

SYNTHESIS, CHARACTERIZATION, REACTIONS AND  
FLUORINE EXCHANGE STUDIES OF PHENYLTELLURIUM(VI) FLUORIDES

BY  
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A thesis submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

DOCTOR OF PHILOSOPHY

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## ABSTRACT

Oxidative fluorinations of phenyltellurium(I,II and IV) compounds by  $\text{XeF}_2$  have been investigated and the new phenyltellurium(VI) pentafluoride,  $\text{PhTeF}_5$ , trans-diphenyltellurium(VI) tetrafluoride, trans- $\text{Ph}_2\text{TeF}_4$ , mer-triphenyltellurium(VI) trifluoride, mer- $\text{Ph}_3\text{TeF}_3$ , triphenyltellurium(VI) difluoride chloride,  $\text{Ph}_3\text{TeF}_2\text{Cl}$  and tetraphenyltellurium(VI) difluoride,  $\text{Ph}_4\text{TeF}_2$ , formed in these reactions have been characterized by  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectroscopy, mass spectrometry and elemental analysis.

Substitution reactions of  $\text{Ph}_n\text{TeF}_{6-n}$  ( $n = 1, 2, 3$ ) with dimethylamine, methanol, water and  $\text{X-SiMe}_3$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) have been investigated and substituted products  $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{HO}, \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ),  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ),  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$ , and  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) formed in these reactions have been characterized by  $^{19}\text{F}$  NMR and mass spectra. Qualitative assignment of fluorine resonances in cis- $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{MeO}, \text{HO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) and  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) have been made on the basis of calculated (empirically) chemical shifts.

A fluoride donor-acceptor reaction between mer- $\text{Ph}_3\text{TeF}_3$  and  $\text{PF}_5$  has been carried out and the novel fluorocation  $\text{Ph}_3\text{TeF}_2^+$  formed in this reaction has been characterized by NMR and chemical reactions.

Intermolecular fluorine exchange in mer- $\text{Ph}_3\text{TeF}_3$  has been initiated by adding  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  and stereoselective fluorine exchange in the system  $\text{Ph}_3\text{TeF}_3$ - $\text{Ph}_3\text{TeF}_2^+$  has been observed.

The progress made in the above oxidative fluorinations and fluoride donor-acceptor reactions has been briefly extended to phosphorus, iodine and tellurium(IV) compounds.



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Md. Kohrshed Alam

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ABBREVIATIONS

aq	aqueous
ax	axial
eq	equatorial
e.s.d	estimated standard deviation
Et	ethyl group
h	hour
Me	methyl group
Ph	phenyl group
R	alkyl group

*To my children,  
Jahangir and Lina*

*To my children,  
Jahangir and Lina*

## 1. INTRODUCTION

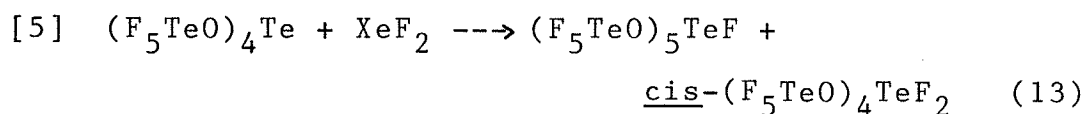
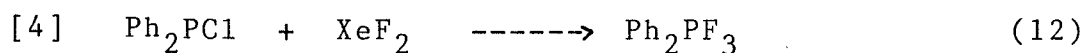
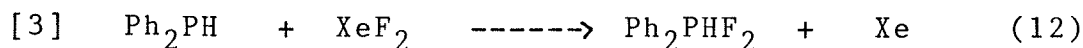
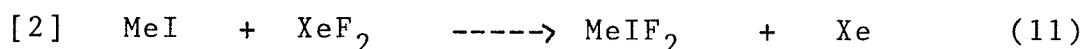
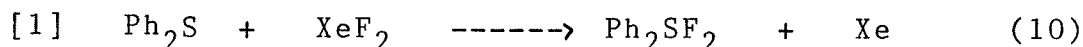
### 1.1 General:

Main group compounds with organic substituents show their highest oxidation state with the highly electronegative fluoride ligand (1) and their stability varies with the stereochemical and electronic environment created by the nature of the attached substituents (1-4). The chemistries of the organo derivatives of group VA fluorides (5) and organoiodine(V) fluorides in group VIIA in the pentavalent state are well known (2,3). No organic substituted chlorine- and bromine-fluorides in high oxidation states have been prepared. Organosulphur(VI) fluorides (6-8) are well known, but the corresponding area of organotellurium(VI) fluorides has been little explored. The first perfluoroalkyltellurium(VI) halide (9) was reported by Passmore and co-workers in 1974.

Since the experimental work to be described in this thesis concerns the preparations of phenyltellurium(VI) fluorides from the oxidative fluorinations of a variety of phenyltellurium compounds with  $\text{XeF}_2$ , and their chemical reactions, the following introduction may serve to familiarize the reader with what is known of the preparations, structure and chemistry of organo derivatives of group VIA fluorides.

## 1.2 Oxidative fluorinations by xenon difluoride:

Main group fluoride derivatives in high oxidation states are frequently obtained by oxidative fluorination of the lower valent compounds. Xenon difluoride readily oxidizes the central element of main group compounds under mild conditions in acetonitrile, methylene chloride, etc. Typical examples of oxidative fluorinations (10-13) by xenon difluoride are given below:



Reaction [3] demonstrates that oxidation of P(III) to P(V) by xenon difluoride occurs without destruction of the P-H bond (12) whereas the P-Cl bond has been converted to P-F in the reaction [4]. In reaction [5], the formation of  $(\text{F}_5\text{TeO})_5\text{TeF}$  as a major product remains unexplained (13).

Considering the influence of reaction conditions upon oxidized product type, it has been found (10) that under mild condition  $\text{Ph}_2\text{SF}_2$  is stable towards further oxidation by xenon difluoride. The reaction of xenon difluoride with an excess of methyl iodide in absence of solvent and at room temperature has been found to produce methyl iodine(III) difluoride in essentially quantitative yield whereas no reaction was observed below  $-40^\circ\text{C}$  (11).

It is interesting to note here that the presence of an  $\alpha$ -hydrogen in the sulphur(II) compounds leads to  $\alpha$ -fluorination in the reaction of xenon difluoride (10,14). Such  $\alpha$ -fluorination reactions, as shown in equation [6], may evolve via the oxidized intermediate  $\text{R}(\text{CH}_3)\text{SF}_2$  (10).



The oxidative fluorinations by xenon difluoride, described above, illustrate the scope of this non-destructive fluorinating agent. The very inert xenon gas is the only side product in the oxidative fluorinations by xenon difluoride and the evolution of xenon gas, as shown in equations [1-3], provides an additional way of monitoring the reaction. Stable solid xenon difluoride is available commercially in very pure form and is inert to nickel, monel, thoroughly dried glass (15) or Teflon apparatus. The slow rate of hydrolysis of xenon difluoride



( $t_{1/2} \approx 7$  hours at  $0^\circ\text{C}$ ) (16) makes it especially favourable for carrying out clean reactions.

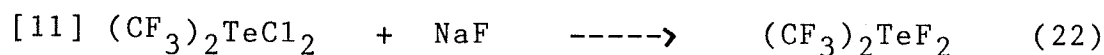
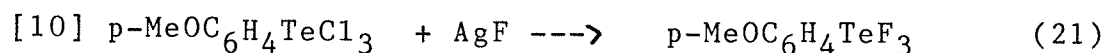
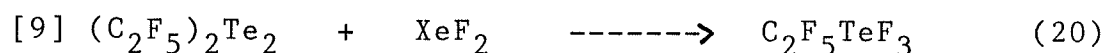
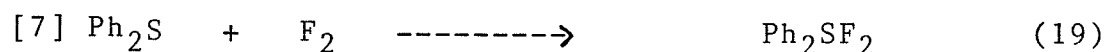
It would be appropriate to discuss, in brief, the fluorinations by some other fluorinating agents. The halogen fluorides, very powerful fluorinating agents, are extremely corrosive and hydrolyze readily. Extensive decomposition of products and even explosions occur in fluorination reactions with  $\text{ClF}$  (9) and  $\text{ClF}_3$  (1) unless the addition of the reagent at low temperature is rigorously controlled. Sulphur tetrafluoride has been widely used for oxidative fluorinations as well as for the selective replacement of doubly bonded oxygen or hydroxyl groups by fluorine (17). The practical disadvantage with  $\text{SF}_4$  is the need for working under pressure. Fluorination with metal fluorides leaves a reactive residue as a by-product (18).

### 1.3 Organo derivatives of chalcogen fluorides:

The chemistry of the organochalcogen(IV) fluorides is well known but comparatively little is known about hexavalent organochalcogen(VI) fluorides. Since the present thesis concerns the preparation of hexavalent phenyltellurium(VI) fluorides, the discussion in this section is organized under the oxidation state categories. This will allow easy comparison of the results recorded in this thesis with related material in the literature.

### 1.3.1 Organochalcogen(IV) fluorides:

Organochalcogen(IV) fluorides, in general, form a well characterized group of compounds with well defined physical and chemical properties. They have been prepared by a variety of methods and some representative examples (9,19-24) are shown below.



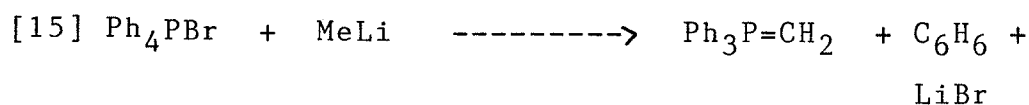
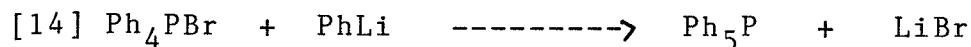
From the above representative examples it is clear that oxidative fluorinations (9,19,20,24) as well as fluoride substitutions (21,22) have been used to prepare organochalcogen(IV) fluorides. Decomposition products  $\text{CF}_4$ ,  $\text{C}_2\text{F}_5\text{Cl}$ ,  $\text{SiF}_4$ , etc. as well as a small amount of a further

oxidized product, trans- $\text{C}_2\text{F}_5\text{TeClF}_4$ , have been identified (9) with  $\text{ClF}$  oxidation in reaction [8].

Thermally stable organochalcogen(IV) fluorides have varying sensitivity to moisture. The monofluoride derivatives are usually reactive. For  $\text{Ph}_3\text{TeF}$  a single peak has been observed in the  $^{125}\text{Te}$  NMR spectrum (25). The author has explained this result as due to ionization as  $\text{Ph}_3\text{Te}^+\text{F}^-$  (25). However, the possibility of intermolecular fluorine exchange in  $\text{Ph}_3\text{TeF}$  in solution has not been investigated. Intermolecular fluorine exchange may also led to a single peak in the  $^{125}\text{Te}$  NMR spectrum of  $\text{Ph}_3\text{TeF}$ . The difluoride derivatives are covalent molecules and the covalent nature has been proven in many cases by the triplet splitting of  $^{13}\text{C}\{-\text{H}\}$  NMR signals (19). Only a few trifluoride derivatives are known. Probably because of extreme reactivity and hydrolytic nature they are very difficult to characterize spectroscopically. Many known examples of trifluoride derivatives do not show fine structure in  $^{19}\text{F}$  NMR spectra (24) perhaps because of impurity catalyzed intermolecular or intramolecular exchange processes.

The examples in the above equations [7-13], clearly demonstrate that perfluoroalkyl and phenyl ligands form stable organochalcogen(IV) fluorides. The stability conferred to high oxidation state compounds by phenyl and perfluoroalkyl ligands, is further illustrated by the existence of stable  $\text{Ph}_4\text{Te}$  (26) and  $(\text{CF}_3)_4\text{Te}$  (27). Further

examples of stabilization of high coordination states by phenyl groups only are given by the fact that stable  $\text{Ph}_5\text{P}$  (28),  $\text{Ph}_5\text{As}$  (29), and  $\text{Ph}_5\text{Sb}$  (30) can be prepared whereas an attempt to make methyltetraphenylphosphorane by the same method gives a four-coordinate ylide:



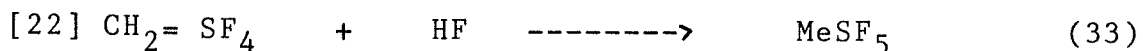
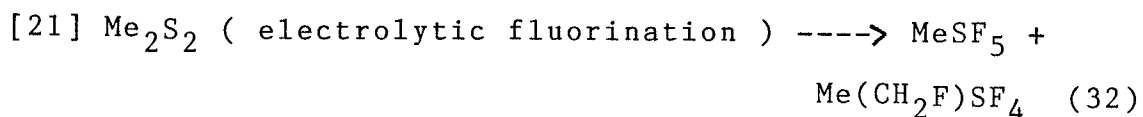
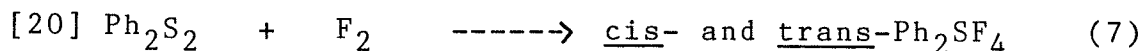
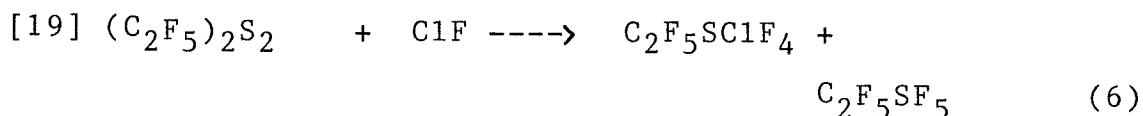
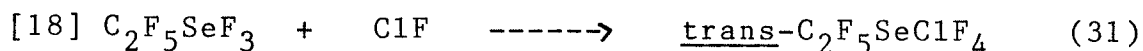
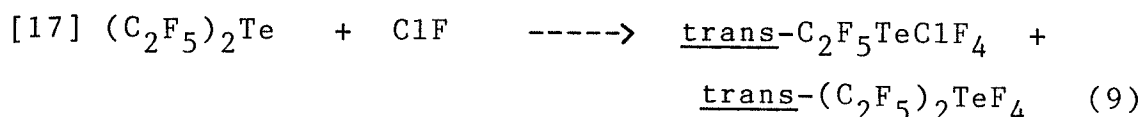
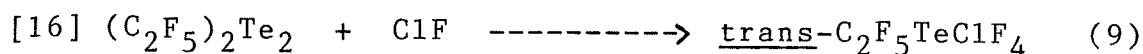
It is interesting to note here that while  $\text{Ph}_3\text{SeF}$  has been prepared (23), an attempt to prepare  $\text{Ph}_4\text{Se}$  led to the formation of biphenyl and  $\text{Ph}_2\text{Se}$  (29). No tetraorganoselenium compound is known yet. Thus, the stability of high coordination state compounds depends on the electronic and stereochemical environment created by the attached ligands.

There are some very interesting chemical features of the representative compounds shown in equations [7-13]. It will be convenient to discuss these aspects, e.g. fluorine exchange processes, spectroscopic properties and solid state structures later in this chapter.

### 1.3.2 Organochalcogen(VI) fluorides:

Organochalcogen(VI) fluorides are extensively

known with sulphur but little is known about selenium and tellurium. Except for  $\text{MeSF}_5$ , all known organochalcogen(VI) fluorides have been prepared by oxidative fluorinations of the corresponding lower valent compounds. Known representative examples of organochalcogen(VI) fluorides (6,7,9,31-33) are presented in equations below:



Oxidative fluorinations by  $\text{ClF}$  in equations [16-19] have been found to produce decomposition products, such as  $\text{Cl}_2$ ,  $\text{C}_2\text{F}_6$ ,  $\text{TeClF}_5$ , etc. and the

decomposition rate has been found to be higher with higher molar ratio of ClF (6,9,31). In most of the above mentioned reactions, oxidized products are separated by simply removing the volatile impurities, by-products and solvents under dynamic vacuum(32,33).

As the above equations [14-20] do not show the experimental details, it would be interesting to describe here one such preparation. Thus, in the preparation of trans-C<sub>2</sub>F<sub>5</sub>TeClF<sub>4</sub>, by Passmore and co-workers, excess ClF (17.5 mmole) was added to (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Te<sub>2</sub> (1.36 mmole) in eight aliquots in a Kel-F vessel held at -78°C. The reaction was complete after 3 hrs at room temperature. The volatile materials at -78°C were found to be Cl<sub>2</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>2</sub>F<sub>5</sub>Cl, TeClF<sub>5</sub>, trans-C<sub>2</sub>F<sub>5</sub>TeClF<sub>4</sub> and ClF (9). Pure trans-C<sub>2</sub>F<sub>5</sub>TeClF<sub>4</sub> was obtained from the least volatile fraction of the mixture. It was also observed that reaction with high molar ratio of ClF at room temperature is extremely exothermic, when the products are C<sub>2</sub>F<sub>6</sub> and TeF<sub>6</sub> as characterized by IR, and a solid mixture of TeCl<sub>4</sub> and TeF<sub>4</sub> as characterized by Raman spectra.

<sup>19</sup>F NMR has been widely used to elucidate the geometry of the products in the above mentioned reactions. Spectroscopic properties and the structure of tellurium(VI) fluoride derivatives will be discussed later in this chapter.

Chalcogen(VI) fluoride derivatives with phenyl substituents are known only for sulphur (7). An

aryliodine(V) fluoride of the neighbouring group VII is also known (3). Thus, it is of interest to synthesize phenyltellurium(VI) fluorides containing one or more phenyl groups.

#### 1.4 Substitution reactions of chalcogen(VI) fluorides with alcohols, amines, water and silicon compounds:

In common with many other high oxidation state fluorides (34,35), chalcogen(VI) fluorides generally react with various nucleophiles. However,  $\text{SF}_6$  is extremely inert chemically, especially towards nucleophiles.  $\text{SF}_6$  and likewise  $\text{MeSF}_5$  (36) are inert to bases. In contrast,  $\text{SClF}_5$  has an extensive chemistry (37). Reactions of  $\text{SClF}_5$  which involve substitution of chlorine are not of great importance to this work. The reactivity of the chalcogen(VI) fluorides increases as the group is descended. Thus,  $\text{TeF}_6$  can directly form a variety of substituted derivatives (39-41). The result of a wide variety of representative substitution reactions of chalcogen(VI) fluorides has been summarized in Table I.

In many cases product formation, defluorination or reduction of products in these reactions has been monitored, mainly by  $^{19}\text{F}$  NMR spectroscopy. Product composition and structure have been determined by mass and NMR spectral studies. Yields in most cases are, at best,

moderate, and usually quite low. Regarding the stability of substituted products, methoxy derivatives are found to be more stable than the corresponding amino derivatives (43).

Table I. Fluoride substitution reactions of chalcogen(VI) fluorides and their derivatives

reactants	products	reference
$\text{TeClF}_5, \text{Me}_3\text{Si-OMe}$	<u>cis-</u> and <u>trans-</u> $\text{MeOTeClF}_4$	38
$\text{TeClF}_5, \text{MeOH}, \text{Na}_2\text{CO}_3$	<u>cis-</u> and <u>trans-</u> $\text{MeOTeClF}_4$	38
$\text{TeF}_6, \text{ROH}, \text{NaF}$	$(\text{RO})_n\text{TeF}_{6-n} (n=1-5)$	39
$\text{TeF}_6, \text{H}_2\text{O}$	$(\text{HO})_n\text{TeF}_{6-n} (n=1-5)$	40,41
$\text{TeF}_6, \text{Me}_3\text{Si-OH}$	$\text{HOTeF}_5$	42
$\text{TeF}_6, \text{Me}_3\text{Si-NR}_2$	$\text{R}_2\text{NTeF}_5, \text{cis-}(\text{R}_2\text{N})_2\text{TeF}_4$	43,44
$\text{SXF}_5 (\text{X=Cl, Br}), \text{Me}_2\text{N-SiR}_3$	$\text{Me}_2\text{NSXF}_4$	45

Besides the information summarized in Table I, several other interesting points may be discussed further. For example, product formations, substitutions and reductions depend very much upon the reaction conditions, such as reactant ratios, solvent, temperature, time of reaction and the nature and source of added nucleophiles.



Thus,  $\text{MeOTeF}_5$  has been formed from the reaction of excess  $\text{TeF}_6$  and  $\text{MeOH}$  in presence of  $\text{NaF}$  whereas cis-( $\text{MeO}$ ) $_2\text{TeF}_4$  has been obtained from the reaction of  $\text{TeF}_6$  and excess  $\text{MeOH}$  in the presence of pyridine (46). Attempts to prepare trisubstituted derivatives resulted in complete decomposition of  $\text{TeF}_6$  (46). Usually multiple substitution occurs if pyridine is used as a base. In such reactions,  $\text{NaF}$  and pyridine combine with the free hydrogen fluoride formed as product in reaction [23].



The following reactions provide excellent examples of the fact that the rate of such reactions depends on the nature of the nucleophile. Thus, methoxy derivatives, e.g.  $\text{MeOTeF}_5$  have been formed in a few hours, but the corresponding reaction of  $\text{TeF}_6$  with ethanol take 3-4 days and propanol and butanol reactions have not been completed after 1 week (39). In contrast to alcohols, triorganosilanol reacts with  $\text{TeF}_6$  to form pentafluoroorthotelluric acid,  $\text{HOTeF}_5$  and fluorosilane  $\text{R}_3\text{SiF}$  (42). In contrast to  $\text{TeF}_6$ ,  $\text{SeF}_6$  does not appear to hydrolyze over a long period of time (40).

Perhaps the reduction of substituted chalcogen(VI) fluorides in the reactions listed in Table I could be stressed here again. For example, some reductions of  $\text{Te(VI)}$  to  $\text{Te(IV)}$  have been observed in the reactions of

$\text{TeClF}_5$  with  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ,  $\text{MeO-SiMe}_3$  and  $\text{Me}_3\text{SiCl}$  (38). In the case of  $\text{Me}_3\text{SiCl}$ , the only characterized product is  $\text{TeCl}_4$ . While  $\text{SXF}_5$  ( $\text{X}=\text{Cl}, \text{Br}$ ) forms  $\text{Me}_2\text{NSXF}_4$  at  $-78^\circ\text{C}$  with  $\text{Me}_2\text{N-SiMe}_3$ ,  $\text{CF}_3\text{SClF}_4$  undergoes defluorination and reduction to  $(\text{Me}_2\text{N})_2(\text{CF}_3)\text{SCl}$  (45). It should be noted that the corresponding oxidized products have not been identified in all such reductions described above.

No such fluoride substitution reaction has yet been investigated for an organotellurium(VI) fluoride.

#### 1.5 NMR spectroscopy of tellurium fluoride derivatives:

The NMR parameters, chemical shifts and coupling constants, are greatly dependent upon the geometry and general bonding situation of a given molecule (47,48). NMR spectroscopy of heavy nuclei often offers unique possibilities for the description of the electronic and steric effects associated with the attached ligands.  $^{125}\text{Te}$  NMR shifts cover a wide range (about 4000 ppm) and because of its sensitivity ( $3.16 \times 10^{-2}$  relative to that of the proton and abundance (6.99%) it is a favourable nuclide for NMR study. The attractive features of  $^{125}\text{Te}$  NMR spectroscopy are that it has spin 1/2 and the pronounced sensitivity of the nuclear shielding and coupling constants to the stereochemical environment and the oxidation state of tellurium (49,50).  $^{123}\text{Te}$  has also spin 1/2, but its abundance is very low (0.87%). From

now on in this thesis  $^{125}\text{Te}$  shifts and coupling constants will be frequently expressed as tellurium chemical shifts and tellurium-element coupling constants unless otherwise specified.

Brief accounts of  $^{125}\text{Te}$  NMR of mainly non-fluoride derivatives have been given elsewhere (51,52). McFarlane et al. (53,54) first determined the  $^{125}\text{Te}$  NMR chemical shifts via proton ( $^1\text{H}$ - $\{^{125}\text{Te}\}$  heteronuclear magnetic double resonance experiments), but since then almost all work has used the FT technique (55,56). Tellurium NMR has recently been utilized to study the exchange reactions (49,57), the solution behaviour (50), the structures (41,58-61) and the oxidation states (49) of tellurium compounds.  $^{125}\text{Te}$  chemical shifts in some selected tellurium fluoride derivatives are shown in Table II. From Table II, it is clear that tellurium chemical shifts are sensitive to the oxidation state of tellurium, the nature and number of attached substituents as well as the stereochemistry created by the attached ligands. For example, the  $^{125}\text{Te}$  chemical shifts in tellurium(IV) compounds are farther downfield than those of tellurium(VI) compounds.

Stepwise replacement of the (HO) group in o-telluric acid,  $(\text{HO})_6\text{Te}$ , by fluorine results in decrements in tellurium chemical shifts (41). Contrary to this trend, tellurium chemical shifts in tellurium(IV) compounds increase toward lowfield with increased electronegativity

of the attached halide (50). Tellurium chemical shifts are also dependent to a certain extent on solvent and concentration (59,62), probably due to state of slight ionization.

The tellurium NMR spectra are of great help in elucidating the geometry of the tellurium fluoride derivatives. For example, Seppelt and co-workers established the mer octahedral geometry (Figure 1) of  $(F_5TeO)_3TeF_3$  from the observed doublet of triplets resonance of the central tellurium (65).

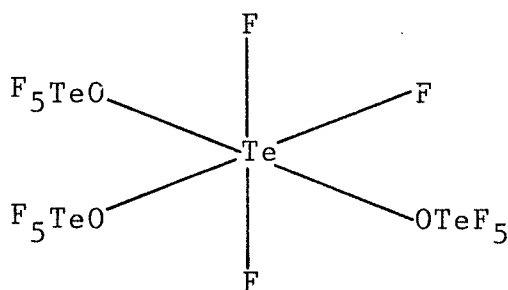


Figure 1. Structure of mer-( $F_5TeO$ ) $_3TeF_3$

Table II. Tellurium-125 chemical shifts in selected tellurium fluoride derivatives

compund	spin system	$\delta$ $^{125}\text{Te}$ in ppm	reference
$(\text{CF}_3)_2\text{TeF}_2$	$a_2x$	1187	63
$\text{TeF}_6$	$a_6x$	545	64
$\text{HOTeF}_5$	$ab_4x$	601	60
$\text{F}_5\text{TeOXe}^+\text{AsF}_6^-$	$ab_4x$	576	64
<u>mer</u> -(HO) $_3\text{TeF}_3$	$ab_2x$	671	41
<u>fac</u> -(HO) $_3\text{TeF}_3$	$a_3x$	678	41
(HO) $_5\text{TeF}$	$ax$	722	41
<u>trans</u> -(HO)(MeO) $\text{TeF}_4$	$a_4x$	640	59
<u>cis</u> -(HO) $_2\text{TeF}_4$	$a_2b_2x$	653	61
$(\text{F}_5\text{TeO})_2\text{TeF}_2$	$a_2x$ Te(IV)	1244.5	65
	$a_4x$ Te(VI)	847.9	
<u>mer</u> -( $\text{F}_5\text{TeO}$ ) $_3\text{TeF}_3$	$a_2bx$ (central Te)	886.4	65
	$a_4bx$ ( $\text{OTeF}_5$ group)	-543.5	

Note: The spin systems are for those fluorines directly bonded to tellurium (x). Positive chemical shifts are downfield of  $\text{Me}_2\text{Te}$ . Chemical shifts are to some extent solvent dependent.

Spin-spin coupling constants between tellurium and other heteroatoms are important parameters of NMR spectra characterizing the chemical bonds and stereochemical features of tellurium compounds. In general, the

tellurium-element coupling constant increases with the oxidation state of tellurium (49) and is dependent upon the number and type of attached substituents (41). The coupling constants in tellurium fluoride compounds are often most readily determined from the positions of the tellurium satellites in fluorine NMR spectra. The existence of  $^{123}\text{Te}$  makes it possible to determine the isotope shift. Spin-spin coupling constants between tellurium and fluorine are of great interest in this thesis and such coupling constants in some selected compounds containing Te(IV) and Te(VI) are presented in Table III for comparison with the results recorded in this thesis.

From Table III it is clear that tellurium-fluorine couplings are much higher in six-coordinate tellurium compounds than in four-coordinate species. Furthermore, such couplings appear to be dependent upon the number and type of substituents as well as their spatial arrangement. The tellurium-fluorine couplings decrease as the number of identical non-fluorine substituents in tellurium(VI) fluoride derivatives decrease.

$^{19}\text{F}$  NMR is frequently used to elucidate the geometry of octahedral tellurium(VI) fluoride derivatives. Thus, Passmore, et al. (9) have established the trans octahedral geometry of  $\text{C}_2\text{F}_5\text{TeClF}_4$  (Figure 2) from its observed single line fluorine resonance ( $a_4$  spin system)

Table III. Tellurium-fluorine coupling constants in some selected tellurium compounds

compound	spin system	$J_{\text{TeF}^a}$	$J_{\text{TeF}^b}$	reference
$\text{Ph}_2\text{TeF}_2$	$a_2x$	540		19
$(\text{CF}_3)_2\text{TeF}_2$	$a_2x$	234		63
$\text{TeF}_6$	$a_6$	3715		65
$\text{Cl}_2\text{NTeF}_5$	$ab_4x$	4136	4399	66
$\text{O}=\text{S}=\text{NTeF}_5$	$ab_4x$	3459	3854	66
$\text{O}=\text{C}=\text{NTeF}_5$	$ab_4x$	3520	3528	66
$\text{B}(\text{trans-O}\text{TeF}_4\text{OMe})_3$	$a_4x$	3631		62
<u>trans</u> - $\text{MeO}\text{TeClF}_4$	$a_4$	3619		38
$\text{HOTeF}_5$	$ab_4x$	3339	3552	41
<u>trans</u> -( $\text{HO}$ ) $_4\text{TeF}_2$	$a_2x$	2895		41
$(\text{HO})_5\text{TeF}$	$ax$	2754		41

Note: The absolute coupling constants are in Hz. The tellurium-fluorine coupling constants are solvent dependent.

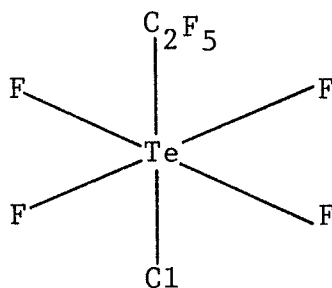


Figure 2. Structure of trans- $\text{C}_2\text{F}_5\text{TeClF}_4$

for fluorines attached to the central tellurium.

Similarly, the cis octahedral geometry of  $\text{MeOTeClF}_4$  has been established from its  $a_2bc$  spin system in its fluorine NMR spectrum (38).

NMR spectra, however, do not yield definitive structural information for compounds of the type  $\text{R}_4\text{TeF}_2$ . For such molecules both cis and trans geometry have equivalent fluorines and thus will display single line fluorine resonance and triplet tellurium resonance for each isomeric form. Complexes having equal numbers of fluorines in different environments are easily recognized by their observed spin system ( $ab$  or  $a_2b_2$  for octahedral species) in fluorine NMR spectra. However, assignment of fluorine resonances from the line patterns is difficult without additional information.

Attempts have been made to overcome the above difficulties by empirical correlation of spectroscopic parameters. Dean and Evans (68) have shown that  $^{19}\text{F}$  NMR



chemical shifts in the series  $L_n\text{SnF}_{6-n}^-$ , relative to  $\text{SnF}_6^{=}$  may be represented by equation [24] where C and T are adjustable constants characteristic of substituent L, and p and q are the number of substituents cis and trans respectively to the resonating fluorine. In octahedral species, q is either 0 or 1 while p ranges from

$$[24] \quad \delta_F = pC + qT$$

0 to 4. The points should therefore fall on two linear lines. Usually two curves are obtained, and the curves are defined by the chemical shifts of known species on the basis of their identity or distinctive line patterns of their spectra, and extrapolation of these curves permits other single line resonances in the fluorine spectrum to be identified or assigned. Such a scheme has been quite successful in helping to make assignments in the system  $(\text{HO})_n\text{TeF}_{6-n}$  (40) but Selig (69) and others (39b) have found that for  $(\text{RO})_n\text{TeF}_{6-n}$  two converging curves are obtained by the relation [24] instead of two parallel lines. Empirical correlation of NMR parameters will be further discussed later in this thesis.

## 1.6 Structures of tellurium fluoride derivatives:

Depending on the number and type of substituents octahedral tellurium(VI) fluoride derivatives may have stereoisomers. As discussed in section 1.5,  $^{19}\text{F}$  NMR often establishes the geometry of many such octahedral derivatives, but fails to yield any structural information for molecules with a single line resonance. Thus, crystal structure analysis is necessary to determine the geometry of many octahedral tellurium(VI) fluoride derivatives. However, the X-ray diffraction technique is limited to solid samples only. Crystallographic data for tellurium(VI) fluoride derivatives are also essential to explain the basicity and hence the reactivity of stereospecific fluorine in a molecule. The fluorine with the longest Te-F bond in a molecule with non-equivalent fluorines will be weakly bonded and thus may be expected to participate easily in chemical reactions or exchange processes. No crystal structure of an organotellurium(VI) fluoride has yet been reported. Known crystal structures of other tellurium(VI) - and tellurium(IV) - fluoride derivatives are discussed in the following paragraphs.

Only one crystal structure analysis of a tellurium(VI) fluoride derivative is known (69), namely that of trans-( $\text{F}_5\text{TeO}$ ) $_4\text{TeF}_2$ . In this molecule the central tellurium is surrounded by two fluorine atoms and four oxygen atoms of the  $\text{OTeF}_5$  groups in a nearly regular

octahedral arrangement with the fluorine atoms in the trans position. The four oxygen atoms deviate only slightly from the plane perpendicular to the axis passing through the central tellurium and two trans fluorines, with the  $\text{TeF}_5$  groups pointing alternately up and down. The average fluorine bond lengths are  $\text{Te-F} = 1.849(8)\text{\AA}$  for the central tellurium and  $\text{Te-F} = 1.808(5)\text{\AA}$  for the  $\text{OTeF}_5$  group. The tellurium-fluorine bonds in the central octahedron ( $1.849\text{\AA}$ ) are somewhat longer than in  $\text{TeF}_6$  ( $1.824\text{\AA}$ ) (70). The cis octahedral geometry of  $(\text{HO})_2\text{TeF}_4$  has recently (1981) been confirmed by X-ray diffraction (71), however, its bond lengths and angles were not reported.

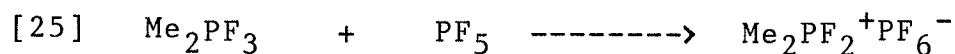
We now turn to the structure analysis of organotellurium(IV) fluorides. Organo derivatives of tellurium(IV) fluorides can be of various structural types, e.g. molecular or a fluorine bridged chain polymer (20,72). As can be seen from the following discussion, the structural type and intermolecular association in tetravalent tellurium fluoride derivatives is clearly governed by the number and type of organic substituents. Crystal structures of  $\text{C}_2\text{F}_5\text{TeF}_3$  (20) and  $\text{Ph}_2\text{TeF}_2$  (72) have recently been reported.  $\text{C}_2\text{F}_5\text{TeF}_3$  has a cis - fluorine bridged polymeric structure with mutually perpendicular polymeric chains. The  $\text{C}_2\text{F}_5$  group of  $\text{C}_2\text{F}_5\text{TeF}_3$  is in the position of an axial fluorine atom in  $\text{TeF}_4$  (73). Chains in  $\text{C}_2\text{F}_5\text{TeF}_3$  are linked by a weak  $\text{Te} \cdots \text{F}$  interaction

[3.168(9)Å] as compared to that in  $\text{TeF}_4$  [2.94(3), 3.01(3)Å].  $\text{Ph}_2\text{TeF}_2$  has a distorted trigonal bipyramidal arrangement in which the fluorine atoms occupy axial positions with only very weak interactions between tellurium and fluorine atoms in adjacent molecules.

### 1.7 Fluoro cations of main group fluorides:

In recent years there has been considerable interest in establishing stereochemical and electronic principles which are operative for the formation of stable fluoro cations of main group compounds. Because of their extreme reactivity and susceptibility to hydrolysis such complexes are very difficult to characterize and isolate.

Fluoro cations are usually prepared from reactions of the parent molecules with a strong fluoride acceptor. For example,  $\text{Me}_2\text{PF}_2^+$  has been prepared (74) from the reaction of  $\text{Me}_2\text{PF}_3$  and  $\text{PF}_5$  according to equation [25].



