ALKYLIMIDOTUNGSTEN FLUORIDES AND RELATED COMPOUNDS

by

OWEN ROSS CHAMBERS

A thesis submitted for the degree
of Ph.D.
on the basis of original research
carried out in the Chemistry Department
of Glasgow University.

Submitted in April 1977.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

ACKNOWLEDGEMENTS.

I would like to thank my supervisors, Dr. J.M. Winfield and Professor D.W.A. Sharp for their help and encouragement during the preparation of this thesis. I would also like to thank Dr. David S. Rycroft for his help in obtaining the 100 MHz ^{19}F n.m.r. spectra.

CONTENTS

SUMMARY

In this work, tungsten hexafluoride derivatives have been prepared containing the strong π-donor ligands, the oxo, the imido and the alkylimido groups, with the main emphasis of the work being on the alkylimido derivatives.

The compounds $WF_4X(MeCN)$, where X = O or NH, have been prepared by the reaction of WF_6 with $(Me_3Si)_2X$ in acetonitrile. When X = NH, the product is unstable to further reaction.

The reactions of primary amines and their trimethylsilyl analogues with tungsten hexafluoride have been investigated. This has resulted in the identification of compounds of the type, $WF_4NMe(L)$, where L = MeCN, EtCN, $(MeO)_2SO$, $EtOC(O)CH_3$ and $(MeO)P(O)Me$, and the salts $RNH_3^+ WF_5NR^-$, where R = Me, Et and $\overset{n}{\underline{Bu}}$. The reaction of the amine, $Me_3SiNHMe$, with WF_6 gave salts of the anions WF_5NMe^- and $W_2F_9(NMe)_2^-$. In addition the compound, $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$, has been identified. The reaction of WF_6 with $\overset{t}{\underline{Bu}}NH_2$ gave a very insoluble 1:3 adduct.

The following techniques have been used in the study of these compounds; elemental analyses, low and high resolution mass spectrometry, infra red spectrometry, Raman spectrometry and n.m.r. spectrometry. The n.m.r. spectra of these compounds have been extensively studied. The n.m.r. evidence shows that the W = N - C skeleton is linear or nearly linear. This is explained in terms of the lone pair of electrons on the nitrogen being fed into empty d-orbitals on the tungsten atom.

The reaction of $TlWF_7$ with $(Me_3Si)_2NMe$ was investigated. The products were Me_3SiF and an insoluble cream solid of the composition, $TlWF_4NMe$. The structure was not found, but i.r. and low temperature Raman evidence suggested that it contains the WF_4NMe moiety. Related reactions were also investigated. X-Ray powder diffraction was used in these investigations along with the previously mentioned techniques.

The reactions of WF_6 with Me_3SnCF_3 and $Me_3SnC_6F_5$ gave charge transfer complexes. The reactions of MoF_6 with Me_4Sn or Me_3SnCF_3 in acetonitrile gave insoluble white solids and MeF, or MeF and CF_4.

CHAPTER ONE

INTRODUCTION

CONTENTS

(i) The Position of Tungsten in the Periodic Table.

Chromium, molybdenum and tungsten constitute Group VI of the d-block of the periodic table. There is a marked difference between the chemistries of chromium and molybdenum, and a lesser difference between the chemistries of molybdenum and tungsten. This is a property of the d-block transition metals and is due to the lanthanide contraction, which has the effect of decreasing the atomic radii of the third row with respect to the second row. There are, however, important differences between the chemistries of molybdenum and tungsten, for example tungsten hexachloride and tungsten hexabromide are known and readily prepared, whereas the corresponding molybdenum hexachloride is little known (1) and the hexabromide is unknown.

There are many differences between the chemistries of the group VI d-block elements and the group VI p-block elements (i.e. O,S, Se, Te and Po), for example S, Se and Te form bivalent hydrides, whereas Cr, Mo and W do not. This reflects the very different relative energies of the d orbitals. In the p-block elements, the d-orbitals are of high energy and take little or no part in chemical bonding; but in the d-block elements the d-orbitals are of low energy and are readily available for chemical bonding.

Many older books classify uranium along with the chromium group, but its chemistry is quite distinct. This is due to uranium possessing low energy f-orbitals which are available for chemical bonding. All modern books place uranium in the actinide group where it more properly belongs.

Table 1 : 1 shows that element 106 is expected to be eka -tungsten, the element below tungsten in the periodic table. Unfortunately it is unlikely that this element will ever be available in quantities of more than a few hundred atoms.

This will permit only tracer studies of its chemistry.

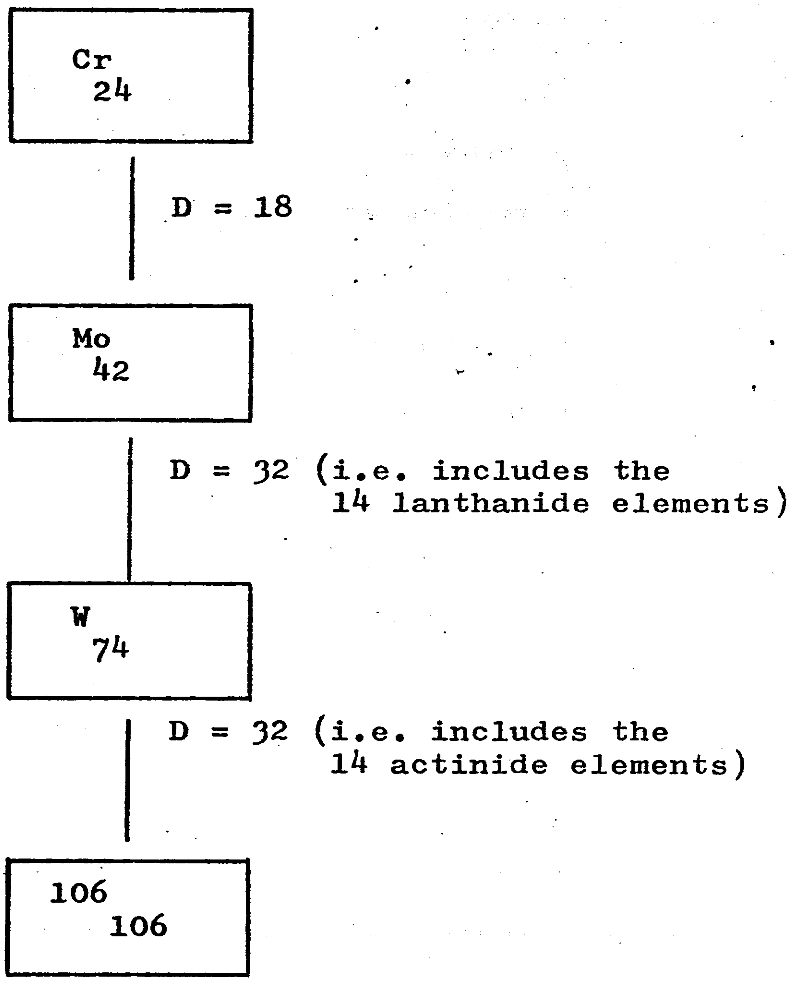
(ii) Elemental Tungsten.

Tungsten is a hard, lustrous, silvery-white metal. It has the highest melting point (3,410°C) of any known metal and its boiling point is probably greater than 6,000°C at atmospheric pressure, since tungsten has a very high heat of vaporization, 853.4kJ mole^{-1} (2). It has a high density, 19.3 g cm^{-3}, which is exceeded only by rhenium, iridium, osmium and platinum and equals that of gold.

Tungsten constitutes about 10^{-4}% of the earth's crust. It is very important industrially and is used extensively in the production of alloy steels. Even a small amount of tungsten produces a large increase in the hardness and mechanical strength of a steel. Its very high melting and boiling points make it an ideal material for the filaments in electric light bulbs.

TABLE 1 : 1

The Identity of Eka-Tungsten



(iii) The Chemistry of Tungsten.

The chemistry of tungsten is very extensive and spans almost 200 years. The work up to 1928 has been exhaustively reviewed by Mellor (3). The more recent work has been reviewed by Parish (4).

The chemistry of tungsten covers nine oxidation states from -2 to +6 and its development has occurred in distinct phases as new skills and techniques have become available and new interests have arisen.

In the early 1780's the tungsten ores wolfram and scheelite were shown to be salts of an unknown acidic metal oxide. In 1783, J.J. and F. de Ellsuyer isolated the metal as a dull grey powder, by reducing the oxide with carbon.

The nineteenth century saw developments in the higher valent state chemistry of tungsten with the preparation of tungsten oxide tetrachloride in 1823, tungsten hexachloride in 1857 and finally, at the turn of the century, tungsten hexafluoride, WF_6 (5, 6).

The early twentieth century workers extended the aqueous solution chemistry with the preparation of anionic halides and cyanide complexes, but very few compounds with a tungsten oxidation state less than W (IV) were prepared.

In 1928, tungsten hexacarbonyl, the first tungsten (0) compound, was prepared. The next thirty five years saw a large expansion in the low valent chemistry of organometallic (8, 9, 10) and carbonyl (7) tungsten compounds. The higher valent states were relatively neglected except for work on the isopolytungstates (11).

The last decade has seen a renewal of interest in the higher valent states of tungsten and it is with these, particularly the fully oxidised tungsten (VI) state, that this work is concerned.

(iv) The Tungsten (VI) State.

Tungsten is very readily oxidized to tungsten (VI) compounds. This is the oxidation state in which it is found in nature, and chlorine, fluorine, oxygen and even bromine all give this oxidation state by direct reaction with the metal. This direct combination of the elements provides the most convenient route for the preparation of the hexahalides (12). The halide and oxide halide chemistry has been extensively reviewed (12, 13, 14, 15, 16). The hexahalide molecules consist of tungsten atoms octahedrally surrounded by the halide atoms. The hexachloride and hexabromide are both black, sublimable, crystalline substances, whereas the hexafluoride is colourless and has a boiling point just below room temperature. All are rapidly hydrolysed in the atmosphere.

Tungsten hexachloride is an important starting material for other tungsten (VI) compounds. Although it is relatively easily reduced, for example with methanol and ethanol it gives tungsten (V) compounds (17), it can successfully be used in the preparation of many tungsten (VI) compounds. For example, tungsten (VI) aryloxides, $W(OAr)_6$, are prepared by reacting the hexachloride with phenols (18, 19, 20, 21). The compounds $W(NMe_2)_6$ (22), $W(CH_2SiMe_3)_6$ (23) and WMe_6 (24) can be prepared by reacting the hexachloride with the corresponding lithio derivative, provided the reaction conditions are carefully controlled to minimise reduced products. Monomethyltungsten (VI) pentachloride, WCl_5Me is prepared from the hexachloride and the milder alkylating agents, trimethylboron, dimethylzine, tetramethyltin and dimethylmercury (25, 26, 27). In the tungsten (VI) compounds which have been described where the structure has been determined, it is found that the central tungsten atom is octahedrally surrounded by substituents. To date, the corresponding molybdenum (VI) compounds are unknown.

Tungsten hexafluoride is the most volatile transition metal hexafluoride, and is the least reactive as a fluorinating and oxidizing agent. Its physical properties, with those of molybdenum hexafluoride for comparison, are given in Table 1:2. The Trouton constants of both compounds show that they are little associated in the liquid state.

The vibrational spectra (34) of both hexafluorides unambiguously demonstrate their octahedral, O_h, symmetry. Later electron diffraction studies also show an octahedral structure (33).

The chemical properties of tungsten and molybdenum hexafluoride are distinct. Molybdenum hexafluoride acts as both a fluorinating and an oxidizing agent whereas tungsten hexafluoride is much less reactive. For example; carbon disulphide reacts with molybdenum hexafluoride to give bis (trifluoromethyl) disulphide, $(CF_3)_2 S_2$, and molybdenum pentafluoride, whereas it is

TABLE 1:2

The physical properties of WF_6 and MoF_6

	MoF_6	ref.	WF_6	ref.
colour	colourless	-	colourless	-
m.p. °C	17.4	28,29	2.0	29,30
b.p. °C	34.0	28,29	17.1	29,30
Trouton Constant	20.5	31	21.5	31
M-F mean bond energy kJ mol^{-1}	439.3	32	506.2	32
length pm	182.0±0.3	33	183.2±0.3	33

unaffected by tungsten hexafluoride (32); and nitric oxide (35) or nitrosyl chloride (36) reduce molybdenum hexafluoride to a molybdenum (V) compound, $NO^+MoF_6^-$, whereas there is no reaction with tungsten hexafluoride.

The comparative reactivities of transition metal hexafluorides have been discussed (12, 37).

The reactivity of transition metal hexafluorides decreases down the periodic table and increases in going from left to right. The higher oxidation states are increasingly stable in going down the periodic table. The increase in reactivity in going from left to right is due to the increasing occupation of the d-orbitals which prevents $p\pi$-$d\pi$ overlap stabilising the metal-fluorine bonds.

Tungsten hexafluoride forms adducts with various donor ligands and is probably the strongest Lewis acid amongst the d-block transition metal hexafluorides (37). To date, adducts with the following ligands have been reported; Me_3P, Me_3N and C_5H_5N (38), Me_2S and Me_2Se (39, 40) and F^- (41).

Both molybdenum and tungsten hexafluoride form highly coloured solutions, involving contact charge transfer complexes in a variety of organic or organometallic solvents (42, 43, 44, 45, 46, 47). Contact charge transfer is the interaction of the donor orbitals on one molecule with the acceptor orbitals on another as thermal motion brings them momentarily into contact. It is thus a donor-acceptor interaction and is probably due to the acceptor properties of WF_6.

Tungsten hexafluoride undergoes ligand substitution reactions with the replacement of one or more fluorines by a chloro, alkoxy, aryloxy and dialkylamino group. Some typical reactions and products are shown in Table 1:3.

The corresponding reactions of molybdenum hexafluoride have been less studied. The compounds $MoF(OMe)_5$ and $MoF_2(OMe)_4$ have been prepared (59), but the less substituted compounds appear to be unstable. The series $(CF_3CH_2O)_nMoF_{6-n}$ (n = 1 - 6) has been prepared by the reaction:-

$$MoF_6 + Me_3SiOCH_2CF_3 \longrightarrow (CF_3CH_2O)_nMoF_{6-n} + Me_3SiF$$

the products depending on the stochiometry and reaction time. When n = 1 - 3, the compounds are unstable to decomposition (60).

A selection of mean bond energies is shown in Table 1:4. This indicates that the thermodynamic driving force for the substitution reactions is the greater bond energy of the M-F bond (M = Si, S and P).

(v) Bonding in the Transition Metals.

For the transition metals, the d-orbitals are of a suitable energy for involvement in bonding. In octahedral complexes, one s-orbital, three p-orbitals and two d-orbitals are of the correct symmetry for σ bonding. The photoelectron spectrum of hexamethyltungsten (VI) indicates strong d and s character for the σ bonds, but a much less pronounced p character (63).

The remaining three d-orbitals are available for π bonding with ligands.

TABLE 1:3

Substitution reactions of tungsten hexafluoride.

Reactant	Molar ratio of the reactant w.r.t. WF_6	Tungsten (VI) product	other products	Ref.
$(RO)_2SO$ (R=Me, Ph)	1	WF_5OR	$ROS(O)F$	48
Me_3SiOMe	1	WF_5OMe	Me_3SiF	49,50
	2	cis $WF_4(OMe)_2$	do.	
	3	$WF_3(OMe)_3$	do.	
	4	cis $WF_2(OMe)_4$	do.	
	5	$WF(OMe)_5$	do.	
$TiCl_4$	1	WF_5Cl	TiF_3Cl	51,52
Me_3SiCl	12	$WF_{6-n}Cl_n$ (n = 1-6)	Me_3SiF	53
Me_3SiNEt_2	1	WF_5NEt_2	Me_3SiF	54,55
	2	$WF_4(NEt_2)_2$	do.	56
	4	$WF_2(NEt_2)_4$	do.	56
$Me_3SiOC_6F_5$	1	$WF_5OC_6F_5$	Me_3SiF	56,57
	2	$WF_{6-n}(OC_6F_5)_n$ (n = 1-6)	do.	
$Me_3SiOCH_2CF_3$	1	$WF_5OCH_2CF_3$	Me_3SiF	58

TABLE 1:4

Average bond energies.

Bond	Average bond energy (kJ. mole^{-1})	Compound	Ref.
Si-C	305	Me_4Si	61
Si-N	335	Si_3N_4(s)	"
Si-Cl	402	$SiCl_4$	"
Si-O	460	SiO_2(c)	"
Si-F	598	Me_3SiF	"
P-Cl	330	PCl_3	"
P-O	368	P_4O_6	"
P-F	498	PF_3	"
S-Cl	272	SCl_2	"
S-F	326	SF_4	62
Sn-Cl	314	Me_4Sn, Me_3SnH	61
Sn-Cl	209	$SnCl_4$	"

For π-acceptor ligands, eg. CO, NO^+ etc., the low valent states are stabilized, since the d-orbitals are filled and can thus act as π-donors. Conversely for π-donor ligands, eg. -F, -OR, =O etc. the high valent state will be stabilized, as the d-orbitals are empty and can thus act as π-acceptors. It is with the latter type of ligand that this work is concerned.

(vi) Oxo, Nitrido and Imido Complexes of Transition Metals.

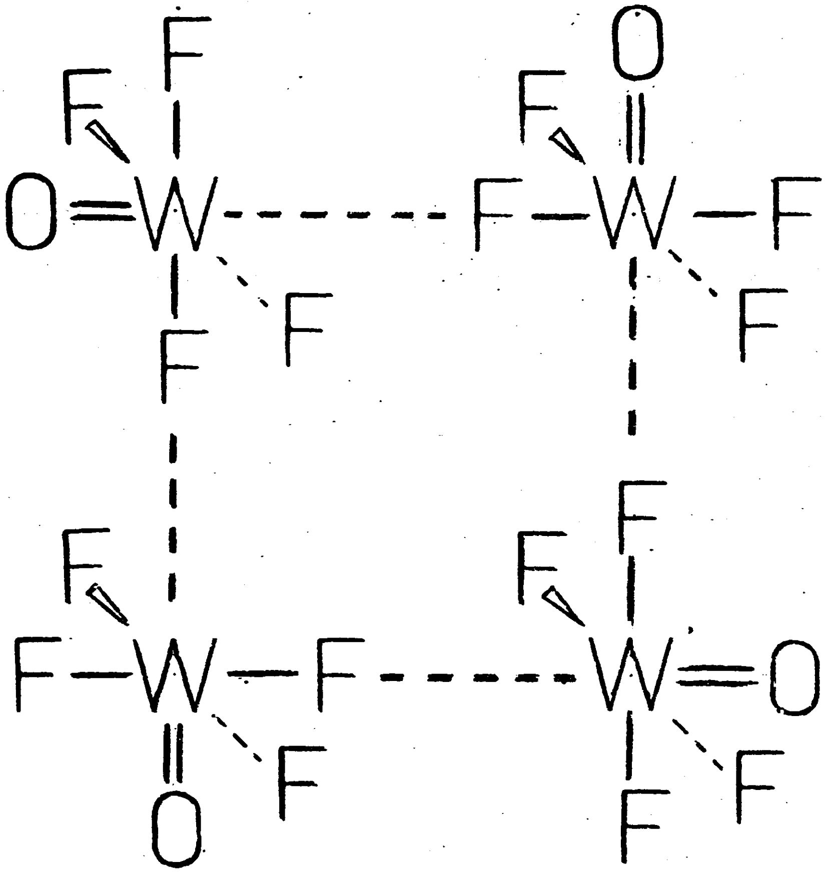
The $p\pi$ -$d\pi$ interaction in mono-oxo compounds of transition metals has various structural and chemical consequences. X-ray crystallography and electron diffraction demonstrate in d^0, d^1 and d^2 transition metal mono-oxo compounds that the M = O bond is generally very short (c.a. 160 pm) consistent with it having a bond order greater than two (64). Chemically the group is unreactive and has little donor properties (64).

These effects can be illustrated by comparing tungsten oxide tetrafluoride with its p-block analogue, tellurium oxide tetrafluoride. The structure of tungsten oxide tetrafluoride is shown in Figure 1:1 (a). It exists as a fluorine bridged tetramer (65). Attempts to prepare tellurium oxide tetrafluoride give a series of polymeric products (66, 67). These are all oxygen bridged. The simplest product, the dimer, is shown in Figure 1:1 (b).

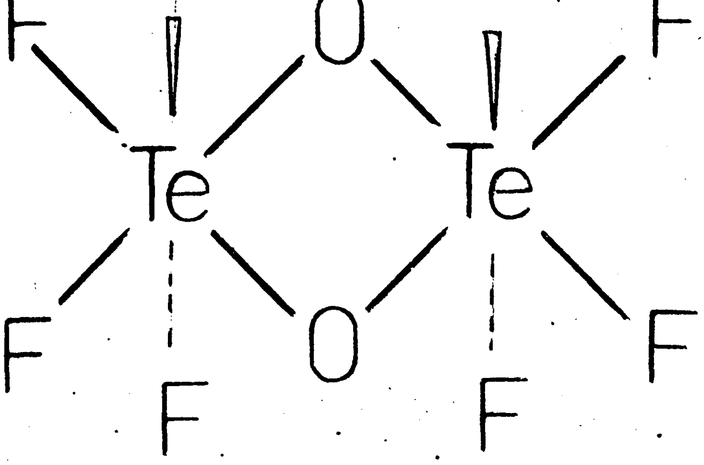
The nitrido ($\equiv$ N) and imido (= NR) groups are isoelectronic with the oxo group and form similar complexes

Figure 1:1

a. the structure of $(WOF_4)_4$; after Bennet, Haas & Purdham (65).



b. the structure of $(TeOF_4)_2$; after Seppelt (66).



with high valent state transition metals. There is strong evidence that they are even better π-donors than the oxo group. For example, a comparison of the rhenium - oxygen, bond stretching force constants in the anions ReO_3N^{2-} and ReO_4^- (68, 69) indicates that replacement of O^{2-} by N^{3-} weakens the remaining Re-O bonds. This implies that nitrogen is competing more effectively for the vacant d-orbitals than the oxygen.

Extensive vibrational spectroscopic studies have been carried out on nitrido complexes and some of the i.r. data are given in table 1:5.

Table 1:6 lists metal-nitrogen bond distances of nitrido and imido complexes. These have been obtained from X-ray diffraction studies. The majority of metal-nitrogen bond lengths are shorter than expected for a double bond and suggest a bond order greater than two. The $(R-\hat{N}-M)$ bond angles in imido complexes are generally very close to 180^o. This is consistent with the lone pair on the nitrogen atom interacting strongly with the vacant d-orbitals on the metal.

The imido complexes of Re(V) are prepared from the corresponding mono-oxo compounds by reaction, either with substituted anilines (87) or with 1, 2 disubstituted hydrazines (88). The displacement of the oxo group can also be used to prepare other imido compounds, eg.

(i) $OsO_4 + H_2NCMe_3 \longrightarrow OsO_3NCMe_3 + H_2O$ (70)

(ii) $VOCl_3 + (Me_3Si)_2NR \longrightarrow VCl_3NR + (Me_3Si)_2O$ (89)

(R = Me, Ph).

Other more specific routes have given some novel

TABLE 1:5

THE v (MN) STRETCHING FREQUENCY (cm^{-1}) IN d^o AND d^2 NITRIDO COMPLEXES.

Compound	d^n	$v(M\equiv N)(cm^{-1})$	Ref.
$KOsO_3N$	0	1023	70,71,72,73,74
$KOs^{18}O_3N$	0	1023	72
$KOsO_3{}^{15}N$	0	992	71, 72,73
K_2OsNCl_5	2	1073	70,71,72,75,76
$K_2Os^{15}NCl_5$	2	1041	71,73
$OsNCl_3(PPh_3)_2$	2	1058	77
$Os^{15}NCl_3(PPh_3)_2$	2	1027	77
$[Ph_4As]^+ [OsNCl_4]^-$	2	1123	73,76
$[Ph_4As]^+ [Os^{15}NCl_4]^-$	2	1085	73,76

TABLE 1:6

METAL-NITROGEN BOND LENGTHS IN SOME d^0 AND d^2 NITRIDO AND IMIDO COMPLEXES.

a) NITRIDO COMPLEXES.

Compound	d^n	(M≡N)pm	Ref.
K_2OsNCl_5	2	161(1)	78
$ReNCl_2(PEt_2Ph)_3$	2	179(1)	79
$ReNCl_2(PPh_3)_2$	2	160(1)	80
$K_2ReN(NC)_4,H_2O$	2	153	81

b) IMIDO COMPLEXES.

Compound	d^n	(M≡N)pm	$R-\hat{N}-M$	Ref.
$WCl_4NC_2Cl_5,CCl_3CN$	0	170(3)	180°	82
$(Cl_5C_2NWCl_2)\mu-Cl_2$	0	171(2)	177(2)°	83
$ReCl_3(p-NC_6H_4OMe)(PEt_2Ph)$	2	170.9(4)	175.8°	84
$ReCl_3(p-NC_6H_4C(O)Me)(PEt_2Ph)_2$	2	169.0(5)	171.8°	84
$ReCl_3(NMe)(PPh_2Et)_2$	2	168.5(11)	173.4(10)°	85
$[H_2NNWCl(diphos)_2]^+BPh_4^-$	2	173	171°	86

diphos = $Ph_2PCH_2CH_2PPh_2$

imido compounds:

(iii) $WCl_6(\text{or } WCl_5) + CCl_3CN \longrightarrow WCl_4NC_2Cl_5\ [(CCl_3CN)]$ (90)

(iv) $W(N_2)_2(\text{diphos})_2 + 2HCl \longrightarrow [WClNNH_2(\text{diphos})_2]^+ + Cl^- + N_2$ (91)

(v) $TaCl_5 + LiNEt_2 \longrightarrow EtN = Ta(NEt_2)_3 + LiCl$ (92,93)

If molybdenum pentachloride is used in reaction (iii) above then a Mo (V) and not a Mo (VI) product is obtained (90), again illustrating the weaker oxidizing power of W (VI) compared with Mo (VI).

(vii) The Object of this work.

The object of the present work was to study tungsten hexafluoride derivatives of two different types of ligands: a) derivatives where the ligand has no π-acceptor or donor properties but forms only a pure σ-bond, and b) derivatives where the ligand is a very strong π-donor. Unfortunately, no satisfactory preparative route could be found for the former and so only the latter types of compounds have been characterized and examined. For the former, attempts were made to prepare perfluoromethyl derivatives of tungsten hexafluoride, it being expected that the high electronegativity of the ligand would stabilize the W (VI) oxidation state. This work is described in Chapter 5.

The remaining chapters describe the work on the preparation and investigation of derivatives containing strong π-donor ligands, the imido and alkylimido groups. The analogy of these groups with the oxo group has already been described. One object of this work was to find the extent of this similarity and to find if there were any significant differences. For example, the oxo group has a markedly higher electronegativity than the imido or alkylimido group and this should affect the relative chemical properties of their respective derivatives. For structural investigations, the alkylimido group is particularly suited to nuclear magnetic resonance studies (see Chapters 2 and 3)

CHAPTER TWO

OXO-IMIDO AND ALKYLIMIDO-TUNGSTEN (VI) TETRAFLUORIDE COMPLEXES.

CONTENTS

(I) INTRODUCTION

(VI) THE REACTION OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE WITH TRIMETHYLPHOSPHITE.

(IX) THE REACTION OF TUNGSTEN HEXAFLUORIDE WITH METHYL (TRIMETHYLSILYL)AMINE.

(X) THE VIBRATIONAL SPECTRA OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE COMPLEXES.

(XIII) EXPERIMENTAL.

(I) INTRODUCTION

(a) General.

The purpose of this part of the work was to study derivatives of tungsten hexafluoride involving π-donor ligands. The ligands investigated were the oxo, the imido and the alkylimido (where the alkyl was methyl, ethyl, normal or tertiary butyl) groups. There has been a great deal of previous work published on oxo ligand derivatives of tungsten hexafluoride (4, 94, 95, 96), however for the imido and alkylimido derivatives there has only been limited previous work (96, 97, 98), and some of this was reported after the completion of the work presented here (98).

The main compounds studied are those of the type $WF_4X(L)$(where X = O, NH and NMe, and L is a donor solvent or ion). Substituted species of the type $W(OR)_nF_{4-n}O$ (n = 1-4) have been previously described (94, 99, 100, 101, 102), and a corresponding methylimido complex has been prepared in the present work.

Many preparative routes have been previously reported for WOF_4 complexes.

eg. $WF_6 + Me_2O \longrightarrow WOF_4,\ Me_2O + MeF$ (49)

$WF_5OMe + (MeO)_3P \longrightarrow (MeO)_3\overset{+}{P}Me\ WOF_5^-$ (103)

In the present work the imido and alkylimido complexes have been prepared by the two general reactions shown below:-

(i) $(Me_3Si)_2NR + WF_6 \longrightarrow (WF_4NR) + Me_3SiF$

(ii) $2H_2NR + WF_6 \longrightarrow H_3NR^+\ WF_5NR^- + HF$

The comparable preparative routes to the analogous oxo complexes have been briefly studied. Tungsten hexafluoride reacts slowly with hexamethyldisiloxane, $(Me_3Si)_2O$, to give tungsten (VI) oxide tetrafluoride, trimethylsilyl fluoride and a brown solid which contains reduced tungsten (49). The partial hydrolysis products of tungsten hexafluoride have been shown to contain the μ-fluorobis (oxotetrafluorotungstate) (VI) anion, $W_2O_2F_9^-$, by ^{19}F n.m.r. spectroscopy. (104).

The structure of tungsten oxide tetrafluoride, which exists as a tetramer, has been extensively studied. Despite initial work suggesting the presence of bridging oxygens (105), it is now well established that the structure consists of asymetric fluorine bridges (106, 65, 108). The structure is shown in Figure 1:1. The structure is disordered however, which led to the original erroneous X-ray structural determination. The bascity of the cis-fluorines is very low as even nitromethane, a very weak donor, breaks up the structure to give a monomeric tungsten oxide tetrafluoride nitromethane complex, $WOF_4,(O_2NCH_3)$ (94).

The oxopentafluorotungstate (VI) and the μ-fluorobis (oxotetrafluorotungstate) (VI) anions, WOF_5^- and $W_2O_2F_9^-$, have been prepared (95, 103, 109). ^{19}F N.m.r. evidence suggests that in both anions the tungsten is octahedrally surrounded by the ligands, and that the anion, $W_2O_2F_9^-$, has a fluorine bridge with a linear or near linear O-W-F-W-O skeleton (103, 109). The inferred structures of the anions are shown in Figure 2:1 and 2.2.

Figure 2:1

The structure of WOF_5^- anion; after Tebbe and Muertties (38).

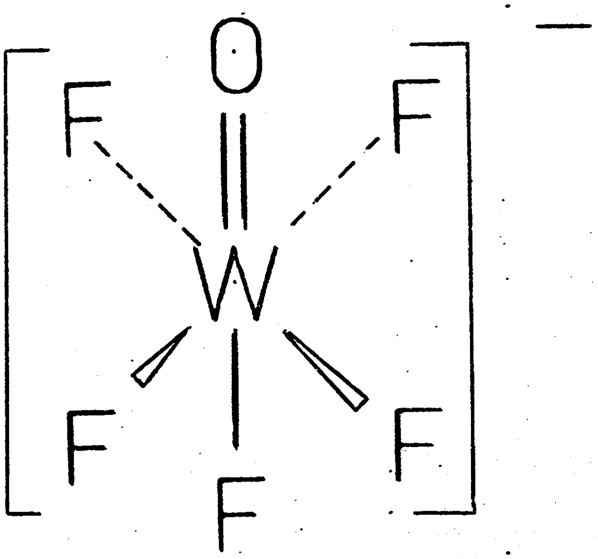
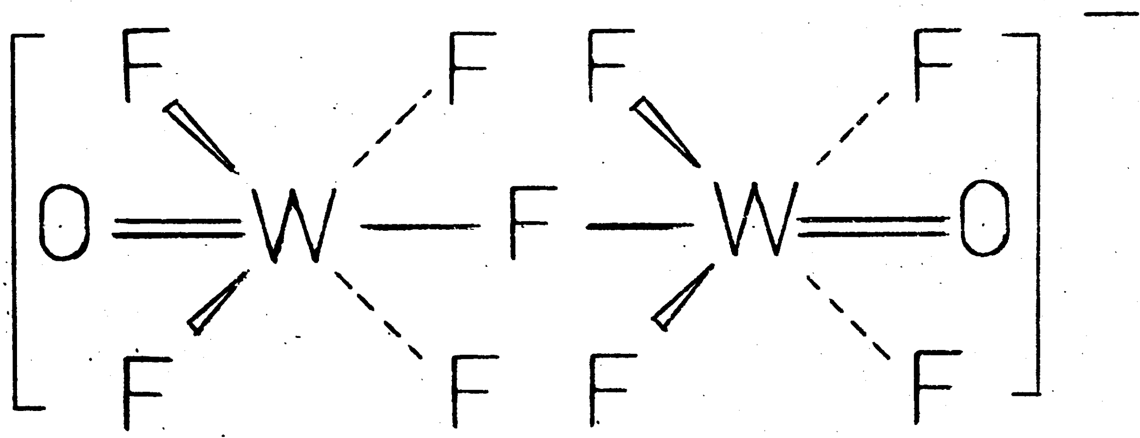


Figure 2:2

The structure of $W_2O_2F_9^-$ anion; after McFarlane, Noble and Winfield (103).



(b) Summary of previous work on the alkylimidotungsten (VI) tetrafluoride system.

The reaction of tungsten hexafluoride with ammonia has been studied as long ago as 1907 (6) and a more recent study has been carried out in 1956 (110). Both investigations found that ammonia reacts with tungsten hexafluoride to give an orange-brown solid. The analytical data on this solid were consistent with the 1:4 adduct, WF_6, $4NH_3$, (110), but no information was obtained as to its structure. The later work also studied the reaction of tungsten hexafluoride with methylamine, and reported that they react together to give a white hygroscopic solid (110). The analysis of the solid suggested the 3:1 adduct, WF_6, $3MeNH_2$, but again no information was obtained as to its structure.

The reaction of osmium tetroxide with ammonia gives osmiamic acid and other nitrido complexes (111, 112, 113), and it is possible that tungsten hexafluoride reacts similarly. Low temperature ^{19}F n.m.r. evidence has been reported recently, which suggests that the following reactions take place in acetonitrile solution (98).

(a) i) $WF_6 + NH_3 \xrightarrow{MeCN} WF_4NH\ (MeCN)$

ii) $WF_4NH\ (MeCN) + HF \xrightarrow{MeCN} WF_5NH^-$

(b) $WF_6 + (Me_3Si)_2NH \xrightarrow{MeCN} WF_4NH\ (MeCN) + 2Me_3SiF$

(c) i) $WF_6 + {}^nBuNH_2 \xrightarrow{MeCN} WF_4N^nBu\ (MeCN)$

ii) $WF_4N^nBu\ (MeCN) + HF \xrightarrow{MeCN} WF_5N^nBu^-$.

No attempt was reported to have been made to isolate the materials formed. The details of these n.m.r. results will be described when appropriate, and their relationship to the results found in this work discussed.

The reaction of tungsten hexafluoride with hexamethyldisilazane, $(Me_3Si)_2NH$, has been investigated, both in the absence of solvent and in acetonitrile (96). In acetonitrile a dark coloured solid was obtained, which was formulated as the complex, $[NH_4]^+[\overline{W}OF_5, MeCN]$. If the reaction was carried out in the absence of a solvent, then a pale yellow solid was produced which gave variable analyses.

The acetonitrile complex of methylimidotungsten (VI) tetrafluoride, $WF_4NMe(MeCN)$, has been isolated as an orange crystalline solid from the following reaction:

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

In the absence of acetonitrile, tungsten hexafluoride and N-methyl hexamethyldisilazane, $(Me_3Si)_2NMe$, react very slowly to give a cream coloured solid and trimethylsilyl fluoride (96). The analyses of this solid were variable and corresponded only approximately to methylimidotungsten (VI) tetrafluoride, WF_4NMe, however it reacted with acetonitrile to give the acetonitrile complex.

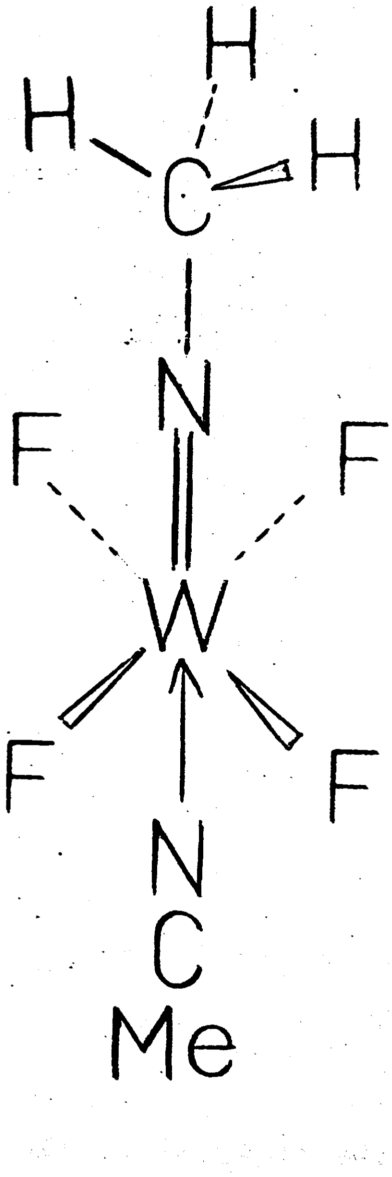
The i.r. spectrum of the complex, $WF_4NMe(MeCN)$, shows the presence of coordinated acetonitrile. It also shows no bands assignable to bridging fluorines.

The ^{19}F n.m.r. spectrum consists of a singlet peak at about 36 p.p.m. to low field of trichlorofluoromethane.

The peak possesses ^{183}W satellites with $^2J(^{19}F-^{183}W) = 46Hz$ (the original work gave this figure erroneously as 56Hz). The ^1H n.m.r. spectrum of a solution in deuteroacetonitrile, CD_3CN, gives two signals of equal intensity at $\delta^1H = 2.04$ and 5.75 p.p.m. The former singlet peak was assigned to coordinated acetonitrile. $^1H-\{^{19}F\}$ And $^1H - \{^{14}N\}$ spin decoupling experiments were carried out on the complex signal at $\delta^1H = 5.75$ p.p.m. These resulted respectively in a 1:1:1 triplet, $^2J(^1H-^{14}N) = 2.8Hz$, and a partially resolved quintet, $^4J(^1H-^{19}F) = 1.3Hz$. The presence of $^1H-^{14}N$ spin-spin coupling fine structure means that the electric field gradient at the imido ^{14}N nucleus must be very small and that the electron density at the ^{14}N nucleus is axially symmetric (see Section 4). This is consistent with a linear (W-N-C) skeleton. It was argued that the n.m.r. evidence strongly suggests a monomeric, octahedral compound, in which the acetonitrile ligand is trans to the methylimido ligand, resulting in four equivalent fluorines (Figure 2:3). It was pointed out that similar structures have been suggested for $WOF_4(L)$ (L= Me_2O or $(MeO)_2P(O)Me$) complexes in solution (48, 49).

Figure 2:3

The structure of $WF_4NMe(NeCN)$; after Harman, Sharp & Winfield (97).



(II) THE 1:1 TUNGSTEN (VI) OXIDE TETRAFLUORIDE, ACETONITRILE COMPLEX.

Tungsten hexafluoride reacts cleanly with hexamethyldisiloxane in acetonitrile according to the following equation:

$$WF_6 + (Me_3Si)_2O \longrightarrow WOF_4(MeCN) + Me_3SiF.$$

A white crystalline solid remains after the removal of the volatile products and its analysis is consistent with its formulation as the 1:1 tungsten (VI) oxide tetrafluoride acetonitrile complex, $WOF_4(MeCN)$. The ^{19}F n.m.r. spectrum of an acetonitrile solution of the solid gives a singlet, with ^{183}W satellites, at $\delta^{19}F = 68.0$ p.p.m. This is the first time that the complex has been isolated though it has previously been reported in solution (94). The infra-red spectrum of the solid is shown in Table 2:1 with suggested assignments. The basis of the assignments of the WOF_4 group will be discussed later. The Dv notation refers to the frequency shift of the ligand vibrations on complexation.

The assignments for the ligand are made by comparison of the spectrum with those of free (114) and complexed (115) acetonitrile. There is a shift to higher frequency of 48cm^{-1} in the (C≡N) stretch of the complex, compared with free acetonitrile. This is characteristic of nitriles that are coordinated via the nitrogen atom, for other donor molecules the effect is generally in the opposite direction. This apparently anomolous shift in frequency has been discussed many times (116, 117, 118). It was concluded that the shift represented a real increase in the force constant, due to the loss of electronic charge from an antibonding orbital.

TABLE 2:1

THE INFRA-SPECTRUM AND TENTATIVE ASSIGNMENTS FOR THE 1:1 TUNGSTEN (VI) OXIDE TETRAFLUORIDE ACETONITRILE COMPLEX, WOF$_4$(MeCN).

Peaks (cm^{-1})	Assignments	Frequency shift from free ligand (cm^{-1})
3270w, 3240w		
3038m		
2984s	v(C-H) (L)	Dv = +40cm^{-1}
2332s	ligand combination	Dv = +33cm^{-1}
2306s	v(C≡N) (L)	Dv = +48cm^{-1}
1486s	CH$_3$def.	
1415 m.br.	CH$_3$def (L)	Dv = -28cm^{-1}
1026 vs	v(W=O)	
944s	v(C-C) (L)	Dv = +25cm^{-1}
814m	overtone of (C-C≡N) bend (L)	
706vs	V(WF$_4$)sym	
638vs br	v(WF$_4$) asym	
507 m.br.	v(WF$_4$ out of plane)	

The spectral region was scanned from 4000 - 350cm^{-1}, using Fluorolube and Nujol mulls between potassium bromide plates.

The free ligand vibrations are after Mulligan and Jacox (114).

(III) THE 1:1 IMIDOTUNGSTEN (VI) TETRAFLUORIDE ACETONITRILE COMPLEX.

Tungsten hexafluoride reacts with hexamethyldisilazane in acetonitrile, propionitrile or ethyl acetate to give pale yellow liquids. These darken, irreversibly, at, or just below room temperature to give deep red solutions. In the absence of a polar solvent reaction occurs at c.a. $-20^{o}C$ to give pale yellow solids of variable composition.

The results of a low temperature ^{19}F n.m.r. study of the pale yellow reaction mixture in propionitrile is summarised in Table 2:2, with recent results reported in the literature (98). Since propionitrile has a similar donor power to acetonitrile, the peak closest to the reported signal of the acetonitrile complex is assigned to the propionitrile complex. Unfortunately in the present work the signal to noise ratio was not good enough to establish whether or not tungsten satellites are present.

Previous work on the tungsten oxide tetrafluoride system has demonstrated that the chemical shifts of the cis-fluorines are related to the donor power of the base (94). The stronger the base is, then the higher the field at which the fluorines resonate. It was observed that acetonitrile, a relatively weak donor, gives a signal

TABLE 2:2

LOW TEMPERATURE ^{19}F n.m.r. STUDIES OF THE $WF_6/(Me_3Si)_2NH$ and WF_6/NH_3 REACTIONS IN NITRILES.

Assignment	Peak shape	Solvent	Temp °C	δ^{19}Fa ppm	δ^{19}Fx ppm	$^2J(^{19}F_a-^{19}F_x)$ Hz	$^1J(^{19}F_a-^{183}W)$ Hz	Ref.
$WF_4NH(MeCN)$	s	MeCN	-50	+42.0	-	-	48	(98)
$WF_4NH(EtCN)$	s	EtCN	-50	+41.3	-	-		*
$WF_4NH(L^1)$	s	EtCN	-50	+38.3	-	-		*
$WF_4NH(L^{11})$	s	EtCN	-50	+35.3	-	-		*
WF_5NH^-	d(Fa) g(Fx)	MeCN	-50	+33.4	-93.5	64	50	(98)

* This work.

to the low field side of the tungsten (VI) oxide tetrafluoride complex range, whereas the fluoride ion, a strong donor, gives a signal to the high field side. This is discussed further in Chapter 3. In table 2:3 the difference in the chemical shifts between the acetonitrile and the fluoride ion complexes of several WF_4X species are indicated. This lends support to the assignment of the imidotungsten (VI) tetrafluoride complexes.

The results obtained from the pale yellow solutions strongly suggest that they contain complexes of the type $WF_4X(RCN)$, and that X is most likely to be the imido group, NH. However, the nitrido group, N^{3-}, is another possibility which cannot be ruled out.

In the previous study of the tungsten hexafluoride/hexamethyldisilazane reaction in acetonitrile only dark coloured solids were isolated (96). Similar difficulty was experienced in this work, but, on one occasion, a pale yellow, fluffy solid was obtained. The analysis of this solid was consistent with the 1:1 imidotungsten (VI) tetrafluoride acetonitrile complex, $WF_4NH(MeCN)$. The i.r. spectrum of this solid is shown in table 2:4. There is a shift to higher frequency of 32 cm^{-1} in the (C≡N) stretch, showing the presence of coordinated acetonitrile. There is a strong absorption in the (N-H) stretch region

TABLE 2:3

THE DIFFERENCE IN THE CHEMICAL SHIFT OF THE CIS-FLUORINES OF THE COMPLEXES $WF_4X(L)$ WHERE L = MeCN AND F^- RESPECTIVELY.

WF_4X	$\delta(WF_4XL) - \delta(WF_4XF)$ (ppm)	Ref.
WF_4O	15.5	(94)
WF_4NMe	9.2	*
WF_4N^nBu	7.7	(98)
WF_4S	7.0	(119, 120)
WF_4NH	8.6	(98)

* This work.

TABLE 2:4

THE INFRA-RED SPECTRUM OF THE 1:1 IMIDOTUNGSTEN (VI) TETRAFLUORIDE ACETONITRILE COMPLEX, $WF_4NH(MeCN)$.

Peak (cm^{-1})	Assignment	Frequency shift from free ligand
3280s	(N-H)st.	
2940m	(C-H)st. (L)	Dv = $-4cm^{-1}$
2317m	ligand combination	Dv = $+18cm^{-1}$
2290m	(C≡N)st. (L)	Dv = $+32cm^{-1}$
1425s	(CH_3) def. (L)	Dv = $-18cm^{-1}$
1261w	(Me_3Si-) impurity	
1060s	(W=N) st.	
1018m	(CH_3) rock (L)	
942w	(C-C)st. (L)	Dv = $+23cm^{-1}$
897w		
852w	(Me_3Si-) impurity	
700w		
614s	(WF_4) asym. st.	

The spectral region was scanned between 3000 - 350cm^{-1} using Fluorolube and Nujol mulls between potassium bromide plates.

The free ligand vibrations are after Mulligan and Jacox (114).

indicating that the imido group is present rather than the nitrido group. The spectrum will be discussed in more detail (see Section 10).

Unfortunately the difficulties involved in the preparation of this compound have not allowed confirmation of its structure. However, the evidence available suggests that in alkylnitriles the reaction between tungsten hexafluoride and hexamethyldisilazane proceeds initially as shown:-

$$WF_6 + (Me_3Si)_2NH \xrightarrow{RCN} WF_4NH(RCN) + 2Me_3SiF$$

The 1:1 imidotungsten (VI) tetrafluoride, alkylnitrile complexes, $WF_4NH(RCN)$, are apparently stable to decomposition in the solid state, but in solution further reaction readily takes place. It has been suggested previously that the final product is $[NH_4]^+ [WOF_5MeCN]^-$ (96). The deep red solutions obtained either show no signals in ^{19}F n.m.r. spectra or, in the case of propionitrile as solvent, weak signals assignable, in all cases, to tungsten (VI) oxide tetrafluoride complexes. The ^1H n.m.r. spectra give a 1:1:1 triplet consistent with the ammonium ion. Removal of solvent leaves dark solids.

Table 2:5 shows the i.r. spectra of $[NH_4]^+ [WOF_5, MeCN]^-$ (96) and the propionitrile analogue. The spectra are similar to the 1:1 imidotungsten (VI) tetrafluoride, acetonitrile complex, $WF_4NH(MeCN)$ (table 2:4), but there are extra peaks in the region 1100-1200cm^{-1}.

The formulation of the product as $[NH_4]^+ [WOF_5MeCN]^-$ is considered unlikely, since the oxopentafluorotungstate (VI) anion, WOF_5^-, is an extremely weak Lewis acid (95), and the ^{19}F n.m.r. spectrum of its solution in acetonitrile

TABLE 2:5

THE i.r. SPECTRA OF $[NH_4]^+$ $[WOF_5, RCN]^-$ WHERE R = Me, Et.

