

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

PHOSPHORUS-FLUORINE CHEMISTRY PART XLII¹. PYRROLE-SUBSTITUTED FLUOROPHOSPHORANES

Michael J. C. Hewson^a; Reinhard Schmutzler^a

^a Lehrstuhl B für Anorganische Chemie der Technischen Universität, Braunschweig, Germany

To cite this Article Hewson, Michael J. C. and Schmutzler, Reinhard(1980) 'PHOSPHORUS-FLUORINE CHEMISTRY PART XLII¹. PYRROLE-SUBSTITUTED FLUOROPHOSPHORANES', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 8: 1, 9 – 26

To link to this Article: DOI: 10.1080/03086648008078156

URL: <http://dx.doi.org/10.1080/03086648008078156>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PHOSPHORUS-FLUORINE CHEMISTRY PART XLII¹. PYRROLE-SUBSTITUTED FLUOROPHOSPHORANES

MICHAEL J. C. HEWSON and REINHARD SCHMUTZLER

*Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstrasse 4,
D-3300 Braunschweig, Germany*

(Received March 16, 1979)

SUMMARY

The silylated compounds, N-trimethylsilyl-pyrrole, **1**, N-trimethylsilyl-2-methylpyrrole, **2**, and N-trimethylsilyl-2,5-dimethylpyrrole, **3**, react with the fluorophosphoranes R_nPF_{5-n} ($n = 0, 1$) to give N-substituted and C-2-substituted fluorophosphoranyl-pyrrole derivatives. The preparation of the corresponding difluorophosphoranyl-pyrrole compounds was carried out by the reaction of the lithium salts of the pyrroles with diphenyltrifluorophosphorane. N-substituted phenyldifluorophosphoranyl - bis(2,5 - dimethylpyrrole), **13**, was obtained from the reaction of phenyltetrafluorophosphorane with the lithium salt of 2,5-dimethylpyrrole, the reaction also producing the monosubstituted phenyltrifluorophosphoranyl-pyrrole derivative, **11**. The N-bonded diphenyl-difluorophosphoranyl derivatives, **10** and **12**, were found to rearrange thermally to give the corresponding C-bonded derivatives, **18** and **19**. The structures of the compounds are deduced from 1H , ^{19}F , ^{31}P n.m.r. spectral data and infrared data. Mass spectral analysis was also employed for identifying the difluorophosphoranes.

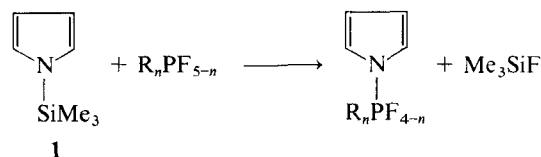
The cleavage reactions of silicon-element bonds by Lewis acid fluorophosphoranes have provided facile methods for the preparation of heteroatom-substituted fluorophosphoranes. Such reactions have been successfully employed in the preparation of fluorophosphoranes,²⁻¹⁷ containing P—N, P—O and P—S bonds. We have found that this principle could also be employed for the preparation of a series of pyrrole-derivatives of fluorophosphoranes. Interest in such compounds arose in connection with the variable temperature ^{19}F n.m.r. studies of fluorophosphoranes containing P—N

bonds.⁴⁻⁶ The reactions did not, however, proceed as first expected. In all cases co-ordination number five at phosphorus was retained except for certain tetrafluorophosphoranes which readily formed phosphonium hexafluorophosphates. The main products were either P—N— or P—C—bonded species, depending on the nature of the pyrrole precursor. The study of the chemistry and stereochemistry of N-fluorophosphoranyl- and C-fluorophosphoranyl-pyrroles is the subject of this paper.

RESULTS AND DISCUSSION

The substitution of pyrrole groups at five-coordinate phosphorus was accomplished by the reaction of the appropriate N-silylpyrrole with the Lewis acid fluorophosphoranes, R_nPF_{5-n} ($n = 0, 1$; R = Me, Et, Ph). Trimethylfluorosilane is formed as the only by-product in almost quantitative yield.^{4-6,14,17}

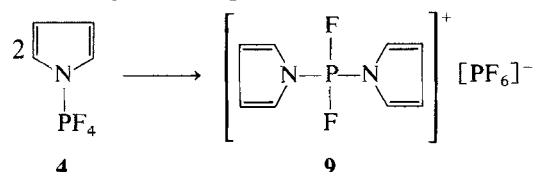
Compound **1**¹⁸ was found to form P-N-bonded fluorophosphoranes according to the equation,



($n = 0$: **4**; $n = 1$; R = Me: **5**; R = Et: **6**; R = Ph: **7**)

The reaction of phosphorus pentafluoride with **1** proceeds below 0°C. However, the covalent tetrafluorophosphorane **4** was not successfully isolated although it was shown to be present in the reaction mixture by n.m.r. spectroscopy. The main product, formed in high yield, was found to be bis(pyrrolyl)difluorophosphonium hexafluorophosphate, **9**, which is presumably formed by

rearrangement of the tetrafluorophosphorane, 4, according to the equation,



The corresponding covalent trifluorophosphoranes were readily isolated, the reactions taking place at higher temperatures. However, formation of ionic species was also noted. This phenomenon has been observed for other amino fluorophosphoranes,^{2,14,19,20}

The reaction of 1 with Ph_2PF_3 proceeds at elevated temperatures (*ca.* 120°C) and large quantities of trimethylfluorosilane are produced. However, isolation of *N*-diphenyldifluorophosphoranyl-pyrrole, 8, proved impossible due to formation of large amounts of intractable material. By employing the lithium salt of pyrrole compound 8 was prepared, a method already applied to the preparation of other pyrrole-phosphorus derivatives.^{21,22} The reaction takes place at room temperature and is exothermic, producing the desired product in high yield in the absence of any polymeric species, in accord with,

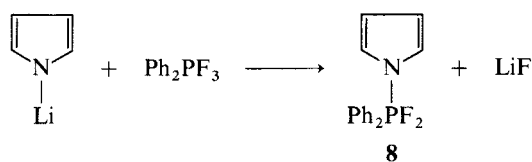
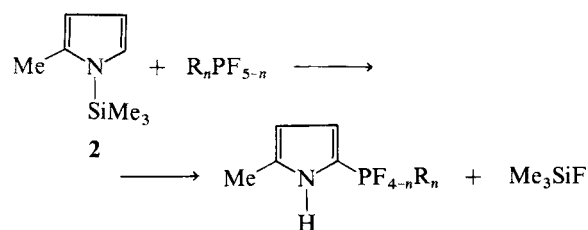


Table II lists the nitrogen-bonded derivatives which were prepared. Compounds 5 and 6 are colourless liquids, whereas compound 7 solidifies to a colourless glassy solid of low melting point. Compounds 8 and 9 are pale yellow crystalline solids. Their stability to hydrolysis is comparable to that of other phosphorus-fluorine compounds.^{2,23}

Compound 2 was found to give rise to formation of P—C bonded fluorophosphoranes according to the equation,



($n = 0$: 15; $n = 1$; R = Et: 16; R = Ph: 17)

The formation of a P—C—bonded fluorophosphorane from the cleavage of a silicon-carbon-bonded precursor has recently been reported;²⁴ methylene(*bis*)tetrafluorophosphorane was produced from the reaction of phosphorus pentafluoride with 1,1,3,3-tetramethyl-1,3-disilacyclobutane. In the present work we have observed the first examples of the cleavage of silicon-nitrogen bonds leading, ultimately, to the formation of P-C-bonded fluorophosphoranes.

Compounds 15–17 were formed under conditions similar to those employed for compounds 4–7. No tendency for rearrangement to ionic species was noted.

The lithium salt of 2-methylpyrrole was employed for the preparation of the α -carbon-bonded difluorophosphorane 18, as similar difficulties were incurred for the reaction of Ph_2PF_3 with 2, as observed for its reaction with 1.

