TOPICS IN THE
CHEMISTRY OF MAIN-GROUP
AND TRANSITION-METAL FLUORIDES

THESIS

submitted to the

UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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September 1974

ACKNOWLEDGEMENTS

I am especially grateful to my supervisor Professor D.W.A. Sharp and to Dr. R. Keat and Dr. J.M. Winfield for their encouragement and advice during the course of this work.

My thanks is also expressed to Dr. A.P. Lane and my postgraduate colleagues for their help in obtaining Raman and mass spectra.

The financial support of the University of Glasgow, in the form of a demonstratorship, is gratefully acknowledged.

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ABSTRACT

Phosphinylamines, $Cl_2P(O)NHR$ (R = Me, Et and Ph), were obtained by the reaction of amine hydrochlorides, $RNH_2.HCl$, with phosphoryl chloride, $P(O)Cl_3$. Fluorination of these derivatives by sodium fluoride produced the compounds $F_2P(O)NHR$. Bis(dichlorophosphinyl)amines, $[Cl_2P(O)]_2NR$, and their fluoro-derivatives were synthesised by the condensation of the phosphinylamines with phosphoryl halides, $P(O)F_nCl_{3-n}$, in the presence of a tertiary amine. The difluoro- derivative, $[FClP(O)]_2NMe$, was obtained as a mixture of diastereoisomers from the reaction of heptamethyldisilazane, $(Me_3Si)_2NMe$, with $P(O)FCl_2$. Attempts to synthesise the difluoro- compounds, $Cl_2P(O)NRP(O)F_2$, from $F_2P(O)NHR$ and $P(O)Cl_3$ resulted in the formation of impure products. Possible reasons for this are discussed. The trifluoro- compounds, $F_2P(O)NRP(O)FCl$, were not prepared. ^1H, ^{19}F and ^{31}P n.m.r. data are given for the diphosphinylamines synthesised, together with their infrared and mass spectra. The spectra are compared with those obtained from the phosphinylamines.

Heptamethyldisilazane, $(Me_3Si)_2NMe$, and tungsten hexafluoride, WF_6, reacted in the absence of a solvent to produce a white solid formulated as WF_4NMe and in the presence of MeCN to produce the complex $WF_4NMe.MeCN$. The coordinated MeCN could be displaced by C_5H_5N (py) forming the complex $WF_4NMe.py$. The adducts were characterised by elemental analyses and by n.m.r. and mass spectroscopy. Their spectra, together with those of $WF_4NMe.CD_3CN$ and $WF_4NMe.C_5D_5N$, are presented and discussed. Possible structures for both WF_4NMe and $WF_4NMe.MeCN$ are

suggested.

A preliminary investigation into the chemistry of $WF_4NMe.MeCN$ showed that the fluorine atoms could be replaced but that the compound did not react with SF_5Cl, SO_2 or CS_2.

Hexamethyldisilazane, $(Me_3Si)_2NH$, and WF_6 reacted in the presence of MeCN to produce a solid whose elemental analysis, infrared and n.m.r. spectra suggest that it has the composition $NH_4^+WOF_5^-.MeCN$.

A reaction carried out between MoF_6 and $(Me_3Si)_2NMe$ in MeCN suggests that MoF_6 reacts in a manner similar to that described for WF_6 but that the reaction products are more susceptible to hydrolysis.

Sulphur chloride pentafluoride, SF_5Cl, reacted exothermically with the chlorophosphines $PhPCl_2$ and Ph_2PCl to produce the corresponding fluorophosphoranes $PhPF_4$ and Ph_2PF_3 along with SCl_2 and Cl_2. When SF_5Cl reacted with $MePCl_2$, although the phosphorane $MePF_4$ was formed, the major product was a white solid which analysed as $CH_{2.3}Cl_5FP$ but which was not further characterised. The reactions between SF_5Cl and the halogen free derivatives $P(NMe_2)_3$ and $P(OMe)_3$ produced SF_4, Cl_2 and other products which were not completely identified but for which structures are suggested. SF_5Cl did not react with either PPh_3 or PCl_3. Reaction schemes for these oxidative fluorinations by SF_5Cl are presented ahd discussed.

A detailed analysis of the vibrational spectra of CF_3SF_4Cl was carried out. This confirmed the evidence from n.m.r. spectroscopy that only the trans isomer of the compound is obtained from the synthesis involving CF_3SF_3, Cl_2 and CsF. The infrared and Raman spectra of other substituted derivatives of SF_6, $CF_3SF_4CF_2CF_2Cl$, $SF_5CF_2CF_2Cl$ and $SF_5CH=CH_2$ are presented and discussed.

INTRODUCTION

The chemistry of fluorine and its derivatives reflects almost two hundred years of chemical research and incorporates much of the Periodic Table. There are three main factors which explain why the chemistry of fluorine is different from that of the other halogens. These have been discussed many times [1,2] but can be summarised as:-

i) The low dissociation energy of the fluorine molecule.

F_2	Cl_2	Br_2	I_2	
37.7	58.2	46.1	36.1	Kcal mole^{-1} [3]

ii) The relatively small size of the fluorine atom and the fluoride ion.

F	Cl	Br	I	O	S	
0.64	0.99	1.14	1.33	0.66	1.04	covalent radius in Å
1.36	1.81	1.95	2.16	1.40	1.84	ionic radius in Å [4]

iii) The relatively high strength of bonds formed between fluorine and other elements [3].

Compound	Bond	Bond Strength (Kcal mole^{-1})
HF	H-F	135.8
HCl	H-Cl	103.3
HBr	H-Br	87.5
PF_3	P-F	119.0
PCl_3	P-Cl	79.0
SiF_4	Si-F	143.0
$SiCl_4$	Si-Cl	96.0
$SiBr_4$	Si-Br	79.0

Some consequences of these physical properties are the high reactivity of the element resulting in combinations with almost every known element, the ability of fluorine to stabilise high oxidation states and the formation of volatile inorganic fluorides.

Research into the chemistry of fluorine derivatives had been hindered by the difficulty of handling them; a problem which has been largely overcome with the use of, for example, suitable glass high-vacuum systems, materials such as "teflon" and all-metal apparatus. These developments, together with some economic factors, resulted in a rapid growth of the subject.

The development of spectroscopy, in particular high-resolution nuclear magnetic resonance spectroscopy, greatly helped investigations into the structure of fluorine compounds. Four factors are considered necessary for the successful study of a nucleus by n.m.r. spectroscopy:-

i) The magnetic moment of the nucleus must be large because the natural sensitivity of a nucleus to n.m.r. detection at constant field strength is proportional to the cube of the magnetic moment,

^{19}F	^{1}H	^{14}N	
2.627	2.793	0.404	nuclear magnetons [5]

ii) The isotope should have a high natural abundance, again because of the problem of sensitivity,

^{19}F is 100% abundant.

iii) The isotope should have a spin quantum number of $I = \frac{1}{2}$ since higher spin quantum numbers have quadrupole moments associated with them which in turn can interact with fluctuating electric field gradients leading to line broadening,

^{19}F $\quad I = \frac{1}{2}$

iv) The nucleus must possess a short relaxation time to avoid saturation of the signal which causes it to broaden and decrease in size. Relaxation times for ^{19}F nuclei are longer than those for ^{1}H nuclei but are still short enough to allow the nucleus to be easily studied.

Thus the nuclear properties of ^{19}F, similar to those of ^{1}H, make it ideal for study by high-resolution n.m.r. spectroscopy. ^{19}F spectra have the added advantage that the range of chemical shifts and coupling constants is large compared with those obtained from ^{1}H spectra, which means that any changes in the magnetic or electronic environment around the nuclei are usually easily observed.

Vibrational spectroscopy has been used in recent years as a tool in structure elucidation. Its usefulness as a tool is that both Raman and infrared spectroscopy are readily applicable to all three states; solid, liquid and gas. A great deal of assistance, in the determination of molecular symmetry, may be gained from a study of the Raman spectrum of a substance since it is often simpler than the infrared spectrum. The difficulty of handling inorganic fluorine compounds is reflected in the relatively small volume of work published on the vibrational spectra of such derivatives, compared with the vast amount of literature on vibrational spectroscopy as a whole. A recent review article summarises the work carried out, so far, on inorganic fluorides [6].

Mass spectrometry is the most recent spectroscopic technique to be utilised widely by inorganic chemists [7]. While it has a general applicability, its use in inorganic fluorine chemistry has been limited but the wider availability of instruments should lead to a development of its use in this subject.

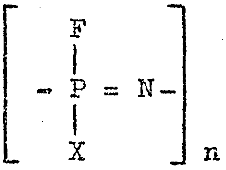
The development of advanced instrumentation in spectroscopy, together with the wider availability of X-ray crystallography, has led to a shift in emphasis in fluorine chemistry research. Previously efforts have been concentrated on the preparation of new types of compounds whereas now the emphasis seems to lie on structure elucidation, determination of bond energies etc. and the theoretical and physicochemical aspects of the element. This trend in research can be seen from a study of recent review articles. A summary of the lower sulphur fluorides, by Seel [8], includes, as a major part of the work, molecular and structural data in contrast to earlier reviews of sulphur fluorine compounds where the emphasis has been on the preparation of the derivatives. Also a paper on the dissociation energy of fluorine starts by summarising older experimental work and concludes with a review of recent various theoretical evaluations of the dissociation energy presenting in some depth the results of new calculations [9].

The work described in this thesis is concerned with some substituted derivatives of main-group and transition-metal halides, mainly fluorides. N.m.r. vibrational spectroscopy and mass spectrometry are used extensively in the study of these derivatives.

INTRODUCTION

In recent years rapid progress has been made in the study of the chemistry of phosphorus-fluorine-nitrogen compounds. The subject has been discussed in several extensive reviews on phosphorus fluorine chemistry [10-12]. However, relatively few fluoro- compounds containing P-N-P linkages have been prepared.

The first examples of phosphorus fluorine compounds containing P=N-P bonds to be discovered were fluorocyclophosphazenes and recently there has been a considerable development of their chemistry [13]. These compounds have the general formula:-



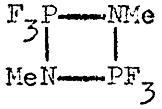
$$\left[-\overset{\displaystyle F}{\underset{\displaystyle X}{P}} = N- \right]_n$$

X = F, Cl, alkyl, aryl, amino etc.

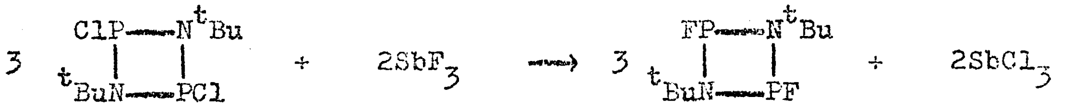
The results of single crystal studies confirm that those compounds which have the formula $(NPR_2)_{3-8}$ are cyclic, while other studies indicate that materials having the formula $(NPR_2)_{n>8}$ are long-chain polymeric species.

Cyclic phosphazenes are found with both planar and puckered phosphorus nitrogen rings. $(NPF_2)_3$ [14], $(NPCl_2)_3$ [15] and $N_3P_3FCl_5$ [16] have planar or nearly planar rings, while the majority of higher cyclic species examined are non-planar.

The first fluorine containing diphosphorus compound with formally saturated P-N-P bridges was fluoro-N,N'-dimethyl-1,3;2,4-diazadiphosphetidine,



This was produced by the reaction of heptamethyldisilazane with phosphorus pentafluoride [17]. An electron diffraction study of this compound demonstrated that the ring is planar with the methyl carbons in the plane of the ring [18]. Other routes to this type of derivative, including P(III) analogues, were later devised. An example of such a route is :-



The first reported acyclic fluorine compounds containing P-N-P linkages were the alkylaminobisdifluorophosphines, $RN(PF_2)_2$ [20]. These were prepared by the series of reactions:-

$$\begin{array}{lcl} RNH_3Cl + 2PCl_3 & \rightleftharpoons & RN(PCl_2)_2 + 3HCl \\ 3RN(PCl_2)_2 + 4SbF_3 & \longrightarrow & 3RN(PF_2)_2 + 4SbCl_3 \\ & & R = Me, Et. \end{array} \qquad (i)$$

Bis(difluorophosphinyl)methylamine and its thio-analogue, $[F_2P(X)_2]_2NMe$ (X = O or S), were among the first acyclic pentavalent phosphorus compounds with P-N-P bridges to be synthesised [21]. They were made by a condensation reaction of the type:-

$$\begin{array}{l} EPF_2NHR + EPF_2Cl \xrightarrow[\text{tertiary amine}]{} F_2P(E)NRP(E)F_2 + \text{amine salt} \\ \qquad\qquad\qquad E = O,S;\ R = Me \end{array} \qquad (ii)$$

Recent studies have produced a series of such derivatives including some chlorofluoro- compounds [22]. These were also made by a reaction of type (ii).

The compounds $F_2PNMePF_4$ and $F_2PNMeP(O)F_2$ have also been synthesised [23]. They were prepared by another route, namely cleavage of a silicon nitrogen bond, for example:-

$$F_2PNMeSiMe_3 + PF_5 \longrightarrow F_2PNMePF_4 + Me_3SiF$$

These acyclic P-N-P compounds were all found to be volatile moisture-sensitive liquids. They are of interest for the following reasons:-

i) They can provide a comparison of the way in which the nitrogen bridge is effective in transmitting electronic effects relative, for example, to the oxygen atom in pyrophosphoryl halides, $[X_2P(O)]_2O$ (X = F,Cl).

ii) They can provide direct comparisons of the properties of P-N-P linkages by reference to spectroscopic properties.

iii) A comparison can be made between the products of fluorination of $[Cl_2P(O)]_2NR$ and, for example, those of $N_3P_3Cl_6$ where fluorination by potassium fluoride in sulphur dioxide takes place by a geminal pathway [24].

With studies of this type in mind, a series of compounds of the type $X_2P(O)NRP(O)X_2$ where X = F,Cl and R = Me,Et,Ph were prepared. Investigation into chloro- and chlorofluoro-derivatives made available information about the electronic environment at phosphorus conferred by fluorine as compared with chlorine.

SUMMARY OF REACTIONS

1. $MeNH_2.HCl + P(O)Cl_3 \xrightarrow[-2HCl]{} Cl_2P(O)NHMe$
2. $EtNH_2.HCl + P(O)Cl_3 \xrightarrow[-2HCl]{} Cl_2P(O)NHEt$
3. $PhNH_2.HCl + P(O)Cl_3 \xrightarrow[-2HCl]{} Cl_2P(O)NHPh$
4. $Cl_2P(O)NHMe + xsNaF \longrightarrow F_2P(O)NHMe + NaCl$
5. $Cl_2P(O)NHEt + xsNaF \longrightarrow F_2P(O)NHEt + NaCl$
6. $Cl_2P(O)NHPh + xsNaF \longrightarrow F_2P(O)NHPh + NaCl$
7. $Cl_2P(O)NHMe + P(O)Cl_3 \xrightarrow[-HCl]{Et_3N} [Cl_2P(O)]_2NMe$
8. $Cl_2P(O)NHEt + P(O)Cl_3 \xrightarrow[-HCl]{Et_3N} [Cl_2P(O)]_2NEt$
9. $Cl_2P(O)NHPh + P(O)Cl_3 \xrightarrow[-HCl]{Et_3N} [Cl_2P(O)]_2NPh$
10. $Cl_2P(O)NHMe + P(O)FCl_2 \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NMeP(O)FCl$
11. $Cl_2P(O)NHEt + P(O)FCl_2 \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NEtP(O)FCl$
12. $Cl_2P(O)NHPh + P(O)FCl_2 \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NPhP(O)FCl$
13. $Cl_2P(O)NHMe + P(O)F_2Cl \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NMeP(O)F_2$
14. $Cl_2P(O)NHEt + P(O)F_2Cl \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NEtP(O)F_2$
15. $Cl_2P(O)NHPh + P(O)F_2Cl \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NPhP(O)F_2$
16. $F_2P(O)NHMe + P(O)F_2Cl \xrightarrow[-HCl]{Me_3N} [F_2P(O)]_2NMe$
17. $F_2P(O)NHEt + P(O)F_2Cl \xrightarrow[-HCl]{Et_3N} [F_2P(O)]_2NEt$
18. $F_2P(O)NHPh + P(O)F_2Cl \xrightarrow[-HCl]{Et_3N} [F_2P(O)]_2NPh$

19. $F_2P(O)NHMe + P(O)Cl_3 \xrightarrow[-HCl]{Et_3N} Cl_2P(O)NMeP(O)F_2$ + other products

20. $(Me_3Si)_2NMe + 2P(O)FCl_2 \longrightarrow [FClP(O)]_2NMe + 2Me_3SiCl$

21. $F_2P(O)NHMe + Et_3N \longrightarrow$ an unidentified mixture of products

22. $F_2P(O)NHMe + P(O)FCl_2 \longrightarrow$ an unidentified mixture of products

23. $[Cl_2P(O)]_2NMe$ + NaF etc. $\longrightarrow [F_2P(O)]_2NMe$ + other products

NOMENCLATURE

A summary of the nomenclature used in describing the phosphorus nitrogen compounds discussed in this chapter is given below:-

i) Phosphinylamines : compounds containing one $>P(O)-N<$ linkage

ii) Diphosphinylamines : compounds containing a $>P(O)-\underset{|}{N}-P(O)<$ linkage

iii) Bis(dihalogenophosphinyl)amines : compounds of the type $X_2P(O)-NR-P(O)X_2$ where $X = F,Cl$; $R = Me,Et,Ph$.

eg. bis(dichlorophosphinyl)methylamine: $[Cl_2P(O)]_2NMe$ and dichlorophosphinyl(difluorophosphinyl)methylamine: $Cl_2P(O)NMeP(O)F_2$

RESULTS

Chloro- and fluorophosphinylamines. The phosphinylamines, $X_2P(O)NHR$ $X = Cl,F$; $R = Me,Et$ and Ph, were prepared with the intention of using them as precursors for the syntheses of the diphosphinylamines, $[X_2P(O)]_2NR$. In view of the fact that, of the series of compounds, only the methyl derivatives had previously been prepared, they were studied in detail to see if any information could be derived from them concerning both the relationship between the chemical shifts of the ^{19}F and ^{31}P nuclei and the substituents attached to these atoms, and possibly about the nature of the phosphorus nitrogen bond.

Preparation of $X_2P(O)NHR$. The chlorophosphinylamines are prepared in an analogous manner to dichlorophosphinylmethylamine according to the following equation:-

$$RNH_2.HCl + POCl_3 \longrightarrow Cl_2P(O)NHR + 2HCl$$ [25]

The fluoro- compounds, $F_2P(O)NHR$, are made by fluorination of the chloro- derivatives with sodium fluoride in a suitable solvent. Full details are given in the Experimental section. Methyl and ethyl dichloro- and difluorophosphinylamines are colourless liquids and the phenyl derivatives are crystalline solids. All the compounds hydrolyse slowly in air.

Characterisation of $X_2P(O)NHR$.

1) N.M.R. Spectra.

^1H Spectra. Details are given in Table 1.1. These can all be interpreted on a first order basis. The ^1H spectra of $Cl_2P(O)NHMe$ and $F_2P(O)NHMe$ have been published several times [25,26] and the results here are in general agreement with those already found. The spectrum of $Cl_2P(O)NHEt$ is more complex and it

TABLE 1.1

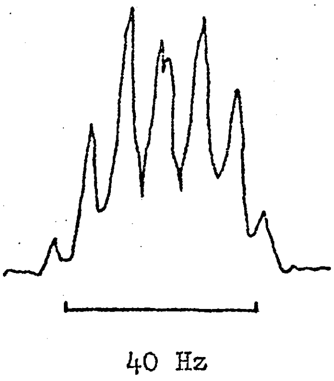
^{1}H N.M.R. Spectra of $X_2P(O)NHR$

	δ_{CH_3}*	δ_{CH_2}	δ_{N-H}	$^3J(P\underline{}NCH)$Hz
$Cl_2P(O)NHMe$	2.77			19.5
$Cl_2P(O)NHEt$	1.78	3.68	6.6	22.0
$F_2P(O)NHMe$	3.02		5.85	14.3
$F_2P(O)NHEt$	1.43	3.30	5.80	13.7

* Throughout this thesis positive values of δ represent downfield shifts from an external reference.

proved difficult to obtain accurate values for some of the coupling constants. In particular, the signal due to the methylene protons is complex since coupling can take place between these protons and the methyl protons, the proton on the nitrogen atom and the phosphorus atom. The spectrum is reproduced in Figure 1.1.

FIGURE 1.1



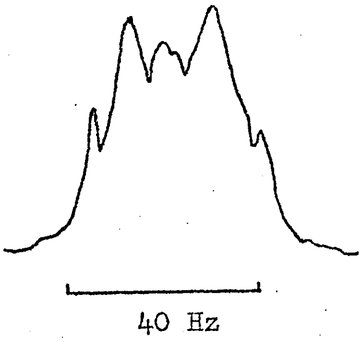
$J(C\underline{H}_2\text{-}N\text{-}\underline{P}) = 22$Hz

$J(C\underline{H}_2\text{-}C\underline{H}_3) = 7.2$Hz

With $F_2P(O)NHEt$ further coupling of the methylene protons to the fluorine atoms is observed. There may be coupling between the phosphorus or fluorine atoms and protons in the phenyl compounds but this was not easily established. Coupling between ^{31}P nuclei and protons has been observed in P-phenyl compounds such as triphenylphosphine and some of its derivatives [27]. With these compounds the coupling was resolved using spin decoupling and solvent shift techniques.

A signal due to the N-H proton is observed in the spectra of these phosphinylamines but only in $Cl_2P(O)NHEt$ does any fine structure appear. Here the signal is a doublet of triplets which is due to coupling between the proton on the nitrogen atom and the phosphorus atom, plus further coupling to the methylene protons of the ethyl group (See Figure 1.2).

FIGURE 1.2



$J(N\underline{H}-\underline{P}) = 16.2Hz$

$J(N\underline{H}-C\underline{H}_2) = 7.8Hz$

^{19}F and ^{31}P Spectra. Details are given in Table 1.2. The ^{31}P spectra of the chlorophosphinylamines consist of a singlet with fine structure, while those of the fluorophosphinylamines all exhibit a triplet. Again, some fine structure is observed. The ^{19}F spectra consist of a simple doublet with the long range coupling constant $J(\underline{F}PNC\underline{H})$ being small and not resolved. There is a shift to high field of the ^{31}P resonance when R = Me,Et is replaced by R = Ph, and when Cl is replaced by F.

TABLE 1.2

^{19}F and ^{31}P N.M.R. Spectra of $X_2P(O)NHR$

	δ_P	δ_F	J(P-F)Hz
$Cl_2P(O)NHMe$	18.4		
$Cl_2P(O)NHEt$	15.6		
$Cl_2P(O)NHPh$	9.0		
$F_2P(O)NHMe$	-0.2	-80.0	1015
$F_2P(O)NHEt$	-3.8	-82.5	1015
$F_2P(O)NHPh$	-8.5	-75.0	1021

To facilitate physical or chemical understanding of the observed trends in chemical shifts nuclear shielding can be divided into a number of physically distinct contributions, an approximation first made by Saika and Slichter [28]. This approach, however, prevents any exact interpretation of observed values of chemical shifts. Nuclear shielding is regarded as being composed of the following contributions:-

A) Magnetic fields arising from local diamagnetic currents.
B) Magnetic fields arising from local paramagnetic currents.
C) Magnetic fields due to induced currents in distant electrons.

It is generally believed that differences in A are responsible for proton chemical shifts while for all other nuclei changes in B are the dominant cause of observed chemical shifts.

The mechanisms contributing to A and B have been classified into through-bond and through-space effects and have been divided into the seven categories:-

i) Inductive and resonance effects.

ii) Magnetic anisotropy effects.
iii) Electric field effects.
iv) Ring current effects.
v) Van der Waals and steric effects.
vi) Intramolecular hydrogen bonding.
vii) Isotope shifts.

These effects have been reviewed recently [29]. The difficulty in interpretation of data arises when more than one mechanism is operating at any one time.

Shielding changes of ^{19}F nuclei in different compounds are generally regarded as being almost entirely due to changes in B, the factor affecting B being changes in the p-electron distribution around the fluorine nucleus; for example, compared with a conventional X-F bond, structures such as $X^{\delta+}-F^{\delta-}$, in which the electronic distribution about the ^{19}F nucleus approximates more to that of the F^{-} ion, are thought to have a more shielded nucleus.

Recent work, however, has shown this to be a possible over-simplification. De Marco and Gatti have observed that substitution of bromine for chlorine at X in CF_3CFXCF_2X produces a deshielding of the fluorines [30]. This is a through-space effect, the importance of which has been discussed elsewhere [31].

Nevertheless, using the approximations described above a good attempt can be made to interpret observed experimental data.

The theory of ^{31}P chemical shifts has been discussed by Van Wazer and Letcher [32]. They concluded that nuclear shielding is again affected by changes in B which are caused by changes in the ionic character of the σ bond between phosphorus and other atoms, and the amount of π-bonding which is present.

The spectra observed in this work have been interpreted in the light of these observations.

The shift to higher field of the resonance of the ^{31}P nuclei in the phosphinylamines, $X_2P(O)NHR$, as detailed in Table 1.2, can therefore be interpreted as being due to an increase in the shielding of the ^{31}P nuclei as R changes from R = Me and Et to R = Ph. The difference in the chemical shift of the ^{31}P nuclei as R changes from Me to Et is small, however, in the phenyl compounds it is possible that the spatial arrangement of the phenyl group relative to the nitrogen atom prevents any delocalisation of the lone pair of electrons on the nitrogen atom. This would have the effect of increasing the electron density around the phosphorus nucleus resulting in an increase in the ^{31}P chemical shift.

Replacement of chlorine attached to phosphorus by fluorine also causes the ^{31}P signal to move upfield. The greater electronegativity of fluorine increases the double bond character of the phosphorus halogen bond thereby increasing the shielding of the ^{31}P nucleus.

2) Infrared Spectra. The infrared spectra were recorded either as liquid films or, in the case of the phenyl compounds, as mulls using both nujol and fluorolube as mulling agents.

There is a certain amount of controversy in the literature about the assignment of phosphorus nitrogen stretching frequencies, especially in fluorine derivatives. This is due to the fact that both phosphorus fluorine and carbon nitrogen stretching frequencies occur in about the same region of the spectrum as that expected for phosphorus nitrogen frequencies. Chittenden and Thomas recommended identification of the peaks due to P-N vibrations by indirect correlations mainly arising from the perturbing effects of P-N bonds on the vibrational frequencies of other bonds in the molecules, such as N-H, P=O etc. [33]. Nyquist et al., however, made the observation that organophosphorus compounds containing the CH_3-NH-P group showed strong bands near 1100 $cm.^{-1}$ which they assigned to asymmetric and symmetric P-N-C stretching modes [34]. In view of the fact that a mixing of the P-N and C-N vibrations almost certainly occurs, the assignment of peaks to ν_{as}(P-N-C) and ν_{s}(P-N-C) seems the best way of interpreting the spectra reported here.

A summary of these bands, together with the assignments made for ν(P-F) and ν(P-Cl) is given in Table 1.3. The complete spectra are detailed in the Experimental section.

Bands assigned to ν_{as}(P-N-C) are shifted to a higher frequency on the substitution of chlorine by fluorine possibly because the increased electronegativity of fluorine causes the lone pair of electrons on the nitrogen atom to be drawn into the P-N bond, thus strengthening the linkage.