Peak (R = Me) (cm^{-1})	Dv (from free ligand) (96)	Peak (R = Et)	Dv (from free ligand)
3270 br.s		3275m	
3020w			
2942m (L)	Dv = $-2cm^{-1}$	2950m	
2310m (L)	Dv = $+11cm^{-1}$		
2277m (L)	Dv = $+30cm^{-1}$	2285s (L)	Dv = $+33cm^{-1}$
1680vbr.m			
1425b r.m (L)	Dv = $-18cm^{-1}$	1422s	
1362w			
1130w		1140m	
1100m			
1060 br.m		1065s	
1020 sh.w (L)		1020s (L)	
940m (L)	Dv = $+21cm^{-1}$	845w	
700s		786w	
650 - 600 b.r.v s		650ssh	
		630vs	

TABLE 2:5 (contd.)

The spectral region (for R = Et) was scanned between 3000 - 350 cm^{-1} using Fluorolube and Nujol mulls between potassium bromide plates.

The free ligand vibrations are after Mulligan and Jacox (114) for acetonitrile, and after Duncan and Janz (123) for propionitrile.

shows the expected AX_4 pattern (94). It is thought more likely that the tungsten is reduced and that the (W=N) linkage is retained, at least to some extent. This view is based on several pieces of evidence:-

(i) The absence, in most cases, of ^{19}F n.m.r. signals is consistent with the presence of a paramagnetic tungsten species.

(ii) There is a strong absorption peak at $1,060cm^{-1}$ in the i.r. of both the acetonitrile and propionitrile complexes. This is nearly the same as the (W=N) stretching vibration in the 1:1 imidotungsten (VI) tetrafluoride acetonitrile complex, $WF_4NH(MeCN)$ (table 2:4); whereas the (W=O) stretching vibration in the corresponding oxo complex (table 2:1) is at $1,026cm^{-1}$.

The reducing species could either be the alkylnitrile ligands or hexamethyldisilazane. Acetonitrile can act as a reducing agent, for example:-

$WCl_6 + MeCN \longrightarrow WCl_4(MeCN)_2 + CCl_3CN + HCl$ (121).

Fluorinated nitriles were not however detected among the products. The i.r. spectra of the solids possess no peaks attributable to (C-F) stretching vibrations (121) though they could have been obscured by the (W=N) stretching vibration,nor were they seen in the i.r. spectra of the volatile products. In the ^{1}H and ^{19}F n.m.r. spectra there were no peaks in the regions expected for fluorinated alkylnitriles (122).

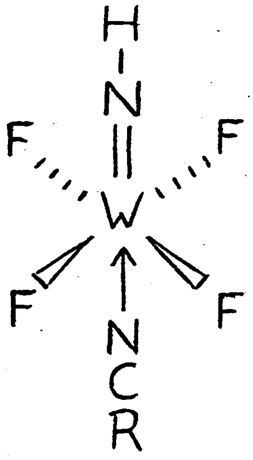
Tungsten hexafluoride is partially reduced by hexamethyldisiloxane (49). It is therefore possible that the reducing agent is the $Me_3SiXSiMe_3$ compounds. The present evidence suggests that this is more likely.

It is thus tentatively suggested that the overall decomposition reaction is:-

$$WF_4NH(MeCN) \longrightarrow NH_4^+ \; WF_4NHMeCN^-$$

where the tungsten is reduced to W(V).

The present work strongly suggests the existence of the compounds:-



R = Me, Et

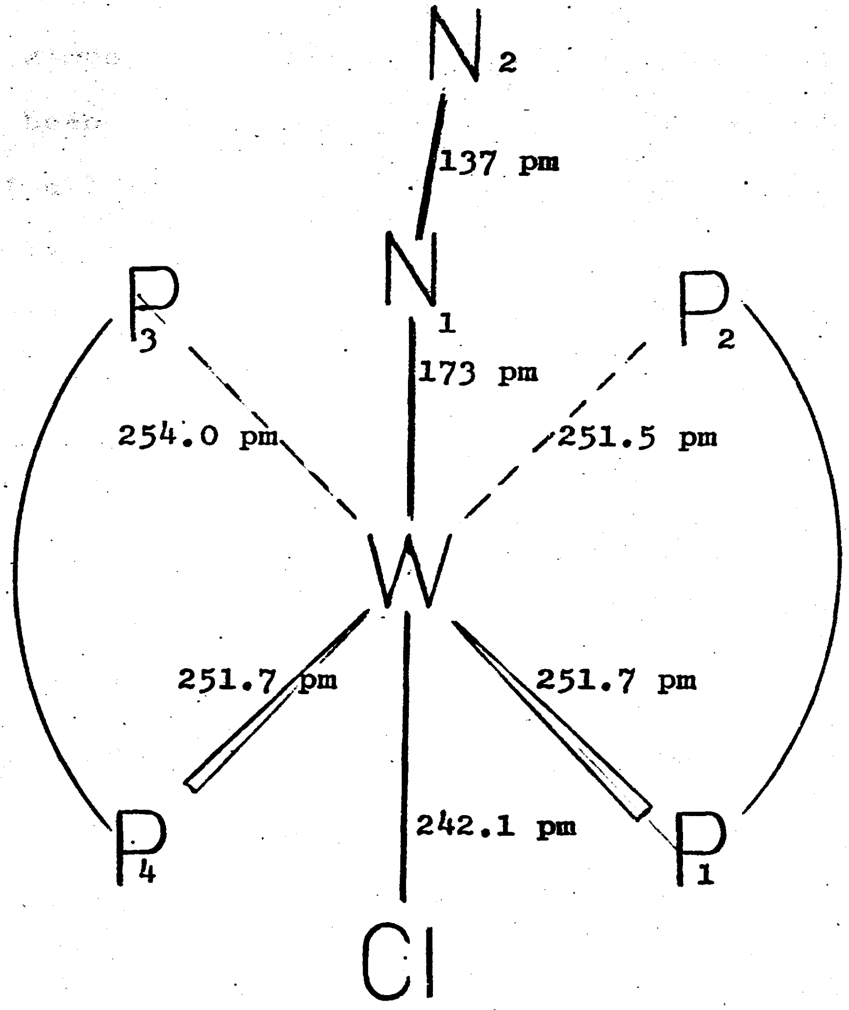
The compounds are stable to decomposition in solutions at low temperatures and in the solid state, but in solution at higher temperatures they readily decompose.

There is good evidence that corresponding d^2 compounds exist, for example the compound $[MoCl(NH)(dpe)_2]^+ \; BPh_4^-$ has recently been prepared (124). The structure of this compound is not yet known, but the structure of the related compound $[WCl(NNH_2)(dpe)_2]^+BPh_4^-$ has been determined by X-ray diffraction and is illustrated in Figure 2:4 (125) (dpe is the bidentate ligand, $Ph_2PCH_2CH_2PPh_2$).

When tungsten hexafluoride is mixed with hexamethyldisilazane in the non-polar solvent, perfluorotoluene, reaction takes place, below room temperature, to give a pale yellow solid of variable composition. The i.r.

Figure 2:4

The Crystal structure of $[WCl(NNH_2)(dpe)_2]^+$ BPh_4^-, after Heath, Mason & Thomas (125)



$W - \hat{N} - N_2 = 171^\circ$

evidence, which is further discussed in Section 10, indicates that the solid consists of impure imidotungsten (VI) tetrafluoride, WF_4NH. Strong peaks are seen in the i.r. spectrum at 1,256 and 855 cm^{-1} and these suggest the presence of a trimethylsilyl group (126, 127). The absence of a strong peak at 910 cm^{-1}, the expected region of any (Si-F) stretching vibration, suggests that the trimethylsilyl group is not present as its fluoride. A possible impurity is trimethylsilylimidotungsten (VI) tetrafluoride, WF_4NSiMe_3. After several days exposure to the normal atmosphere, analysis shows that nearly all the carbon has been lost from the sample. This is to be expected if all the carbon is present in the trimethylsilyl group.

The predominant reaction of tungsten hexafluoride with hexamethyldisilazane in perfluorotoluene can be represented by the following equation:

$$WF_6 + (Me_3Si)_2NH \xrightarrow{CF_3C_6F_5} WF_4NH + 2Me_3SiF$$

However, there is evidence that a competing reaction is also taking place:

$$WF_6 + (Me_3Si)_2NH \xrightarrow{CF_3C_6F_5} WF_4NSiMe_3 + Me_3SiF + HF .$$

(IV) METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE COMPLEXES.

The previous work (96, 97) on the 1:1 imidotungsten (VI) tetrafluoride acetonitrile complex, $WF_4NMe(MeCN)$ has been found to be reproducible and the n.m.r. spectral investigations have been extended to include the ^{14}N chemical shift and further coupling constants. The previously described slow reaction between tungsten hexafluoride and N-methyl hexamethyldisilazane to give pale yellow, polymeric methylimidotungsten (VI) tetrafluoride and trimethylsilyl fluoride has also been found to be reproducible. It has been suggested (96) that the main impurity in methylimidotungsten (VI) tetrafluoride was a compound containing the trimethylsilyl group. This is confirmed to the extent that when donor ligand complexes are prepared from methylimidotungsten (VI) tetrafluoride, then trimethylsilyl fluoride is always observed as a product. There is no strong peak at 910 cm^{-1}, so that the impurity cannot be absorbed or co-ordinated trimethylsilyl fluoride.

In the present work, methylimidotungsten (VI) tetrafluoride complexes have been prepared by the following routes:-

(i) $WF_6 + (Me_3Si)_2NMe \xrightarrow{L} WF_4NMe(L) + 2Me_3SiF$

L = acetonitrile, propionitrile and ethyl acetate.

(ii) $(WF_4NMe)_x + L \longrightarrow WF_4NMe(L)$

L = ethyl acetate and dimethyl sulphite.

In addition the 1:1 complex with dimethyl methylphosphonate, $WF_4NMe[(MeO)_2P(O)Me]$ has been prepared by a route to be described later.

The ^{19}F n.m.r. spectra of solutions of the complexes all show singlets in the region 35-38 p.p.m. downfield from trichlorofluoromethane. These singlets all have ^{183}W satellites with $^{1}J(^{19}F - ^{183}W)$ in the range 44 - 46 Hz. No other ^{19}F n.m.r. signals are observed and thus there is either only one type of fluorine present or else rapid exchange of fluorines. The clearly defined satellites suggest that no fluorine exchange is taking place.

The ^{1}H n.m.r. spectra consist of the ligand signals and a complex peak at 5.5 to 5.7 p.p.m. downfield from tetramethylsilane. $^{1}H - \{^{14}N\}$ Spin decoupling of this peak gives a 1:4:6:4:1 quintet, J = 1.0 to 1.4Hz indicating that the protons are coupled to four other equivalent nuclei with nuclear spin $I = \frac{1}{2}$. $^{1}H - \{^{19}F\}$ decoupling demonstrates that these other nuclei are fluorine atoms, with a chemical shift identical to that of the singlets found in the ^{19}F n.m.r. spectra. The $^{1}H - \{^{19}F\}$ spin decoupling experiment gives a 1:1:1 triplet, J = 2.6 to 2.8Hz. This demonstrates that the protons are coupled to one other nucleus where the nuclear spin, I = 1 i.e. as expected for the ^{14}N nucleus. The complexes are thus similar to the previously described compound, $WF_4NMe(MeCN)$ (96). The n.m.r. data is summarised in Table 2:6.

The presence of the nuclear quadrupole moment associated with the ^{14}N nucleus usually relaxes the coupling of the ^{14}N nucleus to other nuclei. Coupling is observed only when the spin lattice relaxation times of the ^{14}N nucleus is comparable to or greater than the coupling constant. This situation arises when the electric field

TABLE 2:6 - N.M.R. DATA ON $WF_4NMe(L)$ COMPLEXES.

Compound	Solvent	chemical shifts p.p.m.			Coupling constants (Hz)					
		^1H	^{19}F	^{14}N	$^1J(^{183}W-^{19}F)$	$^1J(^{183}W-^{14}N)$	$^2J(^{14}N-^{19}F)$	$^4J(^1H-^{19}F)$	$^2J(^1H-^{14}N)$	$^3J(^{183}W-^1H$
$WF_4NMe(MeCN)$	$MeCN/CD_3CN$	5.53	37.2	24.8	46		±1.3	±1.4	∓2.8	9.2
$WF_4NMe[(MeO)_2SO]$	$(MeO)_2SO$	5.63	38.7	16.1	(±)44	(±)100	±1.3	±1.2	∓2.7	9.4
$WF_4NMe(EtOAc)$	EtOAc	5.50	38.3	15.8			±1.3	±1.3	∓2.8	9.0
$WF_4NMe[(MeO)_2P(O)Me]$	$P(OMe)_3$	5.70	35.5	14.6	46			1.0	2.6	9.2

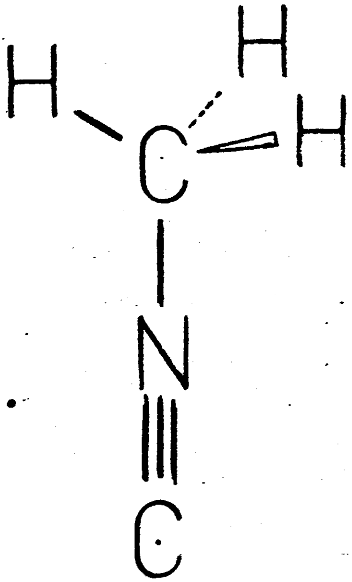
The relative signs of these coupling constants in parenthesis cannot be related to the relative signs of the coupling constants of the same compound out of parenthesis.

gradient around the ^{14}N nucleus is small or zero. The presence of such a small well defined coupling, in the compounds under investigation, implies that the electric field gradient around the nitrogen nucleus is very small. A similar ^{1}H - ^{14}N coupling situation is observed in isonitriles (128), in which the low electric field gradient is thought to be due to axial symmetry at the nitrogen nucleus. The structure and coupling constant of methylisonitrile are shown in Figure 2:5. The evidence thus points to a similar situation in methylimidotungsten (VI) tetrafluoride complexes and the structure in Figure 2:6 is suggested on this basis. The (W-N-C) skeleton is linear resulting in axial symmetry at the ^{14}N nucleus. The magnitude of the coupling constants are consistent with this structure. The $^{2}J(^{1}H - ^{14}N)$ values are similar to those in isonitriles. The $^{4}J(^{1}H - ^{19}F)$ values are similar to those observed in methoxytungsten (VI) fluorides, where $^{4}J(^{1}H - ^{19}F_{cis})$ is in the range 0.9 to 1.2Hz. (49, 50, 103). If the ligand, L, is propionitrile, ethyl acetate, dimethyl sulphite or dimethyl methylphosphonate, then the complex could not be axially symmetric. This would not, however, directly affect the electric field gradient at the nitrogen nucleus, since the magnitude of the electric field gradient varies with r^{-3} (129). The electric field gradient is thus a short range effect. For example, the quadrupole relaxation time in the benzyltrimethylammonium ion, $PhCH_2N^+Me_3$, is as long as it is in the tetramethylammonium ion, Me_4N^+(130).

The i.r. spectra of the acetonitrile, propionitrile and dimethyl sulphite complexes of methylimidotungsten (VI)

Figure 2:5

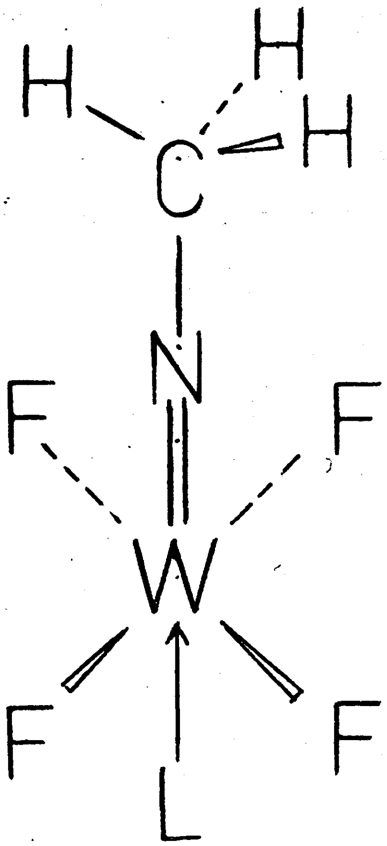
The Structure and coupling constant in Methyl Isonitrile (128).



$^{2}J(^{1}H - ^{14}N)$
$= -2.3 \pm 0.1$ Hz.

Figure 2:6

The Structure of $WF_4NMe(L)$ complexes.



tetrafluoride have been recorded and assignments made. The i.r. spectra of the acetonitrile complex has already been described (96, 97), and the results were found to be reproducible in the present work. The i.r. spectrum of the propionitrile complex shows that the (C≡N) stretching vibration of the propionitrile has been shifted by 46 cm^{-1} to high frequency compared with the free ligand in a similar manner to the acetonitrile complex.

The i.r. spectrum of the 1:1 methylimidotungsten (VI) tetrafluoride dimethyl sulphite complex, $WF_4NMe[(MeO)_2SO]$, is shown in table 2:7. The assignments of the dimethyl sulphite vibrations are based on assignments given in the literature for the free ligand (131, 132). Complexes of sulphite esters have not been extensively investigated, though complexes of trimethylene sulphite with transition metal cations have been prepared (133). The assignments for the WF_4NMe moiety will be discussed later in Section 10. The band at 1,093cm^{-1} is assigned to the (S = O) stretching vibration. This is a drop of 118cm^{-1} compared with the free ligand.

The very strong band at 1,093cm^{-1} is not observed in either the free ligand or in $WF_4NMe(MeCN)$, whereas the free ligand band at 1,211cm^{-1} is absent. There is no other band at a higher energy which can be assigned to the (S = O) stretching vibration, and thus the only alternative would be to assign it to a band of even lower energy.

The dimethyl sulphite ligand could complex via the sulphur atom, the oxo group or the methoxy group, since

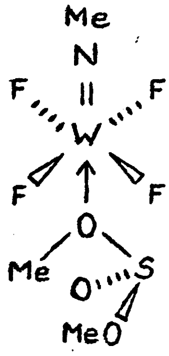
TABLE 2:7

i.r. spectrum of $WF_4NMe[(MeO)_2SO]$

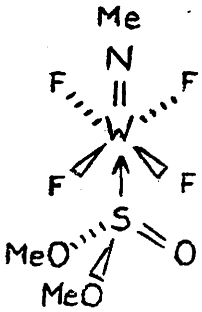
Peak (cm^{-1}).	Assignment	Dv from free ligand
2960m	(CH_3)st.(L)	Dv = 0
2922m.sh.		
2840w	(CH_3)st.(L)	Dv = 0
1450m.br.	CH_3 def. (L)	Dv = -6 cm^{-1}
1430m.br.		
1332s.		
1202m.		
1093vs.	(S = O) st.	Dv = -118 cm^{-1}
970vs. sh.	in phase (C-O-S)st.	Dv = -10 cm^{-1}
950 vs.	out of phase (C-O-S)st.	Dv = -5 cm^{-1}
891w		
766s.sh.	sym (OSO)st.	Dv = +33 cm^{-1}
741s.	asym (OSO)st.	Dv = +55 cm^{-1}
695m.		
663s.		
601vs.	(W-F)st.	
505s.	(W-F)st.	
490s.sh.	(W-F)st.	

The spectral region was scanned from 4,000 - 350 cm^{-1}, using a liquid film between potassium bromide plates.

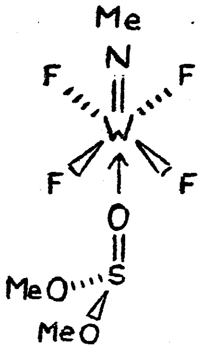
all have electron lone pairs available for donation. There are thus three possible structures for the complex:



(a)



(b)



(c)

The large fall in energy of the (S = O) stretching vibration strongly suggests that complexation occurs in the region of the sulphur or oxo groups as opposed to the methoxy group. In addition, there is very little change in the energy of the (C-O-S) stretching vibration. This favours structures (b) and (c) over (a).

The feasibility of $p\pi$-$d\pi$ bonding, in the sulphur-oxygen bond, has been studied for dimethyl sulphoxide, Me_2SO, and it has been argued from the dipole moment data that $p\pi$-$d\pi$ bonding is sufficient to make the sulphur-oxygen bond order approximately two (206). In going from dimethyl sulphoxide to dimethyl sulphite there is a substantial increase in the energy of the (S = O) stretching vibration. The (S = O) stretching vibration for dimethyl sulphoxide is at 1,055cm^{-1} (134), whereas for dimethyl sulphite it is at 1,211cm^{-1} (131). The greater electronegativity of the methoxy groups over the methyl groups favours this increase in the sulphur-oxygen bond order. For related phosphorus compounds of the type $R_3P = O$ a near linear relationship between the electronegativity of the substituent R and the increasing energy of the (P = O) stretching vibration has been found (135).

If the 1:1 methylimidotungsten (VI) tetrafluoride dimethyl sulphite complex, $WF_4NMe[(MeO)_2SO]$ has the structure (b), then an increase in energy of the (S = O) stretching vibration would be expected, since the electronegativity of the sulphur atom has been increased. Alternatively if the complex has structure (c) then a decrease in energy of the (S = O) stretching vibration would be expected, due to the increased electronegativity of the oxo group. The i.r. evidence strongly favours structure (c).

A similar argument has previously been used for deciding whether dimethyl sulphoxide complexes were through the oxygen or the sulphur atom (134, 136), a decrease in the energy of the (S = O) stretching vibration being taken to mean coordination through the oxygen atom, and an increase in energy of the (S = O) stretching vibration being taken to mean coordination through the sulphur atom. These conclusions were later confirmed by X-ray diffraction crystal structure determinations (137).

(v) POSSIBLE PATHWAYS FOR THE REACTION OF WF_6 WITH $(Me_3Si)_2X$, X = O, NH AND NMe.

The reactions of tungsten hexafluoride with $(Me_3Si)_2X$, where X = O or NMe, proceed similarly i.e. slowly in the absence of a donor solvent and fast when a donor solvent is present. The reaction of tungsten hexafluoride with $(Me_3Si)_2NH$ proceeds rapidly in both the absence and presence of a donor solvent. As the reactions of tungsten hexafluoride with N-methyl hexamethyldisilazane and hexamethyldisiloxane are similar, they will be discussed together.

A possible pathway for the reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane has been previously discussed (96). It was concluded that three steps are involved in the reaction:-

(i) The nucleophilic attack on the tungsten atom by the nitrogen lone pair of electrons to give the complex, WF_6, $(Me_3Si)_2NMe$.

(ii) The decomposition of the 1:1 adduct, $(Me_3Si)_2NMe$, WF_6, with the elimination of trimethylsilyl fluoride to give $WF_5NMeSiMe_3$.

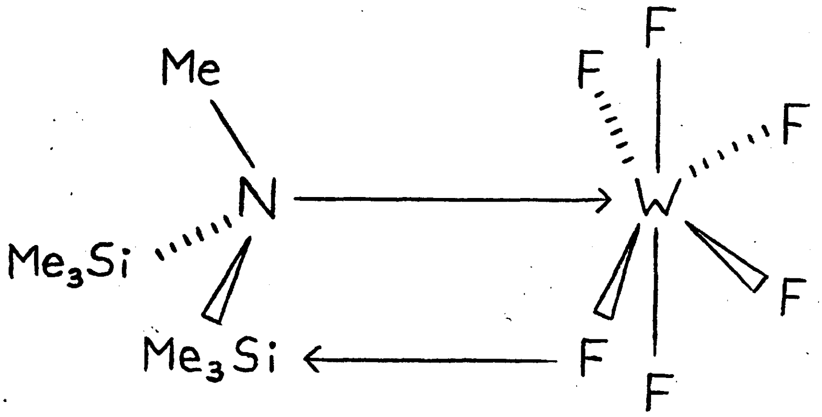
(iii) The elimination of trimethylsilyl fluoride from $WF_5NMeSiMe_3$ to give WF_4NMe.

It was argued that step (i) was slow for the following reason: the lone pair of electrons on the nitrogen atom in $(Me_3Si)_2NMe$ take part in $p\pi$-$d\pi$ 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 the nitrogen (138). Electron diffraction studies of $(R_3Si)_2O$ (R = Me, F, Cl, H) compounds demonstrate that the (Si - O - Si) bond angle is larger than expected and that it increased with the electronegativity of the substituent, R (139, 140), consistent with the presence of $d\pi$ - $p\pi$ bonding in the silicon-oxygen bond. The nitrogen atom in $(Me_3Si)_2NMe$ is thus a very poor donor and the formation of the 1:1 complex is slow.

It is felt that this description is better amended. The low basicity of the nitrogen of $(Me_3Si)_2NMe$ suggests that its 1:1 complex with tungsten hexafluoride is unstable. A contact charge transfer complex is however formed (the deep purple colouration). The following equilibrium should therefore exist and lie well to the left:

$$WF_6 + (Me_3Si)_2NMe \rightleftharpoons WF_6 , (Me_3Si)_2NMe$$

The charge-transfer complex, if the two molecules are of the correct orientation, could react further. It is believed that this is through a concerted process in which steps (i) and (ii) can effectively take place simultaneously. The cyclic transition state is shown in which the fluorine is donating to the silicon, while the nitrogen is donating to the tungsten.

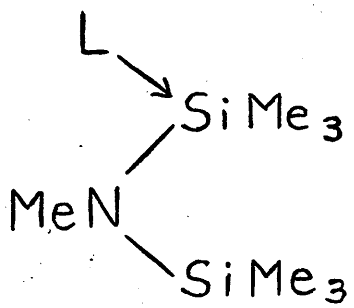


The cyclic transition state would then lead to the elimination of Me_3SiF. The proposed mechanism is consistent with a very slow reaction rate, since the formation reaction, to give the correct orientation for the transition state, should have a very low probability.

There is some low temperature ^{19}F n.m.r. evidence for the compound methyltrimethylsilylamidotungsten (VI) pentafluoride, $WF_5NMe(SiMe_3)$ in the reaction of tungsten hexafluoride and N-methyl hexamethyldisilazane in acetonitrile (96), but it readily gives WF_4NMe and Me_3SiF at higher temperatures. This can be contrasted with the behaviour of tellurium hexafluoride, tungsten hexafluoride's p-block analogue. Tellurium hexafluoride reacts with hexamethyldisilazane to give trimethylsilylamidotellurium (VI) pentafluoride, $TeF_5NHSiMe_3$. This compound is stable at room temperature, and only on reaction with hydrogen fluoride does it give amidotellurium (VI) pentafluoride, TeF_5NH_2 (141). The difference between p- and d- block chemistry can be rationalised in terms of the availability of empty d-orbitals. In the tungsten complex, $WF_5NMe(Me_3Si)$, the nitrogen lone pair will be fed into the vacant d-orbitals on the tungsten. This will drain electrons from the silicon atom making it a more powerful acceptor, and more liable to nucleophilic attack. In contrast, for the tellurium complex, $TeF_5NMe(SiMe_3)$, the vacant d-orbitals on the tellurium are of a much higher energy, there will be little $p\pi - d\pi$ interaction between the orbitals of the nitrogen and tellurium atoms and hence the acceptor properties of the silicon atom will not be enhanced.

The reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane in a donor solvent is very fast and takes place below room temperature. The presence of the donor solvent must therefore increase one or more of the following:- (i) the donor ability of the fluorine atoms, (ii) the donor ability of the nitrogen, and (iii) the acceptor ability of the silicon atom. It is unlikely to increase (iii), but it could increase both (i) and (ii). It can increase (i) by the formation of the seven or eight coordinate complexes, $WF_6(L)$ and $WF_6(L)_2$. In these the electronegativity of the tungsten could be lowered and thus the donor ability of the fluorines enhanced. There is good evidence for the existence of such complexes (38, 39, 40).

If the following complex is formed then the donor abilities of the nitrogen will be enhanced.



Previous experimental evidence, however, suggests that complexes of this type do not form. Visible and ultra-violet absorption investigations indicate that hexamethyldisiloxane does not complex with pyridine or p-toluidene (142). Furthermore the hydrolysis of hexamethyldisilazane is accelerated by acid, but inhibited by small concentrations of the hydroxyl ion. The former will involve electrophilic attack at the nitrogen, whereas the latter will involve nucleophilic attack at the silicon (143). It is still possible for the donor ligand to assist the reaction by coordinating to the silicon atom after the formation of the 1:1 complex, $WF_6,(Me_3Si)_2NMe$, since the silicon will then be a more powerful electrophile. The coordination of the donor ligand should then stabilize the 1:1 complex.

Tungsten hexafluoride reacts rapidly with hexamethyldisilazane below room temperature. This could be explained by the presence of hydrogen fluoride having a catalytic effect upon the reaction.

(VI) THE REACTION OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE WITH TRIMETHYLPHOSPHITE.

(a) Introduction.

An excess of trimethylphosphite, $(MeO)_3P$, reacts slowly with methylimidotungsten (VI) tetrafluoride, WF_4NMe, below, and at room temperature to give an orange solution containing a complex mixture of products. Removal of the volatile products from this solution leaves behind a viscous, orange oil. The nature of the products formed depends on how slowly the mixture is warmed to room temperature. The compounds identified in the reaction mixtures are unchanged trimethylphosphite, dimethyl methylphosphonate, dimethyl fluorophosphite and the 1:1 complexes, methylimidotungsten (VI) tetrafluoride dimethyl methylphosphonate, methylimidomethoxytungsten (VI) trifluoride dimethyl methylphosphonate and cis-methylimidodimethoxytungsten (VI) difluoride dimethyl methylphosphonate.

The identification of the previously characterized compounds, trimethylphosphite, dimethyl methyl phosphonate and dimethyl fluorophosphite is described in Table 2:8. Reaction mixture (a) refers to the solution obtained on warming the mixture rapidly to room temperature, and reaction mixture (b) refers to the solution obtained on warming the mixture slowly to room temperature.

TABLE 2:8

THE IDENTIFICATION BY ^{1}H and ^{19}F n.m.r. STUDIES OF TRIMETHYLPHOSPHITE, DIMETHYL METHYLPHOSPHONATE AND DIMETHYL FLUOROPHOSPHITE IN SOLUTIONS OBTAINED FROM THE REACTION OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE WITH AN EXCESS OF TRIMETHYLPHOSPHITE.

(1) The identification of trimethylphosphite, $(MeO)_3P$.

A strong doublet is observed in the ^{1}H n.m.r. spectra of both reaction mixtures (a) and (b).

n.m.r. parameter (units)	observed (a) and (b)$^{(1)}$	literature	Refs.
$\delta^{1}H$ (p.p.m.)	3.53	3.47	107
$\delta^{31}P$ (p.p.m.)$^{(2)}$	141	140	144
$^{3}J(^{1}H - ^{31}P)^{(3)}$ (Hz)	11	10.7	107

(2) The identification of dimethyl methylphosphonate.

In the ^{1}H n.m.r. spectrum of reaction mixture (b), a pair of strong doublets in the expected intensity ratio of 2:1 is observed. The ^{1}H n.m.r. spectrum of reaction mixture (a) has a significantly weaker pair of doublets in the expected intensity ratio of 2:1. In addition, there is a significant difference in the ^{1}H chemical shifts.

Parameter (units)	observed (a)$^{(1)}$	observed (b)$^{(1)}$	literature	Refs.
δ^{1}Ha(MeOP)(p.p.m.)	3.80	3.54	3.67	145
$\delta^{1}H_b$(Me-P)(p.p.m.)	1.67	1.54	1.43	"
$^{3}J(^{1}H_a - ^{31}P)^{(3)}$(Hz)	11	11	11	"
$^{2}J(^{1}H_b - ^{31}P)^{(3)}$(Hz)	18	18	17.3	"
$\delta^{31}P^{(2)}$(p.p.m.)	34	34	32.4	144

TABLE 2:8 (contd.)

(3) The identification of dimethyl fluorophosphite.

This is not observed in the ^{1}H n.m.r. spectra. The ^{19}F n.m.r. spectra of both reaction (a) and (b) show a strong, widely spaced doublet.

Parameter (units)	observed (a) and (b)(1)	literature	Refs.
$\delta^{19}F$(p.p.m.)	-60.2	-63.1	146
$^{1}J(^{19}F-^{31}P)^{(3)}$(Hz)	1176	1208	"

(1) Where the difference in observed parameters is small then an average is taken. For dimethyl methylphosphonate where the difference is large enough to be significant then the two separate measurements are given.

(2) All the $\delta^{31}P$ parameters are obtained from $^{1}H - \{^{31}P\}$ spin decoupling experiments.

(3) The coupling of the observed nucleus with ^{31}P has been confirmed by ^{1}H or $^{19}F - \{^{31}P\}$ spin decoupling experiments.

(b) The identification and structure of the methylimidotungsten (VI) tetrafluoride dimethyl methylphosphonate complex.

The new complex methylimidotungsten (VI) tetrafluoride dimethyl methylphosphonate is characterized from its ^1H and ^{19}F n.m.r. spectra and its high and low resolution mass spectra. This compound is only observed in reaction (b), where the reaction mixture is very slowly warmed to room temperature. The ^1H n.m.r. spectrum of reaction mixture (b) has a complex peak at $\delta^1H = 5.70$ p.p.m. The ^{19}F n.m.r. spectrum has a singlet peak, with tungsten satellites, at $\delta^{19}F = 35.5$ p.p.m. $^1H - \{^{19}F\}$ Spin decoupling experiments both confirm the relationships of these two peaks and reduce the peak at $\delta^1H = 5.70$ p.p.m. to a 1:1:1 triplet, and a $^1H - \{^{14}N\}$ spin decoupling experiment reduced it to a poorly resolved quintet. The observed n.m.r. parameters are shown in Table 2:6 (this Chapter, section 4). The low resolution mass spectrum has a peak corresponding to the molecular ion, $WF_4NMe[(MeO)_2P(O)Me]^+$, and other peaks corresponding to degradation products. There is no direct evidence that the ligand is not $(MeO)_3P$ as opposed to

$(MeO)_2P(O)Me$, but the latter ligand is preferred by comparison with the other complexes of dimethyl methylphosphonate prepared in the present work for which direct evidence does exist. The coupling, $^3J(^{19}F-^{31}P)$, is not observed in this complex though it is in the corresponding tungsten (VI) oxide tetrafluoride dimethyl methylphosphonate complex (103). The magnitude of the coupling constant is small, 1.5Hz, (103), and the ^{19}F n.m.r. peaks of alkylimidotungsten (VI) tetrafluoride complexes are broader than the corresponding tungsten (VI) oxide tetrafluoride complexes. This is expected since there are two extra couplings, $^2J(^{14}N-^{19}F)$ and $^4J(^1H-^{19}F)$, in the methylimidotungsten (VI) tetrafluoride complexes.

(c) The identification and structure of methylimidomethoxytungsten (VI) trifluoride, dimethyl methylphosphonate, $WF_3(OMe)(NMe)\ [(MeO)_2P(O)Me]$

The compound, methylimidomethoxytungsten (VI) trifluoride dimethyl methylphosphonate, is the main tungsten compound produced in both reactions (a) and (b). Its identification is based on n.m.r., i.r. and mass spectral evidence.

Its ^1H n.m.r. spectrum shows two equally intense peaks, which are upfield from the multiplet peaks of methylimidotungsten (VI) tetrafluoride complexes. These peaks are illustrated in Figure 2:7. One of these peaks is broad, but $^1H-\{^{14}N\}$ spin decoupling reduces it to a quartet (Figure 2:8). This indicates that the methyl protons are coupled to both an ^{14}N nucleus and three equivalent (or nearly equivalent) fluorine atoms. The upfield shift of the methyl protons in the substituted

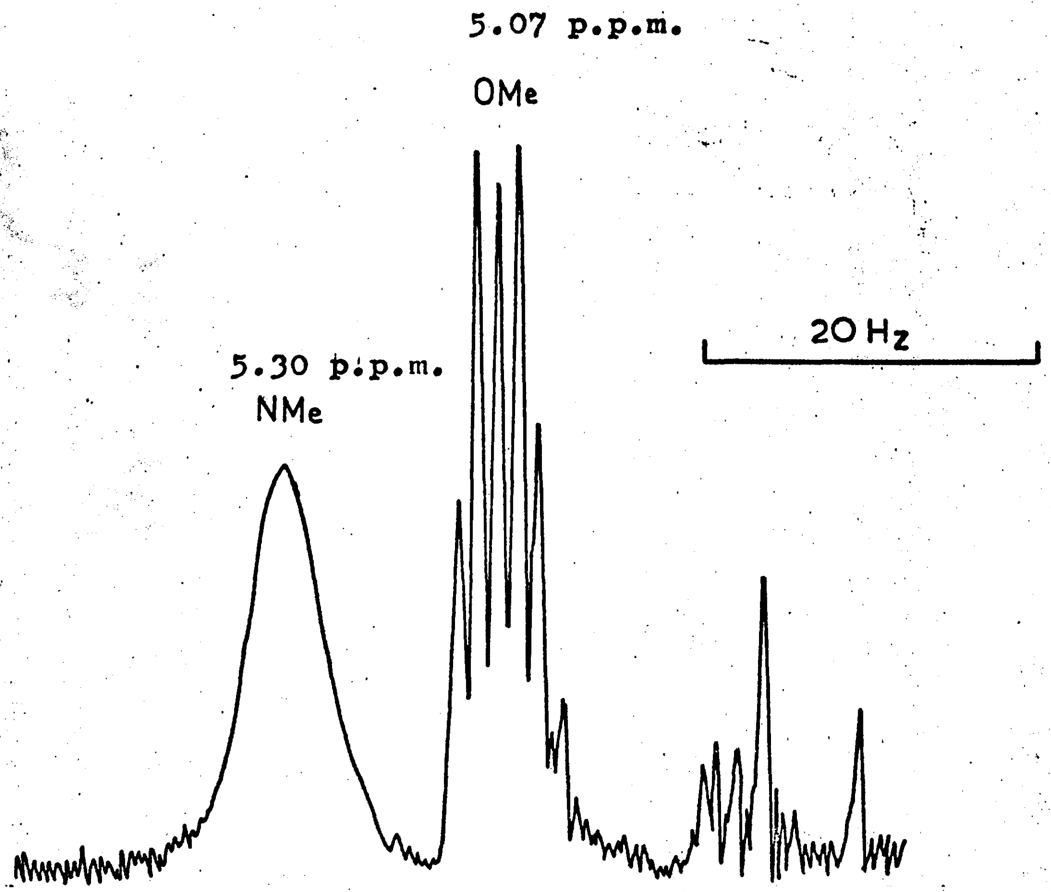


Figure 2:7

The ^{1}H n.m.r. spectrum of $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$ between $\delta^{1}H = 4.5 - 5.5$ p.p.m.

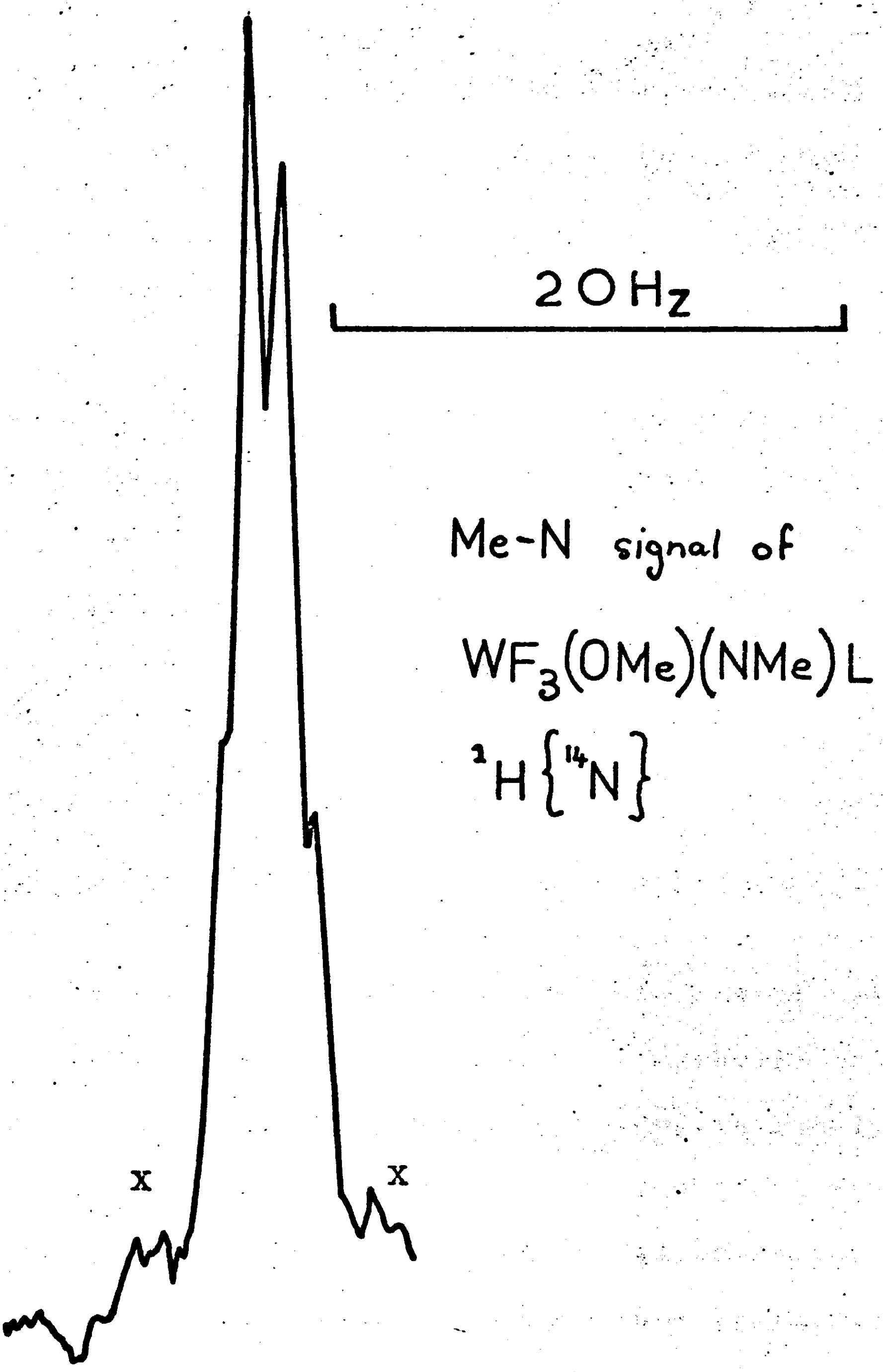


Figure 2:8

$^1H - \{^{14}N\}$ Spin decoupling of the -NMe signal at $\delta\,^1H = 5.30$ p.p.m. in $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$, ^{183}W satellites are marked X.

methylimidotungsten (VI) fluoride complex compared with the non-substituted complexes is similar to an effect observed for the series $WF_{6-n}(OMe)_n$ (n = 1-6), where increasing substitution results in an increasing upfield shift of the methoxy proton resonances. (50). The other peak is a 1:2:2:2:1 multiplet. $^1H-\{^{19}F\}$ decoupling experiments demonstrate that it is a doublet of overlapping triplets (see Chapter 3 Section 3). The ratio of the two ($^1H-^{19}F$) coupling constants c.a. 2:1, is consistent with the single fluorine being trans to the methoxy group and the two other fluorines being cis, since this ratio is observed between cis - and trans - fluorines in methoxytungsten (VI) fluorides.

The ^{19}F n.m.r. spectrum of the methylimidomethoxy tungsten (VI) trifluoride dimethyl methylphosphonate complex is an AB_2 pattern, with tungsten satellites (Figure 2:9). The association of these peaks with the peaks in the ^1H n.m.r. spectrum is confirmed by $^1H-\{^{19}F\}$ spin decoupling, the peak attributed to the protons of the methylimido group is sharpened, though no fine structure is resolved. The AB_2 pattern is approximately 40 p.p.m. upfield from the A_4 spectrum of methylimidotungsten (VI) tetrafluoride complexes, $WF_4NMe(L)$. This compares with a shift of approximately 60 p.p.m. upfield from tungsten (VI) oxide tetrafluoride complexes, $WOF_4(L)$, to methoxytungsten (VI) oxide trifluoride complexes, $WOF_3(OMe)$ (L).

The lack of resolution in the ^1H resonance of the protons of the methylimido group indicates a higher

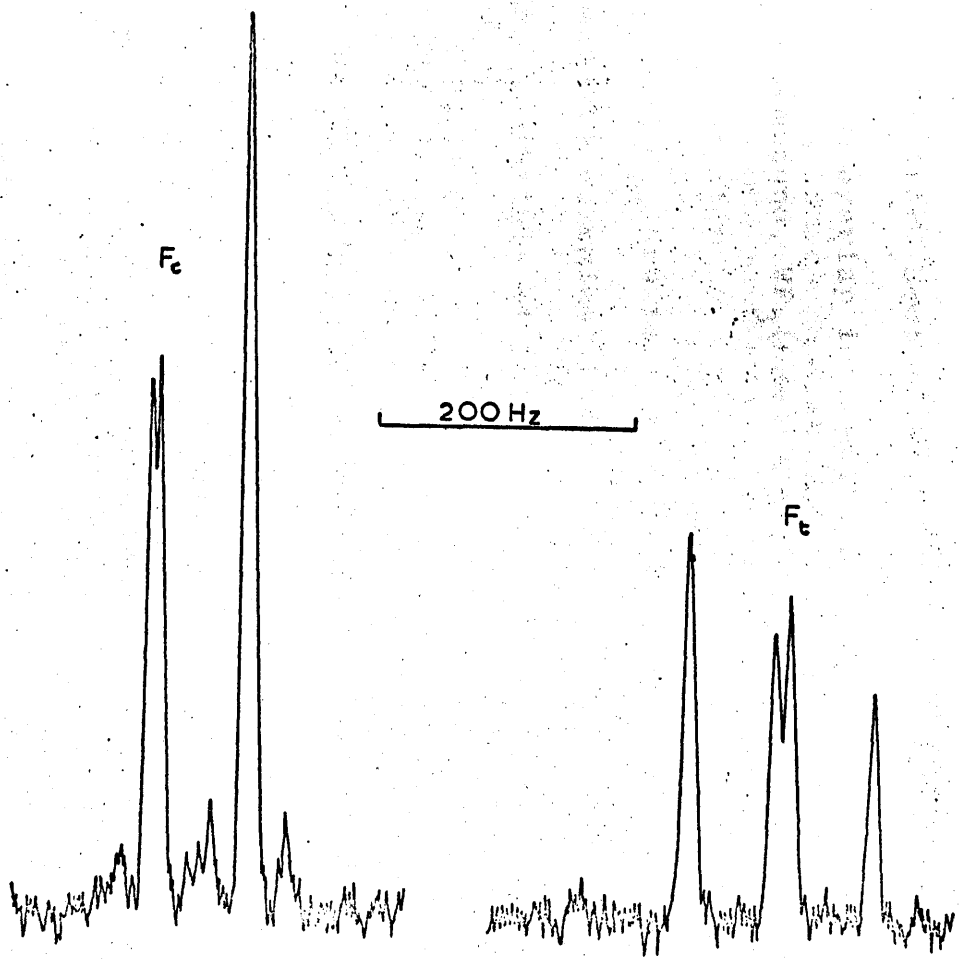


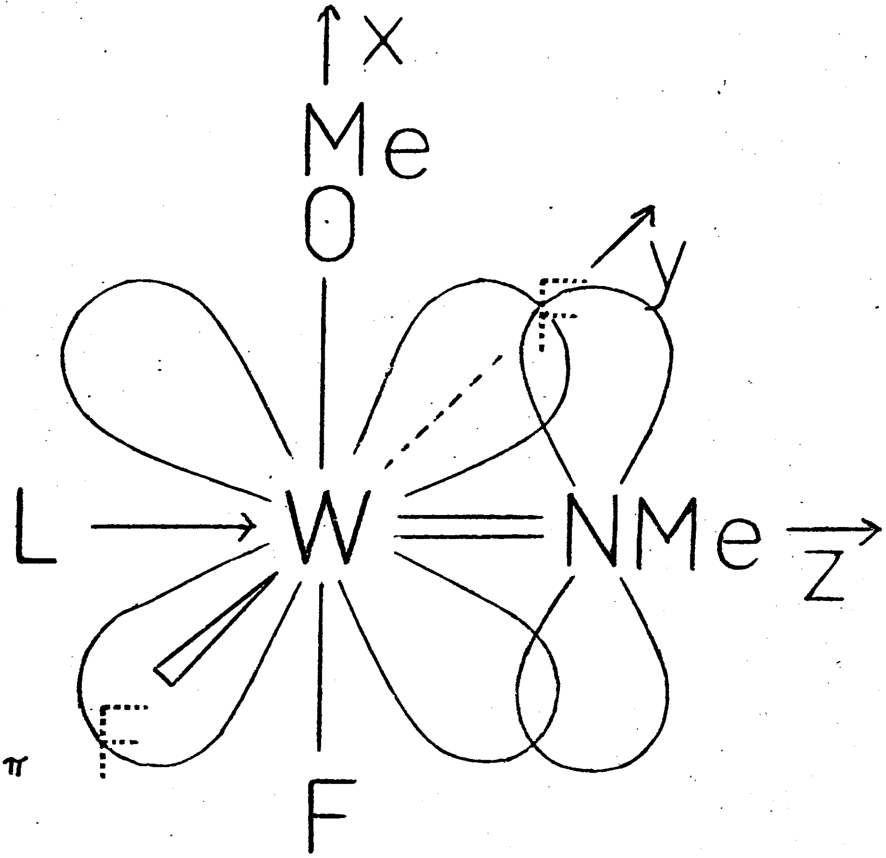
Figure 2:9

The ^{19}F n.m.r. spectrum of $WF_3(OMe)(NMe)[(MeO)P(O)Me]$, recorded at 56.45MHz.

