Preparative and Nuclear Magnetic Resonance Studies of Diazadiphosphetidines. Part V.[1] Chloromethyl Compounds of the Type $[(Cl_xH_{3-x}C)F_2PNMe]_2$

By **Robin K. Harris,* Mark Lewellyn, Mohamed I. M. Wazeer,** and **John R. Woplin,** School of Chemical Sciences, University of East Anglia, Norwich NOR 88C
Richard E. Dunmur, Michael J. C. Hewson, and **Reinhard Schmutzler,** Lehrstuhl B für Anorganische Chemie der Technischen Universität, D3300 Braunschweig, Pockelsstrasse 4, Germany

A series of chlorinated dimethyl tetrafluorodiazadiphosphetidines, $[RF_2PNMe]_2$, where R = $ClCH_2$ (I), Cl_2HC (II), or Cl_3C (III) have been studied. The syntheses of the two new members of this series, (II) and (III), are described. Analyses of the $^{31}P-\{^1H\}$ and $^{19}F-\{^1H\}$ noise-decoupled n.m.r. spectra yielded values for chemical shifts and coupling constants. In addition some ^1H n.m.r. data are given, including results from computer-fitting for (II). The n.m.r. parameters and isomerism of the compounds are discussed.

THE planar four-membered ring structure, $\overline{\text{P–N–P–N}}$, for the diazadiphosphetidines has been confirmed for $[F_3PNMe]_2$ in the gas phase by electron diffraction [2] and for $[Cl_3PNMe]_2$ [3,4] and $[PhF_2PNMe]_2$ in the solid state by X-ray diffraction.[5] Numerous other data have also supported this structure (see refs. 6—10). The ^{19}F n.m.r. spectra of the compounds $[F_3PNMe]_2$ [1a] and $[RF_2PNMe]_2$ [1b] (where R = Me, Et, NEt_2, or Ph) have been analysed and discussed previously. Recently n.m.r. studies were carried out on some unsymmetrical diazadiphosphetidines [1c] and on a range of methyl- and methoxydiazadiphosphetidines.[1d] We report here the preparation of two new tetrafluorodiazadiphosphetidines, $[(Cl_xH_{3-x}C)F_2PNMe]_2$, where $x = 2$ and 3, and present their n.m.r. data, together with those for the case $x = 1$.

The ground-state structure for the tetrafluorodiazadiphosphetidines is such that each phosphorus atom has an approximately trigonal bipyramidal environment with one equatorial and one axial bridging NMe group. Each

---

[1] (a) Part I, R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1966, **10**, 437; (b) Part II, R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 44; (c) Part III, O. Schlak, R. Schmutzler, R. K. Harris, and M. Murray, *J.C.S. Chem. Comm.*, 1973, **23**; (d) Part IV, R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.

[2] A. Almenningen, B. Andersen, and E. E. Astrup, *Acta Chem. Scand.*, 1969, **23**, 2179.

[3] H. Hess and D. Forst, *Z. anorg. Chem.*, 1966, **342**, 240.

[4] L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1966, 1203.

[5] J. W. Cox and E. R. Corey, *Chem. Comm.*, 1967, 123.

[6] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Interscience, London, vol. 2, 1970.

[7] A. F. Grapov, N. N. Mel'nikov, and L. V. Razvodovskaya, *Russ. Chem. Rev.*, 1970, **39**, 20.

[8] R. E. Dunmur and R. Schmutzler, in preparation for submission to *Fortschr. Chem. Forsch.*

[9] A. J. Downs, *Chem. Comm.*, 1967, 628.

[10] M. P. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1770.

NMe group is axial to one phosphorus atom and equatorial to the other. The remaining axial positions are occupied by fluorine atoms so that each phosphorus atom is bonded to one axial and one equatorial fluorine atom. However, intramolecular exchange between axial and equatorial fluorine atoms is rapid on the n.m.r. time-scale.[1] At temperatures below ambient the existence of *gauche*- and *trans*-isomers (see Figure 1) may be detected by n.m.r.[1b] The *gauche* $\rightleftharpoons$ *trans* intramolecular exchange becomes rapid on the n.m.r. time-scale at room temperature and above.

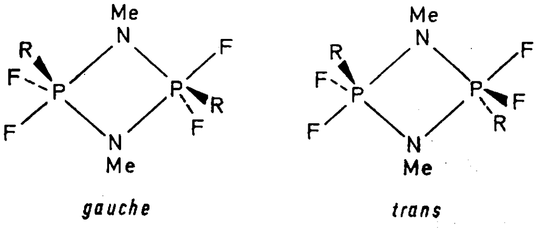


FIGURE 1 *gauche*- and *trans*-Configurations of diazadiphosphetidines, where R = $CH_{3-x}Cl_x$

Several reports have appeared concerning the preparation of diazadiphosphetidines,[11-16] and in general the reactions of fluorophosphoranes with *N*-substituted hexamethyldisilazanes have been found to be useful routes to 2,4-difluorodiazadiphosphetidines,[11-16] Thus, the two new tetrafluorodiazadiphosphetidines (II) and (III) were prepared from the reactions of the corresponding organotetrafluorophosphoranes with *N*-methylhexamethyldisilazane, according to equation (1). Of the tetrafluorophosphorane precursors for (II) and (III), CCl_3PF_4 is a known compound,[17] whereas Cl_2HCPF_4 is new. The preparation of the latter, *via* the dichlorophosphine Cl_2HCPCl_2 and the difluorophosphine Cl_2HCPF_2, both previously unknown, was effected by the reaction sequence (2).