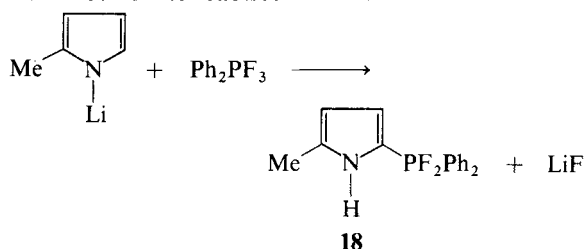
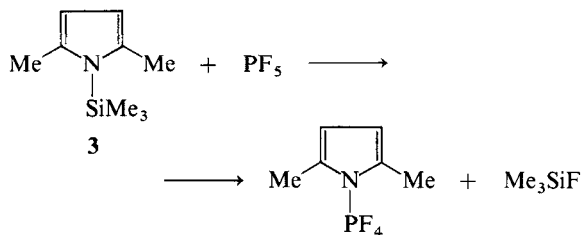
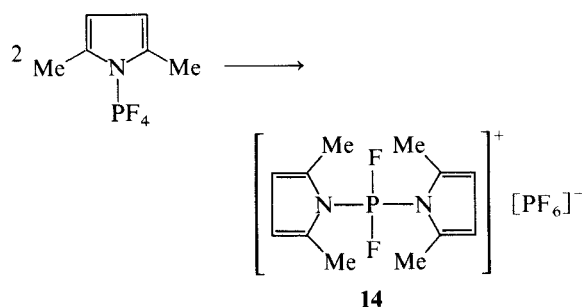


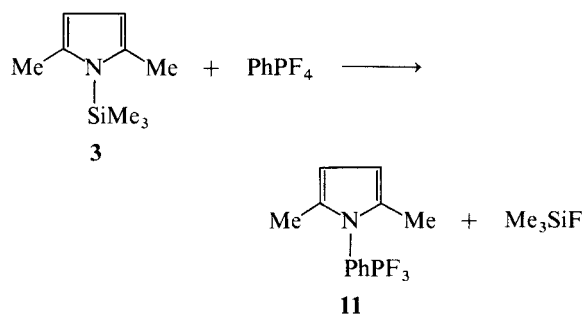
Table III lists the α -carbon-bonded derivatives which were prepared. Compound 15 was isolated as a white crystalline solid. Intermolecular hydrogen bonding is responsible for its solid state.^{25,26} In comparison, compounds 16 and 17 are colourless liquids, steric hindrance reducing the possibility of hydrogen bonding. Compound 18 is a white crystalline solid. The stability of 15 to 19 to moisture is comparable to that of other fluorophosphoranes.^{2,23}

By employing the 2,5-dimethylpyrrole derivative 3²⁷ in which both α -carbon positions are occupied by methyl groups P—N bonded compounds could be obtained from its reaction with PF_5 or PhPF_4 . However, with PF_5 only compound 14, originating from isomerization of an initial tetrafluorophosphorane, was obtained in accord with,



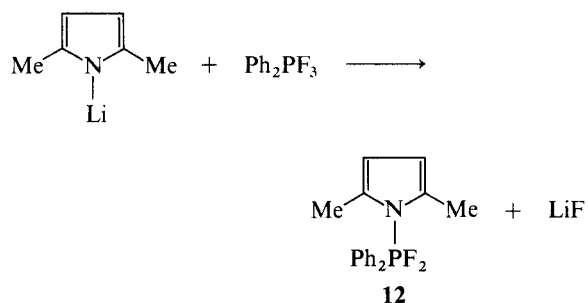


N.m.r. of the reaction mixture indicated the presence of the tetrafluorophosphorane. (See experimental section). The trifluorophosphorane **11** was formed in accord with,

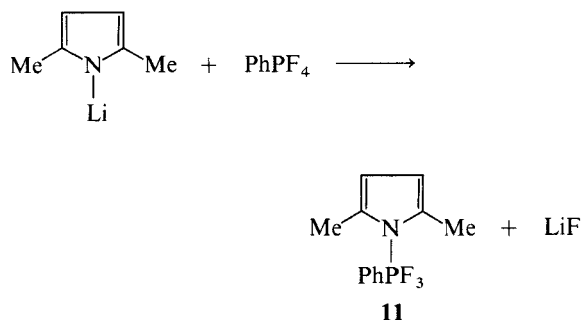


The formation of ionic and polymeric species reduces the yield of **11**, the reaction temperature being above 100°C.

The difluorophosphorane **12** was produced from the reaction of Ph_2PF_3 with the lithium salt of 2,5-dimethylpyrrole.



The reaction of the lithium salt with PhPF_4 produced, depending on the reaction conditions employed, a mono- and/or di-substituted pyrrole derivative. For a molar ratio of 1:1 **11** was obtained in higher yield, the reaction taking place at -10°C and being completed at room temperature.



Addition of PhPF_4 to the lithium salt under similar conditions results in formation of both **11** and a disubstituted derivative **13**. By employing a molar ratio of 2:1 of lithium salt to PhPF_4 , regardless of the mode of addition, compound **13** could be obtained in high yield.

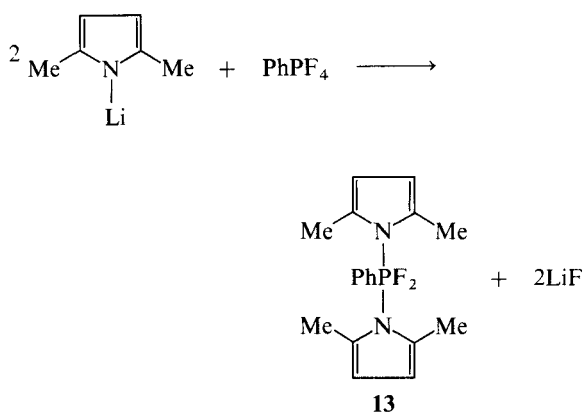
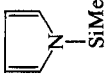
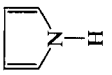
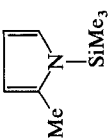
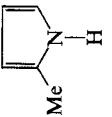
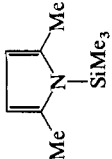
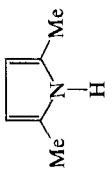


Table II lists the 2,5-dimethyl-N-fluorophosphoranylpyrrole derivatives prepared. Compound **11** is a colourless oily liquid, compounds **12**–**14** are white to pale yellow crystalline solids.











The formation of P—N—bonded compounds can be rationalized in terms of Lewis acid-base reactions between fluorophosphoranes and silylpyrroles, resulting in the cleavage of the Si—N bond and formation of a P—N bond in a concerted one-step process. Electrophilic substitution can occur at the α - or β -carbon of pyrroles^{21,28} although substitution at the α -carbon is preferred due to better mesomeric stabilisation of a transition state. Thus one might explain the formation of P—C—bonded compounds involving **2** in terms of electrophilic attack of $\text{R}_n\text{PF}_{5-n}$ at the α -carbon atom, followed by loss of HF which subsequently cleaves the Si—N bond.

TABLE I
N-trimethylsilyl-substituted pyrroles

Compound	Reactants (mole)	Conditions Temp. °C (hr)	Bp °C/mm	Yield %	Analysis		
					C	H	N
 (1)	 (0.686) (Me ₃ Si) ₂ NH ^a (0.378) (NH ₄) ₂ SO ₄ catalyst	Reflux (16)	153/760	80	See Ref. 44		
 (2)	 (0.65) EtMgBr (0.65) Me ₃ SiCl (0.65) Ether 1.5 l	Reflux (1)	77/26	66	62.8	9.8	9.2
					62.8	9.9	9.1
					Calc. Found		
 (3)	 (0.8) EtMgBr (0.8) Me ₃ SiCl (0.8) Ether 1.5 l	Reflux (1)	93/18	54	See Ref. 27		

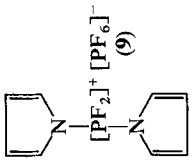
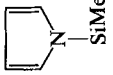
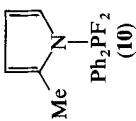
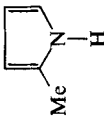
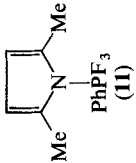
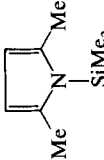
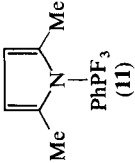
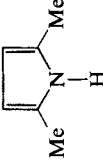
^a Prepared from Me₃SiCl and NH₃ in petroleum ether; R. C. Osthoff and S. W. Kantor, Inorg. Synth., **5**, 55 (1957).