Studies have shown that, while ν(P=O) depends on the electronegativity of the substituents attached to phosphorus, this correlation breaks down when there are alkylamino groups, NHR, present [35]. This is due to the tendency of intramolecular hydrogen bonding to lower the value of ν(P=O).

A band at 1260 $cm.^{-1}$ in each of the chlorophosphinylamines can be readily assigned to ν(P=O). This compares with 1275 $cm.^{-1}$ in $Cl_2P(O)NMe_2$ [35]. The frequency is unaffected by the nature

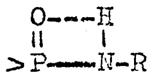
TABLE 1.3

Summary of Infrared Spectra of $X_2P(O)NHR$

	ν(P=O)	ν(PNC)*	ν(PF)	ν(PCl) cm.$^{-1}$
$Cl_2P(O)NHMe$	1260	1090,855		580 vbr
$Cl_2P(O)NHEt$	1260	1080,852		580 vbr
$Cl_2P(O)NHPh$	1260	1105,840		560
$F_2P(O)NHMe$	1327	1125,915	934	
$F_2P(O)NHEt$	1312	1122,900 br	900	
$F_2P(O)NHPh$	1300	1140,910	930	

* These values correspond to ν(P-N-C) asymmetric and symmetric stretching vibrations; the asymmetric being at the higher frequency.

of the substituents on the nitrogen atom but is increased by ~60 cm.$^{-1}$ when the chlorine atoms attached to phosphorus are replaced by fluorine. Again, the frequency is lower than in the corresponding dialkylamino derivatives. In $F_2P(O)NHMe$ ν(P=O) occurs at 1325 cm.$^{-1}$ while in $F_2P(O)NMe_2$ it is at 1365 cm.$^{-1}$ [36]. This suggests that there is a strong degree of intramolecular hydrogen bonding in the compounds, of the type:-



The bands which are assigned to ν(N-H) in the spectra of $X_2P(O)NHR$, which were recorded in the liquid phase, occur at ~3200 cm.$^{-1}$ and are broad and unresolved. The relatively low frequency and the broadness of the bands again indicate the presence of intramolecular hydrogen bonding.

Peaks due to the phosphorus fluorine stretching vibrations are difficult to assign unambiguously, as there is almost certainly coupling of the vibrations with the P-N-C stretching mode. This problem has been encountered with other derivatives [37], but the frequency of the P-F asymmetric stretching vibration probably occurs at ~910 cm.$^{-1}$. Bands due to P-Cl stretches, observed at 580-560 cm.$^{-1}$, are readily identifiable, being very strong and broad. Their frequency varies slightly from compound to compound but no underlying trend in the shift is apparent.

3) Mass Spectra. Only those of the difluorophosphinylamines, $F_2P(O)NHR$, were recorded. The spectra of $F_2P(O)NHEt$ and $F_2P(O)NHPh$, since they are relatively simple, are given in detail in Table 1.4. The spectrum of $F_2P(O)NHMe$ has been published several times [38,39], but is discussed for comparison.

The most intense peak in each spectrum corresponds to a different type of ion in each case. With $F_2P(O)NHMe$ it is the ion $F_2P(O)^+$. In the published spectrum of this compound, the most abundant peak corresponds to the molecular ion, $F_2P(O)NHCH_3^+$ ($F_2P(O)NHCH_3^+$, 23.7%; $F_2P(O)^+$, 8.2%. Intensities are measured here relative to the total ionisation defined as Σ_n(intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak) [39]. It is possible that the spectrum of $F_2P(O)NHMe$ described in this work is unusual. It may have been recorded at a higher temperature or a different ionising voltage from the previously recorded spectrum thus causing the molecule to fragment more easily.

The strongest peak in the spectrum of $F_2P(O)NHEt$ corresponds to loss of a methyl group, $F_2P(O)NCH_2^+$, a not uncommon process

TABLE 1.4

Mass Spectra of $F_2P(O)NHR$

$F_2P(O)NHEt$			$F_2P(O)NHPh$		
m/e	Assignment	Intensity	m/e	Assignment	Intensity
129	$F_2P(O)NHCH_2CH_3^+$	20	178	$F_2P(O)NH_2C_6H_5^+$	10
114	$F_2P(O)NHCH_2^+$	100	177	$F_2P(O)NHC_6H_5^+$	100
112	$F_2PNCH_2CH_3^+$	5	176	$F_2P(O)NC_6H_5^+$	5
110	$FP(O)NHCH_2CH_3^+$	5	158	$FP(O)NHC_6H_5^+$	4
109	$FP(O)NCH_2CH_3^+$	5	157	$FP(O)NC_6H_5^+$	25
101	$F_2P(O)NH_2^+$	10			
94	$FP(O)NCH_2^+$	5	93	$C_6H_5NH_2^+$	10
			92	$C_6H_5NH^+$	40
			91	$C_6H_5N^+$	80
			86	$F_2P(O)H^+$	6
85	$F_2P(O)^+$	10	85	$F_2P(O)^+$	25
82	$FP(O)NH_2^+$	5			
69	F_2P^+	4	69	F_2P^+	20
			66	$FP(O)^+$	80
50	FP^+	8	50	FP^+	12
47	$P(O)^+$	5	47	$P(O)^+$	8
42	$C_2H_4N^+$	25			
41	$C_2H_3N^+$	20			
40	$C_2H_2N^+$	20			
39	C_2HN^+	8			
28	CH_2N^+	5	31	P^+	2

continued

$F_2P(O)NHMe$

m/e	Assignment	Intensity
115	$F_2P(O)NHCH_3^+$	10
114	$F_2P(O)NCH_3^+$	5
101	$F_2P(O)NH_2^+$	40
98	$F_2PNCH_3^+$	4
85	$F_2P(O)^+$	100
66	$FP(O)^+$	3
50	FP^+	2
47	$P(O)^+$	5
30	CH_4N^+	36
29	CH_3N^+	28
28	CH_2N^+	50

Notes:-

i) Intensities are measured as fractions of the most abundant phosphorus containing peak.

ii) Only those peaks $>1\%$ relative intensity above m/e = 28 are detailed.

in organic molecules [40]. The molecular ion is the most abundant peak in the spectrum of $F_2P(O)NHPh$. It seems likely that the delocalisation of electrons which can take place in this ion make it relatively stable.

Peaks corresponding to the loss of OH$^{\bullet}$ are observed in the spectra of $F_2P(O)NHMe$ and $F_2P(O)NHEt$ but not in that of $F_2P(O)NHPh$. This suggests that the hydrogen which is transferred to the oxygen comes from the alkyl group and not from the nitrogen atom.

Diphosphinylamines. This work was undertaken with the aim of preparing a series of derivatives of mono-, di-, tri- and tetrafluoro- substituted derivatives of the tetrachloro-diphosphinylamines, $[Cl_2P(O)]_2NR$, R = Me, Et and Ph.

Preparation of Diphosphinylamines. The bis(dichlorophosphinyl)-amines, $[Cl_2P(O)]_2NR$, are prepared according to the following equation:-

$$Cl_2P(O)NHR \quad + \quad P(O)Cl_3 \quad \xrightarrow[-HCl]{Et_3N} \quad [Cl_2P(O)]_2NR$$

This route has been used previously to synthesise the N-methyl derivative, $[Cl_2P(O)]_2NMe$ [16]. The condensation of $Cl_2P(O)NHEt$ with $P(O)Cl_3$ does not readily go to completion although no difficulty is experienced in the preparation of the N-phenyl derivative.

The syntheses of mono- and gem difluoro- derivatives of $[Cl_2P(O)]_2NR$ can be accomplished by the route:-

$$Cl_2P(O)NHR \quad + \quad P(O)Cl_{3-n}F_n \quad \xrightarrow[-HCl]{Et_3N} \quad Cl_2P(O)NRP(O)Cl_{2-n}F_n$$

There is no n.m.r. evidence that the difluoro- derivative undergoes a rearrangement of the type

$$Cl_2P(O)NRP(O)F_2 \quad \longrightarrow \quad [ClFP(O)]_2NR$$

at room temperature.

TABLE 1.5

δ_{PF_2}	$^1J(PF)$Hz	
-55.6	808.5	(i)
-65.0	921.0	(ii)
-73.0	1015.0	(iii)
-76.5	1021.0	(iv)

Attempts to synthesise the same difluoro- derivative by the alternative route,

$$F_2P(O)NHR \quad + \quad P(O)Cl_3 \quad \xrightarrow[-HCl]{Et_3N} \quad F_2P(O)NRP(O)Cl_2$$

were less successful in that the desired products could not be obtained pure. The impurities consisted of the starting materials and other products, some of which may have been adducts formed between Et_3N and $P(O)Cl_3$ or between Et_3N and $F_2P(O)NHR$. Attempts to prove the existence of an adduct between $P(O)Cl_3$ and Et_3N by n.m.r. spectroscopy were unsuccessful. The slow addition at 0°C of Et_3N to $P(O)Cl_3$ produces a dark red liquid but the ^1H n.m.r. spectrum of the Et_3N remains unchanged. Even when the methyl protons are decoupled from the methylene ones in an attempt to observe coupling to the phosphorus nucleus, no splitting or even broadening of the signal is observed.

When $F_2P(O)NHMe$ is mixed with Et_3N at 0°C in chloroform, and allowed to warm to room temperature, the ^{19}F n.m.r. spectrum of the mixture shows three doublets in addition to one due to $F_2P(O)NHMe$. Table 1.5 gives details of the complete spectrum. When the mixture is refluxed at 60°C for two hours, the appearance of the spectrum changes, there being an increase in the intensity of (iv) while (iii) decreases. A possible interpretation is to propose the self condensation of $F_2P(O)NHMe$. Such a condensation would give rise to the following type of reaction:-

$$F_2P(O)NHMe \xrightarrow[-HF]{Et_3N} F_2P(O)NMeP(O)FNHMe$$

Further condensation could then take place leading to polymeric species.

This difference in mode of activity of $Cl_2P(O)NHMe$ and $F_2P(O)NHMe$ with $P(O)Cl_3$ can be explained in terms of the difference in electronegativity between the chlorine and fluorine atoms. The greater electronegativity of the fluorine atom should make the phosphorus atom in $F_2P(O)NHMe$ more susceptible to nucleophilic attack than the one in $Cl_2P(O)NHMe$, and therefore the fluorine derivative should be able to form a stronger adduct with Et_3N.

Because of the complex nature of the reactions involving $F_2P(O)NHMe$, the trifluoro- derivative $F_2P(O)NRP(O)FCl$ could not be prepared by the route:-

$$F_2P(O)NHMe \quad + \quad P(O)FCl_2 \xrightarrow[-HCl]{Et_3N} F_2P(O)NMeP(O)FCl$$

When this reaction was carried out only an unidentified mixture of products was obtained. It could be seen from the ^{19}F n.m.r. spectrum of the reaction mixture that at least seven different species containing P-F bonds were present, two of which had similar chemical shifts and coupling constants to (ii) and (iv) in Table 1.5, that is products of the reaction between $F_2P(O)NHMe$ and Et_3N.

A possible way of preparing the trifluoro- derivatives may be via the series of reactions:-

$$RNH_2.HCl \quad + \quad P(O)FCl_2 \quad \longrightarrow \quad FClP(O)NHR$$

$$FClP(O)NHR \quad + \quad P(O)F_2Cl \quad \xrightarrow[-HCl]{Et_3N} \quad FClP(O)NRP(O)F_2$$

These were not, however, investigated.
employing the route already known for $[F_2P(O)]_2NMe$:-

$$F_2P(O)NHR \quad + \quad P(O)F_2Cl \quad \xrightarrow[-HCl]{Et_3N} \quad [F_2P(O)]_2NR$$ made

employing the route already known for $[F_2P(O)]_2NMe$:-

$$F_2P(O)NHR \quad + \quad P(O)F_2Cl \quad \xrightarrow[-HCl]{Et_3N} \quad [F_2P(O)]_2NR \qquad [21]$$

It is found that better yields are obtained when the reactions are carried out under nitrogen in the presence of a solvent rather than, as previously described, without solvents.

An isomer of $Cl_2P(O)NMeP(O)F_2$ can be obtained as a mixture of diastereoisomers from the reaction:-

$$2P(O)FCl_2 \quad + \quad (Me_3Si)_2NMe \longrightarrow \quad [FClP(O)]_2NMe \quad + \quad 2Me_3SiCl$$

A pure sample of this compound could not be obtained. It was identified solely from its n.m.r. spectra, which are, however, characteristic and are described in detail later.

All the compounds $[X_2P(O)]_2NR$ are moisture-sensitive liquids or solids and, with the exception of the fluorophosphinylaniline compounds, readily soluble in non-polar solvents.

<u>Characterisation of the Diphosphinylamines.</u> It proved difficult to obtain pure samples of all the diphosphinylamines. This is attributed to two main reasons:-

i) The difficulty of removing all the triethylamine hydrochloride which is a by-product in the reactions and which seems to be slightly soluble in the diphosphinylamines.

ii) The formation of adducts of the type $X_2P(O)NHR.Et_3N$ or $P(O)Cl_{3-n}F_n.Et_3N$, which occurs to a greater or lesser extent in every reaction.

The bis(diphosphinyl)aniline compounds are particularly

TABLE 1.6

^{1}H N.M.R. Spectra of Diphosphinylamines

	δ_{CH_3}	δ_{CH_2}	$^3J(\underline{P}NC\underline{H})$Hz
$Cl_2P(O)NMeP(O)FCl$	3.37		14.1 or 12.1
$Cl_2P(O)NEtP(O)FCl$	2.03	4.37	14.5
$Cl_2P(O)NMeP(O)F_2$	3.87		11.6,11.0
$Cl_2P(O)NEtP(O)F_2$	2.00	4.28	18.0
$F_2P(O)NMeP(O)F_2$	3.49		10.8
$F_2P(O)NEtP(O)F_2$	1.70	4.15	15.0

difficult to isolate since they polymerise if heated above $\sim$180°C under reduced pressure. They could not therefore be distilled from the reaction mixtures.

1) N.M.R. Spectra.

^{1}H Spectra. All the diphosphinylamines give proton spectra which are first order, although weak $^4J(\underline{F}PNC\underline{H})$ coupling sometimes makes it difficult to determine accurate values of $^3J(\underline{P}NC\underline{H})$. Since several of the compounds contain phosphorus in two magnetically different environments, it should be possible to differentiate between the two different values of $^3J(\underline{P}NC\underline{H})$. Only in the cases of $F_2P(O)NMeP(O)Cl_2$ and $FClP(O)NMeP(O)Cl_2$ is it possible to do so. Details of the spectra are given in Table 1.6.

The results in Table 1.6 reveal that there is an increase in the coupling constant $^3J(\underline{P}NC\underline{H})$ on the replacement of methyl by ethyl i.e.

$$^3J(\underline{P}NC\underline{H}_2CH_3) \quad > \quad ^3J(\underline{P}NC\underline{H}_3)$$

TABLE 1.7

^{31}P N.M.R. Spectra of Diphosphinylamines

	$^{\delta}P(O)FCl$	$^{\delta}P(O)Cl_2$	$^{\delta}P(O)F_2$	$^{2}J(\underline{P}N\underline{P})$Hz
$Cl_2P(O)NMeP(O)FCl$	1.3	10.5		21.0
$Cl_2P(O)NEtP(O)FCl$	0.6	9.0		21.0
$Cl_2P(O)NPhP(O)FCl$	-2.5	7.6		41.0
$Cl_2P(O)NMeP(O)F_2$		11.5	-14.4	
$Cl_2P(O)NEtP(O)F_2$		10.5	-15.0	
$Cl_2P(O)NPhP(O)F_2$		n.o.*	n.o.	
$F_2P(O)NMeP(O)F_2$			-14.0	32.2
$F_2P(O)NEtP(O)F_2$			-14.3	34.0
$F_2P(O)NPhP(O)F_2$			-20.0	54.0
$FClP(O)NMeP(O)FCl$				28.2,26.5

* not observed

The nature of the halogen atom attached to phosphorus makes little difference to the magnitude of the coupling constant but it does affect the chemical shift of the protons. They move to lower field being less shielded with increasing electronegativity of the substituents on the phosphorus atom. With the phosphinylamines, $X_2P(O)NHR$, $^{3}J(\underline{P}NC\underline{H})$ decreases when X = Cl is replaced by X = F, therefore the protons in the phosphinylamines are more susceptible to variations in the substituents on phosphorus than are the protons in the diphosphinylamines.

^{31}P Spectra. Details are given in Table 1.7. The ^{31}P spectra of the methyl and ethyl dichlorophosphinylamines are relatively simple to interpret. The resonances due to the two different phosphorus nuclei, when present, are readily distinguishable. The one with the greater number of fluorine atoms attached always occurs at the higher field, since the more fluorine atoms there are attached to phosphorus, the more the phosphorus can take part in π-bonding leading to a greater shielding of the ^{31}P nucleus.

The phenyl derivatives have more complicated spectra, probably due to a greater degree of coupling between the various nuclei. However, they still appear to be first order spectra and a good estimate of the chemical shifts of the ^{31}P nuclei can be made. The spectrum of $[FClP(O)]_2NMe$ was not recorded because of an insufficient amount of sample.

As with the phosphinylamines, the ^{31}P resonances are shifted upfield when R = Me is replaced by R = Et and Ph for presumably similar reasons although in this case the changes in chemical shift are not as large.

^{19}F Spectra. Details of the spectra are given in Table 1.8. Three types of spectra are observed. Those of the mono- and gem difluorophosphinylamines are simple first order spectra. The mono- substituted compounds, $FClP(O)NRP(O)Cl_2$, each have a doublet centred at $\sim$-30ppm from CCl_3F. This is in the region expected for a P(O)FCl group, intermediate between $P(O)F_2Cl$ at δ = -48ppm and $P(O)FCl_2$ at δ = -8ppm. The chemical shift of this group is affected only slightly by the substituent on the nitrogen atom, whereas the coupling constant $^1J(PF)$ is affected rather more, there being a small increase on going from R = Me to R = Et and Ph.

TABLE 1.8

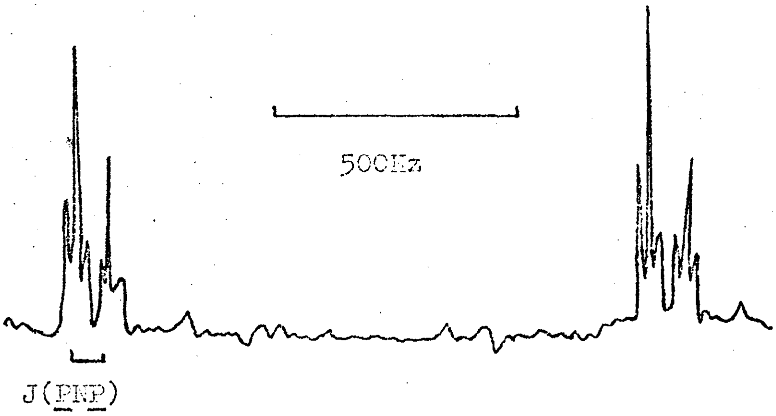
^{19}F N.M.R. Spectra of Diphosphinylamines

	$\delta_{PCl\underline{F}}$	$\delta_{P\underline{F}_2}$	$^1J(\underline{P}\underline{F}Cl)$Hz	$^1J(\underline{P}\underline{F}_2)$
$Cl_2P(O)NMeP(O)FCl$	-31.0		1106	
$Cl_2P(O)NEtP(O)FCl$	-30.0		1128	
$Cl_2P(O)NPhP(O)FCl$	-31.0		1128	
$Cl_2P(O)NMeP(O)F_2$		-68.9		1059
$Cl_2P(O)NEtP(O)F_2$		-66.5		1053
$Cl_2P(O)NPhP(O)F_2$		-70.1		1090
$F_2P(O)NMeP(O)F_2$		-72.3		1053
$F_2P(O)NEtP(O)F_2$		-72.0		1054
$F_2P(O)NPhP(O)F_2$		-76.0		1072
$FClP(O)NMeP(O)ClF$	-30.8,-31.9		1156	

With the gem difluorophosphinylamines, $F_2P(O)NRP(O)Cl_2$, the doublet due to P-F coupling occurs in the region expected for a $-P(O)F_2$ group, ∼-70ppm from CCl_3F. There is a large increase in $^1J(PF)$ on going from R = Me, Et to R = Ph. This increase in coupling constant is observed in the spectra of all the diphosphinylamines and is parallelled by an increase in $^2J(\underline{P}N\underline{P})$. This contrasts with the P(III) analogues $(F_2P)_2NR$ where the magnitudes of $^1J(PF)$ and $^2J(\underline{P}N\underline{P})$ decrease on going from R = Me and Et to R = Ph.[41]. This increase in $^2J(\underline{P}N\underline{P})$ is difficult to explain satisfactorily. A possible explanation is that there is a greater degree of π-bonding between the nitrogen atom and the phenyl group than between the nitrogen and the alkyl groups. This seems unlikely, however, in view of the crystal structure carried out on a related compound $Cl_2P(O)NPhP(S)Cl_2$ [42] which shows little N-phenyl π-bonding, because the phenyl group is at $\sim 90^\circ$ to the P-N-P plane.

The spectrum of bis(chlorofluorophosphinyl)methylamine, $[FClP(O)]_2NMe$, was analysed by the sub-spectral method as an example of an AA'XX' system (neglecting coupling to the alkyl protons) [43]. This method of analysis assumes that the system studied consists of a number of simple systems which contribute independently to the overall spectrum. The procedure is described in detail in reference 43. The spectrum of $[FClP(O)]_2NMe$ consists of a doublet of separation $|J(PF)+J(\underline{P}NP\underline{F})|$ flanked by less intense lines (see Figure 1.3).

FIGURE 1.3



The positions of these lines give $^2J(\underline{P}N\underline{P})$ and indicate that $^1J(PF)$ and $^3J(\underline{P}NP\underline{F})$ are of different relative sign as in the analogous P(III) compounds, $(F_2P)_2NR$ [41]. The presence of two isomers is detected by the occurrence of two sets of doublets with the same fine structure, one set of which occurs at a slightly higher field than the other. Two significantly different values of $^2J(\underline{P}N\underline{P})$ are obtained for the *meso* and *dl* forms.

The tetrafluorophosphinylamines, $[F_2P(O)]_2NR$, have second order ^{19}F n.m.r. spectra. They can be analysed as examples of an $AX_2A'X_2'$ system as has been carried out for $[F_2P(O)]_2NMe$ [44]. The spectra are similar in appearance to that of $[FClP(O)]_2NMe$ consisting of an intense doublet flanked by weaker lines. Broadening effects, including those caused by coupling of the ^{19}F nuclei to the protons present, make it difficult to obtain values for $^{3}J(\underline{P}NP\underline{F})$ and $^{4}J(\underline{F}PNP\underline{F})$ although these were observed in the spectrum of $[F_2P(O)]_2NMe$. The coupling constant $^{2}J(\underline{P}N\underline{P})$ in $[F_2P(O)]_2NMe$ decreased slightly with decreasing temperature (~10Hz from +40°C to -50°C) [44]. The spectrum of $[F_2P(O)]_2NEt$ was recorded at various temperatures down to -60°C to see if a similar change occurred, but the spectrum remained unchanged.

A possible way of comparing the effectiveness of the nitrogen bridge in transmitting electronic effects compared with oxygen or sulphur is to look at the size of the coupling constant $^{2}J(\underline{P}X\underline{P})$. This coupling constant has been shown to be sensitive to details of molecular structure and the electronegativity of substituents [45], but the factors determining its magnitude are not completely understood.

Few fluorine derivatives containing P-O-P linkages have been synthesised and n.m.r. data are not available for all of these. Table 1.9 lists the available data.

A study has been made of the coupling constant $^{2}J(\underline{P}O\underline{P})$ in non-fluorine containing molecules [49]. The magnitude of the coupling constant has been found to lie between 12 and 22 Hz. Substitution by fluorine into a molecule has been observed to lower the magnitude of $^{2}J(\underline{P}O\underline{P})$ substantially. In $[HP(O)_2OP(O)_2H]^{2-}$, $J(\underline{P}O\underline{P})$ = 17Hz [50], while in $[FP(O)_2OP(O)_2F]^{2-}$ it is 2.5Hz.

TABLE 1.9

	$^2J(\underline{P}O\underline{P})$Hz	
$F_2P(O)OP(O)F_2$	0	[46]
FClP(O)OP(O)ClF	21.0	[47]
$[FP(O)_2OP(O)_2F]^{2-}$	2.5	[48]
$F_2P(S)OP(S)F_2$	8.4	[44]

TABLE 1.10

	$^2J(\underline{P}S\underline{P})$Hz	
$F_2P(S)SP(S)F_2$	25.1	[44]
RFP(S)SP(S)FR	13-18	[45]
(R = Me,Et and Ph)		

From the information available it seems likely that the magnitude of $^2J(\underline{P}O\underline{P})$ in any molecule containing fluorine will be small, although perhaps substituents such as $-NMe_2$ on phosphorus might raise it somewhat.

There are even fewer examples available of acyclic fluorine compounds containing P-S-P bridges. A few are listed in Table 1.10.

Obviously there is not enough information available to effectively compare the P-S-P bridge with P-O-P and P-N-P in transmitting electronic effects. However, by comparing the magnitude of $^2J(\underline{P}O\underline{P})$ with those of $^2J(\underline{P}N\underline{P})$ in Table 1.7, where there is a range of 21-54Hz, it is apparent that nitrogen is a much more effective bridge than oxygen in transmitting

TABLE 1.11

Summary of Infrared Spectra of Diphosphinylamines

	ν(P=O)	ν_{as}(PNP)	ν(PF)	ν(PCl) cm.$^{-1}$
$Cl_2P(O)NMeP(O)Cl_2$	1310,1290	912		600
$Cl_2P(O)NEtP(O)Cl_2$	1312,1290,1280	926		
$Cl_2P(O)NPhP(O)Cl_2$	1290			
$FClP(O)NPhP(O)Cl_2$	1323,1298	935	900	598
$FClP(O)NEtP(O)Cl_2$	1325,1298	958	895	598
$FClP(O)NPhP(O)Cl_2$	1310,1295	960	?	562?
$F_2P(O)NMeP(O)Cl_2$	1353,1298	948	905	601
$F_2P(O)NEtP(O)Cl_2$	1347,1295	952	912,895	603
$F_2P(O)NPhP(O)Cl_2$	1327,1295	950	?	598
$F_2P(O)NMeP(O)F_2$	1387,1368	945	938,877	
$F_2P(O)NEtP(O)F_2$	1378 br	960	905,898	
$F_2P(O)NPhP(O)F_2$	1350	940	915,820	

spin coupling effects.

2) Infrared Spectra of Diphosphinylamines. The complete spectra are given in the Experimental section. Bearing in mind that the frequencies of C-N and P-F stretching vibrations occur in the same region of the spectrum as those of P-N, it is possible, by comparing a series of analogous compounds, to extract tentative values for the asymmetric stretching mode of the P-N-P unit. A summary of these, together with assignments made for the P-F, P-Cl and P=O stretching vibrations are given

in Table 1.11. Since the values assigned to ν_{as}(PNP) fall in the same region of the spectrum as P-F stretching frequencies, it is difficult to attach much significance to any observed variation in frequency. The values of ν(PCl) are relatively easy to assign in most of the compounds. They have a very short frequency range. Varying the other substituents on the phosphorus atom appears to have little effect on the P-Cl bond.