$[RF_2PNMe]_2$ (I) R = ClH_2C (III) R = Cl_3C
(II) R = Cl_2HC

$$2RPF_4 + 2MeN(SiMe_3)_2 \longrightarrow [RF_2PNMe]_2 + 4Me_3SiF \qquad (1)$$

R = Cl_2CH or Cl_3C

$$CHCl_3 + PCl_3 + AlCl_3 \longrightarrow [Cl_2HCPCl_3][AlCl_4]$$

Kinnear–Perren complex

$$\Big\downarrow \text{MeOPCl}_2 \qquad (2)$$

$$Cl_2HCPF_4 \xleftarrow[AsF_3]{Cl_2} Cl_2HCPF_2 \xleftarrow{SbF_3} Cl_2HCPCl_2$$

All the diazadiphosphetidines reported here are white crystalline solids and show a stability to hydrolysis better than that observed for organofluorophosphoranes.[11,13,18]

N.m.r. Spectral Analysis.—As has been shown previously [1] for tetrafluorodiazadiphosphetidines of the type discussed here, intramolecular exchange renders the fluorine atoms chemically equivalent on the n.m.r. time-scale, thus reducing the amount of information which can be obtained from the spectra. Thus the room temperature ^{19}F spectra of compounds (I)—(III) indicate that in each case only one fluorine environment is present. The spectral pattern observed when the protons are decoupled is that due to an $[A[X]_2]_2$ spin system,[1b] where A and X refer to ^{31}P and ^{19}F, respectively. Figure 2 shows a typical example. These double resonance spectra were analysed as described previously,[1b] yielding the parameters listed in Table 1, which also includes data [1b] for $[MeF_2PNMe]_2$. The n.m.r. lines are not in general very sharp, probably because of the presence of the quadrupolar nitrogen atoms. This usually leads to considerable uncertainty in L_{FF} ($= {}^4J_{FF} - {}^4J_{FF}'$; see ref. 1*b*), though N_{FF} ($= {}^4J_{FF} + {}^4J_{FF}'$) is generally obtained more accurately.

On cooling the samples to *ca.* -40 °C separate ^{19}F spectra are observed for two different isomeric forms of each diazadiphosphetidine. The isomer giving the high frequency ^{19}F resonance is thought to be the *gauche* form.[1b] The spectrum of each isomer is of the same type as the averaged spectrum observed at room temperature. Exchange between axial and equatorial fluorine atoms for a given isomer is still rapid on the n.m.r. time-scale at the lowest temperatures we have used (down to *ca.* -70 °C).

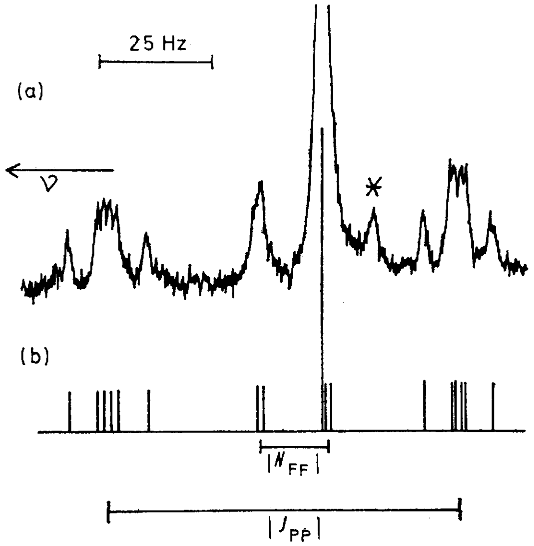


FIGURE 2 ^{19}F-$\{^1H\}$ Decoupled spectra (94·075 MHz) for compound (I) at 90 °C: (a) observed (high frequency region); (b) calculated with the parameters of Table 1 (see ref. 1*b*). The asterisk in (a) indicates an impurity peak. For both (a) and (b) the most intense peak, which is situated at $\nu_F + \frac{1}{2}|N_{PF}|$, has not been taken to its full height

---

[11] R. Schmutzler, *Chem. Comm.*, 1965, 19.

[12] R. Schmutzler, *Angew. Chem.*, 1965, **77**, 530.

[13] R. Schmutzler, in ' Halogen Chemistry,' ed. V. Gutmann, Academic Press, London, 1967, vol. 2, p. 31.

[14] R. Schmutzler, *J.C.S. Dalton*, 1973, 2687.

[15] G. C. Demitras, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, 1964.

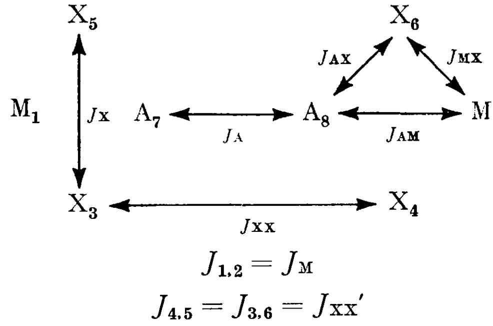
[16] G. C. Demitras, A. G. MacDiarmid, and R. A. Kent, *Chem. and Ind.*, 1964, 1712; G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903.

[17] J. F. Nixon, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1281.

[18] R. Schmutzler, *Adv. Fluorine Chem.*, 1965, **5**, 31.