TABLE II
N-substituted-fluorophosphoranyl pyrrole derivatives

Compound	Reactants (mole)	Conditions Temp. °C (hr)	Bp °C/mm	Yield %	Analysis			
					C	H	F(P)	
 (4)	 (0.095) PF ₅ (0.095)	-78 — +10 (48)	88/10	59			(a)	
 (5)	 (0.096) MePF ₄ (0.096)	100 (6)	64/65	74	35.5 35.7	4.1 4.2	33.7 Calc. 33.4 Found	
 (6)	 (0.12) EtPF ₄ (0.12)	100 (6)	60/22	81	39.3 39.3	4.9 5.0	31.2 Calc. 31.1 Found	
 (7)	 (0.12) PhPF ₄ (0.12)	90 (6)	50/0.05 85/1.0	73			See Ref. 14	
 (8)	 (0.05) Bu ⁿ Li (0.05) Ph ₂ PF ₃ (0.05) Hexane 100 ml.	Reflux (4)	mp. 97-99°	85	66.5 67.5	4.8 4.7	(10.8) Calc. (11.2) Found	

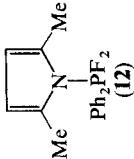
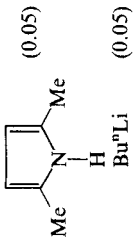
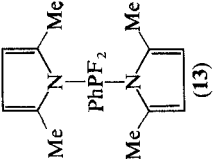
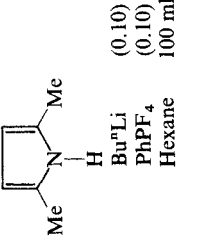
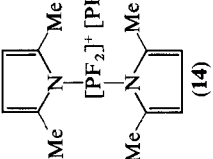
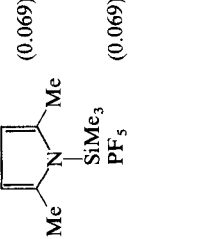
(Continued)

TABLE II (Continued)

Compound	Reactants (mole)	Conditions Temp. °C (hr)	Bp °C/mm	Yield %	Analysis			
					C	H	F(P)	
 (9)	 (0.11)	-78 - +10 (24)	mp. 180 decomposition	91				(d)
 (10)	 (0.05) Bu ⁿ Li Ph ₂ PF ₃ Hexane 100 ml.	25 (12)	mp. 20 (e)	89				(e)
 (11)	 (0.05) SiMe ₃ PhPF ₄	90 (8)	95/0.05	63	55.6 56.0	5.0 4.9	22.0 Calc. 22.0 Found	
 (11)	 (0.05) Bu ⁿ Li PhPF ₄ Hexane 100 ml.	-10 (1) 25 (20)	95/0.05 86/0.01	76	55.6 57.0	5.0 4.9	22.0 Calc. 22.0 Found	

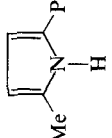
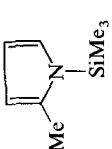
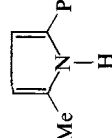
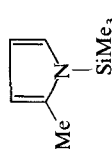
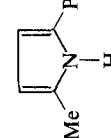
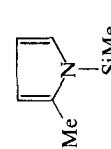
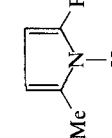
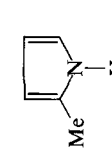
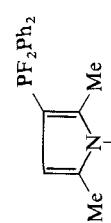
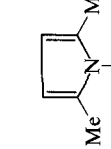
PYRROLE-SUBSTITUTED FLUOROPHOSPHORANES

15

Compound	Reactants (mole)	Conditions Temp. °C (hr)	Bp °C/mm	Yield %	Analysis		
					C	H	F(P)
 (12)	 (0.05) Bu ⁿ Li Ph ₂ PF ₃ Hexane 100 ml.	25 (12)	mp. 62–65 ^f	83	68.1 68.2	5.6 5.6	11.1 Calc. 10.9 Found
 (13)	 (0.10) Bu ⁿ Li PhPF ₄ Hexane 100 ml.	25 (12)	mp. 86–87 ^g	89	64.6 64.1	6.3 6.3	11.4 Calc. 11.4 Found
 (14)	 (0.069) SiMe ₃ PF ₅	–78 – +10 (48)	mp. 180 decomposition	88	35.8 32.6	4.0 4.1	37.6 Calc. 37.6 Found

^a Found to be extremely unstable rearranging to the ionic compound **(9)** characterised spectroscopically^b R. Schmutzler, see reference 14^c Recrystallised from hexane^d Characterised spectroscopically^e Oily brown liquid which converts to P—C—bonded compound on attempted distillation; analysed for compound **(18)**^f Recrystallised from pentane, followed by sublimation at 80°C/0.05 mm using a water cooled finger^g Recrystallised from hexane, sublimation at 70°C/0.05 mm using water cooled finger.

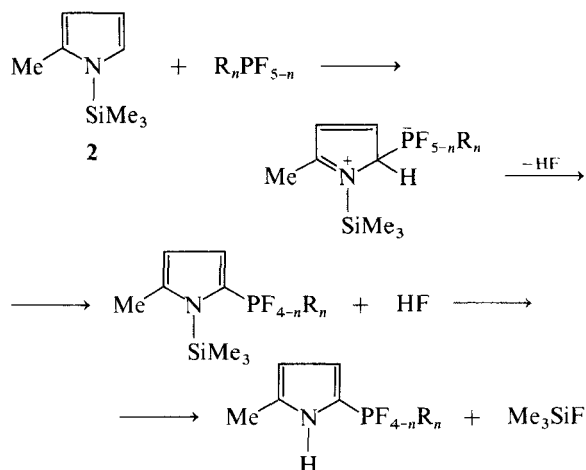
TABLE III
C-substituted-fluorophosphoranyl pyrrole derivatives

Compound	Reactants (mole)	Conditions Temp. °C (hr)	Bp °C/mm	Yield %	Analysis		
					C	H	F
 (15)	 (0.076)	-78 - +10 (48) -78 - +10 (48)	76/25 mp. 44-45	71	32.0 31.9	3.2 3.3	40.6 Calc. 40.0 Found
 (16)	 (0.078)	100 (6)	108/10 88/5	75	42.6 42.6	5.6 5.6	28.9 Calc. 28.7 Found
 (17)	 (0.05)	100 (6)	79/0.05	76	53.9 53.7	4.5 4.4	23.3 Calc. 23.4 Found
 (18)	 (0.05)	Reflux (4)	148/0.05 mp. 117-119 ^a	87	67.4 67.7	5.2 5.2	12.5 Calc. 12.6 Found
 (19)	 (0.05)	Reflux (4)	180/0.05 mp. 104-105 ^b	82			(c)

^a Softening occurs at 100°C

^b Distilled at 180°C/0.05 mm followed by sublimation at 120°C/0.05 mm using water cooled finger

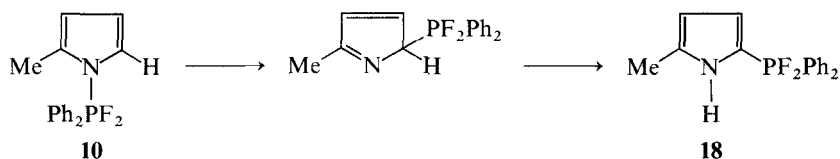
^c Compound characterised spectroscopically and shown to be formed from compound (12). Analysed as compound (12).