Two peaks are assigned in most spectra to ν(P=O) although some splitting of the peaks is observed. The splitting may be due to coupling between the two P=O stretching vibrations such as is found in dicarbonyl compounds [51]. The lower peak at ~1295 cm.$^{-1}$ can be related to the chloro- part of the molecule in chlorofluoro- derivatives since it is at a comparable frequency to ν(P=O) in $[Cl_2P(O)]_2NMe$ and is absent in $[F_2P(O)]_2NMe$. Like ν(PCl) it is unaffected by other substituents on the molecule whereas ν(P=O) related to the fluoro- part of the molecule varies quite significantly as the substituents around it vary.

3) <u>Mass Spectra of Diphosphinylamines</u>. Mass spectroscopy proved to be a useful tool in the identification of the phosphinylamines. It was necessary to use this technique because of the difficulty of obtaining a reasonable quantity of pure material suitable for elemental analyses. Any impurities in the samples appeared to catalyse their polymerisation and their mass spectra contained peaks with m/e values up to ~500. To overcome this the samples were redistilled immediately before their spectra were recorded and the probe temperature was kept as low as possible, usually ~100°C, in case polymerisation of the compounds was taking place in the spectrometer.

In the mass spectra published for other diphosphinyl compounds [21], molecular ions were almost always observed and the spectra exhibited straightforward cracking patterns with either the molecular ion or F_2P^+ the most abundant ions in the spectra.

A similar pattern of behaviour is found here. A molecular ion is observed for every compound except $[F_2P(O)]_2NEt$ where the ion of highest m/e corresponds to $[F_2P(O)]_2NCH_2^+$. The complete spectra are given in the Experimental section, together with the assignments made for the observed peaks.

Three breakdown patterns emerge; a distinct one for each of the methyl, ethyl and phenyl series of compounds. Again, no metastable transitions are observed. The patterns suggested, therefore, are based only on the nature of the ions observed.

The first stage in the fragmentation of the diphosphinylmethylamines involves either the loss of a proton or the cleavage of a phosphorus halogen bond. In compounds containing both chlorine and fluorine it is always a P-Cl bond which is broken first; a fact consistent with the weaker bond strength of P-Cl as compared with P-F. This is followed by the cleavage of a P-N bond and the subsequent breakdown of the individual fragments. The peak corresponding to the ion $X_2P(O)NR^+$ is almost always the most abundant ion in the spectra, suggesting that it is a relatively stable ion.

With the ethyl derivatives the first step in the decomposition is always the loss of a methyl group. This is a common process in organic molecules [40] and not unexpected in this case. The next peaks of highest m/e values correspond to ions of the general formula $[X_2P(O)]_2NH_2^+$ of ~10% relative abundance where X may be Cl, F or a mixture of both. The decomposition of these ions appears to involve the elimination of HCl when a chlorine atom is present, followed by the cleavage of a P-N bond and the subsequent decomposition of the P-N fragments. These two latter steps appear to be the mode of decomposition of $[F_2P(O)]_2NH_2^+$ also.

In the case of the phenyl derivatives the spectra are relatively simple. With the exception of $[F_2P(O)]_2NPh$, the cracking pattern appears to be cleavage of a P-Cl bond followed by the breaking of a P-N bond. $[F_2P(O)]_2NPh$ has a very simple spectrum. The only ions containing P >10% relative intensity correspond to $[F_2P(O)]_2NPh^+$, 10%, and $[F_2P(O)]_2NH_2^+$, 100%,and $F_2P(O)^+$, 80%.

Discussion of Reactions. The syntheses of the diphosphinylamines involves the cleavage of a phosphorus halogen bond in a phosphoryl halide, $P(O)F_nCl_{3-n}$. When the phosphoryl halide contains both chlorine and fluorine atoms the chlorine atom is exclusively displaced, consistent with the better leaving properties of the chloride ion relative to the fluoride ion, and the weaker bond strength of P-Cl as compared with P-F. Similar observations have been made during the syntheses of other phosphorus(V) derivatives [39].

Attempts made to partially fluorinate the tetrachlorophosphinylamines, $[Cl_2P(O)]_2NR$, with a view to obtaining mono-, di-, tri- and tetrafluoro- substituted dreivatives, were not wholly successful. Caesium fluoride, CsF, sodium fluoride, NaF, and antimony trifluoride, SbF_3, were all tried as fluorinating agents. Only with SbF_3 (with a few drops of $SbCl_3$ added as a catalyst) were any fluorinated products obtained. These were largely the fully fluorinated derivatives $[F_2P(O)]_2NR$ which were formed along with other P-F species which could not be fully identified.

This difficulty in fluorination is surprising since the monophosphinylamines are readily fluorinated and since Sowerby has said that the reaction of $[Cl_2P(O)]_2NMe$ with SbF_3, at room temperature, gives fluoro- derivatives [52]. The difficulty of fluorination, however, has been observed previously with other diphosphorus compounds. Attempts to fluorinate $Cl_2P(O)OP(O)Cl_2$ with KSO_2F gave only products involving P-O-P bond cleavage [53], and fluorination of $Cl_2PNMeP(O)Cl_2$ with NaF in sulpholane produced a low yield of $F_2PNMeP(O)F_2$ but large quantities of PF_3 [38]. Fluorination of $(Cl_2P)_2NMe$, however, took place readily with good yields of $(F_2P)_2NMe$ being obtained [20]. It is therefore the P(V) atom which is difficult to fluorinate. This may be due to the increased coordination number of the phosphorus making the formation of an adduct between it and the fluorinating agent more difficult. In addition it has been suggested that the fluorination of $P_3N_3Cl_4(NMe_2)_2$ by SbF_3 involves the coordination of the fluorine to the phosphonitrile by it accepting an electron pair from a ring nitrogen [54]. In compounds containing a $Cl_2P(O)N$-linkage it is possible that SbF_3 could coordinate to the oxygen atom as well as to the nitrogen making chlorine-fluorine exchange more difficult. It was not possible to compare the products of fluorination of $[Cl_2P(O)]_2NR$ with those of $N_3P_3Cl_6$ because of this difficulty of fluorinating $[Cl_2P(O)]_2NR$.

EXPERIMENTAL

Reagents used were obtained from the sources indicated in Table 1.12 and their purity was checked before use by BP and/or infrared spectroscopy. Solvents were dried by conventional means [55]. $P(O)Cl_3$ was purified by distillation. Et_3N was distilled from sodium before use. All operations were carried out under dry nitrogen or on connections to a conventional vacuum line. ^1H, ^{19}F and ^{31}P n.m.r. spectra were measured on a Jeol C60 HL spectrometer operating at 60, 56.4 and 24.3 MHz respectively. The spectra were recorded without using a solvent where possible. $CHCl_3$, $CDCl_3$ and C_6H_6 were used as solvents when necessary. Me_4Si, CCl_3F and 85% H_3PO_4 were used as external references. Mass spectra were recorded on an A.E.I. MS 12 spectrometer operating at 70 Mev. Infrared spectra were obtained as either gas, liquid or mull spectra, as appropriate, on a Perkin-Elmer 457 spectrometer. Elemental analyses were performed by Bernhardt or the analytical laboratories if this university.

Phosphinylamines. Full experimental details and analytical data for new compounds are given in Tables 1.13 and 1.14.

Preparation of Chlorophosphinylamines. In a typical reaction 50 g of amine hydrochloride, $RNH_2.HCl$ (R = Me, Et and Ph), were refluxed with a 3:1 mole excess of $P(O)Cl_3$ until all the salt had dissolved (about two days). Dichlorophosphinylmethylamine, $Cl_2P(O)NHMe$ and dichlorophosphinylethylamine, $Cl_2P(O)NHEt$ were collected by distillation under reduced pressure; dichlorophosphinylaniline, $Cl_2P(O)NHPh$ was crystallised from the reaction mixture and purified by recrystallisation from C_6H_6.

Preparation of Fluorophosphinylamines. Typically a slurry of

TABLE 1.12

Starting Material	Source	Infrared
$P(O)Cl_3$	B.D.H.	[56]
Et_3N	Koch-Light	[57]
$P(O)FCl_2$	PCl_5/H_2PO_4F [58]	[59]
$P(O)FCl_2$	PCl_5/HPO_4F_2 [58]	[59]
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$ [60]	[61]
$MeNH_2.HCl$	B.D.H.	[62]
$EtNH_2.HCl$	B.D.H.	[63]
$PhNH_2.HCl$	B.D.H.	[64]
NaF	B.D.H.	
CsF	Ozark-Mahoning	

NaF in C_6H_6 was stirred for about 15 minutes, cooled to 0°C, then the chlorophosphinylamine added slowly. The mixture was allowed to warm up slowly then refluxed for about 3 hours and filtered. Difluorophosphinylmethylamine, $F_2P(O)NHMe$ and difluorophosphinylethylamine, $F_2P(O)NHEt$ were collected by distillation under reduced pressure; difluorophosphinylaniline, $F_2P(O)NHPh$ was crystallised from solution and purified by recrystallisation from C_6H_6.

Diphosphinylamines. The condensation of phosphoryl halides with dihalogenophosphinylamines was accomplished in diethyl ether solution at 0°C using a 1 mole equivalent of Et_3N. The reaction mixture was allowed to warm to room temperature, then refluxed for about 2 hours, cooled and filtered to remove the $Et_3N.HCl$ formed. The diphosphinylamines were collected, where possible, by distillation under reduced pressure. Full

TABLE 1.13

Preparative Details for Phosphinylamines

Reactants (mmol)		Solvent	Product	MP/BP (mm Hg)	Yield (%)
$MeNH_2.HCl$ (740)	$P(O)Cl_3$ (2220)		$Cl_2P(O)NHMe$	120°(0.01)	95 [25]
$EtNH_2.HCl$ (500)	$P(O)Cl_3$ (1500)		$Cl_2P(O)NHEt$	125°(0.01	95
$PhNH_2.HCl$ (70)	$P(O)Cl_3$ (220)		$Cl_2P(O)NHPh$	92°	90
$Cl_2P(O)NHMe$ (500)	NaF (2000)	MeCN	$F_2P(O)NHMe$	110°(0.01)	90
$Cl_2P(O)NHEt$ (100)	NaF (300)	C_6H_6	$F_2P(O)NHEt$	85°(0.01)	95
$Cl_2P(O)NHPh$ (47)	NaF (140)	C_6H_6	$F_2P(O)NHPh$	45°	75

TABLE 1.14

Elemental Analyses for Phosphinylamines

Compound	Calculated				Found			
	C%	H%	N%	F%	C%	H%	N%	F%
$Cl_2P(O)NHEt$	14.8	3.7	8.6		14.6	3.6	8.4	
$Cl_2P(O)NHPh$	34.3	2.9	6.7		33.6	2.4	6.1	
$F_2P(O)NHEt$	18.6	4.6	10.8	29.45	18.7	4.7	10.7	29.6
$F_2P(O)NHPh$	40.7	3.4	7.9	21.47	39.8	3.25	7.5	21.4

experimental details and some analytical data are given in Tables 1.15 and 1.16; mass and infrared spectra are tabulated below. Mass spectra are presented in the form: m/e, assignment, relative intensity. Relative intensities are expressed as fractions of the most abundant phosphorus containing ion. Only those ions of relative intensity >1% with m/e >30 are detailed.

Bis(dichlorophosphinyl)methylamine, $[Cl_2P(O)]_2NMe$. As complete infrared and mass spectral data have not been published for this compound they are detailed below.

Infrared Spectrum. 2900-2600 *vbr,w*, 1455 *w*, 1310 *s*, 1290 *s*, 1200 *m*, 1040 *m*, 912 *s*, 670 *m*, 600 *s*, 542 *m*, 505 *w*, 480 *w* cm^{-1}.

*Mass Spectrum**. 262, $[Cl_2P(O)]_2NCH_2^+$, 10; 228, $Cl_2P(O)NCH_3P(O)Cl^+$, 100; 212, $Cl_2PNCH_3P(O)Cl^+$, 8; 199, $P_2O_2Cl_3^+$, 10; 192, $[ClP(O)]_2NCH_2^+$, 10; 178, $[ClP(O)]_2N^+$, 6; 146, $Cl_2P(O)NCH_3^+$, 100; 131, $Cl_2P(O)N^+$, 50; 117, $Cl_2P(O)^+$, 40; 101, Cl_2P^+, 65; 94, $ClPNCH_2^+$, 30; 82, $ClP(O)^+$, 30; 66, ClP^+, 25; 60, $PNCH_3^+$, 35; 47, $P(O)^+$, 90; 37, Cl^+, 10; 36, HCl^+, 60;35, Cl^+, 30; 31, P^+, 8.

* Ions are assigned using ^{35}Cl.

Bis(dichlorophosphinyl)ethylamine, $[Cl_2P(O)]_2NEt$.

Infrared Spectrum. 2982 *s*, 2940 *m*, 2895 *w*, 1462 *m*, 1420 *w*, 1385 *s*, 1358 *w*, 1320 *w*, 1312 *sh*, 1290 *s*, 1198 *s*, 1168 *m*, 1115 *br,w*, 1030 *s*, 952 *s*, 920 *s*, 773 *s*, 668 *s*, 605 *vs*, 550 *vs*, 507 *m*, 382 *s* cm^{-1}.

Mass Spectrum. 277, $[Cl_2P(O)]_2NCH_2CH_3^+$, 1; 262, $[Cl_2P(O)]_2NCH_2^+$, 30; 250, $[Cl_2P(O)]_2NH_2^+$, 8; 242, $Cl_2P(O)NCH_2CH_3P(O)Cl^+$, 10; 227, $Cl_2P(O)NCH_2P(O)Cl^+$, 3; 214, $Cl_2P(O)NHP(O)Cl^+$, 8; 192, $[ClP(O)]_2NCH_2^+$, 2; 178, $[ClP(O)]_2N^+$, 4; 160, $(ClP)_2NCH_2^+$, 55; 146, $Cl_2P(O)NCH_3^+$, 30; 117, $Cl_2P(O)^+$, 70; 101, Cl_2P^+, 25; 82, $ClP(O)^+$, 25; 66, ClP^+, 15; 47, $P(O)^+$, 100; 37, Cl^+, 20; 36, HCl^+, 80; 35, Cl^+, 60; 31, P^+, 15.

TABLE 1.15

Preparative Details for Diphosphinylamines

Reactants (mmol)		Product(s)	MP/BP (mm Hg)	Yield (%)
$Cl_2P(O)NHMe$ (200)	$P(O)Cl_3$ (200.5)	$[Cl_2P(O)]_2NMe$	65-70°(0.01)	60 [25]
$Cl_2P(O)NHEt$ (50)	$P(O)Cl_3$ (50.05)	$[Cl_2P(O)]_2NEt$	120°(0.01)	30
$Cl_2P(O)NHPh$ (45.24)	$P(O)Cl_3$ (45.34)	$[Cl_2P(O)]_2NPh$	98-99°	45
$Cl_2P(O)NHMe$ (24)	$P(O)FCl_2$ (24)	$Cl_2P(O)NMeP(O)FCl$	60-62°(0.1)	80
$Cl_2P(O)NHEt$ (16.6)	$P(O)FCl_2$ (16.8)	$Cl_2P(O)NEtP(O)FCl$	108°(0.01)	20
$Cl_2P(O)NHPh$ (53)	$P(O)FCl_2$ (53)	$Cl_2P(O)NPhP(O)FCl$	viscous oil	80
$F_2P(O)NHMe$ (17.38)	$P(O)Cl_3$ (17.45)	$Cl_2P(O)NMeP(O)F_2$ + other products	not purified	
$Cl_2P(O)NHMe$ (31.3)	$P(O)F_2Cl$ (33.5)	$Cl_2P(O)NMeP(O)F_2$	55°(0.01)	10
$Cl_2P(O)NHEt$ (34.4)	$P(O)F_2Cl$ (34.6)	$Cl_2P(O)NEtP(O)F_2$	60°(0.01)	8
$Cl_2P(O)NHPh$ (20.43)	$P(O)F_2Cl$ (20.54)	$Cl_2P(O)NPhP(O)F_2$	-	18
$F_2P(O)NHMe$ (13.92)	$P(O)F_2Cl$ (14.05)	$[F_2P(O)]_2NMe$	65-70°(0.01)	70 [21]
$F_2P(O)NHEt$ (39.57)	$P(O)F_2Cl$ (39.68)	$[F_2P(O)]_2NEt$	65°(0.01)	25
$F_2P(O)NHPh$ (30)	$P(O)F_2Cl$ (30.3)	$[F_2P(O)]_2NPh$	-	5

TABLE 1.16

Elemental Analyses for Diphosphinylamines

Compound	Calculated					Found				
	C%	H%	N%	Cl%	F%	C%	H%	N%	Cl%	F%
$FClP(O)NMeP(O)Cl_2$	5.1	0.9		42.7	24.8*	5.0	1.2		42.7	24.9*
$FClP(O)NPhP(O)Cl_2$	23.2	1.6				22.4	1.7			
$[Cl_2P(O)]_2NEt$	8.6	1.8				8.0	1.9			
$[Cl_2P(O)]_2NPh$	22.0	1.5	4.3			21.9	1.6	4.2		
$[F_2P(O)]_2NEt$	11.3	2.3	6.6		35.7	11.4	2.4	6.5		35.6

* P analysis

Bis(dichlorophosphinyl)aniline.

Infrared Spectrum. A satisfactory infrared spectrum could not be obtained either as a mull or disc; only very broad unresolved bands are observed.

Mass Spectrum. 325, $[ClP(O)]_2NC_6H_5^+$, 100; 290, $Cl_2P(O)NC_6H_5P(O)Cl^+$, 25; 254, $[ClP(O)]_2NC_6H_5^+$, 30; 209, $Cl_2P(O)NHC_6H_5^+$, 20; 191, $Cl_2PNC_6H_4^+$, 20; 173, $ClP(O)NC_6H_5^+$, 35; 117, $Cl_2P(O)^+$, 95; 101, Cl_2P^+, 30; 91, $C_7H_7^+$, 85; 82, $ClP(O)^+$, 25; 77, $C_6H_5^+$, 90; 47, $P(O)^+$, 85; 37, Cl^+, 5; 36, HCl^+, 95; 35, Cl^+, 15; 31, P^+, 3.

Fluorochlorophosphinyl(dichlorophosphinyl)methylamine, $FClP(O)NMeP(O)Cl_2$.

Infrared Spectrum. 2965 w, 1460 w, 1440 w, 1323 vs, 1298 vs, 1210 m, 1050 s, 935 vs, 900 sh,w, 684 s, 598 vs, 540 w, 518 w, 482 w, 445 m, 426 w $cm.^{-1}$

Mass Spectrum. 247, $FClP(O)NCH_3P(O)Cl_2^+$, 10; 212, $FClP(O)NCH_3P(O)Cl^+$, 50; 183, $FCl_2P_2O_2^+$, 5; 176, $FP(O)NCH_2P(O)Cl^+$, 2; 162 $FP(O)NP(O)Cl^+$, 4; 146, $Cl_2P(O)NCH_3^+$, 40; 130, $FClP(O)NCH_3^+$, 100; 117, $Cl_2P(O)^+$, 60; 101, $FClP(O)^+$, 40; 94, $ClPNCH_2^+$, 30; 82, $ClP(O)^+$, 25; 66, ClP^+, 20; 60, $PNCH_3^+$, 10; 47, $P(O)^+$, 100; 37, Cl^+, 5; 36, HCl^+, 90; 35, Cl^+, 15; 31, P^+, 8.

Fluorochlorophosphinyl(dichlorophosphinyl)ethylamine, $FClP(O)NEtP(O)Cl_2$.

Infrared Spectrum. 2990 *w*, 2945 *vw*, 2900 *vw*, 1460 *br,w*, 1390 *w*, 1325 *s*, 1295 *s*, 1173 *m*, 1035 *m*, 985 *s*, 892 *m*, 780 *w*, 675 *m*, 598 *vs*, 515 *w*, 432 *w*, 412 *w* $cm.^{-1}$

Mass Spectrum. 261, $FClP(O)NCH_2CH_3P(O)Cl_2^+$, 10; 246, $FClP(O)NCH_2P(O)Cl_2^+$, 100; 234, $FClP(O)NH_2P(O)Cl_2^+$, 10; 198, $FP(O)NHP(O)Cl_2^+$, 55; 160, $Cl_2P(O)NCH_2CH_3^+$, 60; 146, $Cl_2P(O)NCH_3^+$, 80; 117, $Cl_2P(O)^+$, 85; 101, $FClP(O)^+$, 25; 66, ClP^+, 12; 47, $P(O)^+$, 30; 37, Cl^+, 2; 36, HCl^+, 90; 35, Cl^+, 6.

Fluorochlorophosphinyl(dichlorophosphinyl)aniline, $FClP(O)NPhP(O)Cl_2$.

Infrared Spectrum. 3100 *w*, 2970 *w*, 2800 *vw*, 1603 *m*, 1495 *m*, 1410 *m*, 1310 *sh,m*, 1295 *m*, 1260 *m*, 1220 *w*, 1100 *br,w*, 1030 *w*, 960 *w*, 810 *m*, 750 *m*, 690 *m*, 615 *w*, 560 *m*, 545 *m* $cm.^{-1}$

Mass Spectrum. 309, $FClP(O)NC_6H_5P(O)Cl_2^+$, 30; 274, $FClP(O)NC_6H_5P(O)Cl^+$, 5; 208, $Cl_2P(O)NC_6H_5^+$, 2; 192, $FClP(O)NC_6H_5^+$, 8; 173, $ClP(O)NC_6H_5^+$ 90; 117, $Cl_2P(O)^+$, 100; 101, Cl_2P^+, 80; 91, $C_7H_7^+$, 80; 82, $ClP(O)^+$, 20; 77, $C_6H_5^+$, 15; 65, $C_5H_5^+$, 30; 47, $P(O)^+$, 90; 37, Cl^+, 2; 36, HCl^+, 80; 35, Cl^+, 6; 31, P^+, 10.

Difluorophosphinyl(dichlorophosphinyl)methylamine, $F_2P(O)NMeP(O)Cl_2$.

Infrared Spectrum. 2980 *w*, 2275 *w*, 1353 *s*, 1298 *s*, 1220 *w*, 1070 *m*, 948 *s*, 905 *br,m*, 820 *w*, 733 *m*, 680 *w*, 670 *w*, 650 *w*, 602 *m*, 558 *w*, 542 *w*, 478 *m* $cm.^{-1}$

Mass Spectrum. 231, $F_2P(O)NCH_3P(O)Cl_2^+$, 5; 196, $F_2P(O)NCH_3P(O)Cl^+$, 80; 117, $Cl_2P(O)^+$, 100; 114, $F_2P(O)NCH_3^+$, 85; 85, $F_2P(O)^+$, 22; 69, F_2P^+, 80; 66, ClP^+, 16; 47, $P(O)^+$, 40; 37, Cl^+, 2; 36, HCl^+, 85; 36, Cl^+, 6.

Difluorophosphinyl(dichlorophosphinyl)ethylamine, $F_2P(O)NEtP(O)Cl_2$.

Infrared Spectrum. 3000 w, 2978 vw, 2270 w, 1475 w, 1373 s, 1347 s, 1298 s, 1180 m, 1095 w, 1060 m, 975 s, 952 s, 915 s, 894 m, 785 m, 735 s, 670 w, 665 w, 655 w, 603 s, 562 m, 542 m, 510 m, 475 m, 450 w, 420 w, 380 w cm^{-1}.

Mass Spectrum. 245, $F_2P(O)NCH_2CH_3P(O)Cl_2^+$, 1; 230, $F_2P(O)NCH_2P(O)Cl_2^+$, 80; 218, $F_2P(O)NH_2P(O)Cl_2^+$, 40; 182, $F_2P(O)NHP(O)Cl^+$, 30; 146, $Cl_2P(O)NCH_3^+$, 15; 128, $F_2P(O)NCH_2CH_3^+$, 100; 117, $Cl_2P(O)^+$, 45; 85, $F_2P(O)^+$, 25; 69, F_2P^+, 75; 66, ClP^+, 5; 47, $P(O)^+$, 35; 37, Cl^+, 3; 36, HCl^+, 75; 35, Cl^+, 9.

Difluorophosphinyl(dichlorophosphinyl)aniline, $F_2P(O)NPhP(O)Cl_2$.

Infrared Spectrum. 3075 w, 2900 w, 2890 w, 1605 w, 1600 m, 1503 sh, 1490 m, 1460 w, 1415 m, 1350 m, 1330 s, 1226 m, 1188 m, 1115 w, 1050-1030 br,s, 950 br,m, 835 m, 820 m, 753 m, 692 s, 620 m, 598 vs, 532 s cm^{-1}.

Mass Spectrum. 293, $F_2P(O)NC_6H_5P(O)Cl_2^+$, 95; 258, $F_2P(O)NC_6H_5P(O)Cl^+$, 10; 241, $FP(O)NC_6H_5P(O)Cl^+$, 12; 208, $Cl_2P(O)NC_6H_5^+$, 35; 177, $F_2P(O)NHC_6H_5^+$, 40; 157, $FP(O)NC_6H_5^+$, 90; 117, $Cl_2P(O)^+$, 100; 91, $C_7H_7^+$, 75; 85, $F_2P(O)^+$, 25; 77, $C_6H_5^+$, 20; 69, F_2P^+, 60; 65, $C_5H_5^+$, 12; 47, $P(O)^+$, 60; 37, Cl^+, 4; 36, HCl^+, 75; 35, Cl^+, 12.

Bis(difluorophosphinyl)ethylamine, $[F_2P(O)]_2NEt$.

Infrared Spectrum. 2980 br,w, 1378 s, 1188 m, 1068 m, 1005 s, 960 s, 953 m, 910 w, 875 m, 820 w, 790 w, 652 w, 552 w, 510 s, 430 w cm^{-1}.

Mass Spectrum. 198, $[F_2P(O)]_2NCH_2^+$, 15; 186, $[F_2P(O)]_2NH_2^+$, 5; 155, ?, 12; 128, $F_2P(O)NCH_2CH_3$, 12; 114, $F_2P(O)NCH_3^+$, 16; 104, $P(O)F_3^+$, 35; 85, $F_2P(O)^+$, 100; 47, $P(O)^+$, 80; 31, P^+, 1.

Bis(difluorophosphinyl)aniline. $[F_2P(O)]_2NPh$.

Infrared Spectrum. 3090 *w*, 2980 *w*, 2920 *vw*, 1605 *w*, 1502 *m*, 1425 *w*, 1355 *m*, 1272 *m*, 1232 *w*, 1130 *br,w*, 1075 *br,m*, 940 *m*, 912 *m*, 875 *w*, 820 *m*, 740 *m*, 695 *m*, 650 *w*, 540 *w*, 526 *w*, 490 *m* $cm.^{-1}$

Mass Spectrum. 261, $[F_2P(O)]_2NC_6H_5^+$, 10; 186, $[F_2P(O)]_2NH_2^+$, 100; 177, $F_2P(O)NC_6H_5^+$, 10; 85, $F_2P(O)^+$,80; 77, $C_6H_5^+$, 10; 69, F_2P^+, 8; 50, FP^+, 8; 47, $P(O)^+$, 8.

Preparation of Bis(chlorofluorophosphinyl)methylamine, $[FClP(O)]_2NMe$.

