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THE PREPARATION AND PROPERTIES OF 1-DIFLUOROPHOSPHINO-PYRROLE

D.W.H. RANKIN* and J.G. WRIGHT†

Chemistry Department, University of Edinburgh, West Mains Road,
Edinburgh EH9 3JJ (Gt. Britain)

SUMMARY

Difluorophosphino-pyrrole has been prepared by the reaction of pyrrole with bromo- and chloro- difluorophosphine in the presence of trimethylamine. It is also formed in an exchange reaction between silyl pyrrole and bromodifluorophosphine. It has been characterised by n.m.r., i.r., mass and photoelectron spectroscopy. Reaction with diborane gives a monoborane complex, $H_3B.PF_2(NC_4H_4)$.

INTRODUCTION

Although very many aminodifluorophosphines are known, there are very few in which the nitrogen atom is part of a ring. The few that have been studied include derivatives of pyrrolidine [1], piperidine [2], and morpholine [3], but no derivatives of unsaturated systems or aromatic heterocycles. The latter compounds would be interesting because the nitrogen lone pairs of electrons would be involved in π-bonding with the aromatic system, and would not be fully available for (p → d) π-bonding with phosphorus. As a consequence the P-N bonds should be regarded as effectively single bonds, and in particular it would be expected that the P-N distances would more closely approach the theoretical single-bond length than in other aminodifluorophosphines.

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† Present address: Department of Chemistry, City of London Polytechnic, Jewry Street, London.

The most suitable compound for study is the difluorophosphino-derivative of pyrrole, which should be a simple, low molecular weight species of high volatility. We have therefore prepared this compound, and report here its spectroscopic and chemical properties.

RESULTS AND DISCUSSION

Preparation

When pyrrole was mixed with chloro- or bromo-difluorophosphine in the gas or liquid phase the only reaction that occurred was polymerisation of the pyrrole, apparently catalysed by the phosphine. However, in the presence of trimethylamine, white solids were rapidly formed, and $PF_2(NC_4H_4)$ was formed (equation 1).

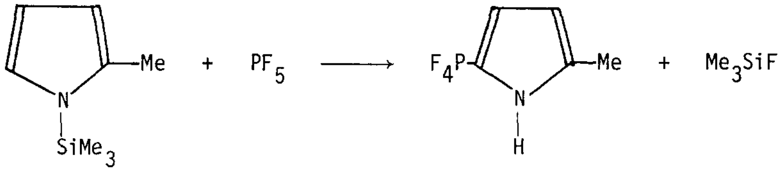
$$PF_2X + HNC_4H_4 + NMe_3 \longrightarrow PF_2(NC_4H_4) + [NHMe_3]X \quad (X = Cl, Br) \qquad (1)$$

There must be some side reactions, as the yield obtained was only about 60%, and the only volatile by-product was PF_3, together with some unreacted PF_2X. The product was a colourless liquid, stable at room temperature for periods of at least several hours. It is therefore more stable than the pyrrolidino derivative, which disproportionates at room temperature [1].

Difluorophosphino-pyrrole was also prepared by an exchange reaction between silyl pyrrole and $PBrF_2$. That this reaction occurs is of interest, as a similar exchange with trisilylamine does not take place, and disilylamine exchanges only one silyl group, to give $PF_2[NH(SiH_3)]$ [4]. It may be that the ease of reaction in the present case reflects the fact that silyl pyrrole has an unusually weak [5] and long [6] Si-N bond.

N.m.r. Spectra

The ^1H, ^{19}F and ^{31}P n.m.r. spectra of $PF_2(NC_4H_4)$ provided unequivocal evidence of its identity, and indicate that the phosphino-group is substituted on nitrogen, not on carbon. This is of interest, as reaction of 1-trimethylsilyl-2-methyl-pyrrole with PF_5 gives 2-methyl-5-tetrafluorophosphoranylpyrrole [7].



The ^{31}P spectrum is a wide triplet due to coupling with two fluorine atoms, with further coupling to ^{14}N (clearly resolved) and to two equivalent protons. The ^{19}F spectrum is also first order, showing coupling only to ^{31}P, but the protons give a deceptively simple second order spectrum, arising from the $[AB]_2X$ spin system. This spectrum has two resonances: one is a triplet, and the other is an apparent quintet, being a triplet of doublets (due to ^{31}P). A similar spectrum of two triplets has been reported for furan [8]. Full analysis of the spectrum in the present case was not possible, as broadening of the lines by ^{14}N obscured finer details, but double resonance experiments confirmed that the β protons were not coupled to either ^{31}P or ^{19}F, while the α protons were coupled to ^{31}P.