The data reported for the separate isomers in Table 1 are therefore average chemical shifts and coupling constants for axial and equatorial fluorine atom environments. The *gauche* $\rightleftharpoons$ *trans* process, which has a higher barrier than the axial $\rightleftharpoons$ equatorial process, still gives rise to some line broadening at room temperature, and the relevant data in Table 1 were mostly obtained at elevated temperatures (up to *ca.* 90 °C). N_{PH} are the same, *i.e.* N_{PH} is negative (irradiation in the low frequency ^{19}F region affects the low frequency half of the methylene ^1H region). The parameters obtained are collected in Table 2.

More detailed attention has been paid to the single resonance ^1H spectrum of $[(Cl_2HC)F_2PNMe]_2$. The relevant spin system (excluding the NMe protons) is $[A[X]_2M]_2$, with $A = {}^{31}P$, $X = {}^{19}F$ and $M = {}^1H$. The $[A[X]_2M]_2$ spin system is characterised by eleven coupling constants (see below):



$$J_{1,2} = J_M \tag{i}$$

$$J_{4,5} = J_{3,6} = J_{XX}' \tag{ii}$$

$$J_{4,7} = J_{6,7} = J_{3,8} = J_{5,8} = J_{AX}' \tag{iii}$$

$$J_{2,3} = J_{2,5} = J_{1,4} = J_{1,6} = J_{MX}' \tag{iv}$$

$$J_{1,8} = J_{2,7} = J_{AM}' \tag{v}$$

Since J_M (= $^6J_{HH}$) is negligibly small and the spectrum is not sensitive to the precise value of J_X (= $^2J_{FF} \approx -50$ Hz) [1c,d] there are only nine effective parameters. It is

TABLE 1

^{19}F and ^{31}P N.m.r. parameters for diazadiphosphetidines $[RF_2PNMe]_2$

R	Isomer	Temp. (°C)	δ_F [a] (p.p.m.)	δ_P [b] (p.p.m.)	$\lvert ^2J_{PP}\rvert$/Hz	$^1J_{PF}$ [c]/Hz	$^3J_{PF}$/Hz	$\lvert N_{FF}\rvert$/Hz	$\lvert L_{FF}\rvert$/Hz
CH_3 [d]	average	+85	−57·76	−50·4	72·2	−891·5	+5·2	16·3	3·7
	gauche	−60	−51·81	−51·2	54·4	−908·2	−6·1	7·2	3·6
	trans	−60	−55·90	−47·4	92·2	−868·0	+18·7	24·8	6·0
CH_2Cl [e]	average	+90	−62·68	−55·1	78·0	−920·5	+8·5	16·0	3·8 ± 0·5
	gauche	−70	−61·4	−56·9	62 ± 1	−931 ± 1	−4 ± 1	11 ± 4	<4
	trans	−70	−64·8	−53·1	90 ± 1	−916 ± 1	+19 ± 1	23 ± 4	<10
$CHCl_2$ [e]	average	+80	−71·94	−62·3	93·5	−946·5	+12·2	18·8 [f] 19·2 [g]	4·5 [f] 5·2 [g]
	gauche	−60	−72·88	−64·8	82·0	−955·1	−2·3	9·2	2·0
	trans	−60	−74·67	−62·1	102·5	−945·2	+18·3	23·5	4·2
CCl_3 [e]	average	+80	−63·47	−59·9	125 ± 1	−975 ± 1	+20 ± 1	24 ± 1	18 ± 3
	gauche	−70	−60·97	−59·0	100 ± 2	−972 ± 2	+1 ± 2	6·8 ± 2	3 ± 2
	trans	−70	−64·65	−60·7	133 ± 1	−971 ± 1	+25 ± 1	26·9 ± 1	18·5 ± 2

[a] With respect to internal $CFCl_3$, positive when the reference is to low frequency; accurate to ±0·01 p.p.m. [b] With respect to 85% H_3PO_4 (external), positive when the reference is to low frequency; *relative* accuracies are ±0·02 p.p.m., but the absolute values may be only accurate to ±0·2 p.p.m. (see the text for the method of obtaining δ_P). [c] Sign assumed (ref. 28). [d] Data from ref 1*b*, except for the δ_P values, which are newly reported here. [e] Errors in coupling constants are in general ±0·5 Hz, except for L_{FF} (accuracy ±1 Hz) and except where otherwise stated. [f] From ^{19}F-{^1H} spectra. [g] From iteratively fitting the ^1H spectrum of the $CHCl_2$ group.

TABLE 2

^1H N.m.r. parameters for diazadiphosphetidines $[RF_2PNMe]_2$ [a-c]

	NMe			R				
R	δ_H [d] (p.p.m.)	$\lvert ^3J_{PH}\rvert$/Hz	$\lvert ^4J_{FH}\rvert$/Hz	δ_H [d] (p.p.m.)	N_{PH} [e]/Hz	L_{PH} [e]/Hz	N_{FH} [e]/Hz	L_{FH} [e]/Hz
CH_3 [f]	2·50	12·5	0·8	1·57	−17·5	*g*	7·4	*g*
CH_2Cl	2·60	12·6	0·5	3·78	−9·2	*g*	5·1	*g*
$CHCl_2$	2·73	12·5	0·7	5·86	−5·04	−4·60	5·37	5·13
CCl_3	2·86	12·7	0·6					

[a] Spectra obtained at ambient temperature (*ca.* 35°). [b] It is assumed that $^5J_{HH} \approx {}^6J_{HH} \approx 0$. [c] Chemical shifts are accurate to ±0·01 p.p.m. Errors in coupling constants are, in general, ±0·1 Hz, except that errors in L_{PH} and L_{FH} may be somewhat larger. [d] With respect to Me_4Si; positive when the reference is to low frequency. [e] See text. [f] Refs. 24 and 25. [g] Not obtained.