However, when both α -carbon positions are occupied as in **3** then N-substitution is preferred. The reaction of the lithiated pyrroles with fluorophosphoranes might conceivably be explained in terms of similar mechanisms.

Formation of the P—C bonded isomer of a fluorophosphoranyl-substituted pyrrole, in preference to the P—N bonded isomer, is, apparently, related to the Lewis acid strength of the fluorophosphorane employed: in most cases, the stronger Lewis acids, especially PF_5 and tetrafluorophosphoranes, give rise, immediately, to the P—C isomer while P—N bonded products (which may, subsequently, undergo rearrangement to P—C bonded isomers) are obtained from trifluorophosphoranes. Also, it would appear important in some cases that methyl substitution in the pyrroles renders the α position particularly susceptible to electrophilic attack.

It has been established for **18** that this compound is formed via the N-bonded isomer **10**. Under mild conditions **10** is formed in high yield. On distillation at *ca.* $+140^\circ\text{C}$ irreversible thermal rearrangement to **18** takes place. This was also observed for compound **12** which could be converted, irreversibly, to the P—C-bonded isomer **19**. This phenomenon is characteristic of N-substituted pyrrole compounds, the rearrangements presumably proceeding via the formation of a pyrrolenine intermediate.²¹

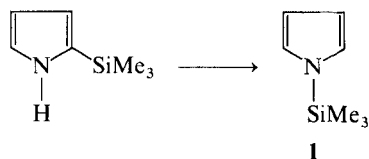


It seems likely that all the reactions discussed here proceed via the formation of P—N-bonded compounds and that thermal rearrangement is easier for the 2-methyl-pyrrole derivatives, although its facility decreases from the tetrafluorophosphorane to the difluorophosphorane. Attempts at following possible thermal rearrangements of compounds **5–8** by ^{19}F n.m.r. proved unsuccessful as at temperatures higher than $+100^\circ\text{C}$ an apparent polymerisation ensued.

All the compounds prepared were characterised by ^1H , ^{19}F , ^{31}P n.m.r. and infrared spectroscopy and elemental analysis. The difluorophosphoranes **8**, **10**, **12**, **13**, **18**, and **19** were also characterised by mass spectral analysis.

NUCLEAR MAGNETIC RESONANCE AND INFRARED DATA

Table IV lists the ^1H n.m.r. data for the trimethylsilylpyrrole precursors. The resonances observed compare with those already reported for the free pyrroles^{21,29,30} except for the absence of the NH resonance which establishes that silylation has occurred at nitrogen. This is confirmed by the infrared spectra which show no NH-frequency expected at about 3400 cm^{-1} .¹³ The α -carbon-bonded isomer of **1** has recently been investigated by Pommier and Lucas and it was shown that it slowly reverts to the Si—N-bonded isomer.²⁸



Tables V and VII list the n.m.r. data for the N-substituted fluorophosphoranyl-pyrrole derivatives and Tables VI and VIII data for the corresponding C-substituted fluorophosphoranyl-pyrrole compounds.

The ^{31}P n.m.r. data are consistent with trigonal bipyramidal structures for the five-coordinate species in which the axial sites are occupied by

TABLE IV
¹H nuclear magnetic resonance data for N-trimethylsilylpyrroles

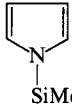
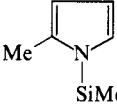
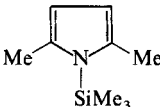
Compound	δ H(ppm)			Multiplicity
 (1)	δ H	-0.28	SiMe ₃	Singlet
	δ H	-6.18	Ring-H 3 & 4	Multiplet
	δ H	-6.62	Ring-H 2 & 5	Multiplet
 (2)	δ H	-0.28	SiMe ₃	Singlet
	δ H	-2.23	CH ₃ -C	Singlet
	δ H	-5.91	Ring-H 3	Multiplet
	δ H	-6.01	Ring-H 4	Complex Quartet
	δ H	-6.55	Ring-H 5	Complex Quartet
 (3)	δ H	-0.33	SiMe ₃	Singlet
	δ H	-2.30	CH ₃ -C	Singlet
	δ H	-5.71	Ring-H 3 & 4	Singlet

TABLE V
 Fluorine-19 and Phosphorus-31 nuclear magnetic resonance data for N-substituted fluorophosphoranyl-pyrrole compounds

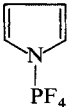

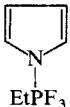
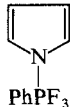
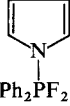
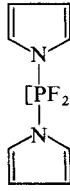
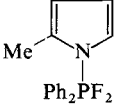
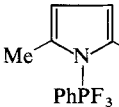
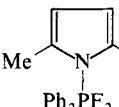
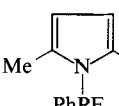
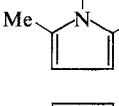
Compound	δ F(ppm)	J(Hz)	δ P(ppm)
 (4) ^a	δ F(av) +55.4	¹ J _{PF(av)} 905	δ P +51.7
 (5)	δ F(ax) +22.1 δ F(eq) +69.9	¹ J _{PF(ax)} 834 ¹ J _{PF(eq)} 978 ² J _{F(ax)F(eq)} 51	δ P +38.9
 (6) ^b	δ F(ax) +33.1 δ F(eq) +72.8	¹ J _{PF(ax)} 868 ¹ J _{PF(eq)} 991 ² J _{F(ax)F(eq)} 55	δ P +38.6
 (7) ^b	δ F(ax) +38.5 δ F(eq) +68.0	¹ J _{PF(ax)} 856 ¹ J _{PF(eq)} 967 ² J _{F(ax)F(eq)} 55	δ P +58.2
 (8) ^c	δ F +34.9	¹ J _{PF} 753	δ P +57.8
 (9) ^d	δ F(an) +72.2 δ F(cat) +76.7	¹ J _{PF(an)} 714 ¹ J _{PF(cat)} 1081	δ P +145.0 ^e

TABLE V (Continued)

Compound	$\delta F(\text{ppm})$	$J(\text{Hz})$	$\delta P(\text{ppm})$
 (10)	δF +27.2	$^1J_{PF}$ 761	δP +52.0
 (11)	$\delta F(\text{ax})$ +23.6 $\delta F(\text{eq})$ +68.7	$^1J_{PF(\text{ax})}$ 884 $^1J_{PF(\text{eq})}$ 996 $^2J_{F(\text{ax})F(\text{eq})}$ 56	δP +46.2
 (12) ^f	δF +26.2	$^1J_{PF}$ 752	δP +50.0
 (13) ^f	δF +9.9	$^1J_{PF}$ 808	δP +53.3
 (14) ^d	$\delta F(\text{an})$ +71.6 $\delta F(\text{cat})$ +76.1	$^1J_{PF(\text{an})}$ 714 $^1J_{PF(\text{cat})}$ 1090	δP +145.0 δP -79.0

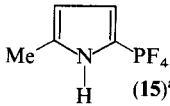
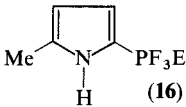
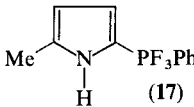
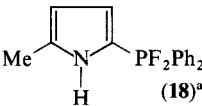
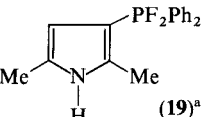
^a Measured only on the reaction mixture^b See Ref. 14^c Benzene solution^d Acetonitrile solution^e δP not observed, compound unstable in solution^f Dichloromethane solvent.