$P(O)FCl_2$ (1.64 g, 12.92 mmol) was added to a stirred solution of $(Me_3Si)_2NMe$ (1.13 g, 6.46 mmol) in diethyl ether at 0°C. When the reaction mixture had been refluxed for ~2 hours, the ^{19}F n.m.r. spectrum showed, in addition to unreacted $P(O)FCl_2$, a doublet centred at $\delta = -34$ppm, $J(PF) = 1134$Hz. After refluxing for 2 days this doublet had decreased in intensity and two other sets of doublets, flanked by weaker lines, had appeared. These latter doublets were assigned to the two diastereoisomers of $[FClP(O)]_2NMe$. The initial one is thought to be due to an intermediate such as $FClP(O)NMeSiMe_3$. The reaction did not go to completion even when the reaction mixture was refluxed for a week and more $P(O)FCl_2$ was added therefore a pure sample could not be obtained.

Reaction between $F_2P(O)NHMe$ and $P(O)FCl_2$. When a 1:1:1 mixture of $F_2P(O)NHMe$, $P(O)FCl_2$ and Et_3N in $CHCl_3$ was refluxed at 40°C for 2 hours a complex mixture of products was formed. These were not identified but a ^{19}F n.m.r. spectrum showed the following sets of doublets attributed to phosphorus fluorine species:- $\delta = -78.3$, $J = 1021$; $\delta = -73.5$, $J = 1060$; $\delta = -71$, $J = 1034$; $\delta = -66$, $J = 925$; $\delta = -64.5$, $J = 997$; $\delta = -43$, $J = 1043$; $\delta = -35.6$ppm, $J = 1109$Hz.

CHAPTER II

THE SYNTHESIS AND PROPERTIES OF SOME NITROGEN DERIVATIVES OF TUNGSTEN HEXAFLUORIDE.

INTRODUCTION

There are now two well established general trends concerning the thermodynamic stability, and hence the reactivity, of transition-metal halides:-

i) In any row of the Periodic Table there is a decrease in the stability of the highest oxidation states with increase in atomic number.

ii) Within any one group of transition-metals the stability of the highest oxidation state increases with increasing atomic number.

These trends have been studied extensively using fluorine derivatives. Since fluorine stabilises higher oxidation states it is possible to obtain, for one metal, a range of compounds each containing the metal in a different oxidation state.

The hexafluorides illustrate the overall trends well. Thus chromium is the only first row metal to form a hexafluoride - and CrF_6 is thermodynamically unstable. In the second row the hexafluorides from molybdenum to rhodium show decreasing stability and no hexafluoride of palladium has been prepared. In the third row, however, with the synthesis in 1972 of AuF_6^- [65], the hexafluorides of all the elements from tungsten to gold have been isolated [66].

The trio of compounds CrF_6, MoF_6 and WF_6 provide a series of compounds on which comparative studies may be carried out, but in practice work has been concentrated on MoF_6 and WF_6 since they are relatively stable. The physical properties of the latter are well established [67]. They are both volatile compounds and are monomeric in the vapour phase. The apparently anomalous order of their boiling points (MoF_6, B.Pt. 34°C; WF_6, B.Pt. 17.1°C) arises because the intermolecular forces are almost identical on the periphery of the molecules, and it is the entropy term which becomes predominant at elevated temperatures. It is a feature of the hexafluorides in general that the compounds of the third row elements are all more volatile than the corresponding second row hexafluorides.

MoF_6 and WF_6 had long been regarded as being chemically very reactive and possessing almost identical chemical properties. However, this assumption was largely based on the fact that they both hydrolyse rapidly and O'Donnell and Stewart have since shown that there is a marked difference in their reactivities. WF_6 is virtually inert both as a fluorinating agent and in halogen exchange reactions, while MoF_6, although shown to be a mild fluorinating agent, readily exchanges its fluorine for chlorine in reactions with, among others, PCl_3 and $AsCl_3$ [68].

Although Ruff and his co-workers studied some transition-metal hexafluorides in the first third of this century [69,70], the first investigation of the chemical properties of WF_6 under strictly anhydrous conditions was carried out by Clark and Emeléus [71]. They studied reactions between WF_6 and various types of compounds. Neither alkali metal fluorides nor sulphur dioxide were found to react with WF_6 , although other workers have prepared and characterised salts of the type RWF_6 (R = K, Rb, Cs) [72, 73]. Sulphur trioxide, however, did react to give an involatile viscous liquid formulated as the fluorosulphate $WF_2(SO_3F)_4$. Reactions with various nitrogen compounds produced the following results:-

i) With ammonia. An orange-brown solid, $(NH_3)_4WF_6$.

ii) With pyridine. A white hygroscopic solid, $(C_5H_5N)_3WF_6$.

iii) With methylamine. A white unstable hygroscopic solid, $(CH_5N)_3WF_6$.

The products of these reactions were identified from analytical results; these indicate that WF_6 does not undergo substitution reactions with amines but instead forms stable adducts. Adducts have also been isolated with sulphur and selenium donors [74]. However, reactions between WF_6 and oxygen donors are more complex. Me_2O, Et_2O and $(Me_3Si)_2O$ react with WF_6 to produce $WOF_4 \cdot OMe_2$, $WOF_4 \cdot OEt_2$ and WOF_4 respectively [75]. The formation of this type of complex demonstrates the great stability of a multiple tungsten oxygen bond.

Charge transfer interactions have been observed between WF_6 and both the group(IV) compounds MX_4 (M = Si, Ge, Sn, X = alkyl; M = C, Si, Sn, X =Cl) and various organic solvents [76-79].

The study of the chemistry of substituted derivatives of WF_6, indeed of all transition-metal halides, has proceeded slowly. Some fully substituted derivatives such as $W(NMe_2)_6$, WMe_6 and $W(OMe)_6$ have been prepared [80-82] although only $W(OMe)_6$ can be synthesised from WF_6; the others are prepared by a reaction of the type:-

$$LiX + WCl_6 \rightarrow WX_6 + LiCl \quad (X = NMe_2, Me)$$

The mono-substituted derivative WF_5Cl, prepared by an exchange reaction between $TiCl_4$ and WF_6, was first reported in 1965 [83], but it is only since the introduction of a type of reaction involving the cleavage of a W-F bond by a Si-X bond (X = Cl, OMe, OPh), that the series $WF_{6-n}X_n$ has been extended. Spectroscopic studies on these compounds suggest that they are monomeric in solution with, in some cases, geometric isomers being present. Recent work, also involving organosilicon compounds as precursors, has produced a series of dialkylamino derivatives $WF_{6-n}(NR_2)_n$ (R = Me,n = 1; R = Et,n = 1,2 and 4.) [84]. The chemistry of these derivatives, in particular their reactions with Me_3SiCl, Me_3SiOMe and $(MeO)_2SO$, has been studied. In each case further substitution of fluorine atoms is achieved. The physical properties of both WF_5NR_2 and $WF_4(NEt_2)_2$ are consistent with their being associated in solution, while $WF_2(NEt_2)_4$ appears to be monomeric.

It was the aim of the work described in this chapter to extend the chemistry of WF_6 with a view to synthesising W=N or W-N-W linkages as there are few examples in transition-metal chemistry of compounds containing these kinds of bonds.

The compounds prepared from the reaction of tungsten oxide tetrachloride, $WOCl_4$, with primary amines were found by analyses to have the composition WOClNR.NHR (R = Me,Et,Ph) [85]. These are red-brown crystalline solids. Evidence from proton magnetic resonance (P.M.R.) and infrared spectra suggested that two different types of tungsten nitrogen bonds were present. The existence of four resonance signals in the P.M.R. spectrum of WOClNEt.NHEt, which was recorded as a 5% solution in chloroform, indicated that the compound contained two non-equivalent methylene groups and hence two non-equivalent tungsten nitrogen bonds. [See Table 2.1] In the infrared spectra of all the compounds, WOClNR.NHR, a band was observed in the 970-950 cm^{-1} range. The authors assigned this band to the W=N stretching frequency.

A second type of compound containing a metal nitrogen double bond was prepared from the reaction

$$VOCl_3 + (Me_3Si)_2NR \longrightarrow VCl_3NR + (Me_3Si)_2O$$

(R = Me,Ph)

TABLE 2.1

P.M.R. of WOClNEt.NHEt

Group	δ(ppm)
$-CH_3$	1.1
$(NH)-\underline{CH}_2$	2.9
-NH-	4.6
$=N-\underline{CH}_2$	7.3

These compounds are also crystalline solids. In this case ν(V=N) was assigned to a band at 985 $cm.^{-1}$ [86].

A compound containing a V=N was also obtained from the following reaction:-

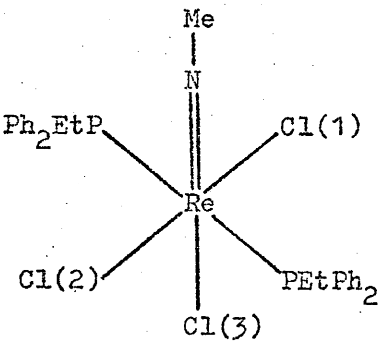
$$NH_4VO_3 \quad + \quad 2HN(SiMe_3)_2 \quad \xrightarrow{-2NH_3} \quad (Me_3SiO)_3V{=}NSiMe_3$$

ν(V=N) was assigned to a band at 990 $cm.^{-1}$ [87].

Bradley and Gitlitz have examined the infrared spectra of alkylamido-trisdialkylamino tantalum compounds, $RN{=}Ta(NR_2)_3$, (R = Et, ^nPr and ^nBu) [88]. They assigned bands in the 620-580 $cm.^{-1}$ range to Ta-N stretching vibrations but were unable to assign any bands to ν(Ta=N). They suggested that these might be in the 1200-1000 $cm.^{-1}$ region and so be obscured by the carbon nitrogen stretches of the ligands. However, the presence of two non-equivalent R groups, =NR and $-NR_2$, was confirmed by the n.m.r. spectra of the compounds, two different signals being obtained for the methylene protons. In $EtN{=}Ta(NEt_2)_3$, for example, the ethylimido methylene quartet was resolved 38.5c/sec downfield from the methylene quartet of the diethylamido groups. The two methyl triplets were also resolved but were too close

(3.7c/sec) to be separated.

The complex $[Re(NMe)Cl_3(PEtPh_2)_2]$ has been shown by X-ray crystallography to have the following structure [89] :-



∠Re=N-Me = 173.4(10)°

Re-Cl(1) = 2.428(6)Å

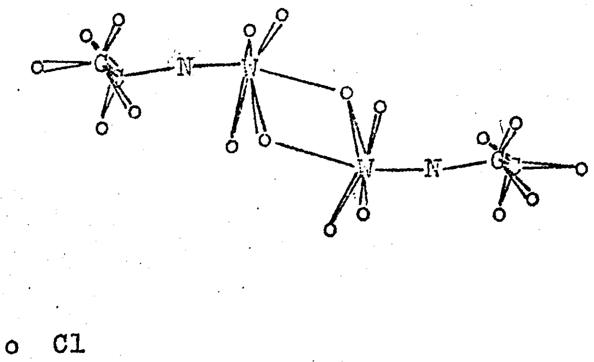
Re-Cl(2) = 2.408(6)Å

Re-Cl(3) = 2.411(6)Å

Re=N = 1.685(11)Å

The notable features of its structure are an almost linear Re-N-Me linkage and a short Re=N bond length. Again the M=N stretching frequency could not be assigned with certainty because the aryl-phosphine ligands absorbed in the same region but a band at ~1090 cm.$^{-1}$ was tentatively assigned to ν(Re=N).

The oxidation of tungsten(V) chloride by trichloroacetonitrile produced on slow recrystallisation from dichloromethane an orange-yellow crystalline solid which analysed as $WCl_6.CCl_3CN$. An X-ray study of this compound showed it to have the following structure [90]:-



The tungsten nitrogen bond length was found to be 1.71Å. This is shorter than those found for tungsten(VI) oxygen multiple bond lengths which lie in the range 1.8-1.9Å, and shorter than W-N single bond lengths which are estimated to lie in the range 2.04-2.07Å [80]. Because of the short W-N distance and the almost linear W-N-C skeleton (the angle = 177°), the tungsten nitrogen linkage was described as W≡N with (p-d)π bonding incorporating the nitrogen lone pair.

A further crystal structure was later carried out on the precursor of $WCl_6.CCl_3CN$ which is $WCl_6.2CCl_3CN$ [91]. The structure showed that this compound contains both trichloroacetonitrile and pentachloroethylnitride groups. The tungsten nitrogen linkage was again proposed as a W≡N since it had the very short bond length of 1.70Å.

Although complete infrared data on the compounds $WCl_6.CCl_3CN$ and $WCl_6.2CCl_3CN$ were not published, a band occurring in the spectrum of each at 1286 $cm.^{-1}$ was assigned as ν(W≡N).

It can be seen from the examples described above that n.m.r. and infrared spectroscopy are important tools in the characterisation of compounds containing transition metal nitrogen multiple bonds. They are used extensively, together with mass spectrometry, to identify the compounds prepared in this work.

SUMMARY OF REACTIONS

1. $WF_6 + (Me_3Si)_2NMe \xrightarrow{\text{1 week}} WF_4NMe + 2Me_3SiF$

2. $WF_6 + F_2PNMeSiMe_3 \xrightarrow{\text{1 week}} WF_4NMe + Me_3SiF + PF_3$

3. $WF_6 + MeNSF_2 \longrightarrow$ polymerisation of $MeNSF_2$

4. $WF_6 + (F_3PNMe)_2 \xrightarrow{\text{1 week}}$ no reaction

5. $WF_4NMe + MeCN \longrightarrow WF_4NMe.MeCN$

6. $WF_6 + (Me_3Si)_2NMe \xrightarrow[\text{immediately}]{MeCN} WF_4NMe.MeCN$

7. $WF_6 + (Me_3Si)_2NMe \xrightarrow{CD_3CN} WF_4NMe.CD_3CN$

8. $WF_4NMe.MeCN + C_5H_5N \longrightarrow WF_4NMe.py + MeCN$

9. $WF_6 + (Me_3Si)_2NMe \xrightarrow{py} WF_4NMe.py + 2Me_3SiF$

10. $WF_6 + (Me_3Si)_2NMe \xrightarrow{C_5D_5N} WF_4NMe.C_5D_5N + 2Me_3SiF$

11. $WF_4NMe.MeCN + Me_3SiCl \xrightarrow{MeCN} WCl_xNMe.MeCN + Me_3SiF$

12. $WF_4NMe.MeCN + Me_3SiOMe \longrightarrow W(OMe)_4NMe$? $+ Me_3SiF$

13. $WF_4NMe.MeCN + SF_5Cl \xrightarrow[h\nu]{MeCN}$ no reaction

14. $WF_4NMe.MeCN + SO_2 \longrightarrow$ no reaction

15. $WF_4NMe.MeCN + CS_2 \longrightarrow$ no reaction

16. $WF_6 + (Me_3Si)_2NH \xrightarrow{-80^{\circ}C}$ peach coloured solid $+ 2Me_3SiF$

17. $WF_6 + (Me_3Si)_2NH \xrightarrow[\text{immediately}]{MeCN} NH_4^+WOF_5^-.MeCN + 2Me_3SiF$

18. $WF_6 + (Me_3Si)_2NH \xrightarrow{CD_3CN} NH_4^+WOF_5^-.CD_3CN$

19. $NH_4^+WOF_5^-.MeCN + C_5H_5N \longrightarrow NH_4^+WOF_5^-.py + MeCN$

20. $NH_4^+WOF_5^-.MeCN + C_5D_5N \longrightarrow NH_4^+WOF_5^-.C_5D_5N + MeCN$

21. $NH_4^+WOF_5^-.MeCN + {}^nBuLi \xrightarrow{C_6H_6}$ no reaction

22. $NH_4^+WOF_5^-.MeCN + Me_3SiCl \xrightarrow{MeCN} NH_4^+WOCl_5^-.MeCN$

23. $MoF_6 + (Me_3Si)_2NMe \longrightarrow$ "MoF_4NMe" $+ 2Me_3SiF$

24. $MoF_6 + (Me_3Si)_2NMe \xrightarrow{MeCN}$ "$MoF_4NMe.MeCN$" $+ 2Me_3SiF$

25. $MoF_6 + (Me_3Si)_2NMe \xrightarrow{C_5H_5N}$ "$MoF_4NMe.py$" $+ 2Me_3SiF$

RESULTS and DISCUSSION

Preparation of WF_4NMe. Tungsten hexafluoride and heptamethyldisilazane react together over a period of a week, in the absence of a solvent, according to equation (1)

$$WF_6 + (Me_3Si)_2NMe \rightarrow \text{cream solid} + Me_3SiF \tag{1}$$

The elemental analyses on the solid were not consistent but suggest that it has the composition WF_4NCH_3. In an effort to obtain consistent analytical data for the compound possible precursors containing an -NMe group were substituted for $(Me_3Si)_2NMe$.

$MeNSF_2$ and WF_6 react below room temperature to produce an orange viscous liquid. This resembles the product formed when $MeNSF_2$ polymerises on standing at room temperature for several hours [92]. It seems likely, therefore, that WF_6 catalyses the polymerisation before the reaction

$$WF_6 + MeNSF_2 \rightarrow WF_4NMe + SF_4 \tag{2}$$

can take place.

No reaction occurs between $(F_3PNMe)_2$ and WF_6 even in the presence of MeCN as a solvent.

$$WF_6 + (F_3PNMe)_2 \not\rightarrow WF_4NMe + PF_5 \tag{3}$$

$F_2PNMeSiMe_3$ and WF_6 react over the period of a week according to equation (4):

$$WF_6 + F_2PNMeSiMe_3 \rightarrow \text{yellow solid} + PF_3 + Me_3SiF \tag{4}$$

It seems likely that this reaction proceeds via an intermediate - possibly $F_2PNMeWF_5$ or $WF_5NMeSiMe_3$. An intermediate of this type was isolated when $F_2PNMeSiMe_3$ reacted with PF_5 in the following way [23]:

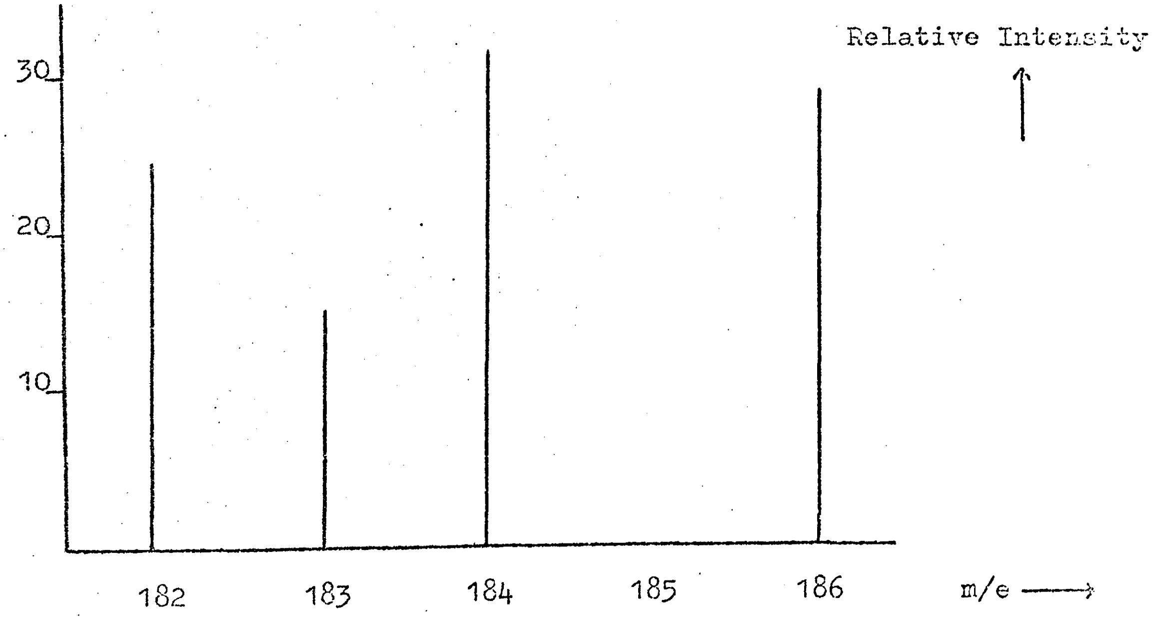
$$PF_5 + F_2PNMeSiMe_3 \rightarrow F_2PNMePF_4 + Me_3SiF \tag{5}$$

However, $F_2PNMePF_4$ dimerised on heating to 80° to produce $(F_3PNMe)_2$

and PF_3. Attempts were made to establish the presence of an intermediate in reaction (4) by studying by infrared spectroscopy at various times during the week the composition of the volatile products. At all times there appeared to be a ~1:1 mixture of PF_3 and Me_3SiF and, therefore, it can be assumed that if an intermediate is formed it is unstable and not isolable. The analyses of the yellow solid formed in (4) corresponded more closely with WF_4NCH_3 than that formed via equation (1) (see Experimental).

Characterisation of WF_4NMe.

1) Mass Spectrum. The mass spectrum has provided valuable evidence in the characterisation of the compound (see Table 2.2). The tungsten atom has four naturally occurring isotopes which have relative abundances of over 1% as shown below:-



This pattern is readily identifiable in a mass spectrum and makes analysis of any spectrum which contains tungsten relatively simple.

Identical spectra are obtained from the samples of WF_4NMe prepared from $WF_6/(Me_3Si)_2NMe$ and $WF_6/F_2PNMeSiMe_3$. The spectrum is simple. Although not confirmed by metastable transitions, there appears to be two breakdown patterns, loss of the NMe group

TABLE 2.2

Mass Spectrum of WF_4NMe

m/e	Assignment	Relative Intensity
291	$WF_4NCH_3^+$	27
272	$WF_3NCH_3^+$	100
262	WF_4^+	44
244	WF_3H^+	5
243	WF_3^+	36
224	WF_2^+	27
205	WF^+	15
29	NCH_3^+	48

Notes:-

i) Intensities are measured as fractions of the most abundant tungsten containing peak.

ii) Only those peaks > 1% relative intensity above m/e = 28 are detailed.

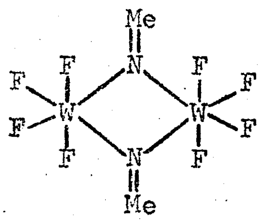
iii) m/e values are given for ^{186}W.

iv) The spectrum was recorded at 250°C. No spectrum was observed if temperatures below this were used.

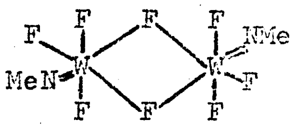
and successive loss of fluorine atoms from the molecular ion and WF_4^+.

The observation of an ion corresponding to $WF_4NCH_3^+$ supports the evidence from the elemental analyses that the compound is WF_4NMe.

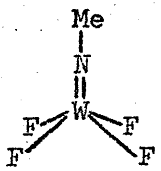
2) <u>Structure and Infrared Spectrum</u>. Assuming that the molecular formula of the compound is WF_4NMe several structures are possible. WF_6 has been shown to be only a weak oxidant [66] so it seems likely that during the reactions undertaken the tungsten atom will retain an oxidation number of six. Some of the possible structures are:-



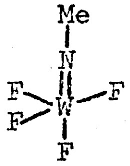
I



II



III



IV

Variations of I and II such as trimeric or tetrameric molecules are also possible. A fluorine-bridged structure would not be surprising in view of the structures determined for analogous apparently five coordinate transition-metal compounds such as NbF_5 and WOF_4. NbF_5 was the first compound of this structural type to be studied. In the solid phase it has been established as a tetrameric molecule with fluorine bridges [93]. Although there has been some controversy about the structure of WOF_4 it now seems certain that it also is a fluorine (as opposed to oxygen) bridged tetrameric species [94, 95]. In fact, the structures which have been determined for both transition-metal pentafluorides and five coordinate fluorine containing derivatives of transition-metals in a +6 oxidation state have shown them all to be bridged species. This suggests that structures III and IV above are unlikely. The infrared spectrum of WF_4NMe is helpful both in eliminating III and IV as possibilities and deciding which of I or II is the more likely structure.

The complete infrared spectrum is given in Table 2.3. There are relatively few bands present suggesting a simple structure. The spectrum is reproducible from sample to sample but in view of the inconsistent analytical data, and hence the possible impurity of the sample, any assignments must be tentative.

It has been suggested from a study of transition-metal fluoride spectra that there are three distinct regions in the spectra due to metal fluorine vibrations:-

i) A metal terminal fluorine stretching region, 800-600 $cm.^{-1}$.
ii) A metal bridging fluorine stretching region, 550-450 $cm.^{-1}$.
iii) A metal fluorine bending region, 350-50 $cm.^{-1}$ [96].

Thus the very strong band at 700-650 $cm.^{-1}$ observed in the spectrum of WF_4NMe is assigned to a tungsten terminal fluorine stretching mode. However, this is also the region where $\nu(W-N)$, if present, would be expected to occur and its presence may be hidden by the strong $\nu(W-F)$. The band at 540-510 $cm.^{-1}$ is in the region expected for a metal bridging fluorine stretch, and is assigned as such. This assignment is confirmed by the

TABLE 2.3

Infrared Spectrum of WF_4NMe

WF_4NMe (cm.$^{-1}$)	Assignment
1412 w	
1335 m	ν(C-N) in secondary amine
1260 w	possibly Me_3Si impurity
890 m	ν(W=N)
855 m	possibly Me_3Si impurity
682 s	ν(W-F) terminal
648 s	ν(W-F) "
540-510 m,br	ν(W-F) bridging

The spectrum was recorded in the solid phase using both nujol and fluorolube as mulling agents.

fact that there is no corresponding band in $WF_4NMe.MeCN$ which has been ascribed a non-bridging structure (vide infra).

No bands at ~3000 cm.$^{-1}$ due to NC-H vibrations are discernible. There is, however, a medium intensity band at 890 cm.$^{-1}$ This is not in the range corresponding to any C-H, C-N or M-F vibration (M = transition metal), nor is it in the region expected for M-N stretching vibrations which should occur from 700-500 cm.$^{-1}$ [88]. A possible impurity in the compound is unreacted $(Me_3Si)_2NMe$ but its spectrum does not have a peak at 890 cm.$^{-1}$ [61]. By comparison with the spectra of the transition-metal compounds containing metal nitrogen multiple bonds described in the Introduction, this band at 890 cm.$^{-1}$ is assigned to a M=N stretching vibration. It occurs 80-100 cm^{-1} lower than other values of $\nu(M=N)$ which have been observed. This is attributed to the greater electronegativity of the fluorine atoms compared with the alkyl and chloro groups present in the other derivatives.

The assignment of bands to bridging fluorine atoms and a W=N bond implies that II is the most likely structure for WF_4NMe. However, no decision can be made about the degree of polymerisation of the molecule.

3) N.M.R. Spectra and Molecular Weight. N.m.r. spectra could not be obtained as WF_4NMe is only soluble in polar solvents with which it reacts. Molecular weight studies, which would have given an indication of the degree of polymerisation, were also ruled out because of the lack of a suitable solvent.

Preparation of $WF_4NMe.MeCN$. Since WF_4NMe reacted with MeCN it was thought that the addition of MeCN to the reaction mixture of WF_6 and $(Me_3Si)_2NMe$ might produce an adduct for which it would be possible to obtain good elemental analyses and which could be studied by n.m.r. spectroscopy. This proved to be the case.