The room temperature single resonance spectra for $[(Cl_xH_{3-x}C)F_2PNMe]_2$ with $x = 1$ or 2 are more complicated. The NMe protons can still be treated simply because they are all effectively magnetically equivalent and are equivalently related to the two PF_2 units. The remaining protons give complex spectra and also complicate the single resonance ^{19}F and ^{31}P spectra. The most difficult case is $[(ClH_2C)F_2PNMe]_2$, since the CH_2 protons are in principle chemically non-equivalent and there are two different values of $^3J_{HF}$. In fact the CH_2 region of the proton spectrum consists of six intense lines with much ill-resolved fine structure. We have carried out an approximate analysis on the assumption that the two values of $^3J_{HF}$ are not significantly different and that $^6J_{HH} \approx 0$. The value of $N_{PH} = {}^2J_{PH} + {}^4J_{PH}$ was obtained readily from ^1H-{^{19}F} decoupling experiments. Computer simulation, on the basis of a reduced spin system, $[A[X]_2M]_2$, assuming $^5J_{FH} \approx {}^4J_{PH} \approx 0$, showed reasonable agreement with the observed spectrum. Partial decoupling experiments of the ^1H-{^{19}F} type established that the signs of N_{PF} (= $^1J_{PF} + {}^3J_{PF}$) and convenient to use the linear combinations (vi)—(xiii) together with J_A.

$$N_{AM} = J_{AM} + J_{AM}' \quad \text{(vi)}$$

$$N_{AX} = J_{AX} + J_{AX}' \quad \text{(vii)}$$

$$N_{MX} = J_{MX} + J_{MX}' \quad \text{(viii)}$$

$$N_{XX} = J_{XX} + J_{XX}' \quad \text{(ix)}$$

$$L_{AM} = J_{AM} - J_{AM}' \quad \text{(x)}$$

$$L_{AX} = J_{AX} - J_{AX}' \quad \text{(xi)}$$

$$L_{MX} = J_{MX} - J_{MX}' \quad \text{(xii)}$$

$$L_{XX} = J_{XX} - J_{XX}' \quad \text{(xiii)}$$

The spectral analysis may be simplified markedly by consideration of subspectral breakdown,[19] with the use of effective Larmor frequencies and 'the X approximation.' The M region of an $[A[X]_2M]_2$ spectrum contains two types of subspectra characterised by m_A and m_X, the quantum numbers for the total z components of the A and X spins, respectively:

$[[x]_2m]_2$ where $m_A = \pm 1$ (subspectral type I)

$[am]_2$ where $m_X = \pm 2$ (subspectral type II)

The effective M Larmor frequencies are as follows:

$$\nu_I = \nu_M \pm \tfrac{1}{2}N_{AM} \qquad \nu_{II} = \nu_M \pm N_{MX}$$

These two types of subspectra clearly contain some lines in common. In addition to these subspectra there will be lines arising from states with $m_A = 0$ and $m_X = 0$ or ± 1. These may be classified according to the quantum numbers for the total z components of spin for the two $[X]_2$ groups, say r and s. Since $|^1J_{PF}|$ is much larger than any of the other coupling constants, states with $m_A = 0$ and $r = \pm 1 = -s$ do not significantly mix and therefore give rise to first-order characteristics in the M region, *i.e.* lines at $\nu_M + (\tfrac{1}{2}L_{AM} + L_{MX})$. Similar conditions do not, unfortunately, hold for states with $m_A = 0$ and $r = \pm 1$, $s = 0$ since when $m_M = \pm 1$ symmetrisation introduces appreciable mixing,[20] and the M transition frequencies cannot be described very simply. The states with $m_A = 0$ and $r = s = 0$ also give in principle a more complicated situation but in the present instance they lead approximately to another subspectrum of type II with effective M Larmor frequency equal to ν_M.

Spectra of the $[AM]_2$ type are well known.[21] In the present instance $J_M \approx 0$ and the m region of the $[am]_2$ subspectra consists of doublets of separation N_{AM} and degenerate mn sub-subspectra with $\nu_m - \nu_n = L_{AM}$ and $J_{mn} = J_{AA}$. Spectra of the $[[X]_2M]_2$ type have been discussed by Lynden-Bell [22] and by Harris and Ditchfield.[23] The outstanding feature of the M region of the type I $[[x]_2m]_2$ subspectra is a 1 : 3 : 1 triplet centred at ν_m with splittings N_{MX}. There are two different mn sub-subspectra (in the present instance each is doubly degenerate because $J_M \approx 0$) centred at $\nu_m + \tfrac{1}{2}N_{MX}$ and at $\nu_m - \tfrac{1}{2}N_{MX}$; these sub-subspectra have $\nu_m - \nu_n = L_{MX}$, with $J_{mn} = N_{XX}$ or $J_{mn} = L_{XX}$. There are additional lines for which there are no explicit expressions.