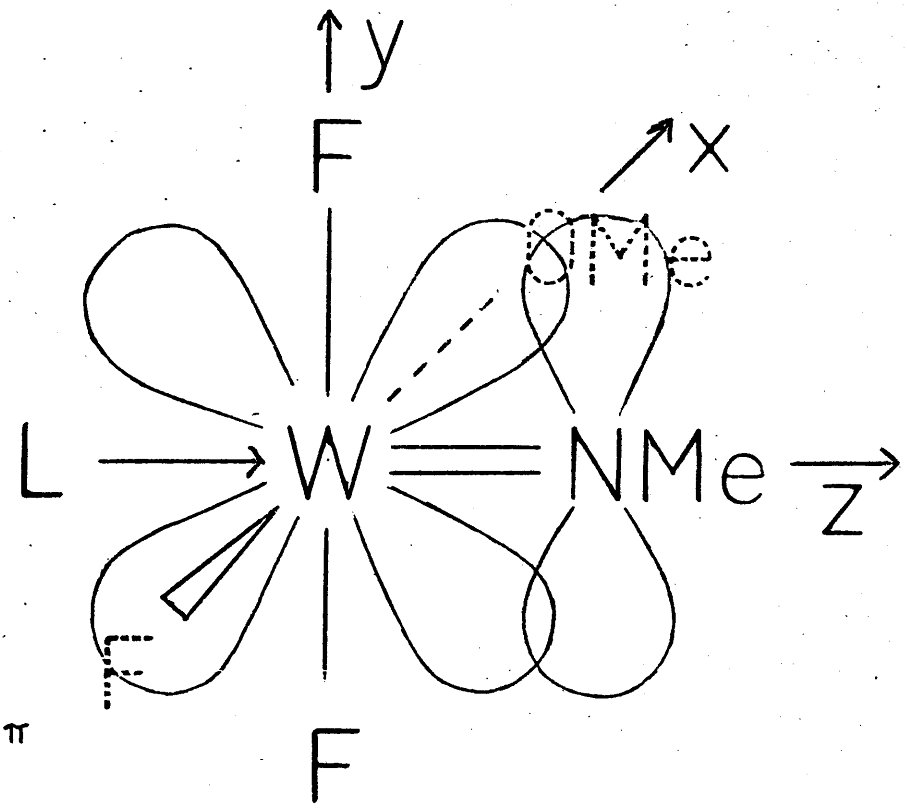
electric field gradient at the nitrogen nucleus than in methylimidotungsten (VI) tetrafluoride complexes. Although the methoxy group introduces asymmetry into the structure the short range nature of the electric field gradient should counteract this effect. It is also unlikely that the methoxy group would produce significant asymmetric bending modes involving the nitrogen atom (see this Chapter, Section 4). Figure 2:10 illustrates the $p\pi$ - $d\pi$ overlap interactions which can take place in the compound, $WF_3(OMe)(NMe)(L)$. The replacement of a fluorine atom by a methoxy group splits the degenerate d_{xz} and d_{zx} orbitals resulting in them having different relative energies (Figure 2:11). This will result in the p orbitals of the nitrogen overlapping to a different extent with the d_{xy} and d_{zy} orbitals. The asymmetry introduced by the methoxy group into the structure can therefore be transmitted to the region of the nitrogen atom by $p\pi$ - $d\pi$ overlap and the axial symmetry at the nitrogen atom lost. A related situation may exist in the compound methylimidorhenium (V) trichloride bis (ethyldiphenylphosphine), $ReCl_3(NMe)(PPh_2Et)_2$. The crystal structure of this compound is shown in Figure 2:12 (85). The compound possesses a near linear (Re-N-Me) skeleton, but the ^1H n.m.r. spectrum shows only ^{31}P coupling to the protons of the methylimido group (88). The fast relaxation of the $^2J(^1H-^{14}N)$ coupling can be explained by the large energy difference between the d_{zx} orbital, which interacts with the p-orbitals on the chlorine atoms, and the d_{yz} orbital which interacts with the

Figure 2:10(a).

The pπ-dπ overlap interactions possible in $WF_3(OMe)(NMe)(L)$, between the tungsten atom and the nitrogen of the imido group.



$(p_x-d_{zx})\pi$



$(p_y-d_{zy})\pi$

Figure 2:10(b).

The pπ-dπ overlap interactions possible in $WF_3(OMe)(NMe)(L)$, between the tungsten atom and the oxygen of the methoxy group.

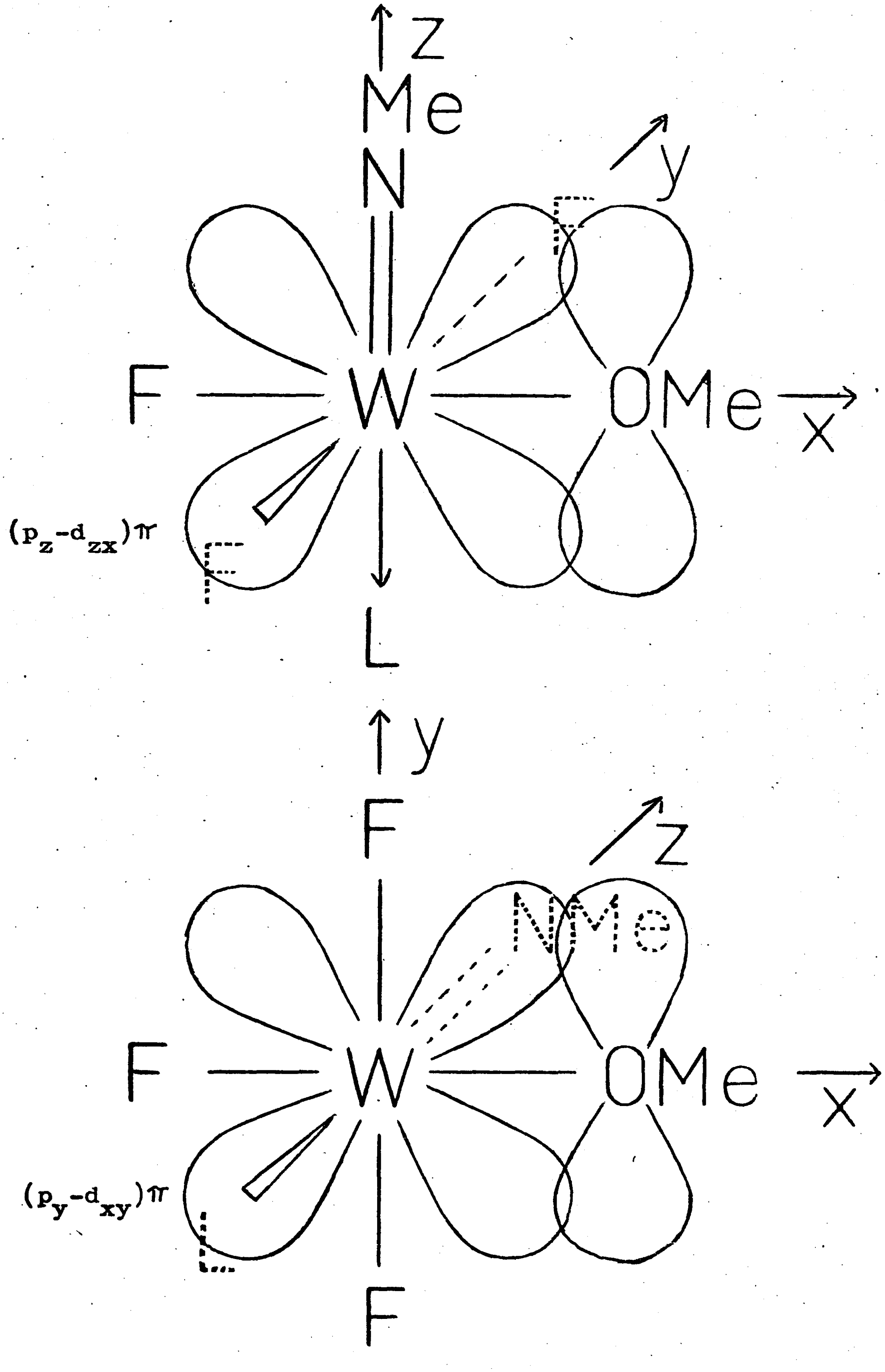
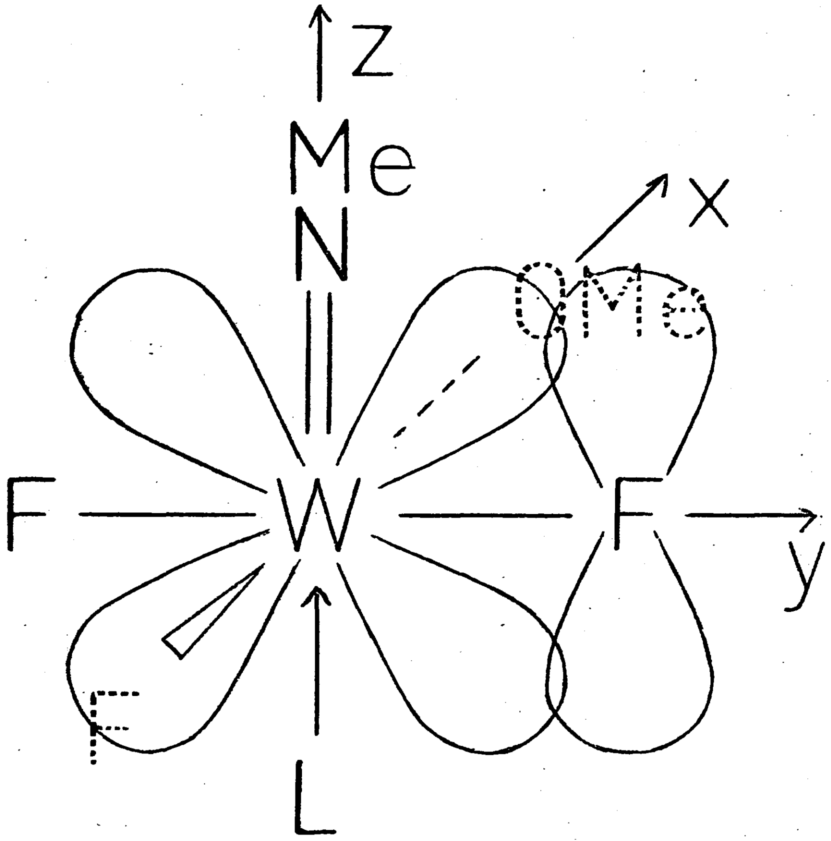
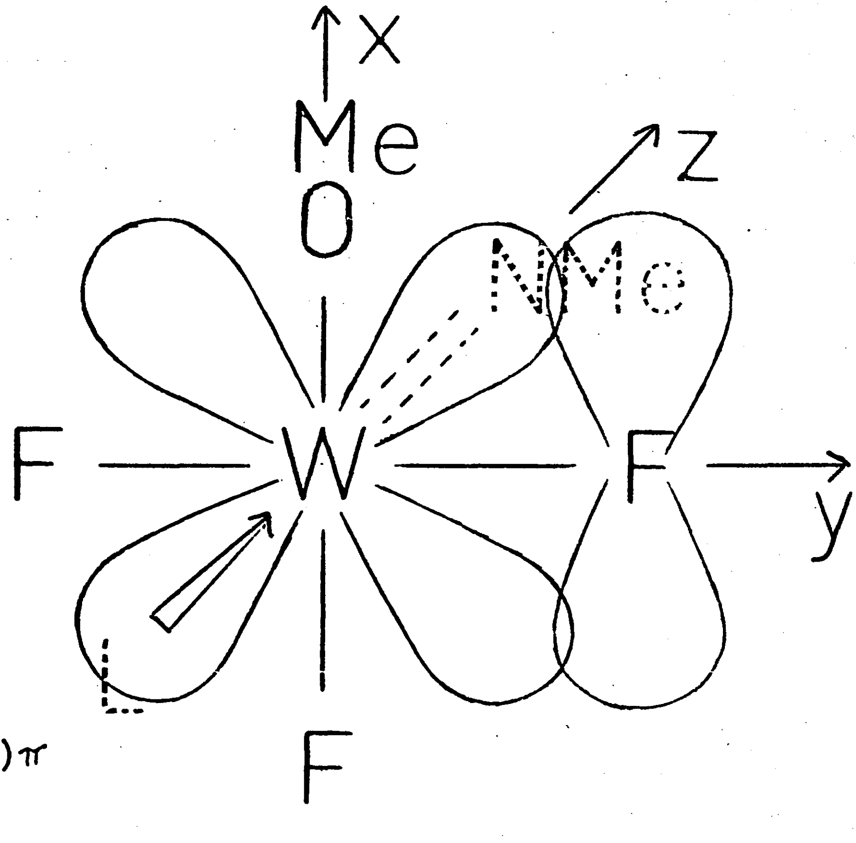


Figure 2:10(c).

The pπ-dπ overlap interactions possible in $WF_3(OMe)(NMe)(L)$, between the tungsten atom and the cis-fluorines.



$(p_z-d_{yz})\pi$



$(p_x-d_{xy})\pi$

Figure 2:11

The splitting of the energy levels of the d-orbitals on lowering the symmetry of octahedral tungsten compounds.

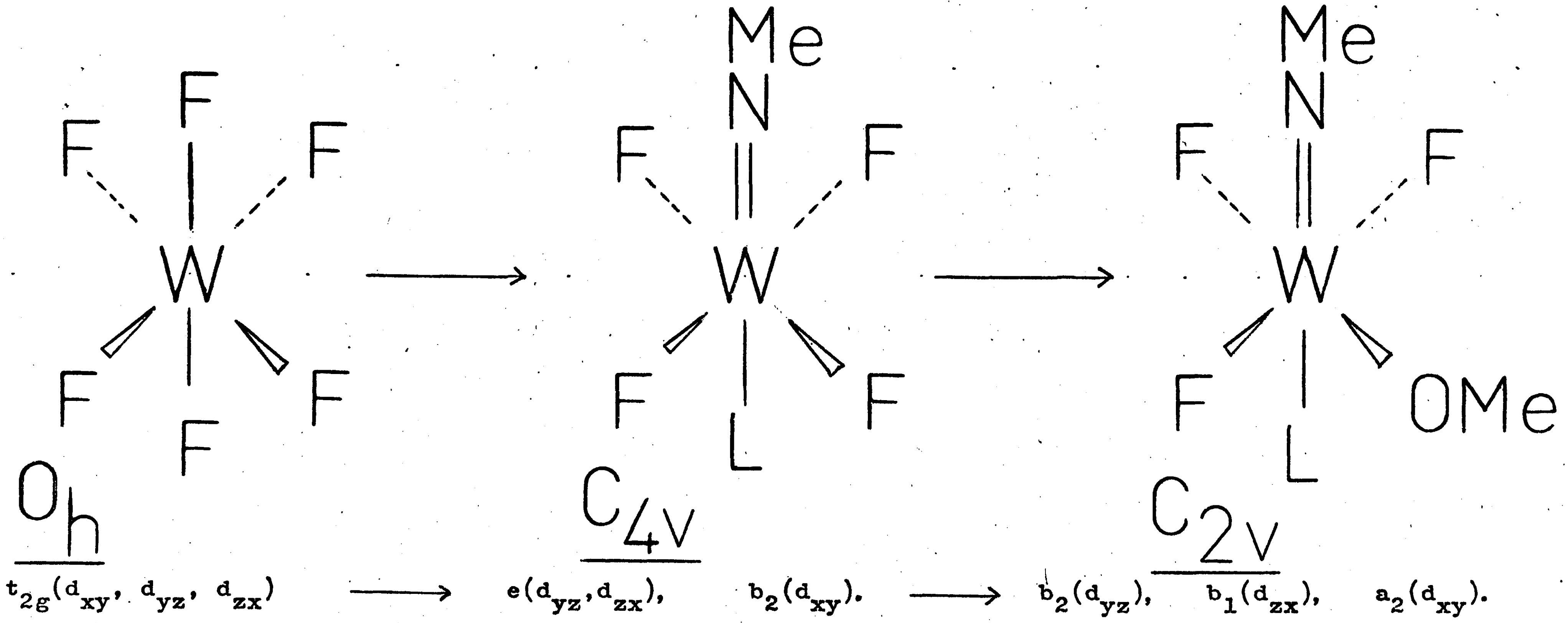
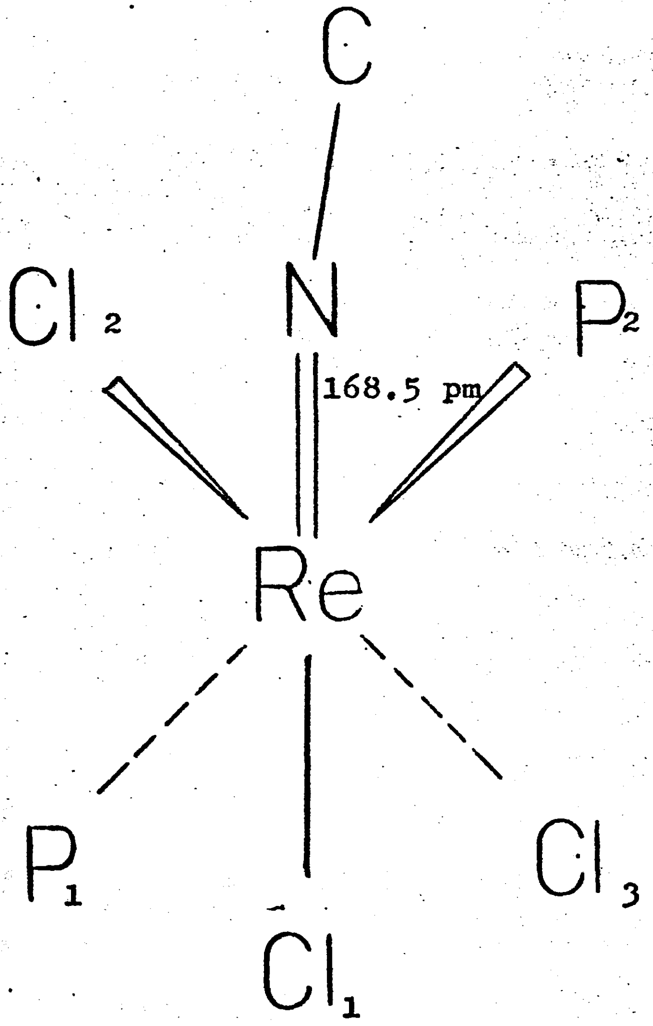


Figure 2:12

The Crystal Structure of $ReCl_3(NMe)(PPh_2Et)_2$; after Bright and Ibers (85).



$C - \hat{N} - Re = 173.4^{\circ}$

p-orbitals on the phosphorous atoms, thus lowering the symmetry at the nitrogen atom.

In reaction (a), where the tungsten hexafluoride and trimethylphosphite reactants are rapidly warmed up to room temperature, relatively pure methylimidomethoxy tungsten (VI) trifluoride dimethyl methylphosphonate is obtained. The ^1H n.m.r. spectrum of the reaction mixture indicates that the ratio of $WF_3(OMe)(NMe):(MeO)_2P(O)Me$ is nearly 1:1. There is a small quantity of cis-methylimidodimethoxytungsten (VI) difluoride dimethyl methylphosphonate present (see this Section part d). The removal of the volatile products from this reaction mixture leaves behind a viscous, orange oil, and the results from the i.r. spectrum are shown in Table 2:9. The assignments for the dimethyl methylphosphonate ligand are based on the spectrum of the free ligand (147), and assignments for the spectra of related organophosphorous compounds (148, 149, 150). It has been reported that in free organophosphorous compounds, the (P = O) stretching mode occurs between 1240 - 1260 cm^{-1} (149), the (P - OC) stretching mode between 950 - 1060 cm^{-1} (150) and the (PO - C) stretching mode for aliphatic substituents between 1168 - 1200 cm^{-1} (150). The absorptions due to the (P = O) and (P - OC) stretching modes are very strong, whereas the absorptions due to (PO - C) stretching modes are medium to weak.

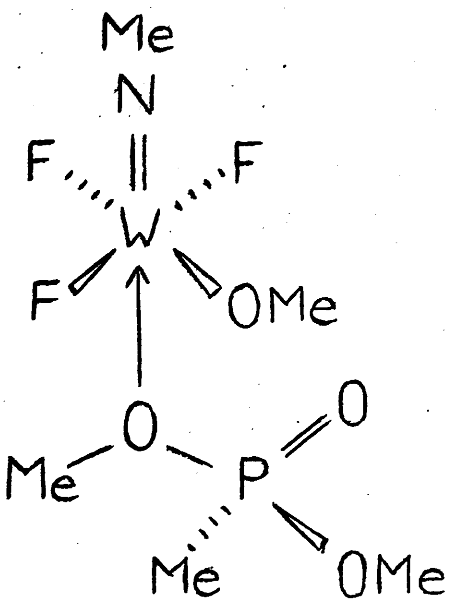
There are two possible ways in which the dimethyl methylphosphonate ligand can complex to the methylimidomethoxytungsten (VI) trifluoride species,

TABLE 2:9

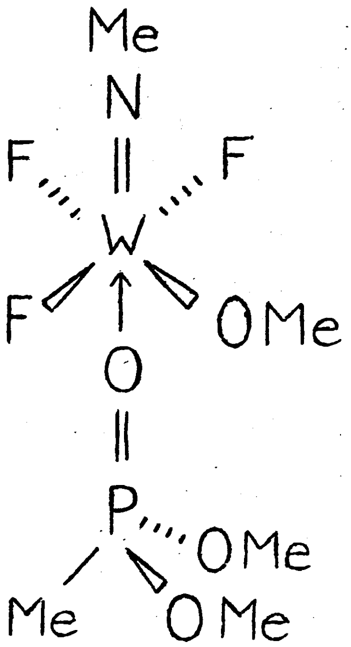
THE INFRA-RED SPECTRUM OF $WF_3(OMe)(NMe)$ $[(MeO)_2P(O)Me]$.

Peak (cm^{-1})	Assignment	Dv from free ligand
3000m	(C-H)st. (L)	Dv = 0
2960s	(C-H)st. (L)	Dv = 0
2930s		
2860m	(C-H)st. (L)	Dv = 0
2824m		
1442m.br.		
1331s		
1316s	asym CH_3 def.(L)	Dv = +2cm^{-1}
1168vs. br	(P = O)st. (L)	Dv = -82cm^{-1}
1060vs. sh.	(P-OR)st. (L)	Dv = 0
1033 vs. br.	(P-OR) (L)	Dv = 0
923s	(L)	Dv = +10cm^{-1}
910m.sh.	(L)	Dv = +10cm^{-1}
840s	(L)	Dv = +19cm^{-1}
800m	(L)	Dv = +21cm^{-1}
731m		
611 s.sh.		
557vs. br.	(W-F)st.	
512vs. br.	(W-F)st.	

Recorded as a liquid film between KBr plates.



(a)



(b)

The major change in the energy of the (P = O) stretching mode suggests that the dimethyl methylphosphonate is complexed through the terminal oxygen atom. The argument for this has already been discussed for the complex, methylimidotungsten (VI) tetrafluoride dimethyl sulphite (see this chapter, Section (IV)).

(d) The tentative identification and structure of cis-methylimidodimethoxytungsten (VI) difluoride dimethyl methylphosphonate, cis - $WF_2(OMe)_2(NMe)\ [(MeO)_2P(O)Me]$.

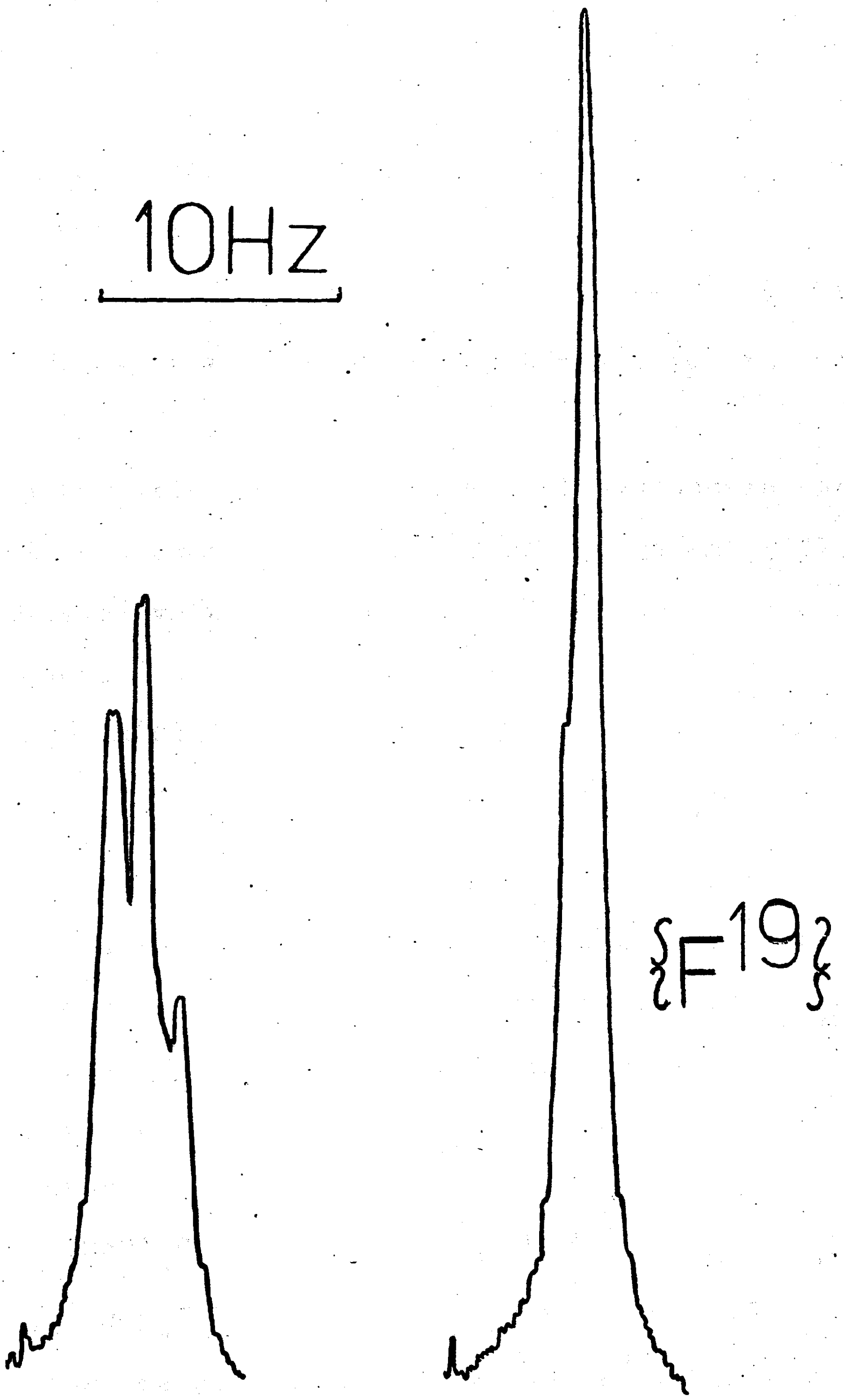
The compound, cis-methylimidodimethoxytungsten (VI) difluoride dimethyl methyl phosphonate, has been tentatively identified in the ^1H and ^{19}F n.m.r. spectra of reaction (a), where the reaction mixture is warmed rapidly to room temperature. The ^{19}F n.m.r. spectrum of the reaction mixture shows a singlet peak at $\delta^{19}F$ = -48.3 p.p.m., that is about 30 p.p.m. upfield from the AB_2 pattern of methylimidomethoxytungsten (VI) trifluoride dimethyl methylphosphonate. This is in the region expected for a disubstituted species, since from ethoxytungsten (VI) oxide trifluoride ethanol, $WF_3(OEt)O(EtOH)$, to diethoxytungsten (VI) oxide difluoride ethanol, $WF_2(OEt)_2O(EtOH)$, there is an upfield shift of about 40 p.p.m. (94). $^1H - \{^{19}F\}$ spin decoupling links this singlet with a triplet at $\delta ^1H = 4.80$ p.p.m., $^4J(^1H-^{19}F) = 1.8Hz$. The results of the spin decoupling experiment are shown in Figure 2:13, and there is some evidence for a separate singlet within this group, which is possibly the methylimido group. The observed peaks in the n.m.r. spectra are assigned to the cis isomer, since the $^4J(^1H-^{19}F)$ coupling constant is similar to that seen in methoxytungsten (VI) fluorides where the methoxide group is trans to a fluorine (50).

(e) A possible pathway for the reaction of methylimidotungsten (VI) tetrafluoride with trimethylphosphite.

The ratio of the products formed in the reaction of methylimidotungsten (VI) tetrafluoride with trimethylphosphite, appears to depend markedly on how fast the reaction mixture is warmed up to room temperature. For reaction (a), where the mixture is warmed up rapidly to room temperature the identified products are $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$, $(MeO)_2PF$ and a small amount of cis-$WF_2(OMe)_2(NMe)$ $[(MeO)_2P(O)Me]$. For reaction (b), where the mixture is warmed up slowly to room temperature the identified products are $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$, $WF_4NMe[(MeO)_2P(O)Me)]$, $(MeO)_2PF$ and significant quantities

Figure 2:13

The peak at $\delta\,^{1}H$ = 4.80 p.p.m. and the effect of $^{1}H - \{^{19}F\}$ spin decoupling.



of free $(MeO)_2P(O)Me$.

A first likely step in the reaction is the formation of a trimethylphosphite complex :-

(i) $(WF_4NMe)_x + (MeO)_3P \longrightarrow WF_4NMe[(MeO)_3P]$

The complex can now decompose by the reaction

(ii) $WF_4NMe[(MeO)_3P] \xrightarrow{(MeO)_3P} WF_3(OMe)(NMe)[(MeO)_3P] + (MeO)_2PF$

and further reaction can take place

(iii) $WF_3(OMe)(NMe)[(MeO)_3P] \xrightarrow{(MeO)_3P}$ cis $WF_2(OMe)_2(NMe)[(MeO)_3P] + (MeO)_2PF$

Reactions (ii) and (iii) are relatively slow with (iii) being slower than (ii).

The formation of dimethyl methylphosphonate can take place via a Michaelis - Arburzov rearrangement (151). This involves valence expansion and is demonstrated in the sequence

(A) - $RB + (R^1O)_3P \longrightarrow (R^1O)_3PR^+ + B^-$

$(R^1O)_3PR^+ + B^- \longrightarrow (R^1O)_2P(O)R + R^1B$

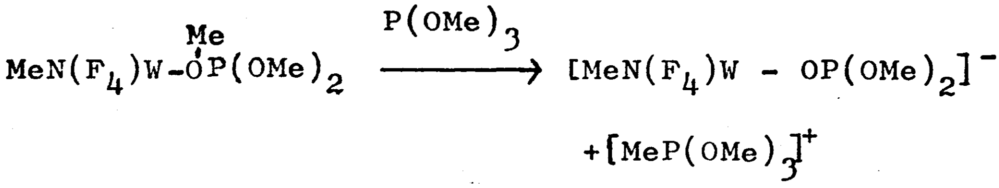
B can be a halogen or another electronegative group which leaves the R group with a slight positive charge. An example of a Michaelis - Arburzov rearrangement is the reaction of methoxytungsten (VI) pentafluoride with trimethylphosphite (48). The intermediate can be isolated in this case

$WF_5OMe + (MeO)_3P \longrightarrow MeP(OMe)_3^+ \; WOF_5^-$

$MeP(OMe)_3^+ \; WOF_5^- \xrightarrow{90^\circ C} MeF + WOF_4[(MeO)_2P(O)Me]$

If for the general reaction (A), $R^1 = R$, then the effect of RB will be to catalyze the conversion of $(RO)_3P$ to $(RO)_2P(O)R$. The conversion of $(MeO)_3P$ is also autocatalyzed by the product, $(MeO)_2P(O)Me$ (152).

A possible reason for the formation of $(MeO)_2P(O)Me$ in the reaction of $(MeO)_3P$ with $(WF_4NMe)_x$ is

(iv) 

$$MeN(F_4)W\text{-}\overset{Me}{O}P(OMe)_2 \xrightarrow{P(OMe)_3} [MeN(F_4)W - OP(OMe)_2]^- + [MeP(OMe)_3]^+$$

The methyltrimethoxyphosphonium ion, $MeP(OMe)_3^+$, can then catalyze the conversion of $(MeO)_3P$ to $(MeO)_2P(O)Me$.

$$\text{(v)}\quad (MeO)_3P + MeP(OMe)_3^+ \longrightarrow (MeO)_2P(O)Me + MeP(OMe)_3^+.$$

The complexes formed in reactions (i), (ii) and (iii) could undergo ligand exchange to give the corresponding dimethyl methylphosphonate complexes. The evidence is consistent with the formation of the dimethyl methylphosphonate complexes terminating the substitution reactions, since $WF_4NMe[(MeO)_2P(O)Me]$ does not react with excess $(MeO)_3P$. If reaction (iv) is slow but relatively temperature independent, whereas reactions (ii) and (iii) are more strongly temperature dependent then this would explain the differing products from reactions (a) and (b).

(VII) THE ALKYLIMIDOPENTAFLUOROTUNGSTATE (VI) ANIONS.

The alkylammonium alkylimidopentafluorotungstate (VI) salts are readily prepared by reacting the corresponding primary amine with an excess (2:1) of tungsten hexafluoride. Reaction takes place at ca. -30°C. The salts have been characterized by their analyses, i.r. spectra and n.m.r. spectra. A stoichiometry of 1:2 was found for the reaction;

$$WF_6 + 2MeNH_2 \longrightarrow MeNH_3^+ \; WF_5NMe^- + HF.$$

The consumption of two equivalents of methylamine in the presence of an excess of tungsten hexafluoride is indirect evidence for the following reaction scheme:

$$\text{(i)}\; WF_6 + MeNH_2 \xrightarrow{\text{fast}} WF_6(MeNH_2)$$

$$\text{(ii)}\; WF_6(MeNH_2) \xrightarrow{\text{slow}} WF_5NHMe + HF$$

$$\text{(iii)}\; WF_6(MeNH_2) + WF_5NHMe \longrightarrow MeNH_3^+ \; WF_5NMe^- + WF_6$$

The absence of methylammonium fluoride suggests that, under the present conditions, hydrogen fluoride does not react with the complex, $WF_6(MeNH_2)$. There is an excess of tungsten hexafluoride present and hence all the methylamine will be present in the complex, $WF_6(MeNH_2)$. Methylamidotungsten (VI) pentafluoride, WF_5NHMe, would be expected to be a very strong acid since the nitrogen is virtually devoid of all base activity (vide infra), and hence should be able to rapidly react with $WF_6(MeNH_2)$. The reactions of tungsten hexafluoride with both ethylamine and n-butylamine proceed in a similar manner to its reaction with methylamine to give ethylammonium ethylimido pentafluorotungstate (VI), $EtNH_3^+ \; WF_5NEt^-$, and n-butylammonium n-butylimidopentafluorotungstate (VI), $Bu^{n}NH_3^{+}WF_5NBu^{n-}$.

The reaction of tungsten hexafluoride with tert-butylamine proceeds in a different manner. The product is a 1:3 adduct which is insoluble in acetonitrile. Although tert-butylamine is reported to have a similar base strength to methylamine and ethylamine (153), the complex, $WF_6(Bu^{t} NH_2)$ could be destabilized for steric reasons, due to the size of the tert-butyl group. The following equilibrium would therefore lie significantly to the left:

$$WF_6 + Bu^{t}NH_2 \rightleftharpoons WF_6(Bu^{t}NH_2)$$

The tert-butylamine is thus available to react with hydrogen fluoride. This would result in the following reaction sequence:

$$\text{(i)} \quad WF_6 + Bu^{t}NH_2 \rightleftharpoons WF_6(Bu^{t}NH_2)$$

$$\text{(ii)} \quad WF_6(Bu^{t}NH_2) \xrightarrow{\text{slow}} WF_5NHBu^{t} + HF$$

$$\text{(iii)} \quad WF_5NHBu^{t} + Bu^{t}NH_2 \xrightarrow{\text{fast}} Bu^{t}NH_3^{+}\ WF_5N^{t}Bu^{-}$$

$$\text{(iv)} \quad HF + Bu^{t}NH_2 \xrightarrow{\text{fast}} Bu^{t}NH_3^{+} + F^{-}.$$

The ^1H n.m.r. spectrum of methylammonium methylimidopentafluorotungstate (VI) in deutero-acetonitrile shows peaks due to the methylammonium cation. Generally the cation signals are poorly resolved with only the methyl signals being observable. The ^1H n.m.r. spectra of the compounds, $EtNH_3^{+}\ WF_5NEt^{-}$ and $Bu^{n}NH_3^{+}\ WF_5NBu^{n-}$, similarly show poorly resolved peaks for their α-methylene protons. The absence of any signal due to the protons on the nitrogen, or, in some cases, an indication that they had collapsed to a broad singlet suggests that some exchange process is taking place.

The ^{1}H n.m.r. spectrum of the methylimidopentafluorotungstate (VI) anion has a broad peak in the same region as the methylimido peak in methylimidotungsten (VI) tetrafluoride complexes. No fine structure can be resolved, but $^{1}H-\{^{14}N\}$ decoupling does sharpen the peak and give information on relative signs of the coupling constants (see Section 13). A possible cause of this broadening is exchange of the trans fluorine, fast enough to affect the small $^{4}J(^{1}H - {}^{19}F_{trans})$ coupling, but not fast enough to affect the large $^{2}J(^{19}F_{cis} - {}^{19}F_{trans})$ coupling. For the ethylimidopentafluorotungstate (VI) anion the methylene group is a quartet, due to coupling with the methyl group protons. The components in this quartet are broad, but $^{1}H-\{^{14}N\}$ decoupling gives no sharpening of the peak. A similar situation is observed for the n-butylimidopentafluorotungstate (VI) anion.

The ^{19}F n.m.r. spectra of the anions, WF_5NMe^-, WF_5NEt^- and $WF_5NBu^{\underline{n}-}$, have all a doublet at 28 p.p.m. downfield from trichlorofluoromethane. In each case there is a much weaker complex signal at about 100 p.p.m. upfield from trichlorofluoromethane. For the anion, WF_5NMe^-, the association of these two peaks has been definitely established by $^{19}F-\{^{19}F\}$ homonuclear decoupling. The two peaks of WF_5NMe^- are shown in Figures 2:14 and 2:15. The doublet is assigned to the cis-fluorines, which are coupled to the lone trans-fluorine. The complex peak at high field is assigned to the trans-fluorine, which is coupled both to the four cis-fluorines and the ^{14}N nucleus.

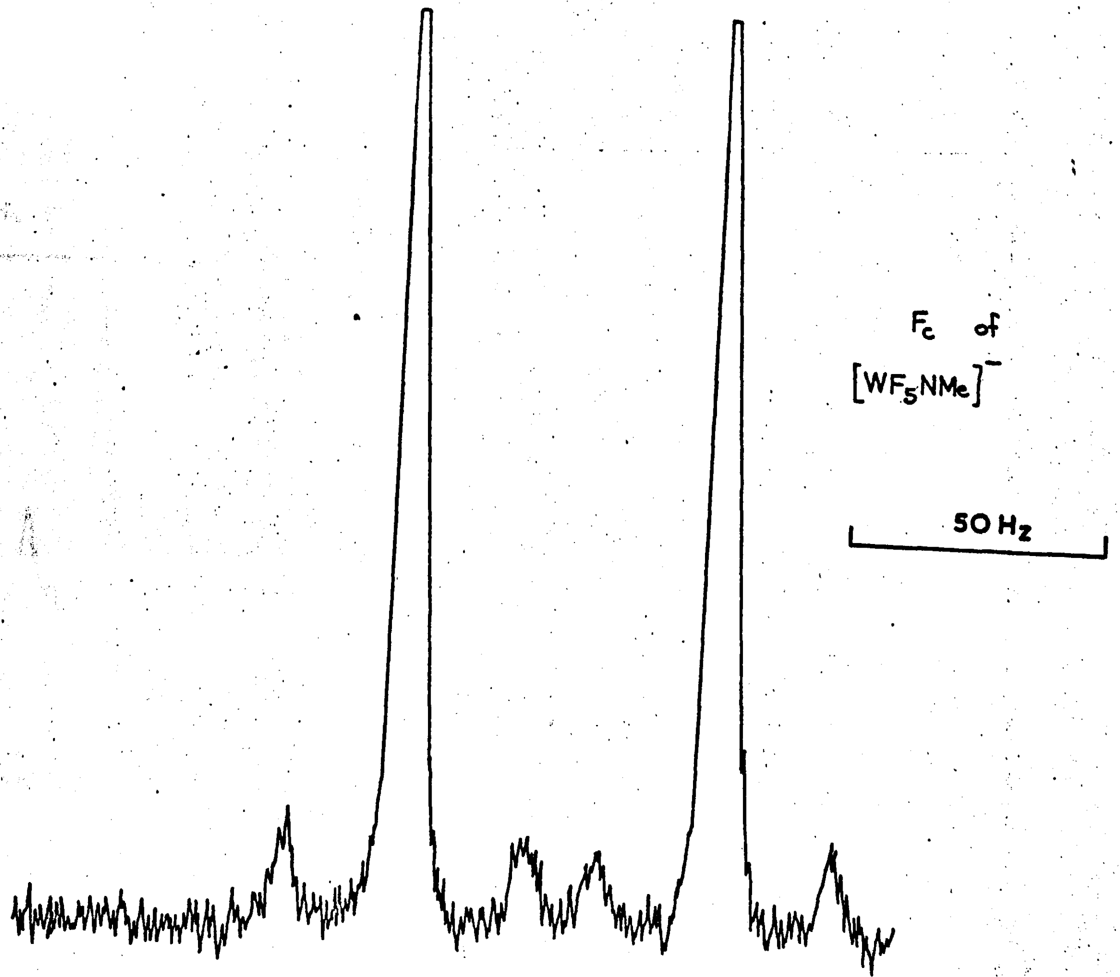


Figure 2:14

The ^{19}F n.m.r. spectrum of WF_5NMe^- showing the peak at $\delta^{19}F = 28.0$ p.p.m.; recorded at 56.45MHz.

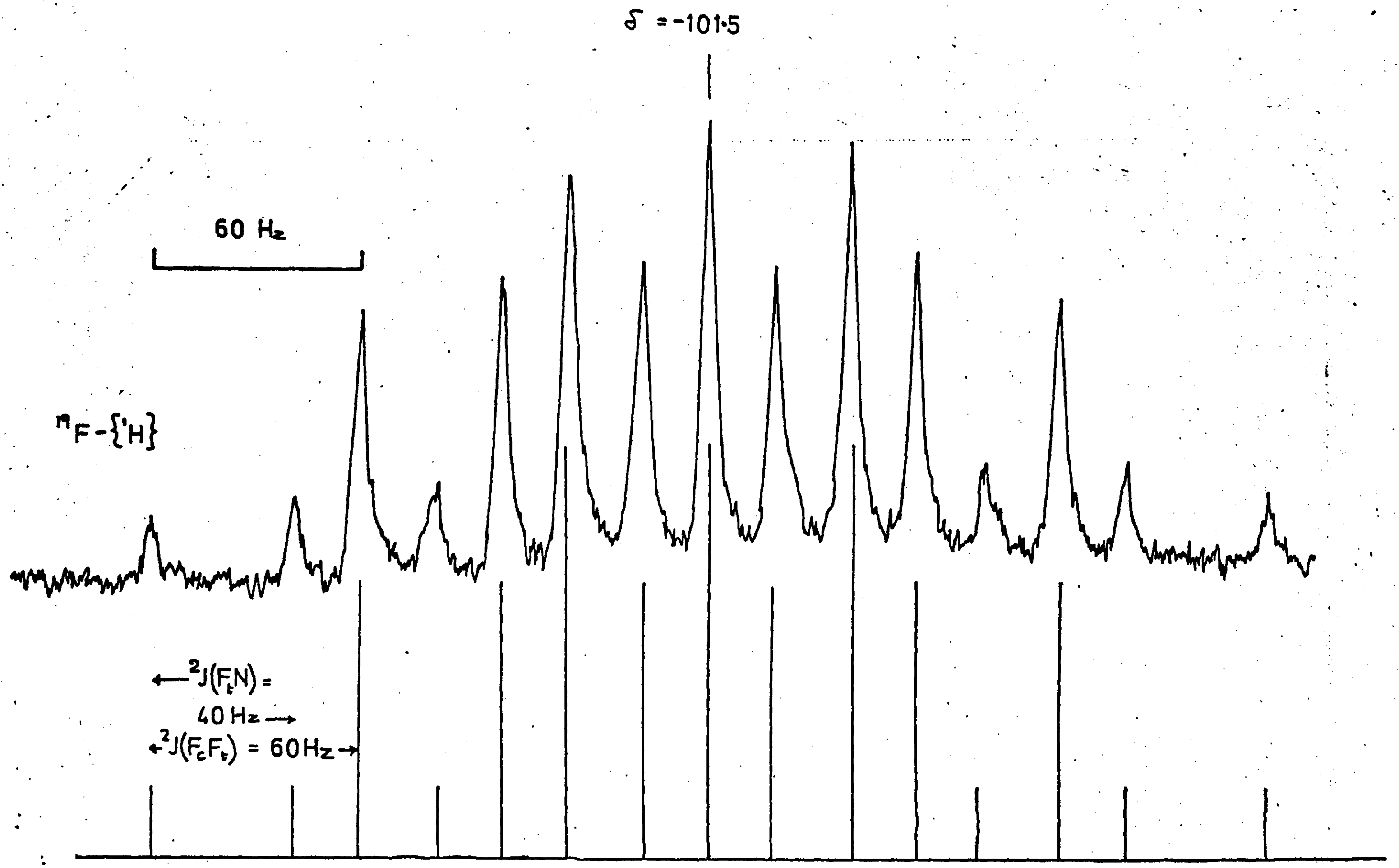


Figure 2:15(a)

The complex peak at $\delta^{19}F$ = -101.5 p.p.m., in the ^{19}F n.m.r. spectrum of WF_5NMe^-, recorded at 94.15 MHz.