The adduct $WF_4NMe.MeCN$ may be prepared in two ways:-

$$WF_4NMe + xsMeCN \longrightarrow WF_4NMe.MeCN \qquad (6)$$

$$(Me_3Si)_2NMe + WF_6 \xrightarrow{MeCN} WF_4NMe.MeCN + 2Me_3SiF \qquad (7)$$

Reaction (7) takes place immediately on warming the reactants from -196°C. It appears to proceed via a purple intermediate which changes at ~-30°C to form an orange crystalline solid. On one occasion a ^{19}F n.m.r. spectrum was obtained of the purple solution. It consisted of a singlet which had a chemical shift of +92.5ppm ; (CCl_3F was used as an external reference). This value of chemical shift is intermediate between that of WF_6 (+165ppm) and that recorded elsewhere for $WF_4NMe.MeCN$ (+35.4ppm). Moreover, it is in the same region as that noted for WF_5NEt_2 (+128ppm) [84]. However, this intermediate species could not be isolated and was not studied further but it is thought from its chemical shift that it is a compound such as $WF_5NMeSiMe_3$ which eliminates Me_3SiF to form the crystalline compound $WF_4NMe.MeCN$.

Characterisation of $WF_4NMe.MeCN$.

1) *Elemental Analysis.* Although agreement between the analysis expected for $WF_4NMe.MeCN$ and that found experimentally is better than for WF_4NMe, consistently low values were obtained for carbon and nitrogen (see Experimental section). A possible explanation for this is that the adduct dissociates over a period of time, resulting in the loss of MeCN.

2) *Mass Spectrum.* The mass spectrum was recorded at various probe temperatures from 110°C to 250°C. At 110°C only the spectrum of MeCN is observed. No other peaks are seen until the temperature reaches 250°C when a spectrum due to $WF_4NMe.MeCN$ is recorded. At this temperature the spectrum of $WF_4NMe.MeCN$ differs from that of WF_4NMe in that additional fragment ions of the WF_4NMe entity are observed and a peak due to the tungsten ion W^+ is recorded. Table 2.4 gives the complete spectrum. The most abundant ion is that due to CH_3CN^+ while the most abundant tungsten containing ion is the same as with WF_4NMe, $WF_3NCH_3^+$.

3) *N.M.R. Spectra.* The adduct $WF_4NMe.MeCN$ is moderately soluble in both MeCN and CD_3CN so a study of its ^{19}F and ^1H n.m.r. spectra can be made. Table 2.5 gives details of the

TABLE 2.4

Mass Spectrum of $WF_4NMe.MeCN$

m/e*	Assignment	Relative Intensity*
291	$WF_4NCH_3^+$	28
272	$WF_3NCH_3^+$	100
262	WF_4^+	44
252	$WF_2NCH_2^+$	5
243	WF_3^+	33
224	WF_2^+	22
205	WF^+	5
186	W^+	2
77	?	8
41	CH_3CN^+	150
40	CH_2CN^+	100
39	$CHCN^+$	50
38	CCN^+	45

* See notes i-iii in Table 2.2

n.m.r. spectra obtained using CD_3CN as a solvent.

^{19}F Spectrum. This consists of a strong single peak with satellites. The distance between these satellites corresponds to the tungsten fluorine coupling constant. The coupling arises from the fact that the ^{183}W nucleus, which is 14% abundant, has a spin of $\frac{1}{2}$ and so coupling between the ^{19}F nucleus and the ^{183}W nucleus gives rise to a doublet. Table 2.6 lists examples of the coupling constant $^2J(F-W)$ found in related W(VI) fluorine compounds. This coupling is not observed with

TABLE 2.5

N.M.R. Spectra of $WF_4NMe.MeCN$

^{19}F	δ_F	+35.4ppm	$^1J(W-F)$	56Hz
^1H	δ_{CH_3CN}	2.1ppm	$^2J(H-N)$	2.8Hz
	δ_{NCH_3}	5.75ppm	$^4J(H-F)$	1.3Hz

TABLE 2.6

Compound	$^1J(F-W)$Hz	
WF_6	44	[97]
WF_5OMe	43	[75]
WOF_4	64	[97]
$WOF_4.OMe_2$	68	[75]
WF_5Cl	25	[98]
WF_4Cl_2(trans)	20	[98]
$WF_4NMe.MeCN$	56	

the tungsten nitrogen derivatives described in reference [84] where only broad signals are obtained. It can be seen that the coupling constant J(F-W) is larger in compounds where the tungsten atom forms a multiple bond to a ligand compared with those compounds where only single bonds are present. Apart from this, however, there is no trend discernible in the magnitude of the coupling constants measured so far.

It was thought that any splitting of the singlet observed in the ^{19}F spectrum might indicate coupling of the ^{19}F nuclei to the protons. However, no coupling is observed even when the sample of $WF_4NMe.MeCN$ in CD_3CN is cooled to ~-50°C where it solidifies.

The value of the chemical shift observed for the ^{19}F nuclei is considerably upfield from those recorded for WF_6 and its complexes [97] suggesting that the ^{19}F nuclei are in a much more shielded environment.

<u>^{1}H Spectrum.</u> This was recorded in both MeCN and CD_3CN solutions. The spectrum in CD_3CN usually consists of a sharp singlet at $\delta = 2.1$ppm, due to MeCN, and a multiplet centred at $\delta = 5.75$ppm due to the -NMe group. However, on some occasions a broad signal is obtained for the MeCN group. A possible explanation for this broadening is that MeCN is alternatively coordinating with and dissociating from the WF_4NMe part of the molecule at a speed which is detectable on the n.m.r. time scale. It is possible that the dissociation process is catalysed by traces of moisture in the solvent. The chemical shift observed for the MeCN (2.0ppm) is almost identical to that recorded for the free MeCN (2.05ppm) [99].

The multiplet due to the NMe protons when expanded shows a group of seven peaks in the ratio 1:2:2:1.5:2:2:1 caused

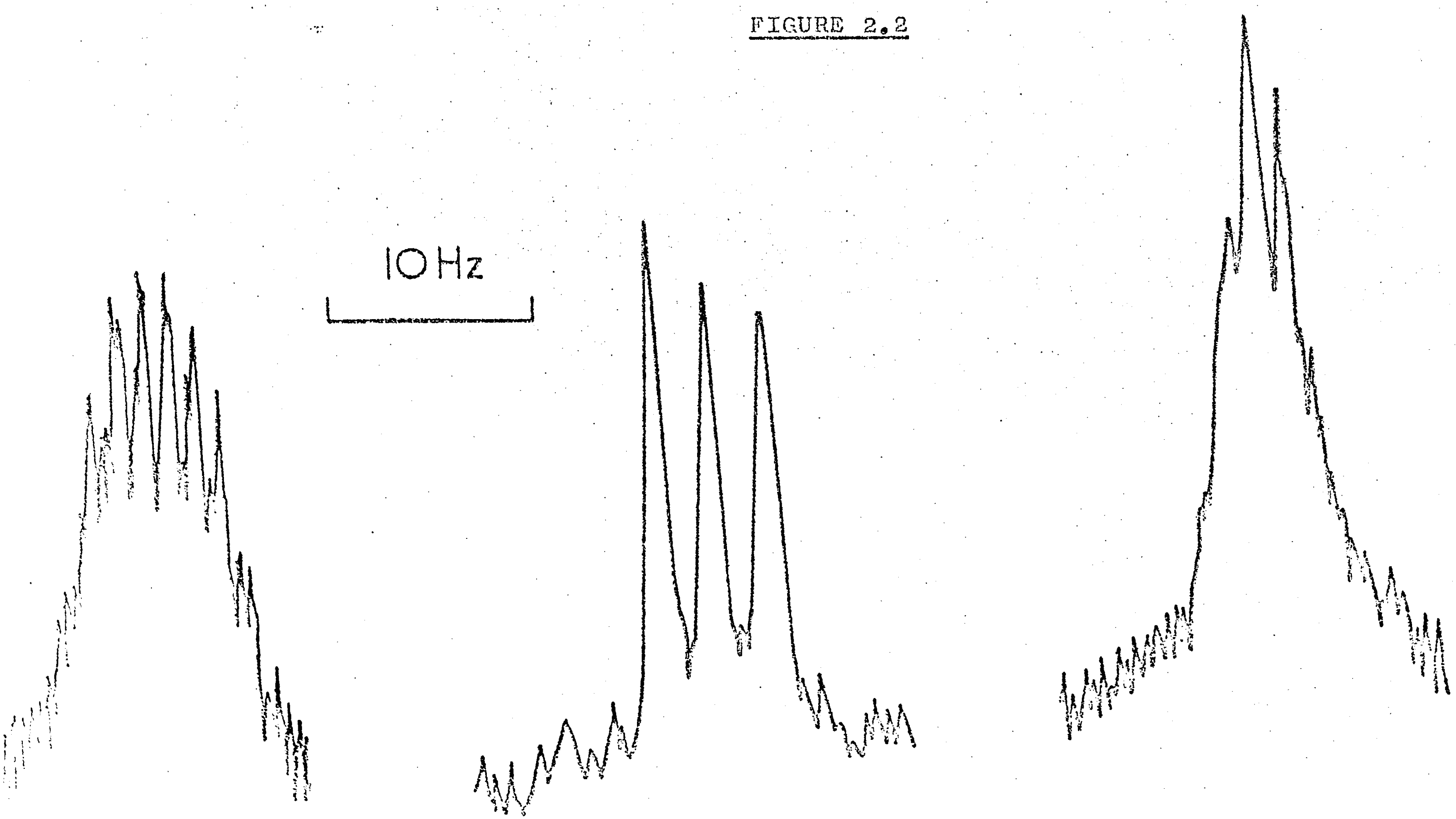
TABLE 2.7

N.M.R. Spectra of Some Isonitriles

Compound	δ_{CH_3} or CH_2 (ppm)	$^2J(H-N)Hz$
$(CH_3)_3CNC$	1.44	3.5
CH_3NC	2.85	2.7
$PhCH_2NC$	4.28	1.3

by coupling of the protons to both the nitrogen and fluorine nuclei. The signal can be simplified by decoupling the proton and fluorine nuclei. If this is done the signal appears as a 1:1:1 triplet (see Figure 2.2). The nitrogen nucleus, ^{14}N, has a nuclear spin of 1 so the signal corresponds to coupling of the protons to ^{14}N. The presence of the nuclear quadrupole moment associated with the ^{14}N nucleus usually relaxes the coupling of ^{14}N nuclei to other nuclei. Coupling of the type J(H-N) has been observed in the ^1H spectra of some other compounds such as those containing the ammonium ion NH_4^+ [100], amides [101] and dry ammonia [102]. The only long range $^{14}N-^1H$ coupling observed until now has been in the spectra of some isonitriles, RNC (see Table 2.7) [103]. The fact that coupling is observed with these compounds indicates that the electric field gradient is unusually small and that the spin lattice relaxation time of the ^{14}N nucleus must be comparable to the coupling constant. It is thought that the low electric field gradient must be due to the axial symmetry of the electron density near the nitrogen atom. Thus observation of this type

FIGURE 2.2



-NMe signal

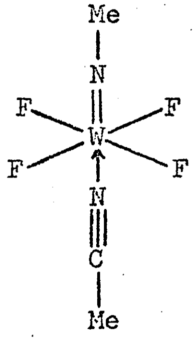
^{19}F decoupled

^{14}N decoupled

of coupling ^2J(H-N) in $WF_4NMe.MeCN$ is an unusual feature of the spectrum. The size of the coupling constant is similar to those observed for the isonitriles. The fact that the coupling is observed suggests that there must be a symmetrical electric field gradient around the nitrogen atom.

When the ^{14}N nucleus is decoupled from the protons a quintet is observed. This corresponds to coupling of the protons to the four ^{19}F nuclei.

Thus the n.m.r. spectra of $WF_4NMe.MeCN$ provide evidence that the compound has the following monomeric structure in solution:-



The existence of only one signal for the ^{19}F nuclei and their coupling to ^{183}W suggests that the four ^{19}F nuclei are equivalent. This means that the -NMe group and MeCN are trans to one another.

4) <u>Infrared Spectrum</u>. Since pure samples of $WF_4NMe.MeCN$ could be obtained its infrared spectrum was studied in more detail than that of WF_4NMe. To help with the assignment of the spectrum a sample of $WF_4NMe.CD_3CN$ was prepared. It can be synthesised in two ways:-

$$WF_4NMe.MeCN \quad + \quad xs\ CD_3CN \quad \longrightarrow \quad WF_4NMe.CD_3CN \quad + \quad MeCN \qquad (8)$$

$$(Me_3Si)_2NMe \quad + \quad WF_6 \quad \longrightarrow \quad WF_4NMe.CD_3CN \quad + \quad 2Me_3SiF \qquad (9)$$

When $WF_4NMe.CD_3CN$ is prepared as in equation (8) its infrared spectrum shows no peaks attributable to MeCN either free or coordinated indicating that complete exchange between MeCN and CD_3CN takes place. However, the samples of $WF_4NMe.CD_3CN$ which were used in the study of its infrared spectrum were obtained according to equation (9) since this method of preparation eliminates the possibility of contamination by MeCN.

Table 2.8 gives details of the observed spectra. The assignments are made by comparison of the spectra with those of free MeCN, CD_3CN [104] and coordinated MeCN [105].

There are fairly large shifts in the frequency of the bands observed in the spectrum of $WF_4NMe.MeCN$ compared with those for WF_4NMe suggesting that the coordination of MeCN to WF_4NMe involves a structural change. A significant difference between the spectra of WF_4NMe and $WF_4NMe.MeCN$ is the absence of the broad band at 540-510 cm^{-1} in the spectrum of the coordinated molecule. Because of this it was assigned as a bridging W-F stretching mode in WF_4NMe. There is a shift to higher frequency of ~40 cm^{-1} in the C≡N stretching frequency of $WF_4NMe.MeCN$ compared with that of free MeCN. This is characteristic of nitriles which are coordinated via the nitrogen atom although studies with other donor molecules might have led one to expect a shift in the opposite direction. This apparently anomalous shift in frequency has been discussed many times before [106,107]. Purcell and Drago concluded that the increase in the frequency of $\nu(C\equiv N)$ upon coordination must be due to an increase in the C≡N force constant. Purcell further went on to propose [108] that all nitriles coordinated to Lewis acids show this increase in force constant due to a strengthening of the σ bonding between carbon and nitrogen. He suggested that in addition to its 's' character the nitrogen lone pair orbital

TABLE 2.8

Infrared Spectra of $WF_4NMe.MeCN$ and $WF_4NMe.CD_3CN$

$WF_4NMe.MeCN$(cm.$^{-1}$)	$WF_4NMe.CD_3CN$(cm.$^{-1}$)	Assignments
3010 m		$\nu(C-H)$ in MeCN
	2980 vw	
2943 m		
2930 sh	2930 w	
2858 w	2858 w	$\nu(C-H)$ in $-NCH_3$
2320 m		combination
	2318 m	$\nu(C\equiv N)$
2295 m		"
	2262 w	$\nu(C-D)$
1410 w	1415 w	
1337 s	1334 s	$\delta(CH_3)$ in $-NCH_3$
1038 m	1028 m	$\nu(C-N)$ or $\nu(W=N)$ or $\nu(C-N=W)$
1025 w,sh	856 m	$\rho(CH_3)$ and $\rho(CD_3)$
947 m		$\nu(C-C)$in MeCN
720 w	720 w	
701 w	700 w	
658 m	658 m	$\nu(W-F)$ terminal
630-600 s	630-600 s	"

These spectra were recorded in the solid phase using both nujol and fluorolube as mulling agents.

TABLE 2.9

ν(M-F) in MF$_5$ (cm.$^{-1}$)		ν(M-F) in MF$_5$.MeCN (cm.$^{-1}$)	
NbF$_5$	746	NbF$_5$.MeCN	710
TaF$_5$	757	TaF$_5$.MeCN	712
MoF$_5$	763	MoF$_5$.MeCN	703

acquires an amount of 'p' character on coordination which means an increasing amount of 's' character in the C≡N bond resulting in an increased force constant.

The strong band in the spectrum of WF$_4$NMe.MeCN at 660-600 cm.$^{-1}$ is assigned to metal fluorine stretching vibrations. This is a decrease of ~30 cm.$^{-1}$ from $\nu_{terminal}$(W-F) in WF$_4$NMe. A similar decrease in the vibrational frequency of terminal metal fluorine bonds has been observed with some transition-metal pentafluorides and their complexes [96] (see Table 2.9), where the coordination number of the central metal atom also did not change on adduct formation.

The assignment of a metal nitrogen stretching frequency is more difficult in the spectra of WF$_4$NMe.MeCN and WF$_4$NMe.CD$_3$CN than with the uncoordinated molecule WF$_4$NMe. There are no bands directly comparable to that at 890 cm.$^{-1}$ in WF$_4$NMe which was tentatively assigned to ν(W=N). The carbon nitrogen stretching frequency in aliphatic amines is said to occur in the range 1230-1030 cm.$^{-1}$ [109]. Therefore, the bands occurring at 1038 and 1028 cm.$^{-1}$ in WF$_4$NMe.MeCN and WF$_4$NMe.CD$_3$CN respectively may be due to ν(W=N) or ν(C-N). However, it is likely that since these two vibrations are expected to have similar energies coupling of the vibrations occurs and the peaks may correspond to ν_{as}(C–N=W).

Preparation of $WF_4NMe.py$. In an attempt to replace the MeCN in $WF_4NMe.MeCN$ by another ligand the following reactions were carried out:-

$$WF_4NMe.MeCN + xsC_5H_5N\ (py) \rightarrow WF_4NMe.py + MeCN \qquad (10)$$

$$WF_6 + (Me_3Si)_2NMe \xrightarrow{py} WF_4NMe.py + 2Me_3SiF \qquad (11)$$

The reactions take place immediately on allowing the mixtures to warm to room temperature. On removal of the volatile products and excess solvent a black crystalline compound is obtained in each case. The solid obtained from reaction (11) analyses as $WF_4NCH_3.C_5H_5N$ (written as $WF_4NMe.py$).

Characterisation of $WF_4NMe.py$.

1) Mass Spectrum. This was recorded at a probe temperature of 110°C. The complete spectrum is given in Table 2.10. The most significant feature of the spectrum is the appearance of a peak corresponding to the ion $WF_4NCH_3.C_5H_5N^+$ in contrast to the spectrum of $WF_4NMe.MeCN$ where a molecular ion is not observed. C_5H_5N has been shown to form stronger complexes with metals in high oxidation states than MeCN [110], and the observation of the ion $WF_4NCH_3.C_5H_5N^+$ is attributed to this. The difference in the spectra of $WF_4NMe.MeCN$ and $WF_4NMe.py$ is not accounted for by a difference in the temperatures at which they were recorded since attempts to record the spectrum of $WF_4NMe.MeCN$ at a probe temperature of ~110°C produced only the spectrum of MeCN. The tungsten containing fragment ions observed in the spectrum of $WF_4NMe.py$ are similar to those obtained for WF_4NMe and $WF_4NMe.MeCN$ indicating a similar breakdown pattern. The most intense peak in all these spectra (apart from those

TABLE 2.10

Mass Spectrum of $WF_4NMe.py$.

m/e*	Assignment	Relative Intensity*
370	$WF_4NCH_3.C_5H_5N^+$	27
351	$WF_3NCH_3.C_5H_5N^+$	100
341	$WF_4.C_5H_5N^+$	72
322	$WF_3.C_5H_5N^+$	10
321	$WF_3.C_5H_4N^+$	20
272	$WF_3NCH_3^+$	95
262	WF_4^+	82
243	WF_3^+	66
224	WF_2^+	66
93	?	100
79	$C_5H_5N^+$	250
78	$C_5H_4N^+$	100
52	$C_4H_4^+$	200
51	$C_4H_3^+$	150
50	$C_4H_2^+$	100
44	?	80
38	$C_3H_2^+$	60

* See notes i-iii in Table 2.2

TABLE 2.11

N.M.R. Spectra of $WF_4NMe.py$

^{19}F	δ_F	+36.6ppm	
^{1}H	δ_H	4.75ppm	-NMe
		6.5 "	pyridine
		6.95 "	pyridine
		8.1 "	pyridine

due to the ligands) corresponds to the loss of one fluorine atom from the molecular ion.

2) N.M.R. Spectra. Details of the spectra are presented in Table 2.11.

^{19}F Spectrum. This consists of a singlet with no resolvable fine structure. It was expected that satellites due to coupling between the ^{19}F and ^{183}W nuclei would be observed as with $WF_4NMe.MeCN$. The fact that these additional peaks were not recorded is possibly due to the spectrum being recorded on solutions of insufficient concentration.

^{1}H Spectrum. A study of this spectrum shows that the molecule contains pyridine and an -NMe group in a 1:1 ratio. The -NMe signal at δ = 4.75ppm is broad with some fine structure visible but due to lack of time no attempt was made to simplify the signal in a manner similar to that achieved for $WF_4NMe.MeCN$.

Apart from that of $[Re(NMe)Cl_3(PEtPh_2)_2]$, the ^{1}H spectra which have been published for compounds containing F-W-N or M=N linkages (M = transition-metal) are all for compounds where the alkyl group is ethyl or a higher alkyl. Thus comparison

TABLE 2.12

Compound	δ_{CH_2} ppm	δ_{CH_3} ppm	
WF_5NEt_2	5.7	1.1	[84]
$[Re(NMe)Cl_3(PEtPh_2)_2]$		0.8	[89]
$CH_3\underset{\sim}{C}\underset{\sim}{H}_2{=}Ta(NEt_2)_3$	4.04		[88]

between the chemical shifts observed here for the methyl protons and those found for analogous compounds is difficult. However, an estimate of the likely chemical shift of the -NMe group can be made. Table 2.12 gives details of analogous compounds. Normally methylene protons are shifted ~0.5ppm downfield from T.M.S. compared with methyl protons in a similar electronic environment [111]. Thus one might expect the methyl protons in $WF_4NMe.MeCN$ or $WF_4NMe.py$ to have a chemical shift of about 4.5ppm. The fact that it is found at 4.75ppm in $WF_4NMe.py$ and 5.75ppm in $WF_4NMe.MeCN$ is indicative of the electronegativity of the fluorine atoms which reduce the electron density around the methyl group. The difference in chemical shift of 1ppm between the acetonitrile and pyridine complexes is accounted for by the greater electron donating power of pyridine as compared to acetonitrile.

3) Infrared Spectrum. To aid the assignment of bands in the infrared spectrum of $WF_4NMe.py$ the compound with the deuterated ligand was prepared as in equation (12):-

$$WF_6 + (Me_3Si)_2NMe \xrightarrow{C_5D_5N} WF_4NMe.C_5D_5N + 2Me_3SiF \qquad (12)$$

The complete spectra of both $WF_4NMe.py$ and $WF_4NMe.C_5D_5N$ are detailed in Table 2.13.

TABLE 2.13

Infrared Spectra of $WF_4NMe.py$ and $WF_4NMe.C_5D_5N$

$WF_4NMe.py(cm.^{-1})$	$WF_4NMe.C_5D_5N(cm.^{-1})$	Assignments
3080 br,w		$\nu(C-\overset{*}{H})$ in pyridine
2960 br,w		$\nu(C-H)$ in -NMe
1615 m	1575 m	in-plane ring deformations
1490 w	1420 br,w	"
1452 m		"
	1350 w	"
1320 m	1325 m	
1224 w		$\delta(C-\overset{*}{H})$ in-plane
1158 m		"
1070 m		
1017 m	1025-1015 br,w	$\nu(W=N)$ or $\nu_{as}(C-N=W)$
	980 m	$\delta(C-\overset{*}{H})$ out-of-plane
956 br,m	960 sh,w	"
898 br,m	898 w	"
	830 m	"
760 br,m	740-720 w	"
688 m		
653 m	651 m	$\nu(W-F)$ terminal
600 br,s	600 br,s	"
	536 m	

These spectra were recorded in the solid phase using both nujol and fluorolube as mulling agents.

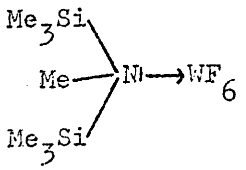
$\overset{*}{H}$ corresponds to either H in C_5H_5N or D in C_5D_5N.

The infrared spectrum of the pyridine molecule is considerably modified on coordination. Detailed studies have been made of the spectrum of pyridine [112] and of its metal complexes [113,114]. Assignments made in these studies have been used here to identify the bands due to pyridine and deuteriopyridine. This means that the bands due to the WF_4NMe part of the complex can be identified and any change in their frequencies from those in $WF_4NMe.MeCN$ can be observed.

There is a small decrease in the WF_4 stretching frequencies on going from the acetonitrile adduct to the pyridine adduct. The other bands corresponding to the WF_4NMe part of the complex are similar to those found in the acetonitrile adduct. Consequently the bands observed at 1017 and 1025 cm.$^{-1}$ in the pyridine and deuteriopyridine adducts respectively are tentatively assigned as $\nu(W{=}N)$ or more likely $\nu_{as}(C{-}N{=}W)$. A more definite assignment cannot be made in view of the occurrence in this region of pyridine bands which may possibly obscure any bands due to the M=N vibration.

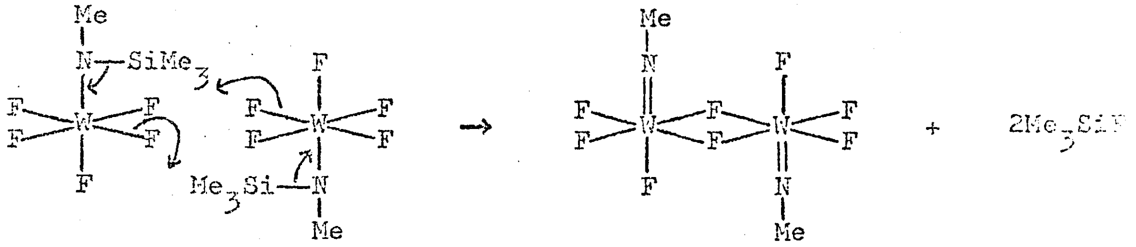
Discussion of Reaction Mechanisms for the Formation of WF_4NMe, $WF_4NMe.MeCN$ and $WF_4NMe.py$.

1) WF_4NMe. The good acceptor properties of WF_6 illustrated by the formation of complexes between it and N-donors [97] suggest that a reaction between WF_6 and $(Me_3Si)_2NMe$ is likely to proceed via a seven coordinate intermediate of the type



$$(\mathrm{Me_3Si})_2(\mathrm{Me})\mathrm{N} \rightarrow \mathrm{WF_6} \qquad \text{(i)}$$

(i) can then eliminate Me_3SiF with the formation of the strong Si-F bond acting as a driving force for the reaction. A process of this type would lead to the formation of $WF_5NMeSiMe_3$ which could then rearrange either inter- or intramolecularly eliminating another molecule of Me_3SiF. A possible mechanism for an intermolecular rearrangement is:-



(ii)

For convenience this mechanism has been illustrated using only two molecules but more may be involved. A rearrangement of the type described could also lead to the formation of a nitrogen-bridged polymer but a fluorine-bridged species seems the more likely from infrared evidence.

The reaction between WF_6 and $(Me_3Si)_2NMe$ is very slow, much slower than, for example, that between WF_6 and Me_3SiNEt_2 which goes to completion within 30 minutes. There are three stages in the suggested process which could determine the rate of reaction:-

i) The nucleophilic attack on tungsten by the nitrogen lone pair of electrons.

ii) The decomposition of the adduct $(Me_3Si)_2NMe.WF_6$ with elimination of Me_3SiF.

iii) The intramolecular rearrangement of $WF_5NMeSiMe_3$.