Clearly similar considerations to the above can be used to discuss the A and X regions also. It can be seen that, provided the M transitions with explicit expressions can be correctly assigned, the magnitudes of all the nine coupling constants mentioned above can be obtained except N_{AX} and L_{AX} (which may be derived from the A or X regions). There are, however, some residual uncertainties, especially of relative signs. The easiest parameters to be obtained (from the six most intense lines) are N_{AM} and N_{MX}. However, for $[(Cl_2HC)F_2PNMe]_2$ the ratio $L^2_{PH}/|J_{PP}|$ is small (*ca.* 0·23 Hz), so the $[am]_2$ subspectra are deceptively simple.[19] Moreover N_{FH} and N_{PH} are not very different, so the gross appearance of the ^1H spectrum ($CHCl_2$ region) for this compound (Figure 3) is that of a septet (*cf.* coupling to a total of six ^{31}P and ^{19}F nuclei). There is sufficient fine structure, however, to make a detailed analysis feasible. The parameters N_{PF}, L_{PF}, N_{FF}, L_{FF}, and J_{PP} were first obtained, as described earlier, from the ^{19}F-{^1H} spectra, though the estimate of

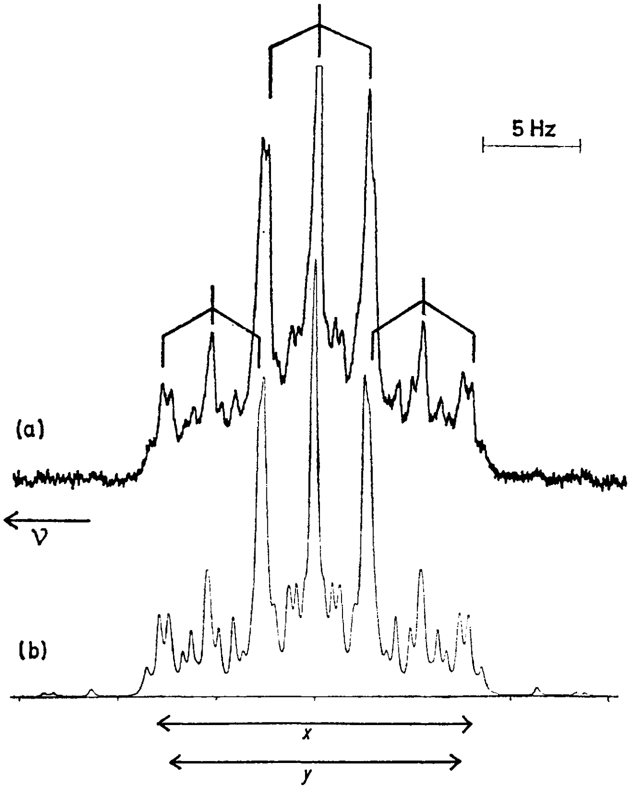


FIGURE 3 100 MHz ^1H Spectrum ($CHCl_2$ region) for compound (II): (a) observed spectrum; (b) spectrum computer-simulated by using the parameters of Tables 1 and 2. The triplets marked have spacing $\tfrac{1}{2}|N_{PH}|$ and origins $\nu_H - N_{FH}$, ν_H, and $\nu_H + N_{FH}$. The separations x and y are $2|N_{FH}| + |N_{PH}|$ and $2|L_{FH}| + |L_{PH}|$, respectively. The most intense peak in (a) has not been taken to its full height

---

[19] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.

[20] R. K. Harris, unpublished work.

[21] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

[22] R. M. Lynden-Bell, *Mol. Phys.*, 1963, **6**, 601.

[23] R. K. Harris and R. Ditchfield, *Spectrochim. Acta*, 1968, **24A**, 2089.

L_{FF} was expected to be crude. Assignment of lines to transitions at $\nu_H \pm (\frac{1}{2}N_{PH} \pm N_{FH})$ and $\nu_H \pm (\frac{1}{2}L_{PH} \pm L_{FH})$ gave estimates for the PH and FH coupling constants. It then proved possible to assign some of the lines of $[mn]_2$ sub-subspectra arising from type I subspectra. Computation gave a simulated spectrum in reasonable agreement with the observed one (Figure 3), and it was possible to assign enough lines to carry out an iterative fitting procedure (keeping $^2J_{FF}$ constant). In fact this resulted (through the use of some rather weak lines in the wings of the spectrum) in defining L_{FF} better than was possible from consideration of the ^{19}F-$\{^1H\}$ spectra. The results for parameters involving ^1H are shown in Table 2.

The sign of N_{FH} (*i.e.* basically $^3J_{FCPH}$) for (II) was found to be positive (with respect to N_{PF} as negative) by ^1H-$\{^{31}P\}$ double resonance experiments.

Similar considerations apply to the ^1H spectrum (PMe region) of $[MeF_2PNMe]_2$, which may be classified as a $[A[X]_2M_3]_2$ spin system. Some preliminary ^1H data [24,25] for this compound are included in Table 2.

The ^{31}P spectra (either single resonance or ^{31}P-$\{^1H\}$ decoupled) were not analysed in detail for any of the compounds since all the parameters could be obtained more accurately from the ^{19}F or ^1H spectra.