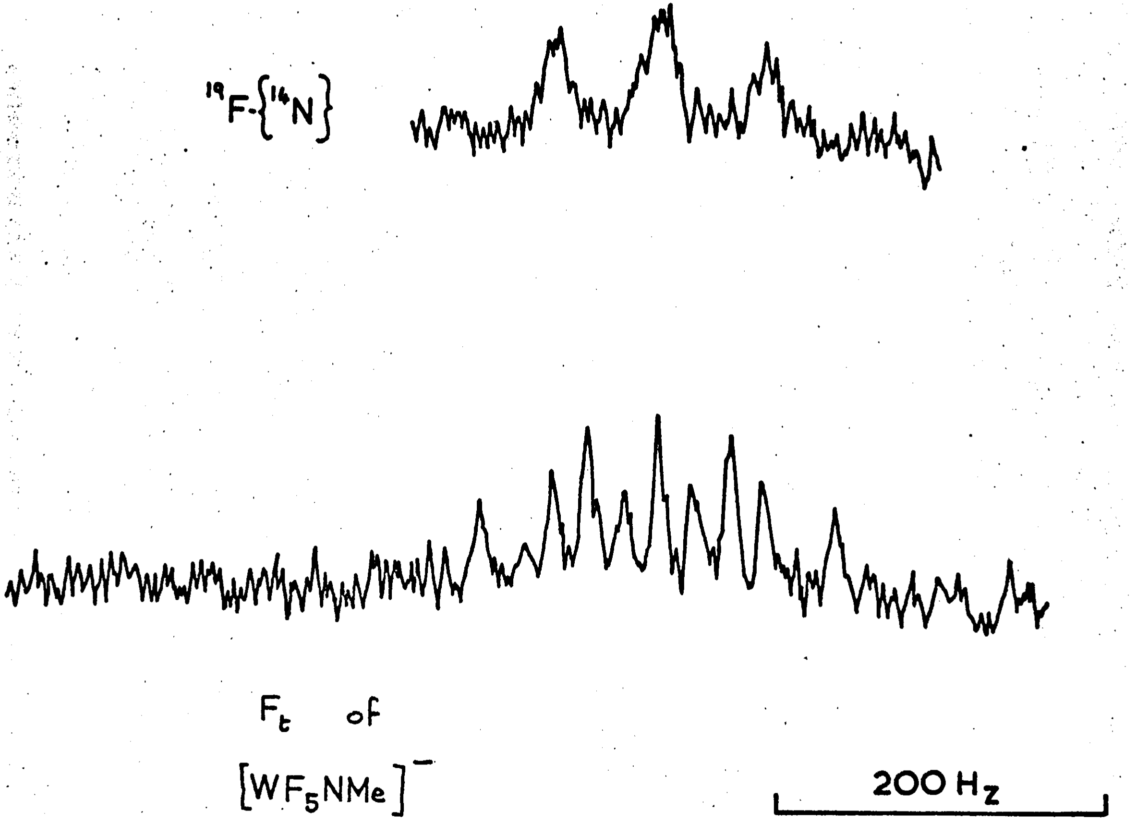
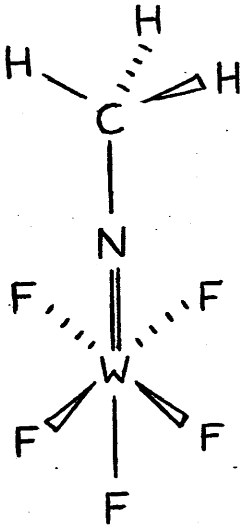


Figure 2:15(b)

The complex peak at $\delta^{19}F$ = -101.5 p.p.m. in the ^{19}F n.m.r. spectrum of WF_5NMe^-, recorded at 56.45MHz., and the $^{19}F - \{^{14}N\}$ spin decoupled spectrum.

$^{19}F - \{^{14}N\}$ Spin decoupling confirms the presence of the nitrogen coupling (Figure 2:15). For the anion, WF_5NEt^-, the multiplet is broad but the ^{14}N - ^{19}F spin coupling is still apparent (Figure 2:16), whereas for the anion, WF_5NBu^{n-}, the multiplet is a quintet in which the ^{14}N - ^{19}F coupling is not observed (Figure 2:17).

The ^1H and ^{19}F n.m.r. data are therefore consistent with the ionic compounds $RNH_3^+WF_5NR^-$ (R = Me, Et and Bu^n) being present in solution. For R = Me, the ^{19}F n.m.r. spectrum suggests that the (C - N - W) skeleton is nearly linear. The n.m.r. evidence is thus consistent with the structure:



The decreasing resolution in the ^{19}F - ^{14}N coupling in going from methyl to ethyl to n-butyl cannot be due directly to the asymmetry of the substituent, since the electric field gradient is a short range effect (see Section 4). A large field gradient could be introduced at the nitrogen atom, due to asymmetric bending modes of the (C - N - W) skeleton:

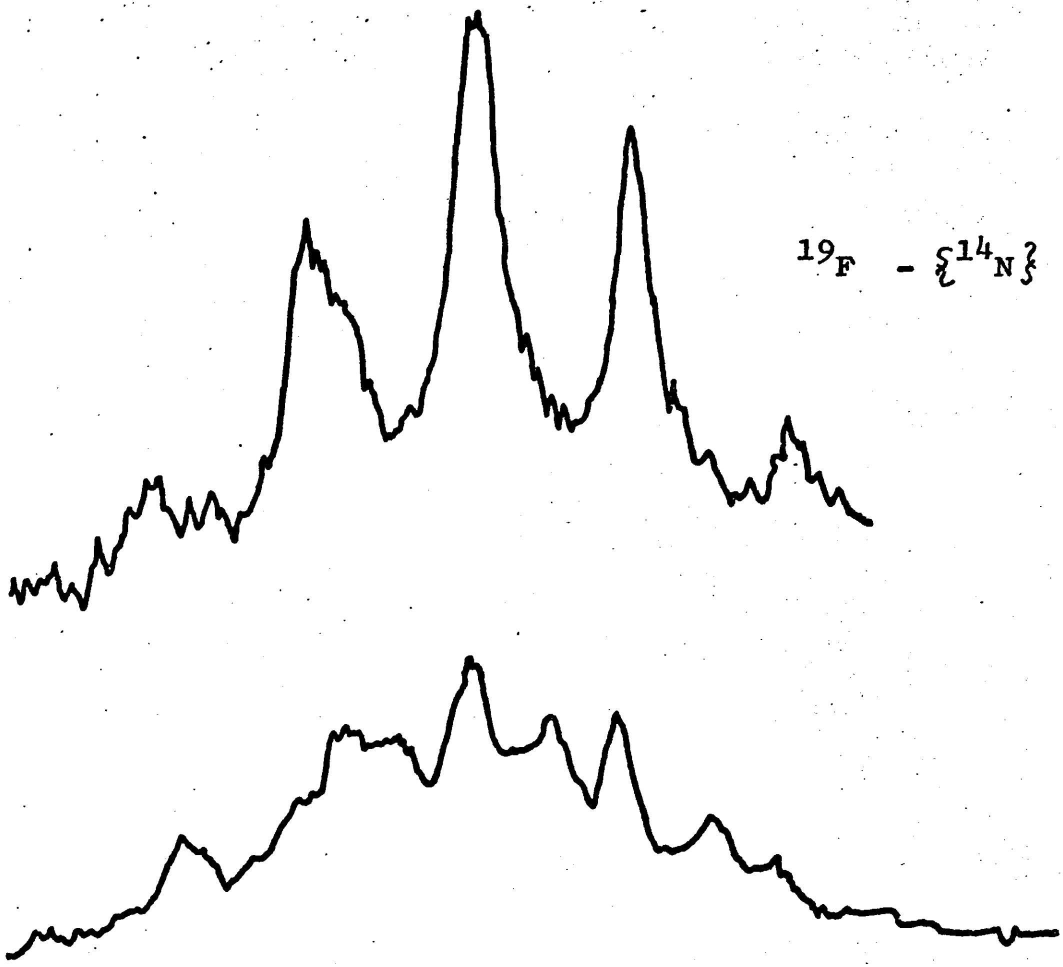


Figure 2:16

The complex peak at $\delta^{19}F$ = -99.5 p.p.m., in the ^{19}F n.m.r. spectrum of WF_5NEt^- and the effect of $^{19}F - \{^{14}N\}$ spin decoupling, recorded at 56.45MHz.

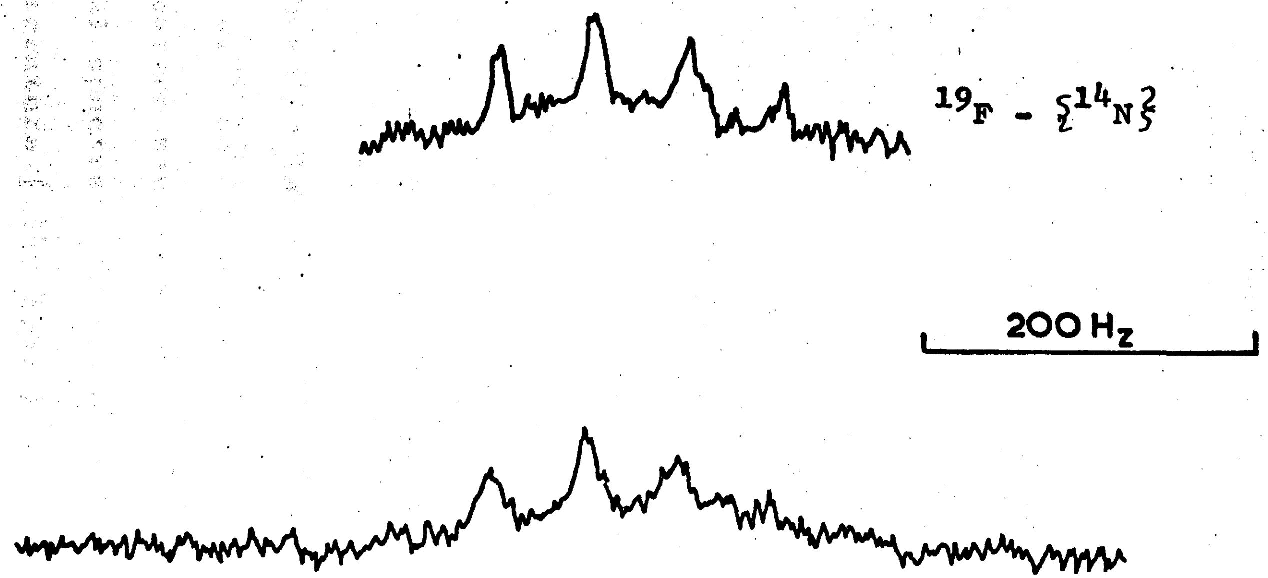
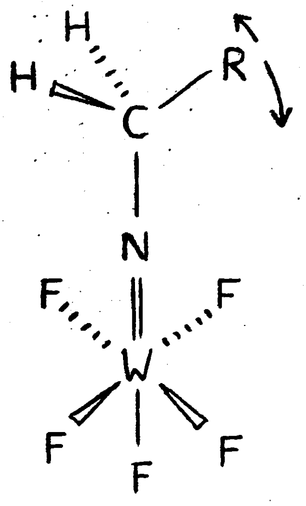


Figure 2:17

The complex peak at $\delta^{19}F = -101$ p.p.m. in the ^{19}F n.m.r. spectrum of WF_5NBu^{n-} and the effect of $^{19}F - \{^{14}N\}$ spin decoupling, recorded at 56.45MHz.



$R = CH_3, C_3H_7$

This results in the (C - N - W) skeleton being on average bent. The asymmetry of the n-butyl group is much greater than that for the ethyl group and thus the average bend greater. The asymmetric bend leads to the electric field gradient at the nitrogen nucleus being greater and the quadrupole relaxation time being shorter. An alternative explanation based on the differing inductive power of the alkyl groups is unlikely, since this difference is small.

The vibrational spectrum of methylammonium methylimidopentafluorotungstate has been extensively studied with the results shown in Table 2:10. The assignments made for the anion will be discussed later (see Section 10).

The cation bands are assigned on the basis of vibrational spectral studies of the methylammonium cation in the literature (154, 155, 156, 157, 158). The spectrum of the methylammonium cation is complex, since Fermi resonance enhances the intensity of many combination bands.

The bands of group A are assigned to both the (N - H) stretch and the first overtone of the (N - H) bend. These

TABLE 2:10

THE VIBRATIONAL SPECTRUM OF $MeNH_3^+$ WF_5NMe^-.

Raman solid (cm^{-1})	I.R. Mull (cm^{-1})	Assignment	Raman solution (cm^{-1})*
	3270 vs.	Cation	
	3185 vs.	Group A	
	3114 vs.	(N - H) stretch	
	2997 s		3004 mP
			2954 wP
	2930 s		2934 sP
	2880 s		
	2788 s	Cation	
	2750 m	Group B	
	2481 m		
	1676 m	Cation	
	1640 s	Group C	
	1617 s		
	1529 s	Cation	
	1520 s	Group D	
	1506 s	(N - H) bend	
	1462 s	Cation or anion	
	1426 m	(C - H) bend	
	1404 m		
1347 vs.	1332 vs.	anion (C-N=W) stretch	1350 vs. P
	1266 m	cation (NH_3) rock	
1111 m.b.r.			1116 mP
			1091 wP
			1052 wP
			1019 wP
	1000 s	cation	1008 wP
	954 vs.	Group E	
	950 vs.		

TABLE 2:10 (contd.)

Raman solid (cm^{-1})	I.R. Mull (cm^{-1})	Assignment	Raman solution (cm^{-1})*
	900w		
718 m	723 vs.	anion	734 wP
670 m			672 mP
			664 mP
630 m	651 vs.	anion	632 sP
625 m			
	586 vs.	anion	
	557 vs. sh	anion	
			547 mP
			508 wP
	481 s	anion	
434 w.br.	431 vs.	anion	439 wP

* Contains $W_2F_9(NMe)_2^-$ as an impurity.

The i.r. spectrum was scanned in the range 4000 - 350 cm^{-1} using Fluorolube and Nujol mulls between potassium bromide plates.

The Raman solid was scanned from 1400 cm^{-1} down, and the Raman solution from 3500 cm^{-1} down.

bands occur at higher frequency than in methylammonium fluoride, $MeNH_3^+F^-$ (157, 158) suggesting little or no hydrogen bonding. For example, in methylammonium fluoride the (N - H) stretching vibration occurs at less than $3135cm^{-1}$, whereas the corresponding fluoroborate salt, where little or no hydrogen bonding is expected, has two strong bands at $3282cm^{-1}$ and $3223cm^{-1}$ (158). The bands in the group B region are assigned to combination bands. These are seen in the i.r. spectra of methylammonium halides (154, 155, 156, 157, 158) though are only weak in the BF_4^- salt (158). The bands in groups C and D are assigned to (N - H) bend vibrations, along with combination bands. The peak at $1266cm^{-1}$ is assigned to an NH_3 rocking mode. This band appears in most $MeNH_3^+$ salts. The bands in group E are assigned to (C - N) stretching and to (CH_3) rocking modes.

The infra-red spectrum of the salt $EtNH_3^+ WF_5NEt^-$ is shown in Table 2:11. There is less published work on the $EtNH_3^+$ cation but a description of its halide salts has been published (156). Group A is assigned to the (N - H) stretching vibrations and, like the corresponding methylammonium derivative, the bands are at a high energy and suggest little or no hydrogen bonding. The bands in Groups C, D, E and F are all consistent with the $EtNH_3^+$ cation.

Table 2:12 shows the infra-red spectrum and assignments of the 3:1 Bu^tNH_2 : WF_6 complex. The i.r. spectra of $^tBuNH_3^+ Cl^-$ and $Bu^tNH_3^+ BCl_4^-$ have been published (158) and the spectra of $Bu^tNH_3^+ Cl^-$, BF_4^- and I^- above 1500 cm^{-1}

TABLE 2:11

THE INFRA-RED SPECTRUM OF $EtNH_3^+ WF_5NEt^-$

I.R. peaks (cm $^{-1}$)	Assignment	
3260s	Cation	(N-H)st Group A
3170s	Cation	
3000s		
2960s		
2861m	Cation	
2740w	"	
2618w	"	Group B Combinationbands
2505w	"	
2340w		Group C
1880w.br.		
1624s	Cation	Group D
1516s		
1476m		
1456m	Anion	
1436w	and Cation.	
1404m		
1376w		
1314vs.	Anion	
1222m	Cation (Group E)	NH_3 rock.
1195s		
1121w		
982m	Cation	Group F
898w		
880m		
805s		

TABLE 2:11 (contd.)

730m	anion
652vs.	anion
600vs.	anion
515m	anion

The 3,000 - 300 cm^{-1} region was scanned, using Fluorolube and Nujol mulls between potassium bromide plates.

TABLE 2:12

INFRA-RED SPECTRUM OF $Bu^{t}NH_2$:WF_6 3:1

Peak (cm^{-1})	Assignment	
3246 s 3180 s 3100 s	cation Group (A)	(N-H)st.
2980 vs. 2938 s 2892 m		
2800 m 2722 m 2602 m 2238 m 2140 s 2021 m	cation Group (B)	combination bands.
1618 s 1520 s	cation Group (C)	(N-H)
1480 m. br.		
1398 s 1362 s	cation or anion CC_3	stretching
1286 vs.	anion	
1221 s	cation NH_3	
962 w 909 w	cation	
735 m 725 m	anion	
651 vs.	anion	

TABLE 2: 12 (contd.)

Peak	Assignment
590v s. br.	anion
550 s br.	anion

The spectrum was recorded in the region 4,000 - 300 cm^{-1} using Nujol and Fluorolube mulls between KBr plates.

have been discussed (156). Bands of groups A, B and C are assigned as previously described for the $MeNH_3^+$ and $EtNH_3^+$ cations. Group D is assigned to stretching vibrations associated with the CC_3 skeleton. In the published spectra there is a third strong band at 1298 and 1291 cm^{-1} respectively, which is presumably obscured by the very strong band at 1286 cm^{-1}.

VIII. THE CHEMICAL PROPERTIES OF THE ALKYLAMMONIUM ALKYLIMIDOPENTAFLUOROTUNGSTATE (VI) COMPOUNDS.

The salts, $MeNH_3^+ WF_5NMe^-$ and $EtNH_3^+ WF_5NEt^-$, are hygroscopic and are slowly hydrolyzed in the moist atmosphere. The adduct, WF_6, $3Bu^tNH_2$, is non-hygroscopic and undergoes no apparent change, but the i.r. spectrum of a sample of the adduct which had been exposed to the atmosphere for several days demonstrated that some hydrolysis had taken place. The peaks assigned to (W - F) stretching modes had decreased in intensity, whereas two new intense peaks had appeared at 944 and 872 cm^{-1}. This suggests that a cis-dioxo complex had formed. For example, the salt $K_2WO_2F_4$, H_2O has two intense peaks in its i.r. spectrum at 959 and 901 cm^{-1}, which were assigned to the cis-(WO_2) symmetric and asymmetric stretching modes respectively (159). Another possibility is the formation of the mixed anion, $WF_4O(NBu^t)^{2-}$. The resistance of the initial adduct, WF_6, $3Bu^tNH_2$, to hydrolysis is demonstrated by the presence of non-hydrolyzed material even after several days exposure to the atmosphere.

If the nitrogen atom in the anions, WF_5NR^-, has some basic properties, then it should be possible to prepare the dialkylamino complexes, WF_5NR_2, from its reaction with a powerful alkyl cation donor. An attempt was made to prepare dimethylamidotungsten (VI) pentafluoride, WF_5NMe_2, by reacting the methylimidopentafluorotungstate (VI) anion, WF_5NMe^-, with methyl fluorosulphate. Methyl fluorosulphate is a very powerful methyl cation donor (160). If the nitrogen atom has some basic character then the following reaction might be expected:

(a) $MeNH_3^+ \; WF_5NMe^- + MeOSO_2F$

$$\longrightarrow MeNH_3^+ \; SO_3F^- + WF_5NMe_2$$

There is no apparent reaction at room temperature. At 90°C the mixture turns green and methyl fluoride is formed. (Methyl fluorosulphate heated to 90°C on its own does not evolve methyl fluoride). This suggests an alternative reaction to the above in which the methyl fluorosulphate is interacting with the trans-fluorine:

(b) $WF_5NMe^- + MeOSO_2F \longrightarrow WF_4NMe(SO_3F)^- + MeF$.

Unfortunately due to lack of time it was not possible to investigate this reaction further.

The presence of methyl fluoride suggests that reaction (b) is much more likely than reaction (a) and that the nitrogen atom in the anion has no basic properties. This is consistent with the nitrogen lone pair electrons interacting strongly with the vacant d-orbitals on the tungsten. The present work implies that it should be possible for the compounds, WF_5NR_2, to behave as alkyl cation donors. The related compound, WF_5OMe, can act in this way (48), for example WF_5OMe reacts with $(MeO)_3P$ to give $(MeO)_3\,PMe^+$ WOF_5^- and with $(MeO)_2SO$ to give a complex mixture of products including WOF_5^- and $W_2O_2F_9^-$. The preparation of diethylamidotungsten (VI) pentafluoride, WF_5NEt_2, has been reported and a brief account has appeared of its reaction with $(MeO)_2SO$ (55, 161). The ^{19}F n.m.r. spectrum of the reaction mixture obtained on mixing $(MeO)_2SO$ and WF_5NEt_2 shows three complex peaks at $\delta^{19}F$ = 61.3, 51.0 and 34.9 p.p.m. These peaks were previously assigned to the complex $WF_4(NEt_2)(OMe)$. (161). The first two peaks are however in the region expected for tungsten oxide tetrafluoride complexes and are better assigned to these species. The peak at $\delta^{19}F$ = 34.9 p.p.m. is very close to the position found for the dimeric anion, $W_2F_9(NMe)_2^-$ (vide infra). A better assignment for this peak is therefore the dimer, $W_2F_9(NEt)_2^-$ or the mixed dimer, $EtNW(F_4)F(F_4)WO^-$. The i.r. spectrum of the reaction has also been described and a strong band reported at 1312 cm^{-1} (161). A conclusion of the present work is that this band is characteristic of the group, $EtN = W$ (see Section 10). The reaction is variable and an ^{19}F n.m.r. study of another reaction mixture has shown no peaks in the $\delta^{19}F$ = 30 - 40 p.p.m. range, and only a weak peak in the i.r. spectrum at 1315 cm^{-1}. The previous work on diethylamidotungsten (VI) pentafluoride is consistent with it acting as an ethyl cation donor.

The chemical properties of the anions, WF_5NR^-, are consistent with the lone pair electrons on the nitrogen having been fed into the vacant d-orbitals on the tungsten. This in turn is consistent with the n.m.r. evidence which suggests a linear, or near linear, (W-N-C) skeleton.

(IX) THE REACTION OF TUNGSTEN HEXAFLUORIDE WITH METHYL (TRIMETHYLSILYL) AMINE.

(a) Introduction.

If an excess (2:1 molar) of tungsten hexafluoride is condensed on to methyl (trimethylsilyl) amine in the presence of a large excess (8:1 molar) of trichlorofluoromethane and the mixture is allowed to warm slowly to room temperature, a reaction takes place to form a solid product, insoluble in CCl_3F, and trimethylsilyl fluoride. The colour of the solid product varies from white to pale - green, and this variation is reflected in the analysis results (see Section XIII). The solid products are completely soluble in acetonitrile, and the ^1H and ^{19}F n.m.r. spectra of these solutions show that they consist of mixtures of the methylammonium salts of the anions, WF_5NMe^- and $W_2F_9(NMe)_2^-$, in varying relative amounts.

(b) The identification of the μ-fluorobis (methylimidotetrafluorotungstate) (VI) anion , $W_2F_9(NMe)_2^-$.

The identification of the μ -fluorobis (methylimidotetrafluorotungstate) (VI) anion is based on the ^{19}F n.m.r. spectra. A typical ^{19}F n.m.r. spectrum of a solution of the solid product in deutero - acetonitrile is shown in the range $\delta^{19}F$ = 25 - 40 p.p.m. in Figure 2:18. This shows the doublet previously assigned to the cis - fluorines of the WF_5NMe^- anion at $\delta^{19}F$ = 28.0 p.p.m., and a further doublet at $\delta^{19}F$ = 35.7 p.p.m. By analogy with the $W_2O_2F_9^-/WOF_5^-$ system it was felt likely that this doublet belonged to the cis - fluorines of the dimeric anion, $W_2F_9(NMe)^-_2$. $^{19}F-\{^{19}F\}$ Spin decoupling demonstrates

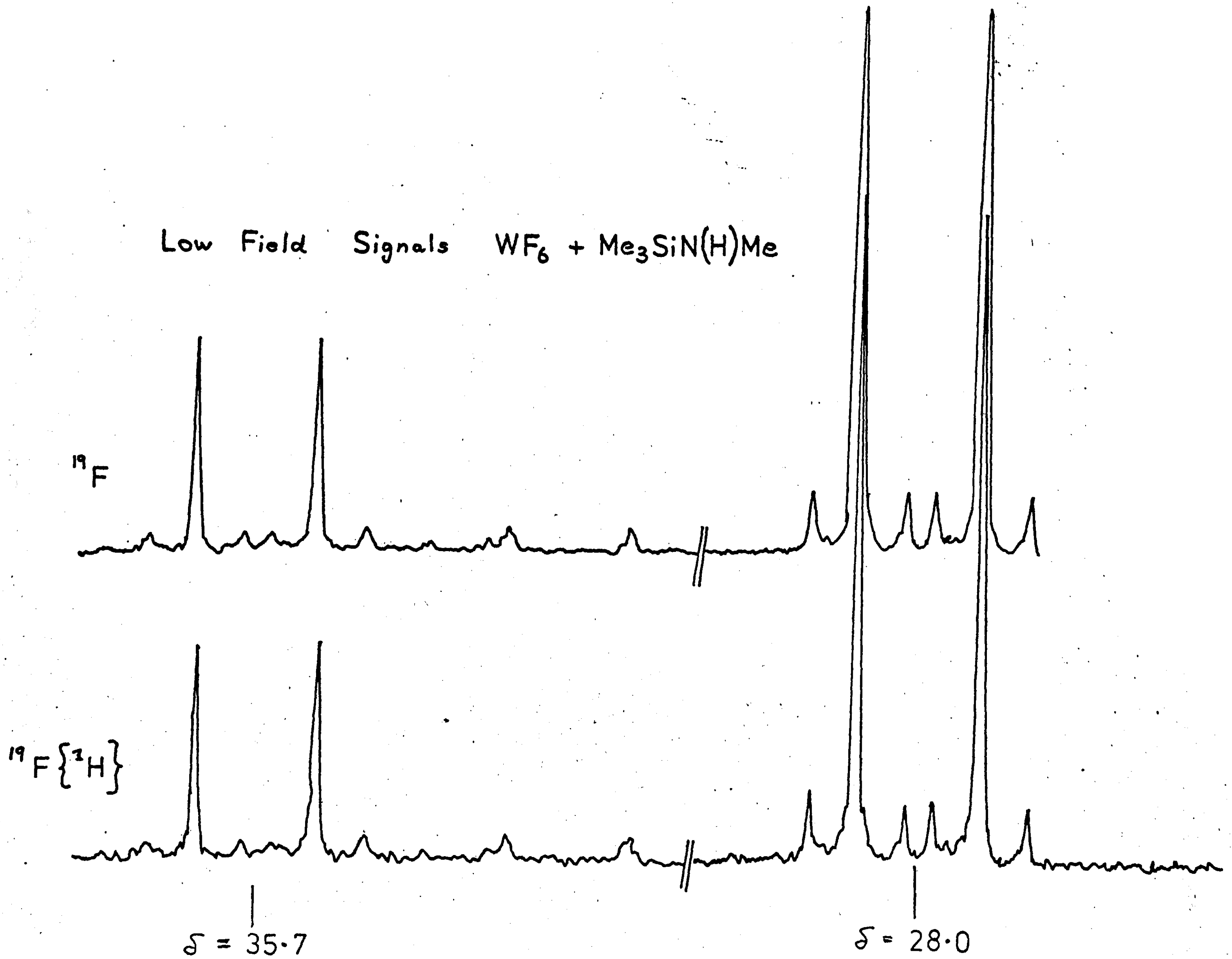


Figure 2:18

The ^{19}F n.m.r. spectrum of the reaction product from WF_6 + $Me_3SiN(H)Me$ dissolved in CD_3CN and the effect of $^{19}F - \{^1H\}$ spin decoupling, recorded at 94.15 MHz.

that the low field doublet is coupled to a fluorine which resonates at $\delta^{19}F = -127.4$ p.p.m. A very complex signal is observed at this position and this is shown in Figure 2:19. If this is the bridging fluorine of the dimeric anion, then it should be coupled to eight equivalent fluorines and two equivalent nitrogens producing a 45 line spectrum. The peak seperations in the signal are consistent with $^{2}J(^{19}F_c - ^{19}F_t) = 60$Hz and $^{2}J(^{14}N - ^{19}F)$ = 26 or 34Hz. The line diagrams in Figure 2:19 show the expected spectra if the fluorine is coupled to eight equivalent fluorines, $^{2}J(^{19}F_c - ^{19}F_t) = 60$Hz and two equivalent nitrogens, $^{2}J(^{14}N - ^{19}F_t) = 26$Hz (b) or 34Hz (c). The intensity relationships show a very good fit for $^{2}J(^{14}N - ^{19}F_t) = 34$Hz.

The observance of $^{2}J(^{14}N - ^{19}F_t)$ coupling suggests that the anion possesses a linear, or near linear, (C - N = W - F - W = N - C) skeleton (Figure 2:20).

(c) Possible reaction pathways.

The solid product formed has a differing composition from reaction to reaction as is shown by both analytical and n.m.r. results. This suggests that several competing reactions are taking place. Initially an equilibrium should be established.

$$WF_6 + Me_3SiNHMe \rightleftharpoons WF_6, Me_3SiN(H)Me.$$

The presence of the trimethylsilyl group should lower the basicity of the nitrogen, in addition its bulk will hinder the formation of the 1:1 complex. The equilibrium will therefore be expected to be well to the left, and there should be significant quantities of free

Figure 2:19
The ^{19}F n.m.r. spectrum of the bridging fluorine in the anion $W_2F_9(NMe)^-$, and theoretical line diagrams.

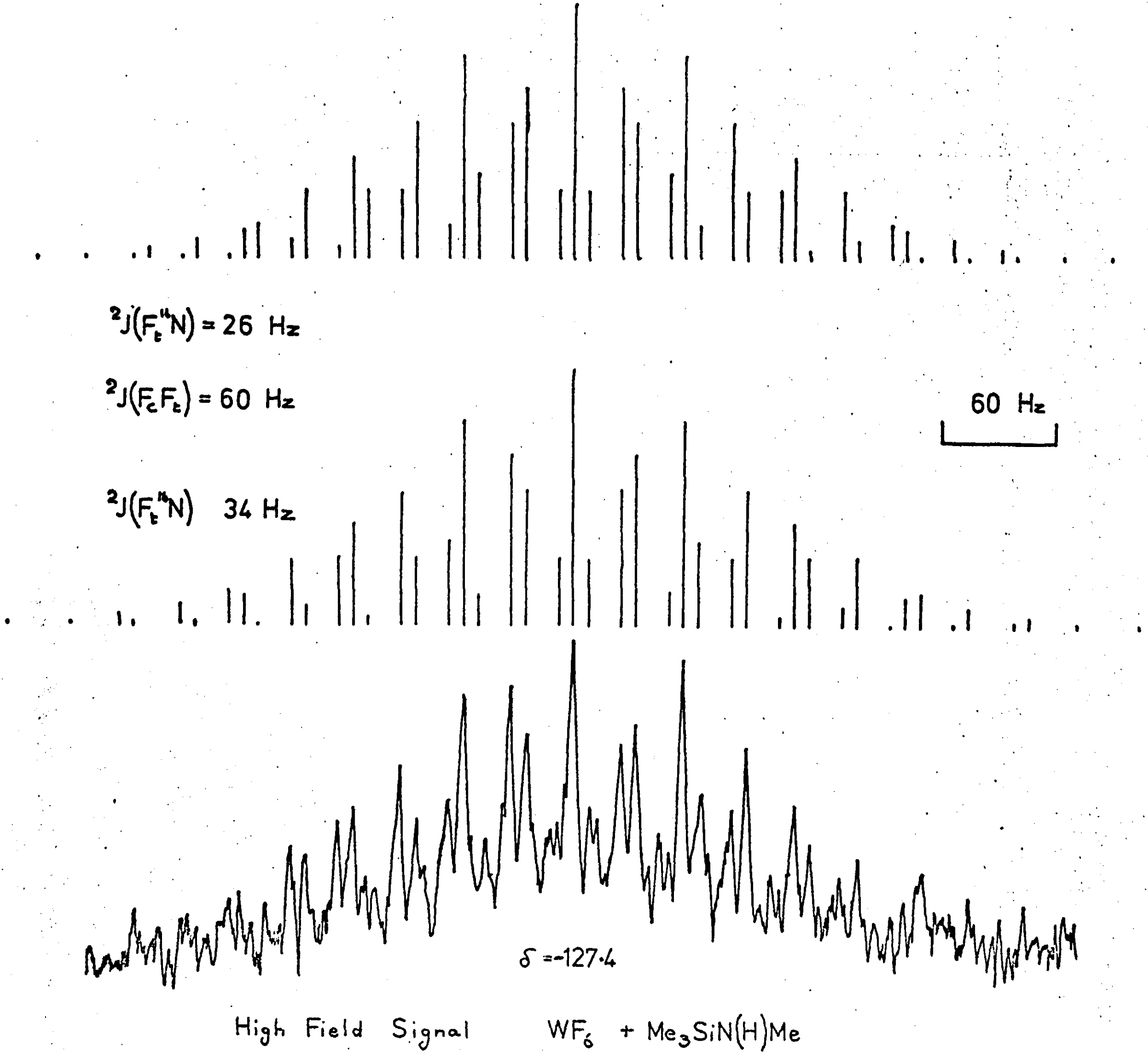
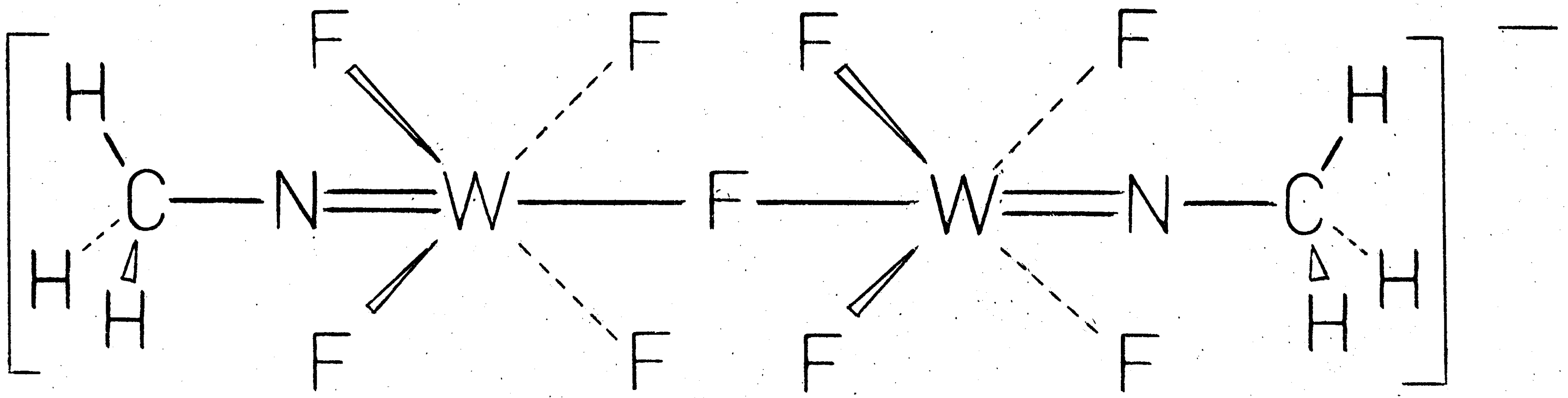


Figure 2:20

The structure of the $W_2F_9(NMe)_2^-$ Anion.



$Me_3SiN(H)Me$ present.

There are two possible ways in which further reaction can take place:

(A) $WF_6, NH(Me)SiMe_3 \longrightarrow WF_5NMe(SiMe_3) + HF$

(B) $WF_6, NH(Me)SiMe_3 \longrightarrow WF_5NMe(H) + Me_3SiF$.

If reaction (A) takes place then the following further reactions could occur:

(i) $WF_5N(SiMe_3)Me \xrightarrow{\text{fast}} WF_4NMe + Me_3SiF$

(ii) $HF + Me_3SiNHMe \xrightarrow{\text{fast}} MeNH_2 + Me_3SiF$

(iii) $WF_6 + MeNH_2 \xrightarrow{\text{fast}} WF_6(NH_2Me)$

(iv) $WF_6(NH_2Me) \xrightarrow{\text{slow}} WF_5N(H)Me + HF$

(v) $WF_6(NH_2Me) + WF_5N(H)Me \xrightarrow{\text{fast}} MeNH_3^+ + WF_5NMe^- + WF_6$

(vi) $WF_4NMe + MeNH_3^+ + WF_5NMe^- \longrightarrow MeNH_3^+W_2F_9(NMe)_2^-$.

Reaction (i) will be fast since the silicon atom in the trimethylsilyl group is a very strong acceptor centre. Reactions (iii), (iv) and (v) have been previously discussed (see Section VII).

The previous work on the $(Me_3Si)_2NH/WF_6$ system suggests that (B) is favoured, but not exclusively. If reaction (A) is autocatalyzed by hydrogen fluoride, then this would provide a possible explanation for the observed products.

(X) THE VIBRATIONAL SPECTRA OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE COMPLEXES.

(a) Introduction.

In compounds derived from the group, WF_4X(X = O, NH, NMe, NEt and $NBu^{\underline{t}}$), prepared in this work, the highest symmetry possible is C_{4v}. This can be lowered, either from the lower symmetry of the ligand or the alkyl substituent. Furthermore, in the solid state compound site asymmetry due to the crystal structure can lower the symmetry further. Tungsten (VI) chloride pentafluoride, WF_5Cl, has been chosen as a model for the assignment of the vibrational spectra of WF_4X compounds. The vibrational spectrum of WF_5Cl has been investigated using gas i.r. spectrometry as well as i.r. investigations of the solid and Raman studies of the liquid (162). The results obtained for WF_5Cl are shown in Table 2:13. Tungsten (VI) chloride pentafluoride is C_{4v} in the gas and liquid states. The splitting of an E band and the appearance of a formally i.r. inactive B_1 band in the i.r. spectrum of the solid is ascribed to lower site symmetry in the solid. Tungsten hexafluoride has site symmetry C_1 in the solid state (163), and a similar packing arrangement would give an even lower site symmetry for WF_5Cl.

(b) Tungsten (VI) oxide tetrafluoride complexes.

Although the structure of the tetramer $(WOF_4)_4$, has been extensively investigated (105, 106, 107, 108), little work has been reported on the structure of the donor ligand complexes of tungsten (VI) oxide tetrafluoride complexes. The crystal structure of the 1:1 tungsten (VI) oxide

TABLE 2:13

VIBRATIONAL ASSIGNMENTS FOR WF_5Cl

(After Adams, Fraser, Morris and Peacock) (162).

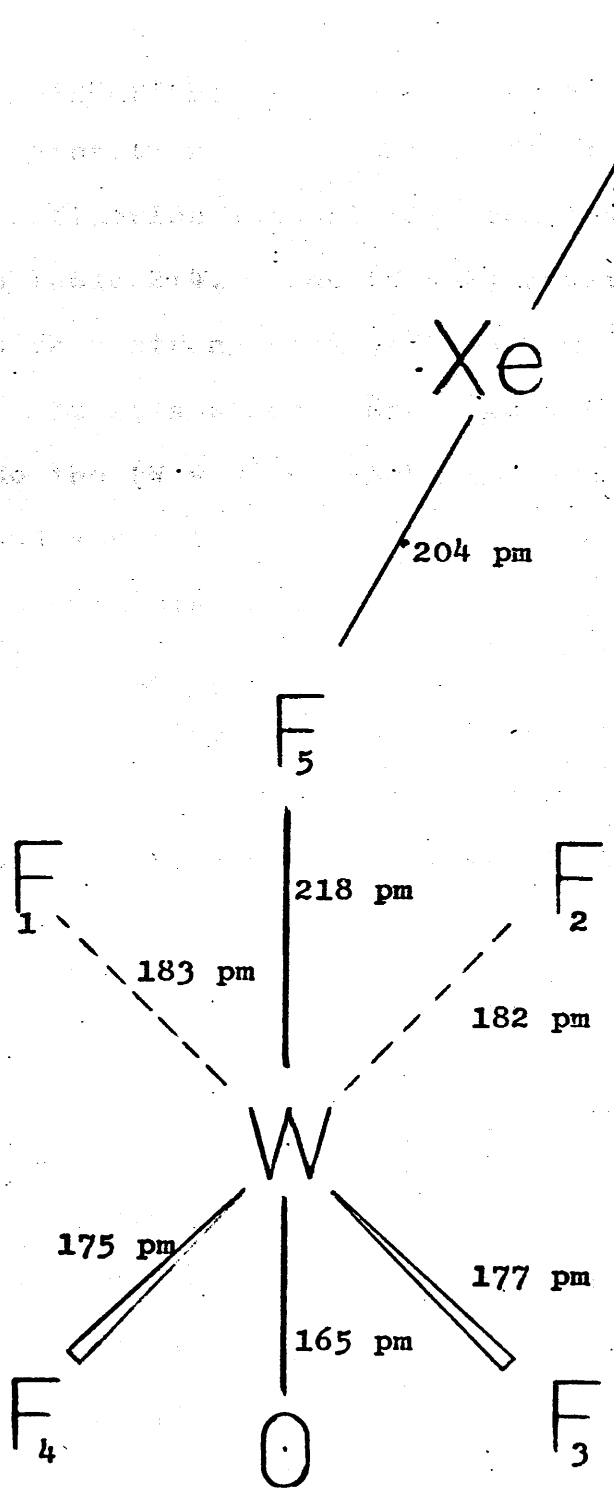
Class	Assignment and Description	Raman	I.R. (solid)
A_1	v_1(W-Cl)	407sP	390s
(I.R. and Raman active)	v_2Vsym(WF_4)	744vs.P	743vs.
	v_3 v(WF_t)	703mP.	704m
	v_4 (WF_4)	257w	243m
B_1			
(Raman only)	v_5 v(WF_4 out of plane)	644w	640s
	v_6 (WF_4)	182w	
B_2 (Raman only)	v_7 (WF_2)	377mD	
E (I.R. and Raman active)	v_8 Vas(WF_4)	661mD	667,655s
	v_9 (WF_4 wag)	307mD	
	v_{10} (WF_4 rock)	290w	
	v_{11} (WF_4 in plane bend)	227w	

tetrafluoride xenon difluoride complex, $WOF_4(XeF_2)$ has been determined from X-ray diffraction studies (164), and is illustrated in Figure 2:21. The tungsten atom and the four cis fluorines are not in the same plane, the cis-fluorines being bent towards the bridging fluorine. The structure is consistent with the ^{19}F n.m.r. evidence for tungsten oxide tetrafluoride complexes in solution (48, 49, 94, 95, 103, 104, 109), which indicate that the complexes are monomeric and that the four fluorines are cis to the oxygen atom. The very short length of the (W = O) bond and the repulsive effect it has on the cis-fluorines are consistent with a high bond order.

In the tungsten (VI) oxide tetrafluoride tetramer a strong broad band is observed in the i.r. spectrum at 1,054 cm^{-1} (105, 108). If the ^{18}O enriched tetramer is studied then this band is considerably weakened and a new band is observed at 997 cm^{-1} (108). The band at 1,054 cm^{-1} is thus assigned to the (W = O) stretching mode. The assignments for the (W-F) stretching modes of the 1:1 tungsten (VI) oxide tetrafluoride acetonitrile complex, $WOF_4(MeCN)$, are made on the basis of the assignments for WF_5Cl and are shown in table 2:1. A significant feature of this spectrum is that the (W = O) stretching vibration is about 20 cm^{-1} lower in energy compared with the tetramer. A similar effect is observed in the 1:1 tungsten (VI) oxide tetrafluoride dimethyl ether complex, $WOF_4(Me_2O)$, where the (W = O) stretching vibration occurs at 1,025 cm^{-1} (49). The (W-F) stretching vibrations are also of a lower energy compared with the tetramer. This latter effect

Figure 2:21

The Crystal Structure from X-ray diffraction of WOF_4, XeF_2; after Tucker, Taylor and Holloway (164).



has previously been observed between the tetrameric pentafluorides of niobium and tantalum and their monomeric, 1:1 acetonitrile complexes (165). The tungsten (VI) oxide tetrafluoride acetonitrile complex shows no bands assignable to bridging fluorines.

(c) Imidotungsten (VI) tetrafluoride complexes.

The vibrational assignments for the 1:1 imidotungsten (VI) tetrafluoride acetonitrile complex, $WF_4NH(MeCN)$, are shown in Table 2:4. The (W = N) stretching vibration is assigned to a strong peak at 1,060 cm^{-1} for the following reason. It is a strong, broad band occurring in a similar region to the (W = O) stretching vibration. The comparative bond strengths of the tungsten-oxygen and tungsten-nitrogen multiple bonds can be compared in a semi-quantitative way. This is because most of the movement of the (W = X) vibration will be concentrated in the light X atom or group. This means that the frequency of vibration will be given approximately by the simple diatomic formula:

$$v = (k/4\pi^2 c^2 m_x)^{\frac{1}{2}} \quad \text{———} \quad (1)$$

where k = force constant, c = speed of light and

m_x = mass of X atom (166).

If the mass of X is changed and the force constant is unchanged then the frequency should vary according to the expression below:-

$$v_2 = v_1(m_{x1}/m_{x2})^{\frac{1}{2}} \quad \text{———} \quad (2)$$

If in $(WOF_4)_4$ an ^{18}O atom is substituted for ^{16}O then a drop in frequency is predicted from 1,054 cm^{-1} to 994 cm^{-1}. This compares with the observed frequency in $(W\ ^{18}OF_4)_4$ of 997 cm^{-1}.

The imido group, NH, is more complex since it is not a single point mass, but because the (N-H) stretching vibration is well removed from the region expected for the (W = N) stretching vibration, it is a feasible approximation to treat the NH group as a single point mass. If the $(W = ^{16}O)$ stretching vibration is taken as 1,026 cm^{-1}, then equation (2) predicts that, assuming the same force constant, a mass of 15 a.m.u. should vibrate at 1,060 cm^{-1}. This is remarkably close to the experimental value, and supports the assumption of the near equality of the force constants of the (W = O) and (W = N) bonds.

The i.r. spectrum of the solid believed to be impure methylimidotungsten (VI) tetrafluoride, WF_4NH, is shown in Table 2:14. There are two strong bands at 1,177 cm^{-1} and 1,094 cm^{-1}. The latter band is in the region where the (W = N) stretching vibration is expected. It is 30 cm^{-1} higher in energy than the (W = N) stretching vibration for the acetonitrile complex, $WF_4NH(MeCN)$, similar to the difference observed between the (W = O) stretching vibrations in $(WOF_4)_4$ and $WOF_4(MeCN)$. Equation (2) predicts, on the basis of a (W = O) stretching vibration at 1,054 cm^{-1}, that the (W = N) stretching vibration for the compound should occur at 1,089 cm^{-1}. This is very close to the experimental value. A possible assignment for the band at 1,117 cm^{-1} is as a vibration associated with the (W-N-Si) skeleton of the compound, trimethylsilylimidotungsten (VI) tetrafluoride, as it is intermediate in energy

TABLE 2:14

THE i.r. SPECTRUM OF METHYLIMIDOTUNGSTEN (VI) TETRAFLUORIDE, WF_4NH.

Peak (cm^{-1})	Intensity	Assignment
3260	vs	(W-H)st.
2959	s	(C-H)st. *
2922	s	(C-H) st. *
2858	m	
1426	vs	(C-H) bend
1349	m	
1256	s	(Me_3Si -) *
1177	s,br	(W = N-Si)st.*
1094	ms,br	(W = N)st.
855	s, br	(Me_3Si -) *
764	s	
724	m	(W = N-Si)st.*
668	s	(W-F)st.
605	s,br	(W-F-W)st.

* (Assigned to the complex, WF_4NSiMe_3) (see Section 4)

+ (Other peaks are observed, but these are not reproducible).

between the (W = N) stretching vibration of the (W = N-H) skeleton, and vibrations associated with the (W = N-C) skeleton (vide infra). It has already been suggested that trimethylsilylimidotungsten (VI) tetrafluoride, WF_4NSiMe_3, is present as an impurity (see Section 4).

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

(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} (165).

The i.r. spectrum of impure methylimido-tungsten (VI) tetrafluoride shows a strong peak in the tungsten - terminal - fluorine stretching region, and a strong peak in the tungsten - bridging - fluorine region. This suggests that it has a polymeric structure similar to tungsten (VI) oxide tetrafluoride. This evidence is not definitive, however, since trimethylsilylimidotungsten (VI) tetrafluoride is present, and is also likely to possess a polymeric fluorine bridged structure.

(d) Alkylimidotungsten (VI) tetrafluoride complexes.

A collation of i.r. data on alkylimidotungsten (VI) fluorides is shown in Table 2:15. The peaks previously assigned to the ligands or the cations have already been discussed and are omitted. The assignments for (W-F) stretching vibrations are discussed first. The bands in group 3 are assigned to the symmetric (W-F) stretching

TABLE 2:15

A COLLATION OF I.R. DATA ON IMIDO AND ALKYLIMIDO TUNGSTEN (VI) FLUORIDES.