The fluoride donor strengths of fluorophosphoranes decrease in the order,  $\text{R}_3\text{PF}_2 > \text{R}_2\text{PF}_3 \gg \text{RPF}_4 > \text{PF}_5$  (75). This order indicates that steric repulsion plays an important role in the fluoride donor properties of a molecule.

Preparation of a fluoro cation for which the parent molecule does not exist is a great challenge to the synthetic chemist. Only three such fluoro cations, namely  $\text{NF}_4^+$  (76-79),  $\text{ClF}_6^+$  (79-81) and  $\text{BrF}_6^+$  (79,82), are known and they can be prepared by oxidation of the corresponding lower fluorides in the presence of a strong Lewis acid and an activation source, such as heat (78,83).

It is clear then that the reactions of fluoro cation preparation are different from those of nucleophilic substitution reactions described in an earlier section. Typical examples of fluoro cations of main group compounds, prepared by different methods under a variety of reaction conditions, are listed in Table IV.

Simple stoichiometries do not give much information about the nature of the products listed in Table IV.  $^{19}\text{F}$  NMR spectroscopy is of great value in elucidating the nature of such fluoro compounds. For example, the appearance of two resonances of equal intensity in the  $^{19}\text{F}$  NMR spectrum of  $\text{ClF}_5\text{-SbF}_5$  system in  $\text{HF-AsF}_5$  solution clearly establishes the presence of the pseudo-trigonal-bipyramidal  $\text{ClF}_4^+$  cation (91). Two overlapping quartets have been observed in the  $^{19}\text{F}$  NMR spectrum of the octahedral  $\text{BrF}_6^+$  cation (92). The two quartets have been assigned to  $^{79}\text{BrF}_6^+$  and  $^{81}\text{BrF}_6^+$ . They arise from spin-spin coupling of six equivalent

Table IV. Fluoro cations of main group compounds

reactants	ionic complex	reference
$\text{NF}_3, \text{KrF}_2, \text{AsF}_5$	$\text{NF}_4^+ \text{AsF}_6^-$	79
$\text{NF}_3, \text{KrFSbF}_6$	$\text{NF}_4^+ \text{SbF}_6^-$	79
$\text{BrF}_5, \text{KrFAsF}_6$	$\text{BrF}_6^+ \text{AsF}_6^-$	82
$\text{ClF}_5, \text{KrF}_2, \text{AsF}_5$	$\text{ClF}_6^+ \text{AsF}_6^-$	83
$\text{PF}_5, \text{SbF}_5$	$\text{PF}_4^+ \text{Sb}_3\text{F}_{16}^-$	84
$\text{TeF}_4, \text{SbF}_5$	$\text{TeF}_3^+ \text{Sb}_2\text{F}_{11}^-$	85
$\text{SeF}_4, \text{NbF}_5$	$\text{SeF}_3^+ \text{NbF}_6^-$	86
$\text{SF}_4, \text{BF}_3$	$\text{SF}_3^+ \text{BF}_4^-$	87
$\text{BrF}_5, \text{SbF}_5$	$\text{BrF}_4^+ \text{Sb}_2\text{F}_{11}^-$	88
$\text{XeF}_4, \text{BiF}_5$	$\text{XeF}_3^+ \text{BiF}_6^-$	89
$\text{MeSF}_5, \text{AsF}_5$	$\text{MeSF}_4^+ \text{AsF}_6^-$	33
$\text{Me}_2\text{NSF}_5, \text{AsF}_5$	$\text{Me}_2\text{NSF}_4^+ \text{AsF}_6^-$	90

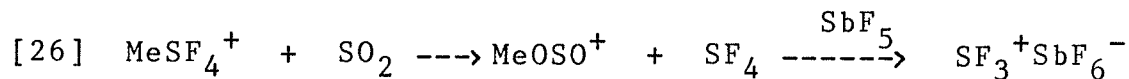
fluorines with  $^{79}\text{Br}$  or  $^{81}\text{Br}$  both with spin 3/2. The  $^{19}\text{F}$  NMR spectrum at low temperature has provided unequivocal proof for the formation of  $\text{Me}_2\text{NSF}_4^+ \text{AsF}_6^-$  (90). The  $a_2b_2$  spin system in the  $^{19}\text{F}$  NMR spectrum for the fluorines in  $\text{Me}_2\text{NSF}_4^+$  shows that the cation exhibits trigonal bipyramidal coordination at the central sulphur with the dimethylamino group at one of the equatorial positions. Firm solid state structural information can obviously lead

to a better understanding of the nature of such fluoro compounds. Thus, the ionic nature as well as substantial fluorine bridging in the systems  $\text{XeF}^+\text{RuF}_6^-$  (93) and  $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$  (94) have been determined by crystallographic studies. Typical chemical reactions and vibrational spectroscopy (82,83) are also used to elucidate the nature of many of the fluoro compounds listed in Table IV.

The formation and stability of fluoro cations depends upon the nature and stoichiometry of the reactants. For example, stable  $\text{ClF}_4^+\text{SbF}_6^-$  can be prepared at room temperature whereas  $\text{ClF}_4^+\text{AsF}_6^-$  is unstable at ambient temperature (95). A further example of the effect of Lewis acid strength upon the formation of fluoro cations is given by the fact that the tendency to form  $\text{NF}_4^+$  salts by thermal activation strongly decreases with decreasing Lewis acid strength (78), i.e.  $\text{SbF}_5 > \text{AsF}_5 > \text{PF}_5 > \text{BF}_3$  (96,97). An example of the effect of ratio of reactants on cation formation is given by the  $\text{BrF}_5$ - $\text{SbF}_5$  system (88). A 1:1 adduct could not be isolated whereas a stable crystalline 1:2 adduct, containing the fluoro cation,  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$ , was isolated under the same reaction conditions (88). Sometimes the yield of fluoro cation is also controlled by the nature of the Lewis acid. For example, the reaction of  $\text{NF}_3$  with  $\text{KrF}_2$  and  $\text{AsF}_5$  produces  $\text{NF}_4^+\text{AsF}_6^-$  in 96.7% yield whereas the corresponding reaction of  $\text{BF}_3$  produces only 30.6% yield of  $\text{NF}_4^+\text{BF}_4^-$  (79).

Fluoro cations may also be obtained by approaches somewhat different from those mentioned above. For example, a tertiary amine of low steric hindrance, e.g.  $\text{Me}_3\text{N}$ , displaces bromide from  $\text{Me}_3\text{NBF}_2\text{Br}$  to form  $(\text{Me}_3\text{N})_2\text{BF}_2^+$  (98).

The only known organochalcogen(VI) fluoro cation,  $\text{MeSF}_4^+$ , listed in Table IV, has been characterized by Seppelt and co-worker (in 1981) at  $-80^\circ\text{C}$  by NMR spectral studies (33). In a reaction mixture of  $\text{MeSF}_5$  and  $\text{SbF}_5$  in  $\text{SO}_2$  at  $-80^\circ\text{C}$ , besides the peaks of the starting compound  $\text{MeSF}_5$  (99), a quintet in the proton spectrum and a quartet in the fluorine spectrum have been assigned to the  $\text{MeSF}_4^+$  cation. The quintet in the  $^1\text{H}$  NMR and a quartet in the  $^{19}\text{F}$  NMR spectra have been thought to be due to the magnetic equivalence of the fluorine atoms through rapid intramolecular exchange. NMR spectra at  $-80^\circ\text{C}$  also show the presence of decomposition products as shown in equation [26]. The compound  $\text{MeSF}_4^+$  has been found to decompose irreversibly at  $20^\circ\text{C}$ .



No fluoride donor-acceptor reaction has yet been reported with organotellurium(VI) fluoride. Thus, the possibility of the formation of fluoro cations of organotellurium(VI) fluorides required investigation.



It would be especially interesting to study the NMR properties of such cation systems.

### 1.8 Fluorine exchange in main group fluorides:

The  $^{19}\text{F}$  nucleus, with spin  $1/2$  and 100% abundance, lends itself convenient study of fluorine exchange processes by the dynamic nuclear magnetic resonance technique (100). The rate of exchange processes, which are in the range of the frequency separation of the spectral lines in question, may vary considerably ( $10^{-1}$  -  $10^{-5}$   $\text{sec}^{-1}$ ). Rapid exchange processes can lead to collapse of spin-spin multiplets or the loss of magnetic non-equivalence of two or more nuclei giving a time averaged single line (101,102). Kinetic information concerning exchange processes can be obtained from a complete line shape analysis of the observed spectra (103).

Both intermolecular and intramolecular fluorine exchange processes in main group fluorides are of interest to the inorganic chemist. Intermolecular exchange will result in loss of spin-spin coupling between the central atom (if the central atom has a convenient spin) and the exchanging ligand while intramolecular exchange will retain such coupling. Thus, NMR may be used to identify intermolecular and intramolecular exchange, or both processes together, in an exchanging system where the central atom has a convenient spin.

In intramolecular processes a permutational or site exchange of ligands occurs without any bond breaking. For example, in the trigonal-bipyramidal  $\text{MF}_5$  molecule (Figure 3) the axial and equatorial fluorines would be exchanging sites without any bond breaking. Thus, all fluorines in the  $\text{MF}_5$  molecule would be equivalent due to intramolecular exchange process.

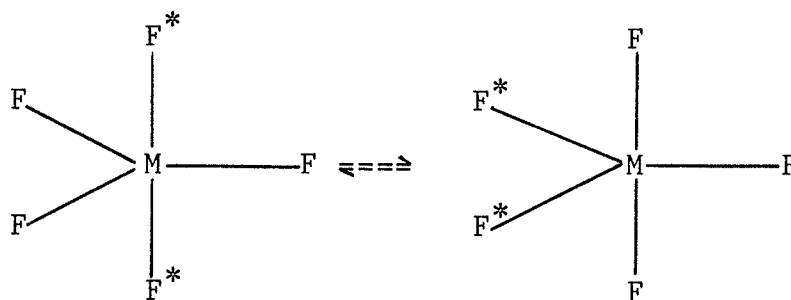
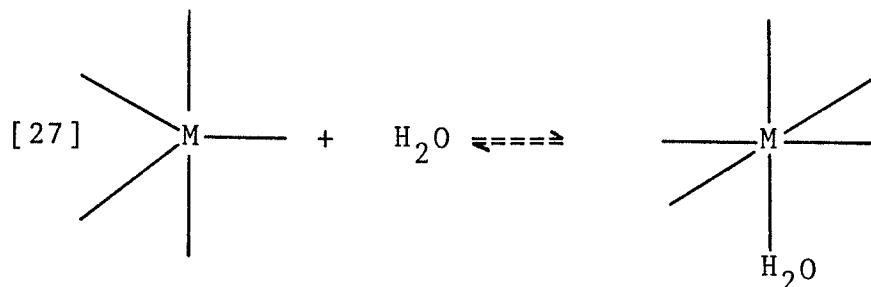


Figure 3. Intramolecular fluorine exchange in a trigonal-bipyramidal  $\text{MF}_5$  molecule.

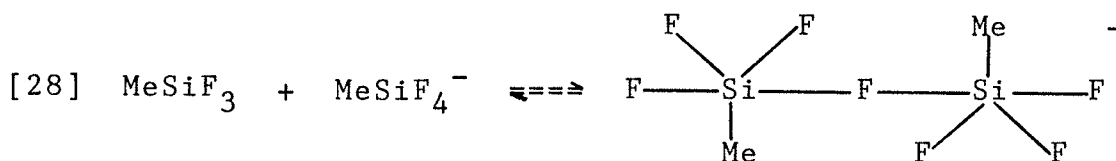
Intramolecular fluorine exchange processes have been reviewed recently (104,105). Exchange of axial and equatorial fluorines in phosphorus, sulphur and silicon fluorides has been explained by various mechanisms; in particular, Berry pseudorotation (106-109), "turnstile" rotation (110), bimolecular exchange (111,112) and impurity catalyzed exchange (113). Janzen et al. (114)

have shown that impurity catalyzed (e.g.  $\text{H}_2\text{O}$ ,  $\text{HF}$ ) axial equatorial fluorine exchange, as observed by  $^{19}\text{F}$  NMR spectroscopy, could also be explained by a rapid equilibrium between five- and six-coordinate geometries, as shown in equation [27].



There have been a number of intermolecular fluorine exchange studies for main group fluoride derivatives. Intermolecular fluorine exchange has been found to be rapid on the NMR time scale in systems such as  $\text{SiF}_5^-$ - $\text{SiF}_6^-$  (115),  $\text{PhPF}_3\text{H}$ - $\text{PhPF}_4\text{H}^-$  (116) and  $\text{PhPF}_4$ - $\text{PhPF}_5^-$  (117). It has been found that upon mixing equimolar amounts of  $\text{MeSiF}_4^-$  ( $\delta_{\text{F}} = -111$  ppm, a quartet with satellites of  $^{29}\text{Si}$ ) and  $\text{MeSiF}_3$  ( $\delta_{\text{F}} = -134.6$  ppm, a quartet resonance with satellites of  $^{29}\text{Si}$ ) in methylene chloride solvent the quartets of the starting compounds are replaced by a broad peak ( $\delta_{\text{F}} = -122$  ppm,  $1/2\Delta \approx 20$  Hz) in the  $^{19}\text{F}$  NMR spectrum, due to rapid intermolecular fluorine exchange (115). The observation of  $^{29}\text{Si}$  satellites in the starting compounds clearly indicates that impurity catalyzed intermolecular fluorine exchange

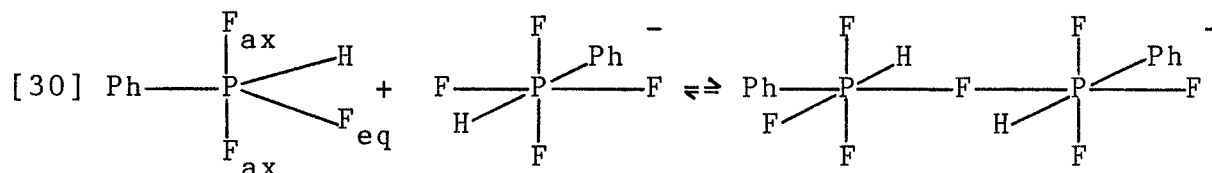
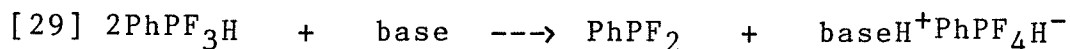
is not occurring. No  $^{29}\text{Si}$  satellites have been observed for the broad peak at -122 ppm because intermolecular fluorine exchange in the system  $\text{MeSiF}_3\text{-MeSiF}_4^-$  removes the spin-spin coupling between fluorine and silicon. This intermolecular fluorine exchange has been explained in terms of coordination changes  $\text{Si } 4 \rightleftharpoons 5$ ,  $\text{F } 1 \rightleftharpoons 2$ , and a fluorine bridged intermediate as shown in equation [28]. Additional support for this mechanism has come from the fact that dilution



of the sample produces a decrease in the exchange rate. The relationship between coordination number and intermolecular fluorine exchange has also been investigated by using a Lewis base to vary the coordination number of silicon. Thus, addition of a large excess of  $\text{NH}_3$  to an equimolar mixture of  $\text{SiF}_5^-$  and  $\text{SiF}_6^-$  has been found to inhibit the exchange, presumably because  $\text{SiF}_5^-$  is converted to  $\text{NH}_3\text{SiF}_5^-$  and intermolecular fluorine exchange between pairs of six-coordinate species is slow on the NMR time scale (115).

The following exchange process provides an excellent example of the fact that base may also promote

exchange by facilitating fluorine transfer between four-, five- and six-coordinate species. Addition of a small amount of triethylamine to a non-exchanging sample of  $\text{PhPF}_3\text{H}$  has been found to cause rapid intermolecular fluorine exchange with the loss of P-F coupling, as observed by the NMR technique (117). It has been suggested that the base reacts with  $\text{PhPF}_3\text{H}$  to generate the anion  $\text{PhPF}_4\text{H}^-$  according to equation [29], and rapid fluorine exchange occurs between five- and six-coordinate



phosphorus species according to equation [30]. In support of equation [30], it has been found that the amount of  $\text{PhPF}_2$  generated is approximately equal to the amount of base added. The observed rate has been found to be first order (within experimental error) in base, in support of the above mechanism which assumes that base produces an equivalent amount of  $\text{PhPF}_4\text{H}^-$ . A similar fluorine bridged intermediate has been proposed for the rapid intermolecular fluorine exchange in the system

$\text{PhPF}_4\text{-PhPF}_5^-$ , from the observed first order rate in  $\text{PhPF}_5^-$ . Exchange in this system has been found to be slightly slower in acetonitrile than in the non-coordinating solvent toluene. This has been attributed to coordination of the donor solvent acetonitrile to the phosphorane, thus preventing the formation of a fluorine bridged intermediate.

In each case discussed above, a fluorine bridged intermediate appears reasonable, but the question of whether an axial or an equatorial fluorine occupies the bridging position in such exchange systems can not be answered because an accompanying intramolecular fluorine exchange process scrambles the axial and equatorial ligands. Thus, while both intermolecular and intramolecular processes have been monitored simultaneously in the  $\text{PhPF}_3\text{H-PhPF}_4\text{H}^-$  system (117), this intramolecular scrambling has removed valuable stereochemical information regarding mechanisms of exchange and reaction. More will be said about this interesting point in fluorine exchange processes later in this thesis.

No fluorine exchange study has yet been reported with an organochalcogen(VI) fluorides. Considering the tetravalent organochalcogen(IV) fluorides, impurity catalyzed intermolecular fluorine exchange has been observed in the  $\text{RSF}_3$  series (118). For  $\text{R}_2\text{SeF}_2$  fluorine exchange has been observed but the mechanism is far from clear (119).

## 2. OBJECTIVES:

It is thus clear from the foregoing discussion that the preparation and chemistry of phenyltellurium(VI) fluorides are not yet known. Thus, to explore the preparations of a series of phenyltellurium(VI) fluorides and to study their chemical reactions and exchange processes this thesis has centered mainly on the following points:

(i) to study reactions of  $\text{XeF}_2$  with  $\text{Ph}_2\text{Te}_2$ ,  $\text{Ph}_2\text{Te}$ ,  $\text{Ph}_2\text{TeF}_2$ ,  $\text{PhTeF}_3$ ,  $\text{Ph}_3\text{TeCl}$ ,  $\text{Ph}_3\text{TeF}$ , and  $\text{Ph}_4\text{Te}$ ;

(ii) to study reactions of the resulting phenyltellurium(VI) fluorides with alcohols, amines, water, and silicon compounds;

(iii) to study reactions of the resulting phenyltellurium(VI) fluorides with the fluoride acceptor  $\text{PF}_5$ ;

and (iv) to initiate and investigate the mechanism of intermolecular fluorine exchange in phenyltellurium(VI) fluorides.

A detailed study of the above reactions and products will be described. In an effort to characterize and to determine the structure and exchange processes of the products the NMR technique was mainly used.

Progress made in the above studies has been extended to other organo-tellurium(IV), -phosphorus(V), -arsenic(V) and -iodine(III) fluorides. For convenience,

these extended experiments have been discussed under the heading "other related studies".

These points, and others, constitute the remaining discussion of this thesis.



### 3. EXPERIMENTAL

#### 3.1 Materials:

Diphenyltellurium dichloride and triphenyltellurium chloride were purchased from K&K and diphenylditelluride and diphenyltellurium from Strem chemicals, Inc. and were used without further purification. Diphenylditelluride and diphenyltellurium were stored in the dark to prevent decomposition by light. Tellurium tetrachloride (Alfa, Ventron division) and benzyltriethylammonium chloride (K&K) were used as purchased. Diphenylmethylphosphine and diphenylmethylarsine were obtained from Strem chemicals, Inc. and stored under dry nitrogen to prevent atmospheric oxidation.  $\text{Et}_2\text{N-SiMe}_3$  and  $\text{Me}_2\text{N-SiMe}_3$  were purchased from Alfa, Ventron division and were distilled before use. Diethylamine, sodium methoxide, sodium fluoride and methyl iodide were purchased from Fisher and were used without further purification.  $\text{MeO-SiMe}_3$  (Petrach Systems, Inc.) and  $\text{HO-SiEt}_3$  (P.S.I) were used as purchased. Phenyllithium [2.4 molar in cyclohexane/diethylether (70/30)] and 2-iodo-1,1,1-trifluoroethane were purchased from Aldrich chemical company, Inc. and were used as purchased.

Gaseous  $\text{PF}_5$  (Allied chemical),  $\text{BF}_3$  (Matheson) and  $\text{SF}_4$  (Matheson) were used as obtained.  $\text{PF}_5$  was found to

contain  $\text{OPF}_3$  which was not removed. Solvents were purified by standard procedures and stored over molecular sieve.

Starting tellurium compounds synthesized by literature procedures are given below:

(i) Triphenyltellurium fluoride,  $\text{Ph}_3\text{TeF}$ , was prepared with some difficulty by the literature method (23,25). Thus, using the literature method (25) for the preparation of  $\text{Ph}_3\text{TeF}$  using glass apparatus almost pure white  $\text{Ph}_3\text{Te}^+\text{BF}_4^-$  was formed in about 72% yield. The formation of  $\text{Ph}_3\text{Te}^+\text{BF}_4^-$  under identical reaction conditions in glass reaction vessel was reproducible.  $\text{Ph}_3\text{Te}^+\text{BF}_4^-$  was characterized by elemental analysis, IR and  $^{19}\text{F}$  NMR,  $^{13}\text{C}$  NMR and  $^{125}\text{Te}$  NMR spectroscopy.

(a)	Analysis:	C%	H%
	Found	47.58	3.28
	Calcd.	48.50	3.39

(b) IR spectrum: A strong absorption at 1030-1090  $\text{cm}^{-1}$  was observed and assigned to  $\text{BF}_4^-$  (120).

(c)  $^{19}\text{F}$  NMR spectrum in acetonitrile: A multiplet centered at -149 ppm was observed and assigned to  $\text{BF}_4^-$ . Coupling to the  $^{11}\text{B}$  (81.17% abundance, spin = 3/2) and the  $^{11}\text{B}$ - $^{10}\text{B}$  (18.8% abundance, spin = 3) isotope shift were clearly observed.

(d)  $^{125}\text{Te}$  NMR spectrum in acetonitrile: The compound displayed a single peak at 768 ppm.

(e)  $^{13}\text{C}$  NMR spectrum in acetonitrile:

$\delta^{13}\text{C}$ in ppm	coupling in Hz
123.5( $\text{C}_1$ ), 135.6( $\text{C}_2$ ), 132.1( $\text{C}_3$ ), 133.9( $\text{C}_4$ )	34.9( $^2\text{J}_{\text{CTe}}$ ), 9.7( $^3\text{J}_{\text{CTe}}$ )

However,  $\text{Ph}_3\text{TeF}$  was prepared by using the literature method (23) and by using Teflon apparatus throughout the reaction, removing the solvent, crystallization and final drying under vacuum. Its  $^{125}\text{Te}$  NMR in methylene chloride showed a single peak at 753 ppm. The  $^{19}\text{F}$  NMR spectrum of  $\text{Ph}_3\text{TeF}$  in methylene chloride displayed a broad ( $1/2\Delta \approx 9$  Hz) peak at -31 ppm.

(ii). Phenyltellurium trichloride,  $\text{PhTeCl}_3$ , was prepared and purified by the literature method (121).

(iii). Tetraphenyltellurium fluoride,  $\text{Ph}_4\text{Te}$ , was prepared by the literature method (26). Its  $^{125}\text{Te}$  NMR spectrum in benzene showed a single peak at 506 ppm. The compound is known to decompose to  $\text{Ph}_2\text{Te}$  and biphenyl in an aromatic solvent (122). This has been reconfirmed by heating the prepared sample in a sealed tube at  $50^\circ\text{C}$  for 1 h, when only the  $\text{Ph}_2\text{Te}$  absorption (688 ppm) appears in the  $^{125}\text{Te}$  NMR spectrum in benzene solution (123).

(iv). Phenyltellurium trifluoride,  $\text{PhTeF}_3$ , was prepared by the published procedure for  $p\text{-MeOC}_6\text{H}_4\text{TeF}_3$  (21).  $\text{PhTeCl}_3$  (0.89 gm, 2.86 mmole) was added to  $\text{AgF}$

(1.3 gm, 10.2 mmole) in toluene (70 mL) and the mixture was heated at 70°C for about 40 minutes with constant stirring. The warm solution was filtered and petroleum ether was added to the filtrate whereupon white  $\text{PhTeF}_3$  crystallized out. Solid phenyltellurium trifluoride was filtered off and dried under vacuum. The yield was about 40%. Phenyltellurium trifluoride was characterized by mass and  $^{19}\text{F}$  NMR spectra. The mass spectrum showed the following characteristic peaks:  $\text{PhTeF}_3^+$  (264,100%),  $\text{PhTeF}_2^+$  (245,72%),  $\text{PhTeF}^+$  (226,10.4%),  $\text{PhTe}^+$  (207,72%),  $\text{TeF}_3^+$  (187,34.6%),  $\text{TeF}_2^+$  (168,90.8%),  $\text{Te}^+$  (130,92.6%). The  $^{19}\text{F}$  NMR spectrum displayed a broad resonance ( $1/2\Delta \approx 364$  Hz) at -78 ppm in acetonitrile. The compound has been found to decompose at 103°C.

(v). Diphenyltellurium difluoride (19) was prepared from the reaction of  $\text{Ph}_2\text{Te}$  and  $\text{XeF}_2$ . Diphenyltellurium (0.15 gm, 0.53 mmole) in methylene chloride (2 mL) was added very slowly through a syringe to a stirred solution of xenon difluoride (0.095 gm, 0.56 mmole) in the same solvent (2 mL) at about 0°C. During addition of diphenyltellurium solution, an exothermic reaction occurs with the evolution of Xe gas and yellow colour of the  $\text{Ph}_2\text{Te}$  disappeared. The reaction solution was dried under vacuum and pure white diphenyltellurium difluoride was obtained by recrystallization from benzene/n-hexane. The yield was 82%. The product was characterized

by its mass spectrum and known  $^{19}\text{F}$  NMR spectrum (19). Its  $^{125}\text{Te}$  NMR spectrum in methylene chloride showed a triplet resonance at 1124 ppm with a separation of 545.5 Hz.

(vi).  $(p\text{-MeOC}_6\text{H}_4)_2\text{TeF}_2$  (21) was prepared by the literature method. Its  $^{19}\text{F}$  NMR spectrum showed a single peak at -123.7 ppm and its  $^{125}\text{Te}$  NMR spectrum displayed a triplet resonance at 1146 ppm with a separation of 588 Hz in chloroform solution.

### 3.2 Physical measurements:

Air sensitive samples were suitably protected from atmospheric decomposition for physical measurements.

Nuclear magnetic resonance spectra were recorded on Varian A 56/60, Bruker WH 90, and Bruker AM 300 spectrometers. For reactive compounds Teflon inserts were used inside the standard NMR tubes. Deuterated solvents were used for recording the NMR spectra on Bruker WH 90 and Bruker AM 300 spectrometers. In  $^1\text{H}$  NMR spectra solvent peaks were used as internal reference.  $\text{C}_6\text{F}_6$  (-162.9 ppm) as internal, 85%  $\text{H}_3\text{PO}_4$  and  $\text{Ph}_2\text{Te}$  as external references were used for  $^{19}\text{F}$  NMR,  $^{31}\text{P}$  NMR and  $^{125}\text{Te}$  NMR respectively. Chemical shifts are reported with respect to  $\text{Me}_4\text{Si}$ ,  $\text{CFCI}_3$ , 85%  $\text{H}_3\text{PO}_4$  and  $\text{Me}_2\text{Te}$  and negative chemical shifts are upfield of these references. Unless otherwise specified the following abbreviations are used: s for singlet, d for

doublet, t for triplet and q for quartet.  $1/2\Delta$  is used to express the half height width of broad resonances. Chemical shifts are reported in ppm and coupling constants in Hz.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 337 grating spectrophotometer. Mass spectra were recorded on a Finnigan 1015 mass spectrometer at 70 eV. Characteristic peaks in the mass spectra (ion mass, relative abundance) are based on the  $^{130}\text{Te}$  and  $^{35}\text{Cl}$  isotopes.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. The X-ray structure analysis of mer- $\text{Ph}_3\text{TeF}_3$  was carried out by Dr. A. S. Secco of this department.

### 3.3 Synthesis:

Reactions were carried out either in a glove box or in a hood under dry nitrogen. Unless otherwise specified, reactions were performed in a Teflon bottle (100 mL) closed by a rubber stopper with an inserted syringe to monitor the evolution of gaseous by-product. Reactants were also added by various syringes through the rubber stopper. Reaction mixtures were stirred by a magnetic stirrer for periods which varied from 10 minutes to 3 days depending on the rate of the specific reaction. Gaseous reactants were mixed through a conventional glass

vacuum line and the attainable vacuum was approximately  $10^{-3}$  cm of Hg. The reaction tubes were flame sealed. Most of the reactions were reproduced several times.

Xenon difluoride reactions were carried out on a 80-150 mg scale. Phenyltellurium(VI) fluorides were prepared by the addition of xenon difluoride to lower valent phenyltellurium compounds and the reaction mixtures stirred until the reactions were judged to be complete by NMR studies. Reactions of xenon difluoride and others were carried out in either acetonitrile, chloroform, or methylene chloride unless otherwise specified.

The yield of products was estimated by  $^{19}\text{F}$  peak integration, based on the added  $\text{C}_6\text{F}_6$  or known internal compounds. The main advantage of this method is that the weight of any non-fluorinated impurity will not influence calculated yields. In all reactions solids were obtained either by evaporating the solvent under vacuum or by adding n-hexane.

### 3.4 Preparation of phenyltellurium(VI) fluorides:

#### 3.4.1 Phenyltellurium(VI) pentafluoride:

To a stirred solution of  $\text{Ph}_2\text{Te}_2$  (51 mg, 0.12 mmole) in methylene chloride or in acetonitrile (about 2 mL) in a Teflon bottle kept at  $-35^\circ\text{C}$  xenon difluoride (107 mg, 0.63 mmole) in the same solvent (about 1 mL) was added

very slowly (about 30 minutes) through a syringe. During each aliquot addition of  $\text{XeF}_2$  solution, an exothermic reaction occurs with the evolution of xenon gas. After the final addition the deep orange colour of the ditelluride disappeared. The reaction solution was allowed to warm slowly to room temperature and stirred at room temperature for an additional 4 h when the clear solution turned to a very faintly straw colour. Solvent and volatile impurities, if any, were then removed under dynamic vacuum at  $-10^\circ\text{C}$ , when pure viscous liquid  $\text{PhTeF}_5$  was obtained. The yield was 54% and the compound was identified by  $^{19}\text{F}$  NMR,  $^{125}\text{Te}$  NMR and mass spectra.  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectral data appear in Tables VI and VII respectively.

Mass spectrum:  $\text{PhTeF}_5^+$  (302,97%),  $\text{TeF}_5^+$  (225,21%),  $\text{TeF}_3^+$  (187,100%),  $\text{TeF}_2^+$  (168,36%).

Phenyltellurium pentafluoride,  $\text{PhTeF}_5$ , was also prepared in about 48% yield from phenyltellurium trifluoride and xenon difluoride. A solution of xenon difluoride (53 mg, 0.31 mmole) in acetonitrile (about 0.6 mL) was added to  $\text{PhTeF}_3$  (80 mg, 0.30 mmole) in the same solvent (1 mL) held at about  $-20^\circ\text{C}$ . The reaction mixture was stirred for 4 h at room temperature and the product, phenyltellurium pentafluoride, was isolated and characterized as described above.



### 3.4.2 Diphenyltellurium(VI) tetrafluoride:

Solid xenon difluoride (119 mg, 0.70 mmole) was added to a stirred solution of diphenyltellurium difluoride (155 mg, 0.48 mmole) in methylene chloride (about 4 mL). The reaction solution was stirred at room temperature for 2 days when a pale yellow solution was obtained. Solvent and volatile impurities, if any, were then removed under vacuum and a white solid was obtained. Pure solid trans-diphenyltellurium(VI) tetrafluoride, trans-Ph<sub>2</sub>TeF<sub>4</sub>, was then obtained by recrystallization from benzene / n-hexane. In some instances the product was also purified by subliming at 65°C under vacuum. The yield was in the range of 60%. <sup>19</sup>F NMR and <sup>125</sup>Te NMR data of the compound appear in Tables VI and VII respectively.

Analysis:	C%	H%
Calcd.	41.62	2.96
Found	40.28	2.82

Mass spectrum: Ph<sub>2</sub>TeF<sub>4</sub><sup>+</sup> (360,13%), Ph<sub>2</sub>TeF<sub>3</sub><sup>+</sup> (341,1%), Ph<sub>2</sub>Te<sup>+</sup> (284,12%), PhTeF<sub>2</sub><sup>+</sup> (245,46%), PhTeF<sup>+</sup> (226,100%), TeF<sub>3</sub><sup>+</sup> (187,13%).

The sublimed product was found to melt at 120°C.

The compound, trans-Ph<sub>2</sub>TeF<sub>4</sub>, was also prepared from the reaction of xenon difluoride and

diphenyltellurium.  $\text{Ph}_2\text{Te}$  (78 mg, 0.27 mmole) solution in methylene chloride (1 mL) was added slowly to a stirred solution of  $\text{XeF}_2$  (118 mg, 0.69 mmole) in the same solvent (about 3 mL) kept at about  $0^\circ\text{C}$ . The reaction mixture was then allowed to warm to room temperature and kept at room temperature for 2 days with occasional stirring. trans- $\text{Ph}_2\text{TeF}_4$  was isolated and purified as described above.

### 3.4.3 Triphenyltellurium(VI) trifluoride:

Solid  $\text{XeF}_2$  (62 mg, 0.36 mmole) was added to a stirred solution of  $\text{Ph}_3\text{TeF}$  (116 mg, 0.30 mmole) in chloroform (3 mL). The reaction solution was stirred for an additional 8 h at room temperature when a very pale yellow solution was formed. Solid product was then precipitated by adding about 15 mL n-hexane to the reaction solution. The solid product, mer-triphenyltellurium(VI) trifluoride, mer- $\text{Ph}_3\text{TeF}_3$ , was then isolated by decanting the liquid, and purified by recrystallization from chloroform / n-hexane. In some instances, the product was purified by subliming at  $102^\circ\text{C}$  under vacuum. A reasonable elemental analysis was obtained only with sublimed product. The yield in several experiments was in the range of 70%. mer- $\text{Ph}_3\text{TeF}_3$  was characterized by elemental analysis and mass and NMR (Tables VI and VII) spectral studies.

Analysis:	C%	H%
Calcd.	51.98	3.64
Found	52.21	3.68

Mass spectrum:  $\text{Ph}_3\text{TeF}_2^+$  (399, 1.3%),  $\text{Ph}_2\text{TeF}_3^+$  (341, 16%),  $\text{Ph}_2\text{TeF}^+$  (303, 12%),  $\text{Ph}_2\text{Te}^+$  (284, 5%),  $\text{PhTeF}_2^+$  (245, 97%),  $\text{PhTeF}^+$  (226, 100%).

The crystalline compound was found to melt at 198°C.

mer- $\text{Ph}_3\text{TeF}_3$  was also prepared in respectable yield (about 63%) from the reaction of  $\text{XeF}_2$  and  $\text{Ph}_3\text{TeCl}$ . Solid  $\text{XeF}_2$  (128 mg, 0.75 mmole) was added to a stirred suspension of triphenyltellurium chloride (158 mg, 0.40 mmole) in chloroform (3 mL). The reaction solution was kept stirring for about 48 h when the solution turned to very light yellow colour. Solvent was then removed under vacuum and the solid product was isolated and purified as described above.

#### 3.4.4 Triphenyltellurium(VI) difluoride chloride:

Solid  $\text{XeF}_2$  (39 mg, 0.23 mmole) was added to a stirred suspension of  $\text{Ph}_3\text{TeCl}$  (92 mg, 0.23 mmole) in acetonitrile at 0°C. The reaction solution was then stirred for 8 h at about 6°C. Solvent was then removed under vacuum and a white solid was obtained. The solid

product, triphenyltellurium(VI) difluoride chloride,  $\text{Ph}_3\text{TeF}_2\text{Cl}$ , was then purified by recrystallization from acetonitrile. The crystallized compound was found to decompose at  $130^\circ\text{C}$ .  $\text{Ph}_3\text{TeF}_2\text{Cl}$  was characterized by elemental analysis and NMR studies. Its  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR properties are listed in Tables VI and VII respectively.