DISCUSSION

The ^{19}F and ^{31}P n.m.r. parameters (Table 2) have values in the same range as those previously reported [1b] for other diazadiphosphetidines. The values of $|^1J_{PF}(av)|$ show a marked trend as the extent of chlorine substitution increases. In all compounds there is an equal weighting from axial and equatorial fluorine atoms, so that variations in $^1J_{PF}$ cannot be attributed to an imbalance. The values for the separate isomers show that $|^1J_{PF}|$ has the same trend for both, but the variation is considerably greater for the *trans*-isomer than for the *gauche*-. In fact for the CCl_3 compound $^1J_{PF}$ is the same for the two isomers within experimental error, whereas for the CH_3 compound the values of $|^1J_{PF}|$ differ by 40 Hz in the two isomers. The dominant effect cannot, therefore, be due to changes in group electronegativity of the CH_xCl_{3-x} substituent (especially in view of the earlier results [1b]), but may arise from geometry changes induced by steric effects. It is interesting to note that $|^1J_{PF}(gauche)| - |^1J_{PF}(trans)|$ is also low (*ca.* 20 Hz) for $[Bu^tF_2PNMe]_2$.[25] The data for the compounds studied here suggest that $^1J_{PF}$ is temperature dependent. The values of $^3J_{PF}$ (av) also show a consistent trend with increasing chlorine substitution. In this case, however, most of the variation can be attributed to changes in the isomer population (see Figure 4) since values of $^3J_{PF}$ for the individual isomers do not vary greatly in the series. However, $^3J_{PF}$ for the *gauche*-isomers does show a consistent trend, even resulting in a change of sign, as the extent of chlorine substitution increases, perhaps as a result of group electronegativity changes. The values of $^2J_{PP}$ (av) also show a marked trend with the extent of chlorine substitution (see Figure 5), the change from the CH_3 compound to the CCl_3 compound being 53 Hz.

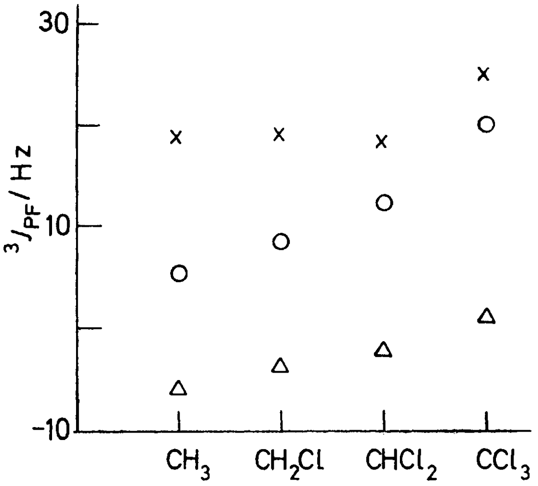


FIGURE 4 Values of $^3J_{PF}$ for diazadiphosphetidines of the type $[(Cl_xH_{3-x}C)F_2PNMe]_2$; ○ high temperature values (weighted averages over the isomer populations); × *trans*-isomer; △ *gauche*-isomer

Again, much of the variation can be attributed to population changes, but results for the *gauche*- and *trans*-isomers also show clear trends, though for the *trans*-isomers $|^2J_{PP}|$ appears to be at a minimum for the CH_2Cl compound. In general the trends are consistent with the marked effect of substituent electronegativity discussed earlier.[1b]

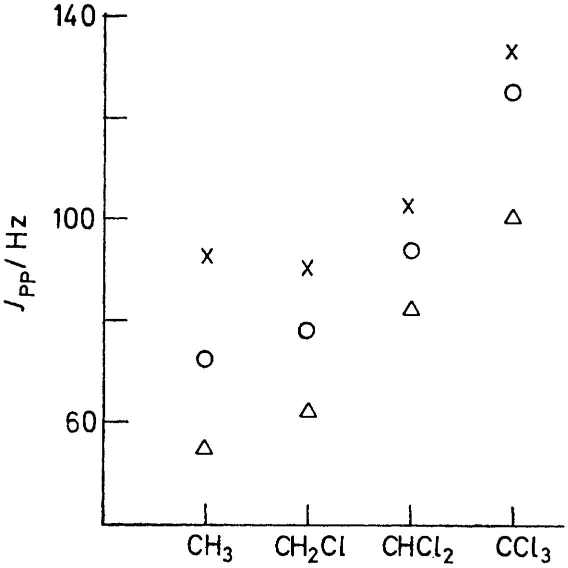


FIGURE 5 Values of $^2J_{PP}$ for diazadiphosphetidines of the type $[(Cl_xH_{3-x}C)F_2PNMe]_2$; ○ high temperature values (weighted averages over the isomer populations); × *trans*-isomer; △ *gauche*-isomer

Unfortunately the available data on N_{FF} and L_{FF} for the present series of compounds are subject to some error and although there are considerable variations in these parameters, no very clear trends emerge.

---

[24] J. R. Woplin, Ph.D. Thesis, University of East Anglia, 1970.
[25] M. I. M. Wazeer and R. K. Harris, unpublished work.

The ^{31}P and ^{19}F chemical shifts of the diazadiphosphetidines are consistent with the presence of five-coordinate phosphorus.[26] For both parameters the shifts are at a minimum (maximum shielding) for the $CHCl_2$ compound. For δ_P this type of situation is common when changes occur in substituents directly bonded to phosphorus, and in that case may be described by the theory of Letcher and van Wazer.[27] However, for directly bonded substituents the effect is normally [1d,27] such that an intermediate compound shows the *minimum* shielding, rather than the maximum. For the present series variations between the isomers do not appear to be significant. Some of the data indicate a temperature dependence of δ_P and/or δ_F, which is not unexpected.