Band	WF_4NMe (cm^{-1})	$WF_4NMe[(MeO)_2SO]$ (cm^{-1})	$WF_4NMe(MeCN)$ (cm^{-1})	WF_5NMe^- (cm^{-1})	WF_5NEt^- (cm^{-1})	$WF_5N^tBu^-$ (cm^{-1})	$WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$ (cm^{-1})
1	1331s	1332s	1330s	1333s	1314s	1286vs	1330s
2	721s			723vs	730m	721m	731m
3	681vs	663s	660m	651vs	652vs	651vs	611s,sh
4	631vs, br.	601 vs,br.	585 vs,br.	586 vs,br. 557	600vs	590 vs,br. 550	556 vs, br. 512 vs, br.
5	505vs, br.						
6		505s			515m		
7			480w	481s 431vs.			

mode of the equatorial fluorines. As has been previously observed between $(WOF_4)_4$ and $WOF_4(MeCN)$, in passing from the tetramer to the donor ligand complex there is a loss in the energy of the (W-F) stretching vibrations. The broad, strong vibrations of group 4 are assigned to the asymmetric (W-F) stretching modes of the equatorial fluorines. These are doubly degenerate for C_{4v} symmetry. For methylimidomethoxytungsten (VI) trifluoride dimethyl methylphosphonate, $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$, two well separated bands are observed in this region. A band is observed at 505 cm^{-1} in the i.r. spectrum of methylimidotungsten (VI) tetrafluoride. This is assigned to the (W-F) stretching vibrations of bridging fluorines, and suggests that the compound is polymeric (see part (e)). The bands of group 6 are assigned to a (WF_4) out of phase stretching mode. For C_{4v} symmetry it is inactive, but, as Table 2:13 shows, it has been observed previously in solid WF_5Cl. The bands in group 7 could not be assigned. The (W-F) stretch of the axial fluorine does not appear to be observed. This is probably because it occurs in the same region as the intense (WF_4) asymmetric stretch.

Groups 1 and 2 are assigned to stretching modes associated with the (C - N = W) skeleton. In this system strong coupling is possible between the (C-N) stretching modes and the (W = N) stretching modes. This would result in the vibrations present being characteristic of the group as a whole and not of individual parts of it. This type of coupling has been fully discussed (166), and there are four requirements: (i) close proximity of the vibrating atoms, (ii) strong forces between the vibrating groups, (iii) approximate equality of the group frequencies and (iv) identical symmetry of the group vibrations. Requirements (i), (ii) and (iv) are clearly met, but requirement (iii) requires further discussion. The (C-N) stretching vibrations in organic compounds occur in the region 1,200 - 1,350 cm^{-1}, and are generally at a higher energy, the higher the electronegativity of the group attached to the nitrogen. The (C-N) stretching vibration in the complexes under discussion is expected to be at the higher end of the range, since the nitrogen substituent is highly electronegative. The position of the (W = N) stretching vibrations is more difficult. A calculation based on equation (2) results in it being shifted to much lower energies, 762 cm^{-1} for NMe, 626 cm^{-1} for NEt and 487 cm^{-1} for $NBu^{\underline{t}}$. These calculations involve gross approximations. As the mass of the substituent increases, the movement of the tungsten atom becomes more significant, and it is now no longer justified to treat the substituent as a point mass. The group 1 vibrations could thus represent a (C-N) stretching mode or an asymmetric stretching mode of the (C - N = W) skeleton; similarly group 2 could represent a (W = N) stretching mode or a symmetric stretching mode of the (C - N = W) skeleton.

Changes of the other tungsten ligands do not affect the position of the group 1 band significantly. Table 2:1 shows that it is fairly constant for the (W = N - Me) group at approximately 1,331 cm^{-1}. If the alkyl group is changed, however, then there is a significant loss in energy. This could be either because the vibration is better represented by a (C-N) stretching mode or else because it is the movement of the carbon which makes the bigger contribution thus making a substitution at the carbon cause a bigger change in the energy of the vibration. X-ray diffraction studies show that compounds of the type $C_2Cl_5NWCl_4(L)$ possess a $(W = NC_2Cl_5)$ skeleton, and that the four remaining chlorines are cis to the pentachloroethylimido group (82, 83). For pentachloroethylimidotungsten (VI) tetrachloride trichloroacetonitrile, $C_2Cl_5NWCl_4$, CCl_3CN a strong band is observed in the i.r. spectrum at 1,285 cm^{-1}, and for the dimer, μ-dichlorobis (pentachloroethylimidotungsten (VI) trichloride), a strong band is observed at 1,290 cm^{-1}. These have been tentatively assigned to the (W = N) stretching vibrations (90). It now seems more accurate to assign them to the asymmetric stretching mode of the (C - N = W) skeleton.

The group 2 vibrations are assigned either to the symmetric (C - N = W) stretching mode or the (W = N) stretching mode.

In oonclusion, there is still much doubt about the assignments for the (C - N = W) stretching modes, but the intense band in the region 1,285 - 1,335 cm^{-1} is a very useful indicator for the presence of the (C - N = W) group.

(XI) THE REACTION OF TUNGSTEN HEXAFLUORIDE WITH TRIMETHYLAMINE.

In the present work the reaction of tungsten hexafluoride with trimethylamine has been briefly studied. Reaction between the two compounds takes place below room temperature to produce an off - white powdery solid. The analytical data on this is consistent with the 1:1 adduct, $WF_5(Me_3N)$. The compound dissolves in deuteroacetonitrile to give a very dark solution. The ^1H n.m.r. of this solution shows a peak at $\delta^1H = 2.67$ p.p.m. which is assigned to coordinated trimethylamine. Other weaker peaks are also observed, but these were not assigned. The ^{19}F n.m.r. spectrum of this solution has no signals, and is thus consistent with reduction to W(V) having taken place.

The ability of trimethylamine to act as a reducing agent has recently been discussed in relation to its reaction with copper dichloride (167). It is suggested that the intermediate formed is the cation, $Me_2N = CH_2^+$. This can react with further trimethylamine to give the cation, $Me_2NCH_2NMe_3^+$. The ^1H n.m.r. spectrum of the adduct, $WF_5(Me_3N)$, does not exclude the presence of this cation.

(XII) THE REACTION OF METHOXYTUNGSTEN (VI) PENTAFLUORIDE WITH N-METHYL HEXAMETHYLDISILAZANE.

The reaction of methoxytungsten (VI) pentafluoride, WF_5OMe, with N-methyl hexamethyldisilazane was investigated as a possible alternative route to methylimidomethoxytungsten (VI) trifluoride complexes. This was based on the expected substitution reaction:

(1) $WF_5OMe + (Me_3Si)_2NMe \longrightarrow WF_3(OMe)(NMe) + 2Me_3SiF$

N-Methyl hexamethyldisilazane reacts slowly with methoxytungsten (VI) pentafluoride at room temperature to give a viscous, brown oil, trimethylsilyl fluoride and methyl fluoride. The brown oil is insoluble in ethyl acetate and perfluorotoluene. The ^1H and ^{19}F n.m.r. spectra are obtained directly from the oil. The ^1H n.m.r. spectrum has several fairly weak peaks, which were not assigned (see Section 13 part xxi), and a strong peak at $\delta^1H = 5.53$ p.p.m. which was assigned to the methyl protons of the methylimidotungsten (VI) tetrafluoride group. The latter peak is broad and no fine structure can be resolved. Two broad signals were observed in the ^{19}F n.m.r. spectrum at $\delta^{19}F = 65$ and 38 p.p.m. On the basis of their chemical shifts, these two peaks are assigned to tungsten (VI) oxide tetrafluoride and methylimidotungsten (VI) tetrafluoride species respectively. A relatively sharp doublet is observed at $\delta^{19}F = 60.5$ p.p.m. and, on the basis of its chemical shift and coupling constant, this is assigned to the dimeric anion, $W_2O_2F_9^-$.

The low resolution mass spectrum of the oil shows peaks attributable to the methoxytungsten (VI) fluorides, $WF_{6-n}(OMe)_n$ (where n = 2 and 3), and methylimidotungsten (VI) tetrafluoride degradation products.

The i.r. spectrum is shown in Table 2:16. The tentative assignments of the peaks are based on their positions. The strong peak at 1,333 cm^{-1} is considered to be characteristic of the (Me - N = W) skeleton (see this Chapter, Section 10).

In the presence of a large excess of ethyl acetate, the reaction of methoxytungsten (VI) pentafluoride with N-methyl hexamethyldisilazane takes place at room temperature to produce a very viscous, insoluble, yellow-brown liquid, a golden-brown solution, and trimethylsilyl fluoride and methyl fluoride. The removal of the volatile products and solvent from the golden-brown solution, leaves a golden-brown oil. The analysis of the soluble oil is close to that expected for the methylimidomethoxytungsten (VI) trifluoride ethyl acetate complex. Other results however indicate that this result must be fortuitous. The ^{1}H n.m.r. spectrum of the soluble oil in ethyl acetate has several peaks. Two peaks at $\delta^{1}H$ = 5.58 and 5.49 p.p.m. are assigned to the methyl protons of methylimidotungsten (VI) tetrafluoride complexes. $^{1}H-\{^{14}N\}$ Spin decoupling sharpens these two peaks, though no fine structure can be resolved. $^{1}H-\{^{19}F\}$ Spin decoupling collapses the peaks to 1:1:1 triplets. The presence of two separate peaks suggests that complexes of methylimidotungsten (VI) tetrafluoride with two different ligands are involved. In addition, the ^{1}H n.m.r. spectrum has a series of broad or complex peaks in the region, $\delta^{1}H$ = 4.60 - 5.22 p.p.m., which are tentatively assigned to higher substituted methoxytungsten (VI) fluorides.

TABLE 2:16

THE I.R. SPECTRUM OF THE BROWN OIL OBTAINED FROM THE REACTION OF TUNGSTEN HEXAFLUORIDE WITH N-METHYLHEXAMETHYLDISILAZANE.

Peak (cm^{-1})	Intensity	Assignment
3,260	s	(N-H) stretch
3,018	w	(C-H) stretch
2,950	m	(C-H) stretch
2,940	m	(C-H) stretch
1,650	w, br.	(N-H) bend
1,585	w, br.	
1,484	s, sh.	(C-H) bend
1,452	s, sh.	
1,435	s	
1,420	s, sh.	
1,415	s, sh.	
1,333	s	(MeN=W) asym. stretch
1,291	w	
1,248	m	
1,151	s	
1,084	s	(W=O) stretch

TABLE 2:16 (contd.)

Peak	Intensity	Assignment
1,014	s.br.	(W=O) stretch
950	m	
926	w	
889	w	
822	w	
701	s	(Me-N=W) sym. stretch
648	s.br.	(W-F) stretch
600	s.br.	(W-F) stretch
458	m	
415	m	

The spectrum was scanned in the region 4,000 - 350 cm^{-1}.

The material was run as a liquid film between KBr plates.

The ^{19}F n.m.r. spectrum of the oil soluble in ethyl acetate has a singlet peak, with tungsten satellites, at $\delta^{19}F = 37.0$ p.p.m., which is assigned to the fluorines of a methylimidotungsten (VI) tetrafluoride complex. Other peaks present in the spectrum are tentatively assigned to mer - $WF_3(OMe)_3$ and fac - $WF_3(OMe)_3$.

The low resolution mass spectrum of the soluble oil has peaks consistent with the presence of $WF_3(OMe)_3$ and WF_4NMe. The mass assignment of the former peak has been confirmed by high resolution mass spectrometry.

The very viscous, insoluble brown oil has only been studied by low resolution mass spectrometry. The low resolution mass spectrum has peaks present consistent with highly substituted methoxytungsten (VI) fluorides.

A possible rationalization of the reaction is

(2) $WF_5OMe + (Me_3Si)_2NMe \xrightarrow{slow} WF_4NMe + Me_3SiF + Me_3SiOMe$

where the trimethylsilyl group preferentially removes the methoxy - group rather than a fluorine atom. The methoxytrimethylsilane can then react further.

(3) $WF_5OMe + Me_3SiOMe \xrightarrow{fast}$ cis - $WF_4(OMe)_2 + Me_3SiF$

(4) cis - $WF_4(OMe)_2 + Me_3SiOMe \xrightarrow{fast}$ mer & fac $WF_3(OMe)_3 + Me_3SiF$

(5) mer & fac $WF_3(OMe)_3 + Me_3SiOMe \xrightarrow{v.\ slow}$ cis - $WF_2(OMe)_4 + Me_3SiF$.

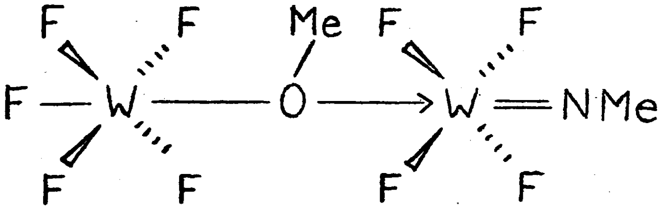
Previous work has shown that reactions (2) and (3) are fast, whereas reaction (5) is slow (50). The main substituted species observed are fac and mer $WF_3(OMe)_3$.

It is probable that the reaction giving rise to methyl fluoride, also results in the formation of tungsten oxide tetrafluoride complexes. The latter are formed when no polar solvent is present, but they have not been identified in the reaction of WF_5OMe with $(Me_3Si)_2NMe$ in ethyl acetate. The identification of methyl fluoride in this reaction, is probably due to its great volatility allowing even small amounts to be identified by gas i.r. spectrometry.

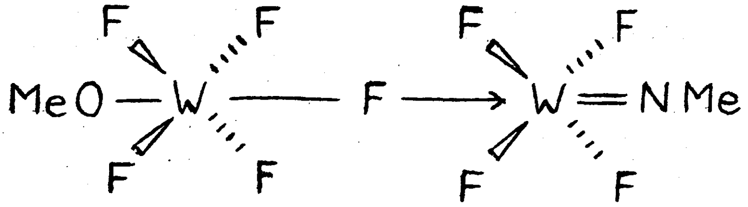
Methoxytungsten (VI) pentafluoride is known to decompose by the reaction

$$WF_5OMe \longrightarrow WOF_4 + MeF$$

The reaction is slow at room temperature but rapid at 135°C. The decomposition reaction is explained on the methyl cation donor properties of WF_5OMe. (48). The presence of the strong acceptor, WF_4NMe, could result in the formation of a methoxy bridged species.



This complex should be an even more powerful methyl cation donator than WF_5OMe, and more liable to eliminate methyl fluoride. The oxygen atom of the methoxy group is, however, a poor donor due to its lone pair electrons interacting with the vacant d-orbitals on the tungsten atom. An alternative is an intermediate bridged through the trans-fluorine.



In this complex the $p\pi - d\pi$ overlap between the p-orbitals of the trans-fluorine and the d-orbitals of the tungsten atom will be decreased and, conversely, the $p\pi - d\pi$ overlap in the (W-O) bond will be increased.

The methyl cation donor properties of the methoxy group will be increased and, hence, elimination of methyl fluoride should more readily occur.

XIII. EXPERIMENTAL

(A) GENERAL

(i) Sources and purification procedures for starting materials.

The starting materials were prepared or obtained commercially as detailed in Table 2:17. The solvents used were dried by standard methods (168). Acetonitrile and propionitrile were dried by refluxing for several hours over phosphorus pentoxide. They were then distilled, and the procedure was repeated two or three times. Dissolved air was removed by cooling to $77^{o}K$ and pumping down to 10^{-3} mm of Hg, repeating this procedure several times. The nitriles were stored under vacuum over molecular sieves (type 4A).

For perfluorotoluene and trimethylphosphite, dissolved air was removed by the procedure described above. They were then distilled and stored over metallic sodium under vacuum.

Tungsten hexafluoride was redistilled and stored over dried sodium fluoride under vacuum. The sodium fluoride had previously been dried by heating to $140^{o}C$ for 12 hours at 10^{-3} mm of Hg.

The other volatile compounds used were similarly degassed and stored over molecular sieves.

(ii) General experimental procedures.

Reactions were carried out in anhydrous conditions under vacuum, using glass reaction vessels with side arms and equipped with Rota-flo, teflon stopcocks. The glass systems were flamed out prior to use to remove adsorbedwater. Glass stopcocks were lubricated with

TABLE 2:17

Sources of Starting Materials.

Starting Material	Source
WF_6	Fluorochem. Ltd., 99%
MeCN	Koch-Light Laboratories or B.D.H. Chemicals Ltd. 98%
C_2H_5CN	B.D.H. Chemicals Ltd.
$(Me_3Si)_2NH$	Ralph Emanual Ltd. 98%
$C_2H_5OC(O)CH_3$	B.D.H. Chemicals Ltd., 'Analar'
$CF_3C_6F_5$	Columbia Organic Chemicals Co. Inc.
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$ (169)
CCl_3F	Fluorochem. Ltd.
CD_3CN	Fluorochem. Ltd.
Me_4Si	Aldrich Chemical Co. Inc.
$(MeO)_2SO$	Aldrich Chemical Co. Inc.
$(MeO)_3P$	Kodak Co.
$(MeO)_2P(O)Me$	Ralph Emanuel Ltd. 97%
$Me_3SiNHMe$	$Me_3SiCl/MeNH_2$ (143)
$MeNH_2$	B.D.H. Chemicals Ltd. 97.8%
$EtNH_2$	B.D.H. Chemicals Ltd. 99.5%
$^{n}BuNH_2$	B.D.H. Chemicals Ltd. 98%
$^{t}BuNH_2$	Koch-Light Laboratories Ltd., Pure.
Me_3N	B.D.H. Chemicals Ltd., 99%

TABLE 2:17 (contd.)

Starting Material	Source	
$MeOWF_5$	$WF_6/(MeO)_2SO$	(48)
$MeOSO_2F$	PCR Inc.,	99%
$(Me_3Si)_2O$	Koch-Light Laboratories Ltd.	Pure.

'Kel F' grease where necessary, otherwise 'Apiezon L' was used. Ground glass joints were either greased or fixed with 'Kel F' wax.

Vacuum was attained by using an Edward's double stage, high vacuum rotary pump in series with a mercury diffusion pump. This resulted in pressures of 10^{-3} mm of Hg or less. Pressures were monitored by a McLeod gauge.

Pressures of volatile compounds required for preparing gas i.r. samples were measured using a mercury manometer. Involatile materials were handled in a Lintott inert atmosphere box.

(iii) Analysis and instrumentation.

All analysis were carried out by A. Bernhardt of West Germany. Carbon and hydrogen were determined by combustion, nitrogen by the Dumas method, while the types of determinations for fluorine and oxygen were not specified. Metals were determined by atomic absorption or another suitable method. Accuracy of the order of ±0.2% or better was claimed.

Low resolution mass spectra were obtained using an A.E.I. M.S.12 spectrometer and high resolution mass spectra were obtained using an A.E.I. M.S.902S spectrometer. Volatile samples were admitted as gases directly into the electron beam, and involatile samples were introduced into the electron beam on a ceramic probe at temperatures between 100 - 280°C.

Infra-red spectra in the range 4,000 to 400 cm^{-1} were recorded on Perkin - Elmer 457 or 577 spectrometers. Gas i.r. spectra samples were contained in 5 cm glass cells with KBr windows. Other samples were recorded as liquid films or mulls between KBr or AgCl plates. The mulling agents, Nujol and Fluorolube were dried over metallic sodium. All the i.r. spectra were referenced using a standard polystyrene film.

Raman spectra were recorded, in the range 4,000 - 100 cm^{-1}, using a Spex - Ramalog spectrometer. The samples, both solids and liquids, were contained in glass capillaries. The following laser excitation lines were utilized: 4765, 4880, 5154, 5682 and 6471 Å.

^{1}H N.m.r. spectra were recorded at 60MHz on a Jeol C60HL high resolution n.m.r. spectrometer. The ^{19}F n.m.r. spectra were either recorded on the same instrument at 56.45MHz, or on a Varian XL100 spectrometer at 94.15MHz.

Spin decoupling and tickling experiments were carried out using either the internal facilities of the XL100 spectrometer for $^{19}F - \{^{1}H\}$ and $^{19}F - \{^{19}F\}$ experiments, or using ancillary instrumentation in conjunction with the Jeol C60HL spectrometer for $^{1}H - \{^{19}F\}$, $^{1}H - \{^{14}N\}$, $^{1}H - \{^{31}P\}$, $^{19}F - \{^{31}P\}$ and $^{19}F - \{^{14}N\}$ decoupling. In the latter case a Schomandl ND100M frequency synthesizer was used to generate the additional frequency required. Where necessary this was amplified by a Jeol heteronuclear spin decoupler, which included white noise modulation facilities. The decoupling frequency was accurately measured (±1Hz) by a Racal 9022 frequency period meter.

^{1}H Chemical shifts were referred to tetramethylsilane, and the convention adopted was that signals to low field (high frequency) of the reference were positive. The chemical shifts of ^{19}F, ^{14}N and ^{31}P nuclei are also expressed using a similar convention. The reference compounds were respectively, internal trichlorofluoromethane,

external nitrate ion, and 75% phosphoric acid.
The ^{14}N chemical shifts were obtained relative to an external ammonium ion in a saturated ammonium nitrate solution in dilute nitric acid, and this was referred to an external nitrate ion using the conversion factor

$$\delta\, ^{14}N(NO_3^-) = \delta\, ^{14}N(NH_4^+) - 354 \text{ p.p.m. } (170)$$

The ^{31}P chemical shifts were obtained relative to dimethyl methylphosphonate and this was then referred to external 75% phosphoric acid using the conversion factor.

$$\delta\, ^{31}P(H_3PO_4) = \delta\, ^{31}P(MeO)_2P(O)Me) + 32.4 \text{ (p.p.m.) } (144).$$

Further details of the n.m.r. techniques are given in Chapter 3.

(B) REACTIONS

(i) The reaction of tungsten hexafluoride with hexamethyldisiloxane in acetonitrile.

A slight excess (approximately 2:1 molar) of tungsten hexafluoride was condensed on to hexamethyldisiloxane in a large excess (approximately 10:1) of acetonitrile. The mixture was allowed to warm slowly to room temperature and gave a clear colourless solution. The solvent and volatile products were removed leaving a white crystalline solid. The volatile material was identified from its gas i.r. spectrum as a mixture of trimethylsilyl fluoride (126), tungsten hexafluoride (34) and acetonitrile (114). The white solid was characterized as tungsten (VI) oxide tetrafluoride acetonitrile, found C7.47, H1.08, F23.66 and W57.88%, $C_2H_3F_4$ NOW requires C7.57, H0.95, F23.97 and W58.04%.

The i.r. spectrum of the white solid was recorded and is shown in Table 2:1 (this Chapter, Section II). The ^{19}F n.m.r. spectrum of the solid in acetonitrile consisted of a singlet at $\delta^{19}F = 68.0$ p.p.m., with tungsten satellites $^{1}J(^{19}F - ^{183}W) = 70Hz$. The literature values for the tungsten (VI) oxide tetrafluoride acetonitrile complex are $\delta^{19}F = 68.5$ p.p.m. and $^{1}J(^{19}F - ^{183}W) = 68Hz$ (109).

(ii) The reaction of tungsten hexafluoride with hexamethyldisilazane in acetonitrile.

Two different products were isolated from this reaction.

(a) Hexamethyldisilazane (0.1656 g, 1.03 mmol) and tungsten hexafluoride (0.5396 g, 1.81 mmol) were condensed into a reaction flask containing acetonitrile

(0.9618 g 23.42 mmol) The mixture was allowed to warm slowly to 0°C. At 0°C a pale yellow solution was obtained and the volatile material was removed, leaving a pale yellow, fluffy powder (0.2365g).

The volatile material was identified by infra-red spectroscopy as a mixture of trimethylsilyl fluoride, a small quantity of tungsten hexafluoride and solvent.

The pale yellow, fluffy solid was characterized as imidotungsten (VI) tetrafluoride acetonitrile, $WF_4NH(MeCN)$, found C7.60, H1.44, F24.26 and N8.46%, $C_2H_4F_4N_2W$ requires C7.61, H1.28, F24.06 and N8.87%. The i.r. spectrum of the solid was recorded and is shown in Table 2:4 (this Chapter, Section III).

It was not possible to repeat the preparation of $WF_4NH(MeCN)$, since further reaction readily took place. Six attempts were made to repeat the above result, a typical result is outlined below.

(b) Hexamethyldisilazane (0.4754g, 1.60 mmol) and tungsten hexafluoride (0.1865g, 1.15 mmol) were condensed into a reaction flask containing acetonitrile (0.9366g, 22.84 mmol). An orange solution was initially formed at 0°C, which turned a deep red after standing at room temperature for a few minutes. The onset of the colour change varied sometimes it occurred during the warm up process, but on one occasion it occurred after standing for 0.5h at room temperature.

The removal of the volatile material left behind a reddish brown solid which could be redissolved in acetonitrile.

The ^{19}F n.m.r. spectrum of the deep red reaction mixture consisted of a signal at $\delta^{19}F = -163.5$ p.p.m. assigned to trimethylsilyl fluoride by comparison with the literature value which is $\delta^{19}F = -164.0$ p.p.m. (171).

The ^1H n.m.r. spectrum consisted of a 1:1:1 triplet at $\delta^1H = 4.90$ p.p.m., J = 54Hz. This was assigned to the ammonium ion. The spectrum of a concentrated solution of ammonium nitrate in dilute nitric acid was recorded and gave $\delta^1H = 6.00$ p.p.m. and $^1J(^1H - ^{14}N) =$ 54Hz. The ^{14}N chemical shift obtained by an $^1H - \{^{14}N\}$ spin decoupling experiment was only 3 p.p.m. downfield from the ^{14}N chemical shift of the authentic ammonium nitrate sample. In addition, an INDOR spectrum of the peak gave the expected quintet.

(iii) <u>The reaction of tungsten hexafluoride with hexamethyldisilazane in propionitrile</u>.

If the reaction was carried out by the procedure used in (i) yellow-brown to dark-red solution were obtained, in four separate runs. The removal of the volatile material from these solutions gave pale to dark brown solids of variable composition. The analysis results from two different preparations were:- (a) Found C5.74, H1.80, F21.33 and N7.64% and (b) C7.93, H1.74, F21.56 and N7.14%.

The volatile materials were identified by infra-red spectroscopy as Me_3SiF, WF_6 and solvent. The i.r. spectrum of the solid products was reproducible and the peaks found are given in Table 2:5 (this Chapter, Section III).

The ^1H n.m.r. spectrum had a 1:1:1 triplet, $\delta^1H = 6.00$ p.p.m., $^1J(^1H - ^{14}N) = 54$Hz assigned to the ammonium ion. The signal assigned to the methylene group of propionitrile was broad at room temperature, but was resolved into a 1:3:3:1 quartet at -20°C. The signal, a triplet, assigned to the methyl group was normal at all temperatures.

The ^{19}F n.m.r. spectrum contained a singlet at $\delta\,^{19}F$ = 67.2 p.p.m. with tungsten satellites, $^{1}J(^{19}F - ^{183}W)$ = 69Hz. The peak was assigned to a tungsten (VI) oxide tetrafluoride complex. The literature value for $\delta\,^{19}F$ in tungsten (VI) oxide tetrafluoride acetonitrile is 68.5 p.p.m. and $^{1}J(^{19}F - ^{183}W)$ = 68Hz (94).

A doublet, approximately twice the intensity of the singlet, was observed at $\delta\,^{19}F$ = 61.7 p.p.m. with $^{2}J(^{19}F_c - ^{19}F_t)$ = 57Hz and tungsten satellites, $^{1}J(^{19}F_c - ^{183}W)$ = 68Hz. The signal was assigned to the equatorial ^{19}F resonance of the $W_2O_2F_9^-$ anion, by analogy with the literature value $\delta\,^{19}F$ = 62.5 p.p.m., $^{2}J(^{19}F_c - ^{19}F_t)$ = 59Hz and $^{1}J(^{19}F - ^{183}W)$ = 72Hz. (109).

In a separate experiment, the ^{19}F n.m.r. spectrum of a reaction mixture which had been allowed to warm only to -40°C was recorded. This contained three peaks at $\delta\,^{19}F$ = 41.3, 38.3 and 35.3 p.p.m. of relative intensity 8:2:7. These were tentatively assigned to $WF_4NH(L)$ species (Table 2:2, this Chapter, Section III).

(iv) The reaction of tungsten hexafluoride with hexamethyldisilazane in ethyl acetate.

The reaction was carried out as described for reaction (ii). The course of the reaction closely followed reaction (ii) (b). A deep red-brown solution was obtained at room temperature and the volatile material was identified as a mixture of Me_3SiF and solvent by gas i.r. spectroscopy.

(v) The reaction of tungsten hexafluoride with hexamethyldisilazane in octafluorotoluene.

Hexamethyldisilazane (0.2330g, 1.44 mmol) was condensed on to a mixture of tungsten hexafluoride (0.4147g, 1.39 mmol) and octafluorotoluene (approximately 1 ml), and the mixture was allowed to warm slowly to room temperature. At approximately 0°C a pale yellow insoluble precipitate was formed. Removal of the volatile material left a pale yellow powder. The volatile material was identified by gas i.r. spectroscopy as a mixture of trimethylsilyl fluoride and solvent. Trap to trap separation of the mixture gave 0.2078g (2.23 mmol) of Me_3SiF.

Analytical data were not reproducible, but the results from two different preparations were as follows: (a) C6.06, H2.06, F24.50, N6.73 and W60.09%, and (b) C5.32, H2.14, F22.31, N8.12 and W54.68%. Required for HF_4NW; C0.00, H0.004, F27.63, N5.09 and W 66.9%.

The low resolution mass spectrum of the solid contained only weak degradation peaks characteristic of WOF_4.

The i.r. spectra of the solids were variable, but the following peaks were always obtained 3260 vs, 2959 s, 2922 s, 2858 m, 1426 vs, 1349 m, 1256 s, 1177 s, br, 1094 ms, br, 855 s, br, 764 s, 724 m, 668 s, 605 s, br cm^{-1}. The low temperature (-196°C) Raman spectrum of one sample contained peaks at 328 s, 285 w,br, 264 s, 139 vs. cm^{-1}.

In separate experiments the donor solvents ethyl acetate acetonitrile and trimethylphosphite were condensed on to the solid, and the mixture allowed to slowly warm to room temperature. In each case dark coloured solutions were obtained which were not investigated further.

The sample corresponding to analysis (b) was exposed to air. Hydrolysis occurred very slowly to give a pale blue solid. Found C0.19, H2.01, F11.91, N6.74, W58.55%; $H_{13} F_4 N_3 O_8 W_2$ required C0.00, H2.07, F12.12, N6.70, W58.69%.

(vi) The reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane in acetonitrile.

The reaction was carried out as previously described (96, 97). N-methyl hexamethyldisilazane (0.2275g, 1.54 mmol) was condensed on to a mixture of tungsten hexafluoride (0.4600g, 1.55 mmol) and acetonitrile (0.6558g, 15.97 mmol). The mixture was allowed to warm slowly to room temperature, and a brown solution was obtained. Removal of the volatile material left a brown solid.

The volatile material was identified by gas i.r. spectroscopy as a mixture of trimethylsilyl fluoride and solvent. The components were separated by trap to trap distillation and 0.1325g (1.44 mmol) of Me_3SiF was obtained. This was a 94% yield based on the quantity of N-methyl hexamethyldisilazane used.

The ^1H n.m.r. spectrum of a solution of the brown solid in deutero-acetonitrile was recorded. It contained a complex peak at $\delta\,^1H = 5.53$ p.p.m., which was assigned to the methylimido group and a singlet at $\delta\,^1H = 1.98$ p.p.m. which was assigned to the acetonitrile of the methylimido-tungsten (VI) tetrafluoride complex. In several preparations it was observed that the intensity of the peak at $\delta\,^1H = 5.53$ p.p.m. was less than the intensity of the acetonitrile peak. It was observed that the paler the colour of the solution then the nearer the intensity ratio was to 1:1. $^{1}H-\{^{19}F\}$ and $^{1}H-\{^{14}N\}$Spin decoupling experiments gave the magnitudes and relative signs of the coupling constants as follows $^{2}J(^{1}H - ^{14}N) = \mp2.8$ Hz, $^{4}J(^{1}H - ^{19}F) = \pm1.4$Hz and $^{2}J(^{14}N - ^{19}F) = \pm1.3$Hz The previously reported values are $\delta^{1}H = 5.73$ p.p.m., $^{2}J(^{1}H - ^{14}N) = 2.8$ Hz and $^{4}J(^{1}H - ^{19}F) = 1.3$Hz (97).

The ^{19}F n.m.r. spectrum of the solution contained a singlet peak at $\delta^{19}F = 37.2$ p.p.m., with tungsten satellites, $^{1}J(^{19}F - ^{183}W) = 46$Hz The previously reported values are $\delta^{19}F = 35.4$ p.p.m. (CCl_3F external) and $^{1}J(^{19}F - ^{183}W) = 56$Hz (97).

The i.r. spectrum of the brown solid was as follows: 3260 vw, 3220 vw, 3018 m, 2955 m, 2930 m, 2860 m, 2658 vw, 2400 vw, 2324 s, 2300 s, 1410 m, 1368 m, 1330 s, 1255 vw, 1168 vw, 1149 vw, 1030 m, 970 w, 943 w, 916 w, 809 w, 736 vw, 720 vw, 700 w, 660 m, 585 s, 480 w, 410 m cm^{-1}.

(vii) The reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane in propionitrile.

The reaction was carried out as described for the previous reaction. The product was a dark brown solution from which a dark brown solid was isolated.

The volatile material was identified from gas i.r. spectroscopy as a mixture of Me_3SiF and solvent.

The low resolution mass spectrum of the brown solid consisted of the peaks shown in Table 2:18 and strong peaks derived from propionitrile. The i.r. spectrum of the solid contained the following peaks: 3260 m, 2993 s, 2950 s, 2918 m, 2298 m, 2248 s, 1680 w, 1604 m, 1461 s,

TABLE 2:18

THE LOW RESOLUTION MASS SPECTRUM OF $WF_4NMe(EtCN)$.

Peak m/e[1]	Relative abundance	Assignment
301	16	
289	32	WF_4NMe^+
270	100	WF_3NMe^+
260	45	WF_4^+
241	45	WF_3^+
222	32	WF_2^+
203	16	WF^+
55	543	$C_2H_5CN^+$
54[2]	3125	$C_2H_4CN^+$

[1] Due to ^{184}W. The characteristic tungsten isotope pattern is observed.

[2] Strongest ligand peak, further degradation peaks observed.

(Carried out at a probe temperature of 270°C)

1427 m, 1331 s, 1235 w, 1182 w, 996 m, 870 m, 830 m, 783 m, 699 m, 668 s, 606 vs cm^{-1}.

(viii) The reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane in ethyl acetate.

This reaction was carried out as previously described for reactions (vi) and (vii). A golden yellow solution was obtained on warming the mixture to room temperature. Removal of the material, volatile at room temperature, gave a dark brown oil. The volatile material was identified as a mixture of Me_3SiF and solvent from gas i.r. spectroscopy. The analysis of the oil was, found C11.91, H2.43, F23.59, N3.68%.

The ^1H n.m.r. spectrum of the reaction mixture contained a complex peak at $\delta\,^1H = 5.50$ p.p.m. $^1H-\{^{19}F\}$ and $^1H-\{^{14}N\}$ spin decoupling experiments reduced it to a 1:1:1 triplet and a 1:4:6:4:1 quintet respectively, and gave $^2J(^1H - ^{14}N) = \mp 2.8$Hz, $^4J(^1H - ^{19}F) = \pm 1.3$Hz, $^2J(^{14}N - ^{19}F) = \pm 1.3$Hz and $\delta\,^{14}N = 13.5$ p.p.m. The spin decoupling experiments also revealed the presence of tungsten satellites, $^3J(^1H - ^{183}W) = 9.0$ Hz.

The ^{19}F n.m.r. spectrum showed a singlet at $\delta\,^{19}F = 38.3$ p.p.m. with tungsten satellites, $^1J(^{19}F - ^{183}W) = 44$Hz. $^{19}F-\{^{14}N\}$ and $^{19}F-\{^1H\}$ spin decoupling experiments both resulted in a sharpening of the singlet peak, but fine structure could not be resolved. The ^{19}F n.m.r. spectrum also contained a weak singlet at $\delta\,^{19}F = 63.6$ p.p.m. This was assigned to tungsten oxide fluoride ethyl acetate, $WOF_4\left[EtOC(O)CH_3\right]$, by analogy with the previously reported value of this compound of $\delta\,^{19}F = 64.9$ p.p.m. (94).

Both the ^1H and ^{19}F n.m.r. spectra of the reaction mixture contain peaks characteristic of trimethylsilyl fluoride.

(ix) The reaction of tungsten hexafluoride with N-methyl hexamethyldisilazane.

A mixture of $(Me_3Si)_2NMe$ and excess WF_6 was allowed to warm slowly from -196°C to room temperature over several hours. A brown-purple solution was obtained whose n.m.r. spectra contained only signals due to WF_6 and $(Me_3Si)_2NMe$.

After 24 hours signals had appeared which were characteristic of Me_3SiF (171, 172), and a small amount of pale yellow solid had been deposited. After a week more powder had deposited and the liquid phase was colourless. The volatile material was removed, and identified from its gas i.r. spectrum as a mixture of WF_6 and Me_3SiF.

The reaction was repeated several times, the solid product obtained varied in colour from pure white to yellow. It was characterized as methylimidotungsten (VI) tetrafluoride on the basis of its i.r. spectrum and its chemical reactions.

The i.r. spectrum (Nujol mull only) contained peaks at 1331 s, 1258 w, 1012 w, 851 w, 721 s, 681 s, 631 vs, 502 vs cm^{-1}.

(x) The reaction of acetonitrile with methylimidotungsten (VI) tetrafluoride.

Excess of acetonitrile was condensed on to the solid obtained from the previous reaction to give a pale yellow solution. Removal of the volatile material left an orange solid.

The ^1H and ^{19}F n.m.r. spectra contained signals identical to those obtained from the product in reaction (v), and these were assigned to methylimidotungsten (VI) tetrafluoride acetonitrile, $WF_4NMe(MeCN)$. An $^1H-\{^{14}N\}$ spin decoupling experiment gave $\delta^{14}N = 24.8$ p.p.m. The ^1H and ^{19}F n.m.r. spectra of the solution contained weak peaks assigned to Me_3SiF. Traces of Me_3SiF were obtained in all reactions of methylimidotungsten (VI) tetrafluoride with donor solvents.

(xi) The reaction of dimethyl sulphite with methylimidotungsten (VI) tetrafluoride.

Excess dimethyl sulphite was condensed on to methylimidotungsten (VI) tetrafluoride, and, on warming to room temperature, a yellow solution was obtained. The removal of the volatile material left behind a yellow, viscous, involatile oil. The low resolution mass spectrum of this oil contained peaks corresponding to the ions, WF_3NMe^+, WOF_3^+ and degradation products. Peaks were also observed corresponding to dimethyl sulphite and its degradation products. The low resolution mass spectrum is shown in Table 2:19. The i.r. spectrum of the oil was recorded and is shown in Table 2:7 (this chapter, Section IV).

The oil was soluble in dimethyl sulphite and the ^1H n.m.r. spectrum of the solution contained a complex signal at $\delta^1H = 5.63$ p.p.m. assigned to the methylimido group of $WF_4NMe[(MeO)_2SO]$. The following n.m.r. parameters were determined from $^1H-\{^{19}F\}$ and $^1H-\{^{14}N\}$ decoupling experiments, $^4J(^1H-{}^{19}F) = \pm 1.2$Hz, $^2J(^1H-{}^{14}N) = \mp 2.7$Hz, $^2J(^{14}N-{}^{19}F) = \pm 1.3$Hz and $\delta^{14}N = 16.1$ p.p.m. Satellite peaks due to ^{183}W were observed on decoupling the signal from which $^3J(^1H-{}^{183}W) = 9.4$Hz was determined. The solution's ^{19}F n.m.r. spectrum

TABLE 2:19

THE LOW RESOLUTION MASS SPECTRUM OF $WF_4NMe[(MeO)_2SO]$.

Peak m/e[1]	Relative abundance	Assignment
333	4.1	
303	65	
291	51	
289[2]	16	WF_4NMe^+
287	71	
270	100	WF_3NMe^+
257	198	WOF_3^+
238	73	WOF_2^+
110[3]	v. strong	$(MeO)_2SO^+$

1) Due to ^{184}W. They show characteristic tungsten isotope pattern.

2) From peak due to ^{183}W and corrected for ^{184}W.

3) Strongest ligand peak. Weaker degradation peaks are also observed.

consisted of a single peak, $\delta\ ^{19}F = 38.7$ p.p.m., with tungsten satellites. $^{19}F-\{^{14}N\}$ Decoupling resulted in the main peak becoming sharper, but no fine structure could be resolved. Similar experiments on the satellite peaks gave $^{1}J(^{19}F - ^{183}W) = \pm 44$Hz and $^{1}J(^{14}N - ^{183}W) = \pm 100 \pm 10$Hz.

(xii) The reaction of ethyl acetate with methylimidotungsten (VI) tetrafluoride.

The reaction was carried out in a similar manner to reactions (x and xi). The initial product was a yellow-green solution. The ^{1}H and ^{19}F n.m.r. spectra of this solution were identical to those assigned to $WF_4NMe\left[EtOC(O)CH_3\right]$ in reaction (viii). Removal of the solvent gave a green solid which gave broad peaks in its i.r. spectrum.

(xiii) The reaction of trimethylphosphite with methylimidotungsten (VI) tetrafluoride.

Excess trimethylphosphite was condensed on to methylimidotungsten (VI) tetrafluoride and, on warming to room temperature, an orange solution was obtained. Removal of the volatile material left an orange oil. The nature of the oil varied depending on whether the reaction mixture was warmed rapidly to room temperature, reaction (a), or whether the reaction mixture was warmed slowly to room temperature, reaction (b).

The ^{19}F n.m.r. spectrum of reaction (b) consisted of three different groups of signals. A singlet at $\delta^{19}F = 35.5$ p.p.m. with ^{183}W satellites, $^{1}J(^{19}F - ^{183}W) = 45$Hz was assigned to the ^{19}F nuclei of methylimidotungsten (VI) tetrafluoride dimethyl methylphosphonate, $WF_4NMe\left[(MeO)_2P(O)Me\right]$. A second order AB_2 spectrum was about 15 p.p.m. to high field of trichlorofluoromethane.

Analysis of the second order spectrum gave the chemical shift of the B_2 groupat $\delta^{19}F = -13.4$ p.p.m. and the A nucleus at $\delta^{19}F = -20.9$ p.p.m. with $^2J(^{19}F_a - ^{19}F_b) = 69Hz$. Satellites due to $^1J(^{19}F_b - ^{183}W) = 55Hz$were observed, but the tungsten satellites of the A signal were not observed. The B_2 and A signals were assigned to the ^{19}F nuclei cis and trans to the methoxy group (Fc and Ft) of the compound, $WF_3(OMe)(NMe)\left[(MeO)_2P(O)Me\right]$. A doublet was observed at $\delta^{19}F = -60.2$ p.p.m. , with $^1J(^{19}F - ^{31}P) = 1176$ Hz . The coupling of the ^{19}F to ^{31}P was confirmed by an $^{19}F-\{^{31}P\}$ spin decoupling experiment. The doublet was assigned to dimethyl fluorophosphite, $(MeO)_2PF$ by analogy with the literature values$\delta^{19}F = -63.1$ p.p.m. and $^1J(^{19}F - ^{31}P) = 1208$ Hz. (146).

The ^{19}F n.m.r. spectrum of the solution obtained in reaction (a) contained the AB_2 spectrum assigned to $WF_3(OMe)(NMe)\left[(MeO)_2P(O)Me\right]$ and the doublet assigned to $(MeO)_2PF$, but the singlet assigned to $WF_4NMe\left[(MeO)_2P(O)Me\right]$was absent. There was an additional weak singlet peak at$\delta^{19}F = -48.3$ p.p.m. and this was tentatively assigned to cis -$WF_2(OMe)_2(NMe)\left[(MeO)_2P(O)Me\right]$.

The ^1H n.m.r. spectrum of reaction (b) was complex. A strong doublet at$\delta^1H = 3.53$ p.p.m., $^3J(^1H - ^{31}P) = 11Hz$, confirmed by $^1H-\{^{31}P\}$ decoupling which gave$\delta^{31}P = 141$ p.p.m., was assigned to unreacted trimethylphosphite by analogy with the reported values for theδ^1H(107),$\delta^{31}P$ (144) chemical shifts and the $^3J(^1H - ^{31}P)$ coupling constant (107, 144). Two doublets at$\delta^1H = 3.54$ p.p.m.

and $\delta^{1}H$ = 1.54 p.p.m., intensity ratio 2:1, were found to correspond to the same ^{31}P chemical shift, $\delta^{31}P$ = 34 p.p.m., by an $^{1}H - \{^{31}P\}$ spin decoupling experiment. These were assigned respectively to the MeO-P and Me-P groups of dimethyl methylphosphonate with $^{3}J(^{1}H - ^{31}P)$ = 11Hz. and $^{2}J(^{1}H - ^{31}P)$ = 18Hz. The literature values are $\delta^{1}H$ = 3.67 p.p.m., $\delta^{1}H$ = 1.43 p.p.m., $^{3}J(^{1}H - ^{31}P)$ = 11Hz., $^{2}J(^{1}H - ^{31}P)$ = 17.3 Hz. (145) and $\delta^{31}P$ = 32.4 p.p.m. (144).

A complex peak at $\delta^{1}H$ = 5.70 p.p.m. was assigned to the methylimido group of the compound, $WF_4NMe\ [(MeO)_2P(O)Me]$. $^{1}H - \{^{19}F\}$ and $^{1}H - \{^{14}N\}$ spin decoupling experiments gave $^{4}J(^{1}H - ^{19}F)$ = 1.0Hz, $^{2}J(^{1}H - ^{14}N)$ = 2.6 Hz., and $\delta^{14}N$ = 14.6 p.p.m. A broad peak at $\delta^{1}H$ = 5.30 p.p.m. was assigned to the methylimido group in the compound $WF_3(OMe)(NMe)\ [(MeO)_2P(O)Me]$. $^{1}H - \{^{14}N\}$ spin decoupling produced a partially resolved quartet, indicating the presence of three ^{19}F nuclei approximately equally coupled to the protons of the methylimido group, the magnitude being 1.2Hz. Decoupling further demonstrated the presence of tungsten satellites with $^{3}J(^{1}H - ^{183}W)$ = 9.5Hz. (see Figures 2:7and 8, this chapter Section VI). $^{1}H - \{^{14}N\}$ spin decoupling gave $\delta^{14}N$ = -1.1 p.p.m. A complex peak at $\delta^{1}H$ = 5.07 p.p.m. was assigned to a MeO-W group in the compound, $WF_3(OMe)(NMe)\ [(MeO)_2P(O)Me]$. $^{1}H - \{^{19}F\}$ Spin decoupling showed that the complex peak consisted of a doublet of overlapping triplets allowing the determination of the relative signs $^{4}J(^{1}H_o - ^{19}F_t)$ = ±2.5 Hz., $^{4}J(^{1}H_o - ^{19}F_c)$ = ±1.2Hz. and $^{2}J(^{19}F_c - ^{19}F_t)$ = ±68.0Hz. The peaks at $\delta^{1}H$ = 5.30 and 5.07 p.p.m. were of equal intensity. Cooling the sample to -30°C produced no significant change in the appearance of the peaks at $\delta\,^1H$ = 5.70, 5.30 and 5.07 p.p.m.

In addition to the above features, the spectrum contained a weak doublet at $\delta\,^1H$ = 0.24 p.p.m., J = 10Hz. assigned to Me_3SiF and unidentified peaks at $\delta\,^1H$ = 7.34, 7.17, 4.83, 4.63, 4.43, 4.23 and 2.43 p.p.m. Two other unidentified peaks were found with ^{31}P coupling at $\delta\,^1H$ = 3.82 p.p.m., $J(^1H - ^{31}P)$ = 11Hz., $\delta\,^{31}P$ = 40 p.p.m., and at $\delta\,^1H$ = 1.93 p.p.m., $J(^1H - ^{31}P)$ = 18Hz., $\delta\,^{31}P$ = 23 p.p.m.

The ^1H n.m.r. spectrum from reaction (a) was similar but less complex. The unidentified peaks at $\delta\,^1H$ = 7.34 and 7.17 p.p.m. were much weaker, and the unidentified peaks at $\delta\,^1H$ = 4.83, 4.63, 4.43 and 4.23 p.p.m. were absent. Unreacted $(MeO)_3P$ was present as before. The peaks due to dimethyl methylphosphonate were much weaker and the methyl phosphorous doublet was shifted downfield to $\delta\,^1H$ = 1.67 p.p.m. The complex peaks at $\delta\,^1H$ = 5.30 and 5.07 p.p.m., assigned to the protons of the MeN and MeO groups in the compound $WF_3(OMe)(NMe)\left[(MeO)_2P(O)Me\right]$, were more intense than in reaction (b). The ratio of these peaks with the peak due to the protons of the Me-P group in dimethyl methylphosphonate was approximately 1:1:1. The peak at $\delta\,^1H$ = 5.70 p.p.m. assigned to the MeN- group in the compound, $WF_4NMe\left[(MeO)_2P(O)Me\right]$ was completely absent. An additional triplet was observed at $\delta\,^1H$ = 4.80 p.p.m., J = 1.8Hz. $^1H - \{^{19}F\}$ spin decoupling established that the splitting was due to coupling with ^{19}F, $\delta\,^{19}F$ = -50 p.p.m. The triplet was tentatively assigned to the methoxy protons in cis $-WF_2(OMe)_2(NMe)\left[(MeO)_2P(O)Me\right]$

The orange oil obtained from reaction (b) was studied by both low and high resolution mass spectrometry with the results shown in table 2:20 and table 2:21.