Since no evidence is found for the existence of $WF_5NMeSiMe_3$ if it is formed it must rearrange quickly indicating that (iii) is a fast process. Complexes of WF_6 previously prepared have been found to be reactive species [97], and the ^{19}F chemical shift of the WF_6 has been found to change on coordination (by 3-30ppm depending on the solvent used). Therefore, if the decomposition of the species $(Me_3Si)_2NMe.WF_6$ is the rate determining step in the reaction, which seems unlikely, it should be possible to detect its presence in the reaction mixture by n.m.r. spectroscopy. $(Me_3Si)_2NMe$ is a poorer nucleophile than C_5H_5N, Me_3N or Me_3SiNEt_2 all of which react quickly with WF_6. This is because the lone pair of electrons on the nitrogen atom in $(Me_3Si)_2NMe$ takes part in (p-d)π-bonding between the nitrogen and silicon atoms and it has been found that the extent of this bonding increases with the number of silicon atoms bound to nitrogen [115]. Because of this it seems likely that the rate determining step in the reaction between WF_6 and $(Me_3Si)_2NMe$ is stage (i), the nucleophilic attack of the nitrogen atom on tungsten.

2) $\underline{WF_4NMe.MeCN}$ and $\underline{WF_4NMe.py}$. The reaction between WF_6 and $(Me_3Si)_2NMe$ takes place immediately in the presence of either MeCN or C_5H_5N which suggests that the solvents are concerned in the rate determining step of the reaction in such a way that they speed it up considerably. WF_6 is known to be monomeric in the liquid phase [116] so the solvent is not breaking up a polymeric structure. In the reaction between WF_6 and $(Me_3Si)_2NMe$ some evidence was found for the existence of an intermediate such as $WF_5NMeSiMe_3$ (see Results section). The use of MeCN as a solvent and the mechanism of reaction of donor solvents in general have been reviewed several times [116,117,118]. From these discussions it seems likely that the first stage in the reaction between $WF_6/(Me_3Si)_2NMe/MeCN$ will be the formation of an adduct $WF_6.MeCN$ which can react more easily with $(Me_3Si)_2NMe$ than can WF_6. This could be because:-

i) The geometry of the seven coordinate adduct is more suitable for the approach of the lone pair of electrons on the nitrogen atom.

ii) The fluorine atoms become more labile on coordination thus facilitating the formation of Me_3SiF.

Reactions of $WF_4NMe.MeCN$. A preliminary investigation was made of the chemical reactions of $WF_4NMe.MeCN$ with a view to substituting the fluorine atoms by other groups.

A) Reaction of $WF_4NMe.MeCN$ with Trimethylchlorosilane. No reaction occurs between excess Me_3SiCl and $WF_4NMe.MeCN$ in the absence of a solvent. However, the addition of MeCN to a reaction mixture containing Me_3SiCl and $WF_4NMe.MeCN$ produces a dark red solution from which a brown crystalline solid, 'A', can be isolated. Me_3SiF is identified as a volatile product so replacement of fluorine by chlorine is thought to have taken place.

$$WF_4NMe.MeCN \quad + \quad xsMe_3SiCl \quad \rightarrow \quad \text{'A'} \quad + \quad Me_3SiF \qquad (13)$$

Characterisation of Brown Crystalline Solid, 'A'.

1) Mass Spectrum. This was recorded at 90°C and details of the spectrum are given in the Experimental section. A complex pattern is observed for the highest set of peaks in the spectrum. This arises from the fact that, as well as observing the pattern due to the four isotopes of tungsten, there is superimposed on this a pattern due to the two naturally occurring isotopes of chlorine, ^{35}Cl and ^{37}Cl. This makes assignment of the set of peaks unambiguous. They correspond to $WCl_3NCH_3^+$. Even though these are the strongest peaks due to tungsten containing ions in the spectrum they are not very strong and it is possible that a set of peaks corresponding to $WCl_4NCH_3^+$ could be observed if a spectrum were recorded at an even lower temperature or a smaller ionising voltage. The fragment ions observed are of a similar

kind to those observed for WF_4NMe corresponding to loss of the -NMe group and successive loss of chlorine atoms.

2) Infrared Spectrum. This was recorded over the range 4000-250 $cm.^{-1}$ and the complete spectrum is given in the Experimental section. It is a simple spectrum similar in pattern to that recorded for $WF_4NMe.MeCN$. It confirms that MeCN is still coordinated to the tungsten atom in 'A' but a significant difference between its spectrum and that of $WF_4NMe.MeCN$ is the absence of the broad band at ~600 $cm.^{-1}$ which was assigned to tungsten fluorine stretching frequencies in $WF_4NMe.MeCN$. This is replaced in the spectrum of 'A' by a very strong peak at 335 $cm.^{-1}$ which is assigned to tungsten chlorine stretching modes by comparison with the spectra of WCl_6 and WF_5Cl [119,120].

3) N.M.R. Spectra.

^1H Spectrum. This was recorded in a solution of CD_3CN. It consists of two broad unresolved peaks of equal intensity which from their chemical shifts of δ = 1.9 and 6.8ppm are assigned to MeCN and -NMe protons respectively. The chemical shift observed for the -NMe protons is downfield from that recorded for the -NMe protons in $WF_4NMe.MeCN$ (δ = 5.75ppm). This is consistent with the reduced electronegativity of chlorine compared with fluorine in that the chlorine atoms will not attract the lone pair on the nitrogen atom as much as the fluorine atoms leaving a greater electron density around the -NMe protons.

^{19}F Spectrum. None was observed as expected.

4) Summary. Unfortunately an insufficient quantity of material was obtained to enable an elemental analysis of the compound to be carried out and time did not permit further

study of the compound, but from the information available it seems likely that the product of reaction (13) is either $WCl_3NMe.MeCN$ or $WCl_4NMe.MeCN$. The fact that all the fluorine atoms in $WF_4NMe.MeCN$ are replaced by chlorine is deduced from the infrared spectrum, and the presence of at least three chlorine atoms attached to tungsten can be assumed from the mass spectrum. If the compound is $WCl_3NMe.MeCN$ it is a derivative of W(V) and therefore paramagnetic. However, no signal was obtained when an e.s.r. spectrum was recorded (in a chloroform solution) which suggests that the compound is $WCl_4NMe.MeCN$. An additional reason for assuming that the compound still contains W(VI) is that Me_3SiCl reacts with WF_6 without reducing it, compounds of the type WF_nCl_{6-n} being obtained [120]. An elemental analysis of 'A' should confirm its composition as $WCl_4NMe.MeCN$.

B) <u>Reaction of $WF_4NMe.MeCN$ with Trimethylmethoxysilane.</u>

When $WF_4NMe.MeCN$ and a large excess of Me_3SiOMe are shaken together for 24 hours in a solution of MeCN, an orange crystalline solid is obtained. Both the elemental analysis and the mass spectrum of the solid are difficult to interpret suggesting that instead of simple replacement of the fluorine atoms in $WF_4NMe.MeCN$ by -OMe, extensive rearrangement takes place possibly with the formation of tungsten oxygen double bonds. Details of the elemental analysis and the mass and infrared spectra of the orange solid are given in the Experimental section.

The infrared spectrum of the compound has no bands in the region 2500-2300 cm^{-1} implying that this compound has no coordinated MeCN - unlike the other compounds examined. There are, however, two strong bands at 570 and 540 cm.$^{-1}$. The latter is in the range of a bridging W-F stretching mode while the former may correspond to a tungsten oxygen stretching vibration, although these occur over a wide range of frequencies (700-300 cm.$^{-1}$) [121]. Medium intensity peaks at 1065 and 1025 cm.$^{-1}$ indicate the presence of W=O bonds.

Only a ^{1}H n.m.r. spectrum could be observed. This consists of a broad singlet at $\delta = 3.5$ppm and a complex multiplet at $\delta = 4.8$ppm. These signals have a ratio of intensities of ~1:4 and from their chemical shifts are assigned to -NMe and -OMe protons respectively.

Obviously this reaction between $WF_4NMe.MeCN$ and Me_3SiOMe will have to be investigated much more thoroughly before an attempt can be made to identify the reaction product. All that can be said at this stage is that it contains W-F, W-OMe and possibly W=O groups. A possible way to study the reaction would be to vary the amount of Me_3SiOMe added to $WF_4NMe.MeCN$ and measure how much Me_3SiF is produced. This would indicate how many fluorine atoms are being replaced.

C) Reactions of $WF_4NMe.MeCN$ with Carbon Disulphide, Sulphur Dioxide and Sulphur Chloride Pentafluoride. These were investigated in an attempt to carry out addition or insertion reactions across the W=N bond.

Both CS_2 and SO_2 were distilled onto $WF_4NMe.MeCN$ and the mixtures shaken together for several days but $WF_4NMe.MeCN$ did not react with either of these compounds.

A solution of $WF_4NMe.MeCN$ in MeCN and SF_5Cl were irradiated by ultra-violet light for 24 hours but again no reaction took place.

It has been suggested, at least with SO_2 [122], that the insertion process into an M-X bond (X = C, N etc.) proceeds by an electrophilic attack on the M-X bond and that the more polar the M-X bond is the more easily the insertion process can take place. Therefore, it is not surprising that there is no reaction between $WF_4NMe.MeCN$ and either CS_2 or SO_2. The lack of reaction between $WF_4NMe.MeCN$ and SF_5Cl can be attributed to the irradiation process being carried out in the liquid phase. This would tend to suppress the formation of $SF_5^\bullet$ and $Cl^\bullet$ radicals from SF_5Cl.

<u>Reaction between Tungsten Hexafluoride and Hexamethyldisilazane.</u>

The reaction between WF_6 and $(Me_3Si)_2NH$ was studied with the aim of producing another compound in the series WF_4NR. WF_6 and $(Me_3Si)_2NH$ react exothermically in the absence of a solvent to produce a peach coloured solid and Me_3SiF. Analytical studies on this solid gave varying results. The solid is insoluble in organic solvents. It seems likely that since the reaction is so vigorous, the N-H bond in $(Me_3Si)_2NH$ is being broken with the probable formation of HF followed by decomposition or polymerisation of the reaction products.

When WF_6 and $(Me_3Si)_2NH$ are mixed together in the presence of MeCN a more moderate reaction takes place and a brown crystalline solid is formed. An elemental analysis of this solid shows that it has the composition $C_2H_5N_2F_5W$ ($WF_5NH_5.MeCN$) instead of the expected $WF_4NH.MeCN$. (No oxygen analysis was performed.)

<u>Characterisation of solid.</u>

1) <u>N.M.R. Spectra.</u> No ^{19}F spectrum could be observed although

TABLE 2.14

^{1}H Spectrum of $WF_6/(Me_3Si)_2NH/MeCN$ Product

δppm			
2.1	CH_3 in MeCN		
5.2	NH_4^+	$^{1}J(H-N)$	54Hz
6.1			
7.0			

infrared and analytical evidence show that the molecule contains fluorine atoms. The ^{1}H spectrum was recorded in CD_3CN. Details of the spectrum are given in Table 2.14. The size of the coupling constant measured [100] and the chemical shift obtained for the ^{14}N nucleus by decoupling studies [123] suggest that the compound contains the ammonium ion, NH_4^+.

2) Infrared Spectrum. To help with the assignment of the spectrum the reaction between WF_6 and $(Me_3Si)_2NH$ was carried out in the presence of CD_3CN and once again a brown crystalline solid was obtained. Details of the spectra of the compounds prepared in both MeCN and CD_3CN are given in Table 2.15. The presence of coordinated MeCN and CD_3CN can be readily seen, while the presence of the NH_4^+ ion is indicated by the bands at 3270, 1680 and 1425 cm^{-1} all of which are characteristic of NH_4^+ [109]. The remainder of the spectrum is assigned by comparison with the spectra of WOF_4 [94] and $NO^+ WOF_5^-$ [124]. These two compounds have bands at 1055 and 1005 cm^{-1} respectively which are assigned as ν(W=O). Thus the medium intencity bands at 1060 cm^{-1} with shoulder peaks at 1020 cm^{-1} in both the compounds prepared here can be assigned as ν(W=O). The ion

TABLE 2.15

Infrared Spectra of $NH_4^+WOF_5^-.MeCN$ and $NH_4^+WOF_5^-.CD_3CN$

$NH_4^+WOF_5^-.MeCN$ (cm.$^{-1}$)	$NH_4^+WOF_5^-.CD_3CN$ (cm.$^{-1}$)	Assignments
3270 br,s	3270 br,s	ν(N-H) in NH_4^+
3020 w	3100 w	
2942 m	2920 w	
	2850 w	
2310 m		combination
	2300 m	ν(C≡N)
2288 m		"
	2265 w	ν(C-D)
	2115 w	
1680 vbr,m	1680 br,w	δ(N-H) in NH_4^+
1425 br,m	1425 br,m	"
1362 w		
1130 w	1130 w	
1100 m	1100 sh,w	
1060 br,m	1060 br,m	ν(W=O)
1020 sh,w	1020 br,m	$\rho(CH_3)$
940 m		ν(C-C)
	850 m	$\rho(CD_3)$
700 s	700 s	
650-600 br,vs	650-600 br,vs	ν(W-F) terminal

These spectra were recorded in the solid phase using both nujol and fluorolube as mulling agents.

WF_6^- is reported to have a characteristic band at 594 cm.$^{-1}$ [125]; thus the presence in the spectra here of very broad bands at 650-600 cm.$^{-1}$ would tend to rule out WF_6^-.

The mass spectrum of the solid, details of which are given in the Experimental section, shows peaks which can be attributed to both WF and WOF species. The highest observed ion, which is also the most abundant tungsten containing ion, corresponds to WF_5^+. In this spectrum there are several sets of peaks having the tungsten isotope pattern which occur below m/e = 186 (the atomic weight of tungsten = 183.86). These have been assigned as doubly charged ions.

To determine whether the reaction product of $WF_6/(Me_3Si)_2NH/MeCN$ contained an acidic N-H linkage a reaction was carried out between it and n-butyl lithium. No reaction occurs between them, identical infrared spectra being obtained for the solid before and after the reaction.

From spectral data and elemental analyses the product obtained from the reaction of WF_6 with $(Me_3Si)_2NH$ in the presence of MeCN is formulated as the salt NH_4^+ WOF_5^-.MeCN.

The formation of the compound NH_4^+ WOF_5^-.MeCN must have arisen from impurities in the starting materials $(Me_3Si)_2NH$ or MeCN. $(Me_3Si)_2O$ is the most likely impurity in $(Me_3Si)_2NH$ and this has been shown to react with WF_6 to form WOF_4 and a brown unidentified solid [126]. WOF_4 reacts with the fluoride ion, F^-, to produce WOF_5^- [97]. It is possible, therefore, that moisture in the starting materials could both convert $(Me_3Si)_2NH$ to $(Me_3Si)_2O$ and react with WF_6 to form HF with these products further reacting to form NH_4^+ WOF_5^-.MeCN. Another possibility for the formation of NH_4^+ WOF_5^-.MeCN is that the expected product of the reaction between WF_6 and $(Me_3Si)_2NH$ in MeCN, namely $WF_4NH.MeCN$, is indeed formed but that it hydrolyses rapidly to form $NH_4^+\ WOF_5^-.MeCN$.

Although some salts of the anion WOF_5^- have been prepared previously there do not appear to be any examples where the ion is coordinated to another ligand.

Reactions with Molybdenum Hexafluoride. Reactions between MoF_6 and $(Me_3Si)_2NMe$ in both MeCN and C_5H_5N were studied briefly to find out if they proceeded in a manner analogous to those between WF_6 and $(Me_3Si)_2NMe$. Preliminary results indicate that MoF_6 reacts in the same way as WF_6 but that the solid products of the reactions are more susceptible to hydrolysis than those from WF_6. The mass spectra of the solids show only peaks corresponding to Mo-O fragments but elemental analyses suggest that compounds MoF_4NMe, $MoF_4NMe.MeCN$ and $MoF_4NMe.py$ are produced. Details of the analyses are given in the Experimental section. This greater susceptibility to hydrolysis is not surprising since MoF_6 itself hydrolyses more readily than WF_6 [67].

SUGGESTED FURTHER STUDIES.

It is obvious from the reactions described in this chapter that a great deal of work remains to be done in this field of chemistry. In particular the section of work which need further investigation are:-

1) Reactions of $WF_4NMe.MeCN$. It has been shown that the fluorine atoms in $WF_4NMe.MeCN$ can be readily replaced by other atoms or groups. A systematic replacement of the fluorine atoms should produce a series of compounds from which geometric isomers could be isolated and from which it might be possible to obtain more information about the frequency of the tungsten nitrogen stretching vibration.

2) Preparation of $WF_4NR.MeCN$. Only the compound where $R = Me$ has been isolated in this work. It should be possible by using the appropriate starting materials to extend the series to $R = H$, Et, Ph.

3) Other Transition-Metal Halides. It is possible that as well as MoF_6 reacting with $(Me_3Si)_2NMe$ in a manner analogous WF_6, other transition-metal halides such as NbF_5 and TaF_5 might do so as well.

4) Structural Investigations. All the compounds prepared in this chapter are crystalline solids and although they are susceptible to hydrolysis X-ray studies on them should be possible. These would be interesting in that they would confirm the structures of WF_4NMe and $WF_4NMe.MeCN$ giving the degree of polymerisation in WF_4NMe and provide information about the length of the $W=N$ bond.

EXPERIMENTAL.

The solvents used, acetonitrile, pyridine and carbon disulphide were dried by standard methods [55] and stored over activated molecular sieves. Other starting materials were prepared or obtained as detailed in Table 2.16. Their purity was checked before use by infrared spectroscopy. References to the spectra are also given in Table 2.16. Spectra and elemental analyses were obtained as in Chapter 1. Tungsten was determined as tungsten trioxide with cinchonine hydrochloride [127]. Reactions were carried out in anhydrous conditions using glass reaction vessels with side-arms and equipped with "teflon" stop-cocks. Solids were handled in a Lintott inert atmosphere box.

Reactions.

1) Preparation of WF_4NMe.

(i) $(Me_3Si)_2NMe$ (1.109 g, 6.33 mmol) was condensed into a reaction vessel with WF_6 (2.195 g, 7.36 mmol) at -196°C and the reactants were allowed to warm to ambient temperature. A cream coloured solid was deposited over a period of a week. The volatile products were removed and separated by fractional distillation into two products identified by their infrared spectra as WF_6 [128] and 1.06 g (11.52 mmol) of Me_3SiF [130]. The cream solid weighed 1.93 g. The theoretical amount calculated for WF_4NMe is 1.82 g. Infrared and mass spectra are tabulated in the Results section. Elemental analyses are given in Table 2.17.

(ii) $F_2PNMeSiMe_3$ (0.78 g, 4.56 mmol) and WF_6 (1.40 g, 4.69 mmol) were condensed together at -196°C and left to warm up to room

TABLE 2.16

Starting Material	Source	Infrared
WF_6	Allied Chemical Co.	[128]
MoF_6	Cambrian Chemicals.	[128]
$(Me_3Si)_2NH$	Hopkins and Williams Ltd.	[61]
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$ [61]	[61]
CD_3CN	Prochem Ltd.	[104]
C_5D_5N	B.D.H.	[129]
$^{n}BuLi$	Alpha Inorganic Inc.	
Me_3SiCl	I.C.I.	[130]
Me_3SiOMe	Pierce Chemicals	[131]
$MeNSF_2$	$MeNH_2/SF_4$ [92]	[92]
$F_2PNMeSiMe_3$	$F_2PCl/(Me_3Si)_2NMe$ [38]	[38]
$(F_3P\text{-}NMe)_2$	$F_5P/(Me_3Si)_2NMe$ [17]	[132]
SF_5Cl	Peninsular Chemicals.	[133]

TABLE 2.17

Elemental Analyses of WF_4NMe

C%	H%	N%	F%	W%	
4.15	1.04	4.85	26.30	63.66	WF_4NMe requires
5.88	1.71	4.83	25.29		$WF_6/F_2PNMeSiMe_3$ product
6.57	1.43	5.36	24.90		$WF_6/(Me_3Si)_2NMe$ product
5.82	2.13		27.93		"

temperature. They were left for one week, by which time a yellow solid had been deposited. This solid had an infrared spectrum identical to that obtained for WF_4NMe prepared as in (i). Details of an elemental analysis are given in Table 2.17. The volatile products were not separated but were identified from their infrared spectra as PF_3 [134], Me_3SiF and WF_6; their total weight was 0.814 g compared with a theoretical weight of 0.862 g based on a 1:1 molar reaction.

(iii) $MeNSF_2$ (0.67 g, 6.76 mmol) and WF_6 (2.30 g, 7.71 mmol) reacted below room temperature to produce an orange viscous liquid for which no ^{19}F n.m.r. spectrum could be obtained and which was assumed to be the product of the polymerisation of $MeNSF_2$.

(iv) $(PF_3NMe)_2$ (0.50 g, 2.15 mmol) and WF_6 (0.77 g, 2.60 mmol) were condensed together and the reaction mixture allowed to stand at room temperature for eight days. An examination of the reaction mixture by infrared spectroscopy showed it to consist only of the starting materials. An excess of MeCN was then added to the reaction mixture but again no reaction occurred.

TABLE 2.18

Elemental Analyses of $WF_4NMe.MeCN$

C%	H%	N%	F%	W%	
10.91	1.82	8.48	23.03	55.75	$WF_4NMe.MeCN$ requires
10.70	1.89	8.24	22.79		$WF_6/F_2PNMeSiMe_3$ then + MeCN
7.72	2.59	7.12	22.03	57.00	"
9.71	0.79	7.65	30.95		$WF_6/(Me_3Si)_2NMe/MeCN$
10.12	1.87	7.88	26.88		"
8.66	1.88	7.97	27.46		"

2) Preparation of $WF_4NMe.MeCN$. $(Me_3Si)_2NMe$ (0.56 g, 3.20 mmol) and WF_6 (1.22 g, 4.09 mmol) were condensed together with an excess of MeCN. They were allowed to warm up slowly and at $\sim -40^{\circ}C$ a reaction took place with the formation of an orange solid. The mixture was shaken for one day to ensure complete reaction whereupon 1.08 g of $WF_4NMe.MeCN$ and 0.51 g (5.90 mmol) of Me_3SiF were obtained. Infrared, n.m.r. and mass spectra are tabulated in the Results section. Results of elemental analyses on $WF_4NMe.MeCN$ prepared in this way and by adding MeCN to WF_4NMe prepared as in 1 (i) and 1 (ii) are given in Table 2.18.

3) Preparation of $WF_4NMe.py$. $(Me_3Si)_2NMe$ (0.62 g, 3.54 mmol) and WF_6 (1.13 g, 3.82 mmol) were condensed into a reaction vessel together with a large excess of C_5H_5N. The reaction mixture was allowed to warm up slowly and then shaken to ensure complete reaction. When the volatile products, Me_3SiF, excess WF_6 and C_5H_5N, were removed 1.20 g (3.30 mmol) of a black solid was obtained. This analysed as $WF_4NCH_3.C_5H_5N$

(Found: C, 19.71; H, 2.36; N, 7.77; F, 20.39. $C_6H_8F_4N_2W$ requires: C, 19.56; H, 2.17; N, 7.61; F, 20.65%). Infrared, n.m.r. and mass spectral data are tabulated in the Results section.

4) Reactions of $WF_4NMe.MeCN$.

(i) With Trimethylchlorosilane. Me_3SiCl was distilled onto a solution of $WF_4NMe.MeCN$ in MeCN. The reaction mixture was shaken over night, then the volatile products were removed and identified by their infrared spectra as Me_3SiCl and Me_3SiF. The mixture of these two could not be separated satisfactorily. An orange crystalline solid formulated as $WCl_4NMe.MeCN$ was left in the reaction vessel. It melted with apparent decomposition at 190°C. Its n.m.r. spectrum is given in the Results section.

Mass Spectrum of $WCl_4NMe.MeCN$ (m/e, assignment, relative intensity) 326, $WCl_3NCH_3^+$, 100; 297, WCl_3^+, 40; 250-255 (complex multiplet), ?, 5; 260, WCl_2^+, 40; 237, $WClN^+$, 10; 223, WCl^+, 30; 140-160 (complex multiplet), ?, 20; 128, ?, 20; 127, ?, 16; 41, CH_3CN^+, 200; 40, CH_2CN^+, 100; 39, $CHCN^+$, 65; 37, Cl^+, 40; 35, Cl^+, 120. These are the only peaks present with >1% relative intensity of m/e >28. m/e values are given for ^{186}W and ^{37}Cl.

Infrared Spectrum of $WCl_4NMe.MeCN$. 2315 s, 2290 s, 1310 s, 1030 w, 950 m, 400 w, 335 vs $cm.^{-1}$.

(ii) With Trimethylmethoxysilane. $WF_4NMe.MeCN$ was shaken with a large excess of Me_3SiOMe in a solution of MeCN. The volatile products were identified from their infrared spectra as Me_3SiF and Me_3SiOMe while an orange crystalline solid remained in the reaction vessel. An elemental analysis of this orange solid gave the following results:- C, 14.37; H, 3.22; N, 4.99; F, 10.14%. This is a ratio of atoms of $C_3H_9NF_{1.5}$.

Mass Spectrum of Solid. 329, $W(OMe)_4NCH_3^+$, 75; 317, $WF_2(OMe)_3^+$, 100; 298, $WF(OMe)_3^+$, 40; 283, $WOF(OMe)_2^+$, 100; 271, $WOF_2(OMe)^+$, 42; 237, WO_2F^+, 30; 147 $WOF_2(OMe)_2^{2+}$, 70; 31, OMe^+, 60; 29, NCH_3^+, 100. Other ions of 1-5% relative intensity are visible from m/e = 90 to m/e = 45. However, the spectrum of the same sample was recorded several times but consistent m/e values were not obtained for these additional peaks.

Infrared Spectrum of Solid. 2930 m, 2822 w, 1460 w, 1438 w, 1315 m, 1168 m, 1090 sh, 1065 m, 1025 m, 605 w, 570 m, 540 m, 503 w $cm.^{-1}$

5) Reaction between WF_6 and $(Me_3Si)_2NH$. When $(Me_3Si)_2NH$ and WF_6 were mixed together in the absence of a solvent an exothermic reaction took place ~-40°C to produce a peach coloured solid, which was insoluble in organic solvents, and Me_3SiF.

Infrared Spectrum of Solid. 3280 m, 1620 w, 1420 br,s, 1260 m, 1175 m, 1100 br,m, 1020 w, 890 sh,w, 850 s, 760 m, 660-600 vs, 450-430 w $cm.^{-1}$

6) Preparation of $NH_4^+WOF_5^-$. MeCN. $(Me_3Si)_2NH$ (0.57 g, 3.34 mmol) and WF_6 (1.187 g, 3.98 mmol) were condensed together with MeCN and allowed to warm to ambient temperature. 0.57 g (6.25 mmol) of Me_3SiF and 1.08 g of an orange solid, formulated as $NH_4^+WOF_5^-$.MeCN, were obtained. The solid melted with decomposition at 114°C. The infrared and n.m.r. spectra are given in the Results section.