Analysis:	C%	H%
Calcd.	50.00	3.50
Found	49.56	3.83

Mass spectrum:  $\text{Ph}_3\text{TeFCl}^+$  (415,5%),  $\text{Ph}_3\text{TeF}_2^+$  (399,25%),  $\text{Ph}_2\text{TeF}_2\text{Cl}^+$  (357,15%),  $\text{Ph}_2\text{TeCl}^+$  (319,78%),  $\text{Ph}_2\text{Te}^+$  (284,29%),  $\text{PhTeClF}^+$  (261,25%),  $\text{PhTeF}_2^+$  (245,100%),  $\text{PhTeF}^+$  (226,85%).

#### 3.4.5 Tetraphenyltellurium(VI) difluoride:

Solid  $\text{XeF}_2$  (29 mg, 0.17 mmole) was added very slowly (about 15 minutes) to a stirred solution of  $\text{Ph}_4\text{Te}$  (62 mg, 0.14 mmole) in benzene (2 mL) at about  $3^\circ\text{C}$ . During each addition of powdered xenon difluoride, an exothermic reaction occurs with the evolution of xenon gas. The reaction mixture was then stirred for an additional 20 minutes at low temperature. A solid was precipitated by adding n-hexane (about 30 mL) to the reaction solution and

keeping the solution in the refrigerator (about 0°C) overnight. The solid product was then filtered off and purified by crystallization from benzene / n-hexane. The yield was 45%. The compound, tetraphenyltellurium(VI) difluoride,  $\text{Ph}_4\text{TeF}_2$ , was identified by mass and NMR (Tables VI and VII) spectral studies.

Mass spectrum:  $\text{Ph}_4\text{TeF}^+$  (457,6%),  $\text{Ph}_3\text{TeF}_2^+$  (399,80%),  $\text{Ph}_2\text{TeF}^+$  (303,100%),  $\text{Ph}_2\text{Te}^+$  (284,97%).

### 3.5 Methoxy derivatives of phenyltellurium(VI) fluorides:

#### 3.5.1.1 Reaction of phenyltellurium(VI) pentafluoride with methanol:

An excess of MeOH (1.97 mmole) was added to a solution of  $\text{PhTeF}_5$  (0.31 mmole) in acetonitrile / methylene chloride (1:1, about 2 mL) in presence of a large excess of NaF (1.8 mmole). The reaction solution was stirred for about 18 h. The solution was then filtered.  $^{19}\text{F}$  NMR examination of the filtrate showed an  $\text{abc}_2$  spin system only. The filtrate was dried under vacuum whereupon a white solid was obtained. The mass spectrum of the solid showed the molecular ion peak for  $(\text{MeO})\text{PhTeF}_4$  along with other fragment peaks.  $^{19}\text{F}$  NMR spectrum was recorded in methylene chloride which showed the  $\text{abc}_2$  spin system for cis- $(\text{MeO})\text{PhTeF}_4$  (data appear in Table XI), as observed in

the reaction solution. The yield was about 67%.

Mass spectrum:  $\text{MeOPhTeF}_4^+$  (314, 27%),  $\text{MeOTeF}_2^+$  (199, 69%),  $\text{TeF}_3^+$  (187, 100%).

### 3.5.1.2 Reaction of phenyltellurium(VI) pentafluoride with MeO-SiMe<sub>3</sub>:

MeO-SiMe<sub>3</sub> (0.35 mmole) was added through a syringe to a solution of PhTeF<sub>5</sub> (0.2 mmole) in methylene chloride (about 1 mL) and the mixture was kept at room temperature for about 12 h with occasional gentle shaking. <sup>19</sup>F NMR examination of the solution showed the abc<sub>2</sub> spin system for cis-(MeO)PhTeF<sub>4</sub>, as described above, along with the resonance for Me<sub>3</sub>SiF(124). A solid product was obtained by removing the dissolved Me<sub>3</sub>SiF and solvent under dynamic vacuum. The mass spectrum of this solid, the same as given above, confirmed the formation of cis-(MeO)PhTeF<sub>4</sub>. The yield was 73% as checked by <sup>19</sup>F peak integration.

### 3.5.2 Reaction of diphenyltellurium(VI) tetrafluoride with methanol:

(i). Excess MeOH (0.61 mmole) was added to a solution of trans-Ph<sub>2</sub>TeF<sub>4</sub> in about 4 mL methylene chloride in the presence of NaF (0.91 mmole). The reaction solution was stirred for two days. During this period the solution

was heated several times (about 20 times) for a short period of time (4 minutes). The solution was then filtered and the filtrate was evaporated under vacuum whereupon a white solid residue was obtained.  $^{19}\text{F}$  NMR and mass spectra of this solid gave evidence for formation of  $(\text{MeO})\text{Ph}_2\text{TeF}_3$ . The yield was 40%.  $^{19}\text{F}$  NMR data for  $(\text{MeO})\text{Ph}_2\text{TeF}_3$  appear in Table XI. The fluorine NMR spectrum of the isolated solid also showed a trace of trans- $\text{Ph}_2\text{TeF}_4$  and about 10%  $\text{Ph}_2\text{TeF}_2$

Mass spectrum of  $(\text{MeO})\text{Ph}_2\text{TeF}_3$ :  $\text{MeOPh}_2\text{TeF}_3^+$  (372, 2%),  $\text{Ph}_2\text{TeF}_3^+$  (341, 100%),  $\text{MeOPhTeF}^+$  (257, 17%),  $\text{MeOTeF}_2^+$  (199, 17%).

(ii). Excess  $\text{MeOH}$  (1.60 mmole) was added to a solution of trans- $\text{Ph}_2\text{TeF}_4$  (0.35 mmole) in acetonitrile (about 4 mL). The reaction mixture was heated in presence of  $\text{NaF}$  (3.23 mmole) at  $53^\circ\text{C}$  for 7 days in a sealed tube. The tube was then opened and the solution was filtered. The filtrate was evaporated under vacuum to leave a white solid residue.  $^{19}\text{F}$  NMR and mass spectral examination of the solid showed the presence of a mixture of  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$  (about 38% yield) and  $\text{Ph}_2\text{TeF}_2$  (about 40% yield).  $^{19}\text{F}$  NMR data for  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$  appear in Table XI.

Mass spectrum:  $\text{Ph}_2\text{MeOTeF}_2^+$  (357, 75.8%),  $\text{Ph}_2\text{MeOTeF}^+$  (365, 5.6%),  $\text{PhMeOTeF}^+$  (257, 100%).

### 3.5.3 Reaction of diphenyltellurium(VI) tetrafluoride with MeO-SiMe<sub>3</sub>:

MeO-SiMe<sub>3</sub> (0.16 mmole) was added to a solution of trans-Ph<sub>2</sub>TeF<sub>4</sub> (0.10 mmole) in methylene chloride (0.5 mL) in an NMR tube and the tube was closed with a cap. The reaction mixture was kept in the tube at room temperature for 3 days. <sup>19</sup>F NMR examination of the solution showed an ab<sub>2</sub> spin system for the reaction product (MeO)Ph<sub>2</sub>TeF<sub>3</sub> (yield 71%) along with the resonance for Me<sub>3</sub>SiF. The <sup>19</sup>F NMR data of (MeO)Ph<sub>2</sub>TeF<sub>3</sub> appear in Table XI. The mass spectrum of the solid obtained by removing the solvent and dissolved Me<sub>3</sub>SiF gave evidence for formation of (MeO)Ph<sub>2</sub>TeF<sub>3</sub>. The mass spectrum of this product is shown in section 3.5.2(i).

### 3.5.4 Reaction of triphenyltellurium(VI) trifluoride with methanol:

MeOH (0.89 mmole) was added to a solution of mer-Ph<sub>3</sub>TeF<sub>3</sub> (0.41 mmole) in chloroform (3 mL) containing NaF (2.80 mmole). The reaction solution was kept at room temperature for three days in a sealed tube with occasional shaking. The solution was then heated at about 45°C for about 30 minutes. The seal was then opened and the solution was filtered. The filtrate was evaporated under vacuum to leave a white solid residue. The product



$\text{Ph}_3(\text{MeO})\text{TeF}_2$  was characterized by  $^{19}\text{F}$  NMR (data appear in Table XI) and mass spectral studies. The fluorine NMR spectrum also showed the formation of about 6%  $\text{Ph}_2\text{TeF}_2$ .

Mass spectrum for  $\text{Ph}_3(\text{MeO})\text{TeF}_2$ :  $\text{Ph}_3\text{MeOTeF}_2^+$  (411, 18%),  $\text{Ph}_3\text{TeF}_2^+$  (399, 37%),  $\text{Ph}_2\text{MeOTeF}_2^+$  (357, 61%),  $\text{Ph}_2\text{MeOTe}^+$  (315, 10%),  $\text{PhMeOTeF}^+$  (257, 93%),  $\text{Ph}_2\text{TeF}^+$  (303, 100%).

### 3.6 Dialkylamino derivatives of phenyltellurium(VI) fluorides:

#### 3.6.1 Reaction of phenyltellurium(VI) pentafluoride with $\text{Me}_2\text{N-SiMe}_3$ :

$\text{Me}_2\text{N-SiMe}_3$  (0.54 mmole) was added to a solution of  $\text{PhTeF}_5$  (0.24 mmole) in methylene chloride (0.42 mmole) in an NMR tube. The reaction mixture was kept in the closed tube at room temperature for 12 h when a yellow solution was formed.  $^{19}\text{F}$  NMR examination of the solution showed an  $\text{abc}_2$  spin system (NMR data are given in Table XI) for the reaction product cis-( $\text{Me}_2\text{N}$ ) $\text{PhTeF}_4$  and a resonance for  $\text{Me}_3\text{SiF}$ . The chemical composition of ( $\text{Me}_2\text{N}$ ) $\text{PhTeF}_4$  was derived from the mass spectrum of the yellow solid obtained by removing the volatile materials and solvent under vacuum.

Mass spectrum of  $(\text{Me}_2\text{N})\text{PhTeF}_4$ :  $\text{Me}_2\text{NPhTeF}_4^+$  (327,65%),  $\text{TeF}_3^+$  (187,100%).

### 3.6.2 Reaction of phenyltellurium(VI) pentafluoride with $\text{Et}_2\text{N-SiMe}_3$ :

$\text{Et}_2\text{N-SiMe}_3$  (0.41 mmole) was added to  $\text{PhTeF}_5$  (0.22 mmole) in methylene chloride / acetonitrile (about 0.40 mL) and the mixture was kept at room temperature for 1 day with occasional gentle shaking. The product, cis- $(\text{Et}_2\text{N})\text{PhTeF}_4$ , was characterized by  $^{19}\text{F}$  NMR and mass spectral studies as described for cis- $(\text{Me}_2\text{N})\text{PhTeF}_4$  in the previous section. Fluorine NMR data are given in Table XI.

Mass spectrum for  $(\text{Et}_2\text{N})\text{PhTeF}_4$ :  $\text{Et}_2\text{NPhTeF}_4^+$  (341,60%),  $\text{TeF}_3^+$  (187,100%).

### 3.6.3 Reaction of diphenyltellurium(VI) tetrafluoride with $\text{R}_2\text{N-SiMe}_3$ (R = Me, Et):

Excess  $\text{R}_2\text{N-SiMe}_3$  (about 0.56 mmole) was added to trans- $\text{Ph}_2\text{TeF}_4$  (0.19 mmole) in chloroform (0.5 mL) and the reaction solution was kept at room temperature for four days in a sealed tube. The reaction solution was then heated for 1 h at about  $35^\circ\text{C}$ . The resulting yellow

solution showed an  $ab_2$  spin system for  $(R_2N)Ph_2TeF_3$  and a single resonance for unreacted trans- $Ph_2TeF_4$  (about 10% on the basis of starting amount) in the fluorine NMR spectrum. The yield of product was 60%. Fluorine NMR data of the product appear in Table XI. Keeping the reaction solution for 12 days at room temperature did not improve the yield. Heating the reaction solution at  $45^\circ C$  for about 3 h did not complete the reaction but rather decreased the yield of reaction product. The yield under this condition was found to be 43%. The  $^{19}F$  NMR spectrum of the reaction solution formed under this drastic condition (heating for a long period) showed the formation of  $Ph_2TeF_2$ .

Mass spectrum of  $(Me_2N)Ph_2TeF_3$ :  $Me_2NPh_2TeF_3^+$  (385, 24%),  $Ph_2TeF_3^+$  (341, 100%).

Mass spectrum of  $(Et_2N)Ph_2TeF_3$ :  $Et_2NPh_2TeF_3^+$  (413, 19%),  $Et_2NPhTeF^+$  (317, 89%),  $PhTeF_2CH_2CH_2^+$  (195, 100%).

#### 3.6.4 Reaction of diphenyltellurium(VI) tetrafluoride with dimethylamine:

$Me_2NH$  (0.65 mmole) was condensed onto a solution of trans- $Ph_2TeF_4$  (0.23 mmole) in chloroform (0.56 mL) at liquid nitrogen temperature. The tube containing the reaction solution was flame sealed and allowed to warm to

room temperature slowly. The solution in the sealed tube was kept at room temperature for 5 days when a dark yellow solution and crystals of dimethylammonium fluoride were formed. The seal was opened and the yellow solution was decanted off from the crystals of dimethylammonium fluoride.  $^{19}\text{F}$  NMR examination of the decanted solution showed two  $\text{ab}_2$  spin systems for the reaction products, the geometrical isomers (labelled as I and II in Table XI) of  $(\text{Me}_2\text{N})\text{Ph}_2\text{TeF}_3$ , in about 65% yield. The ratio of isomer I and isomer II (assignment of NMR data to I and II are shown in Table XI) was found to be 45 : 55 by  $^{19}\text{F}$  peak integration. The  $^{19}\text{F}$  NMR spectrum of the solution also showed the presence of a trace of unreacted trans- $\text{Ph}_2\text{TeF}_4$  and a reduction product  $\text{Ph}_2\text{TeF}_2$ .

The mass spectrum of the yellow solid obtained by removing the solvent and any volatile material gave evidence for the formation of  $(\text{Me}_2\text{N})\text{Ph}_2\text{TeF}_3$ . The characteristic peaks are shown in the previous section (3.6.3).

### 3.6.5 Reaction of triphenyltellurium(VI) trifluoride with dimethylamine:

$\text{Me}_2\text{NH}$  (0.52 mmole) was condensed into a tube containing mer- $\text{Ph}_3\text{TeF}_3$  (0.28 mmole) in chloroform (3 mL) at liquid nitrogen temperature. The tube containing the reaction solution was flame sealed and kept at room

temperature for 5 days. The resulting yellow solution was then heated at about 40°C for about 20 minutes. The seal was then opened and crystals of dimethylammonium fluoride were separated off by decanting the solution.  $^{19}\text{F}$  NMR examination of the decanted solution showed an ab spin system (data appear in Table XI) for the reaction product in 60% yield. The mass spectrum of the solid, obtained by evaporating the solvent and any volatile material under vacuum, did not show a molecular ion peak for the expected product  $(\text{Me}_2\text{N})\text{Ph}_3\text{TeF}_2$ . In fact, the mass spectrum did not show any other peaks which could be assigned as fragment peaks of the assumed product.

### 3.6.6 Reaction of triphenyltellurium(VI) trifluoride with $\text{Et}_2\text{N-SiMe}_3$ :

$\text{Et}_2\text{N-SiMe}_3$  (0.64 mmole) was added to a solution of mer- $\text{Ph}_3\text{TeF}_3$  (0.28 mmole) in chloroform (3 mL) in a Teflon bottle. The solution was kept at room temperature with slow stirring for 3 days and a deep yellow solution was formed. The solution containing the reaction mixture was then heated for 30 minutes at 45°C.  $^{19}\text{F}$  NMR examination of the reaction solution showed an ab spin system for the reaction product in about 42% yield.  $^{19}\text{F}$  NMR data of this product appear in Table XI. The mass spectrum of the vacuum dried solid only showed  $\text{PhF}$  and no peaks assignable to tellurium species. From the observed ab

spin system of the reaction product and observtion of  $\text{Me}_3\text{SiF}$  (in the  $^{19}\text{F}$  NMR spectrum of the unheated reaction product) the compound is probably  $(\text{Et}_2\text{N})\text{Ph}_3\text{TeF}_2$ .

### 3.7 Reaction of phenyltellurium(VI) pentafluoride with water:

$\text{H}_2\text{O}$  (0.20 mmole) was added to a solution of  $\text{PhTeF}_5$  (0.19 mmole) in acetonitrile (0.3 mL) in an NMR tube fitted with a Teflon insert. The NMR tube containing the reaction solution was closed by a plastic cap and the solution was kept at room temperature for 20 minutes with occasional gentle shaking.  $^{19}\text{F}$  NMR examination of the reaction solution showed the formation of cis- and trans-( $\text{HO}$ ) $\text{PhTeF}_4$ . The NMR data for both the isomers appear in Table XI. The approximate cis to trans ratio was 1:3 and the yield was 70% as determined by  $^{19}\text{F}$  peak integration. The solvent was immediately removed under vacuum and the mass spectrum of the solid so obtained supports the chemical composition of ( $\text{HO}$ ) $\text{PhTeF}_4$ .

Mass spectrum for ( $\text{HO}$ ) $\text{PhTeF}_4$ :  $\text{HOPhTeF}_4^+$  (300, 60%),  $\text{HOPhTeF}_3^+$  (281, 5%),  $\text{HOTeF}_4^+$  (223, 16%),  $\text{TeF}_3^+$  (187, 100%).

### 3.8 Preparation of $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$ :

Excess  $\text{PF}_5$  (0.55 mmole) was condensed at liquid nitrogen temperature onto a solution of mer- $\text{Ph}_3\text{TeF}_3$  (0.12 mmole) in methylene chloride (2 mL) in a Schlenk type of tube fitted with a "rotaflo" stop cock. The tube containing the reaction solution was closed by the attached "rotaflo" stop cock and the mixture was slowly allowed to warm to room temperature. The solution in the closed system was kept at room temperature for 1 h when the reaction was completed as judged by the fluorine NMR spectrum. The excess  $\text{PF}_5$  was then vented out through the vacuum line and the solution was transferred to the attached NMR tube which was flame sealed.  $^{19}\text{F}$  NMR examination of the reaction solution in the sealed tube displayed a single line resonance with tellurium satellites for  $\text{Ph}_3\text{TeF}_2^+$  and a doublet resonance for  $\text{PF}_6^-$ . The  $^{125}\text{Te}$  NMR spectrum of the product displayed a triplet resonance due to coupling with two fluorines. NMR properties of the product appear in Table XV. The ratio of fluorine peak areas, as measured by peak integrations, in  $\text{PF}_6^-$  and  $\text{Ph}_3\text{TeF}_2^+$  was 3:1 ( $\pm 4\%$ ). The yield of the product as calculated by the fluorine peak integration based on added  $\text{C}_6\text{F}_6$  was 91%. The product  $\text{Ph}_3\text{TeF}_2^+$  was characterized by its chemical reaction with NaF and benzyltriethylammonium chloride. NaF was added to the product in methylene chloride in a molar ratio of 15:1 and

the mixture was kept at room temperature for 1 day with occasional shaking. The solid was then separated by decantation and  $^{19}\text{F}$  NMR examination of the decanted solution showed the formation of mer- $\text{Ph}_3\text{TeF}_3$  (80% yield) and about 3% fac- $\text{Ph}_3\text{TeF}_3$ . Characterization and NMR properties of fac- $\text{Ph}_3\text{TeF}_3$  will appear later in this thesis. Similarly, excess benzyltriethylammonium chloride was added to the above reaction product in a molar ratio of 20:1 and the solution was kept at room temperature for 20 minutes with gentle shaking.  $^{19}\text{F}$  NMR examination of the solution then showed the formation of  $\text{Ph}_3\text{TeF}_2\text{Cl}$  in almost quantitative yield.

### 3.9 Other related studies:

#### 3.9.1 Oxidative fluorination reactions:

##### 3.9.1.1 Reactions of $\text{XeF}_2$ with $\text{MePh}_2\text{Y}$ ( $\text{Y}=\text{As}, \text{P}$ ):

A solution of  $\text{XeF}_2$  (0.64 mmole) in acetonitrile (1 mL) was added slowly (about 20 minutes) through a syringe to a stirred solution of  $\text{MePh}_2\text{Y}$  (0.69 mmole) in the same solvent (about 2 mL) held at  $-20^\circ\text{C}$ . During addition of xenon difluoride solution xenon gas was evolved. The reaction mixture was allowed to warm to room temperature in about 10 minutes and kept at room temperature for an additional 20 minutes while stirring. The solvent was then



removed under vacuum and a white solid residue was obtained. The products were purified by recrystallization from benzene / n-hexane. The product in each case was characterized by its known  $^{19}\text{F}$  NMR spectrum [ $\text{Y}=\text{As}$  (125),  $\text{P}$  (126)].  $^{19}\text{F}$  NMR peak integration showed the formation of  $\text{MePh}_2\text{YF}_2$  (125,126) in essentially quantitative yield. The mass spectrum in each case showed the molecular ion peak for  $\text{MePh}_2\text{YF}_2$  along with other fragment peaks.

Elemental analysis for  $\text{MePh}_2\text{PF}_2$ :

	C%	F%	H%
Calcd.	55.75	13.56	3.92
Found	55.18	13.25	4.73

#### 3.9.1.2 Reaction of $\text{XeF}_2$ with $\text{CF}_3\text{CH}_2\text{I}$ :

Solid  $\text{XeF}_2$  (89 mg, 0.52 mmole) was added to  $\text{CF}_3\text{CH}_2\text{I}$  (115 mg, 0.54 mmole) in acetonitrile / chloroform (2 mL). The reaction solution was kept stirring at room temperature for 2 days until the reaction was completed as judged by  $^{19}\text{F}$  NMR spectrometry. The reaction product,  $\text{CF}_3\text{CH}_2\text{IF}_2$  (the yield was 62% based on the xenon difluoride used), was characterized by NMR and mass spectral studies. The mass spectrum of the white solid obtained by removing the solvent and unreacted starting compound under vacuum showed the following characteristic peaks:  $\text{CF}_3\text{CH}_2\text{IF}_2^+$

(248,70%),  $\text{CF}_3\text{CH}_2\text{IF}^+$  (229,100%).

$^1\text{H}$  NMR spectrum of  $\text{CF}_3\text{CH}_2\text{IF}_2$  in acetonitrile:

$$\delta \text{H} = 5.08 \text{ ppm}(\text{q}, \text{t})$$

$$J_{\text{CH}_2-\text{CF}_3} = 9.8 \text{ Hz}$$

$$J_{\text{CH}_2-\text{IF}_2} = 8.5 \text{ Hz}$$

$^{19}\text{F}$  NMR spectrum of  $\text{CF}_3\text{CH}_2\text{IF}_2$  in acetonitrile:

The  $\text{CF}_3$  resonance was found at  $-63.2 \text{ ppm}$  (t,t), and the  $\text{IF}_2$  resonance at  $-175.5 \text{ ppm}$  (broad,  $1/2\Delta \approx 16 \text{ Hz}$ ).

### 3.9.1.3 Reaction of $\text{XeF}_2$ with 3,5-dichloro-iodobenzene:

Solid  $\text{XeF}_2$  (121 mg, 0.71 mmole) was added to 3,5-dichloro-iodobenzene (199 mg, 0.72 mmole) in chloroform (3 mL). The reaction solution was kept at room temperature for 2 days with occasional stirring until the reaction was completed as judged by the  $^{19}\text{F}$  NMR spectrum. The product, 3,5-dichlorophenyliodine(III) difluoride was characterized by  $^{19}\text{F}$  NMR and mass spectral studies. The yield was 70%. The mass spectrum of the pale yellow solid obtained by removing the solvent under vacuum showed the molecular ion peak for  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_2$  and other fragment peaks. The  $^{19}\text{F}$  NMR spectrum displayed a broad peak ( $1/2\Delta \approx 4.5 \text{ Hz}$ ) at  $-174.6 \text{ ppm}$  in chloroform solvent.

In an attempt to further oxidize the compound  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_2$ , a mixture of  $\text{XeF}_2$  and  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_2$  (1:1 molar ratio) in chloroform was left at room temperature for 10

days while stirring very slowly. 50% of the difluoride was found to convert to  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_4$  as judged by the  $^{19}\text{F}$  NMR spectrum. The  $^{19}\text{F}$  NMR spectrum of the tetrafluoride displayed a single line resonance at  $-16.3$  ppm in addition to the resonance for the unconverted difluoride (chloroform solvent). The peak at  $-16.3$  ppm may be assigned to the fluorine from the  $\text{IF}_4$  group on the basis that known organoiodine(V) tetrafluorides resonate in this region (1-3).

#### 3.9.1.4 Reaction of $\text{CF}_3\text{CH}_2\text{IF}_2$ with $\text{Ph}_2\text{Te}$ :

$\text{Ph}_2\text{Te}$  (0.31 mmole) was added to a freshly prepared solution of  $\text{CF}_3\text{CH}_2\text{IF}_2$  (0.42 mmole) in acetonitrile and the mixture was stirred at room temperature for 1 h until the colour of diphenyltellurium disappeared.  $^{19}\text{F}$  NMR examination of the solution showed the formation of  $\text{Ph}_2\text{TeF}_2$  in almost quantitative yield with respect to  $\text{Ph}_2\text{Te}$  used. The solid obtained by removing the solvent and any volatile material under vacuum showed the molecular ion peak for  $\text{Ph}_2\text{TeF}_2$ .

#### 3.9.1.5 Reaction of methyliodine(III) difluoride with $\text{Ph}_2\text{Te}$ :

$\text{Ph}_2\text{Te}$  (0.34 mmole) was added to a freshly prepared solution of  $\text{MeIF}_2$  (11) in methylene chloride (about 0.50

mmole) whereupon the colour of the former disappeared immediately. The solution was stirred at room temperature for 20 minutes.  $^{19}\text{F}$  NMR examination of the reaction solution showed the formation of  $\text{Ph}_2\text{TeF}_2$  in essentially quantitative yield.

#### 3.9.1.6 Reaction of $\text{CF}_3\text{CH}_2\text{IF}_2$ with $\text{Ph}_3\text{TeCl}$ :

Solid  $\text{Ph}_3\text{TeCl}$  (85 mg, 0.21 mmole) was added to a freshly prepared solution of  $\text{CF}_3\text{CH}_2\text{IF}_2$  (0.51 mmole) in acetonitrile (about 3 mL) and the reaction solution was stirred at room temperature for 4 h. The solvent was then removed under vacuum whereupon a white solid was obtained. The product, mer- $\text{Ph}_3\text{TeF}_3$ , was purified by recrystallization from chloroform / n-hexane. The product was characterized by the  $^{19}\text{F}$  NMR and mass spectral studies.  $^{19}\text{F}$  NMR examination of the reaction solution also showed the formation of small amounts of  $\text{Ph}_2\text{TeF}_2$ ,  $\text{CF}_3\text{CH}_2\text{Cl}$  (127) and  $\text{CF}_3\text{CH}_2\text{F}$  (127).

#### 3.9.2 Reaction of $\text{BF}_3$ with $\text{Ph}_2\text{TeF}_2$ :

To a solution of  $\text{Ph}_2\text{TeF}_2$  (0.47 mmole) in methylene chloride (3 mL) excess  $\text{BF}_3$  (0.94 mmole) was condensed at liquid nitrogen temperature and the tube containing the reaction mixture was closed by an attached "rotaflo" stop cock. The solution was allowed to warm to room temperature

and kept at room temperature for 2 h whereupon a crystalline white solid was formed. Excess  $\text{BF}_3$  and solvent were then removed under vacuum and the solid so obtained was dissolved in acetonitrile for NMR examination. The  $^{19}\text{F}$  NMR spectrum displayed only a multiplet resonance ( $-149$  ppm) for  $\text{BF}_4^-$ . The reaction was reproduced several times and only in one instance a broad peak ( $1/2\Delta \approx 130$  Hz) at  $-173$  ppm was observed in addition to the resonance for  $\text{BF}_4^-$  in the  $^{19}\text{F}$  NMR spectrum of the reaction product. The reaction product,  $\text{Ph}_2\text{TeF}^+$ , was characterized by its chemical reaction with NaF. To a solution of the isolated solid in acetonitrile a large excess of NaF (in a molar ratio of 1:20) was added and the mixture was kept at room temperature for 2 days with occasional shaking. The solid was filtered off. The solvent from the filtrate was removed under vacuum whereupon a white solid residue was obtained.  $^{19}\text{F}$  NMR examination of this product revealed the formation of  $\text{Ph}_2\text{TeF}_2$  in 80% yield.

### 3.9.3 Reactions of $\text{PF}_5$ with $\text{MePh}_2\text{YF}_2$ ( $\text{Y} = \text{As}, \text{P}$ ):

$\text{PF}_5$  (0.5 mmole) was condensed onto a solution of  $\text{MePh}_2\text{YF}_2$  (0.31 mmole) in acetonitrile (0.5 mL) in an NMR tube at liquid nitrogen temperature and the tube was closed with an attached "rotaflo" stop cock. The reaction mixture was then allowed to warm to room temperature and kept at room temperature for an additional 2 h. Excess  $\text{PF}_5$

was then vented out through a vacuum line and the tube containing the reaction mixture was flame sealed.  $^{19}\text{F}$  NMR examination of the reaction product showed only a doublet resonance centered at  $-73.6$  ppm with a separation of  $709$  Hz for  $\text{PF}_6^-$  anion. In one instance, with the phosphorus compound, the reaction mixture was kept in a flame sealed tube for one month whereupon a doublet of quartets centered at  $-131.8$  ppm with  $^3J_{\text{FH}} = 9$  Hz and  $^2J_{\text{FP}} = 985$  Hz appeared in the  $^{19}\text{F}$  NMR spectrum. This resonance may be assigned to  $\text{MePh}_2\text{PF}^+$ . However, the peak area of the corresponding fluoride anion ( $\text{PF}_6^-$ ) was found to be approximately double that required for the presumed fluoride cation (the doublet resonance at  $-131.8$  ppm). The products in these reactions ( $\text{Y} = \text{As}, \text{P}$ ) were formulated as  $\text{MePh}_2\text{YF}^+$  on the basis of their chemical reactions with  $\text{NaF}$ . Excess  $\text{NaF}$  (in a molar ratio of  $1:24$ ) was added to the reaction product in acetonitrile solvent and the mixture was kept at room temperature for 4 days. The reaction solution was then decanted and the  $^{19}\text{F}$  NMR examination of the decanted clear solution showed the formation of  $\text{MePh}_2\text{YF}_2$  in about 70% yield.

#### 4. RESULTS AND DISCUSSION

##### 4.1 Phenyltellurium(VI) fluorides:

###### 4.1.1 General:

Phenyltellurium(VI) fluorides were prepared from the oxidative fluorination reactions of  $\text{XeF}_2$  with  $\text{Ph}_2\text{Te}_2$ ,  $\text{Ph}_2\text{Te}$ ,  $\text{Ph}_3\text{TeF}$ ,  $\text{Ph}_2\text{TeF}_2$ ,  $\text{PhTeF}_3$ ,  $\text{Ph}_3\text{TeCl}$  and  $\text{Ph}_4\text{Te}$ . The compounds which have been prepared and characterized from these reactions are summarized in Table V - from which it is clear that a variety of phenyltellurium(VI) fluorides containing one to four phenyl groups have been obtained. Furthermore, a compound containing mixed halides,  $\text{Ph}_3\text{TeF}_2\text{Cl}$ , has been obtained.

The products listed in Table V are white solids, except  $\text{PhTeF}_5$  which is a very faint straw coloured viscous liquid. They are stable indefinitely in a Teflon container and under an inert atmosphere.  $\text{PhTeF}_5$  in solution decomposes in contact with glass to a yellow solid which was insoluble in chloroform and methylene chloride and it was not characterized. trans- $\text{Ph}_2\text{TeF}_4$  reacts with water very slowly. Probably the symmetrical octahedral crowding by four fluorines and two phenyl ligands prevents the hydrolysis of the central tellurium. Only 20% of trans- $\text{Ph}_2\text{TeF}_4$  was found to convert to  $(\text{HO})\text{Ph}_2\text{TeF}_3$  in 5 days as checked by  $^{19}\text{F}$  NMR ( $a_{\text{H}_2}$  spin

Table V. Preparative conditions<sup>a</sup> of phenyltellurium(VI) fluorides.

Starting compound	(mmole)	XeF <sub>2</sub> (mmole)	Conditions <sup>c</sup> (solvent)	Major product <sup>b</sup>
PhTeF <sub>3</sub>	0.30	0.31	-20°C, 4 h acetonitrile	PhTeF <sub>5</sub>
Ph <sub>2</sub> Te <sub>2</sub>	0.12	0.63	-20°C, 4 h methylene chloride	PhTeF <sub>5</sub>
Ph <sub>2</sub> Te	0.27	0.69	-2°C, 20 min 2 days methylene chloride	trans-Ph <sub>2</sub> TeF <sub>4</sub>
Ph <sub>2</sub> TeF <sub>2</sub>	0.48	0.70	2 days methylene chloride	trans-Ph <sub>2</sub> TeF <sub>4</sub>
Ph <sub>3</sub> TeF	0.30	0.36	8 h chloroform	mer-Ph <sub>3</sub> TeF <sub>3</sub>
Ph <sub>3</sub> TeCl	0.40	0.75	2 days chloroform	mer-Ph <sub>3</sub> TeF <sub>3</sub>
Ph <sub>3</sub> TeCl	0.23	0.23	0°C, 8 h acetonitrile	Ph <sub>3</sub> TeF <sub>2</sub> Cl
Ph <sub>4</sub> Te	0.14	0.17	7°C, 15 min 10°C, 20 min benzene	Ph <sub>4</sub> TeF <sub>2</sub>



Table V cont'd...

<sup>a</sup>Teflon vessel was used for all reactions.

<sup>b</sup>Trace amount of other isomer, if any, detected in reaction solution is discussed in the text.

<sup>c</sup>Reactions are carried out at room temperature unless otherwise specified.

system,  $\delta_{Fa} = -32.2$  ppm,  $\delta_{Fb} = -63.4$  ppm, and  $J_{FaFb} = 32$  Hz) and mass spectral studies. The mass spectrum shows the molecular ion peak for  $(HO)Ph_2TeF_3$ , and supports the observed  $ab_2$  spin system for the hydrolysed product. Considerable difficulties were encountered in obtaining reasonable elemental analyses, especially with trans- $Ph_2TeF_4$ , and this might be connected with the presence of biphenyl as impurity. Biphenyl may form by decomposition of trans- $Ph_2TeF_4$  during crystallization or sublimation. However, the corresponding reduced product  $Ph_2TeF_2$  could not be observed in the NMR spectrum of the sublimed or crystallized product. Probably the reduced product was always left behind during recrystallization or sublimation. A trace amount of unsublimed solid or viscous yellow oil was seen in several sublimation processes of the reaction products, which was not characterized. Sublimation of the product from the reaction of  $Ph_4Te$  and  $XeF_2$  at  $30-70^\circ C$ , was found to give biphenyl or condensed phenyl compounds, as characterized by mass spectrometry. Above  $70^\circ C$ , only  $Ph_2TeF_2$  was found to sublime as characterized by  $^{19}F$  NMR and mass spectra.

To show the chemical composition of each product, mass spectra of the resulting phenyltellurium(VI) fluorides (Table V) have been reported in the previous experimental section. Isotopes of tellurium and chlorine have been observed in the correct ratios of natural abundance. In addition to the metal-containing peaks,

very intense  $\text{PhF}^+$  and  $\text{PhPh}^+$  peaks have been observed in the mass spectra of phenyltellurium(VI) fluorides. For  $\text{PhTeF}_5$  and trans- $\text{Ph}_2\text{TeF}_4$  molecular ion peaks ( $\text{M}^+$ ) have been observed. For compounds with more than two phenyl substituents, e.g. mer- $\text{Ph}_3\text{TeF}_3$ ,  $\text{Ph}_3\text{TeF}_2\text{Cl}$  and  $\text{Ph}_4\text{TeF}_2$ , the  $[\text{M} - \text{F}]^+$  peak is the highest  $m/z$  peak observed in the mass spectra. For these multisubstituted compounds, the highest peak along with fragment peaks in the mass spectra clearly indicate the molecular composition. For example, in the mass spectrum of mer- $\text{Ph}_3\text{TeF}_3$ , the  $\text{Ph}_3\text{TeF}_2^+$  peak indicates the presence of three phenyl groups and the  $\text{Ph}_2\text{TeF}_3^+$  peak confirms the presence of three fluorine ligands (the mass spectrum is given in section 3.4.3).