The ^1H n.m.r. data, collected in Table 2, are unremarkable. The values of $|{}^4J_{FH}|$, $|{}^5J_{FH}|$, and $|{}^4J_{PH}|$ are small, as expected. The values of $^2J_{PH}$ show a substantial variation with the extent of chlorine substitution, presumably due to electronegativity effects. There is less variation in $^3J_{FH}$. We have shown that $^2J_{PH}$ and $^1J_{PF}$ have the same sign (negative [28,29]), and that $^3J_{FH}$ is positive, in line with literature data.[28] The proton chemical shifts for the PCH_xCl_{3-x} group show a high frequency shift as x decreases, as expected, whereas δ_H for the NMe group remains relatively constant. The results for (II) indicate that $^4J_{PH}$ is negative whereas $^5J_{FH}$ is positive, but the magnitudes involved are small (in the case of $^5J_{FH}$ the value is probably within experimental error of zero).

The values of $^2J_{PP}$ and $^3J_{PF}$, which show clear substituent trends and substantial differences between the isomers, may be used to determine isomer populations in the high temperature region if it is assumed that these coupling constants are temperature-invariant. The results of such calculations are given in Table 3; they show an encouraging agreement between values obtained from the two coupling constants. Also shown in Table 3 are estimations of populations at low temperature from measurements of peak heights for the ' N doublet ' lines. All calculations agree in suggesting that for $[MeNPF_2CH_{3-x}Cl_x]_2$ the isomer populations are roughly equal for $x = 0$ but that the equilibrium shifts progressively in favour of the *trans*-isomer as x increases. This agrees with data [25] for $[RF_2PNMe]_2$ (R = Me, Et, Pr^i, or Bu^t) if regarded as a steric effect, but it must be recalled that assignment of signals to the separate isomers is not unambiguous,[1b] and indeed itself relies on discussion of the expected relative populations. The changes in population between low and high temperatures are not considered to be established well enough for comment.

TABLE 3

Isomer populations [a] for diazadiphosphetidines $[RF_2PNMe]_2$

	R			
Parameter measured [b]	CH_3	CH_2Cl	$CHCl_2$	CCl_3
$^2J_{PP}$ [c]	0·47	0·57	0·71	0·76
$^3J_{PF}$ [c]	0·46	0·54	0·70	0·79
Peak-heights [d]	0·52	0·65	0·69	0·71

[a] The fractional populations of the *trans*-isomer are given. [b] See text. [c] High temperature populations. [d] Low temperature populations.

EXPERIMENTAL

N.m.r. Spectra.—Three n.m.r. spectrometers were used in the present work. Initial single resonance spectra were obtained using a Varian HA 60A spectrometer at 60 MHz for ^1H, 56·4 MHz for ^{19}F, and 24·3 MHz for ^{31}P resonance. Some more detailed work and all ^{19}F-$\{^1H\}$,^1H-$\{^{19}F\}$, and ^1H-$\{^{31}P\}$ heteronuclear double resonance experiments were performed with a Varian HA 100 spectrometer, equipped with a double-tuned probe [24] and used in conjunction with a Schlumberger FSX 3005 frequency synthesiser. These two instruments were used as described earlier [1b] except that the HA 60A instrument was fitted with an external frequency generator to enable the ^{19}F n.m.r. spectra to be measured by the wide-lock technique. The final ^{31}P-$\{^1H\}$ spectra were obtained using a Varian XL 100 spectrometer; the ^2H signal of the CD_2Cl_2 [for (II) and (III)] or $CDCl_3$ [for (I)] solvent was used for field/frequency locking purposes. The ^{31}P chemical shifts were calculated by measuring the ^{31}P resonance frequencies using an r.f. counter, converting to the equivalent frequency for a magnetic field such that the protons in Me_4Si resonate at exactly 100 MHz, subtracting the corresponding scaled ^{31}P frequency for 85% H_2PO_4 (40, 480,720 Hz), and converting to p.p.m. The ^{19}F shifts were obtained directly with respect to internal $CFCl_3$, and the ^1H shifts directly with respect to internal Me_4Si.

N.m.r. tubes were of 5 mm o.d. throughout; samples for the HA 100 and XL 100 were degassed, using the freeze–pump–thaw technique with a vacuum line, and then sealed. Samples for the HA 60 were not degassed. In all cases temperatures were measured using the spectrometer manufacturer's recommended procedure. They are only considered accurate to $\pm 4°$.

Computer-fitting of the ^1H spectrum of (II) was carried out using the program [30] LACX with the I.C.L. 1905E computer at the University of East Anglia. The approximate computer-simulation of (I) was done using the program LAOCOON with an Atlas computer.

The chemical shifts δ_H, δ_F, and δ_P are given in p.p.m. to high frequency of the signals of Me_4Si, $CFCl_3$, and 85% H_3PO_4, respectively.

Preparations.— 2,4-Bis(chloromethyl)-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine (I) was prepared as in ref. 14.

2,4-*Bis*(*dichloromethyl*)-2,2,4,4-*tetrafluoro*-1,3-*dimethyl*-1,3,2,4-*diazadiphosphetidine* (II). (a) *Dichloro*(*dichloromethyl*)*phosphine*. A Kinnear–Perren reaction was conducted, involving chloroform (239 g, 2 mol), phosphorus trichloride (275 g, 2 mol), and aluminium chloride (267 g, 2 mol). The complex thus obtained was treated with methyl dichlorophosphite, as in the case [31] of CCl_3PCl_2. Upon distillation of the reaction mixture at 20 mmHg (without filtration) all product boiling below 100° was collected. Redistillation

---

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

[27] J. H. Letcher and J. R. van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 75; J. R. van Wazer and J. H. Letcher, *ibid.*, p. 169.