Mass Spectrum of $NH_4^+WOF_5^-$.MeCN. 281, WF_5^+, 100; 262, WF_4^+, 50; 259, WOF_3^+, 50; 243, WF_3^+, 48; 224, WF_2^+, 50; 221, WOF^+, 4; 205, WF^+, 30; 186, W^+, 5; 132, WF_4^{2+}, 10; 121.5, WF_3^{2+}, 4; 41, CH_3CN^+, 300; 40, CH_2CN^+, 200; 39, $CHCN^+$, 200.

Results of elemental analyses on $NH_4^+WOF_5^-$.MeCN are given in Table 2.19.

TABLE 2.19

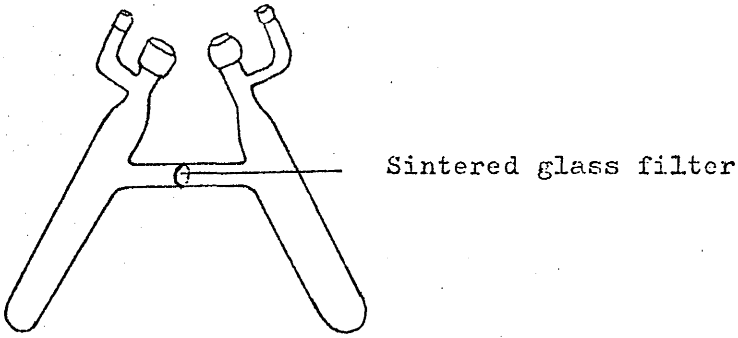
Elemental Analyses of $NH_4^+WOF_5^-.MeCN$

C%	H%	N%	F%	
6.78	1.97	7.91	26.84	$NH_4^+WOF_5^-.MeCN$ requires
6.60	1.48	6.98	23.25	Found
6.94	1.64	8.19	27.80	"
6.45	1.21	7.50	25.69	"
		7.20	23.20	"

7) Reactions of $NH_4^+WOF_5^-.MeCN$.

(i) With n-butyl lithium. The reaction between $NH_4^+WOF_5^-.MeCN$ and n-butyl lithium was carried out in a specially constructed reaction vessel (see Figure 2.3).

FIGURE 2.3



n-Butyl lithium in hexane was put into one side of the reaction vessel which was then taken into a 'dry-box' and $NH_4^+WOF_5^-.MeCN$ put in the other side. The n-butyl lithium solution was poured on the solid and the reaction vessel shaken for 24 hours. The liquid was then separated from the solid using the sintered glass filter and the infrared spectrum of the solid was recorded. This proved to be identical to that of the starting solid $NH_4^+WOF_5^-$.MeCN.

(ii) *With pyridine.* $NH_4^+WOF_5^-$.MeCN (1.1 g, 3.10 mmol) was condensed with excess pyridine and the reaction mixture shaken at room temperature overnight whereupon 1.13 g (2.95 mmol) of a dark grey solid, formulated as $NH_4^+WOF_5^-$.py, were obtained. The reaction was repeated using deuteriopyridine in place of pyridine.

Infrared Spectrum of $NH_4^+WOF_5^-$.py. 3100-3000 br,w, 2150 br,w, 1608 m, 1550 br,w, 1490 m, 1450 w, 1220 m, 1090 m, 1065 m, 1040 m, 1005 m, 890-860 br,m, 750 s, 690 s, 680 s 640 s, 595 vs cm^{-1}.

Infrared Spectrum of $NH_4^+WOF_5^-.C_5D_5N$. 3100-2900 br,w, 2100 w, 1570 br,m, 1440-1420 br,w, 1350 w, 1025-1015 br,m, 895 w, 830 w, 740-720 br,m, 638 s, 595 s, 540 m cm^{-1}.

(iii) *With trimethylchlorosilane.* $NH_4^+WOF_5^-$.MeCN (0.203 g, 0.57 mmol) was condensed with excess Me_3SiCl and the reaction mixture shaken at room temperature overnight. An infrared spectrum of the solid material in the reaction vessel was identical to that of the starting material, $NH_4^+WOF_5^-$.MeCN, indicating that no reaction had occurred. When MeCN was added to the reaction mixture and it was again shaken 0.81 g of a dark brown crystalline was obtained. On the basis of infrared and n.m.r. spectral data the solid was formulated as $NH_4^+WOCl_5^-$.MeCN.

Infrared Spectrum of $NH_4^+WOCl_5^-$.MeCN. 3200 w, 2930 w, 2308 m, 2280 m, 1680 br,w, 1405 br,m, 1080 s, 1030 w, 975 w, 935 m, 850 vbr,m, 338 br,vs cm^{-1}.

N.M.R. Spectrum of $NH_4^+WOCl_5^-.MeCN$. ^1H δ_H = 2.1 MeCN

$$^1J(H\text{-}N) = 54Hz \qquad \left.\begin{array}{l} 5.2 \\ 6.1 \\ 7.0 \end{array}\right\} NH_4^+$$

8) Reactions with MoF_6.

(i) $(Me_3Si)_2NMe$ (0.40 g, 2.29 mmol) and MoF_6 (0.70 g, 3.30 mmol) were condensed together and allowed to warm to ambient temperature whereupon a dark brown solid was deposited. An elemental analysis of the solid gave the following results:- C, 7.58; H, 1.55; N, 5.92; F, 39.48. CH_3F_4NMo requires: C, 5.95; H, 1.49; N, 6.96; F, 37.81%.

Infrared Spectrum of "MoF_4NMe". 2920 vw, 1530 w, 1265 w, 1020 m, 990 w, 630-610 br,s, 520 br,m $cm.^{-1}$

(ii) When $(Me_3Si)_2NMe$ (0.59 g, 3.37 mmol) and MoF_6 (0.8 g, 3.81 mmol) were condensed together in the presence of MeCN 0.77 g (3.2 mmol) of a dark brown solid were obtained. An elemental analysis of the solid gave the following results:- C, 17.33; H, 2.99; N, 11.65; F, 28.03. $C_3H_6F_4N_2Mo$ requires: C, 14.88; H, 2.48; N, 11.57; F, 31.41%.

Infrared Spectrum of "$MoF_4NMe.MeCN$". 3015 w, 2950 w, 2317 m, 2297 m, 1410 w, 1360 w, 1021 w, 940 w, 718 w, 590 vs $cm.^{-1}$

(iii) Excess pyridine was distilled onto "$MoF_4NMe.MeCN$" and the reaction mixture shaken overnight. A black solid was obtained which had the following elemental analysis:- C, 34.58; H, 3.61; N, 11.00; F, 25.07. $C_6H_8F_4N_2Mo$ requires: C,25.71; H, 2.86; N, 10.00; F, 27.14%.

CHAPTER III

THE REACTIONS AND VIBRATIONAL SPECTRA OF SOME DERIVATIVES OF SULPHUR HEXAFLUORIDE.

INTRODUCTION

The sulphur fluorides which are thermodynamically stable with respect to the elements sulphur and fluorine are those found for sulphur in the valency states of six or four while divalent sulphur fluorides readily disproportionate. For other sulphur halides, unless other ligand atoms such as oxygen are present, the stable valency state is two. The only binary halide of tetravalent sulphur is sulphur tetrafluoride, SF_4. This is a very reactive gas, the chemistry of which has been studied extensively and has been summarised in several review articles [135,136]. Sulphur hexafluoride, SF_6 and disulphur decafluoride, S_2F_{10} are the two binary fluorides of hexavalent sulphur. They can both be prepared by the fluorination of sulphur under varying conditions and were thought initially to have similar chemical properties. However, S_2F_{10} was found to be a powerful oxidising agent and it undergoes reactions with halogens and unsaturated hydrocarbons [135,137]. SF_6, on the other hand, has been found to be almost chemically inert. Its reluctance to undergo chemical reactions has been explained in terms of kinetic rather than thermodynamic factors, since, for example, the free energy of hydrolysis of SF_6 is favourable:-

$$SF_6(g) \quad + \quad 3H_2O \quad \longrightarrow \quad SO_3 \quad + \quad 6HF \quad \Delta G^o = -48 \text{ Kcal mole}^{-1}$$

The reaction, however, does not take place. Direct attack of nucleophiles, such as the hydroxyl ion, on the sulphur atom on covalently saturated SF_6 could only take place by extensive electronic rearrangement and may be expected to be difficult. This means that substituted derivatives of SF_6 cannot be made from

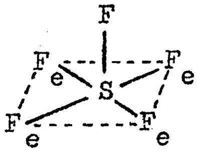
SF_6; other routes to them have had to be devised. Lower fluorides can be attacked and are reactive. Similarly, exchange of fluorine occurs readily between SF_4 molecules but not at all between those of SF_6 [138]. SF_6 does undergo reactions with electrophiles, of the type:-

$$SF_6 + AlCl_3 \xrightarrow[24\ hr]{200^{o}C} AlF_3 + Cl_2 + S_2Cl_2 \quad [139]$$

and it has been possible under extreme conditions to accomplish reactions between SF_6 and metals [140].

A considerable effort has been made to produce substituted derivatives of SF_6 with a view to exploiting its stability for industrial purposes. This has resulted in the syntheses of many perfluoroalkyl derivatives of SF_6, the properties of which have been reviewed several times [141,142]. Since SF_6 itself was of little use in synthesising them most were made by the oxidative fluorination of aliphatic thiols and disulphides. These perfluoroalkyl compounds, R_fSF_5, turned out to be rather unreactive non-toxic liquids and gases. A study of their n.m.r. spectra showed that the SF_5 group contained two different types of fluorine atoms with the stereochemistry based on a pyramid having four equatorially and one axially substituted fluorine atoms, as shown in Figure 3.1

FIGURE 3.1



The synthesis of the compound sulphur chloride pentafluoride, SF_5Cl, meant that a precursor was available for the preparation of inorganic and organic sulphur pentafluorides. SF_5Cl was first reported by George and Cotton in 1959 [143]. They passed a mixture of S_2F_{10} and Cl_2 through a monel tube at 350°C and tentatively identified their product, on the basis of mass spectral evidence, as SF_5Cl. Roberts reported in 1960, as a new compound, the product of a reaction involving the fluorination of SCl_2 [144]. This was characterised by infrared spectroscopy as SF_5Cl and proved to be the same compound as that reported by George and Cotton. Since then the most successful routes to SF_5Cl are those discovered by Muetterties and co-workers:-

$$SF_4 + Cl_2 + CsF \longrightarrow SF_5Cl + CsCl \qquad [145]$$

and a revised method by Roberts <u>et</u> <u>al</u>.:-

$$SF_4 + ClF \longrightarrow SF_5Cl \qquad [146]$$

SF_5Cl is a colourless gas (B.Pt. = -21°C) and its structure, which has been established from a study of its microwave spectrum [147], is that of a monosubstituted octahedron.

The chemistry of SF_5Cl has been dominated by its ability to form, with ease, the SF_5 radical. This can be achieved either thermally or photochemically. It has been found that although SF_5Cl does not react with saturated hydrocarbons it adds across multiple bonds in unsaturated systems such as olefins or acetylenes in reactions of the type:-

$$SF_5Cl + RCH{=}CH_2 \longrightarrow RCHCl{-}CH_2SF_5 \qquad [148, 149]$$

The products obtained in these reactions with olefins or fluoro-olefins are generally those expected if SF_5Cl reacts by a free radical mechanism. Isomers can be obtained and separated by gas chromatography but so far no compounds have been synthesised containing two $-SF_5$ groups.

Evidence for the existence of the SF_5^- anion was first discussed by Muetterties <u>et</u> <u>al</u>.[145]. A 1:1 adduct of CsF and SF_4 gave a white powder which analysed as $CsSF_5$. They concluded that the compound was a salt containing the anion SF_5^-. Cl_2 converted this salt to SF_5Cl at 60°C; a temperature much lower than that required for the synthesis involving SF_4, CsF and Cl_2. They therefore suggested that $Cs^+SF_5^-$ is an intermediate in this synthesis and that the rate determining step is the absorption of SF_4 by CsF:-

$$CsF \quad + \quad SF_4 \quad \rightleftharpoons \quad Cs^+SF_5^-$$

The anion SF_5^- has also been made by the reaction:-

$$SF_4 \quad + \quad Me_4NF \quad \longrightarrow \quad Me_4N^+SF_5^- \qquad [150]$$

Several reactions have been reported where it is not clear whether SF_5Cl was reacting as $SF_5^\bullet$ and $Cl^\bullet$ radicals, although in some cases it seems likely that it was. These reactions are described below:-

i) <u>With CO and $Fe(CO)_5$</u>. Attempts to prepare iron carbonyl derivatives containing $-SF_5$ groups by the reaction of SF_5Cl with $Fe(CO)_5$ were unsuccessful. The only products isolated were brown solids containing terminal CO groups but no S-F bonds. When CO was reacted with SF_5Cl, COFCl was the predominant product [151].

ii) <u>With $B_2(NMe_2)_2$</u>. Fluorination of $B_2(NMe_2)_2$ with an excess of SF_5Cl gave BF_3, Cl_2 and SF_4 [152].

iii) <u>With $PhHC{=}CHPh.Pt(PPh_3)_2$</u>. When $PhHC{=}CHPh.Pt(PPh_3)_2$ and SF_5Cl were mixed together a high yield of an orange solid, $PtCl(SF_5)(PPh_3)_2$, was isolated [153].

iv) <u>With Amines</u>. SF_5Cl and Me_3N reacted in the following way:-

$$\begin{tikzcd}
SF_5Cl \quad + \quad 2NMe_3 \arrow[r, "-78^\circ"'] & SF_5Cl.2NMe_3 \text{ (white solid) } [92] \arrow[d, "25^\circ C"] \\
& SF_4 \quad + \quad (Me_3N)_2ClF
\end{tikzcd}$$

It was suggested that the white solid had the formula

$(Me_3N.NMe_3)^{2+}Cl^-SF_5^-$, analogous to $Cs^+SF_5^-$ and $Me_4N^+SF_5^-$. With a primary amine the reaction was as follows:-

$$2SF_5Cl \quad + \quad 4MeNH_2 \longrightarrow MeN{=}NMe.HCl.HF + MeNH_2.HCl + SF_4$$

$$MeNSF_2$$

The compound SF_5Br has also been prepared and reactions similar to those of SF_5Cl can be carried out using it [154]. SF_5I has not been isolated.

The synthesis, in 1969, of CF_3SF_4Cl by the following reaction,

$$CF_3SF_3 + Cl_2 + CsF \longrightarrow CF_3SF_4Cl \qquad [155]$$

made available the grouping $-SF_4Cl$ which could be introduced into organic derivatives. Reactions similar to those carried out for SF_5Cl have been studied using CF_3SF_4Cl [156].

It was the aim of the work described in this chapter to extend the chemistry of SF_5Cl by studying its reactions with some phosphorus(III) derivatives. These were chosen, as a preliminary investigation in this department of a reaction between diphenylchlorophosphine, Ph_2PCl, and SF_5Cl suggested that the oxidation of P(III) to P(V) was taking place [157]. It was thought that such an oxidation process could take place by the addition of $SF_5^\bullet$ and $Cl^\bullet$ radicals to the lone pair of electrons on P(III) and might lead to P-S-F linkages.

When this work was started little information had been published about the infrared and Raman spectra of substituted SF_6 derivatives. Detailed studies were confined to SF_5Cl [133] and CF_3SF_5 [158,159]. Therefore, the vibrational spectra of a series of substituted SF_6 compounds have been studied. Those chosen were CF_3SF_4Cl, $CF_3SF_4CF_2CF_2Cl$, both of which were prepared in this department, $SF_5CF_2CF_2Cl$ and $SF_5CH{=}CH_2$. Since the commencement of this work two papers have appeared containing infrared and Raman data on similar S(II), S(IV) and S(VI) derivatives [160,161].

SUMMARY OF REACTIONS

1. $SF_5Cl + PhPCl_2 \longrightarrow PhPF_4 + SCl_2 + Cl_2$

2. $SF_5Cl + Ph_2PCl \longrightarrow Ph_2PF_3 + SCl_2 + Cl_2$

3. $SF_5Cl + MePCl_2 \longrightarrow MePF_4 + SCl_2 + Cl_2$ + white solid

4. $SF_5Cl + P(OMe)_3 \longrightarrow (MeO)_2PF_2OPF_2(OMe)_2? + SF_4$

$+ Cl_2 + S +$ white solid

5. $SF_5Cl + P(NMe_2)_3 \longrightarrow F_2P(NMe_2)_3 + SF_4 +$ brown solid

6. $SF_5Cl + PPh_3 \longrightarrow$ no reaction

7. $SF_5Cl + PCl_3 \longrightarrow$ no reaction

RESULTS

Reactions of Sulphur Chloride Pentafluoride with Phosphines.

A) With Phenyl- and Diphenylchlorophosphine. SF_5Cl reacts with phenyldichlorophosphine, $PhPCl_2$ and diphenylchlorophosphine, Ph_2PCl in a 1:1 molar ratio below room temperature to produce the fluorophosphoranes $PhPF_4$ and Ph_2PF_3 respectively. In addition to these P(V) fluorides, SCl_2, SF_5Cl and a trace amount of Cl_2 are observed as volatile products in each case. It has been noted that when a large excess of Ph_2PCl is reacted with SF_5Cl some SF_4 is formed [157].

B) With Methyldichlorophosphine. When SF_5Cl reacts with methyldichlorophosphine, $MePCl_2$, the phosphorane $MePF_4$ is observed as a volatile product along with SCl_2, Cl_2 and excess SF_5Cl. However, the major product is a white solid soluble in MeCN which analyses as $CH_{2.3}Cl_5FP$. Its infrared spectrum indicates the presence of P-Cl and P-F bonds. The complete spectrum is given in the Experimental section. When the ^1H and ^{19}F n.m.r. spectra were recorded in CD_3CN, no ^{19}F signal was obtained and the ^1H spectrum consisted of a single peak at $\delta = 2.72$ppm. This is a rather low chemical shift and may correspond to a grouping such as $ClCH_2-$. It is thought that this compound is a salt but further investigations of its properties are necessary before it can be identified.

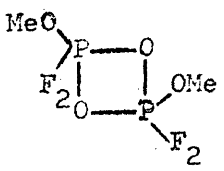
C) With Trimethylphosphite. SF_5Cl and trimethylphosphite, $P(OMe)_3$, react exothermically below room temperature to produce a complex mixture of products. The volatile products consist of SF_4, $S(O)F_2$ (a trace amount), Cl_2 and a colourless liquid which is not very volatile. Two solids are formed; a white solid soluble in MeCN and a trace amount of a yellow solid which is soluble in CS_2 and is assumed to be sulphur. The white solid was not identified. The n.m.r. spectra of the colourless liquid are given below:-

^1H	$\delta = 3.55$	doublet	$J(PH) = 14.7Hz$
^{19}F	$\delta = -62.2$	doublet	$J(PF) = 733Hz$

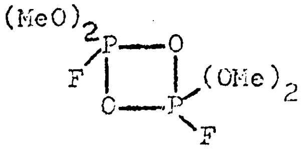
The ^1H chemical shift suggests the presence of a methyl group attached to oxygen while the coupling constant is consistent with the presence of P-OMe linkage. The existence of P-F bonds in the compound is confirmed by its ^{19}F n.m.r. spectrum which is a doublet. There are no peaks in the infrared spectrum of the compound (detailed in the Experimental section) in the region 1350-1250 cm^{-1}, which eliminates the presence of a P=O bond in the molecule. The n.m.r. parameters obtained here are identical to those observed for a product of a reaction between SF_4 and $P(OMe)_3$ which occurred at ∽-100°C when the reactants were allowed to warm up from -196°C [162]. The product was not identified but was postulated as $(MeO)_2PF_2OPF_2(OMe)_2$ formed by:-

$$2(MeO)_3PF_2 \longrightarrow (MeO)_2PF_2OPF_2(OMe)_2 + 2Me_2O$$

Dimethylether was identified as a product. If the compound were $(MeO)_2PF_2OPF_2(OMe)_2$ it would be the first example of two five coordinate P(V) atoms linked by an oxygen bridge. However, it seems probable that it would rearrange and more likely structures for the unidentified phosphorus compound are:-



or



These are consistent with the infrared and n.m.r. spectra observed but the reaction will have to be studied in more detail before an unambiguous identification can be made.

D) With Trisdimethylaminophosphine. The reaction between trisdimethylaminophosphine, $P(NMe_2)_3$, and SF_5Cl was only studied briefly as they react explosively in glass reaction vessels. When the reaction is carried out in a monel bomb a mixture of three volatile products is obtained, SF_4, $S(O)F_2$ (a trace amount) and a colourless liquid which has an infrared spectrum very similar to that of $F_2P(NMe_2)_3$ [163]. A yellow-brown unidentified solid is left in the bomb.

E) Other Reactions. SF_5Cl does not react with either PCl_3 or PPh_3.

Discussion of Reactions. SF_5Cl does not add to the lone pair of electrons on P(III) as $SF_5^{\bullet}$ and $Cl^{\bullet}$ radicals but does act as an oxidative fluorinating agent. This oxidation of P(III) to P(V) takes place under very mild conditions. Similar oxidative fluorinations of the type,

$$3RPCl_2 \quad + \quad 4MF_3 \quad \longrightarrow \quad 3RPF_4 \quad + \quad 2M \quad + \quad 2MCl_3 \quad M = Sb, As$$

take place ~50°C over a period of two hours [164]. These reactions were investigated by Schmutzler who also studied reactions between chlorophosphites, $(RO)_nPCl_{3-n}$, dialkylaminodichlorophosphines, $(R_2N)_nCl_{3-n}$, and Group(V) fluorides [165,166]. He found no evidence in these latter reactions for oxidation-reduction processes leading to fluorophosphoranes. Some reaction, however, was observed between $(^nBu)_3P$ and SbF_3 but the products could not be identified [167]. Schmutzler concluded that for oxidation to take place it was necessary to have electron donating substituents and at least one chlorine atom attached to phosphorus. The mechanism for the oxidative fluorination process is thought to be via an adduct of the type $Cl_2RP.MF_3$ followed by fluorine chlorine exchange.

In view of the fact that the reaction between SF_5Cl and $P(OMe)_3$ produces the same product as that between SF_4 and $P(OMe)_3$, it seems likely that SF_4 is an intermediate in the fluorination reactions described in this work.

SF_4 has been found to function as an oxidative fluorinating agent towards phosphines of various kinds to produce fluorophosphoranes:-

$$PPh_3 \quad + \quad SF_4 \quad \longrightarrow \quad Ph_3PF_2 \qquad [168]$$

Fairly stringent conditions were required for PPh_3 (~10 hours at 100-150°C) but PMe_3 was readily converted at room temperature to Me_3PF_2 [169].

Some SF_5Cl was recovered in most of the reactions here with phosphines which suggests that they do not react in an exactly 1:1 molar ratio.

A possible reaction scheme for these oxidative fluorinations is the addition of the radical $F^\bullet$ to the phosphorus atoms:-

$$PhPCl_2 \quad + \quad SF_5Cl \quad \longrightarrow \quad PhPF_2Cl_2 + SF_4 + SCl_2 + 2F^\bullet \qquad (i)$$

$$PhPF_2Cl_2 \quad + \quad SF_4 + F^\bullet \quad \longrightarrow \quad PhPF_4 \quad + \quad SCl_2 \quad + \quad Cl_2 \qquad (ii)$$

The addition step (i) could take place with each of the phosphorus compounds. The intermediate formed by the addition of $2F^\bullet$ to $P(OMe)_3$ would be the alkoxyfluorophosphorane $F_2P(OMe)_3$. Compounds of this type have been shown to be thermodynamically unstable [170] and it is likely that $F_2P(OMe)_3$, if formed, would rearrange to form a cyclic compound. The reaction scheme would stop at (i), thus some SF_4 is observed. The compounds formed by the addition of $2F^{\bullet}$ to the chlorophosphines, R_nPCl_{3-n} and $P(NMe_2)_3$ would be stable and thus are either isolated, as with $P(NMe_2)_3$, or further fluorinated, as with R_nPCl_{3-n}. The formation of the white solid in the reaction of SF_5Cl with $MePCl_2$ may be due to the intermediate reacting with the chlorine produced; it is possible that the methyl group is chlorinated.

An alternative reaction scheme is possible. The radicals $F^{\bullet}$ and $Cl^{\bullet}$ could add to the P(III) atoms:-

$$\begin{array}{lllllll} Ph_2PCl & + & SF_5Cl & \longrightarrow & Ph_2PFCl_2 & + & SF_4 \quad \text{(i)} \\ Ph_2PFCl_2 & + & SF_4 & \longrightarrow & Ph_2PF_3 & + & SCl_2 \quad \text{(ii)} \end{array}$$

A reaction scheme of this type would explain why no SCl_2 is observed when SF_5Cl reacts with $P(OMe)_3$. $FClP(OMe)_3$ could also rearrange to form a cyclic compound, therefore, the reaction would again stop at (i). It is possible that both reaction schemes can and do take place.

The fact that no reaction is observed with PCl_3 suggests that, as with the chlorophosphites, $(RO)_nPCl_{3-n}$, studied by Schmutzler, the phosphorus atom must have at least one electron donating substituent before it can be oxidatively fluorinated. Presumably the electron donating group is necessary to increase the basicity of the P(III) atom. It is probable that the bulkiness of the three phenyl groups around phosphorus in PPh_3 is responsible for the lack of reaction between SF_5Cl and PPh_3. Perhaps the use of more stringent conditions, such as those used in the reaction of SF_4 with PPh_3, might cause them to react.

The mechanisms proposed above may be checked in several ways. The rearrangement of the intermediate, either $F_2P(OMe)_3$ or $FClP(OMe)_3$, to form a cyclic compound should be accompanied by the elimination of either MeF or MeCl. The presence of these could be detected by infrared spectroscopy.

$PhPCl_2$ and SF_5Cl were condensed into an n.m.r. tube and allowed to warm up slowly in the n.m.r. spectrometer from -78°C to +33°C in an attempt to identify any of the intermediate species postulated, from their n.m.r. spectra. However, only SF_5Cl and $PhPF_4$ were observed, but a reinvestigation of this and the other reactions, under more controlled conditions, perhaps employing a solvent to moderate the speed of the reactions, might produce some evidence for the existence of the intermediates.

The reactions described here involving SF_5Cl as an oxidative fluorinating agent certainly suggest that the chemistry of SF_5Cl is not confined to that of the $SF_5^{\bullet}$ radical and it may prove useful as a fluorinating agent when very mild conditions are required.

Infrared and Raman Spectra of CF_3SF_4Cl.

When the compound CF_3SF_4Cl is prepared from CF_3SF_3, CsF and Cl_2, there is the possibility of the formation of both cis and trans isomers. Trans isomers have been reported for XSF_4Y, where X and Y were two perfluoroalkyl groups [171,172,173], but n.m.r. spectra of disubstituted derivatives containing S-O linkages (X,Y = OSO_2F [174], OSF_5 [175] and OCF_3 [176]), showed the presence of only the cis isomers. The only reported case in which both of the possible isomers of a compound XSF_4Y have been isolated is that of $(CF_3)_2CFSF_4N{=}SF_2$ [177] where the isomers were separated by gas chromatography and again characterised by n.m.r. spectroscopy. The ^{19}F n.m.r. spectrum of CF_3SF_4Cl indicates that only the trans isomer is formed [155]. It is possible, both with CF_3SF_4Cl and the other derivatives where only the trans isomer was found, that the cis isomer was formed but its presence was not detected by n.m.r. spectroscopy. The $-SF_4-$ group of the cis isomers contain three magnetically different types of fluorine atoms resulting in second order spectra which have a greater number of lines than the first order spectra of the trans isomers and therefore are more difficult to detect [177].