The n.m.r. parameters are listed in Table 1. It should be noted that the ^{31}P chemical shift is to low frequency of those of other aminodifluorophosphines [9,10]. This probably reflects a lower interaction between the nitrogen lone pair of electrons and the phosphorus 3d orbitals in the pyrrole derivative.

TABLE 1

N.m.r. Parameters for $PF_2(NC_4H_4)^a$

$\delta(^1H_\alpha)$/ppm	7.17
$\delta(^1H_\beta)$/ppm	6.49
$\delta(^{19}F)$/ppm	-64.6
$\delta(^{31}P)$/ppm	132.0
$^1J(^{31}P^{19}F)$/Hz	1256.9
$^1J(^{31}P^{14}N)$/Hz	39
$J(^1H_\alpha{}^1H_\beta)$/Hz	2.1^b
$^3J(^{31}P^1H_\alpha)$/Hz	4.5

(a) Studied in CCl_3D at 295 K

(b) Apparant splitting of triplets: see text

Other couplings were not resolved

TABLE 2

Gas Phase i.r. Spectrum of $PF_2(NC_4H_4)$

Frequency/cm^{-1}	Assignment
3160 vw	C-H stretch
3124 vw	
1547 w	Ring Stretch
1540 w	
1473 m	
1462 sh	
1437 w	
1432 w	
1400 vw	
1298 w	
1242 m	C-H in-plane def.
1213 s	
1205 s	
1072 s	Ring stretch and P-N stretch?
1042 m	
982 w	
866 s	C-H out-of-plane def. and PF_2 stretch
850 vw	
828 vw	
825 vw	
787 vw	C-H out-of-plane def.
780 vw	
734 s	
700 vw	Ring in-plane def.
652 vw	
616 w	Ring out-of-plane def.
610 w	
557 s	
435 w	PF_2N def.
418 w	
411 w	
365 w	
327 w	
246 w	
226 w	
202 w	

Infra-red Spectrum

The i.r. spectrum of $PF_2(NC_4H_4)$ in the gas phase (Table 2) has been assigned by comparison with the spectra of unsubstituted pyrrole [11], other substituted five-membered rings [12] and other aminodifluorophosphines [10]. The assignment of the P-N stretching mode is made very tentatively: it could well lie with the P-F stretching modes at about 850 cm^{-1}, in which case the band at 1042 cm^{-1} would probably be a C-H in-plane deformation mode.

Of particular importance is the absence of any band that can be associated with N-H stretching. The i.r. spectrum of 2-methyl-5-tetrafluorophosphoranylpyrrole contained a strong absorption at 3450 cm^{-1} [7] : the absence of such a band in the present case clearly indicates that the $-PF_2$ group is bound to the nitrogen.

Mass Spectrum

There are few prominent ions in the mass spectrum, recorded in Table 3, and the major species present corresponds to the parent ion. The main fragmentation paths involve simple cleavage of the P-N bond, yielding $[PF_2]^+$ or $[NC_4H_4]^+$.

TABLE 3

Mass Spectrum

m/e	Relative Abundance	Ion
135	100	$[PF_2(NC_4H_4)]^+$
109	10	$[PF_2(NC_2H_2)]^+$
108	6	$[PF_2(NC_2H)]^+$
96	10	$[PF_2(NCH)]^+$, $[P(NC_4H_3)]^+$
69	61	$[PF_2]^+$
66	30	$[NC_4H_4]^+$
39	26	$[NC_2H]^+$, $[C_3H_3]^+$
38	6	$[NC_2]^+$, $[C_3H_2]^+$

Photo-electron Spectrum

Details of the He(I) photo-electron spectrum of $PF_2(NC_4H_4)$ are given in Table 4. The similarities between this spectrum and that of unsubstituted pyrrole [13] indicate that no disruption of the ring π-system has occurred, and that the pyrrole ring has retained its aromaticity, and make assignment of the spectrum straightforward. None of the peaks showed vibrational fine structure, unlike those in the spectrum of pyrrole.

TABLE 4

He(I) Photoelectron Spectrum

Ionisation potential (eV)	Assignment
8.85	C-C π
9.85	C-C π
11.20	P $3p_z$
13.25	
14.10	C-C, C-N, C-H bonding 2p
14.65	
15.55	P-N σ
16.55	F $2p_\pi$
18.4	C-C, C-N, C-H bonding 2s
>19	P-F σ

Reactions with Hydrogen Halides

A rapid reaction occurred between HCl or HBr and $PF_2(NC_4H_4)$ in solution in CCl_3D at room temperature, with the quantitative formation of PF_2X and polymerised pyrrole. This shows that the formation of an ammonium salt is not necessary to drive this type of reaction to completion.