fluorine atoms, with the remaining groups occupying equatorial sites.^{2,32} The room temperature ^{19}F n.m.r. data for the fluorophosphoranes are consistent with those already reported.^{2,23} A delabelling of the axial and equatorial fluorine occurs for the tetrafluorophosphoranes^{2,23} due to a "pseudorotation" process causing positional exchange of the fluorine atoms.³³ The trifluorophosphoranes all show distinct axial and equatorial fluorine environments, and the difluorophosphoranes have axial fluorine atoms, only giving rise to one resonance.^{2,23} The ionic species, fluorophosphonium hexafluorophosphates, also show n.m.r. data which are characteristic.^{23,32}

The low temperature ^{19}F n.m.r. spectrum of **15** (recorded on a solution of *ca.* 50% in toluene) shows three distinct fluorine atom resonances at -50°C . The room temperature doublet collapses and a complex 24 line spectrum is observed. The axial fluorine atoms, F^1 and F^2 , become chemically and magnetically non-equivalent, A and B, respectively whilst the equatorial fluorine atoms, F^3 and F^4 , remain equivalent, M_2 . The ratio of the chemical shift difference between $F^1(\text{A})$ and $F^2(\text{B})$ to the coupling constant, $^2J_{F^1F^2}$ is such that an AB type spectrum is seen.³⁴ Six ab sub-spectra,³⁴ the AB part of an ABXM_2 spin system ($X = ^{31}\text{P}$ and $M = \text{F-equatorial}$) are observed and Figure 1

TABLE VI

Fluorine-19 and phosphorus-31 nuclear magnetic resonance data for 2-methyl-5- and 2,5-dimethyl-3-fluorophosphoranyl compounds

Compound	$\delta F(\text{ppm})$		$J(\text{Hz})$		$\delta P(\text{ppm})$	
 (15) ^a	$\delta F(\text{av})$	+ 60.8	$^1J_{\text{PF}(\text{av})}$	895	δP	+ 61.5
	$\delta F^{1\text{ b}}$	+ 50.4	$^1J_{\text{PF}^1}$	856		
	δF^2	+ 46.6	$^1J_{\text{PF}^2}$	838		
	δF^3	+ 73.2	$^1J_{\text{PF}^3}$	967		
	δF^4	+ 73.2	$^1J_{\text{PF}^4}$	967		
			$^2J_{\text{F}^1\text{ F}^2}$	17		
			$^2J_{\text{F}^1\text{ F}^3}$	76		
			$^2J_{\text{F}^2\text{ F}^3}$	66		
 (16)	$\delta F(\text{ax})$	+ 39.8	$^1J_{\text{PF}(\text{ax})}$	772	δP	+ 26.6
	$\delta F(\text{eq})$	+ 83.7	$^1J_{\text{PF}(\text{eq})}$	963		
			$^2J_{\text{F}(\text{ax})\text{F}(\text{eq})}$	46		
 (17)	$\delta F(\text{ax})$	+ 30.8	$^1J_{\text{PF}(\text{ax})}$	866	δP	+ 51.8
	$\delta F(\text{eq})$	+ 65.9	$^1J_{\text{PF}(\text{eq})}$	975		
			$^2J_{\text{F}(\text{ax})\text{F}(\text{eq})}$	58		
 (18) ^a	δF	+ 49.3	$^1J_{\text{PF}}$	626	δP	+ 63.2
 (19) ^a	δF	+ 34.8	$^1J_{\text{PF}}$	626	δP	+ 47.8

^a Benzene solution^b 50 % toluene solution at -50°C .

TABLE VII

^1H nuclear magnetic resonance data of N-substituted fluorophosphoranyl pyrrole compounds

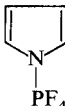
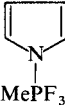
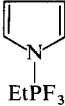
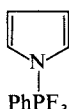
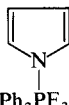
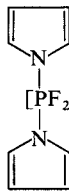
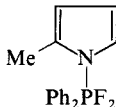
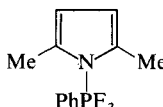
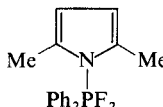
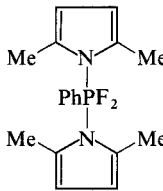
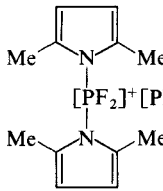
Compound	$\delta H(\text{ppm})$	Remarks
 (4)	δH -6.30	Ring-H 3 & 4
	δH -7.08	Ring-H 2 & 5
 (5)	δH -1.80	CH_3
	δH -6.20	Ring-H 3 & 4
	δH -7.10	Ring-H 2 & 5
 (6)	δH -1.18	CH_3
	δH -2.25	CH_2
	δH -6.26	Ring H 3 & 4
	δH -7.16	Ring-H 2 & 5

TABLE VII (Continued)

Compound	$\delta H(\text{ppm})$			Remarks	
 PhPF_3 (7)	δH	−6.25	Ring-H 3 & 4	Complex Multiplet	
	δH	−7.10	Ring-H 2 & 5	Complex Multiplet	
	δH	−7.50	Phenyl Ring	Complex Multiplet	
 Ph_2PF_2 (8) ^a	δH	−6.55	Ring-H 3 & 4	Complex Multiplet	
	δH	−7.46	Ring-H 2 & 5	Complex Multiplet	
	δH	−7.80	Phenyl Ring	Complex Multiplet	
 $[\text{PF}_2]^+[\text{PF}_6]^-$ (9) ^b	δH	−6.10	Ring-H 3 & 4	Complex Quartet	
	δH	−6.80	Ring-H 2 & 5	Complex Multiplet	
 Ph_2PF_2 (10)	δH	−2.76	Ring CH_3	Singlet	
	δH	−6.50	Ring-H 3	Complex Multiplet	
	δH	−6.63	Ring-H 4	Complex Multiplet	
	δH	−7.66	Ring-H 5	Complex Multiplet	
	δH	−8.08	Phenyl Ring	Complex Multiplet	
 PhPF_3 (11)	δH	−2.16	Ring CH_3	Singlet	
	δH	−5.76	Ring-H 3 & 4	$^4J_{\text{HP}}$ 6.0 Hz ^c	
	δH	−7.56	Phenyl Ring	Complex Multiplet	
 Ph_2PF_2 (12) ^a	δH	−2.00	Ring CH_3	Singlet	
	δH	−5.85	Ring-H 3 & 4	$^4J_{\text{HP}}$ 6.0 Hz ^c	
	δH	−7.71	Phenyl Ring	Complex Multiplet	
 PhPF_2 (13) ^b	δH	−2.06	Ring CH_3	Singlet	
	δH	−5.88	Ring-H 3 & 4	$^4J_{\text{HP}}$ 6.0 Hz ^c	
	δH	−7.72	Phenyl Ring	Complex Multiplet	
 $[\text{PF}_2]^+[\text{PF}_6]^-$ (14)	δH	−2.26	Ring CH_3	Singlet	
	δH	−6.06	Ring-H 3 & 4	Singlet	

^a Dichloromethane solution^b Acetonitrile solution^c Assigned from $^1\text{H}\{-^{31}\text{P}\}$ measurement.