The i.r. spectrum of the orange oil obtained from reaction (a) was recorded and the results are given in table 2:9 (this chapter, Section VI).

(xiv) The reaction of tungsten hexafluoride with methylamine.

Tungsten hexafluoride (3.6885g, 12.4mmol) was condensed on to methylamine (0.1605g, 5.17 mmol), and the mixture was allowed to warm up slowly, reaction taking place between -60 and -50°C. After the mixture had warmed up to room temperature, the volatile material was removed leaving behind a white solid. The solid was characterized as methylammonium methylimidopentafluorotungstate (VI), $MeNH_3{}^+WF_5NMe^-$,found C6.88, H2.53, F28.07, N8.01, W54.42%. $C_2H_9F_5N_2W$ requires :- C7.06, H2.65, F27.94, N8.24, W54.12%.

The volatile material (0.8107g) was identified by gas i.r. spectroscopy as mainly WF_6 with a small quantity of SiF_4. Thus 2.7 mmol of tungsten hexafluoride had been consumed in the reaction. This was consistent with a reaction stochiometry of $MeNH_2:WF_6$ of 2:1.

The i.r. and Raman spectra of solid $MeNH_3{}^+WF_5NMe^-$ were recorded and are shown in Table 2:8 (this chapter, Section VII).

The ^1H and ^{19}F n.m.r. spectra of a solution of the compound in CD_3CN were run. The ^1H n.m.r. gave broad singlets at 5.50 p.p.m., assigned to the WF_5NMe^- anion,

TABLE 2:20.

LOW RESOLUTION MASS SPECTRUM OF THE MIXTURE OF $WF_4NMe\ [(MeO)_2P(O)Me]$ and $WF_3(OMe)(NMe)\ [(MeO)_2P(O)Me]$ OBTAINED FROM REACTION (b).

Peak m/e[1]	rel. intensity	Assignment[1]
413	4	$WF_4NMe,(MeO)_2P(O)Me^+$
394	6	$WF_3NMe,(MeO)_2P(O)Me^+$
393	11	$WF_3NMe,(MeO)_2P(O)Me(-H)^+$
384	7	$WF_3,(MeO)_2P(O)Me^+$
366	2	
350	6	
335	4	
301	33	$WF_3(OMe)(NMe)^+$
300	100	$WF_3(OMe)(NMe)(-H)^+$
293	11	
289	87	WF_4NMe^+
282	131	$WF_2(OMe)(NMe)^+$
281	149	$WF_2(OMe)(NMe)(-H)^+$
270		WF_3NMe^+
269	408	$WF_3NCH_2^+$
260	124	WF_4^+
259	149	WF_2NCH^+ or $WF_2OCH_3^+$
241	149	WF_3^+
222	120	WF_2^+
203	37	WF^+
184	11	W^+
124	strong	$(MeO)_2P(O)Me^+$
109	strong	$(MeO)_2P(O)^+$

[1] Peaks assigned to ^{184}W containing ions all show the characteristic tungsten isotope pattern.

TABLE 2:21

HIGH RESOLUTION MASS SPECTRA OF THE MIXTURE OF $WF_4NMe\ [(MeO)_2P(O)Me]$ and $WF_3(OMe)(NMe)\ [(MeO)_2P(O)Me]$ FROM REACTION (b).

Peak (found)	Calc.	Assignment
280.98417	280.98491	$^{184}WF_2(OMe)(NMe)^+(-H)$
269.97195	269.97274	$^{184}WF_3NMe^+$

and at 2.51 p.p.m. assigned to the methyl group of the $Me\overset{+}{N}H_3$, cation. However the protons attached to the nitrogen were not observed. The ^{19}F n.m.r. gave a doublet at $\delta^{19}F$ = 28.0 p.p.m., assigned to the cis fluorines of the anion WF_5NMe^-, and a complex peak at $\delta^{19}F$ = -101.5 p.p.m. assigned to the trans fluorine. Further n.m.r. investigations carried out on the anion, WF_5NMe^-, are reported in part (xix) of the experimental section.

(xv) The reaction of tungsten hexafluoride with ethylamine.

This was carried out as described for the previous reaction. The white product was characterized as ethylammonium ethylimidopentafluorotungstate (VI), found C13.14, H3.95, F25.70, N7.69, W49,81%, $C_4H_{13}F_5N_2W$ requires C13.04, H3.53, F25.82, N7.61 and W50.00%.

The i.r. spectrum of $EtNH_3^+WF_5NEt^-$ was recorded and the results are shown in Table 2:9. (this chapter, Section VII).

The ^1H n.m.r. spectrum of $EtNH_3^+WF_5NEt^-$ dissolved in CD_3CN was recorded. A relatively weak, broad singlet at δ^1H = 8.63 p.p.m. was not assigned. A very broad peak at δ^1H = 6.70 p.p.m. was assigned to the protons attached directly to the nitrogen in the cation $EtNH_3^+$. A broadened, but well resolved, quartet at δ^1H = 5.80 p.p.m., $^3J(^1H - ^1H)$ = 7.1Hz. was assigned to the methylene group of the anion WF_5NEt^-. A very broad singlet at δH^1 = 3.10 p.p.m. was assigned to the methylene protons of the $EtNH_3^+$ cation. A strong triplet at δ^1H = 1.20 p.p.m., $^3J(^1H - ^1H)$ = 7.1Hz. was assigned to the methyl group of both the cation $EtNH_3^+$ and the anion, WF_5NEt^-.

The ^{19}F n.m.r. spectrum gave a doublet at

$\delta^{19}F$ = 27.6 p.p.m. and a complex peak at $\delta^{19}F$ = -99.5 p.p.m. The doublet had tungsten satellites and gave $^{1}J(^{19}Fc - ^{183}W)$ = 49 Hz. and $^{2}J(^{19}F_c - ^{19}F_t)$ = 60 Hz. $^{19}F - \{^{14}N\}$ high power, noise modulated spin decoupling gave no sharpening of the doublet. A similar experiment on the complex peak at $\delta^{19}F$ = -99.5 p.p.m. simplified it to a quintet with $^{2}J(^{19}F_c - ^{19}F_t)$ = 60 Hz. The non-decoupled peak was broadened, but it was consistent with a $^{2}J(^{14}N - ^{19}F_t)$ = 36 Hz.

(xvi) The reaction of tungsten hexafluoride with n-butylamine.

This reaction was carried out as the previous two reactions. The white solid obtained was dissolved in CD_3CN and its n.m.r. spectra studied.

The ^{1}H n.m.r. spectrum gave a broad peak at $\delta^{1}H$ = 6.73 p.p.m. which was assigned to the protons attached directly to the nitrogen in the cation $BuNH_3^+$. A broadened triplet was seen at $\delta^{1}H$ = 6.23 p.p.m., $^{3}J(^{1}H - ^{1}H)$ = 6Hz. This was assigned to the α methylene group of the anion $WF_5N^{n}Bu^-$. A broad peak was observed at $\delta^{1}H$ = 3.33 p.p.m. and this was assigned to the methylene group of the cation $\overset{n}{Bu}NH_3^+$. A complex group of peaks centred at $\delta^{1}H$ = 2.03 p.p.m. was assigned to the β and γ methylene groups of both the anion and cation. Another complex peak at $\delta^{1}H$ = 1.30 p.p.m. was assigned to the terminal methyl group of both the anion and the cation.

The ^{19}F n.m.r. gave a doublet at $\delta^{19}F$ = 28.7 p.p.m. and a complex peak at $\delta^{19}F$ = -101 p.p.m. The doublet gave $^{2}J(^{19}F_c - ^{19}F_t)$ = 59Hz., and its tungsten satellites gave $^{1}J(^{19}F_c - ^{183}W)$ = 47 Hz.

It was assigned to the four cis fluorines of the anion, WF_5NBu^{n-}. The literature values are $\delta^{19}F$ = 28.8 p.p.m., $^2J(^{19}F_c - ^{19}F_t)$ = 60 Hz. and $^1J(^{19}F_c - ^{183}W)$ = 50 Hz. (98). The complex peak at $\delta^{19}F$ = -101 p.p.m. consisted of a broadened quintet. $^{19}F - \{^{14}N\}$ high power, noise modulated decoupling sharpened the quintet. The quintet gave $^2J(^{19}F_c - ^{19}F_t)$ = 59 Hz. The complex peak was assigned to the trans fluorine of the anion WF_5NBu^{n-}. The literature value is $\delta^{19}F$ = -99.5 p.p.m. (98).

The ^{19}F n.m.r. also gave an extra doublet at $\delta^{19}F$ = 34.1 p.p.m., $^2J(^{19}F - ^{19}F)$ = 60 Hz. (cf aged solutions of $Me\overset{+}{N}H_3WF_5NMe^-$) which was not assigned.

(xvii) The reaction of tungsten hexafluoride with t-butylamine.

The reaction was carried out as the previous three reactions. The product was a white solid which analyzed as a 3:1 adduct: C27.80, H6.31, F22.26, N8.22 W35.51%, $C_{12}H_{29}F_6N_3W$ requires :- C27.85, H6.38, F22.05, N8.12, W35.59%.

The infra-red spectrum of the solid was recorded and the results are shown in Table 2:12.

The product appeared to be insoluble in CD_3CN. The ^{19}F n.m.r. spectrum showed a very weak doublet at $\delta^{19}F$ = 28.0 p.p.m. which was tentatively assigned to the anion WF_5NBu^{t-}.

The product underwent no apparent change on exposure to air, but infra-red spectra indicated that some hydrolysis had occurred. The infra-red spectrum of a sample which had been exposed to air for several days gave peaks at:- 3057 vs. br., 2980 vs., 2930 vs., 2830 s, 2728 m, 2624 m, 2521 m, 2390 v w., 2100 w, 1985 v w., 1684 m.br., 1626 m, 1531 s, 1483 m, 1408 m, 1381 m, 1365 v w., 1303 s, 1226 s, 1176 w, 1135 w, 996 w, 944 v s., 872 v s., 793 w, 734 w, 722 w, 699 w, 652 w, 597 v s., 582 v s., 457 v s. and 346 v s. cm^{-1}.

(xviii) The reaction of methylammonium methylimidopentafluorotungstate (VI) with methyl fluorosulphate.

(a) Methyl fluorosulphate was condensed on to solid methylammonium methylimidopentafluorotungstate (VI) and the mixture was allowed to warm to room temperature. The volatile material was removed and gas i.r. spectroscopy identified this as methyl fluorosulphate, by comparison with an authentic sample. The remaining white solid was dissolved in deutero-acetonitrile. The ^{19}F n.m.r. of the solution showed only signals of the methylimidopentafluorotungstate (VI) anion. There was thus no evidence of any reaction.

(b) A mixture of methyl fluorosulphate and methylammonium methylimidopentafluorotungstate (VI) was heated to 90° C, with agitation, for two hours. The solid dissolved to give a pale green solution. Methyl fluorosulphate and methyl fluoride were identified in the solid by gas i.r. spectroscopy.

In a separate experiment it was demonstrated that methyl fluorosulphate did not decompose on its own when held at 90° C for two hours.

(xix) The reaction of tungsten hexafluoride with methyl (trimethylsilyl) amine.

An excess (>2:1 molar) of tungsten hexafluoride was condensed on to methyl (trimethylsilyl) amine in the presence of a large excess of trichlorofluoromethane, and the mixture was allowed to warm slowly to room temperature.

The appearance of the product varied, being either a white or a yellow-green solid (four separate reactions were carried out). All products were insoluble in trichlorofluoromethane. Sometimes during the warm up process fumes were observed and in these cases the product was coloured. The volatile material was removed and identified by gas i.r. spectroscopy as a mixture of tungsten hexafluoride, trichlorofluoromethane and trimethylsilyl fluoride.

A sample of the yellow green solid analyzed as C7.24, H2.57, F27.66, N8.04, W53.94%, $C_2H_{10}F_5N_2W$ requires C7.05, H2.65, F27.94, N8.23, W54.12%. A sample of the white solid analyzed as C6.00, H2.40, F28.64, N7.24, W55.88%.

The i.r. spectrum of the white solid was as follows: 3273 v s., 3241 v s. sh., 3180 v s., sh., 3138 v s., 3000 s, 2940 m, 2895 m, 2800 m, 2586 w, 2498 w, 1635 m, 1619 m, 1527 m, 1496 w., s h., 1467 w, 1428 w, 1408 w, 1333 s, 1267 w, 998 m, 956 s, 891 m, 835 w, 723 m, 649 s, 598 v s., 515 s. sh., 422 v s., cm^{-1}.

A Raman spectrum of the white solid dissolved in CD_3CN consisted of peaks at 3004 m.(P), 2954 w.(P), 2934 s.(P), 1019 w.(P), 1008 w.(P), 734 w.(P), 706 v.w., 672 m.(P), 664 m.(P), 632 s.(P), 547 m.(P), 508 w.(P), 439 w.(P), 408 w.(P), 326 w.(P), 296w.(P), 201 w.(P) cm^{-1}. The Raman spectrum of the yellow-green solid dissolved in acetonitrile in the region 1100 - 200 cm.$^{-1}$, was as follows: 1090 w. br .(P), 998 w.(P), 753 w.(P), 660 m.(P), 652 m.(P), 628 s.(P), 535 w.(P), 420 w. br . (P), 283 w.(P), 204 w.(P), cm.$^{-1}$.

The ^{1}H and ^{19}F n.m.r. spectra of several samples were recorded in deutero-acetonitrile solution. Most solutions became yellow-green on standing but then underwent no further change even after several weeks at room temperature. The spectra, which are described in detail below, indicate that all solutions contained a mixture of methylammonium salts of the methylimidopentafluorotungstate (VI) and the μ-fluorobis (methylimidotetrafluorotungstate)(VI) anions, WF_5NMe^- and $W_2F_9(NMe)_2^-$. The relative concentrations of the anions depended on the past history of the sample. Reactions which had given yellow-green solids had greater amounts of $W_2F_9(NMe)_2^-$ in solution.

The ^{1}H n.m.r. spectra of the solutions contained broad peaks at $\delta^{1}H$ = 5.50 p.p.m. and 2.51 p.p.m. One sample also showed a very broad 1:1:1 triplet at $\delta^{1}H$ = 7.20 p.p.m., separation J = 52Hz. The broad peak at $\delta^{1}H$ = 2.51 p.p.m. and the triplet at $\delta^{1}H$ = 7.20 p.p.m. were assigned to the methylammonium cation. The ^{1}H spectrum of an authentic sample of methylammonium chloride dissolved in dilute, aqueous hydrochloric acid contained the triplet at $\delta^{1}H$ = 7.60 p.p.m., $^{1}J(^{1}H - {}^{14}N)$ = 50 Hz., and a quartet at $\delta^{1}H$ = 2.93 p.p.m., $^{3}J(^{1}H - {}^{1}H)$ = 6 Hz. The literature values are $\delta^{1}H$ = 2.66 and 7.39 p.p.m. and $^{1}J(^{1}H - {}^{14}N)$ = 54 Hz. (173).

The broad singlet at $\delta^{1}H$ = 5.50 p.p.m. was assigned to the methylimido group of the anion, WF_5NMe^-. $^{1}H - \{^{19}F\}$ Spin decoupling had no visible effect on this peak. $^{1}H - \{^{14}N\}$ Decoupling sharpened the peak, but no fine structure could be resolved except for tungsten satellites, $^{3}J(^{1}H - ^{183}W) = 10$ Hz. A $^{1}H - \{^{14}N\}$ spin decoupling experiment on the satellites showed that $^{3}J(^{1}H - ^{183}W)$ was of opposite sign to $^{1}J(^{14}N - ^{183}W)$. $^{1}H - \{^{14}N\}$ Spin decoupling of the main peak demonstrated that $\delta^{14}N = -1.2$ p.p.m., and that $^{4}J(^{1}H - ^{19}F_t)$ and $^{2}J(^{14}N - ^{19}F_t)$ were of the same sign. The magnitude of $^{4}J(^{1}H - ^{19}F)$ was approximately 1 Hz. Most samples contained two additional broad peaks in the ^{1}H n.m.r. which were a broad singlet at $\delta^{1}H = 4.82$ p.p.m. and a much weaker singlet at $\delta^{1}H = 5.10$ p.p.m. The former peak was assigned to the methylimido group of the dimeric anion, $W_2F_9(NMe)_2^-$. $^{1}H - \{^{19}F\}$ and $^{1}H - \{^{14}N\}$ spin decoupling experiments were without visible effect on either peak.

All ^{19}F n.m.r. spectra contained a doublet at $\delta^{19}F = 28.0$ p.p.m. and a complex peak at $\delta^{19}F = -101.5$ p.p.m. These peaks were assigned to the cis and trans ^{19}F nuclei, F_c and F_t, of the anion WF_5NMe^- respectively. The doublet and its tungsten satellites were studied by ^{19}F homonuclear decoupling experiments. These gave $^{1}J(^{19}F_t - ^{183}W) = \mp 36$ Hz., $^{1}J(^{19}F - ^{183}W) = \pm 47$ Hz. and $^{2}J(^{19}F_c - ^{19}F_t) = 60$ Hz. They also confirmed the chemical shift of the fluorine, which was responsible for the doublet, at $\delta^{19}F = -101.5$ p.p.m. $^{19}F - \{^{14}N\}$ spin decoupling experiments gave $^{2}J(^{14}N - ^{19}F_t) = \pm 40$ Hz. and $^{1}J(^{14}N - ^{183}W) = \pm 70$ Hz. and confirmed $\delta^{14}N = -1.2$ p.p.m., and a $^{19}F - \{^{183}W\}$ spin decoupling experiment gave

$\delta\,^{183}W$ = +520 ±10 p.p.m.

The complex peak at $\delta\,^{19}F$ = -101.5 p.p.m. was simplified to a 1:4:6:4:1 quintet by high power, noise modulated $^{19}F - \{^{14}N\}$ spin decoupling. The complex peak was consistent with the coupling constants, $^{2}J(^{19}F_{c} - {}^{19}F_{t})$ = 60 Hz. and $^{2}J(^{14}N - {}^{19}F_{t})$ = 40 Hz. (see Figure 2:15).

Most samples contained a further doublet at $\delta\,^{19}F$ = 35.7 p.p.m. and a complex peak at $\delta\,^{19}F$ = -127 p.p.m. The association of these two signals was confirmed by ^{19}F homonuclear decoupling. The doublet and its tungsten satellites gave $^{2}J(^{19}F_{c} - {}^{19}F_{t})$ = 60 Hz. and $^{1}J(^{19}F_{c} - {}^{183}W)$ = 47 Hz. The tungsten satellites of the doublet were broad and $^{19}F - \{^{1}H\}$ produced very slight sharpening (see Figure 2:18). They were consistent with being broad quintets where $^{4}J(^{19}F_{c} - {}^{19}F_{c}{}^{1})$ = ca. 1 Hz. The complex signal was consistent to a single fluorine being coupled to eight equivalent fluorine and two equivalent nitrogen nuclei with $^{2}J(^{19}F_{c} - {}^{19}F_{t})$ = 60 Hz. and $^{2}J(^{14}N - {}^{19}F_{t})$ = 34 Hz. 32 Of the expected 45 lines were observed (see Figure 2: 19).

(xx) The reaction of tungsten hexafluoride with trimethylamine.

This reaction was carried out using a procedure similar to that described for the other amines. The product was an off-white powder characterized as a 1:1 tungsten pentafluoride trimethylamine adduct.

Found: C10.55, H3.00, F28.21, N4.28, W54.08%. $C_3H_9F_5NW$ requires: C10.65, H2.66, F28.10, N4.14 and W54.43%.

The solid dissolved in CD_3CN to give a very deep brown-red solution. No signals were observed in the ^{19}F n.m.r. spectrum of this solution. The ^{1}H n.m.r. spectrum contained weak, fairly broad peaks at $\delta^{1}H = 7.15$ and 6.90 p.p.m. and stronger sharper peaks at $\delta^{1}H = 3.36$ and 3.10 p.p.m. A stronger sharp peak was observed at $\delta^{1}H = 2.67$ p.p.m. This last peak was assigned to coordinated trimethylamine. The others were not assigned. The literature value for free trimethylamine is $\delta^{1}H = 2.12$ p.p.m. (174).

(xxi) The reaction of methoxytungsten (VI) pentafluoride with N-methyl hexamethyldisilazane.

N-methyl hexamethyldisilazane (0.483 g., 2.77 mmol) was condensed on to methoxytungsten (VI) pentafluoride (0.7306g, 2.36 mmol). The mixture was allowed to warm slowly to 0° C at which point the mixture was pale yellow. At room temperature an orange brown viscous liquid formed. The volatile materials (0.4908g) were removed and these were identified by gas i.r. spectroscopy as a mixture of Me_3SiF and MeF. (175).

Data for the low resolution mass spectrum of the involatile product are shown in table 2:22 with the assignments made.

The i.r. spectrum of the involatile product contained the following peaks: 3260 s., 3018 w., 2950 m., 1650 w.br., 1585 w.br., 1484 w. sh ., 1452 s. sh ., 1435 s., 1420 s. sh., 1415 s. sh., 1333 s., 1291 w., 1248 m., 1151 s., 1084 s. br., 1014 s. br., 950 m., 926 w., 889 w., 822 w., 701 s., 648 s. br., 600 s. br., 458 m., 415 m. cm^{-1}.

The product was insoluble in both ethyl acetate and perfluorotoluene, therefore its n.m.r. spectra were obtained from the neat oil. The ^{19}F n.m.r. spectrum contained a very broad signal at $\delta^{19}F = 65$ p.p.m., width at half height = 280 Hz. There were major peaks within

TABLE 2:22

LOW RESOLUTION MASS SPECTRUM OF THE INVOLATILE PRODUCT FROM REACTION (xxi).

Peak m/e[1]	relative intensity	Assignment[2]
333	2	$WF_3(OMe)_3^+(-H)$
321	11	$WF_4(OMe)_2^+(-H)$
315	5	$WF_2(OMe)_3^+$
314	3	$WF_2(OMe)_3^+(-H)$
303	25	
291	19	
287	112	$WF_4NMe^+(-2H)$
272	17	
269	100	$WF_3NMe^+(-H)$
257	511	WOF_3^+

Further degradation peaks of WOF_3^+ are seen.

[1] All the peaks show the characteristic tungsten isotope pattern.

[2] ^{184}W

the broad signal, a singlet at $\delta^{19}F = 66$ p.p.m. and a doublet at $\delta^{19}F = 60.5$ p.p.m. J = 60 Hz. were distinguished. The singlet was assigned to a tungsten (VI) oxide tetrafluoride complex and the doublet to the μ-fluorobis (oxotetrafluorotungstate)(VI) anion, $W_2O_2F_9^-$. The literature values for the anion are $\delta^{19}F = 62.6$ p.p.m. and $^2J(^{19}F_c - {}^{19}F_t) = 59$ Hz. (109). A further broad signal was observed at $\delta^{19}F = 38$ p.p.m., width at half height = 150 Hz which was assigned to a methylimidotungsten (VI) tetrafluoride species.

The ^1H n.m.r. spectrum contained fairly broad signals at $\delta^1H = 5.98$, 5.85, 4.50, 4.30, 4.02, 3.83, 3.70 and 3.20 p.p.m.

The peaks at $\delta^1H = 4.50$ and 4.02 p.p.m., and at $\delta^1H = 4.30$ and 3.83 p.p.m. appeared to be doublets with J = 28 Hz. None of these peaks could be assigned. A strong peak at $\delta^1H = 5.53$ p.p.m. was tentatively assigned to the methyl protons of a methylimidotungsten (VI) tetrafluoride complex.

(xxii) The reaction of methoxytungsten (VI) pentafluoride with N-methyl hexamethyldisilazane in ethyl acetate.

N-methylhexamethyldisilazane was condensed on to a slight excess (>1:1 molar) of methoxytungsten (VI) pentafluoride in a large excess (>10:1 molar) of ethyl acetate. The mixture was allowed to warm slowly to room temperature. The products were a golden brown solution and a yellow-brown very viscous liquid. When the volatile material was removed from the solution a golden-brown oil was left behind. The volatile material was identified by gas i.r. spectroscopy as a mixture of solvent, Me_3SiF and MeF.

The analysis of the soluble golden-brown oil gave: C18.44, H3.59, F14.85, N3.41, W47.52%.

The low resolution and high resolution mass spectral data for the soluble golden-brown oil are shown in Tables 2:23 and 2:24. The low resolution mass spectral data for the insoluble product is given in Table 2:25.

The ^1H and ^{19}F n.m.r. spectra of the soluble species were recorded in a solution in ethyl acetate. The ^1H n.m.r. spectrum was complex. Two peaks at $\delta^1H = 5.58$ and 5.49 p.p.m. were assigned to the protons in the methylimido groups of $WF_4NMe(L)$ complexes. $^1H - \{^{14}N\}$ Spin decoupling sharpened both peaks but fine structure could not be resolved. $^1H - \{^{19}F\}$ Spin decoupling sharpened the peaks and fine structure could be resolved giving in both cases $^2J(^1H - ^{14}N) = 2.4$ Hz. A series of broad or complex peaks were observed at $\delta^1H = 5.22, 4.97, 4.90, 4.84, 4.77$ and 4.60 p.p.m. These are consistent with higher substituted methoxytungsten (VI) fluorides, but it was not possible to assign each individually. ^1H Resonances for the compounds $WF_{6-n}(OMe)_n$ occur in the range $\delta\,^1H = 5.9$ to 4.8 p.p.m. (131). A very weak doublet assigned to trimethylsilyl fluoride was observed at high field.

The ^{19}F n.m.r. spectrum contained a singlet at $\delta^{19}F = 37.0$ p.p.m. with tungsten satellites, $^1J(^{19}F - ^{183}W) = 42$ Hz. The peak was assigned to a WF_4NMe, L complex. A doublet, about half the intensity of the singlet peak, was observed at $\delta^{19}F = 35.5$ p.p.m. Its separation, 58 Hz., was characteristic of a $^{19}F - ^{19}F$ coupling in a cis-WF_2 group and it contained ^{183}W satellite peaks,

TABLE 2:23

LOW RESOLUTION MASS SPECTRUM OF REACTION (xxii) SOLUBLE PRODUCT.

Peak m/e[1]	relative intensity	Assignment[2]
345	3	
333	13	$WF_3(OMe)_3^+(-H)$
315	41	
303	53	
284	35	
281	39	
269	100	$WF_3NMe^+(-H)$
257	42	WOF_3^+
238	20	WOF_2^+

[1] All peaks show characteristic tungsten isotope pattern.

[2] ^{184}W

TABLE 2:24

HIGH RESOLUTION MASS SPECTRUM OF REACTION (xxii) SOLUBLE PRODUCT.

m/e found	m/e calculated	Assignment
332.99353	332.99354	$^{184}WF_3(OMe)_3^+(-H)$

TABLE 2:25

LOW RESOLUTION MASS SPECTRUM OF INSOLUBLE PRODUCT FROM REACTION (xxii).

Peak m/e[1]	Relative intensity	Assignment[2]
313	2	$WF_2(OMe)_3(-2H)^+$
299	25	$WF_2(O)(OMe)_2(-H)^+$
287	28	$WF_3(O)(OMe)(-H)^+$
281	22	$WF(O)(OMe)_2^+$
280	25	$WF(O)(OMe)_2(-H)^+$
269	100	$WF_3NMe(-H)^+WF_2(O)(OMe)^+$
257	71	WOF_3^+
238	4	WOF_2^+

---

[1] All peaks show characteristic tungsten isotope pattern.

[2] ^{184}W

$^{1}J(^{19}F - ^{183}W) = 47$ Hz. This peak was assigned to the two cis fluorines of mer - $WF_3(OMe)_3$. The literature values for mer - $WF_3(OMe)_3$ are $\delta^{19}F = 35.0$ p.p.m., $^{2}J(^{19}F_c - ^{19}F_t) = 60$ Hz. and $^{1}J(^{19}F - ^{183}W) = 45$ Hz. (98). A singlet peak was observed at $\delta^{19}F = 17.0$ p.p.m. and this was assigned to fac - $WF_3(OMe)_3$. The literature value for fac - $WF_3(OMe)_3$ is $\delta^{19}F = 17.7$ p.p.m. (50). A very complex group of peaks were observed at $\delta^{19}F = 0 - 5$ p.p.m., and these were not assigned.

CHAPTER 3

FURTHER DISCUSSION ON THE N.M.R. RESULTS

I. INTRODUCTION

In this work high resolution nuclear magnetic resonance spectroscopy has been used extensively to investigate the structures of the compounds prepared. Some aspects, eg. nuclear quadrupole broadening, have already been discussed in Chapter 2. In this chapter some of the basic theory and techniques used will be described and some of the results of a more comparative character will be discussed.

High resolution nuclear magnetic resonance (n.m.r.) spectroscopy has been used by chemists as an aid to the study of molecular structure and reaction mechanisms for about 25 years. Atomic nuclei may possess a spin defined by the nuclear spin quantum number I. This idea was originally put forward by Pauli (176) to explain some of the details of hyperfine structure found in optical atomic spectra. Depending on the particular isotope, I may have the values, 0, 1, 3/2, ... For nuclei having I values other than zero, rotation of the electrically charged nucleus gives rise to a magnetic moment If an external magnetic field, Bo, is applied to a system of nuclei with magnetic moments, then the different orientations of the nuclei have different energies:

(i) $$E = -\frac{m \mu B_o}{I}$$

where m may have the values I, I-1, ...-(I-1). The separation between successive energy levels is:-

(ii) $$\Delta E = \frac{\mu B_o}{I}$$

The allowed transitions between the different energy levels are for m = ±1. Radiation of the appropriate frequency can cause transitions between levels. Since $E = hv$, this can be expressed by the equation below:-

$$\text{(iii)} \quad v = \frac{\mu \, Bo}{Ih}$$

The magnetic moment and angular momentum behave as if they were parallel or anti-parallel vectors. It is convenient to define a ratio between them which is called the magnetogyric ratio, γ , where

$$\text{(iv)} \quad \gamma = \frac{2\pi}{h} \cdot \frac{\mu}{I}$$

γ Has a characteristic value for each magnetically active nucleus and is positive for parallel and negative for anti-parallel vectors. Incorporating the magnetogyric ratio, equation (iii) becomes:-

$$\text{(v)} \quad v = \frac{\gamma Bo}{2\pi}$$

The values of I depend on the spin alignments of the protons and neutrons within the nucleus. There are three important consequences of this:

(a) All even-even nuclei have $I = 0$.

(b) All even-odd and odd-even have $I = \frac{2n-1}{2}$ where $n = 1, 2, 3......$

(c) All odd-odd nuclei have $I = n$ where $n = 1, 2, 3.....$

If $I > 1/2$ the nucleus possesses an electric quadrupole moment, Q. This means that the distribution of charge in the nucleus is non-spherical and that it can interact with electric field gradients arising from the electric charge distribution within the molecule. This interaction provides a means by which the nucleus can exchange energy with the molecule in which it is situated. Some of the consequences of this have already been described in Chapter 2.

In this work the nuclei, ^{1}H, ^{14}N, ^{19}F, ^{31}P and ^{183}W have been used as n.m.r. probes. The n.m.r. properties of these nuclei are shown in Table 3:1. Chemical and structural information has been deduced from three n.m.r. phenomena, (a) chemical shift (b) spin-spin coupling and (c) quadrupole relaxation.

The general texts consulted in this work are given in the reference section (179, 180, 181). In addition, a recent review by Harris (178) on some of the less common nuclei, and a review by Witanowski and Webb on nitrogen n.m.r. spectroscopy (182) have also been consulted.

TABLE 3:1

THE N.M.R. PROPERTIES OF SOME NUCLEI (177, 178).

Nucleus	Natural abundance %	Spin I	Magnetic moment nuclear magnetons	n.m.r. frequency MHz.[1]	Relative receptivity[2]	Quadrupole moment $Q/10^{-28}m^2$
^{1}H	99.98	½	2.79268	100.000	1.000	0
^{14}N	99.63	1	0.40347	7.224	1×10^{-3}	1.6×10^{-2}
^{19}F	100.0	½	2.62727	94.077	0.8328	0
^{31}P	100.00	½	1.1305	40.481	0.0663	0
^{183}W	14.4	½	0.116205	4.161	1.04×10^{-5}	0

[1] At a field of 23 K.Gauss (23T); [2] At constant magnetic field; relative to receptivity of a proton. The receptivity is defined here as $\gamma^3 N\ (I+1)$.

II. SIGNAL TO NOISE ENHANCEMENT

The equipment used for obtaining the n.m.r. spectra has already been described. A significant improvement in ^{19}F n.m.r. spectra from the 60MHz spectrometer was obtained by the use of filtering in combination with very slow sweep times. This is due to the following reasons.

The output of an n.m.r. spectrometer consists of random noises at all frequencies and a slowly varying d.c. voltage which is the signal. A degree of separation can be achieved by using a resistor capacitor network. The RC network will offer a high impedance to high frequencies (depending on the RC time constant), and hence remove much of the noise. If the signal voltage is varying too fast, however, the RC network can distort the signal and decrease the resolution and, therefore, a high RC time constant must be used in conjunction with a very slow scan speed. For example, the spectrum of the trans fluorine in the methylimidopentafluorotungstate anion, WF_5NMe^-, was recorded with an RC time constant of 10 sec. and a scan speed of 0.007 cm/sec. For an 18 p.p.m. scan, this corresponded to a scan speed of 0.2Hz/sec.

A drawback of this technique is that the r.f. irradiating power must be reduced because the slow passage increases saturation effects. The saturation effects are caused by the depletion of the excess nuclei in the low energy state with regard to the high energy state, i.e. population levels of the two energy states are being equalized.

(III) MAGNETIC DOUBLE RESONANCE.

The normal effect of applying a sufficiently strong second r.f. field at the resonance frequency of one nucleus in a spin system is to remove the coupling to other nuclei, whose resonances are consequently simplified. The irradiation induces rapid transitions between the spin states of the first nucleus. As a result the information which is normally transmitted to the other nuclei about these spin states is lost.

In most modern spectrometers an audio side-band mode of operation is used in which the central radio frequency (60 or 100 MHz.) is modulated by a frequency of a few kilohertz. This generates an r.f. energy spectrum consisting of the centreband together with two sidebands at the audio frequency, and one of these is used to record the normal n.m.r. spectrum. This technique is adopted because it makes the achievement of a stable base-line easier.

Homonuclear double resonance experiments can be performed by simply adding a second audio-frequency oscillator.

In the present work, the $^{19}F - \{^{19}F\}$ experiments were carried out on the Varian XL100 spectrometer in this way.

Heteronuclear decoupling experiments are normally carried out by using a second r.f. generator. Heteronuclear decoupling provides a valuable route for obtaining the chemical shifts of nuclei which are of low sensitivity to detection, provided they are coupled to an ^{1}H or an ^{19}F nucleus. The detection takes place at the ^{1}H or ^{19}F frequencies and hence the sensitivity is correspondingly high. In this work the chemical shifts of ^{14}N, ^{31}P and ^{183}W nuclei have been obtained by this method.

The precision of obtaining chemical shifts is improved by the spin tickling technique. The nucleus is irradiated with very low r.f. power. This does not collapse the observed signal but it does perturb it and hence the decoupling frequency can be measured very accurately. The observed signal will be perturbed each time the frequency coincides with a line in the irradiated nucleus' spectrum. The degree of perturbation depends on the intensity of the line in the irradiated nucleus' spectrum. By fixing the main frequency on to a transition in the spectrum of the observed nucleus and sweeping through the decoupling frequencies, the spectrum of the decoupled nucleus may be recorded. This is known as inter-nuclear double resonance spectroscopy (INDOR). In the present work the homonuclear INDOR spectrum of the trans-fluorine in $^{183}WF_5NMe^-$ was obtained, by observing the two outer ^{183}W satellites of the cis-fluorines and sweeping the trans fluorine frequency. The signal/noise ratio was relatively poor, and progressive and regressive effects complicated the intensity relationships, but the spectra enabled $^1J(^{19}F_t - {}^{183}W)$ to be measured fairly accurately.

Spin tickling is of special value for the determination of the relative signs of coupling constants. Absolute signs of coupling constants cannot be determined by this method, since the relative signs obtained are invariant with respect to the reversal of all the signs in the molecule.

The method has been used for measuring the relative signs of coupling constants in the present study as is illustrated for the compound $WF_3(OMe)(NMe)\left[(MeO)_2P(O)Me\right]$. The structure of this compound is shown in Figure 3:1. The ^1H n.m.r. spectrum of the methoxy group attached to the tungsten atom is shown in Figure 3:2.

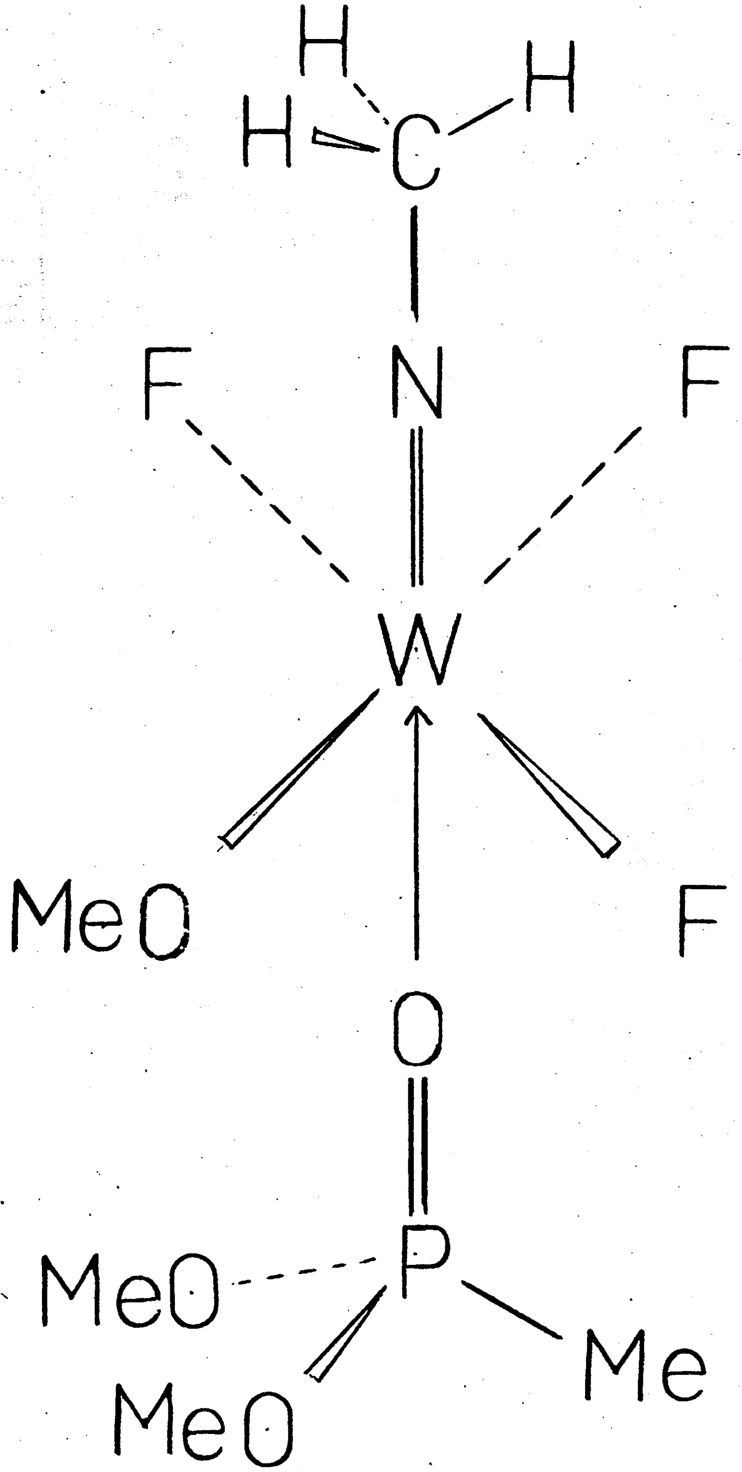
The protons of the -OMe group are coupled to two types of ^{19}F nuclei. Two equivalent ^{19}F nuclei are cis to the -OMe group and one ^{19}F nucleus is trans. The ^{19}F n.m.r. spectrum which consists of an AB_2 spectrum has been shown earlier (see Chapter 2, Figure 2:9).

In spectra (c) and (d) of Figure 3:2 the sample has been irradiated with low r.f. power at the high field (low frequency) and low field (high frequency) sides respectively of the F_t triplet. Irradiation at the high field side of the F_t triplet results in the collapse of the high field doublet in the -OMe spectrum and irradiation at the low field side results in the collapse of the low field doublet in the -OMe spectrum. This indicates that $^4J(^1H - {}^{19}F_t) / {}^1J(^{19}F_c - {}^{19}F_t) > 0$ i.e. $^4J(^1H-{}^{19}F_t)$ and $^1J(^{19}F_c - {}^{19}F_t)$ are of the same sign. Spectrum (b) of Figure 3:2 shows the trace obtained when the decoupling frequency corresponds to the position of the central peak of the F_t triplet, this gives no information about the relative signs of the coupling constants.

Spectra (e) and (f) of Figure 3:2 are recorded when the decoupling frequency is at the high field (low frequency) side of the F_c doublet and at the low field (high frequency) side of the F_c doublet respectively. In this case it is the high field triplet (e) and the low field triplet (f) which are collapsed. This indicates that

Figure 3:1

The Structure of $WF_3(OMe)(NMe)$ [$(MeO)_2P(O)Me$]



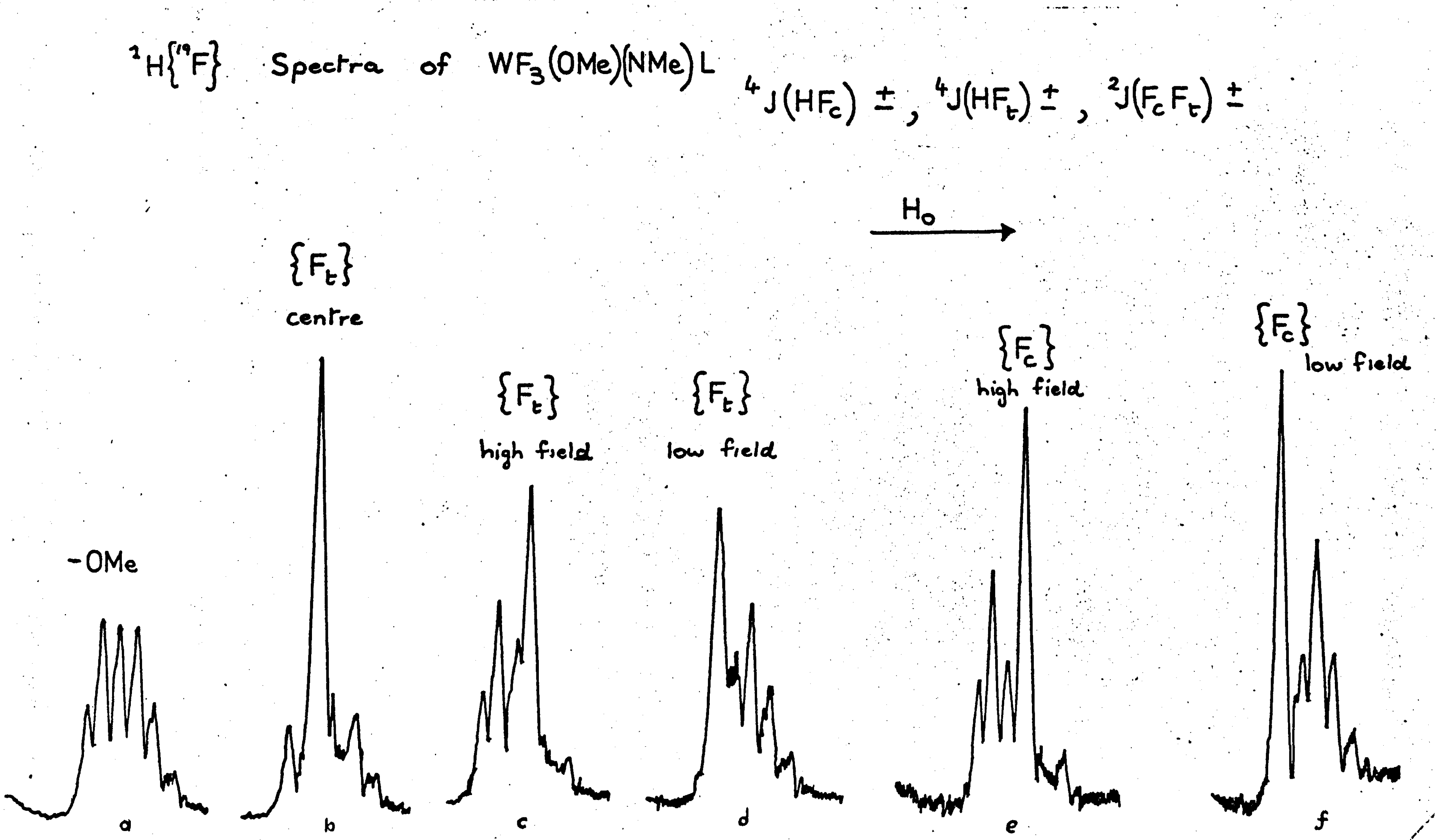


Figure 3:2

The ^1H n.m.r. spectra of the WOMe group in $WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$ at different ^{19}F decoupling frequencies.

${}^4J({}^1H - {}^{19}F_c)$ and ${}^2J({}^{19}F_c - {}^{19}F_t)$ are of the same sign.

By coupling these two results it can be stated that ${}^4J({}^1H - {}^{19}F_c)$ and ${}^4J({}^1H - {}^{19}F_t)$ are of the same sign.

Magnetic double resonance experiments can also be used to measure the coupling constant between two nuclei, which cannot be directly observed. The technique was utilized to measure ${}^2J({}^{14}N - {}^{19}F)$ in $WF_4NMe(L)$ compounds ($L = (MeO)_2SO$, EtOAc and MeCN) since ${}^{19}F$ n.m.r. spectroscopy did not resolve this coupling. Figure 3:3 shows the ${}^1H$ n.m.r. spectra due to the -NMe group and (ii), (iii) and (iv) recorded at different r.f. decoupling frequencies of very low power. These spectra were recorded in the field sweep mode at 60 MHz. The ${}^{19}F$ n.m.r. spectrum should be a 1:1:1 triplet (neglecting ${}^1H - {}^{19}F$ spin couplings) and hence the apparent value of ${}^2J({}^{14}N - {}^{19}F)$ is 4 Hz. This is not the real coupling constant, since the field sweep mode was used.