$^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectral data of the phenyltellurium(VI) fluorides are listed in Table VI and Table VII respectively - from which it is clear that all the compounds listed are of covalent molecular octahedral structure in organic solvents. Some  $^{123}\text{Te}$ -F coupling constants, measured from the satellite peaks in  $^{19}\text{F}$  NMR spectra, are included in Table VII for easy comparison with  $^{125}\text{Te}$ -F coupling constants which can be obtained from both  $^{125}\text{Te}$  NMR and  $^{19}\text{F}$  NMR spectra. For simplicity of discussion, magnetically non-equivalent fluorines in a molecule are assigned as  $\text{F}^a$  for lower field resonance,  $\text{F}^b$  for the next highest field and  $\text{F}^c$  for the next highest field resonances. In  $^{19}\text{F}$  NMR spectra, satellites for  $^{125}\text{Te}$  isotope ( $\mu = -0.8824$  nuclear magnetons,  $I = 1/2$  and

Table VI.  $^{19}\text{F}$  NMR data of phenyltellurium(VI) fluorides.

Compound (solvent)	Spin System	$\delta_{\text{F}^a}$ ppm	$\delta_{\text{F}^b}$ ppm	$J_{\text{F}^a\text{F}^b}$ Hz
$\text{PhTeF}_5$				
acetonitrile	$ab_4$	-36.8	-53.4	148.3
chloroform	$ab_4$	-38.3	-54.6	148
$\text{Ph}_2\text{TeF}_4$				
methylene chloride	$a_4$	-56.2		
acetonitrile	$a_4$	-56.9		
$\text{Ph}_3\text{TeF}_3$				
chloroform	$ab_2$	-8	-99	40
methylene chloride	$ab_2$	-2.5	-97.6	39
$\text{Ph}_4\text{TeF}_2$				
chloroform	$a_2$	-33.7		

Table VII. Tellurium NMR data for phenyltellurium(VI) fluorides.

Compound (solvent)	Spin system	$\delta_{125\text{Te}}$	$J_{125\text{TeF}^a}$	$J_{125\text{TeF}^b}$
		in ppm	$J_{(123\text{TeF}^a)^*}$	$J_{(123\text{TeF}^b)^*}$
			in Hz	in Hz
PhTeF <sub>5</sub> acetonitrile	ab <sub>4</sub> x	711	2955	3615
Ph <sub>2</sub> TeF <sub>4</sub> methylene chloride	a <sub>4</sub> x	805	3002 (2503)	
Ph <sub>3</sub> TeF <sub>3</sub> methylene chloride	ab <sub>2</sub> x	786	2860 (2346)	2081 (1709)
Ph <sub>3</sub> TeF <sub>2</sub> Cl chloroform	abx	778	2580	1902
Ph <sub>4</sub> TeF <sub>2</sub> chloroform	a <sub>2</sub> x	659	2058	

\* Coupling constants measured from the satellites in  $^{19}\text{F}$  NMR spectra.

6.99% abundance) have always been observed and in very intense spectra satellites for  $^{123}\text{Te}$  isotope ( $\mu = -0.7319$  nuclear magnetons,  $I = 1/2$  and 0.87% abundance) have also been observed. The ratio of  $^{125}\text{Te} - ^{19}\text{F}$  to  $^{123}\text{Te} - ^{19}\text{F}$  coupling constants, e.g. 1.19 for trans- $\text{Ph}_2\text{TeF}_4$  is in good agreement with the ratio of  $^{125}\text{Te}$  and  $^{123}\text{Te}$  nuclear magnetons (1.20) (coupling constant values are in Table VII). Further, the observed resonance intensities of satellite peaks are also in qualitative agreement with the  $^{125}\text{Te}/^{123}\text{Te}$  isotope abundance (7.9:1.0). As an example, the satellite peaks for tellurium isotopes in the  $^{19}\text{F}$  NMR spectrum of trans- $\text{Ph}_2\text{TeF}_4$  are shown in Figure 4.

The observed  $^{125}\text{Te}$  chemical shifts of phenyltellurium(VI) fluorides (Table VII) are comparable with those of six-coordinate  $(\text{HO})_n\text{TeF}_{6-n}$  (41) and  $\text{XYTeF}_4$  ( $X = \text{HO}$ ,  $Y = \text{MeO}$ ;  $X = Y = \text{MeO}$ ) (59). A direct comparison of  $^{125}\text{Te}$  chemical shifts of  $\text{Ph}_n\text{TeF}_{6-n}$  with  $(\text{HO})_n\text{TeF}_{6-n}$  will appear later in this section in Figure 11. NMR parameters for  $\text{Ph}_2\text{TeF}_2$  and  $(p\text{-MeOC}_6\text{H}_4)_2\text{TeF}_2$ , obtained in this work are given in Table VIII for comparison with those of phenyltellurium(VI) fluorides. It is clear from Tables VII and VIII that the absolute values of  $^{125}\text{Te} - ^{19}\text{F}$  coupling constants in six-coordinate phenyltellurium(VI) fluorides are much higher than those of four-coordinate aryltellurium(IV) fluorides. However, such couplings in phenyltellurium(VI) fluorides are very close to those found for six-coordinate tellurium(VI) fluoride

Table VIII.  $^{125}\text{Te}$  NMR data of  $\text{Ph}_2\text{TeF}_2$  and  $(p\text{-MeOC}_6\text{H}_4)_2\text{TeF}_2$ .

Compound	$\delta^{125}\text{Te}$ in ppm	$J_{\text{TeF}}$ in Hz	Solvent
$\text{Ph}_2\text{TeF}_2$	1124(t)	545.5	methylene chloride
$(p\text{-MeOC}_6\text{H}_4)_2\text{TeF}_2$	1146(t)	588	chloroform

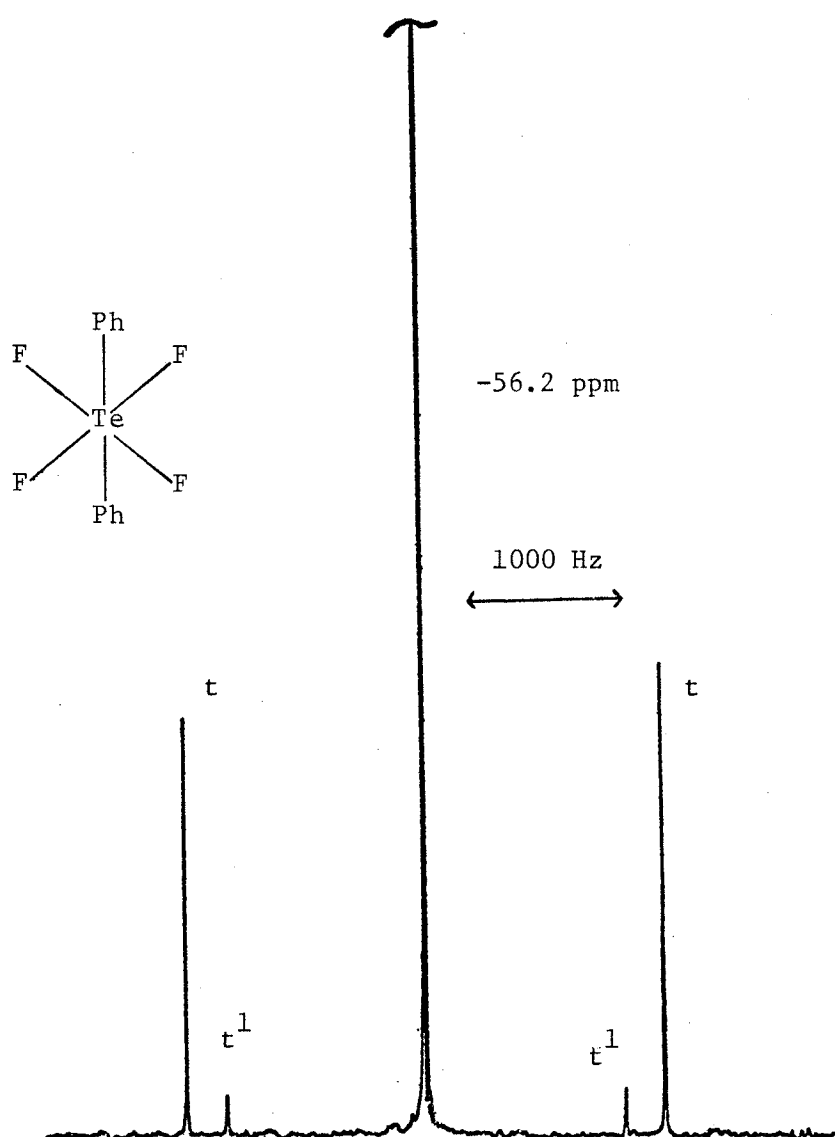


Figure 4.  $^{19}\text{F}$  NMR spectrum of  $\text{trans-Ph}_2\text{TeF}_4$  in methylene chloride.  $t$  and  $t^1$  are the satellite peaks for  $^{125}\text{Te}$  and  $^{123}\text{Te}$  isotopes, respectively.



derivatives, e.g.  $(\text{HO})_n\text{TeF}_{6-n}$  (41).

The actual  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectra of  $\text{PhTeF}_5$  are shown in Figures 5 and 6 respectively. The spectrum in Figure 5 clearly shows that the  $^{19}\text{F}$  NMR spectrum of  $\text{PhTeF}_5$  has a typical  $ab_4$  pattern with  $F^a$  resonance downfield to  $F^b$  resonance and  $R \approx 0.105$  ( $R = J_{\text{FaFb}} / \nu_o \delta_{ab}$  where  $J_{\text{FaFb}}$  is the coupling constant and  $\nu_o \delta_{ab}$  is the chemical shift difference between non-equivalent fluorines a and b). The  $ab_4$  spectrum for  $\text{PhTeF}_5$  has been simulated by the computer program LAME (128, 129). Each transition was numerically assigned (130) and the approximate values of  $J_{\text{FaFb}}$  and  $\nu_o \delta_{ab}$  were obtained from the following (131) relations:

$$[31] \quad \Delta(11,12) = \Delta(13,14) = \Delta(15,16) = \Delta(19,20) = 2\nu_o \delta_{ab}$$

$$[32] \quad \Sigma(1,10) = \nu_o \delta_{ab} - 5/2 J_{\text{FaFb}}$$

$$[33] \quad \Sigma(5,17) = \nu_o \delta_{ab} + 5/2 J_{\text{FaFb}}$$

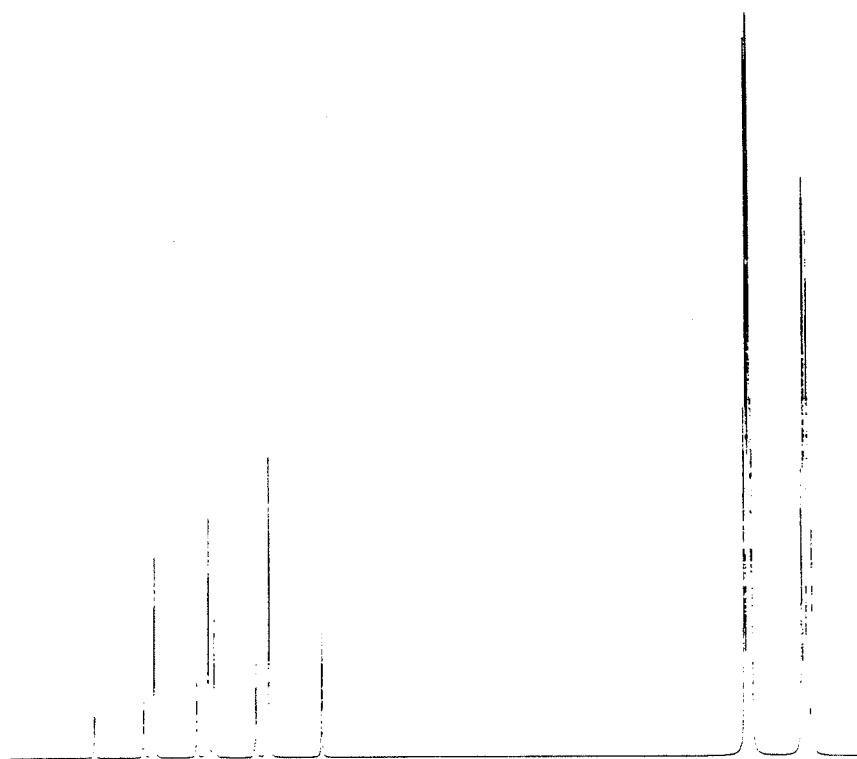
$$[34] \quad \Sigma(7,18) = \nu_o \delta_{ab} - 3/2 J_{\text{FaFb}}$$

$$[35] \quad \Sigma(19,21) = \nu_o \delta_{ab} + 3/2 J_{\text{FaFb}}$$

$\Delta(i,j)$  is the separation in Hz between peaks numbered  $i$  and  $j$ .  $\Sigma(i,j)$  is the sum of the frequencies of the  $i$ th and  $j$ th transitions relative to the origin.

The crude values of the coupling constant and chemical shift difference were given as input to the program which refined the values to give a good fit in a very few iterations. The calculated value of  $R$  is found to be 1.14 and the coupling constant ( $J_{\text{FaFb}}$ ) is 149.9 Hz.  $^{125}\text{Te}$

(S)



(E)

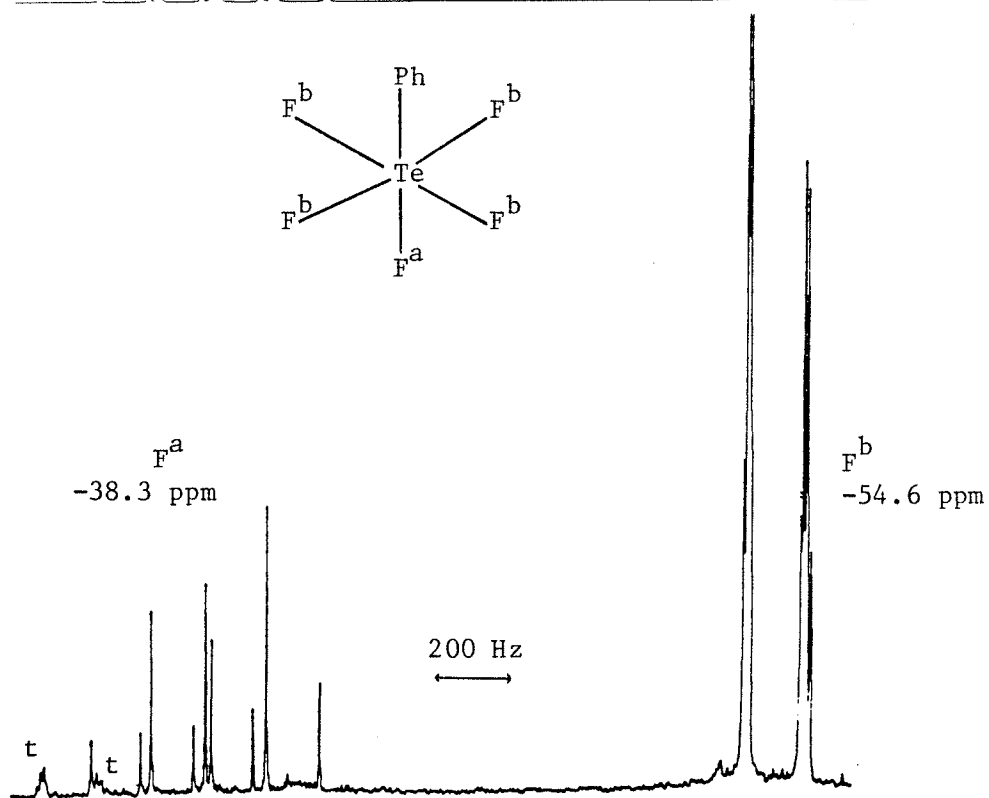


Figure 5.  $^{19}\text{F}$  NMR spectrum of  $\text{PhTeF}_5$ . E is the experimental and S is the simulated spectrum. t is the  $^{125}\text{Te}$  satellite for  $\text{F}^b$  fluorines.

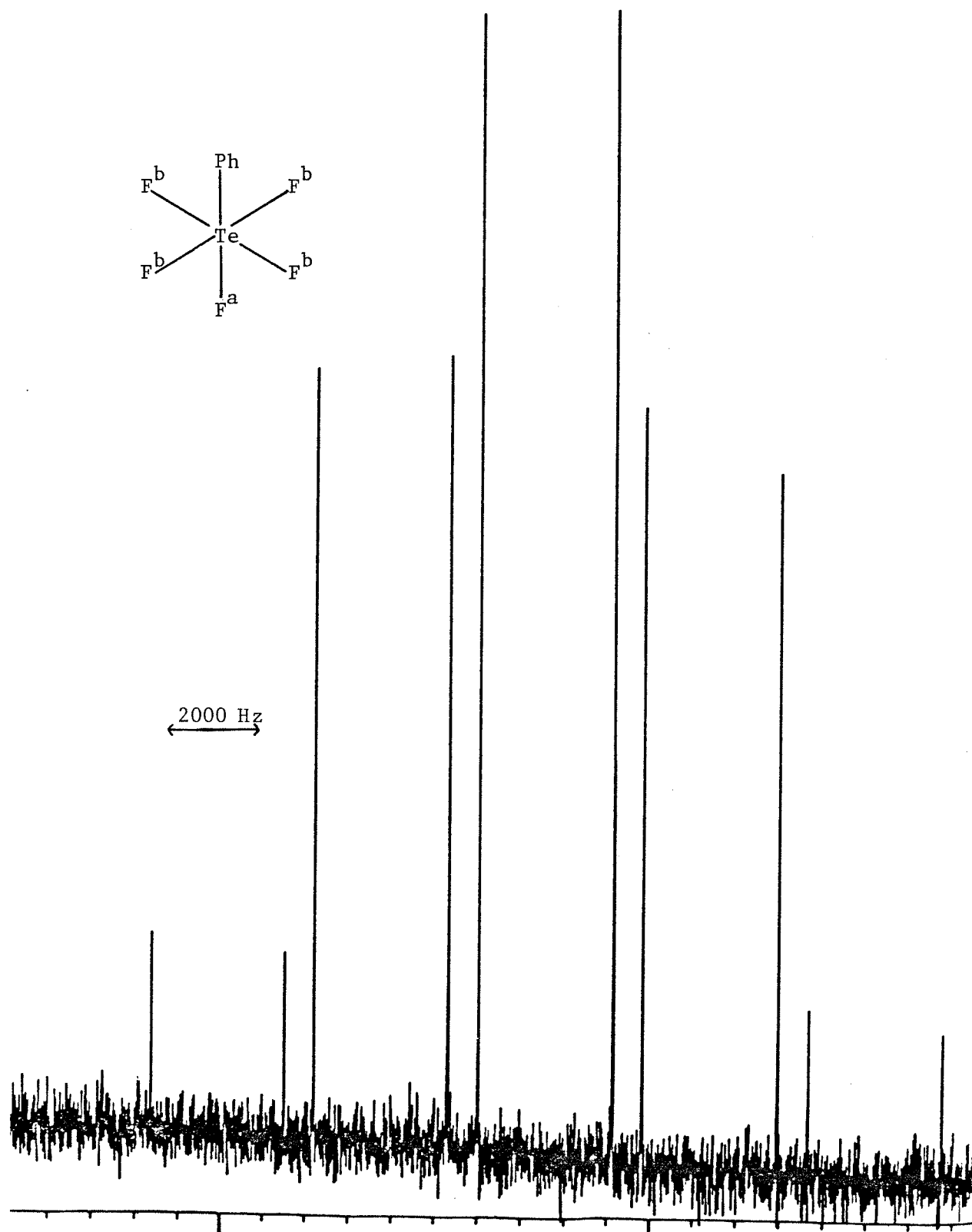


Figure 6.  $^{125}\text{Te}$  NMR spectrum of  $\text{PhTeF}_5$ .

satellites have been observed in the  $^{19}\text{F}$  NMR spectrum of  $\text{PhTeF}_5$ . However, the tellurium-fluorine couplings in  $\text{PhTeF}_5$  were measured clearly from the first order  $^{125}\text{Te}$  NMR spectrum. Similar  $ab_4$  patterns in  $^{19}\text{F}$  NMR spectra have been found for octahedral  $\text{XTeF}_5$  [ $\text{X} = \text{OH}$  (132),  $\text{OMe}$  (46),  $\text{Me}_2\text{N}$  (43)] compounds, with  $\text{F}^a$  resonance downfield from the  $\text{F}^b$  resonance. The  $J_{\text{F}^a\text{F}^b}$  value for  $\text{PhTeF}_5$  is slightly smaller and the chemical shift difference between a and b fluorines is slightly higher than those found for  $\text{XTeF}_5$  [e.g.  $\text{X} = \text{OH}$  (132),  $\text{OMe}$  (46)]. However, the chemical shift difference and fluorine-fluorine coupling constant in  $\text{PhTeF}_5$  are very close to those of  $\text{CF}_3\text{SF}_5$  (6).

In mer- $\text{Ph}_3\text{TeF}_3$ , the fluorine-fluorine coupling constant is much smaller and the chemical shift difference between a and b fluorines is much higher than those in mer- $\text{X}_3\text{TeF}_3$  [ $\text{X} = \text{OH}$  (40),  $\text{OMe}$  (39)]. Thus, the phenyl substituent appears to shift apart the axial and equatorial fluorines much more than hydroxyl or methoxy groups in tellurium(VI) fluoride derivatives.

The  $^1\text{H}$  NMR spectra of all phenyltellurium(VI) fluorides show two sets of multiplets in an intensity ratio of approximately 3:2. The  $^1\text{H}$  NMR spectrum of mer- $\text{Ph}_3\text{TeF}_3$  is given in Figure 7, as a representative spectrum of phenyltellurium(VI) fluorides. The less intense low field multiplet has been assigned to ortho protons and the corresponding high field multiplet to meta and para protons. Similar assignments for phenyl proton

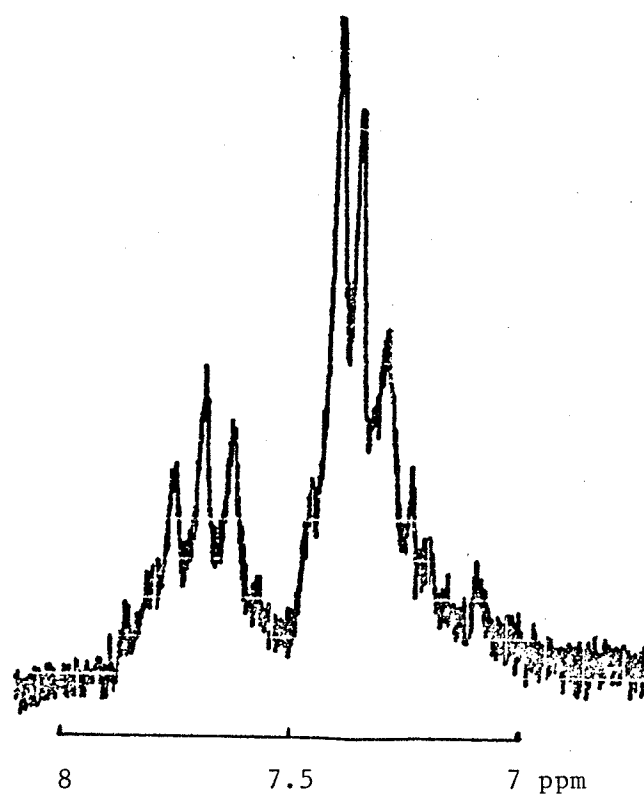


Figure 7.  $^1\text{H}$  NMR spectrum of mer- $\text{Ph}_3\text{TeF}_3$  in chloroform solution.

resonances have been made for triphenyltin(IV) halides (with equivalent phenyl groups) which show the similar  $^1\text{H}$  spectra (133).  $^1\text{H}$  NMR spectra of phenyltellurium(VI) fluorides do not provide any useful information regarding the structures and will not be discussed further here.

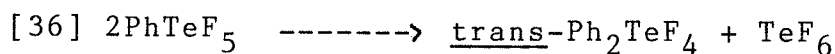
Turning now to the differential solvent effects on chemical shifts, it can be seen from the data in Table VI that the fluorine resonances of phenyltellurium(VI) fluorides are to some extent solvent dependent (about 2 ppm). Such solvent effects on fluorine chemical shifts have been widely observed in NMR spectroscopy (134). The chemical shift for  $\text{F}^a$  fluorine of mer- $\text{Ph}_3\text{TeF}_3$  in the polar chloroform solvent is at higher field than in the relatively less polar methylene chloride solvent (Table VI). This can be attributed to an intermolecular exchange process in mer- $\text{Ph}_3\text{TeF}_3$  in the more polar chloroform solvent. The intermolecular exchange process in mer- $\text{Ph}_3\text{TeF}_3$  will be discussed in a later section in this thesis.

#### 4.1.2 Reactions and products:

As seen in Table V, phenyltellurium(VI) fluorides containing one to four phenyl ligands are formed by the oxidative fluorination of Te(I), Te(II) and Te(IV) compounds with  $\text{XeF}_2$ .

The formation of  $\text{PhTeF}_5$  from the exothermic reaction of  $\text{Ph}_2\text{Te}_2$  with  $\text{XeF}_2$  proceeds through the

intermediate  $\text{PhTeF}_3$  as checked by  $^{19}\text{F}$  NMR and mass spectrometry. Thus, the product obtained from the reaction of  $\text{Ph}_2\text{Te}_2$  and  $\text{XeF}_2$  in about 1:3 molar ratio at about  $-25^\circ\text{C}$  was found to be  $\text{PhTeF}_3$ , as checked by  $^{19}\text{F}$  NMR and mass spectra. In the preparation of  $\text{PhTeF}_5$  at slightly above  $-15^\circ\text{C}$ , a small amount (about 5 - 10%) of trans- $\text{Ph}_2\text{TeF}_4$  is formed, as checked by  $^{19}\text{F}$  NMR spectroscopy. The formation of trans- $\text{Ph}_2\text{TeF}_4$  in this reaction by a ligand redistribution process is unlikely, because  $\text{PhTeF}_5$  is found to be stable at room temperature. Furthermore, in such a ligand redistribution process according to equation [36], the fluorine resonance for  $\text{TeF}_6$  was not observed. Thus, the formation of trans- $\text{Ph}_2\text{TeF}_4$  in the reaction of  $\text{Ph}_2\text{Te}_2$  and  $\text{XeF}_2$  at slightly above  $-15^\circ\text{C}$  can not be explained without further information.



While the fluorination of  $\text{Ph}_2\text{Te}$  with  $\text{XeF}_2$  at low temperature gave  $\text{Ph}_2\text{TeF}_2$  almost instantaneously (section 3.1.v), when the reaction was carried out at room temperature for 2 days with a large excess of  $\text{XeF}_2$ , trans- $\text{Ph}_2\text{TeF}_4$  was obtained.  $^{19}\text{F}$  NMR examination of the reaction solution of  $\text{Ph}_2\text{TeF}_2$  and  $\text{XeF}_2$  also shows the formation of about 1 - 2 % (based on the amount of trans- $\text{Ph}_2\text{TeF}_4$  peak) cis- $\text{Ph}_2\text{TeF}_4$  ( $a_2b_2$  spectrum,  $\delta_{\text{Fa}} = -34.8$  ppm,  $\delta_{\text{Fb}} = -77.7$  ppm,  $J_{\text{FaFb}} = 88$  Hz,  $J_{\text{TeFa}} = 2880$  Hz,  $J_{\text{TeFb}} = 2685$

Hz, in chloroform), characterization of which will be discussed in the next section. This trace amount of cis- $\text{Ph}_2\text{TeF}_4$  stays without any increase or decrease in fluorine peak intensity in an NMR tube for a few days, suggesting that its formation in an oxidative fluorination reaction is probably kinetically controlled. However, purification of the major reaction product by crystallization or sublimation removes completely this trace amount of cis- $\text{Ph}_2\text{TeF}_4$ .

Turning now to the reaction of  $\text{Ph}_3\text{TeCl}$  and  $\text{XeF}_2$ ,  $\text{Ph}_3\text{TeCl}$  is oxidized to  $\text{Ph}_3\text{TeF}_2\text{Cl}$  in an equimolar reaction whereas a large excess of  $\text{XeF}_2$  produced mer- $\text{Ph}_3\text{TeF}_3$ . These results might suggest that an oxidative fluorination of  $\text{Ph}_3\text{TeCl}$  to  $\text{Ph}_3\text{TeF}_2\text{Cl}$  followed by a substitution reaction is a more likely mechanism in the formation of mer- $\text{Ph}_3\text{TeF}_3$ . In the formation of mer- $\text{Ph}_3\text{TeF}_3$  from the reaction of  $\text{Ph}_3\text{TeCl}$  and  $\text{XeF}_2$  a small amount (about 2% based on the amount of mer- $\text{Ph}_3\text{TeF}_3$ ) of fac- $\text{Ph}_3\text{TeF}_3$  (a  $3$  spin system,  $\delta_{\text{F}a} = -50$  ppm,  $J_{\text{TeF}} = 2244$  Hz as measured from  $^{125}\text{Te}$  satellites in chloroform) was observed by  $^{19}\text{F}$  NMR spectrometry. Characterization of fac- $\text{Ph}_3\text{TeF}_3$  will be discussed in the following paragraph. The structure of fac- $\text{Ph}_3\text{TeF}_3$  appears in Figure 8.

The most interesting preparation in this work is  $\text{Ph}_4\text{TeF}_2$  with four phenyl ligands, which is formed from the instantaneous exothermic reaction of  $\text{Ph}_4\text{Te}$  with  $\text{XeF}_2$  in benzene. In fact, this is the only reaction of  $\text{XeF}_2$  in



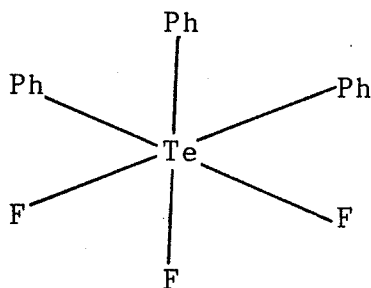


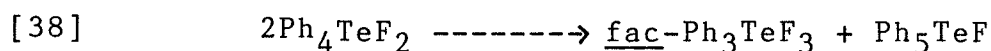
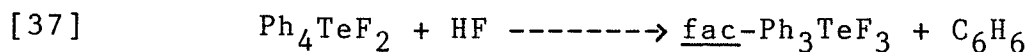
Figure 8. Structure of fac- $\text{Ph}_3\text{TeF}_3$

benzene solvent described in this thesis. Benzene was used in this reaction because  $\text{Ph}_4\text{Te}$  is known to react with chloroform to form  $\text{Ph}_3\text{TeCl}$ . In some instances, fac- $\text{Ph}_3\text{TeF}_3$  (about 8 - 10% based on the amount of  $\text{Ph}_4\text{TeF}_2$ ) was observed in the preparation of  $\text{Ph}_4\text{TeF}_2$  from the reaction of  $\text{Ph}_4\text{Te}$  and  $\text{XeF}_2$  at above  $15^\circ\text{C}$ . Attempts to separate the two components by fractional crystallization from chloroform or methylene chloride were unsuccessful, probably because of very similar solubility. However, fac- $\text{Ph}_3\text{TeF}_3$  has been separated (in about 15% yield) by preparative TLC ( $R_f \approx 0.9$ ) with chloroform solvent. The separated compound shows a single peak ( $\delta_{\text{F}} = -50$  ppm,  $J_{\text{TeF}} = 2244$  Hz in chloroform) in its  $^{19}\text{F}$  NMR spectrum and the characteristic peaks in its mass spectrum are  $\text{Ph}_3\text{TeF}_2^+$  (399, 2%),  $\text{Ph}_2\text{TeF}_3^+$  (341, 18%),  $\text{Ph}_2\text{TeF}^+$  (303, 8.1%),  $\text{PhTeF}_2^+$  (245, 90%) and  $\text{PhTeF}^+$  (226, 100%). Thus, the mass spectral

peaks suggest that the compound has three phenyl groups and three fluorines along with tellurium. As the fluorine NMR spectrum shows a single fluorine resonance line, the structure of this compound with the above chemical composition should be as shown in Figure 8. Unfortunately because of the very poor yield its  $^{125}\text{Te}$  NMR spectrum could not be obtained. Because of the extreme difficulty in the preparation of  $\text{Ph}_4\text{Te}$  and also the very poor yield of probable fac- $\text{Ph}_3\text{TeF}_3$ , further investigation of this interesting compound has been suspended.

The probable formation of fac- $\text{Ph}_3\text{TeF}_3$  in the reaction of  $\text{Ph}_4\text{Te}$  and  $\text{XeF}_2$ , as described above, is unlikely to occur according to equation [37] for the following reasons. Although, HF can be expected to form from the reaction of  $\text{XeF}_2$  with moisture in the organic solvent two independent reactions of HF with trans- $\text{Ph}_2\text{TeF}_4$  and mer- $\text{Ph}_3\text{TeF}_3$  did not show the formation of  $\text{PhTeF}_5$  and  $\text{Ph}_2\text{TeF}_4$  respectively, by the cleavage of phenyl ligand. What is surprising is that reactions of anhydrous HF with trans- $\text{Ph}_2\text{TeF}_4$  and mer- $\text{Ph}_3\text{TeF}_3$  were found to produce small amounts of  $\text{Ph}_2\text{TeF}_2$  in about 5-6 h. The formation of  $\text{Ph}_2\text{TeF}_2$  may be due to reductive elimination of ligands in phenyltellurium(VI) fluorides in the presence of HF as catalyst in such reduction processes. A ligand rearrangement process in  $\text{Ph}_4\text{TeF}_2$  to form fac- $\text{Ph}_3\text{TeF}_3$  according to equation [38] has not been observed. Thus, the formation of fac- $\text{Ph}_3\text{TeF}_3$  in the above mentioned

reaction can not be explained without additional information.



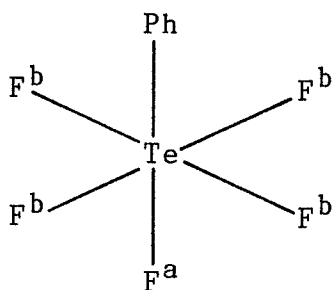
In one instance, in the reaction mixture of  $\text{Ph}_4\text{Te}$  and  $\text{XeF}_2$  a new peak, other than those of  $\text{Ph}_4\text{TeF}_2$  and fac- $\text{Ph}_3\text{TeF}_3$  as discussed above, at -42.4 ppm in the  $^{19}\text{F}$  NMR spectrum with  $^{125}\text{Te}$  satellites ( $J_{\text{TeF}} = 1380$  Hz) and a corresponding doublet resonance at 559 ppm with a separation of 1380 Hz in the  $^{125}\text{Te}$  NMR spectrum appears. An attempt to separate this compound by fractional crystallization inadvertently lost it. These NMR observations do suggest that this tellurium compound has only one fluorine. Without having a mass spectrum of the separated compound its chemical composition could not be established. However, in this reaction the formation of  $\text{Ph}_5\text{TeF}$ , probably by ligand redistribution, can be expected. As discussed in section 1.3.2, the reaction of  $\text{XeF}_2$  with  $(\text{F}_5\text{TeO})_4\text{Te}$  is also instantaneous, exothermic and produces  $(\text{F}_5\text{TeO})_5\text{TeF}$  (13). An attempt has been made to characterize this compound by empirical correlation of  $^{125}\text{Te}$  chemical shifts, which will be discussed in a later section.

#### 4.1.3 Structure of phenyltellurium(VI) fluorides by NMR studies:

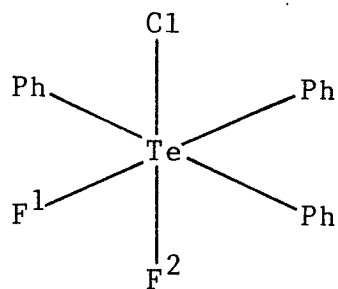
It is clear from the earlier discussion (section 1.5) that  $^{125}\text{Te}$  NMR and  $^{19}\text{F}$  NMR are valuable tools in elucidating the geometry of many octahedral tellurium(VI) fluoride derivatives. In general, the chemical shift difference between non-equivalent fluorine atoms are quite large and the satellites due to tellurium-fluorine spin-spin coupling are of great help in the interpretation of the spectra.