TABLE VIII

¹H nuclear magnetic resonance data of 2-methyl-5- and 2,5-dimethyl-3-fluorophosphoranyl pyrrole compounds

Compounds	δ H(ppm)			Remarks
 (15) ^a	δ H	-2.34	Ring CH ₃	Singlet
	δ H	-6.16	Ring-H 3	Complex Multiplet
	δ H	-7.22	Ring-H 4	Complex Multiplet
	δ H	-9.96	NH	Broad Singlet
 (16)	δ H	-1.15	Ethyl CH ₃	³ J _{HP} 26.0 Hz
	δ H	-2.20	Ethyl CH ₂ ^b	³ J _{HH} 7.0 Hz
				² J _{HP} 17.0 Hz ^c
				³ J _{HH} 7.0 Hz
				³ J _{HF(ax)} 10.0 Hz ^d
	δ H	-2.20	Ring CH ₃ ^b	Singlet
	δ H	-5.96	Ring-H 3	Complex Multiplet
	δ H	-7.00	Ring-H 4	Complex Multiplet
	δ H	-8.91	NH	Broad Singlet
 (17)	δ H	-2.36	Ring CH ₃	Singlet
	δ H	-5.90	Ring-H 3	Complex Multiplet
	δ H	-6.05	Ring-H 4	Complex Multiplet
	δ H	-7.50	Phenyl Ring	Complex Multiplet
	δ H	-8.50	NH	Broad Singlet
 (18) ^e	δ H	-2.35	Ring CH ₃	Singlet
	δ H	-6.18	Ring-H 3	Complex Multiplet
	δ H	-7.25	Ring-H 4	Complex Multiplet
	δ H	-7.50	Phenyl Ring	Complex Multiplet
	δ H	-9.26	NH	Broad Singlet
 (19) ^e	δ H	-2.22	Ring CH ₃ (2)	Singlet
	δ H	-2.42	Ring CH ₃ (5)	Singlet
	δ H	-6.38	Ring-H 4	Complex Multiplet
	δ H	-7.70	Phenyl Ring	Complex Multiplet
	δ H	-8.93	NH	Broad Singlet

^a Acetonitrile Solution^b Overlap of these two resonances^c Obtained from ³¹P spectrum^d Obtained from ¹⁹F spectrum^e Dichloromethane solution.

shows the ¹⁹F experimental and computed n.m.r. band shapes for one half of the axial fluorine atom resonances consisting of 3 ab sub-spectra. The spectrum was simulated by the computer program³⁵ NMR ITERATIVE. The equatorial fluorine atoms, F³ and F⁴, give rise to a resonance consisting of six lines, a doublet of triplets, which are broad, probably due to unresolved coupling to the axial fluorine atoms.

This is believed to be the first example of the observation of different fluorine atom environments (relative to the n.m.r. time scale) for P—C—bonded tetrafluorophosphoranes.^{2,23} Previous examples have included, for example,

the P—N—bonded aminotetrafluorophosphoranes^{2,4,5,6,14,36-39} and P—S—bonded organothio - tetrafluorophosphoranes^{14,40,41}. In these cases the results were interpreted in terms of reduced rotation about the P—N or P—S bond, plus a reduction in the rate of positional exchange of the fluorine atoms through an intramolecular process. For **15** the rate of the positional exchange of fluorine is believed to decrease due to formation of intermolecular hydrogen bonds. Figure 2 indicates the formation of the hydrogen bond with a bond length for H . . . F of 3.03 Å^{25,26}. Thus one can formulate an intermolecular dependence of the "pseudorotational" process. The asymmetric

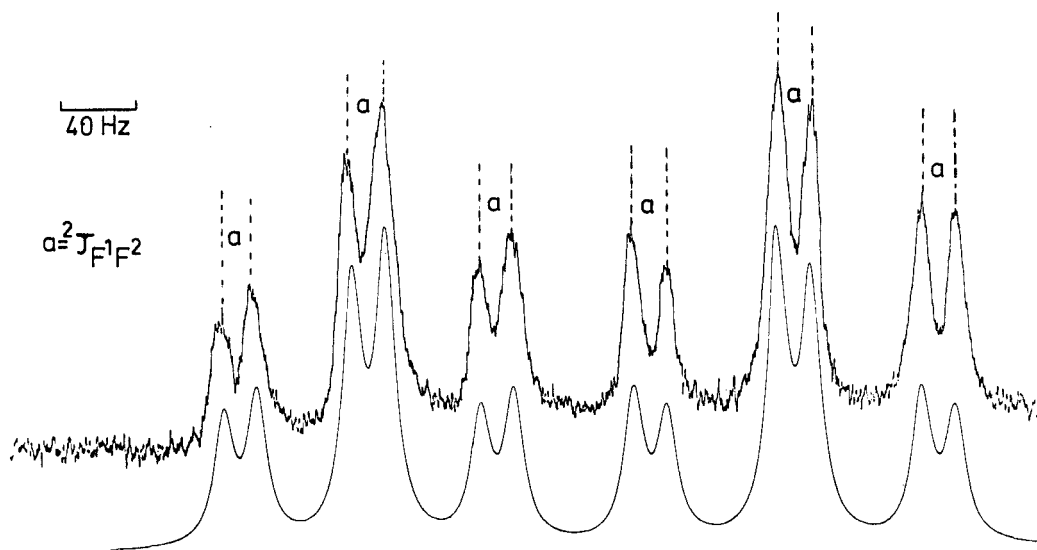


FIGURE 1 The ^{19}F experimental and computed n.m.r. band shapes for the low field sub-spectra of compound (15) at -50° . Three of the six ab sub-spectra in the AB part (F^1 and F^2) of an ABM_2X (where $\text{M} = \text{F}^3$ eq and F^4 eq and $\text{X} = \text{P}$) spin system are shown.

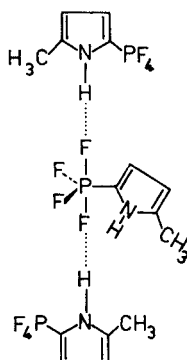


FIGURE 2 Intermolecular hydrogen bond formation for compound (15). The $\text{H} \cdots \text{F}$ bond distance is 3.03 Å.

nitrogen atom renders the two axial fluorine atoms magnetically non-equivalent. Qualitative experiments have shown that the n.m.r. spectrum is concentration dependent supporting the formulation of an intermolecular process.

Solutions of 16 and 17 in toluene show no significant change in their ^{19}F n.m.r. spectra even at -90°C . This can be explained by the larger molecules being unable to form intermolecular hydrogen bonds and normal spectral observations are made.^{2,23}

All the N-substituted compounds, except 10, show no spectral changes at low temperatures. For 10 coalescence of the ^{19}F resonance at -100°C

was observed indicating magnetic non-equivalence. This is expected due to the presence of a prochiral center at nitrogen. We were, however, unable to resolve the spectrum to the expected ABX type.³⁰ (Where A and B = axial F's and X = P).

Compounds 10 and 12 were shown to rearrange thermally in an irreversible process to their P—C—bonded isomers, 18 and 19, respectively. At $+100^\circ\text{C}$ the P—N—bonded isomers are stable, at $+130^\circ\text{C}$ slow rearrangement occurs, and at $+150^\circ\text{C}$ the rearrangement is rapid and goes to completion. On cooling to $+100^\circ\text{C}$ no reversal of this process is seen. These rearrangements were followed by ^{19}F n.m.r.

The ^1H n.m.r. data for all the compounds prepared do not vary significantly from those already reported for other pyrrole systems.^{21,29} The presence or absence of the NH resonance at high field is indicative of the formation of either the C-substituted or N-substituted compounds. Significantly, substitution at the β -carbon atom in 19 causes the two methyl groups at the α -positions to become magnetically non-equivalent and two resonances are observed.

In all cases infrared spectral data were obtained and the appearance of an absorption at approximately 3400 cm^{-1} attributed to the NH stretching frequency³¹ indicated substitution at carbon. This absorption was absent in the case of the P—N—bonded compounds.

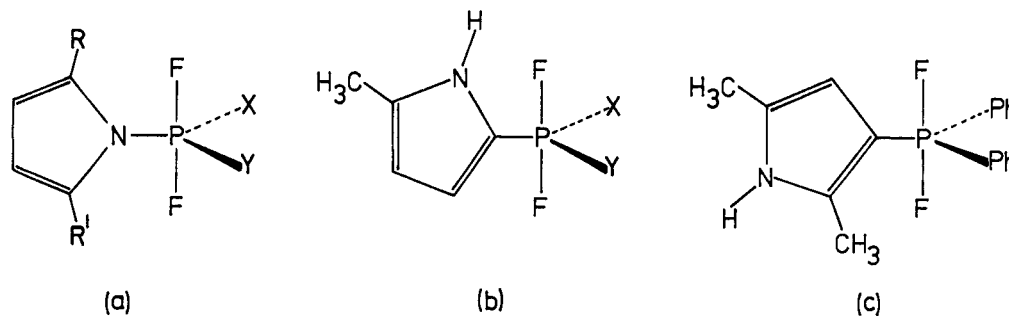


FIGURE 3 Suggested structures for fluorophosphoranyl-pyrrole derivatives. (a) $X = Y = F$ and $R = R' = H$, $X = F$, $Y = Me, Et, Ph$ and $R = R' = H, Me.$, $X = Y = Ph$, $R = R' = H, Me$ or $R = H$ and $R' = Me$, (b) $X = Y = F$, $X = F$ and $Y = Et, Ph$, $X = Y = Ph$, (c) Formed from the thermal rearrangement of (a) where $R = R' = Me$ and $X = Y = Ph$.