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

[29] R. R. Dean and W. McFarlane, *Chem. Comm.*, 1967, 840.

[30] C. W. Haigh, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 311.

[31] M. Fild and R. Schmutzler, *Inorg. Synth.*, 1970, **12**, 290.

through a 30 cm Vigreux column gave the dichlorophosphine (208 g, 56%), b.p. 84—86° at 18 mmHg (lit.,[32] 36—37° at 8 mmHg) (Found: C, 6·5; Cl, 76·4. $CHCl_4P$ requires C, 6·5; Cl, 76·3%), δ_H 6·0, $|J_{PH}|$ 12·5 Hz, δ_P 143·6. In the reported preparation,[32] $MePCl_2$ instead of $MeOPCl_2$ was employed as a reducing agent for the Kinnear–Perren complex.

(b) *Dichloromethyl(difluoro)phosphine.* The difluorophosphine was obtained through chlorine–fluorine exchange in Cl_2HCPCl_2 (81 g, 0·43 mol), by adding antimony trifluoride (52 g, 0·3 mol) in small portions with stirring. Distillation after 2 h heating (60°) gave the *difluorophosphine* (42 g, 64%), b.p. 55—56° (Found: C, 8·2; H, 0·9; F, 22·3. $CHCl_2F_2P$ requires C, 7·85; H, 0·7; F, 24·85%), δ_H 5·39, $|J_{FH}|$ 7·0 Hz, $|J_{PH}|$ 5·6 Hz, δ_F −96·8, $|J_{PF}|$ 1232 Hz, δ_P 159·5.

(c) *Dichloromethyl(tetrafluoro)phosphorane.* Using a vacuum line, the foregoing difluorophosphine (21 g, 0·14 mol), arsenic trifluoride (12 g, 0·09 mol), and chlorine (10·6 g, 0·145 mol) were condensed into a Monel cylinder at −196 °C. The cylinder was then shaken for 16 h. The contents of the cylinder were condensed, under vacuum, into a round-bottomed flask and distilled at atmospheric pressure to give the *tetrafluorophosphorane* (20 g, 76%), b.p. 52—53°, which was extremely moisture-sensitive; δ_H 5·84, $|J_{FH}|$ 5·0 Hz, $|J_{HP}|$ 3·7 Hz, δ_F −58·0, $|J_{FP}|$ 970 Hz, δ_P −52·4.

(d) *Reaction of dichloromethyl(tetrafluoro)phosphorane with heptamethyldisilazane.* Using the reported [14] procedure, the phosphorane (10·0 g, 0·052 mol) was added slowly with stirring and cooling to heptamethyldisilazane (9·1 g, 0·052 mol),[33] and the mixture was then heated to 60° for 12 h. Fluoro(trimethyl)silane (8·0 g, 83%) was collected in a trap, and was identified from its ^1H n.m.r. spectrum. The solid (9·0 g, 94%) remaining was sublimed at 80° and 0·1 mmHg to give the pure *diazadiphosphetidine* (II) (5·0 g, 52%) as a white crystalline solid, m.p. 83—84° (Found: C, 13·3; H, 2·2; F, 20·7; N, 7·6. $C_4H_8Cl_4F_4N_2P_2$ requires C, 13·2; H, 2·2; F, 20·9; N, 7·7%).

Preparation of 2,4-*Bis(trichloromethyl)*-2,2,4,4-*tetrafluoro*-1,3-*dimethyl*-1,3,2,4-*diazadiphosphetidine* (III). A similar reaction of tetrafluoro(trichloromethyl)phosphorane (11·2 g, 0·05 mol) [17] and heptamethyldisilazane [33] for 0·5 h (exothermic) was carried out. After further heating to 70° for 0·5 h formation of fluoro(trimethyl)silane (8·2, g 89%) was observed. Sublimation of the solid product gave the *diazadiphosphetidine* (III) (10·2 g, 95%) as a white crystalline solid, m.p. 83—85° (Found: Cl, 49·1; F, 17·5; P, 14·5. $C_4H_6Cl_6F_4N_2P_2$ requires Cl, 49·15; F, 17·6; P, 14·3%).

We are grateful to Dr. R. Kebabcioglu for obtaining some preliminary n.m.r. spectra of compound (II) and to Dr. K. M. Worvill for assistance with computations. One of us (R. E. D.) is grateful to Albright & Wilson (Mfg) Ltd. for a maintenance grant; M. L. thanks the United States–United Kingdom Commission for a Fulbright–Hays Student Grant. The international collaboration required in this project was made possible through the support of the N.A.T.O. Scientific Affairs Division. We are grateful to Verband der Chemischen Industrie (Fonds der Chemischen Industrie), Frankfurt am Main, for assistance. Professor H. Jonas and Dr. R. Schliebs, Bayer A.G., Leverkusen, are thanked for generous supplies of some phosphorus compounds and chloro(trimethyl)silane.

[4/1509 *Received, 22nd July,* 1974]

---

[32] V. A. Shokol, V. F. Gamaleya, and G. I. Derkach, *Zhur. obshchei Khim.*, 1969, **39**, 856.

[33] S. W. Kantor and R. C. Osthoff, *Inorg. Synth.*, 1957, **5**, 58.