The ${}^1H$ and ${}^{19}F$ n.m.r. spectra are shown schematically in Figure 3:4, with the relative value of the ${}^4J({}^1H - {}^{19}F)$ coupling constants reduced for clarity. (A), (B) and (C) are the three peaks in the ${}^1H$ n.m.r. spectrum and (1), (2) and (3) are the three peaks in the ${}^{19}F$ n.m.r. spectrum. (A) is observed and is decoupled by r.f. irradiation at (3) the value of which is 56, 454, 440 Hz. (C) is decoupled by r.f. irradiation at (1) the value of which is 56, 454, 448 Hz. Thus the apparent value of $2 \times {}^2J({}^{14}N - {}^{19}F)$ is 8.0 Hz. However at (C) the field strength is 0.093 p.p.m. higher than it is at (A). To decouple (A) at this field strength requires a frequency at (3) which is 0.093 p.p.m. higher than is (A). Therefore the

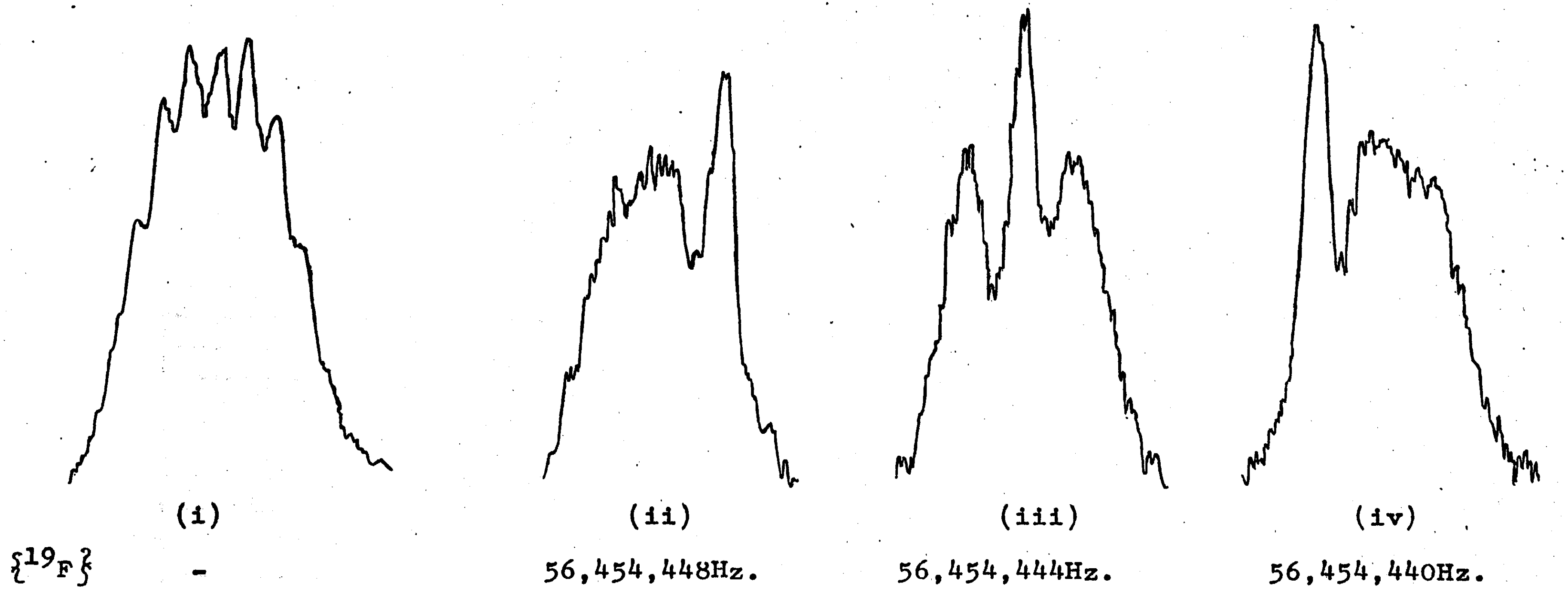
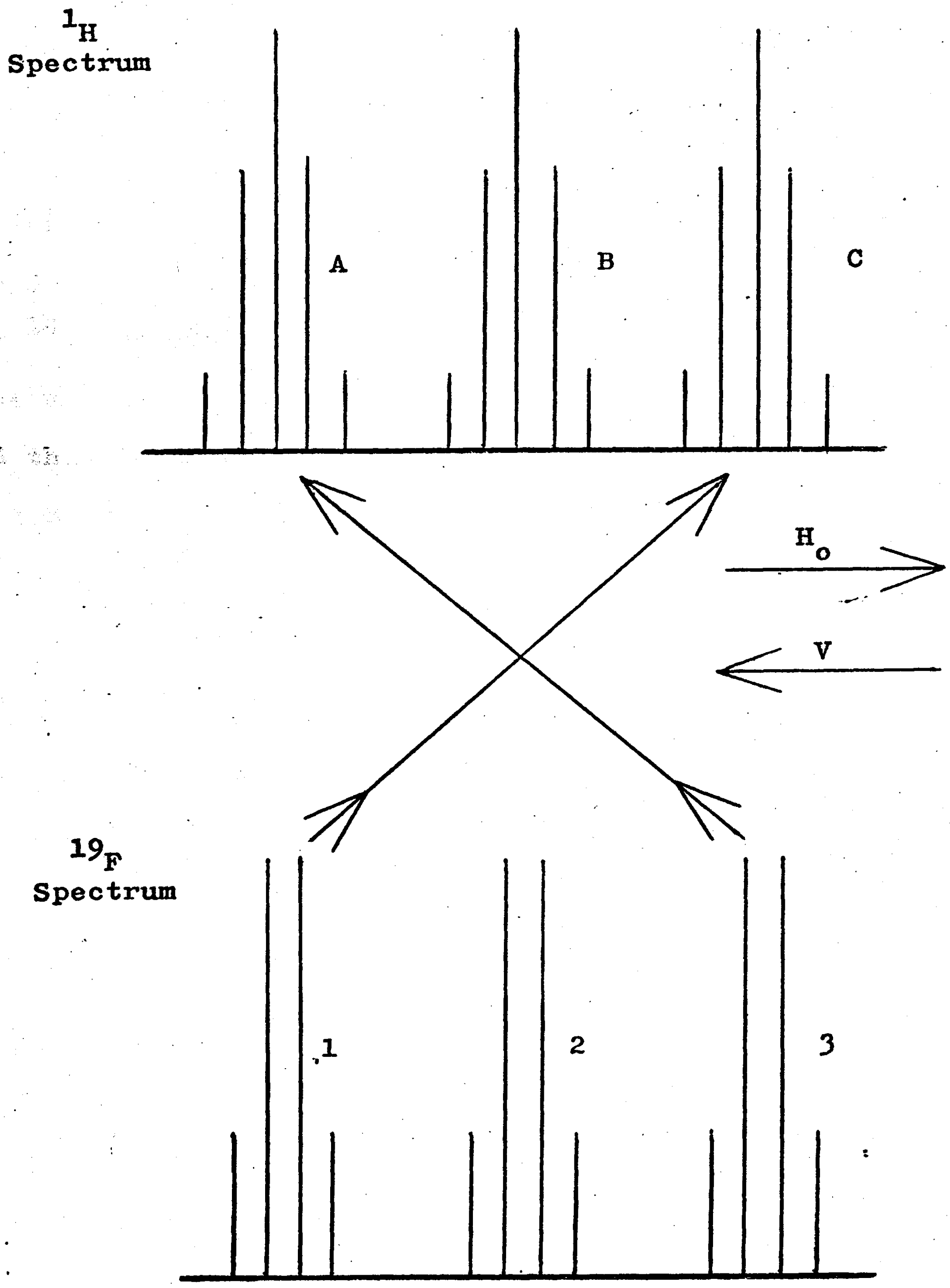


Figure 3:3

^{1}H N.m.r. spectra of the -NMe group in WF_4NMe $(MeO)_2SO$ at different $\{^{19}F\}$ decoupling frequencies.

Figure 3:4

The ^{1}H and ^{19}F n.m.r. spectra of $WF_4NMe(L)$ shown diagrammatically.



decoupling frequency is 5.3 Hz. higher than it would be if the field strength had remained constant. From an apparent value for $2 \times {}^{2}J({}^{14}N - {}^{19}F) = 8.0$ Hz., 5.3 Hz. must be subtracted to give the actual value. The result is $2 \times {}^{2}J({}^{14}N - {}^{19}F) = 2.7$ Hz. and hence ${}^{2}J({}^{14}N - {}^{19}F) =$ 1.3 Hz. The error in this result is probably very small and no more than ±0.1 Hz. This experiment demonstrates that ${}^{2}J({}^{1}H - {}^{14}N)$ and ${}^{2}J({}^{14}N - {}^{19}F)$ are of opposite sign.

The same situation should occur for the ${}^{1}H - \{{}^{14}N\}$ experiments on the same compounds, however in this case 0.093 p.p.m. is equivalent to a change of only 0.4 Hz. in the ${}^{14}N$ frequency. The apparent ${}^{2}J({}^{14}N - {}^{19}F)$ in this case should be 1.7 Hz. based on a real value of 1.3 Hz. and this is in good agreement with the experimental value of 1.8 Hz.

IV. CHEMICAL SHIFTS

The chemical shift of a nucleus is dependent upon its nuclear screening parameter. The general expression for the nuclear screening parameter for a nucleus A may be divided into diamagnetic, paramagnetic and long range terms.

$$\sigma_A = \sigma_A^{dia} + \sigma_A^{para} + \sum_B \sigma_{AB} \quad - (1)$$

(183, 184, 185). It is generally accepted that the chemical shifts of all but the lightest nuclei are dominated by the paramagnetic contribution to the nuclear screening parameter (186). This can be expressed by a relation of the type (187);

$$\sigma_A^{para} = - \frac{Q}{DE} \quad \underline{\qquad\qquad} \quad (2)$$

Q depends on the electronic imbalance in the valence orbitals. In general as the effective electronegativity of attached atoms or groups increases, so Q tends to increase and the resonance moves to lower field. DE is the energy of electronic excitation to a state of the correct symmetry to be mixed with the ground state by the magnetic field. The latter parameter is relatively constant in a series of closely related compounds except when a transition metal is involved. For a transition metal variations in DE may be dominant, the ^{59}Co chemical shifts of a series of compounds have been satisfactorily explained on this basis (188, 189). In compounds of the type $WF_4NMe(L)$ it is expected that the chemical shifts of both the ^{19}F and the ^{14}N nuclei are dominated by the Q term, whereas the ^{183}W chemical shifts are dominated by the DE term, since it is a transition metal. The chemical shifts of the ^{19}F and ^{14}N nuclei should thus depend on the effective electronegativity of the tungsten atoms.

In the series of compounds, $WF_{6-n}(OMe)_n$ (n = 0 - 5), the chemical shifts of the ^{19}F nuclei are nearly linearly related to the degree of substitution of the fluorines by the methoxy group (50).

The ^{19}F chemical shift in complexes of the type $WOF_4(L)$ have been studied (94). It was found that the ^{19}F chemical shift is almost linearly related to the donor strength of the ligand, L, as the donor strength increased then the ^{19}F chemical shift moved up field. The donor strengths given were those based on Gutmann (190).

Table 3:2 shows the ^{19}F chemical shifts of the $WF_4NMe(L)$ complexes studied in this work. The ^{19}F chemical shifts are those expected from the comparable work on the $WOF_4(L)$ complexes with the exception of the acetonitrile complex which occurs at a slightly higher field than expected. This relationship can be readily explained on the basis of the Q term being dominant. The weaker the donor, the higher is the effective electronegativity of the tungsten and hence the ^{19}F resonance is shifted to lower field.

In the alkylimidopentafluorotungstate (VI) anions, changes in the alkyl group do not significantly affect the chemical shift of either the cis or the trans fluorine nuclei.

The ^{14}N chemical shifts of $WF_4NMe(L)$ complexes are shown collated in Table 3:3. The ^{14}N values appear to

TABLE 3:2

THE ^{19}F CHEMICAL SHIFTS OF $WF_4NMe(L)$ COMPLEXES AND RELATED COMPOUNDS.

Complex	Spectral Type [a]	$\delta^{19}F$ p.p.m. [b]			Solvent
$WF_4NMe(MeCN)$	A_4	+37.2		(s)	$MeCN, CD_3CN$
$WF_4NMe[(MeO)_2SO]$	A_4	+38.7		(s)	$(MeO)_2SO$
$WF_4NMe(EtOAc)$	A_4	+38.3		(s)	EtOAc
$W_2F_9(NMe)_2^-$	A_8X	+35.7	(Fa)	(d)	$MeCN, CD_3CN$
		-127.4	(Fx)	(c)	
$WF_4NMe[(MeO)_2P(O)Me]$	A_4	+35.5		(s)	$(MeO)_2P(O)Me$
WF_5NMe^-	A_4X	+28.0	(Fa)	(d)	$MeCN, CD_3CN$
		-101.5	(Fx)	(c)	
WF_5NEt^-	A_4X	+27.6	(Fa)	(d)	CD_3CN
		-99.5	(Fx)	(c)	
$WF_5N^nBu^-$	A_4X	+28.7	(Fa)	(d)	CD_3CN
		-101.0	(Fx)	(q)	
$WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$	A_2B	-13.4	(Fa)	(d)	$(MeO)_2P(O)Me$
		-20.9	(Fb)	(t)	
cis $WF_2(OME)_2(NMe)[(MeO)_2P(O)Me]$	A_2	-58.3		(s)	$(MeO)_2P(O)Me$

(a) This neglects coupling to the protons.

(b) All referenced to CCl_3F internal, estimated error ±0.2 p.p.m.

TABLE 3:3

THE ^{14}N CHEMICAL SHIFTS OF $WF_4NMe(L)$ COMPLEXES AND RELATED COMPOUNDS.

Complex	Spectral Type[a]	$\delta^{14}N$ p.p.m.[b]	Solvent
$WF_4NMe(MeCN)$	A	+24.8	CD_3CN, MeCN
$WF_4NMe[(MeO)_2SO]$	A	+16.1	$(MeO)_2SO$
$WF_4NMe(EtOAc)$	A	+15.8	EtOAc
$WF_4NMe[(MeO)_2P(O)Me]$	A	+14.6	$(MeO)_2P(O)Me$
WF_5NMe^-	AM	-1.2	CD_3CN
$WF_3(OMe)(NMe)[(MeO)_2P(O)Me]$	A	-1.1	$(MeO)_2P(O)Me$

[a] This does not include coupling to the protons or the small $^2J(^{14}N-^{19}F_c)$ coupling.

[b] All referenced to NH_4^+ external (saturated NH_4NO_3 solution in dilute nitric acid) and then adjusted to NO_3^- as reference using the relationship $\delta^{14}N(NO_3^-) = \delta^{14}N(NH_4^+) - 353.5$ p.p.m. (170). Estimated error ±0.2 p.p.m.

be similarly dependent on the donor strength of the ligands. The ^{14}N chemical shift in the acetonitrile complex occurs at a surprisingly low field, opposite to the effect in the ^{19}F chemical shift. There are two possible explanations for the anomolous behaviour of the acetonitrile complex; (i) it is a solvent effect, (ii) the acetonitrile ligand has a different relative effect upon the equatorial and axial orbitals of the tungsten than the other ligands studied. The latter is a possibility, since acetonitrile is a radically different ligand from the others studied in the present work eg. on complexation the v ($C \equiv N$) of acetonitrile increases in energy whereas for dimethyl sulphite and ethyl acetate the v ($S = O$) and v ($C = O$)decrease in energy. If the latter is correct then it suggests a possible way of investigating the different bonding properties of ligands.

In the complex, $WF_3(OMe)(NMe)\left[(MeO)_2P(O)Me\right]$, the substitution of a fluorine by a methoxy group has a much more marked effect upon the ^{19}F chemical shifts than the ^{14}N chemical shift. The ^{19}F resonances are shifted to high field by about 50 p.p.m. from the unsubstituted complex, whereas the ^{14}N resonances are shifted only by about 16 p.p.m. to high field. The diagrams in Figure 2:10show that both the d_{xy} and d_{zx} orbitals of the tungsten are available for overlap with the p orbitals of the oxygen. If the oxygen p_z orbital is overlapping with the tungsten d_{zx}, then the effective electronegativity of the tungsten along the z-axis and the x-axis should be lowered, ie. with respect to the methylimido group and the trans-fluorine. This should result in a shift to higher field of the ^{14}N resonance of the methylimido group and the ^{19}F resonance of the trans-fluorine. If the oxygen p_y orbital is overlapping with the d_{xy} orbital then the effective electronegativity of the tungsten atom will be reduced along the x and the y axis. This should result in a shift upfield of the ^{19}F resonances of both the cis and the trans fluorines. The experimental chemical shifts suggest that the latter situation is dominant.

The analogous $WOF_3(OR)(L)$ system has been previously studied (109). The general structure of these compounds is shown in Figure 3:5. It has been observed that the chemical shift difference between the trans-fluorines and the cis-fluorines depends on the donor strength of the ligand L. In the complex, $WOF_3(OEt)(MeCN)$, the ^{19}F resonance of the cis-fluorines occurs upfield of the trans-fluorine resonance. This suggests very little $\pi(p_z - d_{xy})$ overlap and very strong $\pi(p_y - d_{xz})$ overlap.

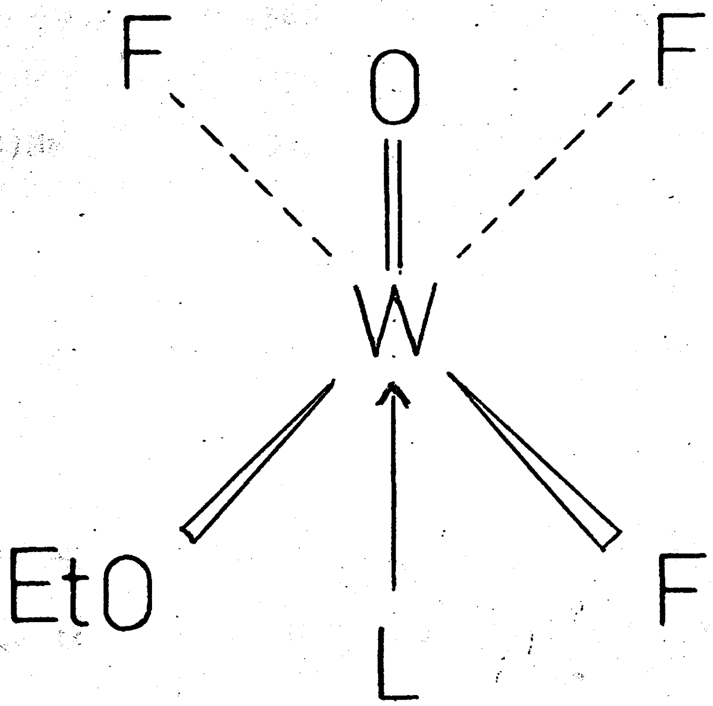
The ^{183}W chemical shift of the anion WF_5NMe^- has been obtained, and is given in Table 3:4, with some previously obtained values for ^{183}W chemical shifts.

The ^{183}W chemical shifts have been previously discussed (103). It was concluded that DE is the dominant term in equation (2) and that DE is small, resulting in a non-linear relationship.

It has been observed (103), that increasing methoxy substitution in the series $WF_{6-n}(OMe)_n$ results in a shift downfield for the ^{183}W resonances, and this trend is explained by the overlap of the unused 2p orbitals of the oxygen with the $5d_{xy}$, $5d_{yz}$ and $5d_{xz}$ orbitals of the tungsten, which leads to a suitable excited state of low energy. The extent of this interaction with the 2p

Figure 3:5

The structure of $WF_3(OEt)(L)$ complexes after Buslaev et al (109).



L = EtOH or MeCN.

TABLE 3:4

SOME ^{183}W CHEMICAL SHIFTS.

Compound	$\delta(^{183}W)$p.p.m.[a]	Reference
WF_6	0	103
WF_5OMe	+41	"
cis $WF_4(OMe)_2$	+160	"
mer$WF_3(OMe)_3$	+464	"
cis $WF_2(OMe)_4$	+604	"
WOF_4,OMe_2	+566	"
$WOF_4,(Me)_2SO$	+533	"
$WOF_4,(MeO)_2P(O)Me$	+529	"
WOF_5^-	+605	"
WF_5NMe^-	+520	This work*
$W_2O_2F_9^-$	+617	103

[a] Using WF_6 as an external reference.

* I would like to thank W. McFarlane for making this measurement.

orbitals of fluorine would be less and so DE should be larger in the more fully fluorinated derivatives.

In the present work the infra-red evidence (see Chapter 2 Section X) has suggested that the tungsten-nitrogen and tungsten-oxygen bonds have very similar strengths for compounds of the type, $WF_4X(L)$. The ^1H n.m.r. evidence for a linear C - N = W skeleton suggests a large degree of overlap of the 2p orbitals on the nitrogen with the $5d_{xy}$ and $5d_{zy}$ orbitals on the tungsten. The difference in the ^{183}W chemical shifts on going from WF_5NMe^- to $WOF_5^=$ is thus rather surprising, but it is, however, in the direction expected if Q is the dominant term. For these two anions, therefore, it appears that the electronic structure is similar enough for the ^{183}W chemical shift to be dominated by the electronegativity of the attached groups rather than changes in the excitation energy.

(V) SPIN-SPIN COUPLING CONSTANTS

If a pair of nuclei with spin $I \geq \frac{1}{2}$ are placed in proximity to each other their spins may be coupled, that is they may interact so that different combinations of the allowed spin states differ in total energy. There are several mechanisms by which nuclear spins may be coupled, and those which arise when the nuclei are connected by a sequence of chemical bonds are of the greatest interest to chemists. The degree of coupling is measured by the coupling constant J (in Hertz). The value of the coupling constant is independent of the field strength. The interaction between a pair of coupled nuclei may be positive or negative, that is the state of lower energy may be the state with the spins anti-parallel or it may be the state with the spins parallel, and which is of the lower energy determines the sign of the coupling constant. If the relative chemical shift of two coupled nuclei is of similar magnitude to their coupling constant, then a second order spectrum is obtained, the effects due to spin coupling and chemical shift have similar energy and become intermingled, leading to alterations in relative line intensities and in line positions. At high enough field strengths it should be possible to remove any second order effect, since chemical shift increases with field strength. In practice this is not always possible and various ways of analysing second order spectra have been developed (180, 181). Second order spectra can also contain extra information, for example the relative signs of the coupling constants. In this work only a relatively simple AB_2 spectrum has been encountered (see Chapter 2, Section VI).

Various calculations have shown that nuclear spin-spin coupling between directly bound elements should be dominated by the Fermi contact interaction unless this happens to be very small (191, 192). The Fermi contact interaction depends on the magnitude of the valence electron density at the nucleus. Since the s-orbitals are the only orbitals to have contact with the nucleus, the Fermi contact interaction will depend on the s character of the bond. There is also a dependence on the s-overlap integral which can lead to coupling constants of either sign. The reduced coupling constant, is defined in order to eliminate dependence on individual nuclear properties.

$$K_{AB} = \frac{2\,J_{AB}}{\hbar\gamma_A\gamma_B} \qquad \text{— (1)}$$

All known $^{1}K(^{19}F - M)$ coupling constants whose signs have been determined are negative but not all known $^{1}J(^{19}F - M)$ are negative. The reduced coupling constant involves the magnetogyric ratio, γ , which can be negative eg. for ^{15}N, ^{29}Si, ^{119}Sn and ^{125}Te. Therefore if one nucleus has a positive magnetogyric ratio and the other a negative magnetogyric ratio K and J will be of opposite signs, for example in TeF_6. In WF_6 the reduced coupling constant $^{1}K(^{19}F - {}^{183}W)$ is 103×10^{20} cm^{-3} which is small compared with $^{1}K(^{19}F - {}^{125}Te)$, -1030×10^{20} cm^{-3} in TeF_6, and $^{1}K(^{19}F - {}^{119}Sn)$, -368×10^{20} cm^{-3} in SnF_6^{2-} (193, 194). The absolute sign of $^{1}K(^{183}W - {}^{19}F)$ in WF_6 is at present, unknown. There are various ways of obtaining the absolute signs of coupling constants. The direct method is to partially orientate the molecule, either by dissolution in a liquid crystal or by the application of a strong (ca.20 kv/cm) electric field (195, 196).

An indirect method for finding the absolute sign of a coupling constant involves comparing the relative sign of the coupling constant with one whose absolute value is known. It is very common for $^{1}J(^{1}H - ^{13}C)$, which is always positive, to be used for this purpose.

A tentative assignment for the absolute sign of $^{1}J(^{19}F - ^{183}W)$ in WF_6 can be made from the following argument. It has been found that ^{19}F nuclei can participate in 'through space coupling' and semi-empirical theories suggest that this contribution is always positive (197, 198). Recently the low temperature ^{19}F n.m.r. spectrum of $WF_6(Me_2S)_2$ has been obtained (40). This shows a group of two fluorines and of four fluorines with a coupling constant $^{2}J(^{19}F_1 - ^{19}F_2) = 95$ Hz. In octahedral tungsten-fluorine compounds the fluorine-fluorine distance is at about the limit when the 'through space coupling' starts becoming effective, therefore any further steric crowding, such as is involved in the formation of an eight coordinate complex, should result in a positive 'through space' contribution to $^{2}J(^{19}F - ^{19}F)$. The drop in effective electronegativity of the tungsten should also increase the 'through space' contribution (197). In octahedral tungsten-fluorine compounds $^{2}J(^{19}F - ^{19}F)$ is in the range 55 - 70 Hz.

The trend observed is therefore consistent with a positive $^{2}J(^{19}F - ^{19}F)$ coupling constant. The work on the anion WOF_5^- (103) shows that $^{1}J(^{19}F_c - ^{183}W)$ has the same sign as $^{2}J(^{19}F_c - ^{19}F_t)$ and that $^{1}J(^{19}F_t - ^{183}W)$ has the opposite sign. The chemical shifts suggest that the cis-fluorines in both anions are similar in their bonding to the fluorines in WF_6. Therefore $^1J(^{19}F - ^{183}W)$ in WF_6 is positive.

Table 3:5 shows the n.m.r. data on WF_5NMe^-, $W_2F_9(NMe)_2^-$, $WF_4NMe[(MeO)_2SO]$ and WF_5NEt^- along with some oxygen analogues for comparison. The main similarity between WOF_5^- and WF_5NMe^- is that $^1J(^{19}F_c - ^{183}W)$ and $^2J(^{19}F_t - ^{183}W)$ are of opposite signs. Although it was not possible to obtain the values of the relative signs of the coupling constant for the anion $W_2F_9(NMe)_2^-$ the same situation probably applies here as well. This effect has been previously discussed (103), and it was concluded that the observed trends in the coupling constants can be accounted for by changes in the energy of the W 6s orbital relative to the F_t 2s orbital leading to alterations in the s-overlap integral which dominates the sign and magnitude of the Fermi contact contribution. The possibility of a significant orbital contribution to the coupling constants cannot be excluded because of the relatively small magnitudes of the coupling constants.

Although only two values have been measured for $^1J(^{14}N - ^{183}W)$, they suggest that its value depends markedly on the ligand, the lower the basicity of the ligand then the greater the magnitude of the coupling constant. This could be because the $p\pi - d\pi$ overlap is making a significant contribution to the coupling constant. There could be a close relationship between the ^{14}N chemical shift and the $^1J(^{14}N - ^{183}W)$ terms.

TABLE 3:5

N.M.R. DATA ON SOME ALKYLIMIDO AND OXOTUNGSTEN (VI) FLUORIDES.

Compound	WF_5NMe^-	${}^{b}WOF_5^-$	$W_2F_9(NMe)_2^-$	${}^{b}W_2O_2F_9^-$	WF_4NMe $[(MeO)_2SO]$	WF_5NEt^-
$\delta\,{}^{19}F_c$(p.p.m.)	+28.0	+53.5	+35.7	+65.5	+38.7	+27.6
$\delta\,{}^{19}F_t$ "	-101.5	-78.5	-127.4	-139.5	-	-99.5
$\delta\,{}^{1}H$ "	+5.52	-	+4.80	-	+5.63	+5.80 (CH_2)
$\delta\,{}^{14}N$ "	-1.2	-	?	-	+16.1	?
$\delta\,{}^{183}W$ "	+520±10	+605	?	+617	?	?
${}^{1}J({}^{19}F_c-{}^{183}W)$Hz	±47	±71	47	±70	(±)44[a]	49
${}^{1}J({}^{19}F_t-{}^{183}W)$"	∓36	∓58	?	∓49	-	?
${}^{2}J({}^{19}F_c-{}^{19}F_t)$"	(±)60	±53	60	±58	-	60
${}^{1}J({}^{14}N-{}^{183}W)$"	±70	-	?	-	(±) 100±10[a]	?

TABLE 3:5 (CONTD.)

N.M.R. DATA ON SOME ALKYLIMIDO AND OXOTUNGSTEN (VI) FLUORIDES.

Compound	WF_5NMe^-	$^bWOF_5^-$	$W_2F_9(NMe)_2^{-b}$	$W_2O_2F_9^-$	WF_4NMe $[(MeO)_2SO]$	WF_5NEt^-
$^2J(^{19}F_c-^{14}N)$Hz	<3	-	<3	-	±1.3	<3
$^2J(^{19}F_t-^{14}N)$"	(±) 40	-	34	-	-	36
$^3J(^1H-^{183}W)$ "	∓10	-	?	-	?	?
$^4J(^1H-^{19}F)$ "	<3	-	<3	-	±1.2	<6
$^2J(^1H-^{14}N)$ "	<3	-	<3	-	∓2.7	<6

[a] The relative signs of these coupling constants in parenthesis cannot be related to the relative signs of the coupling constants of the same compound out of parenthesis.

[b] From reference (103).

CHAPTER 4

THE REACTIONS OF N-METHYL HEXAMETHYLDISILAZANE WITH FLUOROTUNGSTATES (V) AND (VI) AND WITH THE N-METHYLIMIDOPENTAFLUOROTUNGSTATE (VI) ANION.

CONTENTS

(I) INTRODUCTION

Several studies of the behaviour of tungsten hexafluoride towards ionic fluorides, in the presence of bromine and bromine trifluoride (199), iodine pentafluoride (200), or chlorine trifluoride (201), have suggested the formation of $M[WF_7]$ and $M_2[WF_8]$ salts (M = Na, Cs or NH_4). More recently a study has been carried out on the reaction of tungsten hexafluoride with ionic fluorides in the presence of acetonitrile, and Raman and ^{19}F n.m.r. spectral evidence has been obtained for the existence of the WF_7^- anion in both the solid state and solution (41). In this latter work, thallium (I) heptafluorotungstate was obtained as a white solid and the related copper (II) salt as a blue solid.

Many metals are oxidized by tungsten hexafluoride in the presence of acetonitrile to give hexafluorotungstate (V) salts (202). These salts are often contaminated with the heptafluorotungstate (VI) anion, since WF_6 is a stronger fluoride ion acceptor than WF_5 (41, 202). The thallium (I) and silver (I) hexafluorotungstate (V) salts can however be obtained relatively pure by this method.

Following from the work described in Chapter 2, it was felt likely that the reaction of N-methyl hexamethyldisilazane with heptafluorotungstate (VI) salts might provide an alternative route to the preparation of salts of the methylimidopentafluorotungstate (VI) anion, by the following reaction;

$$MWF_7 + (Me_3Si)_2NMe \xrightarrow{MeCN} MWF_5NMe + 2Me_3SiF$$

The result obtained for this work (where M = Tl) is described in this chapter, along with preliminary work carried out on related reactions.

(II) THE REACTION OF N-METHYL HEXAMETHYLDISILAZANE WITH THALLIUM (I) HEPTAFLUOROTUNGSTATE (VI) IN ACETONITRILE.

If N-methyl hexamethyldisilazane is condensed on to a solution of thallium (I) heptafluorotungstate (VI) in acetonitrile and the mixture is allowed to warm up to room temperature, then a cream precipitate and an orange-yellow liquid are obtained. Removal of the volatile products from the liquid leaves behind a small quantity of an unidentified, viscous, yellow-orange oil. The volatile products have been identified by gas i.r. spectroscopy as trimethylsilyl fluoride and acetonitrile. The cream coloured solid can be repeatedly washed with acetonitrile, to free it of soluble impurities and dried under vacuum. Three separate analyses of this cream coloured solid have been carried out from two separate preparations. These analyses characterized the cream solid as $TlWF_4NMe$. The results of these analyses are shown in Table 4:1. The quantity of trimethylsilyl fluoride produced in the reaction has been measured and is consistent with a $TlWF_7:(Me_3Si)_2NMe$ reaction ratio of 2:3. The overall reaction can thus be represented by the following equation;

$$2TlWF_7 + 3(Me_3Si)_2NMe = 2TlWF_4NMe + 6Me_3SiF + (MeN).$$

The fate of the extra methylimido group is unknown.

The cream solid, $TlWF_4NMe$, is slowly hydrolyzed in air to a white solid. The X-ray powder photograph of $TlWF_4NMe$ has been recorded, and a comparison of this with the X-ray powder photograph of thallium fluoride shows that it does not contain free thallium fluoride.

TABLE 4:1

The analytical data characterizing $TlWF_4NMe$

Sample	C%	H%	F%	N%	W%
A(1)	2.49	0.74	15.62	3.01	37.31
A(2)	2.53	0.78	15.75	2.93	37.00
B	2.61	0.65	15.65	2.72	37.39
CH_3NF_4TlW (calculated)	2.43	0.65	15.42	2.84	37.32

$TlWF_4NMe$ begins to decompose in glass at 180°C and decomposition is rapid at 235 - 245°C. The course of the decomposition has been followed by gas infra-red spectroscopy, where the only volatile product detected was silicon tetrafluoride. The volatile decomposition product thus appears to be hydrogen fluoride, which then reacts with the glass of the reaction vessel to give silicon tetrafluoride. The analytical data on the blue-black glassy substance which is left behind is consistent with this, and further suggests that only one equivalent of hydrogen fluoride is evolved. The overall decomposition reaction can thus be represented by the equation:

$$TlWF_4NMe \xrightarrow{240^{\circ}} TlWF_3NCH_2 + HF$$

Methyl fluorosulphate reacts with $TlWF_4NMe$ at 66°C to give methyl fluoride and an insoluble yellow solid.

The i.r. and Raman spectral data for $TlWF_4NMe$ are shown in Table 4:2. The assignments made are based on those given in Chapter 2 for $WF_4NMe(L)$ complexes. The i.r. spectrum is very similar to that of $WF_4NMe(L)$ complexes, see Table 2:15 This suggests that the cream solid contains the (WF_4NMe) unit.

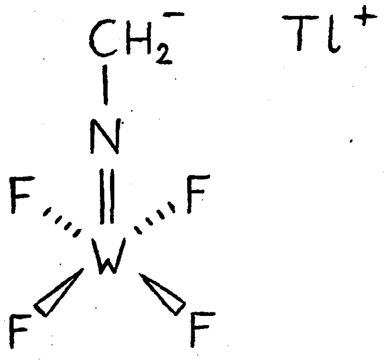
The analytical data suggest that the tungsten has been reduced in the reaction to either W(V), or an equal mixture of W(IV) and W(VI). A possible alternative is that a proton has been lost, since this would not significantly change the analytical results due to the low atomic weight of hydrogen. This last possibility

TABLE 4:2

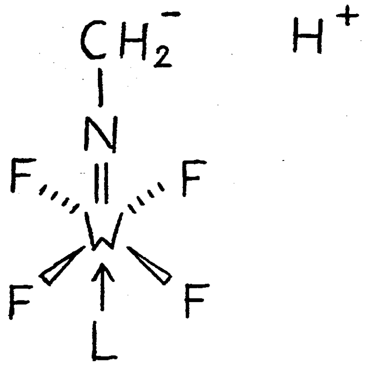
The vibrational spectra of solid $TlWF_4NMe$

Infra-red (cm^{-1}) (mull)	low temp Raman (-197°C)(cm^{-1})	assignment
2960m		(C-H)st.
2930m		(C-H)st.
2860w		
2640w		
1456w		
1426m	1431w	(C-H)bend
	1410s	
1406w	1404m	
1396w	1398w	
	1387m	
	1367m	
1330s	1348s	(C-N=W)st
	1165w	
	1148s	
	1142m	
	853m	
	831w	
	827m	
	814s	
731s	781s	(C-N=W)st
650s		(W-F)st
577 vs,br.		(W-F)st
540 m,sh.		(W-F)st(Bridging fluorine)
430vs	477s	
	335vs	
	307m	
	300m	
	288m	
	268vs	

suggests the structure below:



This, in turn, suggests the possibility that the compounds, $WF_4NMe(L)$, could be formulated as below:



Although there is no direct evidence against this formulation, the ^1H n.m.r. spectra of the WF_5NEt^- and $WF_5NBu^{\underline{n}-}$ anions show that there is no such ionization in these cases and hence that it is very unlikely that there is ionization for the $WF_4NMe(L)$ compounds. The similarity of the i.r. spectra of $TlWF_4NMe$ with the $WF_4NMe(L)$ compounds suggest in turn that such a structure is unlikely for the thallium compound. This implies that some or all of the tungsten must have been reduced.

$TlWF_4NMe$ is diamagnetic. This does not exclude the W(V) oxidation state, since there are many examples where oxidation states with formally unpaired electrons give compounds which are diamagnetic eg. $Cl_5RuORuCl_5{}^-$ (203).

The absence of coordinated acetonitrile in $TlWF_4NMe$ is consistent with the thallium being present as Tl(I), since this coordinates only very poorly whereas Tl(III) coordinates strongly (204). Further if Tl(III) were present this would imply a very reduced state for the tungsten.

The vibrational spectral evidence suggests that a fluorine bridged polymer based on the WF_4NMe species is present. The oxidation state would either be W(V) or an alternating mixture of W(IV) and W(VI).

By analogy of the reaction of tungsten hexafluoride with hexamethyldisiloxane, where reduced tungsten is produced along with tungsten oxide tetrafluoride (49), the probable reducing agent is N-methyl hexamethyldisilazane.

(III) REACTIONS OF HEXAMETHYLDISILAZANE AND N-METHYL HEXAMETHYLDISILAZANE WITH FLUOROTUNGSTATES (V) AND (VI) AND THE METHYL IMIDO PENTAFLUOROTUNGSTATE (VI) ANION.

The following reactions have been briefly studied, and their relationship to the preparation of $TlWF_4NMe$ considered.

(i) $TlWF_7 + (Me_3Si)_2NH \xrightarrow{MeCN}$

(ii) $MeNH_3{}^{+}\ WF_5NMe^{-} + (Me_3Si)_2NMe \xrightarrow{MeCN}$

(iii) $Cu(MeCN)_5{}^{2+}\ 2WF_7 + (Me_3Si)_2NMe \xrightarrow{MeCN}$

(iv) $AgWF_6 + (Me_3Si)_2NMe \xrightarrow{MeCN}$

(v) $TlWF_6 + (Me_3Si)_2NMe \xrightarrow{MeCN}$

(vi) $TlWF_7 + (Me_3Si)_2O \xrightarrow{MeCN}$

The reaction of $TlWF_7$ with $(Me_3Si)_2NH$ in acetonitrile gives a pale brown powder and Me_3SiF. The powder has been characterized as $TlWF_4NH$ by analysis. The vibrational spectral data on $TlWF_4NH$ are shown in Table 4:3 along with tentative assignments for the bands. The vibrational spectra are consistent with the presence of the (WF_4NH) species. The compound appears to be analogous to $TlWF_4NMe$.

It is possible that the methylimidopentafluorotungstate (VI) anion is an intermediate in the reaction of thallium (I) heptafluorotungstate (VI) with N-methyl hexamethyldisilazane i.e. that it is initially formed and then reacts very rapidly with further N-methyl hexamethyldisilazane. The reaction of methylammonium methylimidopentafluorotungstate (VI) with N-methyl hexamethyldisilazane in acetonitrile is complex. The reaction at room temperature gives trimethylsilyl fluoride and a viscous green

TABLE 4:3

The vibrational spectra of $TlWF_4NH$

infra-red (mull)	Raman *	assignment
3270s		(N-H)st
2930m		(C-H)st
2858m		(C-H)st
2270w		
1680m		(N-H) bend
1423s		(C-H) bend
1301vw		
1257w		Me_3Si - (impurity)
1086s		W = N
986m		
946m		
877s		
	810w	
722m		
	600w	
575 vs,br.		(W-F)st
	505m	
430 m,br.		
	380vs	
	318s	
	298s	
	230vs	

* low temperature (-197°C)

liquid. The i.r. spectrum of the green liquid shows a strong peak at 1328 cm^{-1} characteristic of the (W = NMe) group. The viscous green liquid readily redissolves in acetonitrile to give a green solution, and from this solution an insoluble white solid is slowly deposited. The i.r. spectrum of the white solid is similar to that obtained for the viscous green liquid.

The reaction of pentakis (acetonitrile) copper (II) bis (heptafluorotungstate) (VI) with N-methyl hexamethyldisilazane in acetonitrile is also complex. Initially, trimethylsilyl fluoride and a brown-green solid are obtained. On standing the solid slowly turns a pale-yellow. Both solids are soluble in acetonitrile. The i.r. spectrum of the pale yellow solid shows a strong band at 1,331 cm^{-1} indicating the presence of the (W = NMe) group.

The reactions of N-methyl hexamethyldisilazane with silver (I) and thallium (I) hexafluorotungstates (V) in acetonitrile at room temperature give trimethylsilyl fluoride and involatile brown solids which are soluble in acetonitrile. The i.r. spectra of both solids have strong peaks at about 1332 cm^{-1}. This is consistent with the presence of the (W = NMe) group. The brown solids are very rapidly hydrolyzed in air to deep blue-purple solids. If $TlWF_4NMe$ were a W(V) compound then it is very likely that it would be formed in the reaction of thallium (I) hexafluorotungstate (V) with N-methyl hexamethyldisilazane. Its non-formation suggests that $TlWF_4NMe$ is not a W(V) compound.

The reaction of thallium (I) heptafluorotungstate (VI) with hexamethyldisiloxane in acetonitrile gives trimethylsilyl fluoride and bulky white solids of variable composition. The analyses of these solids suggests that some reduction of the tungsten has taken place. The i.r. spectrum of one of the solids indicates that it contains the cis-WO_2 group, by comparison with previously published work on fluorotungsten (VI) salts containing this group (205, 159, 207).

EXPERIMENTAL

(i) General

The starting materials were obtained as detailed in Tables 2:1 and 4:4. The solvents were purified as previously described in Chapter 2. The general experimental procedures and instrumentation have also been previously described in Chapter 2.

X-ray powder photography was utilized in the work described in this chapter. Attempts to index the powder photographs were made by the methods described by D'Eye and Wait in their textbook on the subject (208). The X-ray powder photographs in this work were all taken using CoKα radiation which has a wavelength of 179.02 pm. The samples were powdered and placed into fine Lindemann glass capillaries in the inert atmosphere box. The end of the capillary was then sealed with plasticine. The dimensions of the circular camera were such that by measuring the diameter of the spacings in millimeters, the Bragg angle, could be obtained directly by dividing by four. The distances between the crystal planes d, could then be determined by using the Bragg equation.

$$d = \frac{\lambda}{2\sin\theta}$$

(ii) The reaction of N-methyl hexamethyldisilazane with thallium (I) heptafluorotungstate (VI) in acetonitrile.

The preparation of $TlWF_7$ has been previously described (41). Thallium fluoride (0.2910 g, 1.30 mmol) was placed in a flask and acetonitrile (0.8398 g, 20.5 mmol)

TABLE 4:4

Starting Material	Source
TlF	K & K., I.C.N. Pharmaceuticals Ltd.
CuF_2	Ozark Mahoning
$TlWF_7$	ref. (41) and see text.
$TlWF_6$	ref. (202) and see text.
$AgWF_6$	ref. (202) and see text.
$Cu(WF_7)_2$, 5MeCN	ref. (41) and see text.

was added by distillation, followed by tungsten hexafluoride (0.4279 g, 1.10 mmol). The mixture was shaken at room temperature. The thallium fluoride almost completely dissolved. The solution was refrozen and N-methyl hexamethyldisilazane (0.3490 g, 1.99 mmol) was added by distillation. The reaction mixture was allowed to slowly warm up from -80°C, being agitated at the same time. At low temperatures a purple colouration was initially observed but this disappeared at higher temperatures. Finally, a white precipitate and an orange-yellow solution were obtained.

The volatile products were distilled off and collected to give 1.2983 g of a clear, pale-yellow liquid. Gas i.r. spectroscopy identified the compounds as trimethylsilyl fluoride and acetonitrile. The volatile products were seperated by trap to trap distillation to give trimethylsilyl fluoride (0.3259 g, 3.54 mmol). This suggests a reaction ratio for $TlWF_7$: $(Me_3Si)_2NMe$ of 1: 1.6.

The solid was washed with fresh acetonitrile and then pumped dry. The product was a cream coloured powder. Three separate analyses from two separate preparations have been carried out. The analytical results are shown in Table 4:1. These characterized the cream powder as $TlWF_4NMe$.

The acetonitrile washings were yellow, and left a small quantity of a yellow-orange viscous liquid on removal of the acetonitrile.

The cream coloured solid hydrolyzed slowly in air to give a white solid. When dropped into water it hissed and gave a white solid. After several hours standing in water this turned the characteristic bright yellow of tungstic acid.

The i.r. and low temperature Raman spectra of the cream coloured solid were recorded and the results are shown in Table 4:2.

The cream coloured solid was insoluble in both acetonitrile and hexafluorobenzene and thus it was not possible to obtain its n.m.r. spectra.

The X-ray powder photograph of the cream coloured solid was recorded and the results are shown in Table 4:5. The X-ray powder photograph of thallium fluoride was also recorded on the same equipment and no correspondence was observed between the two photographs. Attempts to index the powder photograph were not successful although they demonstrated that the compound did not possess a cubic or tetragonal structure, and neither, probably, a hexagonal, rhombic or orthorhombic structure.

The magnetic moment of the cream coloured solid was determined by the Gouy Method (209). The compound was found to be diamagnetic, with a magnetic susceptibility of -186×10^{-6} g atom. If corrections are made for the estimated diamagnetic contributions of the Tl, F, N, C and H atoms (209), then the magnetic susceptibility becomes -97×10^{-6} g atom. This work also gave the bulk density of the compound as 1.87 g cm^{-3}.

(iii) The thermal decomposition of $TlWF_4NMe$.

Approximately 1 g of $TlWF_4NMe$ was placed in a glass reaction flask and the temperature was slowly raised. At 180°C a small quantity of a volatile material was

TABLE 4:5

THE X-RAY POWDER DATA FOR $TlWF_4NMe$.

Band no.	intensity	$\sin^2\theta$	d(pm)
1	m	0.00585	1170
2	s	0.00668	1095
3	m	0.02570	558.3
4	s	0.05147	394.5
5	s	0.05253	390.5
6	s	0.05842	370.3
7	vw	0.06450	352.4
8	vw	0.07007	338.1
9	s	0.07322	330.8
10	vw	0.07678	323.0
11	vw	0.08942	299.3
12	m	0.09370	292.4
13	m	0.10385	277.8
14	w	0.11433	264.7
15	vw	0.12726	250.9
16	w	0.13972	239.5
17	w	0.15773	225.4
18	m	0.17743	212.5
19	w	0.17901	211.6
20	w	0.20259	198.9
21	w	0.21579	192.7
22	m	0.22739	187.7
23	vvw	-	-
24	vvw	-	-
25	m	0.27612	170.3

evolved and SiF_4 was identified by gas i.r. spectroscopy (210). At 235 - 245°C copious quantities of volatile materials were evolved and gas i.r. spectroscopy again identified SiF_4. Severe etching of the glass flask and manifold were noted. After approximately 15 minutes the evolution of volatile material ceased. The flask was then allowed to cool. The product remaining in the flask was a blue-black, glassy solid. The analysis of this solid was C2.50, H0.31, F12.32, N2.93, W38.69%. CH_2F_3NTlW requires C2.54, H0.42, F12.05, N2.96, W38.90%.

The i.r. spectrum of the blue-black, glassy solid had the following peaks: 2920 mbr, 1430 mbr, 1151 mbr, 1080 mbr, 970 w, 942 w, 889 w, 721 s, 575 vs.br, 501 vs.br (cm^{-1}).

(iv) The reaction of $TlWF_4NMe$ and methyl fluorosulphate.

A large excess of $MeOSO_2F$ was distilled into a reaction flask containing $TlWF_4NMe$. The mixture was then heated to 66°C and shaken for 1 hour. The cream coloured solid became more yellow, but no other change was apparent. However, i.r. spectroscopy identified MeF in the volatiles. As previously described in Chapter 2, $MeOSO_2F$ heated alone to 90°C for 2 hours produced no detectable MeF.

(v) The reaction of hexamethyldisilazane with thallium (I) heptafluorotungstate (VI) in acetonitrile.

The preparation of thallium (I) heptafluorotungstate was carried out as previously described, in the literature (41).

Thallium fluoride (0.2509 g, 1.13 mmol) was placed in a flask and acetonitrile (c.a. 1 ml) was added by distillation, followed by an excess (1:1) of tungsten hexafluoride. The mixture was shaken at room temperature until all the thallium fluoride had dissolved. Unreacted tungsten hexafluoride was removed by pumping until a precipitate began to appear.

Hexamethyldisilazane (0.1511 g, 0.94 mmol) was added by distillation to the resultant solution of $TlWF_7$ and the temperature of the solution was slowly raised. At -52°C a yellowish colouration was observed which darkened as warming continued. At 0°C a reddish brown precipitate was obtained. The liquor was decanted off the precipitate and the solid washed several times with fresh acetonitrile, and dried under vacuum. The product was a pale yellow-brown solid. Trimethylsilylfluoride was identified in the volatile products by gas i.r. spectroscopy.

The analysis of the pale yellow-brown solid gave C0.16, H0.35, F16.00, N3.08, W38.53.

HF_4NTlW requires C0.00, H0.21, F15.87, N2.92, W38.41%.

The vibrational spectra of the product are shown in Table 4:3.

(vi) The reaction of methylammonium methylimidopentafluorotungstate (VI) with N-methyl hexamethyldisilazane in acetonitrile.