The vibrational spectra of CF_3SF_4Cl were examined to confirm the structure of trans CF_3SF_4Cl.

The trans isomer can be treated as a molecule possessing C_{4v} symmetry (see below) while the point group for the cis isomer is C_s. Under C_{4v} symmetry three of the fundamental frequencies (b_1 and b_2) are Raman active but infrared inactive, and one (a_2) is inactive in both. For C_s symmetry all the fundamentals are both Raman and infrared active. The number of polarised Raman lines also differ significantly; fifteen for C_s and six for C_{4v}. Experimentally, therefore, the two point groups C_{4v} and C_s are readily distinguishable.

Analysis of Spectra. To find out the number and kind of vibrational modes expected for trans CF_3SF_4Cl the molecule can be considered as consisting of two parts, XSF_4Cl and CF_3. A similar analysis has been carried out for CF_3SF_5 [159] where the assumption made, that the CF_3- group is free to rotate about the C-S bond and can therefore be considered as a single substituent, was shown to be justified. XSF_4Cl can then be expected to obey the selection rules for a molecule of C_{4v} symmetry and the CF_3, C_{3v} symmetry.

The irreducible representation of internal motion for CF_3SF_4Cl including the CF_3- group is:-

$6a_1(R,p;IR)$ + a_2(inactive) + $2b_1(R,dp)$ + $b_2(R,dp)$ + $7e(R,dp;IR)$

This includes three modes arising from the interaction of CF_3 and $-SF_4Cl$, by analogy with CF_3SF_5. The irreducible representation is worked out in detail in Appendix 1.

Table 3.1 lists the complete spectra observed for CF_3SF_4Cl while Table 3.2 gives a list of the fundamental frequencies. The fundamental frequencies of CF_3SF_5 and SF_5Cl are presented in Tables 3.3 and 3.4 as they are used to assign the spectra of CF_3SF_4Cl and are referred to frequently.

From the irreducible representation it can be seen that only the a_1 and e modes are both infrared and Raman active, which enables them to be distinguished from the remaining modes. The number of bands coincident in the infrared and Raman should therefore be thirteen; only ten of these are observed over the range scanned in the infrared, 4000-200 $cm.^{-1}$.

There is no band in the Raman spectrum corresponding to the very strong infrared peak at 867 $cm.^{-1}$. By comparison with the spectra of CF_3SF_5, SF_5Cl and SF_5O^- [178] this strong band is assigned to the asymmetric stretching vibration of the $-SF_4-$ group. Since there is little change in the polarisability of the molecule during this vibration it is expected that the band due to it would be weak in the Raman. This was the case with both CF_3SF_5 and SF_5Cl.

A band occurring at 420 $cm.^{-1}$ in the Raman spectrum, which is assigned to an in-plane deformation of the $-SF_4-$ group, should have a corresponding infrared band but this is not observed; the other $-SF_4-$ in-plane deformation is only weakly active in the infrared.

TABLE 3.1

Vibrational Spectra of CF_3SF_4Cl

Coincidences	Infrared (cm.$^{-1}$)	Raman (cm.$^{-1}$)		pol	Assignments
1.	1255 vs	1258	3	dp	ν_{11}
2.	1162 s	1160	5	p	ν_1
	1160 sh				
	1128 m	1120	1	dp	?
	1123				
	867 vs				ν_{12}
	794				
3.	790 vs	788	34		ν_2
	785				
		769	1		$2\nu_{16}$
	745 w	748	1		$\nu_{14} + \nu_{17}$
	712 w				$\nu_5 + \nu_6$
4.	685 vvs	674	33	p	ν_3
	655				
5.	651 m	648	89	p	ν_4
	647				
	618 vw	620	9		ν_8
6.	610 vw	610	7		ν_{13}
7.	570 w	570	4	dp	ν_{14}
	538 w	533	7		ν_{10}
	477 w				$\nu_4 - \nu_{17}$
8.	424 vw	425	25	p	ν_5
		420	22		ν_{15}
9.	380 vw	386	12		ν_{16}
10.	296 w	293	100	p	ν_6
		275	24		ν_9
		170	34		ν_{17}

TABLE 3.2

Fundamental Frequencies of CF_3SF_4Cl

Number	Species	Assignment	(cm.$^{-1}$)
1.	a_1	CF_3 sym. stretch	1160
2.		CF_3 sym. deformation	790
3.		SF_4 square stretch	685
4.		SF_4 out-of-plane deformation	651
5.		SCl stretch	425
6.		CS stretch	296
7.	a_2	inactive	
8.	b_1	SF_4 square stretch	620
9.		SF_4 out-of-plane deformation	275
10.	b_2	SF_4 in-plane deformation	533
11.	e	CF_3 antisym. stretch	1255
12.		SF_4 antisym. square stretch	867
13.		SF wagging	610
14.		CF_3 antisym. deformation	570
15.		SF_4 in-plane deformation	420
16.		SF_4Cl rocking	386
17.		CF_3 rocking	170

TABLE 3.3

Fundamental Frequencies of CF_3SF_5

Number	Species	Assignment	(cm.$^{-1}$)
1.	a_1	CF_3 sym. stretch	1168.3
2.		SF axial stretch	883.3
3.		CF_3 sym. deformation	754.8
4.		SF_4 square stretch	691.9
5.		SF_4 out-of-plane deformation	612.4
6.		CS stretch	324.5
7.	a_2	torsion	
8.	b_1	SF_4 square stretch	627
9.		SF_4 out-of-plane deformation	262
10.	b_2	SF_4 in-plane deformation	501
11.	e	CF_3 antisym. stretch	1256
12.		SF_4 square stretch	902
13.		SF wagging	590
14.		CF_3 antisym. deformation	558
15.		SF_4 in-plane deformation	424.5
16.		SF_5 rocking	319.7
17.		CF_3 rocking	219.6

TABLE 3.4

Fundamental Frequencies of SF_5Cl

Number	Species	Assignment	($cm.^{-1}$)
1.	a_1	SF axial stretch	854
2.		SF_4 square stretch	707.1
3.		SF_4 out-of-plane deformation	601.9
4.		SCl stretch	401.7
5.	b_1	SF_4 square stretch	625
6.		SF_4 out-of-plane deformation	271
7.	b_2	SF_4 in-plane deformation	505
8.	e	SF_4 square stretch	909
9.		SF_4 wagging	579
10.		SF_4 in-plane deformation	441
11.		SF_5 rocking	398.5

The infrared spectrum was not recorded below 200 cm.$^{-1}$. There is a medium intensity peak in the Raman spectrum at 170 cm.$^{-1}$ which is assigned to a CF_3 rocking mode.

The ten coincident bands which are observed are readily distinguishable as a_1 and e modes since the a_1 modes are polarisable while the e modes are depolarised. Most of the assignments made for these fundamentals are very similar to the corresponding modes in CF_3SF_5 and SF_5Cl. Two observations require further comment:-

i) The small increase in the frequency of the S-Cl stretching vibration on going from SF_5Cl to CF_3SF_4Cl.

ii) The decrease of ~30 cm.$^{-1}$ in the frequency of the C-S stretching vibration on going from CF_3SF_5 to CF_3SF_4Cl.

The frequencies of these vibrations will depend on the masses of the atoms involved in the bond, the force constant of the bond and any coupling of vibrations which may occur.

Since the increase in mass when a fluorine atom is replaced by a CF_3- group should decrease ν(S-Cl), the shift in frequency in (i) cannot be due solely to the mass effect. The increase may be caused by the difference in electronegativity between the F and CF_3 entities. The CF_3- group, being less electronegative than F, should cause an increase in the electron density in the S-Cl bond resulting in an increased force constant, which would be reflected in a greater vibrational frequency.

In (ii) the force constant of the C-S bond is likely to increase when F is replaced by Cl, which should result in an increase in ν(C-S). The mass effect should be smaller than in (i) (F replaced by Cl as compared with F replaced by CF_3), therefore the decrease observed in ν(C-S) may be caused by the coupling of

TABLE 3.5

Compound	ν(C-S) (cm.$^{-1}$)	
$CF_3S^{II}Cl$	468	[179]
$CF_3S^{II}SCF_3$	447	[179]
$CF_3S^{II}CF_3$	480	[161]
$CF_3S^{IV}(O)CF_3$	468	[161]
$CF_3S^{VI}F_5$	324	[159]
$(C_2F_5)S^{VI}F_4$	695	[180]
CF_3SF_4Cl	296	

vibrations of similar energies. However, a decrease of ∽30 cm.$^{-1}$ is small in comparison with the range of frequencies quoted for ν(C-S) in other derivatives. Table 3.5 lists some of these values. From the information available it appears that ν(C-S) depends a great deal on the the nature of the substituents attached to the sulphur atom and very little on the oxidation state of the sulphur. The range of ∽300 cm.$^{-1}$ quoted for ν(C-S) may be indicative of the difficulty in assigning bands to C-S stretching vibrations.

The assignments made for the remaining fundamental frequencies, b_1 and b_2, are again very similar to those in CF_3SF_5. There are very weak bands in the infrared spectrum corresponding to ν_8 and ν_{10} which should be Raman active only. Their observation may indicate a lowering of the symmetry of the molecule but only six polarised Raman bands are observed which indicates that the molecule is of C_{4v} symmetry and that the spectrum represents only the trans isomer of CF_3SF_4Cl.

These assignments of the fundamental frequencies leaves six bands unassigned. They are assumed to be due to overtones and combinations and, with one exception, are assigned as such. Under C_{4v} symmetry no combinations of b_1 and b_2 with a_1 fundamentals are allowed and none are observed. The exception is the weak band at $\sim$1120 cm.$^{-1}$ in both the Raman and infrared spectra, which remains unassigned.

Vibrational Spectra of $CF_3SF_4CF_2CF_2Cl$, $SF_5CF_2CF_2Cl$ and $SF_5CH=CH$.

These vibrational spectra are presented in full but they have not been analysed in detail. They were chosen for study since, together with CF_3SF_4Cl, they provide a series of compounds where a comparison may be made of the effect on the $-SF_4-$ group of varying the substituents around sulphur. They can be prepared in the following ways [156,148,149]:-

$$\begin{array}{lclcll} CF_3SF_4Cl & + & CF_2CF_2 & \longrightarrow & CF_3SF_4CF_2CF_2Cl & + \text{ higher polymers} \\ SF_5Cl & + & CF_2CF_2 & \longrightarrow & SF_5CF_2CF_2Cl & + \text{ higher polymers} \\ SF_5Cl & + & CH_2CH_2 & \longrightarrow & SF_5CH_2CH_2Cl & + \text{ higher polymers} \\ & & & & -HCl \Big\downarrow \text{ base} & \\ & & & & SF_5CHCH_2 & \end{array}$$

The spectra are assigned by comparison with those of CF_3SF_5, SF_5Cl and pentafluoroethylhalides [181].

A) $CF_3SF_4CF_2CF_2Cl$. Table 3.6 gives details of the observed infrared and Raman spectra. In the spectra of $CF_3SF_4CF_2CF_2Cl$ almost all of the bands occur in both the infrared and Raman spectra indicating the low symmetry of the molecule. Bands which can be assigned to vibrations of the CF_3- and $-SF_4-$ groups occur at similar frequencies to the corresponding vibrations in CF_3SF_4Cl. However, because of the greater number of bands present, there is more ambiguity about the assignment of some bands; $\nu(CF_3-S)$ and $\nu(CF_2-S)$ in particular. Since the masses of CF_3S and CF_2S are

TABLE 3.6

Vibrational Spectra of $CF_3SF_4CF_2CF_2Cl$

Infrared (cm^{-1})	Raman (cm^{-1})		pol	Assignments
1259 vs	1260	3		$\nu(CF_3)$ antisym.
1222 m				$\nu(CF_2)$
1156 m	1150	3		$\nu(CF_3)$ sym.
1058 w	1065	14	dp	?
960 w				
932 w	932	1		$\nu(CCl)$
855 vs	850	1		$\nu(SF_4)$
801 w	792	3		
780 vw	780	5		$\delta(CF_3)$
760 vw	760	4		$\nu(CC)$
	755			
702 m	707	36	p	$\nu(SF_4)$
680 s	674	2		$\nu(SF_4)$
660 s				$\delta(SF_4)$ out-of-plane
	650	9		
635 vw	635	100	p	$\nu(SF_4)$
605 m	604	14	dp	$\delta(SF_4)$ out-of-plane
570 m	570	1		$\delta(CF_3)$
	548	2		$\delta(SF_4)$ in-plane
470 w	480	9	p	$\delta(CCl)$
	440	26		$\delta(SF_4)$ in-plane
	380	5		$\delta(CF_2)$
	328	9		$\nu(CF_3S)$
	289	11		$\nu(CF_2S)$
	242	21		CF_3 rocking
	196	65	p	CF_2Cl rocking

similar, $\nu(CF_3-S)$ should occur at a higher frequency than $\nu(CF_2-S)$ if the electronegativities of each group are considered. In view of this $\nu(CF_3-S)$ and $\nu(CF_2-S)$ are assigned to bands at 328 and 289 cm.$^{-1}$ respectively although, because of the number of bands in this region, these assignments must be tentative. Risgin and Taylor, in their discussion of the spectra of pentafluoroethylhalides [181], decided that there was probably a considerable mixing of the C-Cl, C-F and C-C stretching vibrations. It is reasonable to assume that this probably occurs in the CF_2CF_2Cl part of $CF_3SF_4CF_2CF_2Cl$, therefore the assignments made are unlikely to correspond to pure vibrations.

B) $\underline{SF_5CF_2CF_2Cl}$. Details of the spectra are given in Table 3.7. There are no unusual features in the spectra of this compound. The frequencies of the vibrations associated with the CF_2CF_2Cl part of the molecule occur at slightly higher frequencies than those in $CF_3SF_4CF_2CF_2Cl$ which may reflect the greater electronegativity of F as compared with CF_3 in an analogous manner to the increase in $\nu(S-Cl)$ observed on going from SF_5Cl to CF_3SF_4Cl.

C) $\underline{SF_5CH=CH_2}$. Details of the spectra are given in Table 3.8. This was chosen for study as it provides an example of an electron donating group attached to sulphur. The infrared spectrum has previously been published [149]. As might be expected the vibrations associated with the $-SF_4-$ group occur at a much higher frequency than those in SF_5Cl, CF_3SF_5 or CF_3SF_4Cl reflecting the greater electron density in the S-F bonds due to the $-CH=CH_2$ group. The axial S-F bond is not affected to the same extent.

It is difficult to assign any band to the C-S stretching vibration. It is expected that it will be at a higher frequency than in any of the other compounds studied, therefore it may be

TABLE 3.7

Vibrational Spectra of $SF_5CF_2CF_2Cl$

Infrared (cm.$^{-1}$)	Raman (cm.$^{-1}$)		pol	Assignments
1215 s				
1190 m				$\nu(CF_2)$
1145 s				$\nu(CF_2)$
1078 m	1080	17	dp	
1052 m				
948 s				$\nu(CF_2Cl)$
896 vs	900	3		$\nu(SF_4)$
835 m	825	3		$\nu(SF)$ axial
790 vs				
680 m	694	100		$\nu(SF_4)$
600 m	612	13		$\delta(SF_4)$ out-of-plane
580 w				SF_4 wagging
	550	12		SF_4 wagging
	490	14		$\delta(SF_4)$ in-plane
	445	30	p	$\delta(CCl)$ or $\delta(SF_4)$ in-plane
	418	14		SF_5 rocking
	369	10		$\delta(CF_2)$
	320	27	dp	$\nu(CF_2S)$
	268	12		$\delta(SF_4)$ out-of-plane
	212	46		CF_2Cl rocking
	141	31		

TABLE 3.8

Vibrational Spectra of $SF_5CH=CH_2$

Infrared (cm.$^{-1}$)	Raman (cm.$^{-1}$)		pol	Assignments
3100 vw				ν(CH) antisym. in CH_2
3060 w				ν(CH) antisym. in CHR
2980 sh,w				ν(CH) sym. in CH_2
2940 w				ν(CH) sym. in CHR
2880 vw	2820	33	p	
1920 sh,w				
1905 w	1896	23	p	
	1610	8	p	ν(C=C)
1560 w				
1460 w				
1390 m				$\delta(CH_2)$ in-plane
1365 sh,w				
	1330	7		
1280 vw				δ(CH) in-plane
1242 vw				δ(CH) in-plane
1130 br,w				δ(CH) in-plane
1040 m				$\delta(CH_2)$ out-of-plane
960 vs				$\nu(SF_4)$ or δ(CH) out-of-plane
870 vvs				ν(SF) axial
790 m	800	6	p	$\nu(SF_4)$
655 m				$\nu(SF_4)$
590 s				SF wagging
562 s				$\delta(SF_4)$ in-plane
460 br,w	450	43	p	$\delta(SF_4)$ in-plane
365 vw				?
	330	20	p	?

TABLE 3.9

Compound	$\nu_{as}(SF_4)$	$\nu_s(SF_4)$	$\nu(CS)$	$cm.^{-1}$
CF_3SF_4Cl	867	685	296	
$CF_3SF_4CF_2CF_2Cl$	855	680	328,289*	
$SF_5CF_2CF_2Cl$	896	694	320	
$SF_5CH=CH_2$	960	790	-	
CF_3SF_5	902	691.9	324	[159]
SF_5Cl	909	707.1	-	[133]
* $\nu(CF_2S)$				

part of the band at 450 $cm.^{-1}$ assigned to an in-plane deformation of the $-SF_4-$ group, but without data from analogous compounds it is impossible to assign it unambiguously.

There is no absorption in the infrared spectrum corresponding to the Raman peak at 1610 $cm.^{-1}$ assigned to $\nu(C=C)$. This is not surprising since C=C bonds usually absorb only very weakly in the infrared region of the spectrum.

Most of the remaining bands can be assigned to C-H stretches and deformations.

Discussion of Spectra. The analyses of the spectra obtained here show how sensitive the $-SF_4-$ is to changes in the other substituents around the central sulphur atom. Table 3.9 lists the observed frequencies for $\nu_{as}(SF_4)$ and $\nu_s(SF_4)$. There is a variation of $\sim$100 $cm.^{-1}$ in the value of $\nu_{as}(SF_4)$. Since this is usually a very strong peak in the infrared spectrum and easily identifiable, it may be possible to use this band as a guide to the nature of substituents in unknown derivatives.

In addition to information about S-F stretching vibrations, the spectra studied in this work provide a series of ν(C-S), few examples of which, in fluorine compounds, have previously been published. However, because of the difficulty of assigning peaks to C-S stretching vibrations, it is not possible to speculate, with any degree of certainty, about the factors which affect its frequency.

EXPERIMENTAL

The materials used were obtained as detailed in Table 3.10. All compounds were redistilled several times before use and their purity was checked by infrared spectroscopy. Reactions were carried out in glass reaction vessels on a conventional vacuum line. ^1H and ^{19}F n.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 60 and 56.4MHz respectively. Routine infrared spectra were recorded on a Perkin-Elmer 457 spectrometer, while the spectra used in the vibrational studies of SF_6 derivatives were obtained from a Perkin-Elmer 225 spectrometer. Polarised Raman spectra were recorded using a 90^o scattering geometry on a Spex Ramalog 4 spectrophotometer at a resolution of 2 $cm.^{-1}$. The instrument was calibrated to ± 1 $cm.^{-1}$ using the plasma lines of an argon laser. The 488.0 nm line of a Coherent Radiation 52G argon ion laser was used as the exciting source.

Reaction between SF_5Cl and $PhPCl_2$. $PhPCl_2$ (1.37 g, 7.6 mmol) and SF_5Cl (1.24 g, 7.65 mmol) were condensed together at -196^oC and allowed to warm up slowly. A reaction took place $\sim -30^oC$ to produce $PhPF_4$, identified by its n.m.r. spectrum [186] and SCl_2 identified by infrared spectroscopy [187]. Traces of a greenish-yellow gas which reacted with mercury were observed. This was presumed to be chlorine.

Reaction between SF_5Cl and Ph_2PCl. Ph_2PCl (0.78 g, 3.53 mmol) and SF_5Cl (0.58 g, 3.55 mmol) reacted $\sim -30^oC$ to produce Ph_2PF_3, identified by n.m.r. spectroscopy [166] and analysis (Found:- C, 59.15; H, 2.25; F, 22.98; P, 11.75 $C_{12}H_{10}F_3P$ requires: C, 59.38; H, 1.74; F, 23.56; P, 12.81%). SCl_2 and Cl_2 were

TABLE 3.10

Starting Material	Source	Infrared
SF_5Cl	I.C.I. (Mond Division) (a gift)	[133]
$MePCl_2$	Albright and Wilson (a gift)	[182]
$PhPCl_2$	B.D.H.	[183]
Ph_2PCl	B.D.H.	[182]
$P(OMe)_3$	Hopkins and Williams Ltd.	[184]
$P(NMe_2)_3$	Aldrich Chemicals	[185]
CF_3SF_4Cl	$CF_3SF_3/CsF/Cl_2$ [155] (prepared by G.Haran)	
$CF_3SF_4CF_2CF_2Cl$	CF_3SF_4Cl/CF_2CF_2 [156] (prepared by G.Haran)	
$SF_5CF_2CF_2Cl$	I.C.I. (Mond Division) (a gift)	
$SF_5CH{=}CH_2$	I.C.I. (Mond Division) (a gift)	

again observed.

Reaction between SF_5Cl and $MePCl_2$. $MePCl_2$ (0.67 g, 5.7 mmol) and SF_5Cl (0.93 g, 5.75 mmol) reacted -50°C to produce $MePF_4$, identified by infrared and n.m.r. spectroscopy [188,186] and SCl_2 and SF_5Cl identified by infrared spectroscopy. Cl_2 was also produced. The main product of the reaction was a white solid (0.25 g) which had the following elemental analysis:- C, 4.81; H, 0.97; Cl, 73.3; F, 8.02; P, 13.04%. This corresponds to the atomic ratio $CH_{2.3}Cl_5FP$.

Infrared Spectrum of Solid. 3010 w, 2980 w, 2920 w, 2895 w, 905 br,m, 880 sh, 840 br,s, 795 w, 563 m, 535 w, 495 w, 450 br,m cm^{-1}.

Reaction between SF_5Cl and $P(OMe)_3$. $P(OMe)_3$ (0.61 g, 4.97 mmol) and SF_5Cl (0.81 g, 5.00 mmol) reacted at $\sim$-70°C to produce SF_4 and $S(O)F_2$ (a trace amount) as volatile products. Both were identified by infrared spectroscopy [189,190]. Trace amounts of Cl_2 and S were also observed. Two other products were formed:-

i) A white solid soluble in CD_3CN which had the following ^1H n.m.r. spectrum:- δ = 2.54 br; δ = 2.85 br; δ = 3.64 singlet; δ = 3.82 singlet ppm.

ii) A colourless not very volatile liquid which had the following spectra:-

^1H N.M.R. Spectrum δ = 3.55 doublet J(PH) = 14.7Hz; δ = 3.88 br.

^{19}F N.M.R. Spectrum δ = -62.2 doublet J(PF) = 733Hz.

Infrared Spectrum. 3020 w, 2980 w, 2870 w, 1190 m, 1110 s, 1060 m, 850 m, 825 m, 460 w cm^{-1}.

Reaction between SF_5Cl and $P(NMe_2)_3$. $P(NMe_2)_3$ (0.53 g, 3.27 mmol) and SF_5Cl (0.54 g, 3.31 mmol) reacted explosively in glass. In a monel reactor they produced SF_4, $S(O)F_2$ (a trace amount) and a colourless which had an infrared spectrum similar to that of $F_2P(NMe_2)_3$ [163].

Infrared Spectrum of Liquid. 3010 *sh*, 2960 *m*, 2920 *sh*, 2895 *s*, 2840 *w*, 1460 *br.m*, 1300 *br,s*, 1230-1200 *br,w*, 1020 *vs*, 990 *sh*, 950 *m*, 875 *vs*, 825 *vs*, 775 *vs*, 700 *w*, 515 *br,m*, 430-420 *br* $cm.^{-1}$

A yellow-brown solid was left in the reaction vessel.

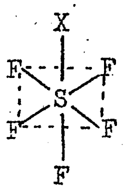
APPENDIX 1

Determination of the Irreducible Representation for CF_3SF_4Cl.

The molecule can be considered as consisting of two parts, XSF_4Cl and CF_3, and the irreducible representation found for each part.

i) XSF_4Cl. This has C_{4v} symmetry. The reducible representation can be found by considering the cartesian displacement vectors which do not change positions as a result of the symmetry operations in the point group C_{4v}. The character table for C_{4v} is reproduced below.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x,y)(R_x, R_y)	(xz, yz)



By inspection the reducible representation for CF_3SF_4Cl is:-

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
21	3	-3	5	3

The number and kind of irreducible representations which make up this reducible one can be found using the formula:-

$$a_j = 1/g\sum n_r \chi(R)\chi_i(R)$$

where a_j = the number of times the jth irreducible representation occurs in the reducible representation.

$\chi(R)$ = the reducible representation.

$\chi_i(R)$ = the irreducible representation (from the character table)

n_r = the number of elements in the class.

g = the number of symmetry operations in the group.

Using this, the irreducible representation for XSF_4Cl is:-

$$5A_1 + A_2 + 2B_1 + B_2 + 6E$$

However, this includes translational and rotational as well as vibrational modes. From the character table the translational and rotational modes have the symmetry:-

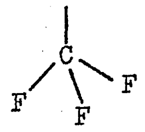
$$A_1 + A_2 + 2E$$

Therefore, the irreducible representation for the vibrational modes of XSF_4Cl is:-

$$4A_1 + 2B_1 + B_2 + 4E$$

ii) <u>CF_3</u>. In a similar way, the irreducible representation for CF_3 can be worked out. The CF_3 group has C_{3v} symmetry. The character table for C_{3v} is given below.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$



The reducible representation, by inspection, is:-

E	$2C_3$	$3\sigma_v$
12	0	2

This can be reduced giving an irreducible representation:-

$$3A_1 + A_2 + 4E$$

Those corresponding to translations and rotations are:-

$$A_1 + A_2 + 2E$$

This leaves the irreducible representation for the vibrational modes of CF_3 as:-

$$2A_1 + 2E$$

The total number of vibrational modes expected for any molecule is 3n-6, where n = the number of atoms in the molecule. Therefore, the number expected for CF_3SF_4Cl is 24. The irreducible representations calculated above give only 21. The three missing modes must be due to the interaction of the CF_3 and SF_4Cl parts of the molecule. By analogy with CF_3SF_5 the interactions have the symmetry A_2 (inactive) and E. Again, by analogy with CF_3SF_5 [159], the irreducible representation for the whole molecule can be written as the sum of the individual components:-

$$4A_1 + 2B_1 + B_2 + 4E + 2A_1 + 2E + A_2 + E$$

giving:-

$$\boxed{6A_1 + A_2 + 2B_1 + B_2 + 7E}$$

APPENDIX 2

Abbreviations used in Text.

s	strong
m	medium
w	weak
br	broad
sh	shoulder
v	very
ν_s	symmetric stretch
ν_{as}	asymmetric stretch
δ	bend
ρ	rock
mmol	millimoles

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