Thus, from the observed spin systems in the  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectra (Tables VI and VII), the octahedral geometry of  $\text{PhTeF}_5$  and  $\text{Ph}_3\text{TeF}_2\text{Cl}$ , trans octahedral geometry of  $\text{Ph}_2\text{TeF}_4$  and mer octahedral geometry of  $\text{Ph}_3\text{TeF}_3$  have been unequivocally assigned. Structures of  $\text{PhTeF}_5$ ,  $\text{Ph}_3\text{TeF}_2\text{Cl}$ , and trans- $\text{Ph}_2\text{TeF}_4$  are shown in Figure 9. It is not possible to elucidate the cis or trans geometry of  $\text{Ph}_4\text{TeF}_2$  from the NMR spectra because both the isomers (Figure 9) have equivalent fluorines and will display a single line fluorine resonance.

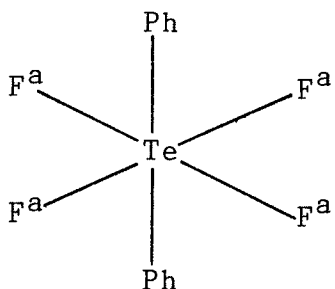
In the case of  $\text{Ph}_3\text{TeF}_2\text{Cl}$ , assignment of fluorine resonances (Table VI) to  $\text{F}^1$  and  $\text{F}^2$  fluorines in the structure shown in Figure 9 remains unsettled. However, by considering the fact that in mer- $\text{Ph}_3\text{TeF}_3$  and  $\text{PhTeF}_5$  the fluorine trans to the phenyl group resonates downfield to the fluorine trans to fluorine and since chlorine is very



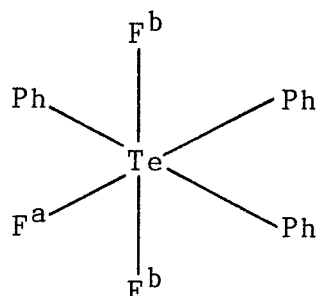
$ab_4x$  spin system of  
 $PhTeF_5$



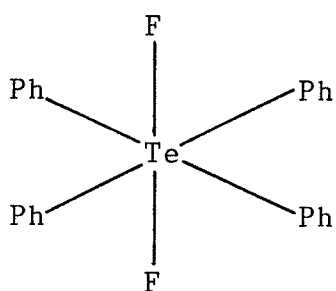
$abx$  spin system of  
 $Ph_3TeF_2Cl$



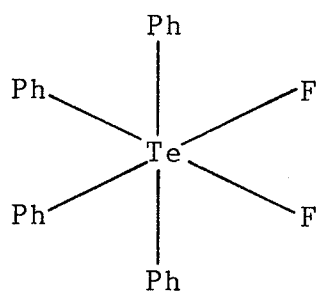
$a_4x$  spin system of  
trans- $Ph_2TeF_4$



$ab_2x$  spin system of  
mer- $Ph_3TeF_3$



trans isomer of  
 $Ph_4TeF_2$



cis isomer of  
 $Ph_4TeF_2$

Figure 9. Structures of  $PhTeF_5$ , trans- $Ph_2TeF_4$ ,  $Ph_3TeF_2Cl$ , mer- $Ph_3TeF_3$  and trans- and cis- $Ph_4TeF_2$ .

similar to fluorine then  $F^1$  may be tentatively assigned to the downfield resonance (-1.5 ppm in methylene chloride; Table VI) and accordingly the high field resonance at -86.4 ppm can be assigned to  $F^2$ . There are ample precedents in the literature with downfield resonances for the fluorine trans to relatively less electronegative substituents in octahedral tellurium compounds (39,43).

From Table VI it is clear that only one isomeric form of a phenyltellurium(VI) fluoride is formed from the oxidative fluorination reactions investigated in this work. The formation of one isomeric form in these reactions is probably due to steric demands of Ph groups. In this connection, in octahedral compounds often only one isomeric form occurs as the major product and cis- / trans-isomers are only rarely observed (13). In summary, while an X-ray diffraction study is required to determine the structure of  $Ph_4TeF_2$ , the  $^{19}F$  NMR and  $^{125}Te$  NMR data have established the geometry of other phenyltellurium(VI) fluorides.

#### 4.1.4 Crystal and molecular structure of *mer*- $Ph_3TeF_3$ :

A single crystal of mer- $Ph_3TeF_3$  was grown from chloroform and n-hexane. mer- $Ph_3TeF_3$  has non-equivalent fluorines (see Table VI) and obviously its weakly bonded fluorine (the fluorine with a relatively longer Te-F bond in the molecule) will be involved in a faster

intermolecular fluorine exchange process. Thus, in an attempt to predict the stereospecific fluoride reactivity in solution and to determine the solid state structure of a representative of phenyltellurium(VI) fluorides, a crystal structure of mer- $\text{Ph}_3\text{TeF}_3$  was determined by Dr.A.S.Secco.

The slightly distorted octahedral environment of the central tellurium in mer- $\text{Ph}_3\text{TeF}_3$  is given in Figure 10 along with atomic numberings. The bond distances and angles are shown in Table IX. The bond angles deviate slightly from octahedral geometry. No short intermolecular interactions occur and thus the geometry of the molecule is determined solely by intramolecular forces. From the bond length data in Table IX, it is clear that  $\text{Te-F}_3$  bond is significantly longer than  $\text{Te-F}_1$  and  $\text{Te-F}_2$  bond lengths.  $\text{F}_3$  in Figure 10 is labelled as  $\text{F}^a$  and  $\text{F}_1$  and  $\text{F}_2$  (in Figure 10) as  $\text{F}^b$  fluorines in the structure of mer- $\text{Ph}_3\text{TeF}_3$  (Figure 9). Thus,  $\text{F}^a$  fluorine is expected to be more reactive than  $\text{F}^b$  fluorines.

No other crystal structure of an organotellurium(VI) fluoride has been reported, and thus direct comparison of bond lengths and angles of mer- $\text{Ph}_3\text{TeF}_3$  with another organotellurium(VI) fluoride is not possible. However, the  $\text{Te-F}$  distances (Table IX) in mer- $\text{Ph}_3\text{TeF}_3$  are slightly longer than in trans-( $\text{F}_5\text{TeO}$ ) $_4\text{TeF}_2$  [1.849(8)Å average] (69). Known  $\text{Te-F}$  distances in  $\text{Te(VI)}$  compounds lie in the range from 1.80 to 1.86Å (70) and are shorter than in

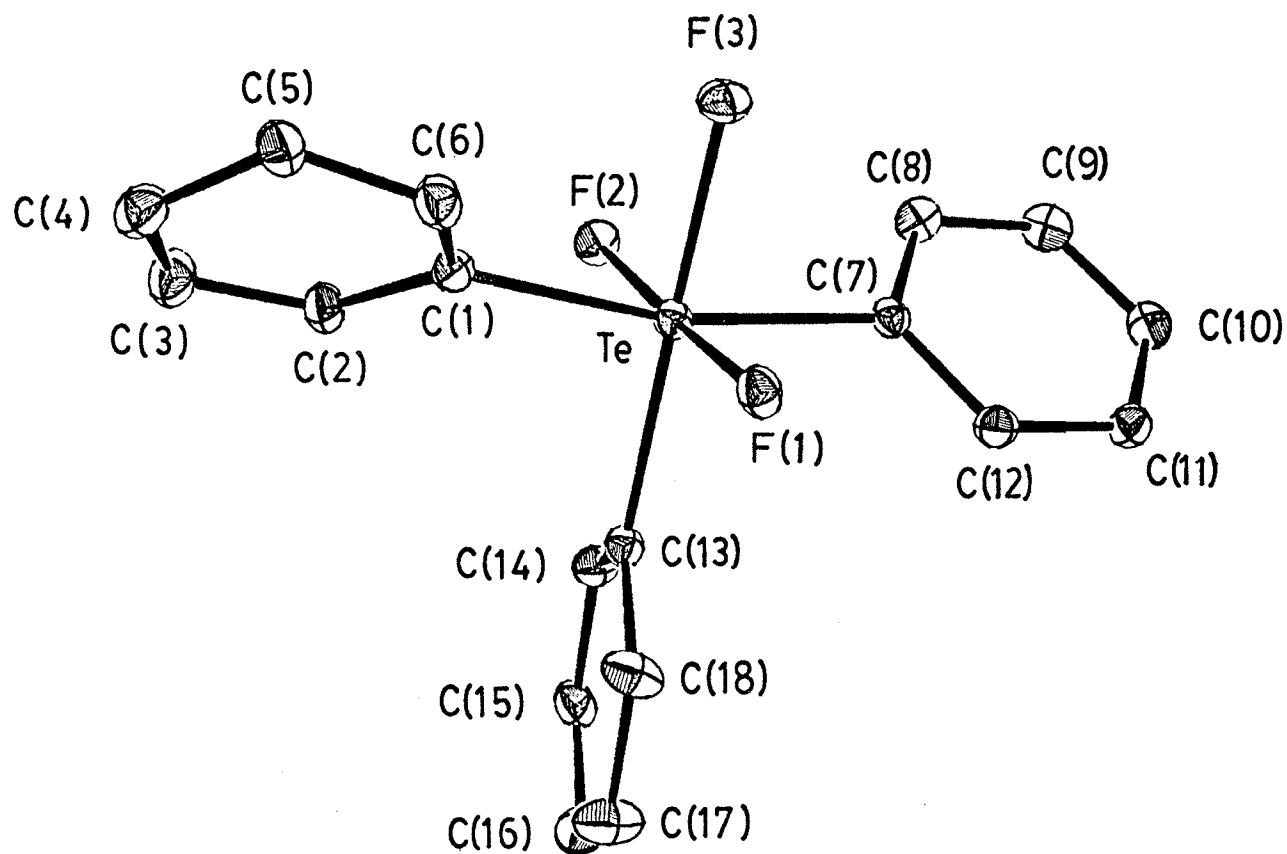


Figure 10. The molecular structure of  $\text{mer-Ph}_3\text{TeF}_3$ .



Table IX. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in mer- $\text{Ph}_3\text{TeF}_3$  (e.s.d's in parentheses).

Bond lengths		Bond angles	
atoms	lengths	atoms	angle
$\text{Te-F}_1$	1.918(1)	$\text{F}_1\text{-Te-F}_2$	176.2(1)
$\text{Te-F}_2$	1.919(1)	$\text{F}_1\text{-Te-F}_3$	87.9(1)
$\text{Te-F}_3$	1.954(1)	$\text{F}_1\text{-Te-C}_1$	89.2(1)
$\text{Te-C}_1$	2.112(2)	$\text{F}_1\text{-Te-C}_7$	90.5(1)
$\text{Te-C}_7$	2.110(2)	$\text{F}_1\text{-Te-C}_{13}$	92.0(1)
$\text{Te-C}_{13}$	2.129(2)	$\text{F}_2\text{-Te-F}_3$	88.4(1)
		$\text{F}_2\text{-Te-C}_1$	89.4(1)
		$\text{F}_2\text{-Te-C}_7$	90.1(1)
		$\text{F}_2\text{-Te-C}_{13}$	91.7(1)
		$\text{F}_3\text{-Te-C}_1$	83.9(1)
		$\text{F}_3\text{-Te-C}_7$	84.1(1)
		$\text{F}_3\text{-Te-C}_{13}$	178.9(1)
		$\text{C}_1\text{-Te-C}_7$	168.0(1)
		$\text{C}_1\text{-Te-C}_{13}$	97.2(1)
		$\text{C}_7\text{-Te-C}_{13}$	98.4(1)

Te(IV) compounds (1.86 - 2.06Å) (135).

Crystal structure analyses of some other phenyltellurium(VI) fluorides are in progress.

#### 4.1.5 Empirical correlations of NMR parameters of phenyltellurium(VI) fluorides:

As discussed previously (section 1.5), simple NMR spectral lines do not yield structural information for some geometrical isomers of octahedral fluoride derivatives. In some octahedral fluoride systems empirical correlations of chemical shifts have been used with some success to identify the unknown species in solution and assign resonances (40,67). The interest of this thesis was to search for some empirical correlations of chemical shifts and coupling constants of phenyltellurium(VI) fluorides prepared in the present work to identify some traces of other isomers formed in reaction solutions which could not be separated or characterized by other means.

Accordingly,  $^{125}\text{Te}$  chemical shifts of known  $\text{Ph}_n\text{TeF}_{6-n}$  ( $n = 1, 2, 3$  and  $4$ ) are plotted against the number of phenyl substituents and the resulting curve is extrapolated to  $n = 5$ . The plot is shown in Figure 11 - from which it is clear that the extrapolation uniquely fits the observed  $^{125}\text{Te}$  chemical shift of the proposed  $\text{Ph}_5\text{TeF}$  (section 4.1.2) formed in the reaction of

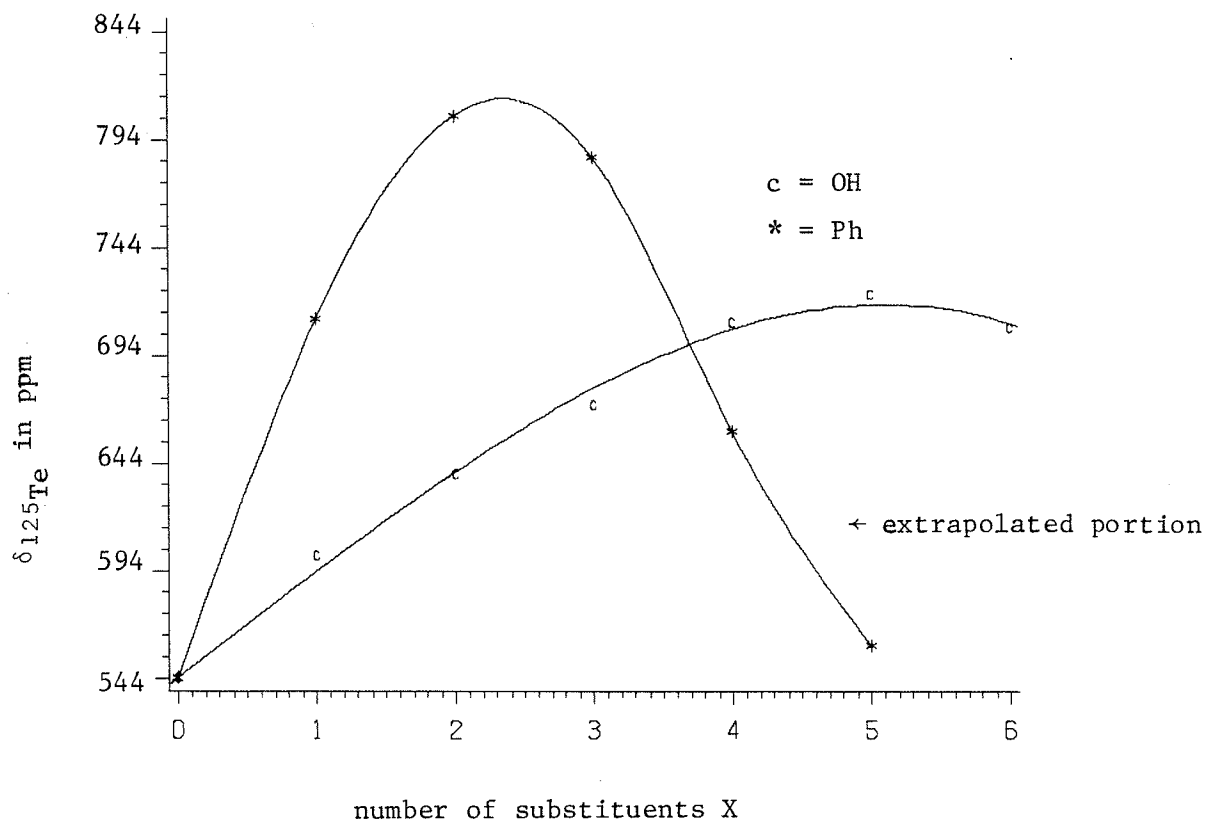


Figure 11. Plots of  $^{125}\text{Te}$  chemical shifts in  $\text{X}_n\text{TeF}_{6-n}$  ( $\text{X} = \text{Ph}, \text{OH}$ ) vs. number of substituents X.

$\text{Ph}_4\text{Te}$  and  $\text{XeF}_2$ . Thus, the compound with a single line fluorine resonance at  $-42.4$  ppm and with  $J_{\text{TeF}} = 1370$  Hz in the reaction mixture of  $\text{Ph}_4\text{Te}$  and  $\text{XeF}_2$  can reasonably be assigned to  $\text{Ph}_5\text{TeF}$ . A similar plot of the known  $^{125}\text{Te}$  chemical shifts in  $(\text{HO})_n\text{TeF}_{6-n}$  is included in Figure 11 for comparison. From Figure 11 it is also clear that the  $^{125}\text{Te}$  chemical shifts of phenyltellurium(VI) fluorides are in the range of six-coordinate hydroxy derivatives of tellurium(VI) fluorides.

In the reaction solution of  $\text{Ph}_2\text{TeF}_2$  and  $\text{XeF}_2$  two triplets ( $a_2b_2$  spin system) of about 1 - 2% with respect to the major product trans- $\text{Ph}_2\text{TeF}_4$  were observed in the  $^{19}\text{F}$  NMR spectrum. However, during the purification of the major reaction product by crystallization or sublimation, this trace amount of compound with  $a_2b_2$  spin system was inadvertently lost. The appearance of an  $a_2b_2$  spin system in the  $^{19}\text{F}$  NMR spectrum indicates that the compound has a total of four fluorines in two different environments. However, additional information is required to identify the other two non-fluorine substituents. Therefore, an attempt has been made to characterize this compound by empirical correlations of  $J_{\text{FaFb}}$  in the series  $\text{Ph}_n\text{TeF}_{6-n}$ . Considering the geometrical models, in the series  $\text{Ph}_n\text{TeF}_{6-n}$  only three compounds with  $n = 1, 2$  and  $3$  have non-equivalent fluorines and thereby have fluorine-fluorine couplings. Two ( $n = 1, 3$ ) out of these three

compounds have been formed as major products in the oxidative fluorination reactions investigated in the present work and they are well characterized by the NMR spectroscopic technique. The remaining ( $n = 2$ ) compound of this series with non-equivalent fluorines is cis- $\text{Ph}_2\text{TeF}_4$ . A plot of  $J_{\text{FaFb}}$  against the number of phenyl groups for  $\text{PhTeF}_5$  and mer- $\text{Ph}_3\text{TeF}_3$  linearly fits the experimental value of the above  $a_2b_2$  system in the position of two phenyl substituents (figure 12). A similar plot of  $J_{\text{FaFb}}$  for the known  $(\text{MeO})_n\text{TeF}_{6-n}$  ( $n = 1, 2, \text{ and } 3$ ) compounds (68) also shows a linear relationship (plot included in Figure 12 for comparison). This result clearly indicates that the species with the  $a_2b_2$  spin system ( $\delta_{\text{Fa}} = -34.8$  ppm,  $\delta_{\text{Fb}} = -77.7$  ppm and  $J_{\text{FaFb}} = 88$  Hz) observed in the reaction mixture of  $\text{Ph}_2\text{TeF}_2$  and  $\text{XeF}_2$  is cis- $\text{Ph}_2\text{TeF}_4$  (Figure 13). The  $J_{\text{FaFb}}$  (97 Hz) for cis- $\text{Ph}_2\text{SF}_4$  (8) is very similar to the value for cis- $\text{Ph}_2\text{TeF}_4$ , as characterized by empirical correlation of fluorine-fluorine coupling constants in phenyltellurium(VI) fluorides.

The assignment of fluorine resonances in cis- $\text{Ph}_2\text{TeF}_4$  (Figure 13) has to be settled. An attempt has been made to assign fluorine resonances by plotting fluorine trans to fluorine resonances in  $\text{PhTeF}_5$  and mer- $\text{Ph}_3\text{TeF}_3$  (structures in Figure 9) against the number of phenyl groups. The result is shown in Figure 14 - from which it is clear that the resonance at  $-77.7$  ppm is well

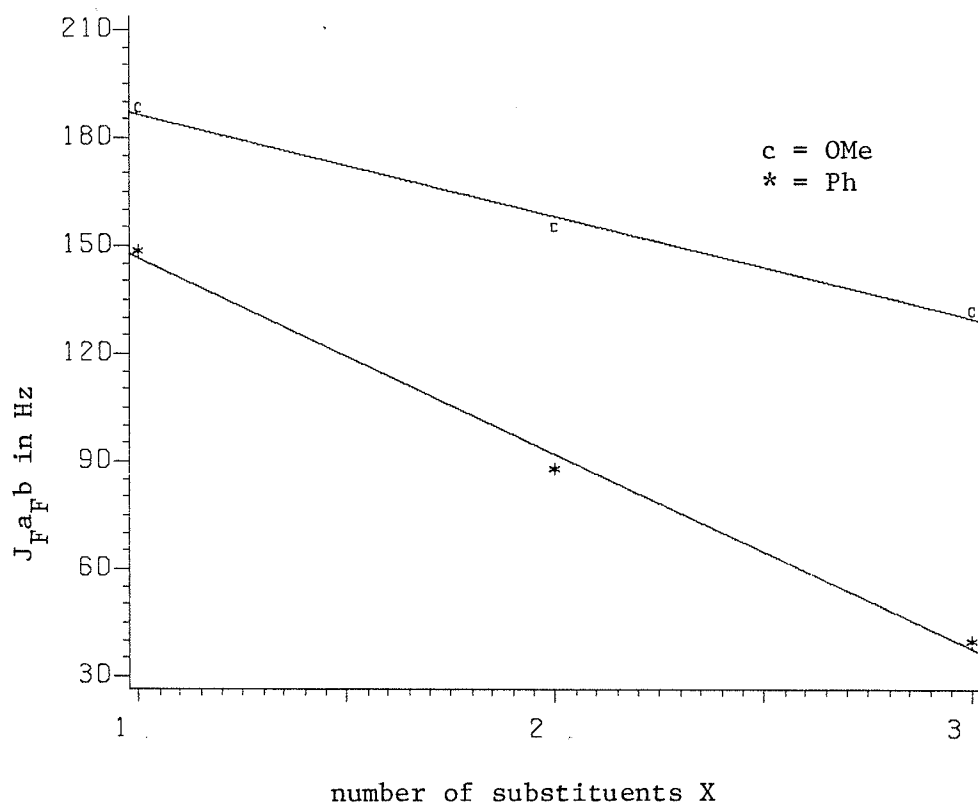


Figure 12. Plots of fluorine-fluorine coupling constants ( $J_{F^a_b}$ ) in  $X_n\text{TeF}_{6-n}$  ( $X = \text{Ph}, \text{OMe}$ ) vs. number of substituents X.

fitted for  $F^2$  fluorines of cis- $\text{Ph}_2\text{TeF}_4$  as shown in Figure 13. Accordingly, the resonance at -34.8 ppm can be

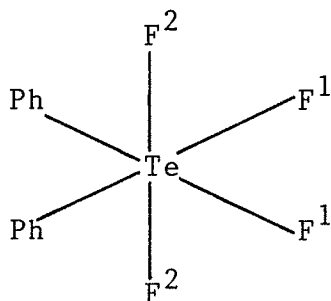


Figure 13. Structure of cis- $\text{Ph}_2\text{TeF}_4$

assigned to  $F^1$  fluorines in the structure shown in Figure 13. This result is again in agreement with the tentative assignment made for  $\text{Ph}_3\text{TeF}_2\text{Cl}$  in the previous section, on the assumption that fluorine trans to phenyl resonates downfield from fluorine trans to fluorine in such octahedral systems. A plot of  $\delta_F$  for  $(\text{MeO})_n\text{TeF}_{6-n}$  ( $n = 1, 2$  and  $3$  and with non-equivalent fluorines) (68) against  $\delta_F$  for  $\text{Ph}_n\text{TeF}_{6-n}$  ( $n = 1, 2, 3$  with non-equivalent fluorines) shows a linear relationship, as shown in Figure 15.

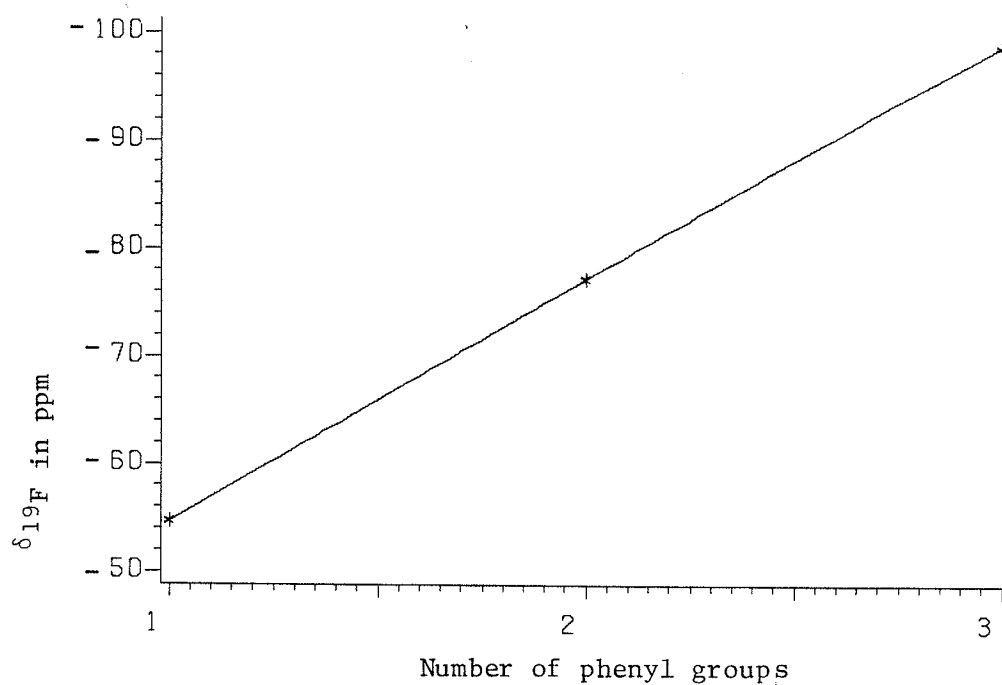


Figure 14. Plot of fluorine chemical shifts for fluorine trans to fluorine in  $\text{Ph}_n\text{TeF}_{6-n}$  ( $n = 1, 2$  and  $3$ ) with non-equivalent fluorines vs. the number of phenyl groups.



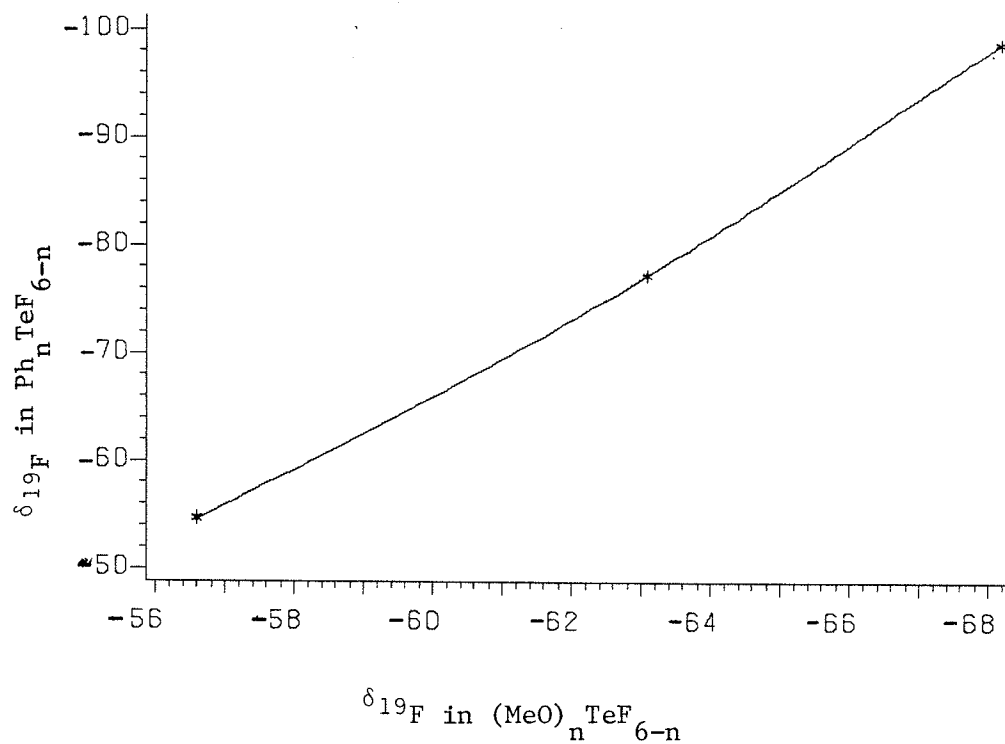


Figure 15. Plot of fluorine chemical shifts of fluorine trans to fluorine in  $\text{PhTeF}_{6-n}$  with non-equivalent fluorines vs. similar fluorine chemical shifts in  $(\text{MeO})_n\text{TeF}_{6-n}$ .

#### 4.2 Reactions of Phenyltellurium(VI) fluorides with alcohols, amines, water and silicon compounds:

Reactions of  $\text{PhTeF}_5$ , trans- $\text{Ph}_2\text{TeF}_4$  and mer- $\text{Ph}_3\text{TeF}_3$  with alcohols, amines, water and silicon compounds have been investigated under different reaction conditions. Products from these reactions were characterized by  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and mass spectral studies and are listed in Table X. NMR studies and empirical calculations of  $^{19}\text{F}$  chemical shifts were used to elucidate the nature and kinds of products obtained in these reactions.

The  $^{19}\text{F}$  NMR data of these reaction products are recorded in Table XI, - from which it is clear that a variety of spin systems have been obtained. An actual  $^{19}\text{F}$  NMR spectrum of cis-( $\text{MeO}$ ) $\text{PhTeF}_4$  is shown in Figure 16.

For convenience and easy comparison, reactions of the same phenyltellurium(VI) fluoride with all the nucleophilic reactants (Table X) will be discussed together. We may start here with the reactions of  $\text{PhTeF}_5$ . It is clear from Table XI that mono substituted products cis- $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{OH}, \text{OMe}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) are obtained from the reactions of  $\text{PhTeF}_5$  with methanol, amine, water and silicon compounds. In the case of water the trans product is also obtained. Random substitution of fluorine would lead to a four fold predominance of the cis isomer. However, from the  $^{19}\text{F}$  NMR peak integration, the approximate cis-to-trans ratio in ( $\text{HO}$ ) $\text{PhTeF}_4$  was found to

Table X. Reactions of phenyltellurium(VI) fluorides with alcohols, amines, water and silicon compounds.

Reactants <sup>a</sup>	Conditions <sup>e</sup> (solvent)	Substituted products <sup>b</sup>
PhTeF <sub>5</sub> , MeOH	NaF, 12 h methylene chloride	<u>cis</u> -(MeO)PhTeF <sub>4</sub>
PhTeF <sub>5</sub> , MeO-SiMe <sub>3</sub>	12 h methylene chloride	<u>cis</u> -(MeO)PhTeF <sub>4</sub>
PhTeF <sub>5</sub> , R <sub>2</sub> N-SiMe <sub>3</sub> (R=Me, Et)	12 h methylene chloride	<u>cis</u> -(R <sub>2</sub> N)PhTeF <sub>4</sub>
PhTeF <sub>5</sub> , H <sub>2</sub> O	1 h acetonitrile	<u>cis</u> -and <u>trans</u> - (HO)PhTeF <sub>4</sub>
<u>trans</u> -Ph <sub>2</sub> TeF <sub>4</sub> , MeOH	NaF, 4 days methylene chloride	(MeO)Ph <sub>2</sub> TeF <sub>3</sub>
<u>trans</u> -Ph <sub>2</sub> TeF <sub>4</sub> , MeOH	NaF, 53°C, 7 days acetonitrile	(MeO) <sub>2</sub> Ph <sub>2</sub> TeF <sub>2</sub>
<u>trans</u> -Ph <sub>2</sub> TeF <sub>4</sub> , MeO-SiMe <sub>3</sub>	3 days methylene chloride	(MeO)Ph <sub>2</sub> TeF <sub>3</sub>
<u>trans</u> -Ph <sub>2</sub> TeF <sub>4</sub> , Me <sub>2</sub> NH	5 days chloroform	(Me <sub>2</sub> N)Ph <sub>2</sub> TeF <sub>3</sub> <sup>c</sup>
<u>trans</u> -Ph <sub>2</sub> TeF <sub>4</sub> , R <sub>2</sub> N-SiMe <sub>3</sub> (R = Me, Et)	4 days chloroform	(R <sub>2</sub> N)Ph <sub>2</sub> TeF <sub>3</sub>
<u>mer</u> -Ph <sub>3</sub> TeF <sub>3</sub> , MeOH	NaF, 5 days 45°C, occasionally chloroform	(MeO)Ph <sub>3</sub> TeF <sub>2</sub>
<u>mer</u> -Ph <sub>3</sub> TeF <sub>3</sub> , Me <sub>2</sub> NH	5 days chloroform	(Me <sub>2</sub> N)Ph <sub>3</sub> TeF <sub>2</sub> <sup>d</sup>
<u>mer</u> -Ph <sub>3</sub> TeF <sub>3</sub> , Et <sub>2</sub> N-SiMe <sub>3</sub>	42°C, occasionally chloroform, 2 days	(Et <sub>2</sub> N)Ph <sub>3</sub> TeF <sub>2</sub> <sup>d</sup>

## Table X cont'd...

<sup>a</sup>Nucleophilic reactants are in 3-10 molar excess.

<sup>b</sup>Products are characterized by <sup>19</sup>F NMR and mass spectra unless otherwise specified.

<sup>c</sup>Two geometrical isomers (two  $ab_2$  spin systems in <sup>19</sup>F NMR spectrum) are observed.

<sup>d</sup>Products are identified only by <sup>19</sup>F NMR.

<sup>e</sup>Reactions are carried out at room temperature unless specified.

Table XI.  $^{19}\text{F}$  NMR data of amino, alkoxy, and hydroxy derivatives of phenyltellurium(VI) fluorides.

Compound solvent	Spin system	Chemical shift in ppm	Coupling constant in Hz
<u>cis</u> -(MeO)PhTeF <sub>4</sub> methylene chloride	abc <sub>2</sub>	$\text{F}^{\text{a}} = -44.8$ $\text{F}^{\text{b}} = -49.4$ $\text{F}^{\text{c}} = -59.6$	$\text{TeF}^{\text{a}}=3308$ $\text{F}^{\text{a}}\text{F}^{\text{b}}=147$ $\text{TeF}^{\text{b}}=2940$ $\text{F}^{\text{b}}\text{F}^{\text{c}}=129$ $\text{TeF}^{\text{c}}=3292$ $\text{F}^{\text{c}}\text{F}^{\text{a}}=105$
<u>cis</u> -(Me <sub>2</sub> N)PhTeF <sub>4</sub> acetonitrile	abc <sub>2</sub>	$\text{F}^{\text{a}} = -33$ $\text{F}^{\text{b}} = -46$ $\text{F}^{\text{c}} = -72.9$	$\text{TeF}^{\text{a}}=3100$ $\text{F}^{\text{a}}\text{F}^{\text{b}}=150$ $\text{TeF}^{\text{b}}=3392$ $\text{F}^{\text{a}}\text{F}^{\text{c}}=104$ $\text{TeF}^{\text{c}}=3115$ $\text{F}^{\text{b}}\text{F}^{\text{c}}=122$
<u>cis</u> -(Et <sub>2</sub> N)PhTeF <sub>4</sub> acetonitrile	abc <sub>2</sub>	$\text{F}^{\text{a}} = -30.9$ $\text{F}^{\text{b}} = -40.2$ $\text{F}^{\text{c}} = -68.7$	$-$ $\text{F}^{\text{a}}\text{F}^{\text{b}}=153$ $-$ $\text{F}^{\text{a}}\text{F}^{\text{c}}=105$ $-$ $\text{F}^{\text{b}}\text{F}^{\text{c}}=120$
<u>cis</u> -(HO)PhTeF <sub>4</sub> acetonitrile	abc <sub>2</sub>	$\text{F}^{\text{a}} = -28$ $\text{F}^{\text{b}} = -44$ $\text{F}^{\text{c}} = -51.6$	$-$ $\text{F}^{\text{a}}\text{F}^{\text{b}}=147$ $-$ $\text{F}^{\text{a}}\text{F}^{\text{c}}=116$ $-$ $\text{F}^{\text{b}}\text{F}^{\text{c}}=105$
<u>trans</u> -(HO)PhTeF <sub>4</sub> acetonitrile	a <sub>4</sub>	$\text{F}^{\text{a}} = -47.4$	$\text{TeF}^{\text{a}}=3445$ $(2884)^*$

Table XI cont'd...