MASS SPECTRAL DATA FOR DIFLUOROPHOSPHORANES

In all cases the molecular ion was observed, in agreement with data for other difluorophosphoranes.⁴² Formation of the most abundant fragment was dependent on the nature of the pyrrole derivative. For the P—N—bonded compounds $Ph_2PF_2^+$ (m/e 223) resulting from cleavage of the P—N bond is the most abundant fragment. For **13** cleavage of one P—N bond leads to the base peak at m/e 240 by loss of one pyrrole group. Loss of the second pyrrole entity also occurs and the ion $PhPF_2^+$ (m/e 146) is also present. For the P—C—bonded compounds the most abundant fragment is caused by loss of hydrogen fluoride from the parent molecule as in compound **18**, producing an ion at m/e 283; or by loss of a phenyl group in compound **19**, through cleavage of a P—C bond forming an ion at m/e 240. The loss of HF for the P—N—bonded compounds is either not observed or insignificant, suggesting the necessity of an NH bond for its occurrence. In all cases successive cleavage of P—F and P—C bonds is observed.

All the data are consistent with trigonal bipyramidal structures for the compounds prepared in which the axial positions are occupied by fluorine atoms and the remaining groups take up equatorial positions. The data also suggest that the pyrrole rings which can be considered as π -donor systems are oriented in the axial plane,⁴³ thus accounting for the differing axial fluorine atoms, as in compounds **10** and **15**. Figure 3 shows the suggested structures of these pyrrole derivatives.

EXPERIMENTAL

Nuclear Magnetic Resonance data were obtained on a Varian Associates 60 MHz HA/HR-60 and a Jeol C-60HL spectrometer. The Varian instrument was fitted with an external frequency generator to enable measurement of the ^{19}F n.m.r. spectra by extended lock technique. 1H spectra were measured at 60 MHz using Me_4Si as internal standard; ^{19}F spectra at 56.4 MHz using CCl_3F as internal standard and ^{31}P spectra at 24.3 MHz using sealed capillaries containing 85% H_3PO_4 as external standard. CCl_3F in sealed capillaries was used as an external standard for the high temperature ^{19}F measurements. All the samples were measured as neat liquids except where otherwise stated. The abbreviations ax and F^1 and F^2 refer to axial fluorine atoms; eq and F^3 and F^4 refer to the equatorial fluorine atoms; cat and an refer to cation and anion, respectively, and av refers to average chemical shift and coupling constant for the fluorine atoms.

The usual precautions required in handling moisture sensitive compounds were observed. Organic solvents were dried by standard procedures. N.m.r. samples were prepared in an atmosphere of dry nitrogen or dry argon. Phosphorus pentafluoride was obtained from U.S. Agrichemicals, Decatur, Ga. Pyrrole and 2,5-dimethylpyrrole were obtained from Cilag Chemie, Basel, Switzerland. 2-Methylpyrrole was prepared from 2-pyrrole-aldehyde⁴⁴ by reduction with hydrazine hydrate.⁴⁵ For synthesis of fluorophosphoranes, see Ref. 46 and 47.

The silylamines employed were N-trimethylsilylpyrrole **1**,¹⁸ N-trimethylsilyl-2-methylpyrrole **2**, and N-trimethylsilyl-2,5-dimethylpyrrole **3**.²⁷ They were prepared by standard literature methods and are listed in Table I. Characterisation was carried out by infrared and 1H n.m.r. spectroscopy; Table IV lists the n.m.r. data.

The following examples of the synthesis of the silylamines, tetra-, tri-, and di-fluorophosphoranes illustrate the procedures used in the preparation of the compounds discussed. Data pertinent to the preparation of these compounds, including analyses, are listed in Tables I–III.

N-Trimethylsilyl-2-methylpyrrole (**2**). *N*-Trimethylsilyl-2-methylpyrrole was prepared in a manner similar to that previously described for the preparation of N-trimethylsilyl-2,5-dimethylpyrrole.²⁷ The preparation was carried out on a 0.65

mole scale and the product was purified by vacuum distillation affording a colourless liquid (66% yield) of b.p. 77°C/26 mm. The liquid was stored with exclusion of light at low temperatures in a glass vial.

2-Methyl-5-tetrafluorophosphoranylpyrrole (15). Phosphorus pentafluoride (9.5 g; 0.76 mole) was condensed onto compound **2** (11.6 g; 0.076 mole) in vacuo in a glass reaction tube at -196°C. The tube was sealed and left in a dry-ice/acetone bath at -78°C for two days, during which time the temperature rose to room temperature. The tube was then opened, trimethylfluorosilane (6.6 g; 94%) was allowed to evaporate at room temperature into a -78°C trap, and the remaining semi-solid residue was extracted with three times 20 ml of benzene. Vacuum distillation, after removal of the benzene gave the desired product **15** (10.1 g; 71%) as a colourless liquid of b.p. 76°C/25 mm which subsequently solidified, m.p. 44-45°C.

2-Methyl-5-phenyltrifluorophosphoranylpyrrole (17) Phenyltetrafluorophosphorane (9.2 g; 0.05 mole) and compound **2** (7.6 g; 0.05 mole) were charged, under an atmosphere of dry nitrogen, into a glass reaction tube connected to a vacuum line. The tube was cooled to -196°C, evacuated and sealed. After allowing the tube to warm up to room temperature it was heated at +100°C for 6 hours. After cooling to room temperature and further cooling to -196°C the tube was opened and Me₃SiF collected in a trap at -78°C on warming once again to room temperature. (3.8 g; 83%). Distillation of the remaining product in vacuo gave compound **17** (9.3 g; 76%) as a colourless liquid of b.p. 79°C/0.05 mm.

N-methyltrifluorophosphoranylpyrrole (5) As described in the previous experiment methyltetrafluorophosphorane (11.8 g; 0.096 mole) was allowed to react with compound **1** (13.4 g; 0.096 mole) in a sealed glass reaction tube. Trimethylfluorosilane (7.4 g; 84%) was collected. The remaining liquid was distilled at reduced pressure affording compound **5** (12.1 g; 74%) as a colourless liquid of b.p. 64°C/75 mm.

N-Phenyltrifluorophosphoranyl-2,5-dimethylpyrrole (11) 2,5-Dimethylpyrrole (4.75 g; 0.05 mole) in 100 ml of dry hexane was placed in a flask fitted with a reflux condenser topped by a drying tube, and a pressure-equalising dropping funnel. The system was flushed with dry nitrogen and n-butyllithium (3.2 g; 0.05 mole), as a 15% solution in hexane, was added to the pyrrole through the dropping funnel over a period of 0.5 hr. An exothermic reaction was observed which was moderated by cooling. On completion the reaction mixture was transferred under an atmosphere of dry nitrogen to a dropping funnel attached to another flask containing phenyltetrafluorophosphorane (9.2 g; 0.05 mole) in 50 ml. hexane. The contents of the flask were cooled to -10°C and the lithiated pyrrole was slowly added over a period of 1 hr. The reaction mixture was then allowed to warm up to room temperature and stirring was continued for 20 hours. After filtration in an atmosphere of dry nitrogen the filtrate was distilled in order to remove the solvent and the remaining liquid was distilled under reduced pressure. Compound **11** was obtained as a colourless liquid (9.8 g; 76%) of b.p. 86°C/0.01 mm.