Methylammonium methylimidopentafluorotungstate (VI) (0.6560 g, 1.33 mmol) was placed in a reaction flask and dissolved in c.a. 2 ml of acetonitrile. N-Methyl hexamethyldisilazane (0.2692 g, 1.54 mmol) was then condensed into the reaction flask and the mixture was allowed to warm slowly to room temperature. At room temperature, a green solution was obtained which underwent no change after several hours shaking. The volatile products were then distilled off leaving a green, very viscous liquid. Trimethylsilyl fluoride and acetonitrile were identified in the volatile products by i.r. spectroscopy. The volatile products were separated by trap to trap distillation. This produced trimethylsilyl fluoride (0.2852 g, 3.1 mmol).

A liquid film i.r. spectrum of the viscous liquid gave peaks at 3259 vs, 3170 vs. sh., 2903 m, 2799 m, 2580 vw, 2482 vw, 2299*w, 2258 m*, 1690 m, 1610 mbr., 1514 m, 1461 s, 1422 m, 1372 $\overset{*}{\text{m}}$, 1328 s, 1279 m, 1106 s, 1099 msh, 1089 w, 1012 m, 947 mbr., 918 $\overset{*}{\text{w}}$, 852 mbr., 791 msh., 731 sbr., 720 ssh., 649 s, 685 vs. br. and 6800 - 412 vs. vbr. (overlapping peaks) (cm^{-1}). Peaks assigned to uncoordinated acetonitrile are marked by an asterisk.

The viscous, green liquid was miscible with acetonitrile to givea green solution, from which a white solid slowly precipitated.

The analysis of the white solid was C10.09, H3.60, F21.94, N11.70 and W52.48%.

$C_3H_{13}F_4N_3W$ requires C10.26, H3.70, F21.65, N11.93 and W52.42%.

The i.r. spectrum (Nujol mull) of the white solid was recorded. 3258 s, 3165 s, 3139 s, 2640 w, 2579 w, 2459 w, 2312 w, 1610 s, 1599 s, 1518 s, 1425 s, 1327 s, 1291 s, 1102 s, 1090 s, 1070 m, 1039 w, 1019 m, 864 m, 940 m, 849 s, 835 s, 789 s, 730 s.br, 647 w, 623 s, 561 vs. br, 515 vs., 500 vs., 475 vs., 465 vs., 454 vs. and 421 vs. (cm^{-1}).

An attempt to obtain the ^{1}H and ^{19}F n.m.r. spectra of the green solution failed due to the rapid deposition of solid.

The X-ray powder photograph of the white solid was obtained and the results are shown in Table 4:6.

(vii) The reaction of N-methyl hexamethyldisilazane with pentakis (acetonitrile) copper (II) bis (heptafluorotungstate)(VI) in acetonitrile.

Copper (II) bis (heptafluorotungstate) (VI) was prepared as previously reported in the literature (41). Copper (II) bis (heptafluorotungstate) (VI) (0.3542 g, 0.6 mmol) was placed in a reaction flask and dissolved in approximately 1 ml of acetonitrile. N-Methyl hexamethyldisilazane (0.1460 g, 0.83 mmol) was then distilled into the flask and the mixture was allowed to slowly warm up. At -16°C a green solution was obtained and a white precipitate. At -5°C the white precipitate redissolved and a dark, brown-green solution was produced. The volatile products were removed from the solution, leaving behind a dark-green solid.

The volatile products were investigated by i.r. spectroscopy and both Me_3SiF and MeCN were identified. These were separated by trap to trap distillation and trimethylsilyl fluoride (0.1432 g, 1.56 mmol) was recovered. This is a 94% recovery of Me_3SiF based on $(Me_3Si)_2NMe$.

The dark green solid turned a golden-brown colour on standing for several hours at room temperature. The i.r. spectrum of the golden-brown solid was recorded; 3230 mbr., 3200 m, 3004 m, 2942 m, 2855 m, 2660 w, 2480 vw, 2400 w, 2303 m, 2278 m, 1700 w, 1622 w, 1428 m, 1410 m,

TABLE 4:6

THE X-RAY POWDER DATA ON THE WHITE SOLID PRODUCED IN THE REACTION OF $[MeNH_3]^+$ $[WF_5NMe]^-$ WITH $(Me_3Si)_2NMe$.

Band no.	intensity	$\sin^2\theta$	d(pm)
1	s.br.	0.01743	678.0
2	s.br.	0.01842	659.5
3	w	0.02166	608.2
4	s.br.	0.02380	580.2
5	s.br.	0.02542	561.4
6	s.br.	0.02912	524.5
7	w.br.	0.03797	459.4
8	v.w.	0.04484	422.7
9	m	0.05976	366.2
10	m	0.06918	340.3
11	m	0.08043	315.6
12	m	0.09168	295.6
13	m	0.09421	291.6
14	w	0.11726	261.4
15	w	0.13402	244.5

1365 m, 1331 s, 1148 vw, 1082 m, 978 s, 948 vw, 935 vw, 928 vw, 890 w, 730 s, 612 s, 601 vs, 517 vs, 438 vs, 418 vs, (cm^{-1}).

The golden-brown solid was analysed: C15.68, H2.54, F18.08, N11.50, Cu7.48, W44.16%. This adds up to 99.44%, thus indicating that there has been no hydrolysis. $C_{11}H_{24}F_8N_7CuW_2$ requires C15.86, H2.52, F18.26, N11.77, Cu7.63, W44.20%.

(viii) <u>The reaction of N-methyl hexamethyldisilazane with silver (I) hexafluorotungstate (V) in acetonitrile</u>.

Silver (I) hexafluorotungstate (V), $AgWF_6$, was prepared as previously described in the literature (202).

Silver (I) hexafluorotungstate (V) (0.7797 g, 1.92 mmol) was dissolved in approximately 1 ml of acetonitrile and N-methyl hexamethyldisilazane (0.3023 g, 1.73 mmol) was added by distillation. After being warmed up to room temperature, a dark coloured solution was produced. The removal of the volatile products from this solution left behind a dark-brown solid.

The volatile products were investigated by i.r. spectroscopy and Me_3SiF and MeCN were identified. These were separated by trap to trap distillation and 0.2926 g (3.18 mmol) of Me_3SiF were recovered, a 92% yield based on $(Me_3Si)_2NMe$.

The following analytical data were obtained on the brown solid: C11.86, H1.71, F19.42, N7.21, Ag13.34, W45.85%. This gives a total of 99.39% and indicates that little hydrolysis has taken place. The i.r. spectrum of the brown solid was recorded (Nujol mull only); 2310 s, 2293 s, 1331 vs, 1175 w, 1030 m, 1020 m.sh., 972 m, 940 m, 889 w, 845 w, 721 s, 699 s, 661 vs., 590 vs. br., 521 vs. br., (cm $^{-1}$).

(ix) The reaction of N-methyl hexamethyldisilazane with thallium (I) hexafluorotungstate (V) in acetonitrile.

Thallium (I) hexafluorotungstate (V) was prepared as previously described in the literature (202).

Thallium (I) hexafluorotungstate (V) (0.5115 g, 0.67 mmol) was placed into a reaction flask and approximately 1 ml of acetonitrile was distilled on. N-Methyl hexamethyldisilazane (0.0913 g, 0.52 mmol) was then distilled on and the mixture was left to warm up to room temperature. A dark-brown solution was obtained. The volatile products were pumped off leaving behind a dark, brown-grey solid. On exposure to the atmosphere this immediately turned a deep blue-purple colour.

The i.r. spectrum of the grey solid was recorded: 3262 m, 3018 m, 2945 m, 2322 m, 2300 m, 2289 w, 1410 m, 1332 s, 1169 w, 1030 m, 981 w, 944 m, 918 w, 893 w, 809 w, 720 s, 710 s, 593 vs., 520 vs. sh., 410 vs. (cm^{-1}).

(x) The reaction of hexamethyldisiloxane with thallium (I) heptafluorotungstate (VI).

$TlWF_7$ was prepared as previously described (41). It was dissolved in acetonitrile and a slight excess (1:1) of $(Me_3Si)_2O$ was distilled in, and the mixture was allowed to warm slowly to room temperature. The product was a bulky white solid, however the analyses of this material from two different preparations were not reproducible,

C2.63, H0.32, F10.26, N0.48 and W54.25%

C0.04, H0.02, F10.94 and W41.68%

The infra red spectrum of the first sample was recorded: 3420 m, 3200 m, 2950 m, 2870 m, 2420 m, 2400 m, 2360 m, 1617 m, 1430 m. br., 1410 m.br., 1301 vw, 1260 vw, 1201 vw, 1150 vw, 1021 w, 990 s, 898 vs. br., ('tailing' to 770), 730 vs, 610 vs.

I.r. spectroscopy identified Me_3SiF in the volatile products from the reaction.

CHAPTER 5

THE REACTIONS OF MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES WITH TRIMETHYLTIN DERIVATIVES.

CONTENTS

(I) INTRODUCTION

(II) RESULTS AND DISCUSSION

(III) EXPERIMENTAL

(b) Reactions

I. INTRODUCTION

(a) Trifluoromethyltungsten (VI) fluoride compounds.

In compounds of the type $WF_{6-n}(CF_3)_n$ (n = 1 - 6), the trifluoromethyl group should form only a σ bond to the tungsten similar to the methyl group in hexamethyltungsten (VI) (63). These compounds should thus possess very interesting chemical and structural properties which differ markedly from the properties of other tungsten hexafluoride derivatives. For example, trifluoromethyltungsten (VI) pentafluoride should have the trans-fluorine-tungsten bond shorter than the cis-fluorine-tungsten bond, since the $-CF_3$ group would not compete for the vacant d-orbitals on the tungsten. This should reverse the positions of the cis-fluorines and trans-fluorine resonances in the ^{19}F n.m.r. spectrum from that found in methoxytungsten (VI) fluorides (50), and give information about the degree of π - bonding in the tungsten-fluorine bond. Furthermore, a compound of the type $W(CF_3)_4F_2$ could possess a high degree of resistance to hydrolysis because of steric crowding around the tungsten hindering any nucleophilic attack.

(b) Preparative route.

The preparation of compounds of the type, $WF_{6-n}(CF_3)_n$ (n = 1 - 6), was attempted from the reaction of tungsten hexafluoride with trimethyltrifluoromethyltin, Me_3SnCF_3. There were four reasons for choosing this route (i) the Sn - C bond is considerably weaker than the Si - C bond (see Chapter 1, table 1:4), (ii) the compound $[Me_3Sn]^+ [CF_3BF_3]^-$ can be successfully prepared by this route (211),

(iii) trimethyltin fluoride is an insoluble polymeric solid whose formation should be highly favoured (212), and (iv) tetramethyltin reacts with tungsten hexachloride to give methyltungsten (VI) pentachloride, $MeWCl_5$ and trimethyltin chloride (25).

(II) RESULTS AND DISCUSSION.

(a) The reaction of trimethyltin derivatives with tungsten hexafluoride.

It has been previously reported that tungsten hexafluoride and tetramethyltin form a highly coloured solution together, which n.m.r. and Raman spectral evidence indicates is a mixture of tungsten hexafluoride and tetramethyltin. The intense colour was ascribed to a charge transfer complex (44). Contact charge transfer occurs during random encounters whenever a donor and acceptor are sufficiently close to one another provided that the overlap integral between appropriate donor and acceptor orbitals is appreciable.

Charge transfer absorbtion can occur even if no stable complex is formed (213).

In the present work the reaction of tungsten hexafluoride with trimethyltrifluoromethyltin and trimethylpentafluorophenyltin was found to give highly coloured liquids. The ^1H and ^{19}F n.m.r. spectra of these liquids show peaks due only to the starting materials. It was concluded that charge transfer complexes were formed, but that the reaction proceeded no further.

(b) The reaction of trimethyltin derivatives with molybdenum hexafluoride.

It has been previously reported that molybdenum hexafluoride reacts with tetramethyltin to give unidentified solid products. (44). In this work molybdenum hexafluoride was reacted with Me_4Sn, Me_3SnCF_3 and $Me_3SnC_6F_5$. The results are summarized in table 5:1. The use of the donor solvent, acetonitrile, results in a much cleaner reaction giving white solids.

TABLE 5:1

THE REACTION OF MoF_6 WITH Me_3SnR, where R = Me, CF_3 AND C_6F_5, IN VARIOUS SOLVENTS.

Reaction No.	R	Solvent	Ratio of Reactants	Products	Ratio of Products	Ratio of reactant to products
(I)	Me	$n\text{-}C_6F_{14}$	$Me_4Sn:MoF_6 = 1:1$	black solid		
(II)	Me	MeCN	$Me_4Sn:MoF_6 = 1:1$	white solid MeF^b sticky red solid		$Me_4Sn:MeF = 2:1$
(III)	CF_3	MeCN	$Me_3SnCF_3:MoF_6 = 1:2$	white solid MeF^a $CF_4{}^a$	$MeF:CF_4 = 3:1^c$	$Me_3SnCF_3:MeF/CF_4 = 1.6:1$
(IV)	C_6F_5	C_6F_6	$Me_3SnC_6F_5:MoF_6 = 1:2$	brown solid MeF^a		

a) Identified by gas i.r. spectroscopy.

b) Identified by gas i.r. spectroscopy and molecular wt. measurement.

c) Determined from vapour density measurement.

Reaction (II) was the most extensively studied. The products are a red sticky soluble solid, a white insoluble solid and methyl fluoride. The red sticky solid dissolves in water to give trimethyltin fluoride as a precipitate and a red solution. The red solution turns blue after standing in the air for several days. This is consistent with the red solution being due to a Mo(III) or Mo(IV) species (214). The analysis of the white solid corresponds approximately to Me_3SnMoF_7, 3MeCN. The i.r. spectrum of this solid contains peaks due to coordinated acetonitrile. The (C≡N) stretching vibration is shifted to a higher energy by 40 cm^{-1} with respect to the free ligand. There are peaks at 792 and 562 cm^{-1} characteristic of trimethyltin species, and a strong peak at 596 cm^{-1} consistent with an (Mo-F) stretching vibration.

A very tentative reaction sequence is:

$$\text{(i)}\ MoF_6 + Me_4Sn \xrightarrow{MeCN} Me_3SnF + \underset{\text{(red solid)}}{\text{Mo(IV) (or III) species}} + MeF.$$

The Me_3SnF can now either react with the Mo(IV) species to give an Mo(IV)/Me_3SnF complex or with further MoF_6.

$$\text{(ii)}\ MoF_6 + Me_3SnF \xrightarrow{MeCN} Me_3SnMoF_7,\ 3MeCN$$

The reaction of MoF_6 with Me_3SnCF_3 appears to proceed in a similar manner. The white solid in this case being possibly a mixture of $Me_2(CF_3)SnMoF_7$,3MeCN and Me_3SnMoF_7,3MeCN.

In this latter reaction the ratio of MeF:CF_4 of 3:1 suggests that the rate of formation of RF is independent of R.

The reactions which take place in the absence of acetonitrile give dark coloured solids which are probably mixtures of compounds.

The work on the reactions of tungsten hexafluoride and molybdenum hexafluoride with trimethyltin derivatives suggests that this does not provide a suitable route to the desired derivatives of the hexafluorides, but that instead reduced species and trimethyltin salts are formed. The possibility of MoF_5Me being formed as an intermediate species, however, cannot be excluded.

(III) EXPERIMENTAL

(a) General.

The solvents used were obtained and purified as previously described. The sources of the compounds used are summarized in Table 5:2.

The compound trimethyltrifluoromethyltin was prepared in a steel bomb by the reaction

$Me_6Sn_2 + CF_3I \xrightarrow{80^oC} Me_3SnCF_3 + Me_3SnI$ (215).

Two other products were observed in this reaction which were not mentioned in the original report (215). These were tetramethyltin and trimethyltin fluoride, (identified by i.r. spectroscopy). The former compound was separated from Me_3SnCF_3 by repeated trap to trap distillation.

Trimethylpentafluorophenyltin was prepared by the following series of reactions.

(1) $3Me_4Sn + SnBr_4 \longrightarrow 4Me_3SnBr$ (216, 217)

(2) $C_6F_5Br + Mg \xrightarrow{Et_2O} C_6F_5MgBr$ (218).

(3) $Me_3SnBr + C_6F_5MgBr \xrightarrow{Et_2O} Me_3SnC_6F_5 + MgBr_2$ (219).

The final product was isolated as previously described (219) and stored over activated molecular sieves, type 4A, prior to use.

The general experimental techniques and instrumentation have been previously described. Molecular weights of volatile compounds were obtained, by measuring the pressure of a known weight of the volatile compound in a system which had been previously calibrated with n-pentane.

TABLE 5:2

SOURCES OF CHEMICALS

Compound	Source
MoF_6	Fluorochem. Ltd. (Ozark-Mahoning Co.)
Me_4Sn	Alfa Products (99.5%)
$SnBr_4$	B.D.H. Chemicals Ltd. (min. assay 97%)
Me_3SnBr	$SnBr_4/Me_4Sn$
$Me_3SnC_6F_5$	Me_3SnBr/C_6F_5MgBr (218, 219)
C_6F_5Br	Imperial Smelting Co. Ltd.
Me_6Sn_2	M. & T. Chemicals Inc.
CF_3I	Fluorochem. Ltd.
Me_3SnCF_3	Me_6Sn_2/CF_3I (215)

(b) REACTIONS

(i) Reaction of tungsten hexafluoride with trimethyltrifluoromethyltin.

Tungsten hexafluoride (0.3943 g, 1.32 mmol) was condensed on to trimethyltrifluoromethyltin (0.2356 g, 1.01 mmol) and the reaction mixture was allowed to warm slowly to room temperature.

The product was a mobile red liquid. The ^{1}H and ^{19}F n.m.r. spectra contained only peaks assignable to WF_6 and Me_3SnCF_3. The infra-red and mass spectra of the volatile materials showed only WF_6 and Me_3SnCF_3.

(ii) The reaction of tungsten hexafluoride and trimethylpentafluorophenyltin.

Trimethylpentafluorophenyltin (0.7360 g, 2.22 mmol) was placed in a flask and tungsten hexafluoride (0.6261 g, 2.10 mmol) was distilled on. The reaction mixture was then allowed to warm up slowly to room temperature. A reddish orange liquid was obtained. ^{1}H and ^{19}F n.m.r. spectra of this liquid contained only peaks assignable to tungsten hexafluoride and trimethylpentafluorophenyltin.

(iii) The reaction of molybdenum hexafluoride and tetramethyltin in normal perfluorohexane.

Molybdenum hexafluoride (0.4386 g, 2.09 mmol) was distilled on to a mixture of n-perfluorohexane (1 ml) and tetramethyltin (0.3700 g, 2.07 mmol). The mixture was then allowed to slowly warm up to room temperature. The reaction began at -72°C when a greenish colour formed. As the warming up continued the colour became progressively darker until at room temperature a black solid and a clear liquid were obtained.

The volatile products were identified by gas infra-red spectroscopy as a mixture of methyl fluoride and solvent.

The i.r. spectrum of the black solid contained the following peaks 3000 m, 2927 m, 2394 w, 1405 m, 1206 w, 1022 w, 805 m, 700 m, 642 m, 506 m, cm^{-1}.

(iv) <u>The reaction of molybdenum hexafluoride and tetramethyltin in acetonitrile</u>.

Molybdenum hexafluoride (0.7581 g, 3.58 mmol) was distilled on to a mixture of acetonitrile (1.2588 g, 30.67 mmol) and tetramethyltin (0.6699 g, 3.75 mmol). The reaction mixture was then allowed to slowly warm to room temperature. At -20°C there was a bright yellow solution with a small amount of white solid. As the solution warmed to room temperature the yellow colour darkened until it was a golden brown colour. After three days more white solid was deposited and the solution became reddish brown in colour. Some of the white solid was separated into a side-arm and washed by backdistilling acetonitrile on to it and then decanting the acetonitrile off. The volatile material was removed leaving a white solid in the side-arm and a red heterogeneous material in the main reaction vessel.

The volatile products were seperated by trap to trap distillation. The low boiling point fraction was identified as methyl fluoride by gas i.r. spectroscopy and molecular weight determination (found 36.5 g $mole^{-1}$, calc. for MeF 34.0 g, mole $^{-1}$). The high boiling point fraction was found to be a mixture of acetonitrile and unreacted tetramethyltin by i.r. gas and liquid film spectroscopy. The yield of methyl fluoride was 0.0654 g (1.92 mmol).

The sticky red solid dissolved in water to give a red solution and a grey-white solid. The red solution turned blue after standing in air for three days. The grey-white solid was identified as trimethyltin fluoride by i.r. spectroscopy. The white solid was tentatively characterized as Me_3SnMoF_7, 3MeCN.

Found C21.02, H2.87, F26.32, N8.02%, $C_9H_{18}F_7$ Mo Sn requires C20.95, H3.52, F25.87, N8.16%.

The i.r. spectrum of the white solid contained the following peaks (Nujol only) 2322 m, 2299 s, 1359 s, 1027 m, 952 m, 815 w, 792 w.br., 721 w, 596 vs, 562 s cm^{-1}.

The Raman spectrum of the white solid contained peaks assigned to coordinated acetonitrile and a broad peak at 450 cm^{-1}.

(v) The reaction of molybdenum hexafluoride and trimethyltrifluoromethyltin in acetonitrile.

Molybdenum hexafluoride (0.7349 g, 3.50 mmol) was distilled on to a mixture of acetonitrile (0.8630 g, 21 mmol) and trimethyltrifluoromethyltin (0.4805 g, 1.87 mmol). The reaction mixture was allowed to slowly warm up to room temperature. A bright yellow solution was initially obtained which, after two hours at room temperature, darkened to a deep red-brown colour and deposited a white solid.

The volatile products were identified as carbon tetrafluoride and methyl fluoride by i.r. and mass spectrometry. They were seperated from solvent and unreacted trimethyltrifluoromethyltin by trap to trap distillation. The apparent molecular weight of the MeF/CF_4 mixture was found to be 48 g mole $^{-1}$ which corresponds to a $MeF:CF_4$ ratio of 3:1. The total weight of this mixture was 0.0556 g.

The mass spectrum of the white solid was recorded and this showed peaks due to Me_3Sn^+ and Me_2SnF^+ and their degradation products. The removal of the volatile material from the brown solution left a brown sticky material.

(vi) The reaction of trimethylpentafluorophenyltin and molybdenum hexafluoride in hexafluorobenzene.

Molybdenum hexafluoride (0.5936 g, 2.83 mmol) was distilled on to a mixture of hexafluorobenzene (1 ml) and trimethylpentafluorophenyltin (0.4520 g, 1.37 mmol). The mixture was allowed to slowly warm to room temperature. The product at room temperature was a very deeply coloured solution, and a small quantity of dark solid. Methyl fluoride was identified by i.r. spectroscopy as the main volatile component at -68^oC. The ^1H n.m.r. spectrum of the coloured liquid contained weak broad peaks at $\delta^1H = 4.83, 2.58, 1.37$ and -1.32 p.p.m. The ^{19}F n.m.r. spectrum contained weak broad peaks at $\delta^{19}F = -90.9, -119.3, -138.3$ and -146.9 p.p.m.

Removal of the volatile material from the coloured liquid resulted in a chocolate coloured solid. The i.r. spectrum of this solid contained the following bands

(Nujol mull only): 1645 s, 1513 s, 1378 s, 1283 m, 1211 w, 1180 vw, 1141 w, 1073 vs , 1055 w, 1029 m, 1011 m, 968 vs, 818 s, 801 s, 701 vs , 651 vs ,580 m, 525 s, 470 vs, cm^{-1}.

The low resolution mass spectrum of the solid material showed a peak consistent with $Me(C_6F_5)SnF^+$ and further degradation peaks. No molybdenum isotope pattern was observed.

REFERENCES

(1) M. Mercer, Chem Comm., 1967, 119.

(2) I. Dellien, F.M. Hall and L.G. Hopler, Chemical Reviews, 1976, 76, 283.

(3) J.W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 11, Longmans, Green and Co., London, 1931.

(4) R.V. Parish, 'The Inorganic Chemistry of Tungsten', in H.J. Emeleus and A.G. Sharpe (eds.), Advances in Inorganic and Radiochemistry, 1966, 9, 315 - 354.

(5) O. Ruff and F. Eisner, Chem. Ber. 1905, 38, 742.

(6) O. Ruff, F. Eisner and W. Heller, Z. anorg. Chem., 1907, 52, 256.

(7) E.W. Abel, Quart. Rev., 1963, 17, 133.

(8) M.L.H. Green and P.L.I. Nagy, Advan. Organometal. Chem., 1964, 2, 235.

(9) R.G. Guy and B.L. Shaw, Advan. Inorg. Chem. Radiochem., 1962, 4, 78.

(10) M.D. Rausch, Can. J. Chem., 1963, 41, 1289.

(11) D.L. Keppert, Progr. Inorg. Chem., 1962, 4 199.

(12) J.H. Canterford and R. Colton, 'Halides of the Second and Third Row Transition Metals', Wiley - Interscience, London, 1968.

(13) J.E. Fergusson, 'Halide Chemistry of Chromium, Molybdenum and Tungsten', in V. Gutmann (Ed), 'Halogen Chemistry, Vol. 3, 227-302, Academic Press, London and New York, 1967.

(14 and 15) J.M. Winfield (pp 271 - 298) and R. Colton (pp 299 - 338) in D.W.A. Sharp (ed.) 'M.T.P. International Review of Science, Inorganic Chemistry, Vol. 5, Series One, Butterworths, 1972.

(16) J.M. Winfield (pp 1 - 28) in D.W.A. Sharp (ed.) 'M.T.P. International Review of Science, Inorganic Chemistry, Vol. 5, Series Two', Butterworths, 1974.

(17) O.J. Klejnot, Inorg. Chem., 1965, 4, 1668.

(18) H. Funk and W. Baumann, Z. anorg. Chem., 1937, 231, 264.

(19) S. Prasad and K.S.R. Krishnaiah, J. Indian Chem. Soc., 1960, 37, 681.

(20) P.I. Mortimer and M.I. Strong, Austral J. Chem., 1965, 18, 1579.

(21) W. Beck, H. Stetter, S. Tadros and K.E. Schwarzhaus, Chem. Ber., 1967, 100, 3944.

(22) D.C. Bradley, M.H. Chisolm, C.E. Heath and M.B. Hursthouse, Chem. Comm., 1969, 1261.

(23) G. Yagupsky, W. Mowat, A. Shortland and G. Wilkinson, Chem. Comm., 1970, 1389.

(24) A. Shortland and G. Wilkinson, J.C.S. Dalton, 1973, 873.

(25) W. Grahlet and K.H. Thiele, Z. anorg. Chem., 1971, 383, 144.

(26) C. Santini-Scampucci and J.G. Reiss, J. Organometal Chem., 1974, 73, C13.

(27) C. Santini-Scampucci and J.G. Reiss, J.C.S. Dalton, 1976, 195.

(28) T.A. O'Donnell, J. Chem. Soc., 1956, 4681.

(29) G.H. Cady and G.B. Hargreaves, J. Chem. Soc., 1961, 1563.

(30) E.J. Barber and G.H. Cady, J. Phys. Chem., 1956, 60, 505.

(31) O. Ruff and E. Ascher, Z. anorg. Chem., 1931, 196, 413.

(32) T.A. O'Donnell and D.F. Stewart, Inorg. Chem., 1966, 5, 1434.

(33) H.M. Seip and R. Seip, Acta. Chem. Scand., 1966, 20, 2698.

(34) T.G. Burke, D.F. Smith and A.H. Nielsen, J. Chem. Phys., 1952, 20, 447.

(35) J.R. Geichman, E.A. Smith, S.S. Trond and P.R. Ogle, Inorg. Chem., 1962, 1, 1012.

(36) J.R. Geichman, E.A. Smith and P.R. Ogle, Inorg. Chem., 1963, 2, 1012.

(37) N. Bartlett, Angew. Chem. internat Edit., 1968, 7, 433.

(38) F.N. Tebbe and E.L. Muetterties, Inorg. Chem., 1968, 7, 172.

(39) A.M. Noble and J.M. Winfield, Inorg. Nucl. Chem. Letters, 1968, 4, 339.

(40) A. Steigel and S. Brownstein, J. Amer. Chem. Soc., 1974, 96, 6227.

(41) A. Prescott, D.W.A. Sharp and J.M. Winfield, J.C.S. Dalton, 1975, 934.

(42) H.F. Priest and W.C. Schumb, J. Amer. Chem. Soc., 1948, 70, 2291.

(43) H.J. Clese, A.M. Noble and J.M. Winfield, Spectrochim Acta, 1969, 25A, 293.

(44) R.R. McLean, D.W.A. Sharp and J.M. Winfield, J.C.S. Dalton, 1972, 676.

(45) P.R. Hammond and R.R. Lake, Chem. Comm., 1968, 987.

(46) P.R. Hammond, J. Phys. Chem., 1970, 74, 647.

(47) P.R. Hammond and W.S. McEwan, J. Chem. Soc. (A), 1971, 3812.

(48) A.M. Noble and J.M. Winfield, J. Chem. Soc. (A), 1970, 501.

(49) A.M. Noble, and J.M. Winfield, J. Chem. Soc. (A), 1970, 2574.

(50) L.B. Handy, K.G. Sharpe and F.E. Brinckmann, Inorg. Chem., 1972, 11, 523.

(51) B. Cohen, A.J. Edwards, M. Mercer and R.D. Peacock, Chem. Comm., 1965, 322.

(52) G.W. Fraser, M. Mercer and R.D. Peacock, J. Chem. Soc. (A), 1967, 1091.

(53) G.W. Fraser, C.J.W. Gibbs and R.D. Peacock, J. Chem. Soc. (A), 1970, 1708.

(54) A. Majid, R.R. McLean, T.J. Ouelette, D.W.A. Sharp and J.M. Winfield, Inorg. Nucl. Chem. Letters, 1971, 6, 53.

(55) A. Majid, R.R. McLean, D. W.A. Sharp and J.M. Winfield, Z. anorg. Chem., 1971, 385, 85.

(56) A. Majid, D.W.A. Sharp, J.M. Winfield and I. Hanley, J.C.S. Dalton, 1973, 1876.

(57) F.E. Brinckmann and R.B. Johannsen, J. Fluorine Chem. 1971/72, 1, 493.

(58) F.E. Brinckmann, R.B. Johannsen, R.F. Hammerschmidt and L.B. Handy, J. Fluorine Chem., 1975, 6, 427.

(59) D.W. Walker and J.M. Winfield, J. Fluorine Chem., 1971/72, 1, 376.

(60) L.B. Handy, J. Fluorine Chemistry, 1976, 7, 641.

(61) D.A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' 158, Cambridge University Press, 1968.

(62) F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', (Third Edition), Wiley, New York.

(63) L. Gulyer, G. Wilkinson and D.R. Lloyd J.C.S. Chem. Comm., 1975, 497.

(64) W.P. Griffith, Coord. Chem. Rev., 1970, 5, 459.

(65) M.J. Bennet, T.E. Haas and J.T. Purdham, Inorg. Chem., 1972, 11, 207.

(66) K. Seppelt, Angew. Chem. internal Edit., 1974, 13, 92.

(67) I. Beattie, R. Crocombe, A. German, D. Jones, C. Marsden, G. Van Schalkwyk and A. Buckovsky, J.C.S. Dalton, 1976, 1381.

(68) A Müller, B. Krebs and W. Holtje, Spectrochim Acta, 1967, 23A, 2753.

(69) B. Krebs and A. Müller, J. Inorg. Nucl. Chem., 1968, 30, 463.

(70) A.F. Clifford and C.S. Kobayashi, Inorg. Syn., 1960, 6, 204.

(71) J. Lewis and G. Wilkinson, J. Inorg. Nucl. Chem., 1968, 6, 12.

(72) K.H. Schmidt, V. Fleming and A. Müller, Spectrochim Acta, 1975, 31A, 1913.

(73) R.J. Cullin, W.P. Griffith and D. Pawson, J. Mol. Struct., 1973, 19, 531.

(74) A. Müller, F. Bollmann and E.J. Baran, Z. anorg. Chem., 1969, 370, 238.

(75) W.P. Griffith, J. Chem. Soc., 1965, 3694.

(76) W.P. Griffith and D. Pawson, J.C.S. Dalton, 1973, 1315.

(77) W.P. Griffith and D. Pawson, J.C.S. Chem. Comm., 1973, 418.

(78) D. Bright and J.A. Ibers, Inorg. Chem., 1969, 8, 709.

(79) P.W.R. Carfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 1967, 6, 197.

(80) R.J. Doedens and J.A. Ibers, Inorganic Chem., 1967, 6, 204.

(81) W.O. Davies, N.P. Johnson, P. Johnson and A.J. Graham, Chem. Comm., 1969, 736.

(82) M.G.B. Drew, K.C. Moss and N. Rolfe, Inorg. Nucl. Chem. Letters, 1971, 7, 1219.

(83) M.G.B. Drew, G.W.A. Fowles, D.A. Rice and N. Rolfe, Chem. Comm., 1971, 231.

(84) D. Bright and J.A. Ibers, Inorg. Chem., 1968, 7, 1099.

(85) D. Bright and J.A. Ibers, Inorg. Chem., 1969 8, 703.

(86) G.A. Heath, R. Mason and K.M. Thomas, J. Amer. Chem. Soc., 1974, 96, 259.

(87) J. Chatt, J.D. Garforth, N.P. Johnson and G.A. Rowe, J. Chem. Soc., 1964, 1012.

(88) J. Chatt, J.R. Dilworth and G.J. Leigh, J. Chem. Soc. (A), 1970, 2239.

(89) A. Slavisch, Z. anorg. Chem., 1970, 374, 291.

(90) G.W.A. Fowles, K.C. Moss, D.A. Rice and N. Rolfe J.C.S. Dalton, 1973, 1871.

(91) J. Chatt, G.A. Heath and R.L. Richards, J.C. S. Dalton, 1974, 2074.

(92) D.C. Bradley and I. Thomas, Can. J. Chem., 1962, 40, 1355.

(93) D.C. Bradley and M.H. Gitlitz, J. Chem. Soc. (A), 1969, 980.

(94) Yu. A. Buslaev, Yu. V. Kokunov, V.A. Bochkareva, M.P. Gustyakova and D.N. Suglobov, Russ. J. Inorg. Chem. 1974, 19, 652.

(95) R. Bougon, T. Bui Huy and P. Charpin, Inorg. Chem. 1975,14, 1822.

(96) Mary Harman, Ph.D., Thesis, University of Glasgow, 1973.

(97) M. Harman, D.W.A. Sharp and J.M. Winfield, Inorg. Nucl. Chem. Letters, 1974, 10, 183.

(98) Yu. V. Kokunov, Yu. D. Chubar, V.A. Bochkareva and Yu. A. Buslaev, Koord. Khim., 1975, 1, 1100.

(99) H. Funk, W. Weiss and G. Mohaupt, Z. anorg. Chem., 1960, 304, 238.

(100) Yu. A. Buslaev, Yu. V. Kokunov and V.A. Bochkareva, Russ. J. Inorg. Chem., 1971, 16, 1393.

(101) Yu. A. Buslaev, Yu. V. Kokunov, V.A. Bochkaneva and E.M. Shustorovich, Russ J. Inorg. Chem., 1972 17, 1675.

(102) Yu. A. Buslaev, Yu. V. Kokunov, V.A. Bochkareva and E.M. Shustorovich, J. Inorg. Nucl. Chem., 1972, 34, 2861.

(103) W. McFarlane, A.M. Noble and J.M. Winfield, J. Chem. Soc. (A), 1971, 948.

(104) Alexander M. Noble, Ph.D. Thesis, University of Glasgow, 1970.

(105) A.J. Edwards and G.R. Jones, J. Chem. Soc. (A), 1968, 2074.

(106) I.R. Beattie and D.J. Reynolds, Chem. Comm., 1968, 1531.

(107) G. Mavel and G. Martin, J. Chim. phys., 1962, 59, 762.

(108) L.B. Asprey, R.R. Ryan and E. Fuckushima, Inorg. Chem., 1972, 11, 3122.

(109) Yu A. Buslaev, Yu. V. Kokunov and V.A. Bochkareva, Zhur. Strukt. Khim., 1972, 13, 611.

(110) H.C. Clark and H.J. Emeléus, J. Chem. Soc., 1957, 4778.

(111) M.L. Hair and P.L. Robinson, J. Chem. Soc., 1960, 2775.

(112) G.W. Watt and E.M. Potrafke, J. Inorg. Nucl. Chem., 1961, 17, 248.

(113) G.W. Watt and N.C. McMordie Jr., J. Inorg. Nucl. Chem., 1965, 27, 2013.

(114) D.E. Mulligan and M.E. Jacox , J. Mol. Spectroscopy, 1962, 8, 126.

(115) J. Reedijk, A.P. Zuur and W.L. Groenveld, Rec. Trav. chim., 1967, 86, 1127.

(116) K.F. Purcell and R.S. Drago, J. Amer. Chem. Soc. 1966, 88, 919.

(117) K. Nakamoto, 'Infra-red Spectra of Inorganic and Coordination Compounds', Wiley-Interscience, New York and London, 1970, p. 178.

(118) K.F. Purcell, J.Amer. Chem. Soc., 1967, 89, 247.

(119) Yu. A. Buslaev, Yu. V. Kokunov and Yu. D. Chubar, Doklady Akad. nauk SSSR, 1974, 217, 93.

(120) Yu. A. Buslaev, Yu. V. Kokunov and Yu. D. Chubar, Doklady Akad. nauk SSSR, 1973, 213, 1083.

(121) R.G. Jones and W.J. Orville-Thomas, J. Chem. Soc. 1965, 4632.

(122) G.P. Van der Kilen and Z. Eeckhaut, J. Mol. Spectroscopy, 1963, 10, 141.

(123) N.E. Duncan, and G.J. Janz, J. Chem. Phys., 1955, 23, 434.

(124) J. Chatt and J.R. Dilworth, J.C.S. Chem. Comm., 1975, 983.

(125) G.A. Heath, R. Mason and K.M. Thomas, J. Amer. Chem. Soc., 1974, 96, 259.

(126) H. Bürger, Spectrochim Acta., 1968, 24A, 2015.

(127) H. Kriegsmann, Z. anorg. Chem.,1958, 294, 113.

(128) I.D. Kuntz Jr., P. Van R. Schleyer and A. Allerhand, J. Chem. Phys., 1961, 35, 1533.

(129) W. Gordy, Disc. Faraday Soc., 1955, 19, 14.

(130) R.A. Ogg and J.D. Ray, J. Chem. Phys., 1957, 26, 1339.

(131) P. Klaeboe, Acta. Chem. Scand., 1968, 22, 2817.

(132) P.V. Huong and E. Raducanu, J. Mol. Struct., 1974, 23, 81.

(133) P.W.N.M. Van Leeuwen and W.L. Groeneveld, Rec. Trav. chim , 1967, 86, 1217.

(134) F.A. Cotton, R. Francis and W.D. Horrocks, J. Phys, Chem., 1960, 64, 1534.

(135) F.A. Cotton, R.D. Barnes and E. Bannister, J. Chem. Soc., 1960, 2199.

(136) F.A. Cotton and R. Francis, J. Amer. Chem. Soc., 1960, 82, 2986.

(137) M.J. Bennett, F.A. Cotton and D.L. Weaver, Nature, 1966, 212, 286.

(138) E.A.V. Ebsworth, 'Volatile Silicon Compounds', Pergamon Press, 1963, Ch. 5, p. 101 - 121.

(139) B. Csakvarie, Z.S. Wagner, P. Gömöny, F.C. Mÿlhoff, B. Rozsondai and I. Hargittai, J. Organometal Chem., 1976 107, 287.

(140) W. Airey, C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick and D.W.J. Cruickshank, Trans. Faraday Soc. 1970, 66, 551.

(141) K. Seppelt, Inorg. Chem., 1973, 12, 2837.

(142) C. Eaborn., J. Chem. Soc., 1955, 2047.

(143) R.O. Sauer and R. Hasek, J. Amer. Chem. Soc., 1946, 68, 241.

(144) V. Mark, G.D. Dungan, M. Crutchfield and J. Van Wazer, in 'Topics in Phosphorus Chemistry', Edit. M. Grayson and E.J. Griffiths, Wiley, (1967) 145.

(145) M.Y. De Wolf, J. Mol. Spectroscopy, 1965, 18, 59.

(146) D.H. Brown, K.D. Crosbie, G.W. Fraser and D.W.A. Sharp, J. Chem. Soc. (A), 1969, 872.

(147) C.I. Meyrick and H.W. Thompson, J. Chem. Soc., 1950, 225.

(148) L.J. Bellamy, 'The Infra-Red Spectra of Complex Molecules', Methuen and Co. Ltd., 2nd Edition, 1958, p.311.

(149) L.C. Thomas and R.A. Chittenden, Spectrochimica Acta, 1964, 20, 467.

(150) L.C. Thomas and R.A. Chittenden, Spectrochimica Acta, 1964, 20, 489.

(151) R.G. Harvey and E.R. De Sombre, 'Topics in Phosphorus Chemistry', 1964, 1, 57.

(152) D.H. Brown, G.W. Fraser, A. McAuley and D.W.A. Sharp, J. Chem. Soc. (A), 1969, 872.

(153) H.K. Hall, J. Amer. Chem. Soc., 1957, 79, 5441.

(154) A. Thêorêt and C. Sandorfy, Spectrochimica Acta, 1967, 23A, 519.

(155) A. Cabana and C. Sandorfy, Spectrochimica Acta, 1962, 18, 843.

(156) B. Chenon and C. Sandorfy, Can J. Chem. 1958, 36, 1181.

(157) R.D. Waldron, J. Chem. Phys., 1953, 21, 734.

(158) W. Kynaston, B.E. Lavecombe and H.S. Turner, J. Chem. Soc., 1960, 1772.

(159) W.P. Griffith and T.D. Wickins, J. Chem. Soc. (A), 1968, 400.

(160) M.G. Ahmed, R.W. Alder, G.H. James, M.L. Sinnot and M.C. Whiting, Chem. Comm., 1968, 1533.

(161) Abdul Majid, Ph.D. Thesis, University of Glasgow, 1972.

(162) D.M. Adams, G.W. Fraser, D.M. Morris and R.D. Peacock, J. Chem. Soc. (A), 1968, 1131.

(163) S. Siegel and D.A. Northrop, Inorg. Chem., 1966, 5, 2187.

(164) P.A. Tucker, P.A. Taylor, J.H. Holloway and D.R. Russell, Acta Cryst. (B), 1975, 31, 906.

(165) J.C. Fuggle, Ph.D. Thesis, University of Glasgow, 1972.

(166) R.C. Lord and F.A. Miller, Appl. Spectroscopy,1956, 10, 115.

(167) T.A. Lane and J.T. Yuke, Inorg. Chem., 1976, 15, 484.

(168) D.D. Perrin, W.L.F. Armarego and D.R. Perrin, 'Purifications of Laboratory Chemicals', Pergamon Press, 1966.

(169) L. Birkofer and G. Schmidtberg, Chem. Ber., 1971, 104, 3831.

(170) D. Herbison-Evans and R.E. Richards, Mol. Physics, 1964, 8, 19.

(171) R.B. Johannesen, F.E. Brinckmann and T.D. Coyle, J. Phys. Chem., 1968, 72, 660.

(172) H. Schmidbaur, J. Amer. Chem. Soc., 1963, 85, 2336.

(173) E. Grunwald, P.J. Karabatsos, R.A. Kromhout and E.L. Purlee, J. Chem. Phys., 1960, 33, 556.

(174) G. Van Dyke Tiers, 'Characteristic Nuclear Magnetic Resonance (N.M.R.), Shielding Values, (Spectra Positions) for Hydrogen in Organic Structures.'
Part I, 'Tables of values for a variety of organic compounds,' Minnesota Mining and Manufacturing Company, 1958.

(175) R. Mecke and F. Langenbucker, 'Infra-red Spectra of Selected Chemical Compounds.' Heyden, London, 1965, MeF No. 1687.

(176) W. Pauli, Naturwiss, 1924, 12, 741.

(177) 'Handbook of Chemistry and Physics', ed. R.C. West, Chemical Rubber Company, Cleveland, 55th Edn., 1974, and refs. therein.

(178) R.K. Harris, Chem. Soc. Revs., 1976, 5, 1.

(179) J.W. Akitt, 'N.M.R. and Chemistry', Chapman and Hall, London, 1973.

(180) J.A. Pople, W.G. Schneider and H.J.Bernstein, 'High-resolution Nuclear Magnetic Resonance', McGraw-Hill, New York, 1959.

(181) J.W. Emsley, J. Feeney and L.H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Oxford, London, Pergamon Press, 1965, Vols. I and II.

(182) M. Witanowski and G.A. Webb, Annual Reports on N.M.R. Spectroscopy, 1972, 5A, 395.

(183) J.A. Pople, J. Chem. Phys. 37, 53.

(184) J.A. Pople, J. Chem. Phys., 1962, 37, 60.

(185) J.A. Pople, Discuss. Faraday Soc., 1963, 34, 7.

(186) A. Saika and C.P. Slichter, J. Chem. Phys., 1954, 22, 26.

(187) C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 1964, 40, 1714.

(188) S.S. Dharmatti and C.R. Kanekar, J. Chem. Phys., 1959, 31, 1436.

(189) G.P. Betteridge and R.M. Goulding, J. Chem. Phys., 1969, 51, 2497.

(190) V. Gutmann, Chemistry in Britain, 1971, 7, 102.

(191) J.A. Pople and D.P. Santry, Mol. Phys., 1964, 8, 1.

(192) W. McFarlane, Quart. Rev., 1969, 23, 187.

(193) G.W. Fraser, R.D. Peacock and W. McFarlane, Mol. Phys., 1969, 17, 291.

(194) P.A.W. Dean and D.F. Evans, J. Chem. Soc. (A), 1968, 1154.

(195) A.D. Buckingham and K.A. McLauchlan, Progress in N.M.R. Spectroscopy, 1967, 2, 63.

(196) A.D. Buckingham and K.A. McLauchlan, Procc. Chem. Soc., 1963, 144.

(197) R.D. Chambers, L.H. Sutcliffe and G.J.T. Tiddy, Trans. Faraday Society, 1970, 66, 1025.

(198) T. Schaeffer, W. Niemczura and K. Marat, J.C.S. Faraday II, 1975, 71, 1526.

(199) B. Cox, D.W.A. Sharp and A.G. Sharpe, J. Chem. Soc., 1956, 1242.

(200) G.B. Hargreaves and R.D. Peacock, J. Chem. Soc., 1958, 2170.

(201) N.S. Nikolaev and V.F. Sukoverkhov, Doklady Akad. Nauk S.S.S.R., 1961, 136, 621.

(202) A. Prescott, D.W.A. Sharp and J.M. Winfield, J.C.S. Dalton, 1975, 936.

(203) J.D. Dunitz and L.E. Orgel, J. Chem. Soc.,1953, 2594.

(204) A.G. Lee, 'The Chemistry of Thallium', Elsevier, London, 1971.

(205) Yu. A. Buslaev and R.L. Davidovitch, Russ. J. Inorg. Chem., 1968, 13, 656.

(206) C.W.N. Cumper and S. Walker, Trans. Faraday Soc., 1956, 52, 193.

(207) R. Mattes, G. Muller and H.J. Becher, Z. anorg. Chem., 1972, 389, 177.

(208) R.W.M. D'Eye and E. Wait, 'X-Ray Powder Photography in Inorganic Chemistry', Butterworth, London, 1960.

(209) B.N. Figgis and J. Lewis, 'The Magnetochemistry of Complex Compounds', in J. Lewis and R.G. Wilkins, (Eds.), 'Modern Coordination Chemistry', Wiley, New York, 1960.

(210) J. Heicklen and V. Knight, Spectrochim Acta, 1964, 20, 295.

(211) R.D. Chambers, H.C. Clark and C.J. Willis, J. Amer. Chem. Soc., 1960, 82, 6238.

(212) G.P. Van der Kelen, E.V. Van den Berghe and L. Verdonck 'Organotin Halides', in A.K. Sawyer (Ed.), 'Organotin Compounds', Vol.I, Dekker, New York, 1971.

(213) L.E. Orgel and R.S. Mulliken, J. Amer. Chem. Soc. 1957, 79, 4839.

(214) F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', (Third Edition), Wiley, New York.

(215) H.C. Clark and C.J. Willis, J. Amer. Chem. Soc., 1960, 82, 1890.

(216) K. Moedritzer, Organometallic Chem. Rev., 1966, 1, 179.

(217) K. Moedritzer, Advance in Organometallic Chem., 1968, 6, 171.

(218) E. Nield, R. Stephens and J.C. Tatlow, J. Chem. Soc., 1959, 166.

(219) R.D. Chambers and T. Chivers, J. Chem. Soc., 1964, 4782.