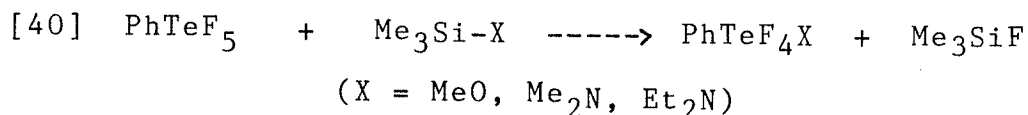
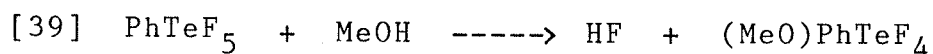
(MeO)Ph <sub>2</sub> TeF <sub>3</sub>	ab <sub>2</sub>	F <sup>a</sup> = -32.4	TeF <sup>a</sup> =2918	F <sup>a</sup> F <sup>b</sup> =29
methylene chloride		F <sup>b</sup> = -75.6	TeF <sup>b</sup> =2762	
(Me <sub>2</sub> N)Ph <sub>2</sub> TeF <sub>3</sub> (I)	ab <sub>2</sub>	F <sup>a</sup> = -8.4	TeF <sup>a</sup> =2798	F <sup>a</sup> F <sup>b</sup> =40
acetonitrile		F <sup>b</sup> = -87.6	TeF <sup>b</sup> =2462	
(Me <sub>2</sub> N)Ph <sub>2</sub> TeF <sub>3</sub> (II)	ab <sub>2</sub>	F <sup>a</sup> = -19.8	TeF <sup>a</sup> =2680	F <sup>a</sup> F <sup>b</sup> =66
acetonitrile		F <sup>b</sup> = -53	TeF <sup>b</sup> =2378	
(Et <sub>2</sub> N)Ph <sub>2</sub> TeF <sub>3</sub>	ab <sub>2</sub>	F <sup>a</sup> = -12.7	TeF <sup>a</sup> =2789	F <sup>a</sup> F <sup>b</sup> =42
chloroform		F <sup>b</sup> = -85	TeF <sup>b</sup> =2457	
Ph <sub>2</sub> (MeO) <sub>2</sub> TeF <sub>2</sub>	a <sub>2</sub>	F <sup>a</sup> = -57.4	TeF <sup>a</sup> =2668	
chloroform				
(Me <sub>2</sub> N)Ph <sub>3</sub> TeF <sub>2</sub>	ab	F <sup>a</sup> = -7	TeF <sup>a</sup> =2374	F <sup>a</sup> F <sup>b</sup> =72
methylene chloride		F <sup>b</sup> = -64.8	TeF <sup>b</sup> =2078	
(MeO)Ph <sub>3</sub> TeF <sub>2</sub>	ab	F <sup>a</sup> = -29.4	TeF <sup>a</sup> =2604	F <sup>a</sup> F <sup>b</sup> =53
methylene chloride		F <sup>b</sup> = -75	TeF <sup>b</sup> =2069	
(Et <sub>2</sub> N)Ph <sub>3</sub> TeF <sub>2</sub>	ab	F <sup>a</sup> = -11.3	-	F <sup>a</sup> F <sup>b</sup> =50
acetonitrile		F <sup>b</sup> = -74.4		

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\*<sup>123</sup>Te-<sup>19</sup>F coupling constant measured from satellite peaks. - not observed due to dilution of samples. I and II are two geometrical isomers.

be 1:3. There are ample precedents for similar reaction products in the literature. For example, the reactions of excess methanol and excess  $\text{Me}_2\text{N-SiMe}_3$  with  $\text{TeF}_6$  produce only the cis isomers,  $\text{X}_2\text{TeF}_4$  [ $\text{X} = \text{MeO}$  (39),  $\text{Me}_2\text{N}$  (43)] while the hydrolysis of  $\text{TeClF}_5$  produces cis- and trans- $\text{HOTeClF}_4$  (136).

The HF generated in the reaction of  $\text{PhTeF}_5$  with  $\text{MeOH}$ , according to equation [39], as well as in other  $\text{MeOH}$  reactions to be described later, was neutralized by the presence of excess  $\text{NaF}$ .  $\text{PhTeF}_5$  reacts smoothly with silicon-containing compounds to produce the corresponding substituted products cis- $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{MeO}$ ,  $\text{Me}_2\text{N}$ ,  $\text{Et}_2\text{N}$ ), because of the easy formation of  $\text{Me}_3\text{SiF}$  in such bond-scission reactions [40]. The formation of  $\text{Me}_3\text{SiF}$  was confirmed by its known  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR spectra (124).



Mass spectra of the solid products from the reactions of  $\text{PhTeF}_5$  are consistent with the formation of  $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{OMe}$ ,  $\text{NMe}_2$ ,  $\text{NEt}_2$ ,  $\text{OH}$ ). The observed  $\text{abc}_2$  spin-system in  $^{19}\text{F}$  NMR spectra of  $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{OH}$ ,  $\text{OMe}$ ,  $\text{Me}_2\text{N}$ ,  $\text{Et}_2\text{N}$ ) clearly establish their cis octahedral

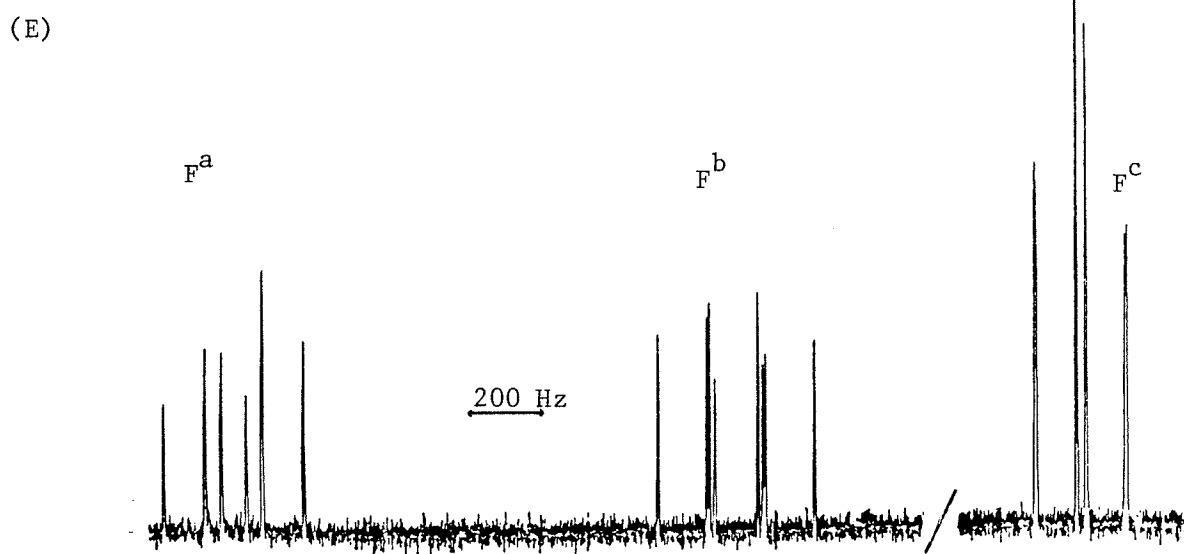
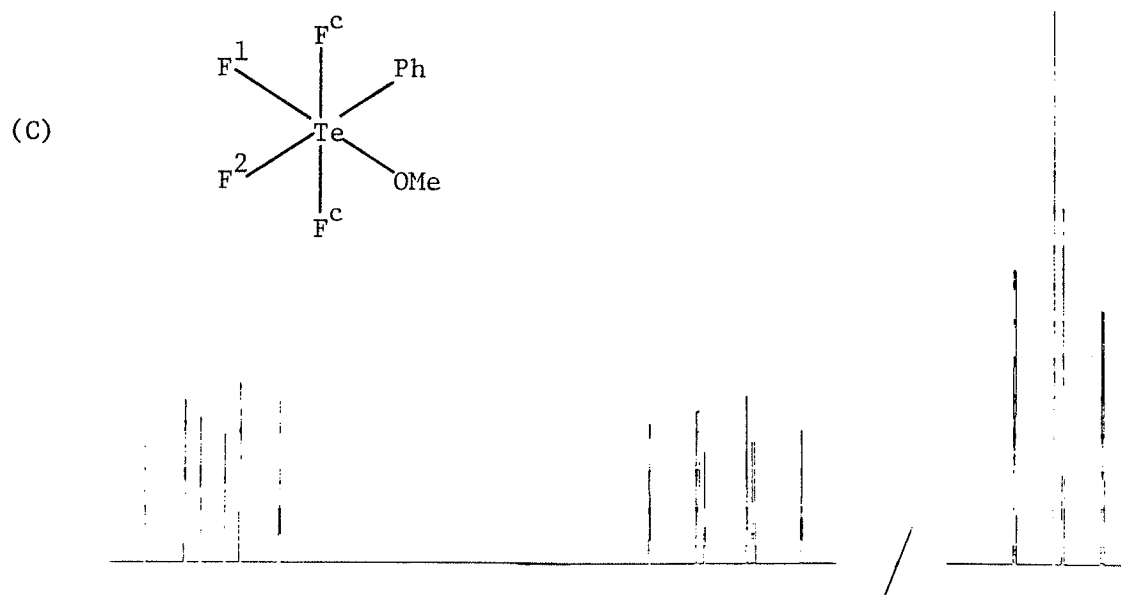


Figure 16. <sup>19</sup>F NMR spectrum of cis-(MeO)PhTeF<sub>4</sub>.  
 E is the experimental and C the calculated spectrum.  
 Assignment of F<sup>a</sup> and F<sup>b</sup> resonances to F<sup>2</sup> and F<sup>1</sup> are  
 discussed in the text.



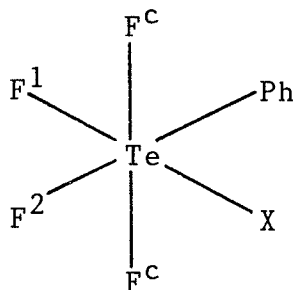


Figure 17. Structure of cis-PhTeF<sub>4</sub>X (X=HO, MeO, Me<sub>2</sub>N, Et<sub>2</sub>N)

geometry, as shown in Figure 17. The <sup>19</sup>F NMR spectra of cis isomers (abc<sub>2</sub> spin system) were simulated by the computer program LAME (128, 129), as discussed before. The simulated spectrum for cis-(MeO)PhTeF<sub>4</sub> is shown in Figure 16, as a representative example. In the calculated spectrum for cis-(MeO)PhTeF<sub>4</sub> shown in Figure 16 the calculated coupling constant values are J<sub>TeF<sup>a</sup></sub> = 148.4 Hz, J<sub>TeF<sup>b</sup></sub> = 130.2 Hz and J<sub>TeF<sup>c</sup></sub> = 106.2 Hz. From the peak intensities (theoretically 1:1:2 for an abc<sub>2</sub> spin system for cis-PhTeF<sub>4</sub>X) and splitting patterns (theoretically a doublet of doublets for the c<sub>2</sub> resonance) the highest field fluorine resonance (F<sup>C</sup> resonances in Table XI) in the <sup>19</sup>F NMR spectrum of cis-PhTeF<sub>4</sub>X (X = HO, MeO, Me<sub>2</sub>N, Et<sub>2</sub>N) has been unequivocally assigned to F<sup>C</sup> fluorines in the cis octahedral structure shown in Figure 17. However, the abc<sub>2</sub> spin systems do not directly dictate which of the F<sup>a</sup> and F<sup>b</sup> resonances in cis-PhTeF<sub>4</sub>X (X = HO, MeO, Me<sub>2</sub>N,

Et<sub>2</sub>N) (Table XII) should be assigned to F<sup>1</sup> and F<sup>2</sup> in the cis structure shown in Figure 17. To solve this crucial point, the <sup>19</sup>F chemical shifts of F<sup>1</sup>, F<sup>2</sup> and F<sup>C</sup> in the structure shown in Figure 17 (X = HO, MeO, Me<sub>2</sub>N, Et<sub>2</sub>N) have been calculated by the method of Dean and Evans (67) with adjustable parameters determined from known fluorine chemical shifts of XTeF<sub>5</sub> [X = Ph of the present work, HO (40,41), MeO (39b), Et<sub>2</sub>N (44), Me<sub>2</sub>N (44)]. As a representative example, the empirical calculation of fluorine chemical shifts for cis-(MeO)PhTeF<sub>4</sub> is shown below.

It has been discussed previously that the <sup>19</sup>F chemical shifts ( $\delta_F$ ) in substituted octahedral fluoride derivatives may be represented by relation [24]  $\delta_F = pC + qT$ , where C and T are empirical constants characteristic of the substituent and p and q are the number of substituents cis and trans respectively to the fluorine whose resonance ( $\delta_F$ ) is to be fit by the above equation [24]. Though the fit is seldom perfect, it has been found to be good enough to make the relationship useful for the series (MeO)<sub>n</sub>WF<sub>6-n</sub> (88) and (HO)<sub>n</sub>TeF<sub>6-n</sub> (40). Empirical constants for the MeO substituent trans (labelled as Tome) and cis (labelled as Come) to the resonating fluorine in MeOTeF<sub>5</sub> are calculated from the known chemical shifts of MeOTeF<sub>5</sub> (39b) and TeF<sub>6</sub> (65).

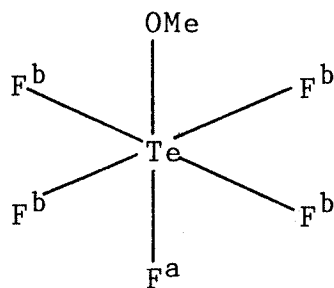


Figure 18. Structure of  $\text{MeOTeF}_5$

In the above structure (Figure 18), the chemical shift of  $\text{F}^b$  fluorines is  $-58.2$  ppm and that of  $\text{F}^a$  is  $-45.7$  ppm with respect to  $\text{CFCl}_3$ . These chemical shifts relative to  $\text{TeF}_6$  ( $-54.4$  ppm) are then  $-3.8$  ppm and  $8.7$  ppm for  $\text{F}^b$  and  $\text{F}^a$  fluorines respectively.  $\text{F}^b$  and  $\text{F}^a$  fluorines are cis and trans respectively to OMe. Thus, from relationship [24] the following values are obtained:

$$\begin{aligned}
 -3.8 &= p\text{Come} + q\text{Tome} \\
 [41] \quad -3.8 &= \text{Come} \quad (\text{for } \text{F}^b \quad q = 0 \text{ and } p = 1) \\
 \text{Similarly, } 8.7 &= \text{Tome} \quad [42] \text{ as for } \text{F}^a \text{ fluorine} \quad p = 0 \\
 &\text{and } q = 1.
 \end{aligned}$$

Empirical constants for phenyl groups trans (labelled as Tph) and cis (labelled as Cph) have been calculated from the measured chemical shifts of  $\text{PhTeF}_5$  ( $\text{ab}_4$  spin system) from the present work. The chemical

shifts of  $F^a$  and  $F^b$  fluorines in  $\text{PhTeF}_5$  appear in Table VI.

$$p\text{Cph} + q\text{Tph} = (54.4 - 53.4)$$

$$[43] \quad \text{Cph} = 1.0 \text{ as } q = 0 \text{ and } p = 1 \text{ for } F^b \text{ fluorines.}$$

$$[44] \quad \text{Tph} = 17.6 \text{ as } p = 0 \text{ and } q = 1 \text{ for } F^a \text{ fluorine.}$$

With known  $\text{Come}$ ,  $\text{Tome}$ ,  $\text{Cph}$  and  $\text{Tph}$  the empirical chemical shifts of fluorines in cis-( $\text{MeO}$ ) $\text{PhTeF}_4$  (Figure 17,  $X = \text{MeO}$ ) have been calculated as follows:

$$\begin{aligned} F^c &= \text{Come} + \text{Cph} \\ &= -3.8 + 1.0 \\ [45] \quad &= -2.8 \end{aligned}$$

Therefore, the  $^{19}\text{F}$  chemical shift of  $F^c$  fluorines in cis-( $\text{MeO}$ ) $\text{PhTeF}_4$  with respect to  $\text{CFCl}_3 = (-2.8 - 54.4) = -57.2$  ppm.

$$\begin{aligned} F^1 &= \text{Cph} + \text{Tome} \\ &= 1.0 + 8.7 \\ [46] \quad &= 9.7 \end{aligned}$$

Therefore, the  $^{19}\text{F}$  chemical shift of  $\text{F}^1$  fluorine in cis-(MeO)PhTeF<sub>4</sub> with respect to CFC1<sub>3</sub> = (9.7-54.4) = -44.7 ppm.

$$\begin{aligned} \text{F}^2 &= \text{Come} + \text{Tph} \\ &= -3.8 + 17.6 \\ [47] &= 13.8 \end{aligned}$$

Therefore, the  $^{19}\text{F}$  chemical shift of  $\text{F}^2$  fluorine in cis-(MeO)PhTeF<sub>4</sub> with respect to CFC1<sub>3</sub> = (13.8-54.4) = -40.6 ppm.

From the order of decrease of chemical shifts in calculated and observed values (Table XI), tentative assignments of observed resonances (especially for  $\text{F}^a$  and  $\text{F}^b$  resonances) to fluorines in the structure shown in Figure 17 have been made as shown in Table XII. Similar assignments of fluorine resonances in cis-(MeO)TeClF<sub>4</sub> (Figure 19) have been made (38) on the basis of calculated chemical shifts using the same method (67). As the differences between  $\text{F}^a$  and  $\text{F}^b$  chemical shifts in cis-PhTeF<sub>4</sub>X (Table XI) are small, the assignment of resonances shown in Table XII on the basis of empirical calculations should be tested by a different method. In any future extension of this work magnetic double resonance experiments might be useful to confirm this tentative assignment of fluorine resonances in  $\text{abc}_2$  spectra of

Table XII. Calculated chemical shifts in cis-PhTeF<sub>4</sub>X (X = MeO, Me<sub>2</sub>N, Et<sub>2</sub>N, HO) and assignment of their observed resonances to fluorines in the structure shown in Figure 17.

X	Calculated Chemical Shifts	Observed Chemical Shifts*	Observed chemical shifts assigned to fluorines in figure 17
MeO	for F <sup>c</sup> -57.2	F <sup>c</sup> = -59.6	F <sup>c</sup> to F <sup>c</sup>
	for F <sup>1</sup> -44.7	F <sup>b</sup> = -49.4	F <sup>b</sup> to F <sup>1</sup>
	for F <sup>2</sup> -40.6	F <sup>a</sup> = -44.8	F <sup>a</sup> to F <sup>2</sup>
Me <sub>2</sub> N	for F <sup>c</sup> -58.6	F <sup>c</sup> = -72.9	F <sup>c</sup> to F <sup>c</sup>
	for F <sup>2</sup> -42	F <sup>b</sup> = -46	F <sup>b</sup> to F <sup>2</sup>
	for F <sup>1</sup> -36.4	F <sup>a</sup> = -33	F <sup>a</sup> to F <sup>1</sup>
Et <sub>2</sub> N	for F <sup>c</sup> -54.9	F <sup>c</sup> = -68.7	F <sup>c</sup> to F <sup>c</sup>
	for F <sup>2</sup> -38.3	F <sup>b</sup> = -40.2	F <sup>b</sup> to F <sup>2</sup>
	for F <sup>1</sup> -32.9	F <sup>a</sup> = -30.9	F <sup>a</sup> to F <sup>1</sup>
HO	for F <sup>c</sup> -48	F <sup>c</sup> = -51.6	F <sup>c</sup> to F <sup>c</sup>
	for F <sup>1</sup> -42	F <sup>b</sup> = -44	F <sup>b</sup> to F <sup>1</sup>
	for F <sup>2</sup> -31.4	F <sup>a</sup> = -28	F <sup>a</sup> to F <sup>2</sup>

\*Observed resonances in abc<sub>2</sub> spectra of cis-PhTeF<sub>4</sub>X as recorded in Table XI.

cis-PhTeF<sub>4</sub>X (X = OH, OMe, NMe<sub>2</sub>, NEt<sub>2</sub>).

The <sup>1</sup>H NMR spectrum of the MeO group in cis-(MeO)PhTeF<sub>4</sub> is shown in Figure 20. The spectrum shows a broadish four line grouping centered at 4.07 ppm with a separation of 1.16 Hz. A quartet resonance does not support the structure of cis-(MeO)PhTeF<sub>4</sub>. It is reasonable to view this spectrum as an overlapped doublet of triplet resonances caused by two equivalent cis fluorines (F<sup>C</sup> fluorines in Figure 17, X = MeO) and one non-equivalent cis fluorine (F<sup>2</sup> in Figure 17, X = MeO)) assuming the trans coupling (due to F<sup>1</sup>) is either zero or very small. Thus, assuming a zero trans coupling (due to F<sup>1</sup> in Figure 17), the a<sub>2</sub>bx<sub>3</sub> spectrum for the x transitions has been simulated by using the observed line positions as input which fits exactly with the experimental spectrum (Figure 20). The calculated coupling constant values are J<sub>xFa</sub> = 1.16 Hz and J<sub>xFb</sub> = 1.157 Hz. The <sup>1</sup>H NMR spectra of cis-PhTeF<sub>4</sub>X (X = Me<sub>2</sub>N, Et<sub>2</sub>N) were recorded but fine structure due to H-F coupling was not observed.

The trans octahedral geometry of (HO)PhTeF<sub>4</sub> has been established from the single peak in its <sup>19</sup>F NMR spectrum and a quintet resonance in its <sup>125</sup>Te NMR spectrum (δ<sup>125</sup>Te = 738 ppm, J<sub>TeF</sub> = 3445 Hz in chloroform). The <sup>19</sup>F chemical shift for trans-(HO)PhTeF<sub>4</sub> has been calculated and the calculated shift (-48 ppm) fits very well with the observed chemical shift (-47.4 ppm).

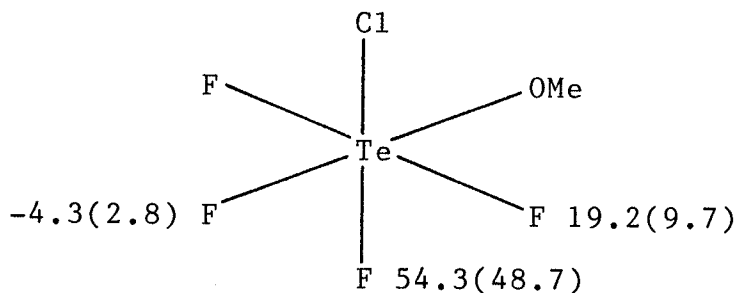


Figure 19. Structure of cis-MeOTeClF<sub>4</sub>. Numerical values are observed (calculated) chemical shifts in ppm.

The cis-(MeO)PhTeF<sub>4</sub> compound is stable under inert atmosphere for an indefinite period of time. The amino derivatives decompose slowly as checked by <sup>19</sup>F NMR peak integration and forms a yellow solid which was not soluble in either chloroform or methylene chloride and it was not characterized. The hydroxy derivatives react with glass to form an insoluble viscous liquid.

We now turn to the diphenyl derivatives formed in the reactions of trans-Ph<sub>2</sub>TeF<sub>4</sub> with methanol, amine, water and silicon compounds. The mass spectra of the mono substituted products, Ph<sub>2</sub>TeF<sub>3</sub>X (X = MeO, Me<sub>2</sub>N, Et<sub>2</sub>N) formed in these reactions clearly show the molecular ion peak along with fragment peaks.

From the NMR data in Table XI it is clear that, except in the reaction with Me<sub>2</sub>NH (Table X), only one isomeric form is obtained in the above reactions. The



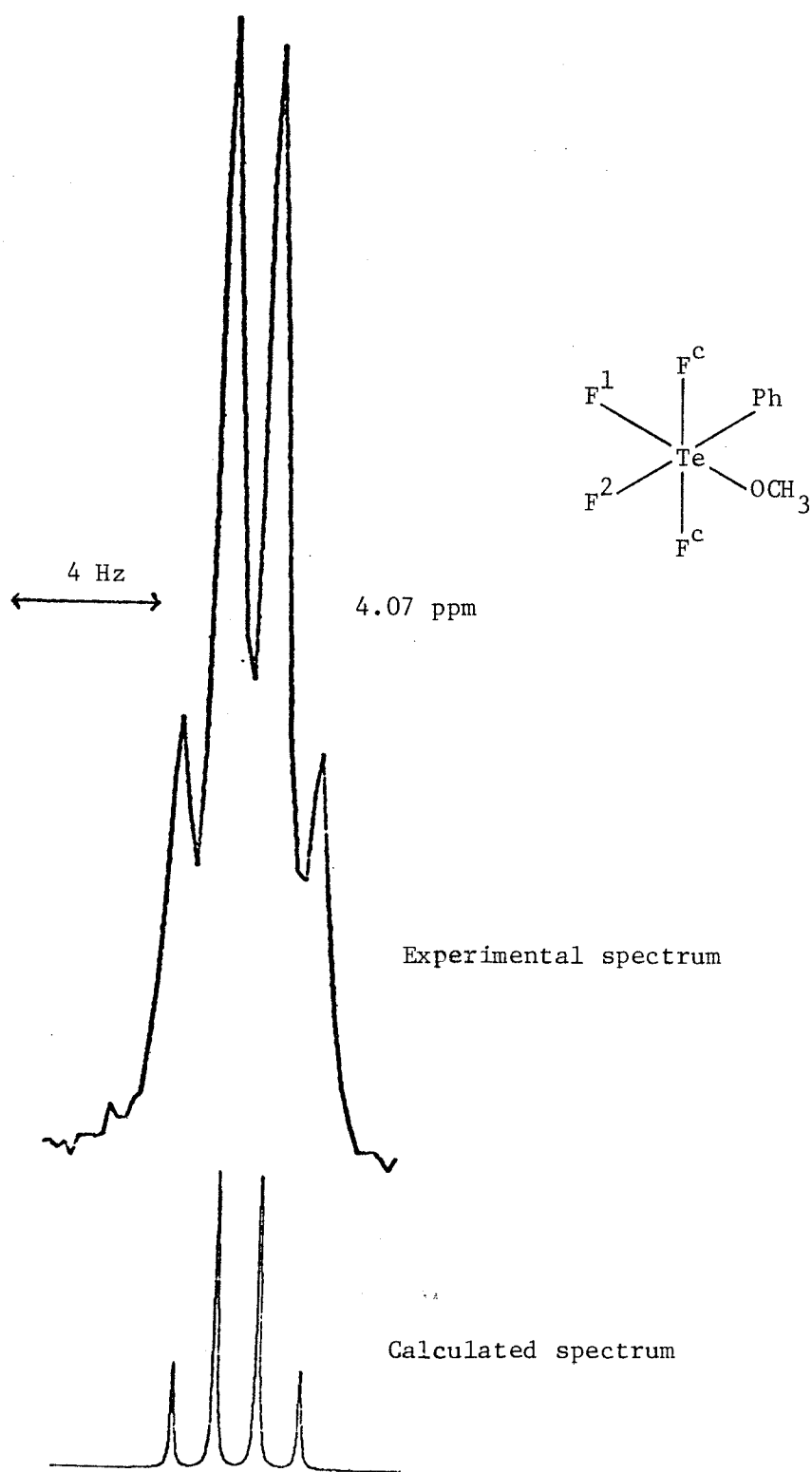


Figure 20.  $^1\text{H}$  NMR spectrum of the MeO region in cis-(MeO)PhTeF<sub>4</sub>.

reaction of trans- $\text{Ph}_2\text{TeF}_4$  with  $\text{Me}_2\text{NH}$  has been reproduced several times and the two geometrical isomers I and II (Table XI) are formed each time. Isomer I is formed in both  $\text{Me}_2\text{NH}$  and  $\text{Me}_2\text{N-SiMe}_3$  reactions and its chemical shifts in  $^{19}\text{F}$  NMR spectra are very close to that of  $(\text{Et}_2\text{N})\text{Ph}_2\text{TeF}_3$  (Table XI). The mono substituted products,  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) can have three geometrical isomers as shown in Figure 21. All three isomers in Figure 21 have  $\text{ab}_2$  spin systems in their fluorine NMR spectra and thus it is not possible to assign the geometry of the products  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) formed in the reactions of trans- $\text{Ph}_2\text{TeF}_4$ .

As can be seen from Table XI, the rate of substitution reactions in trans- $\text{Ph}_2\text{TeF}_4$  are much slower than  $\text{PhTeF}_5$  reactions. In fact, a trace amount of unreacted trans- $\text{Ph}_2\text{TeF}_4$  was observed in the  $^{19}\text{F}$  NMR spectra of several reaction products. Except for the reactions of silicon-containing compounds,  $\text{Ph}_2\text{TeF}_2$  was always formed in about 5 - 15% yield as observed in  $^{19}\text{F}$  NMR spectra of the reaction products. Attempts to force the reaction of trans- $\text{Ph}_2\text{TeF}_4$  towards completion by heating at higher temperature or constant heating for longer times resulted in more of the reduction product  $\text{Ph}_2\text{TeF}_2$ . However, the corresponding oxidized product could not be identified in any reaction. The products  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) are stable under an inert atmosphere and in organic solvents.

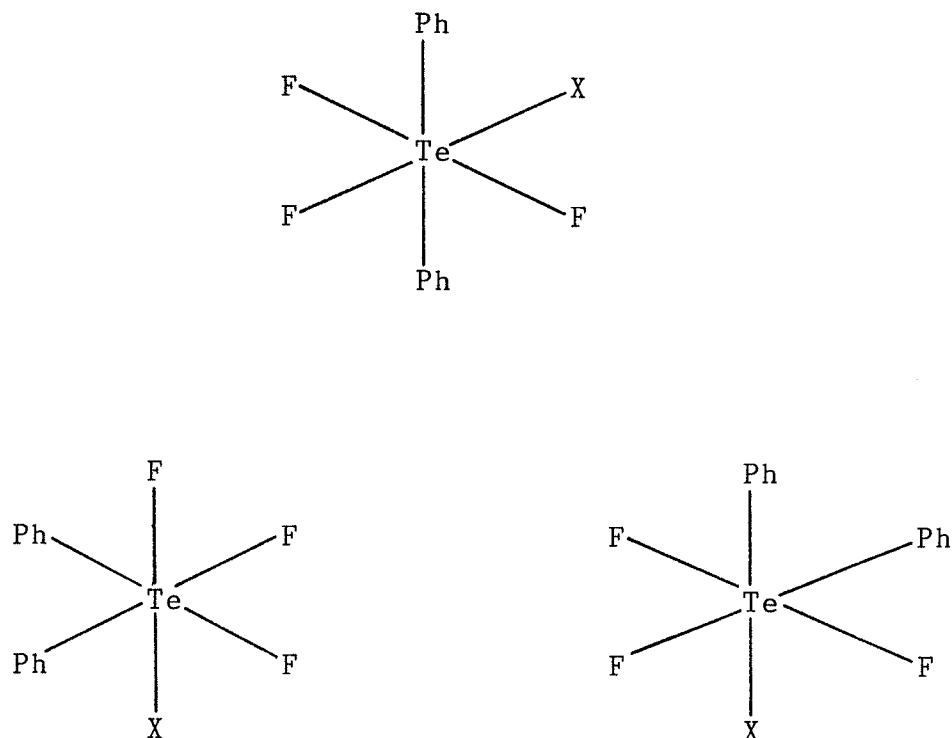


Figure 21. Possible geometrical isomers of  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ )

Only under drastic reaction conditions can the disubstitution product  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$  be obtained from the reaction of trans- $\text{Ph}_2\text{TeF}_4$  with methanol. The product shows a broad peak ( $\delta_{\text{H}} = 3.6$  ppm,  $1/2\Delta = 1.5$  Hz in chloroform) for the MeO group protons in its  $^1\text{H}$  NMR spectrum. A single line  $^{19}\text{F}$  NMR spectrum (Table XI) for the product  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$  suggests one of the structures shown in Figure 22. From the simple NMR data it is not possible to

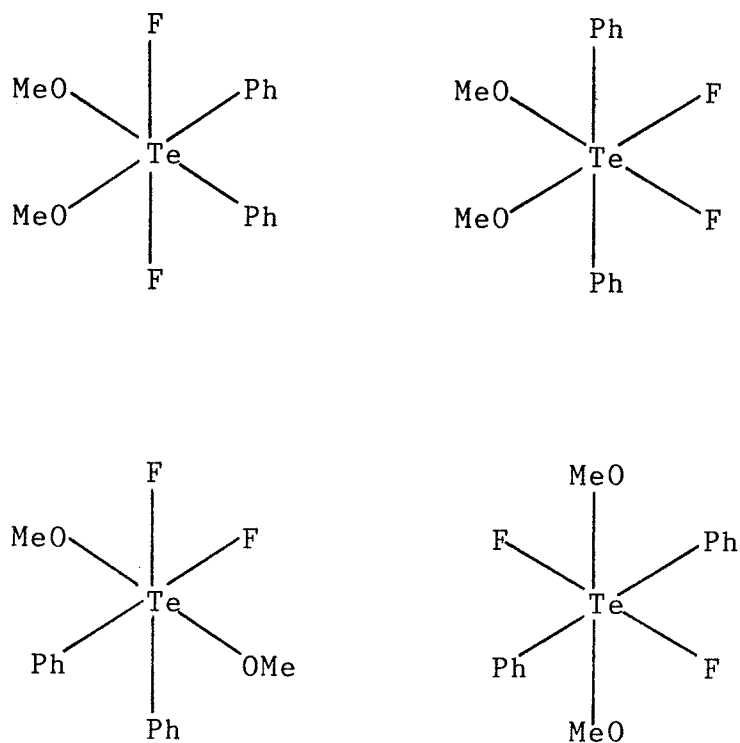


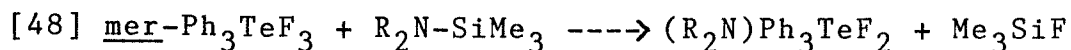
Figure 22. Possible isomers of  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$  with equivalent fluorines.

assign the structure of  $(\text{MeO})_2\text{Ph}_2\text{TeF}_2$ .

mer- $\text{Ph}_3\text{TeF}_3$  reacts similarly with  $\text{Me}_2\text{NH}$ ,  $\text{MeOH}$  and  $\text{Me}_2\text{N-SiMe}_3$ , however, but at a slower rate than trans- $\text{Ph}_2\text{TeF}_4$ . In reactions with  $\text{Me}_2\text{NH}$  and  $\text{MeOH}$ , the reduced product  $\text{Ph}_2\text{TeF}_2$  was observed by  $^{19}\text{F}$  NMR studies. The corresponding oxidized product could not be observed again.

The mass spectrum of the compound  $(\text{MeO})\text{Ph}_3\text{TeF}_2$  clearly shows its molecular ion peak along with other fragment ion peaks. No reasonable mass spectrum was

obtained from the vacuum dried reaction products of mer- $\text{Ph}_3\text{TeF}_3$  with  $\text{Me}_2\text{NH}$  and  $\text{R}_2\text{N-SiMe}_3$ . The observed ab spin system (two fluorines in non-equivalent environments) in the  $^{19}\text{F}$  NMR spectra of these reaction products can only be assumed to be due to mono substituted  $(\text{R}_2\text{N})\text{Ph}_3\text{TeF}_2$  ( $\text{R} = \text{Me}, \text{Et}$ ). In the reactions with  $\text{R}_2\text{N-SiMe}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) the formation of  $\text{Me}_3\text{SiF}$  was observed by  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR spectrometry. However, as these reactions were not done in a sealed tube in order to avoid the danger of breaking the sealed NMR tube in the NMR probe due to the pressure of liberated  $\text{Me}_3\text{SiF}$ , the ratio of fluorine in  $\text{Me}_3\text{SiF}$  to that of fluorine attached to tellurium (ab spin system) was not determined. However, the formation of  $\text{Me}_3\text{SiF}$  and the observation of an ab spin system for substituted products do suggest that the products in these reactions are  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ), according to equation [48]. No further studies have been made to characterize these compounds.