N-Diphenyldifluorophosphoranylpyrrole (8) Pyrrole lithium (4.15 g; 0.05 mole) was prepared as described in the preceding experiment. Diphenyltrifluorophosphorane (12.1 g; 0.05 mole) in 50 ml. of dry hexane was then added over a period of 0.5 h with occasional cooling. On completion the reaction mixture

was refluxed for 1 hr. After filtration of the hot reaction mixture a white crystalline solid separated from the filtrate, and was recrystallised twice from hexane. Yield 12.3 g; (85%); m.p. 97-99°C.

Bis(2,5-dimethylpyrrol)-difluorophosphonium Hexafluorophosphate (14) Phosphorus pentafluoride (8.8 g; 0.069 mole) was allowed to react with **3** (11.6 g; 0.069 mole) in a manner similar to that described for the preparation of **15**. On opening the tube Me₃SiF (5.1 g; 80%) was collected. The remaining solid was washed several times with dry hexane. Analysis and n.m.r. spectra suggested that the product as obtained was of satisfactory purity. N.m.r. data of the reaction mixture indicate the existence of a tetrafluorophosphorane intermediate: $\delta F(av) + 52.4$ ppm; $\delta P + 48.3$ ppm and $^1J_{PF} 922$ Hz. Compound **14** was obtained as a yellow-white crystalline solid (12.4 g; 88%) which was found to decompose gradually upon heating up to and above 180°C.

ACKNOWLEDGEMENTS

We are indebted to Dr. R. Schliebs and Prof. H. Hoffmann of Bayer A. G. for some organo-phosphorus intermediates; thanks are also due to Hoechst A. G. and BASF A. G. for various chemicals and solvents employed in this work. The Jeol n.m.r. instrument was provided through Deutsche Forschungsgemeinschaft. Support through Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. We would like to thank the department of mass spectrometry of the Gesellschaft für Biotechnologische Forschung m.b.H., 3301 Stöckheim-Braunschweig for measurements made on the difluorophosphoranylpyrrole compounds. We would also like to thank Dr. C. Glidewell (University of St. Andrews) for helpful discussions during the course of this work.

REFERENCES

1. Part XLI.: W. Althoff, M. Fild, H. P. Rieck, and R. Schmutzler, *Chem. Ber.*, **111**, 1845 (1978).
2. R. Schmutzler, in *Halogen Chemistry*, ed. V. Gutmann, Academic Press, London and New York, 1967, Vol. 2, p. 31.
3. M. Fild, M. J. C. Hewson, S. C. Peake, and R. Schmutzler, *Inorg. Chem.*, **10**, 2723 (1971).
4. M. J. C. Hewson, S. C. Peake, and R. Schmutzler, *Chem. Comm.*, **1971**, 1454.
5. M. J. C. Hewson and R. Schmutzler, *Z. Naturforsch.*, **27B**, 879 (1972).
6. S. C. Peake, M. J. C. Hewson, O. Schlak, R. Schmutzler, R. K. Harris, and M. I. M. Wazeer, *Phosphorus and Sulfur*, **4**, 67 (1978).
7. R. E. Dunmur and R. Schmutzler, *J. Chem. Soc.*, (A), **1971**, 1289.
8. G. O. Doak and R. Schmutzler, *Chem. Comm.*, **1970**, 476.
9. G. O. Doak and R. Schmutzler, *J. Chem. Soc.*, (A), **1971**, 1295.
10. J. G. Riess, D. U. Robert, G. N. Flatau and C. Demay, *Chem. Comm.*, **1972**, 1127.
11. D. U. Robert, G. N. Flatau, A. Cambon and J. Costa, *Tetrahedron*, **29**, 1877 (1973).
12. J. G. Riess, D. U. Robert and J. Costa, *J. Chem. Soc. Chem. Comm.*, **1973**, 745.

13. D. U. Robert, D. J. Costa and J. G. Riess, *J. Chem. Soc. Chem. Comm.*, **1975**, 29.
14. R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, **1973**, 2687 (and references therein).
15. R. K. Harris, M. Lewellyn, M. I. M. Wazeer, J. R. Woplin, R. E. Dunmur, M. J. C. Hewson, and R. Schmutzler, *J. Chem. Soc. Dalton Trans.*, **1975**, 61.
16. R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsenges. Phys. Chem.*, **76**, 45 (1972).
17. M. J. C. Hewson and R. Schmutzler, *Inorg. Synth.*, **18**, 179 (1978).
18. R. Fessenden and D. F. Crowe, *J. Org. Chem.*, **25**, 598 (1960).
19. R. Schmutzler, *J. Am. Chem. Soc.*, **86**, 4500 (1964).
20. M. J. C. Hewson, S. C. Peake, and R. Schmutzler, unpublished results.
21. A. Gossauer, in *Organische Chemie in Einzeldarstellungen*, ed. H. Bredereck, K. Hafner and E. Müller, Springer Verlag, Berlin, Heidelberg, New York, 1974, Vol. 15, p. 1.
22. J. J. Mrowca, U.S. Pat. 3816452 (to E. I. duPont de Nemours and Co., Inc.) 1974.
23. R. Schmutzler, in *Advances in Fluorine Chemistry*, ed. M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths London, 1965, Vol. 5, p. 31.
24. W. Althoff, M. Fild, H. Koop, and R. Schmutzler, *J. Chem. Soc. Chem. Comm.*, **1975**, 468.
25. M. J. C. Hewson, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc. Chem. Comm.*, **1973**, 190.
26. W. S. Sheldrick, *J. Chem. Soc. Dalton Trans.*, **1973**, 2301.
27. J. Nagy, P. Hencsei and E. Gergö, *Z. Anorg. Allg. Chemie.*, **367**, 295 (1969).
28. J. C. Pommier and D. Lucas, *J. Organometal. Chem.*, **57**, 139 (1973).
29. R. L. Hinman and S. Theodoropoulos, *J. Org. Chem.*, **28**, 3052 (1963).
30. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press Ltd., 1965, Vol. 1 and 2, p. 457, 787.
31. N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy"; Academic Press International Edition, New York and London, 1964, p. 237, 279.
32. J. F. Nixon and R. Schmutzler, *Spectrochim. Acta.*, **20**, 1835 (1964).
33. R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
34. P. Diehl, R. K. Harris, and R. G. Jones, *Prog. NMR Spectrosc.*, **3**, 1 (1967).
35. R. K. Harris and M. Kinns, *Nuclear Magnetic Resonance Programs*, Atlas Computer Laboratory, Chilton (U.K.), 1974.
36. E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).
37. F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **7**, 172 (1968).
38. J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, **10**, 1538 (1971).
39. R. Goodrich-Haines and J. W. Gilje, *Inorg. Chem.*, **15**, 470 (1976).
40. R. B. Johannesen, S. C. Peake and R. Schmutzler, *Z. Naturforsch.*, **29B**, 669 (1974).
41. S. C. Peake and R. Schmutzler, C.N.R.S. Symposium, Paris, May 1969, *Actes*, Vol. **182**, p. 101 (1970).
42. T. A. Blazer, R. Schmutzler, and I. K. Gregor, *Z. Naturforsch.*, **24B**, 1081 (1969).
43. R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).
44. R. M. Silverstein, E. E. Ryskiewicz, and C. Willard, *Org. Synth.*, **36**, 74 (1956).
45. A. J. Castro, J. F. Deck, M. T. Hugo, E. J. Lowe, J. P. Marsh, and R. J. Pfeiffer, *J. Org. Chem.*, **28**, 857 (1963).
46. R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).
47. R. Schmutzler, *Inorg. Synth.*, **9**, 65 (1967).