Reaction with Diborane

When excess B_2H_6 was allowed to react with $PF_2(NC_4H_4)$ in an n.m.r. tube at room temperature, yellow solids were formed, and n.m.r. spectra showed that the BH_3 adduct, $H_3B.PF_2(NC_4H_4)$ had been formed, together with smaller amounts of $H_3B.PF_3$ and $H_3B.PF_2H$, identified by their n.m.r. parameters. The formation of the last species is interesting, as it implies that reduction of the phosphine by borane has occurred, presumably with oxidation of the diborane to a higher borane. Overlapping of peaks in the n.m.r. spectra prevented verification of this.

TABLE 5

N.m.r. Parameters for $H'_3B.PF_2(NC_4H_4)^a$

$\delta(^1H_\alpha)$/ppm	7.11
$\delta(^1H_\beta)$/ppm	6.50
$\delta(^1H')$/ppm	0.89
$\delta(^{19}F)$/ppm	-69.6
$\delta(^{31}P)$/ppm	124.0
$^1J(^{31}P^{19}F)$/Hz	1228.5
$^1J(^{11}B^1H')$/Hz	106
$^1J(^{31}P^{11}B)$/Hz	56.2
$^2J(^{31}P^1H')$/Hz	19.4
$^3J(^{19}F^1H')$/Hz	17.6

a) Studied in CCl_3D at 295 K.
Other couplings were not resolved: see text

N.m.r. parameters of the borane adduct are listed in Table 5. The fairly high chemical shift of the borane protons and low values for BH and PB couplings imply that the free phosphine is of low basicity [14,15], consistent with the idea that there is little delocalisation of electrons from nitrogen to phosphorus. The ring proton spectra were not sufficiently well resolved to be fully analysed, but their symmetry implies that the $-PF_2$ group has remained bound to the nitrogen atom. All the couplings are consistent with the proposed formulation.

EXPERIMENTAL

All volatile compounds were handled using a Pyrex glass vacuum line, fitted with Sovirel greaseless taps. Silyl pyrrole [16], $PBrF_2$ and $PClF_2$ [17] were prepared by standard procedures. N.m.r. spectra were recorded using Varian Associates EM360 and XL100 spectrometers, i.r. spectra with a Perkin-Elmer 557 spectrometer (4000 - 200 cm^{-1}), mass spectra with a double-focussing AEI MS902 instrument operating at 70 eV, and u.v. photoelectron spectra with a Perkin-Elmer PS16 spectrometer with He(I) (21.22 eV) excitation.

Preparation of $PF_2(NC_4H_4)$

Dry pyrrole (0.082 g, 1.2 mmol) was condensed into a glass ampoule (40 ml) with $PClF_2$ (1.4 mmol) and NMe_3 (1.4 mmol). On warming to room temperature white solids were formed, and the reaction was shown by i.r. spectroscopy to be complete after 30 minutes. Fractionation of the volatile products yielded difluorophosphino-pyrrole (0.7 mmol, 58%), passing a trap held at 227 K but retained at 209 K. A mixture of PF_3 and $PClF_2$ (0.45 mmol) was recovered from a trap held at 77 K.

In a similar reaction pyrrole (0.146 g, 2.2 mmol), $PBrF_2$ (2.3 mmol) and NMe_3 (2.3 mmol) reacted completely in 30 seconds at room temperature, yielding $PF_2(NC_4H_4)$ (1.24 mmol, 56%) and a mixture of PF_3 and $PBrF_2$ (0.60 mmol).

Reaction of $PBrF_2$ with $SiH_3(NC_4H_4)$

Excess $PBrF_2$ (0.3 mmol) and $SiH_3(NC_4H_4)$ (0.2 mmol) were warmed to room temperature in an n.m.r. tube with CCl_3D solvent. N.m.r. spectra were run immediately, and showed the presence of $PF_2(NC_4H_4)$, $SiBrH_3$ and a trace of SiH_4 and pyrrole polymer.

Reactions of $PF_2(NC_4H_4)$ with HCl and HBr

The room temperature reactions of $PF_2(NC_4H_4)$ (0.35 mmol) with equimolar quantities of HCl or HBr were carried out in n.m.r. tubes, with CCl_3D as solvent. ^1H and ^{31}P n.m.r. spectra showed that $PClF_2$ or $PBrF_2$ and pyrrole polymer were rapidly and quantitatively formed.

Reaction of $PF_2(NC_4H_4)$ with B_2H_6

Excess B_2H_6 (0.4 mmol) was condensed with $PF_2(NC_4H_4)$ (0.6 mmol) in an n.m.r. tube, with CCl_3D as solvent. N.m.r. spectra were recorded at room temperature.

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