The geometry of the compounds  $(\text{R}_2\text{N})\text{Ph}_3\text{TeF}_2$  ( $\text{R} = \text{Me}, \text{Et}$ ) and  $(\text{MeO})\text{Ph}_3\text{TeF}_2$  have been established (Figure 23) from ab spin systems in their  $^{19}\text{F}$  NMR spectra. As discussed previously for  $\text{abc}_2$  spin systems, the observed fluorine resonances in  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ; see Table XI for chemical shifts) are assigned to  $\text{F}^1$  and  $\text{F}^2$  in

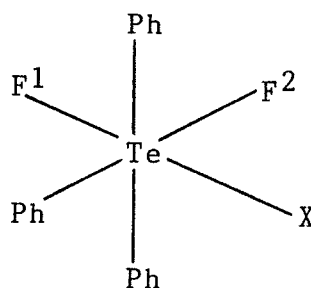


Figure 23. Structure of  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X}=\text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) with ab spin system in  $^{19}\text{F}$  NMR.

Table XIII. Calculated chemical shifts of fluorines in structure shown in Figure 23 and assignment of observed resonances (Table XI) to  $\text{F}^1$  and  $\text{F}^2$ .

X		calculated chemical shift ppm		observed chemical shift ppm	assignment of observed resonance
MeO	$\text{F}^1$	-89.2	$\text{F}^b$	-75	$\text{F}^b$ to $\text{F}^1$
	$\text{F}^2$	-6.7	$\text{F}^a$	-29.4	$\text{F}^a$ to $\text{F}^2$
$\text{Me}_2\text{N}$	$\text{F}^1$	-80.98	$\text{F}^b$	-64.8	$\text{F}^b$ to $\text{F}^1$
	$\text{F}^2$	-8.1	$\text{F}^a$	-7	$\text{F}^a$ to $\text{F}^2$
$\text{Et}_2\text{N}$	$\text{F}^1$	-77.48	$\text{F}^b$	-74.4	$\text{F}^b$ to $\text{F}^1$
	$\text{F}^2$	-4.49	$\text{F}^a$	-11.3	$\text{F}^a$ to $\text{F}^2$

the structure shown in Figure 23 on the basis of calculated chemical shifts (67). The adjustable constants were determined from the known chemical shifts of mer- $\text{Ph}_3\text{TeF}_3$  (Table VI),  $\text{MeOTeF}_5$  (39b),  $\text{Me}_2\text{NTeF}_5$  (44) and  $\text{Et}_2\text{NTeF}_5$  (44). The calculated values and assignment of resonances to  $\text{F}^1$  and  $\text{F}^2$  of the structure in Figure 23 are shown in Table XIII.

The  $^1\text{H}$  NMR spectra of the compounds  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) have been recorded. They are generally very poorly resolved in the region of alkyl protons and provide no structural information.

#### 4.3 Formation of $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$ :

As discussed in section 1.7, the only known organochalcogen(VI) fluoro cation  $\text{MeSF}_4^+$  has been characterized at low temperatures by NMR studies (33).  $\text{PF}_5$  is a good fluoride acceptor and many ionic complexes have been prepared from its reaction with strong fluoride donor compounds (75). One of the objectives of the present work was to establish whether five-coordinate phenyltellurium(VI) fluoride cations could be prepared from reactions of phenyltellurium(VI) fluoride with  $\text{PF}_5$ . It would be especially interesting to study the  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR properties of such systems.

Table XIV. NMR spectral data of  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  in methylene chloride solvent

	chemical shift in ppm			coupling constant in Hz		
	$^{19}\text{F}$	$^{31}\text{P}$	$^{125}\text{Te}$	FP	$^{125}\text{TeF}$	$^{123}\text{TeF}$
$\text{Ph}_3\text{TeF}_2^+$	-123(s)		894(t)		1600	1323
$\text{PF}_6^-$	-73.6(d)	-143.6(h)		709		

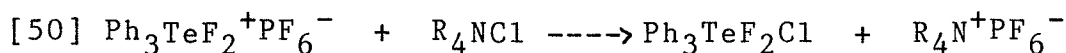
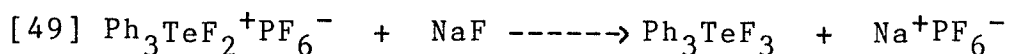
note: h is heptet

In this connection, it was found that the reaction of mer- $\text{Ph}_3\text{TeF}_3$  with excess  $\text{PF}_5$  (1:10 molar ratio) in methylene chloride produced  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  in almost quantitative yield.  $^{19}\text{F}$  NMR,  $^{31}\text{P}$  NMR and  $^{125}\text{Te}$  NMR spectral parameters of the resulting  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  are given in Table XIV.

The preparation of the ionic product  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  has been reproduced several times under identical reaction conditions. As discussed in the experimental section,  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  has been characterized by its chemical reaction with NaF and triethylbenzylammonium chloride. The products  $\text{Ph}_3\text{TeF}_2\text{Cl}$  and mer- $\text{Ph}_3\text{TeF}_3$  obtained from the



reactions of triethylbenzylammonium chloride and NaF with  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  have been characterized by their  $^{19}\text{F}$  NMR spectra (Table VI).



As checked by the  $^{19}\text{F}$  NMR spectroscopy, the compound  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  was found to decompose to mer- $\text{Ph}_3\text{TeF}_3$  and a trace amount of fac- $\text{Ph}_3\text{TeF}_3$ , after evaporation of the solvent containing  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$ , in about 2 days. A trace amount (about 8 - 12% with respect to  $\text{PF}_6^-$  as checked by  $^{19}\text{F}$  peak integrations) of a doublet resonance centered at -84.5 ppm was observed in the  $^{19}\text{F}$  NMR spectrum ( $J = 985$  Hz in methylene chloride) when the solution containing  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  was in contact with atmospheric moisture (Figure 24). The fluorine spectrum in Figure 24 also shows a weak but sharp doublet signal centered at -88.3 ppm ( $J_{\text{FP}} = 1062$  Hz) for  $\text{OPF}_3$ . This doublet resonance for  $\text{OPF}_3$  is labelled as "a" in the spectrum in Figure 24.  $\text{OPF}_3$  is a volatile gas and its intensity in the spectrum was found to decrease with time. The  $^{31}\text{P}$  NMR spectrum of this solution shows a corresponding broad triplet at -21.1 ppm ( $J_{\text{PF}} = 985$  Hz) in addition to the heptet resonance for  $\text{PF}_6^-$  (Figure 24). From the observed  $^{31}\text{P}$  chemical shift ( $\delta^{31}\text{P} = 21.1$  ppm), the P-F coupling

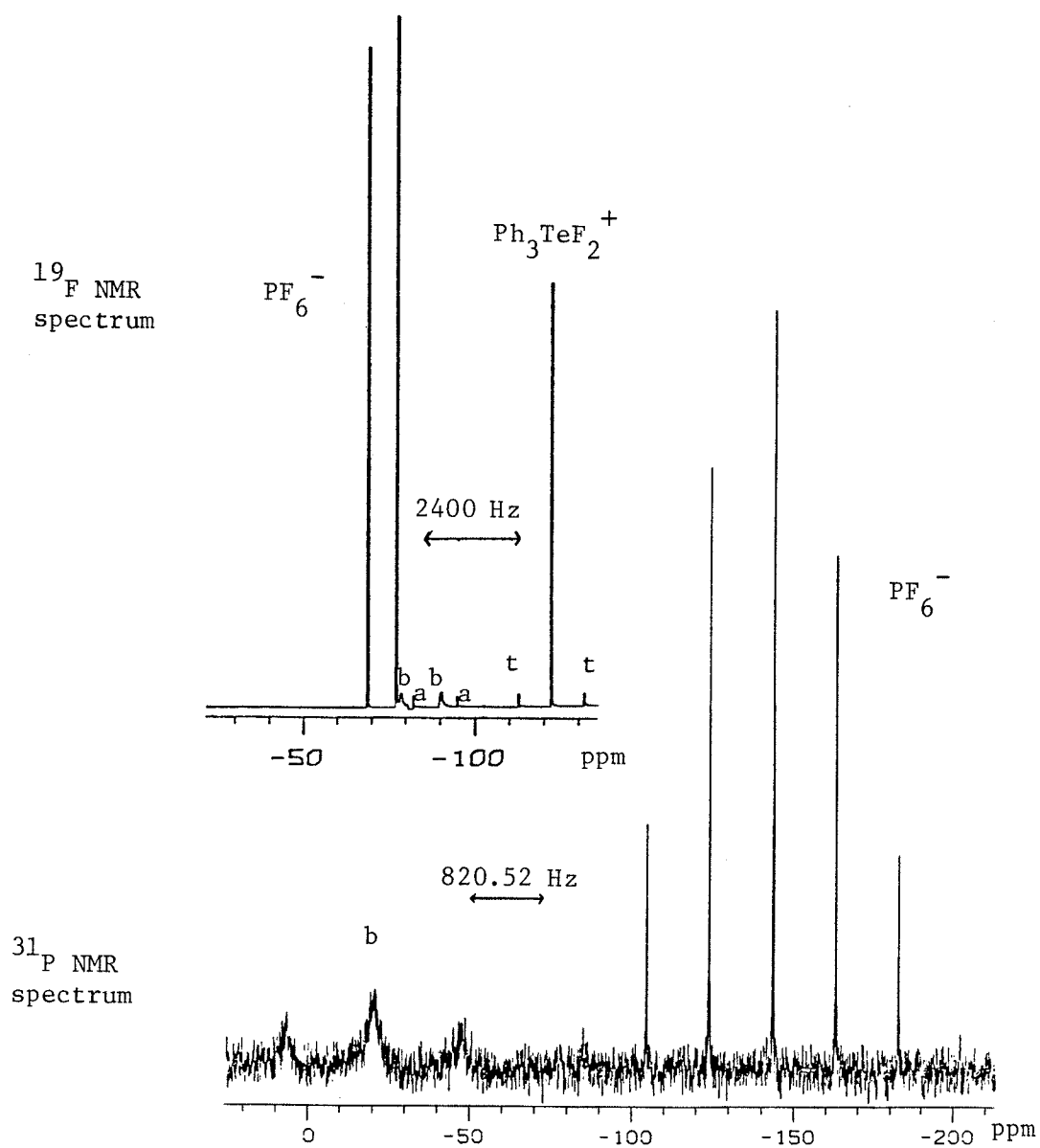
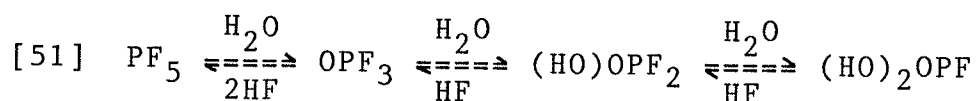


Figure 24.  $^{19}\text{F}$  NMR and  $^{31}\text{P}$  NMR spectra of  $\text{Ph}_3\text{TeF}_2^+ \text{PF}_6^-$ .  
 t is the satellite peak of  $^{125}\text{Te}$  isotope. a and b peaks  
 are discussed in the text.

constant (985 Hz) and the spin system in both  $^{31}\text{P}$  NMR and  $^{19}\text{F}$  NMR spectra this impurity has been characterized as  $(\text{HO})\text{OPF}_2$  (137-139). The resonance for  $(\text{HO})\text{OPF}_2$  is labelled as "b" in the spectra shown in Figure 24. This impurity is probably formed by hydrolysis of  $\text{PF}_5$ . The broadish ( $1/2\Delta \approx 10$  Hz) appearance of the fluorine resonances is probably due to an exchange process (140) as shown in equation [51].



The presence of  $(\text{HO})_2\text{OPF}$  in this solution has been deduced from the low temperature NMR spectrum, which will be discussed in the next section. This hydrolysis impurity  $(\text{HO})\text{OPF}_2$  did not appear in the solution containing  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  kept in a flame sealed dry NMR tube.

It is recognized that this  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  ionic compound is probably the most important preparation during this study and it is imperative that molecular weight, conductivity, infrared and X-ray crystallographic data should be obtained at the earliest opportunity.

#### 4.4 Fluorine exchange in the $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+$ system:

As discussed in section 1.8, intermolecular fluorine exchange processes involving a fluorine bridged intermediate do not identify the fluorine which occupies the bridging position because an accompanying rapid intramolecular process scrambles stereospecific fluorines in such systems. Thus, the main interest in this thesis was to investigate whether such valuable stereochemical information regarding the mechanism of exchange processes could be obtained with the fluoride systems prepared in the present work. mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  has non-equivalent fluorines and according to its solid state structure (described in section 4.1.4) the  $\text{F}^{\text{a}}$  fluorine is expected to be more reactive and more basic. It was therefore envisaged that mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  would be a valuable system for obtaining stereochemical information about fluorine exchange processes.

In this connection it was found that the  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+$  system meets these criteria. According to known processes (115-117), rapid intermolecular fluorine exchange was initiated by adding six-coordinate mer- $\text{Ph}_3\text{TeF}_3$  to five-coordinate  $\text{Ph}_3\text{TeF}_2^+$  and the mechanism of exchange process was studied by means of NMR spectroscopy.

$\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  was added as a solution in methylene chloride to mer- $\text{Ph}_3\text{TeF}_3$  in the same solvent. Solutions were added through various syringes and the contents were

gently shaken to ensure complete mixing. Several experiments were made at different concentrations of reactants which were determined by repeated integration of  $^{19}\text{F}$  NMR peaks. The concentrations were estimated to be accurate to  $\pm 5\text{--}6\%$  when determined by this technique.

On mixing known amounts of  $\text{mer-Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  and  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  and recording the  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectra, the following observations are made:

1. The  $J_{\text{FaFb}}$  coupling in  $\text{mer-Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  is lost as  $\text{Ph}_3\text{TeF}_2^+$  is added to  $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  (Figure 25, peak at  $-110.31$  ppm). The doublet resonance for  $(\text{HO})\text{OPF}_2$ , an impurity usually formed in  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  solutions, also appears (labelled as "a") in the spectrum shown in Figure 25. Further, peaks for  $\text{fac-Ph}_3\text{TeF}_3$  (labelled as "d") and  $\text{trans-Ph}_2\text{TeF}_4$  (labelled as "e") also appear in this spectrum. These were present as impurities in the starting compound  $\text{mer-Ph}_3\text{TeF}_3$ . The presence or absence of these impurities did not affect the exchange process. The  $^{125}\text{Te}$  satellites are labelled as "t" and  $^{123}\text{Te}$  satellites as "t<sup>1</sup>" in the spectrum shown in Figure 25 as well as in other spectra to be described next.

2. The  $\text{Te-F}^{\text{b}}$  coupling in  $\text{mer-Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  is retained (Figure 25), but the  $\text{Te-F}^{\text{a}}$  coupling is lost as  $\text{Ph}_3\text{TeF}_2^+$  is added to  $\text{mer-Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$ .

3. The  $\text{Te-F}$  coupling in  $\text{Ph}_3\text{TeF}_2^+$  is retained during the exchange process.

4. The fluorine chemical shift of  $\text{F}^{\text{b}}$  in  $\text{mer-}$

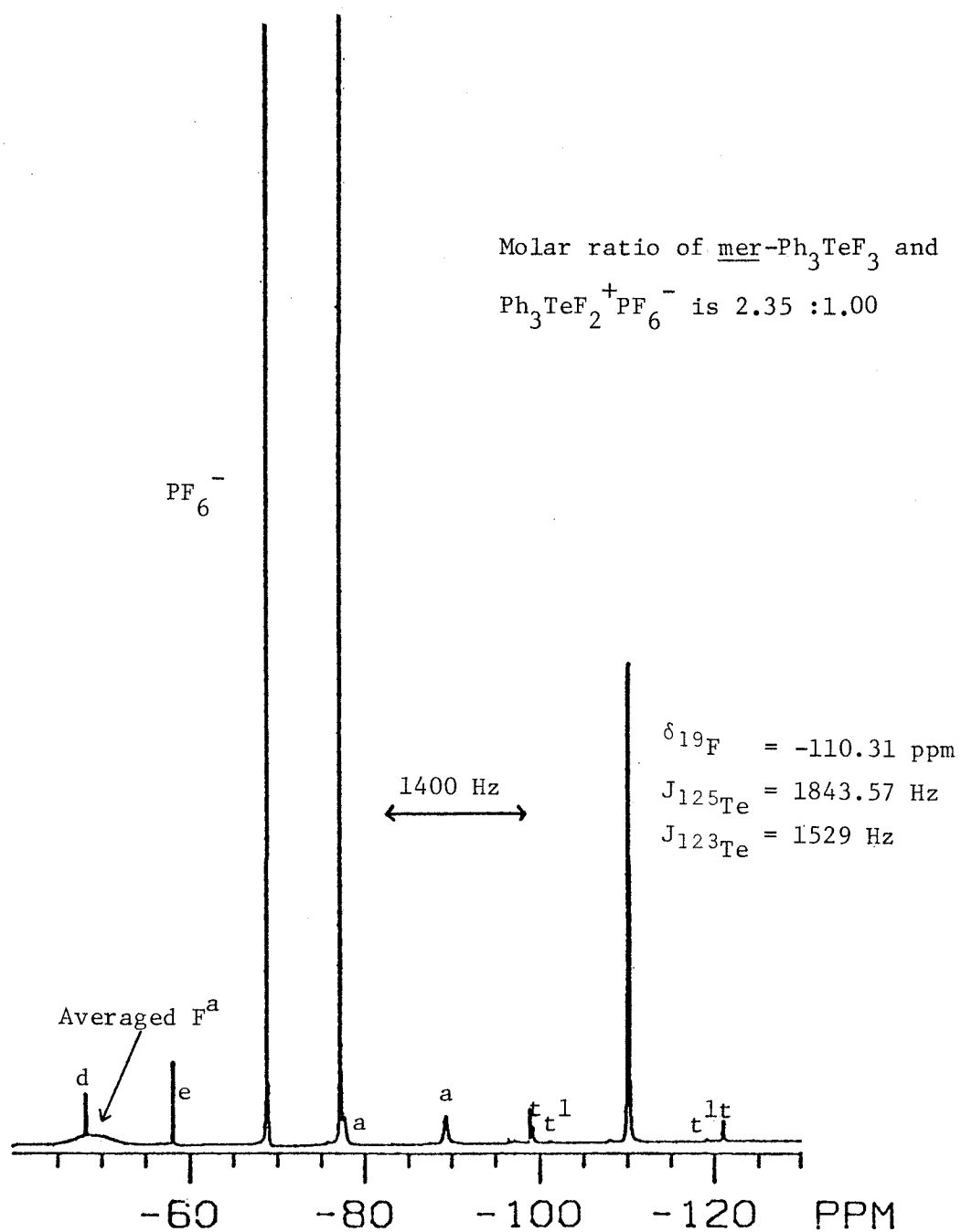


Figure 25.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$ . Peaks a, d and e are discussed in the text. t and  $t^1$  are the satellites caused by the  $^{125}\text{Te}$  and  $^{123}\text{Te}$  isotopes, respectively.

$\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  moves toward high field as  $\text{Ph}_3\text{TeF}_2^+$  is added, but the  $\text{Te}-\text{F}^{\text{b}}$  coupling is retained.  $^{19}\text{F}$  NMR spectra with different concentrations of reactants appear in Figures 25 and 26. The spectrum in Figure 26 also shows the doublet resonance (labelled as "a") for  $(\text{HO})\text{OPF}_2$ .

5. The  $\text{F}^{\text{a}}$  fluorine resonance in  $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  moves upfield as  $\text{Ph}_3\text{TeF}_2^+$  is added to  $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$ . Chemical shifts at different concentrations of reactants are shown in Figures 25 and 26 and the chemical shift of  $\text{F}^{\text{a}}$  fluorine in rigid mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  appears in Table VI.

6. The  $^{125}\text{Te}$  NMR spectrum with any proportions of reactants is always a triplet due to coupling with two  $\text{F}^{\text{b}}$  fluorines (Figure 27). The spectrum shown in Figure 27 is for a solution containing mer- $\text{Ph}_3\text{TeF}_3$  and  $\text{Ph}_3\text{TeF}_2^+$  in a molar ratio of 4.95:1.00.

7. The average fluorine chemical shift of  $\text{F}^{\text{b}}$  fluorines and the  $\text{TeF}^{\text{b}}$  coupling constant in mixed mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$ - $\text{Ph}_3\text{TeF}_2^+$  solutions is very close to the weighted averaged chemical shifts and coupling constants of mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  and  $\text{Ph}_3\text{TeF}_2^+$  (Table XV).

8. The average chemical shift and coupling constant in the  $^{125}\text{Te}$  NMR spectrum obtained on mixing  $\text{Ph}_3\text{TeF}_2^+$  and mer- $\text{Ph}_3\text{TeF}_3$  is, again, very close to the weighted average values.

9. The internal consistency of ratios of chemical shifts and coupling constants in both  $^{125}\text{Te}$  NMR and  $^{19}\text{F}$  NMR spectra of mixed mer- $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  and  $\text{Ph}_3\text{TeF}_2^+$

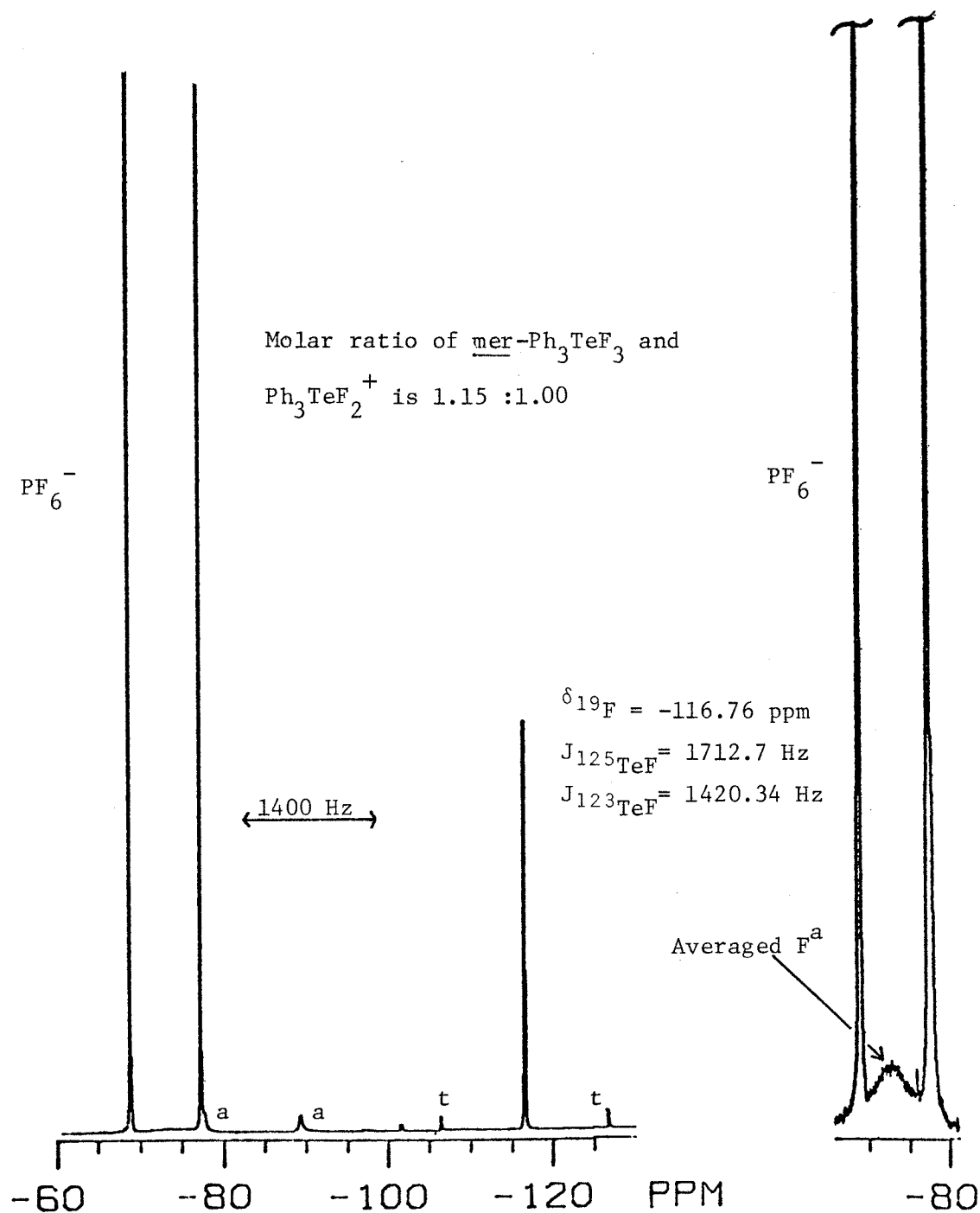


Figure 26.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3$ - $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$ .

The doublet resonance labelled as a is discussed in the text. t is the satellite caused by the  $^{125}\text{Te}$  isotope. The  $^{123}\text{Te}$  satellites have been observed in the amplified spectrum (not shown).



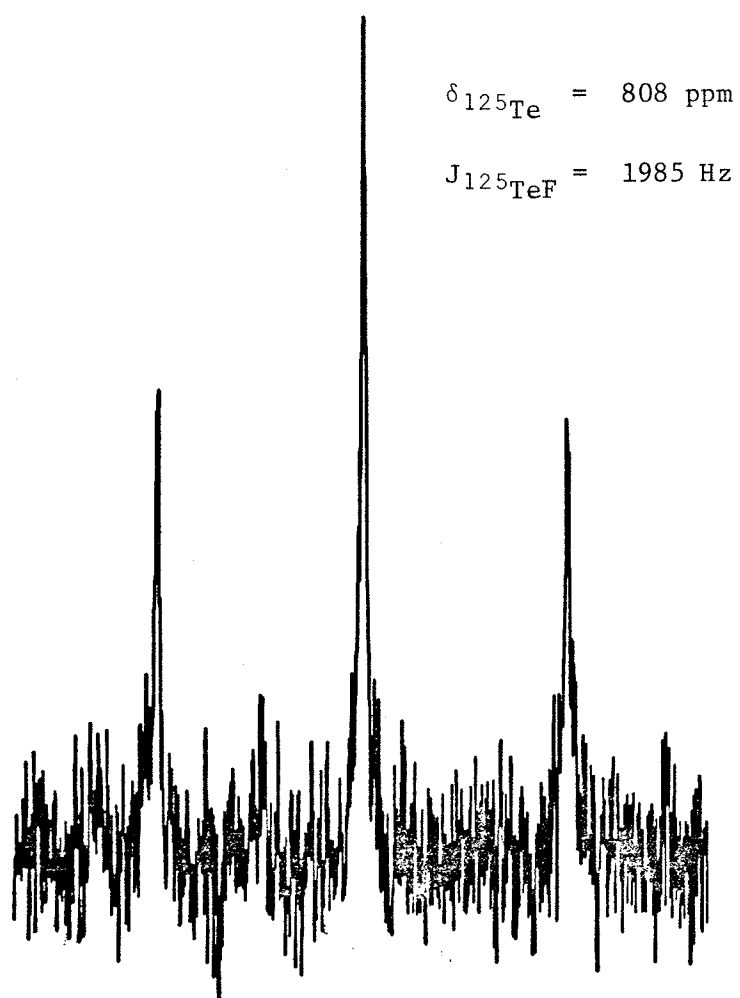


Figure 27.  $^{125}\text{Te}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+$ .

solutions is retained.

10. By lowering the temperature of the solution containing  $\text{Ph}_3\text{TeF}_2^+$  and  $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$  the averaged  $\text{F}^{\text{a}}$  resonance moves downfield and the averaged  $\text{F}^{\text{b}}$  fluorines move very slightly upfield. Spectra shown in Figures 28-32 clearly display these results. The temperature dependent spectra shown in Figures 28-32 are for a solution containing mer- $\text{Ph}_3\text{TeF}_3$  and  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  in a molar ratio of 2.59:1.00.

A trace of a new doublet (Figures 31 & 32) appears at  $-93^\circ\text{C}$  and also at  $-106^\circ\text{C}$ . From its chemical shift ( $-81.8$  ppm) and coupling constant (976 Hz) this doublet resonance is assigned to  $(\text{HO})_2\text{OPF}$  (137-139). This doublet resonance for  $(\text{HO})_2\text{OPF}$  is labelled as "f" in the spectra shown in Figures 31 and 32. Further, the original broad doublet for  $(\text{HO})\text{OPF}_2$  became sharp at  $-93^\circ\text{C}$ .

11. The exchange in the system  $\text{Ph}_3\text{TeF}_3$ - $\text{Ph}_3\text{TeF}_2^+$  could be completely halted in a few minutes by adding excess triethylbenzylammonium chloride (about 20 molar ratio excess on the basis of added  $\text{Ph}_3\text{TeF}_2^+$ ), when the products formed are mer- $\text{Ph}_3\text{TeF}_3$  and  $\text{Ph}_3\text{TeF}_2\text{Cl}$  as characterized by  $^{19}\text{F}$  NMR spectrometry.

These results clearly demonstrate that fluorine exchange in the  $\text{Ph}_3\text{TeF}_3$ - $\text{Ph}_3\text{TeF}_2^+$  system does not lead to intramolecular scrambling of  $\text{F}^{\text{a}}$  and  $\text{F}^{\text{b}}$  fluorines of  $\text{Ph}_3\text{TeF}^{\text{a}}\text{F}^{\text{b}}_2$ . It is only  $\text{F}^{\text{a}}$  which is involved in an intermolecular exchange process according to the mechanism

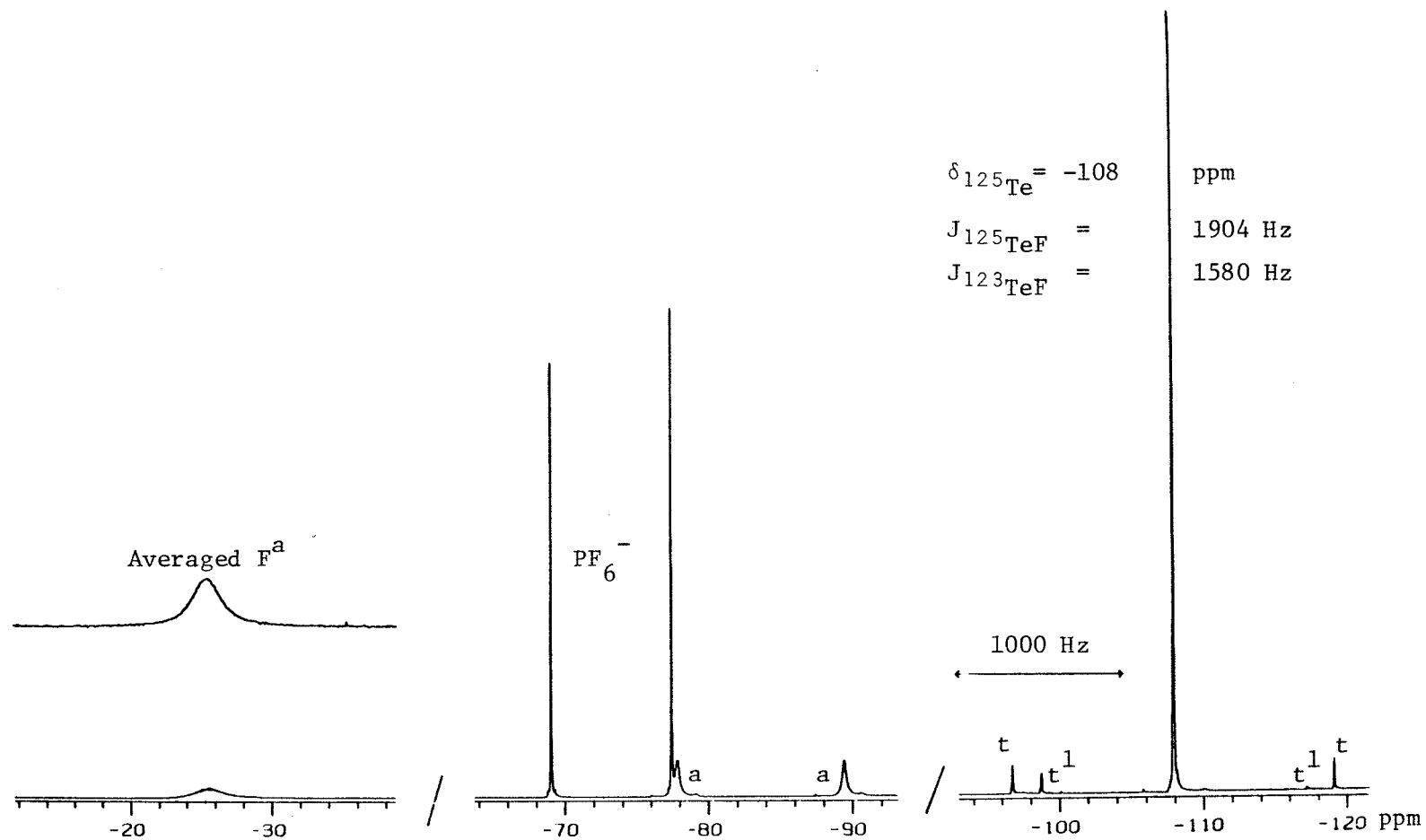


Figure 28.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$  at  $24^\circ\text{C}$ .

Peaks a, t and t<sup>1</sup> are discussed in the text.

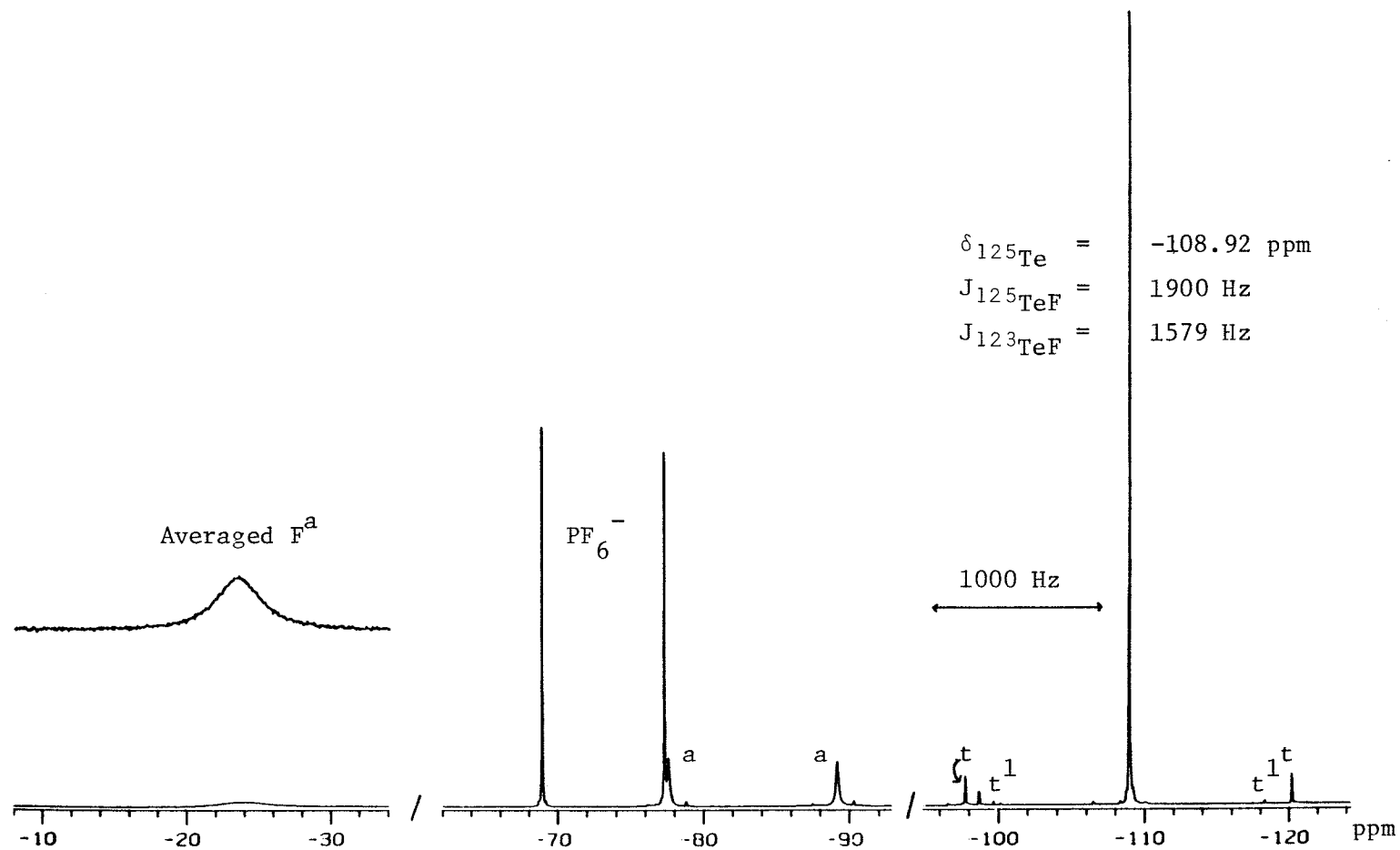


Figure 29.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$  at  $-13^\circ\text{C}$ .

Peaks a, t and  $t^1$  are discussed in the text.

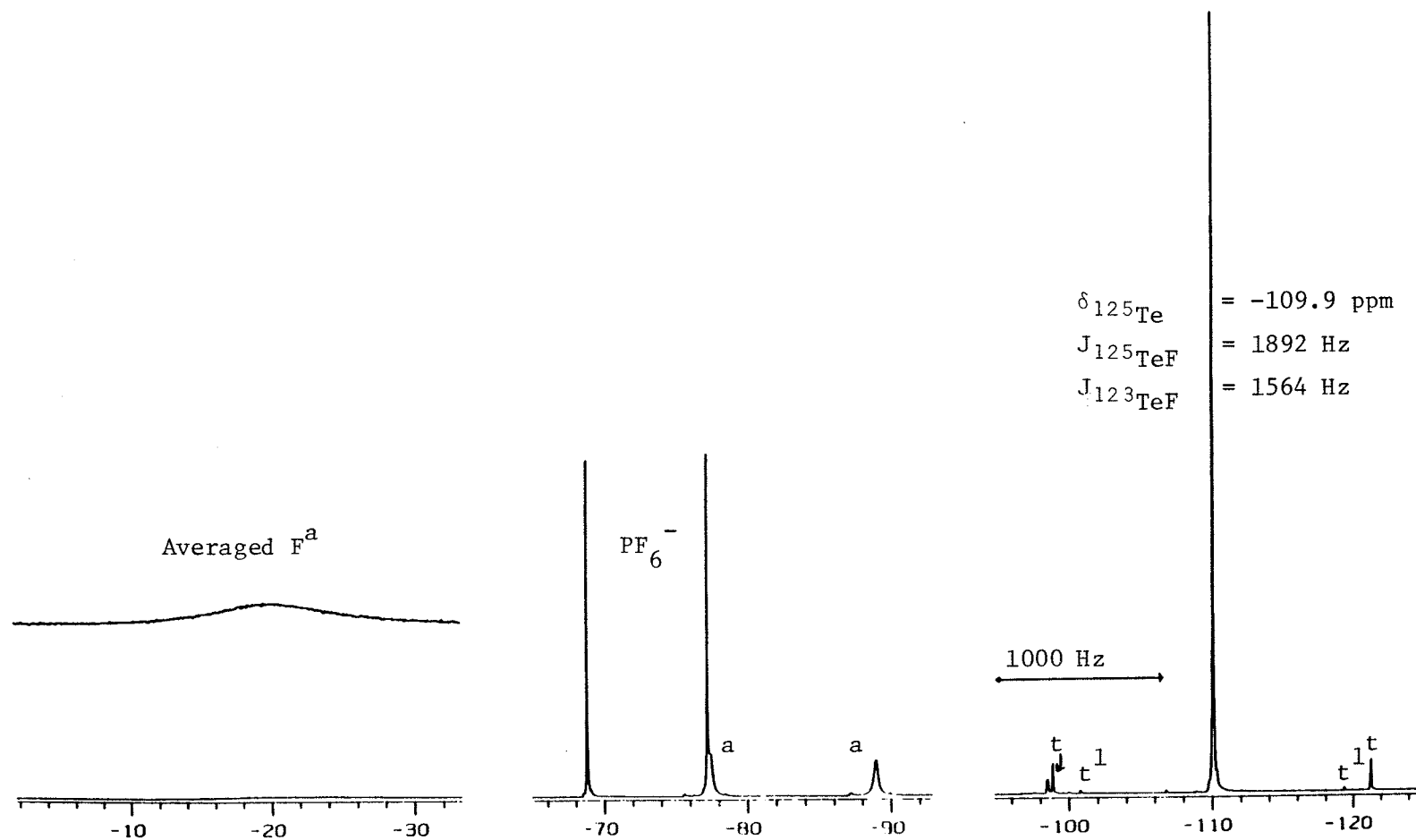


Figure 30.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$  at  $-53^\circ\text{C}$ .

Peaks a, t and  $t^1$  are discussed in the text.

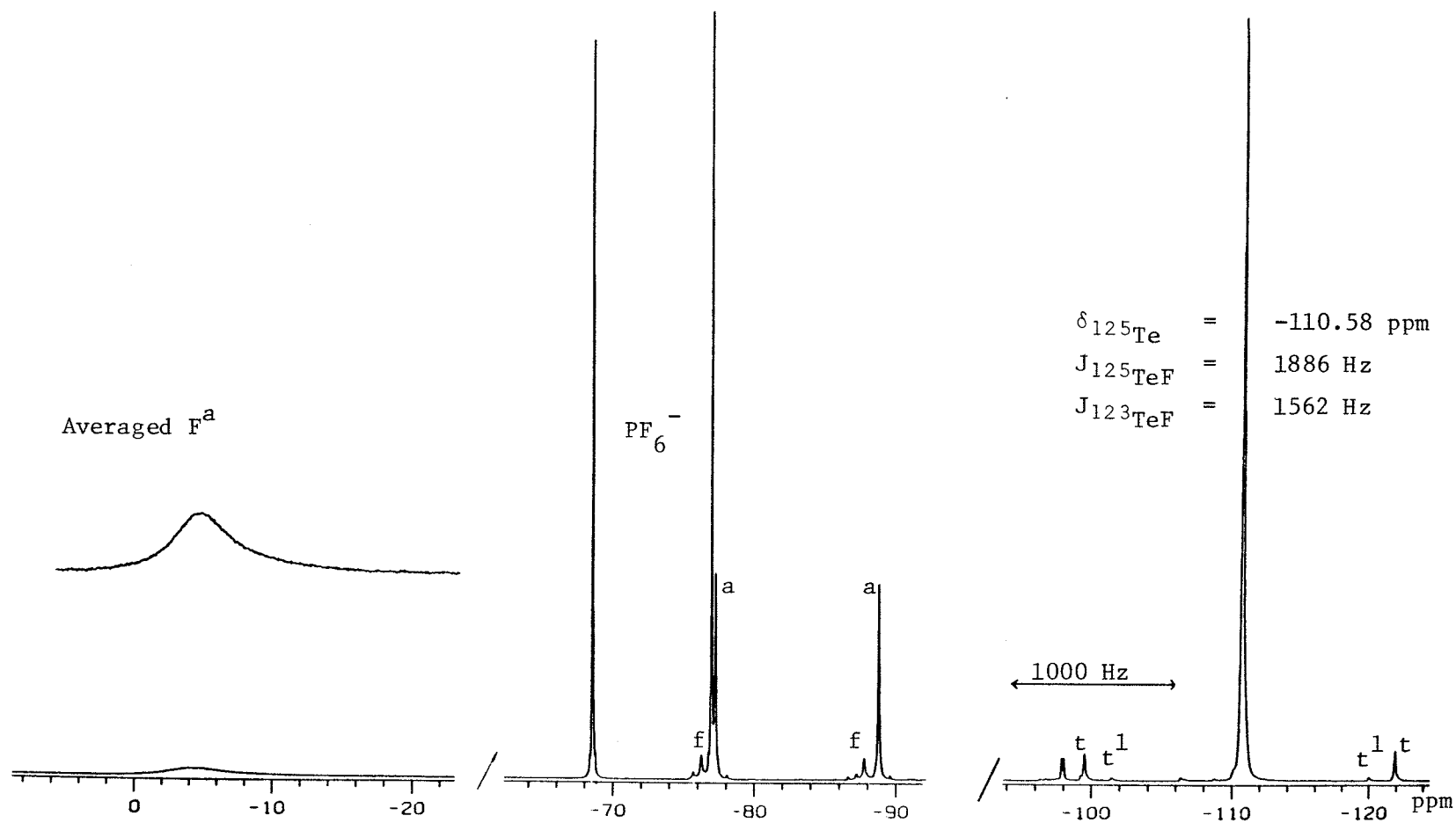


Figure 31.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$  at  $-93^\circ\text{C}$ .  
 $t$  and  $t^1$  are the satellite peaks of  $^{125}\text{Te}$  and  $^{123}\text{Te}$  isotopes respectively.  
 Peaks  $a$  and  $f$  are discussed in the text.

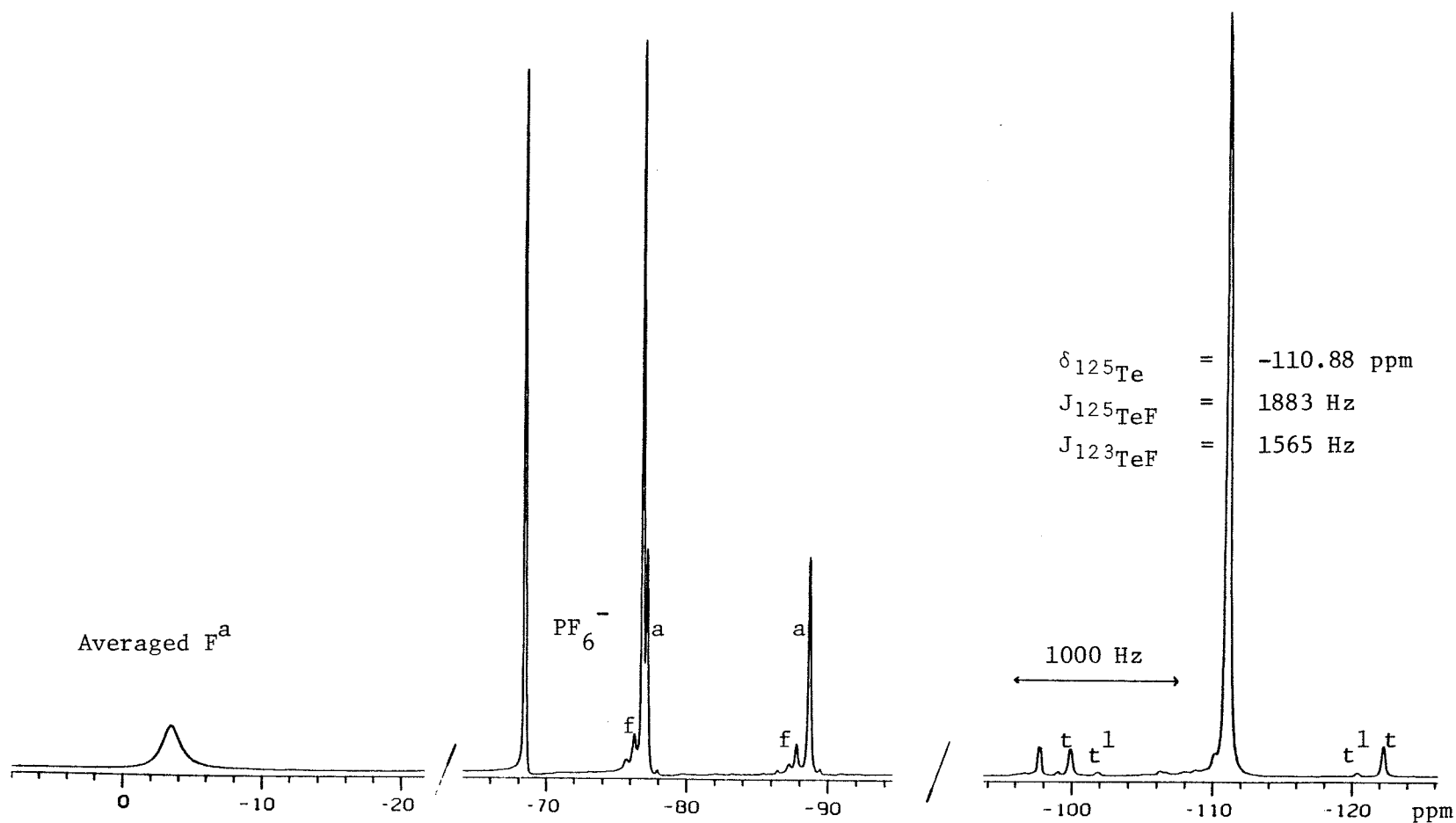


Figure 32.  $^{19}\text{F}$  NMR spectrum of the system  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+\text{PF}_6^-$  at  $-106^\circ\text{C}$ .

$t$  and  $t^1$  are the satellite peaks of  $^{125}\text{Te}$  and  $^{123}\text{Te}$  isotopes respectively.

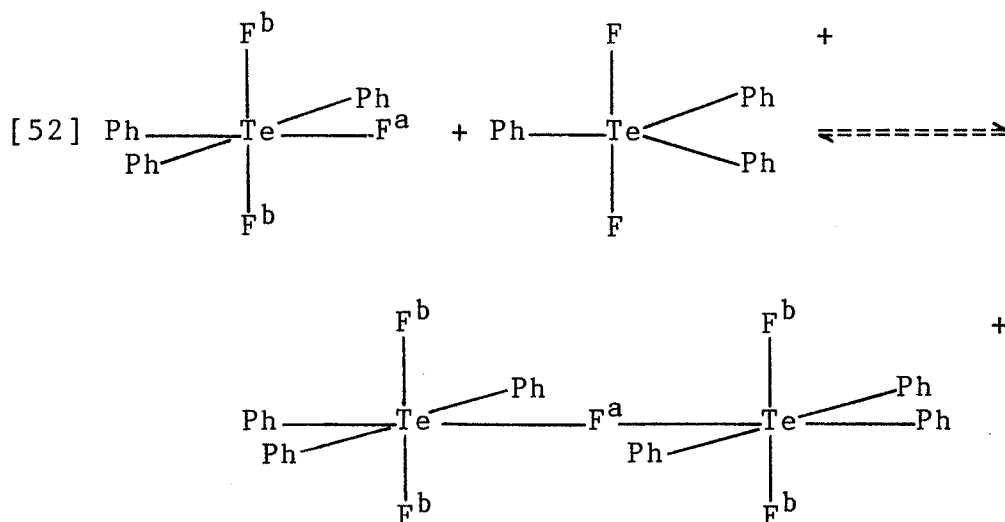
Peaks  $a$  and  $f$  are discussed in the text.

Table XV. Average chemical shift and coupling constant in  $\text{Ph}_3\text{TeF}_3\text{-Ph}_3\text{TeF}_2^+$  system obtained by adding mer- $\text{Ph}_3\text{TeF}_3$  ( $54 \times 10^{-4}$  mmole) to  $\text{Ph}_3\text{TeF}_2^+$  ( $37 \times 10^{-4}$  mmole) in a molar ratio of 1.45:1.00.

average $\delta_{\text{F}^b}$ ppm	average $J_{\text{F}^b\text{Te}}$ Hz	ratio of chemical shift (D-C)/(D-A)	ratio of coupling constant ( $D^1\text{-C}^1$ )/( $D^1\text{-A}^1$ )
-115.8	1739	1.4	1.4

Note: D and  $D^1$  are the chemical shift (-98 ppm) and Te-F coupling constant (2081 Hz) respectively for  $\text{F}^b$  fluorines in  $\text{Ph}_3\text{TeF}^{\text{aF}^b}_2$ . C and  $C^1$  are the chemical shift (-123 ppm) and Te-F coupling constant (1600 Hz) for fluorines in  $\text{Ph}_3\text{TeF}_2^+$ . A and  $A^1$  are the chemical shift and Te-F coupling constant observed upon mixing the components  $\text{Ph}_3\text{TeF}_2^+$  and  $\text{Ph}_3\text{TeF}^{\text{aF}^b}_2$ .

and intermediate shown in equation [52].





It has also been observed that by adding suitable reagents exchange can be initiated in either the cation or anion of  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$ . Adding mer- $\text{Ph}_3\text{TeF}_3$  introduces exchange in the tellurium-containing species, as described above, but does not involve  $\text{PF}_6^-$ , since the doublet of  $\text{PF}_6^-$  in the  $^{19}\text{F}$  NMR spectrum is not affected. Conversely, adding excess  $\text{PF}_5$  to  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  introduces rapid exchange among the phosphorus species, due to rapid exchange in the  $\text{PF}_5\text{-PF}_6^-$  system, but the  $\text{Ph}_3\text{TeF}_2^+$  species is unaffected (Figure 33). Rapid intermolecular fluorine exchange has been found to occur in the similar system  $\text{PhPF}_4\text{-PhPF}_5^-$  (117). The spectrum shown in Figure 33 also shows the fluorine resonances (labelled as "a") for  $\text{OPF}_3$ , which may be formed by hydrolysis of  $\text{PF}_5$  or also from the  $\text{PF}_5$  cylinder as an impurity.

It should also be noted here that the doublet resonance for  $(\text{HO})\text{OPF}_2$  became sharp at  $-93^\circ\text{C}$  and a trace of another new doublet at  $-81.8$  ppm ( $J = 976$  Hz) appears. This new doublet can be assigned to  $(\text{HO})_2\text{OPF}$  from the chemical shift and coupling constant. This result can reasonably be due to an exchange process, as shown previously in equation [51].

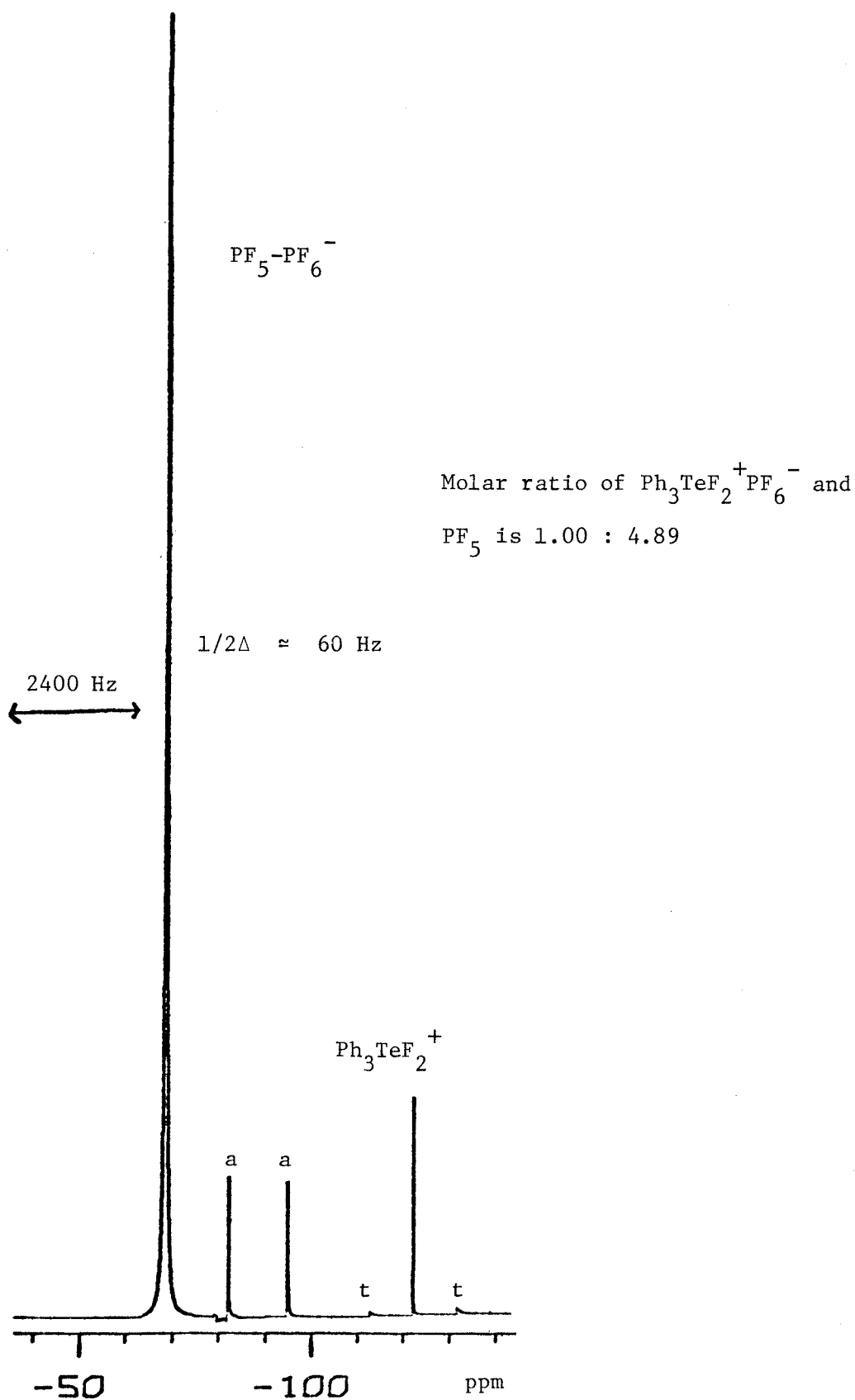


Figure 33.  $^{19}\text{F}$  NMR spectrum of  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  in presence of  $\text{PF}_5$ .

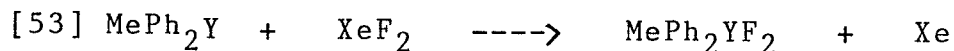
t is the satellite caused by  $^{125}\text{Te}$  and a is the resonance for  $\text{OPF}_3$ .

#### 4.5 Other related studies:

##### 4.5.1 Oxidative fluorinations by xenon difluoride and organoiodine(III) difluorides:

Mild non-destructive oxidative fluorination by xenon difluoride has been well discussed in the introduction to this thesis. Using xenon difluoride as an oxidative fluorinating agent, phenyltellurium(VI) fluorides containing one to four phenyl ligands have been prepared in the present work. Thus, extension of the use of xenon difluoride to oxidize P(III) and As(III) compounds with phenyl and alkyl substituents was of interest.

In this connection, it was found that the reaction of  $\text{XeF}_2$  with  $\text{MePh}_2\text{Y}$  ( $\text{Y} = \text{As}, \text{P}$ ) in acetonitrile solvent produced the known compounds  $\text{MePh}_2\text{YF}_2$  ( $\text{Y} = \text{As}, \text{P}$ ) in essentially quantitative yield. The products  $\text{MePh}_2\text{YF}_2$



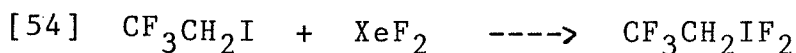
(As, P) were characterized by their known NMR spectra [ $\text{Y} = \text{As}$  (125),  $\text{Y} = \text{P}$  (126)] as well as by mass spectra and elemental analyses. The  $^1\text{H}$  NMR spectrum of  $\text{MePh}_2\text{AsF}_2$  in acetonitrile displays a triplet resonance for the Me group centered at 2.39 ppm with a separation of 8.6 Hz. This triplet splitting of the methyl resonance is due to

coupling with two equivalent fluorines. The  $^{19}\text{F}$  NMR spectrum (chloroform) of  $\text{MePh}_2\text{AsF}_2$  displays a quartet resonance (-78.8 ppm) due to coupling with three methyl protons.  $^1\text{H}$  NMR spectra of  $\text{MePh}_2\text{YF}_2$  ( $\text{Y} = \text{As}, \text{P}$ ) display two sets of multiplets in the region of 7.3 to 8.4 ppm in an intensity ratio of approximately 1.0:1.5. As discussed with phenyltellurium(VI) fluorides, the downfield multiplet set can be assigned to the ortho protons. Accordingly, the upfield more intense multiplet set can be assigned to meta and para protons. The resonance of the methyl protons in  $\text{MePh}_2\text{PF}_2$  in chloroform shows a doublet of triplets (2.35 ppm) due to coupling with phosphorus and two equivalent fluorines ( $J_{\text{HP}}=17.15$  Hz,  $J_{\text{HF}}=13$  Hz). Its  $^{19}\text{F}$  NMR spectrum in chloroform displays a doublet of quartets (-30.5 ppm) with  $J_{\text{FP}} = 630$  Hz. The multiplet resonance in its  $^{31}\text{P}$  NMR spectrum is centered at -41.1 ppm.

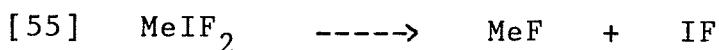
As xenon difluoride readily converts P(III) to P(V), As(III) to As(V) and Te(I,II and IV) to Te(VI) compounds it seemed reasonable that oxidation of organoiodine compounds might also be accomplished under mild conditions. In fact, it is possible to prepare  $\text{MeIF}_2$  by  $\text{XeF}_2$  oxidation (11). Powerful fluorinating agents such as  $\text{F}_2$ ,  $\text{BrF}_3$  and  $\text{ClF}_3$  which have been used to prepare perfluoroiodine(III and V) fluorides (1-4,141,142), would not be applicable to the synthesis of alkyl iodine fluorides owing to their destruction of alkyl groups.

Thus, oxidative fluorinations by xenon difluoride have been extended in the present work to oxidize  $\text{CF}_3\text{CH}_2\text{I}$  and 3,5-dichloro-iodobenzene.

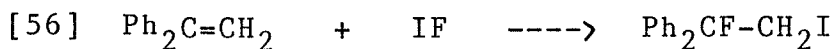
Accordingly, it was found that the reaction of  $\text{XeF}_2$  with  $\text{CF}_3\text{CH}_2\text{I}$  in acetonitrile or chloroform produced  $\text{CF}_3\text{CH}_2\text{IF}_2$  smoothly in 62% yield. The rate of oxidation of  $\text{CF}_3\text{CH}_2\text{I}$  has been found to be slower than of  $\text{MeI}$ , as



$\text{CF}_3\text{CH}_2\text{IF}_2$  is formed in 2 days whereas  $\text{MeI}$  is converted to  $\text{MeIF}_2$  in 20 minutes (11). The fluorine chemical shift of the  $\text{IF}_2$  group in  $\text{CF}_3\text{CH}_2\text{IF}_2$  is close to that of  $\text{MeIF}_2$  (11). The compound  $\text{CF}_3\text{CH}_2\text{IF}_2$  is more stable than  $\text{MeIF}_2$ , as 60% remains after 5 days in the Teflon container. It decomposes in presence of moisture and in contact with glass to a yellowish solid which was not characterized. Usually, organoiodine(III) fluorides decompose with time. Although the exact decomposition mechanism is not known yet, decomposition invariably fluorinates the attached organic group with the breaking of the iodine-carbon bond. For example, it has been found in the present work that  $\text{MeIF}_2$  decomposes to  $\text{MeF}$  and  $\text{IF}$  according to equation [55], as observed by NMR studies of systems in a sealed tube.



The decomposition product MeF has been characterized by its known  $^1\text{H}$  NMR (143) and  $^{19}\text{F}$  NMR (144) spectra as well as by the mass spectra of the evolved gas. The other decomposition product IF has been trapped by 1,1-diphenylethene and methylene cyclohexane. Thus, adding excess methylene cyclohexane to a freshly prepared solution of  $\text{MeIF}_2$  in acetonitrile and allowing time for decomposition (approximately 1 h for a solution of about 0.31 mmole at room temperature in a Teflon container), it was found that 1-iodomethyl-cyclohexyl fluoride was produced, as characterized by its known  $^{19}\text{F}$  NMR spectrum (145). The  $^{19}\text{F}$  NMR spectrum of this decomposed solution did not show any other fluorine signal. Similarly, 1,1-diphenylethene was found to produce  $\text{Ph}_2\text{CF-CH}_2\text{I}$  due to addition of IF according to equation [56], as characterized by mass, known  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra (146). It may tentatively be speculated that, like other organoiodine(III) difluorides (1-4),  $\text{CF}_3\text{CH}_2\text{IF}_2$  may decompose to  $\text{CF}_3\text{CH}_2\text{F}$  and IF in an inert atmosphere.



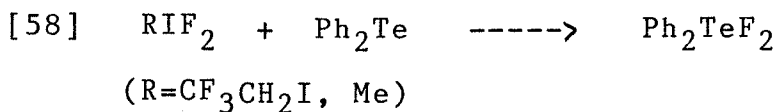
Similarly, 3,5-dichlorophenyliodine(III) difluoride is formed in 2 days from the oxidative reaction of  $\text{XeF}_2$  with 3,5-dichloro-iodobenzene. The fluorine



chemical shift of 3,5-dichlorophenyliodine(III) difluoride is close to that of  $\text{MeIF}_2$ . The compound decomposed slowly, 25% remains after about 20 h, to a pale yellowish solid which was not characterized.  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_2$  was found to be further oxidized very slowly by  $\text{XeF}_2$ ; only 50% was converted to  $\text{Cl}_2\text{C}_6\text{H}_3\text{IF}_4$  in about 10 days. The tetrafluoride was identified only by its fluorine chemical shift (-16.3 ppm). Fluorine chemical shifts of organoiodine(V) fluorides are close to this region (3).

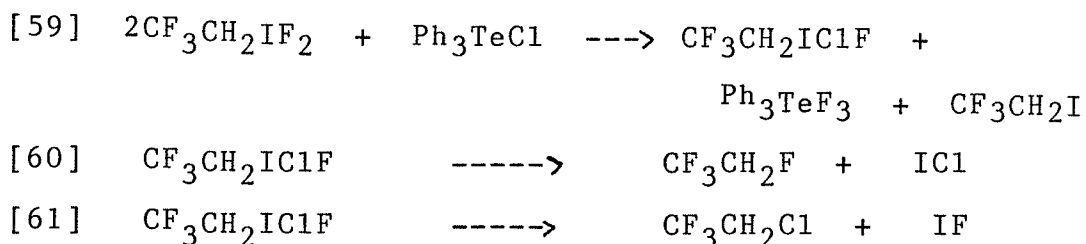
The use of organoiodine(III) difluorides in organic fluorinations is still very limited (147,148), possibly because of the difficulty in their preparation and storage. It is the synthesis of  $\text{MeIF}_2$  from the reaction of  $\text{XeF}_2$  and  $\text{MeI}$  which makes this potential fluorinating agent readily available (11). No oxidative fluorination by organoiodine(III) difluorides has yet been reported. It was thus of interest to this thesis to investigate the possibility of oxidative fluorination by organoiodine(III) difluorides.

Accordingly, reactions of  $\text{CF}_3\text{CH}_2\text{IF}_2$  and  $\text{MeIF}_2$  with  $\text{Ph}_2\text{Te}$  in an organic solvent were found to produce  $\text{Ph}_2\text{TeF}_2$  in a high yield. As for  $\text{XeF}_2$  oxidation, the other product



in reaction [58] may be expected to be  $\text{RI}$ . In these

experiments some MeI and  $\text{CF}_3\text{CH}_2\text{I}$  were present in the starting fluorinating agents. These were retained to prevent the faster decomposition of the starting compounds. Thus, the formation of RI in equation [58] was not characterized by NMR peak integration. Further oxidation of  $\text{Ph}_2\text{TeF}_2$  by  $\text{MeIF}_2$  was not found to occur in about 8 h at room temperature.  $\text{CF}_3\text{CH}_2\text{IF}_2$  was found to convert  $\text{Ph}_3\text{TeCl}$  to mer- $\text{Ph}_3\text{TeF}_3$  at a much faster rate than did  $\text{XeF}_2$ .  $^{19}\text{F}$  NMR examination of the reaction mixture of  $\text{CF}_3\text{CH}_2\text{IF}_2$  and  $\text{Ph}_3\text{TeCl}$  also shows the formation of traces of  $\text{CF}_3\text{CH}_2\text{Cl}$  and  $\text{CF}_3\text{CH}_2\text{F}$ , as characterized by their known  $^{19}\text{F}$  NMR spectra (127). The mechanism of formation of  $\text{CF}_3\text{CH}_2\text{Cl}$  and  $\text{CF}_3\text{CH}_2\text{F}$  in this reaction has not been studied. One possible way of formation of these halogenated organic compounds may be according to the following reactions:



It is thus clear that organoiodine(III) difluorides are potential oxidative fluorinating agents and may find valuable use in conditions where  $\text{XeF}_2$  can not be used. In any future extension of this work, it would be

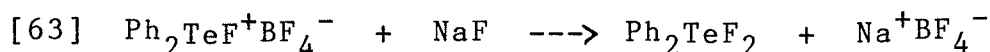
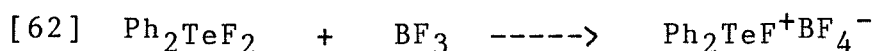


very valuable to investigate the mechanism of formation of the halogenated compounds in the above reactions.

#### 4.5.2 Formation of $\text{Ph}_2\text{TeF}^+$ and $\text{MePh}_2\text{YF}^+$ ( $\text{Y} = \text{AS}, \text{P}$ ):

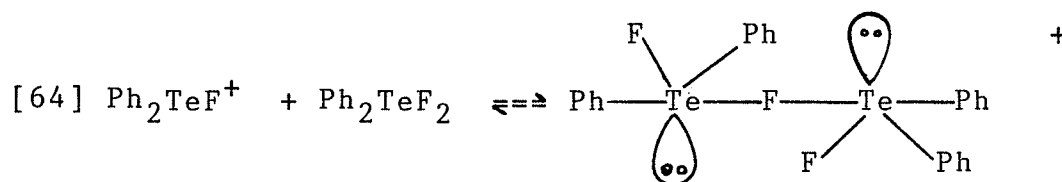
It has been discussed in the introduction to this thesis that fluoro cations of main group fluorides are generally formed in fluoride donor-acceptor reactions. A novel fluoro cation  $\text{Ph}_3\text{TeF}_2^+$  has been prepared in the present work from such a donor-acceptor reaction. A further interest of this thesis was to explore the possibility of formation of fluoro cations of main group compounds with organic substituents and with systems other than tellurium(VI) derivatives.

Accordingly, it was found that the reaction of  $\text{BF}_3$  with  $\text{Ph}_2\text{TeF}_2$  formed  $\text{Ph}_2\text{TeF}^+$  in chloroform / methylene chloride solvent. The compound was characterized by its



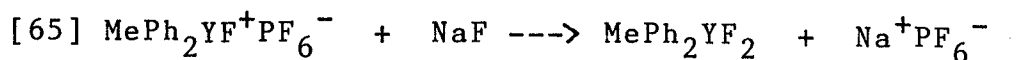
chemical reaction with NaF, when  $\text{Ph}_2\text{TeF}_2$  was formed. The insolubility of the compound resulting from the reaction of  $\text{Ph}_2\text{TeF}_2$  and  $\text{BF}_3$  in methylene chloride, in which the starting compound  $\text{Ph}_2\text{TeF}_2$  is highly soluble, and high solubility in polar acetonitrile supports the above ionic

formulation of the compound. The fluorine resonance for  $\text{Ph}_2\text{TeF}^+$  could not be observed. The presumed disappearance of fluorine signal for the cationic fluoride may be attributed to an intermolecular fluorine exchange of the type shown in equation [64].



The appearance of a broad peak at  $-173$  ppm in the  $^{19}\text{F}$  NMR spectrum of the reaction product, and only in one instance, may be indicative of the fact that the presumed exchange process shown in equation [64] is dependent on the concentration of the components. In any future extension of this work low temperature  $^{19}\text{F}$  NMR spectrum studies would be of great help to elucidate the nature of the resulting compound and to understand its fluorine exchange process.

Similarly, reactions of  $\text{PF}_5$  with  $\text{MePh}_2\text{YF}_2$  ( $\text{Y} = \text{As}, \text{P}$ ) in acetonitrile produced the cationic fluorides  $\text{MePh}_2\text{YF}^+$  ( $\text{As}, \text{P}$ ), as characterized by the reaction of the resulting compound with  $\text{NaF}$  in acetonitrile. The fluorine resonances



for the cations  $\text{MePh}_2\text{YF}^+$  ( $\text{Y} = \text{As}, \text{P}$ ) could not be observed perhaps because of an intermolecular fluorine exchange process of the type discussed above. In one instance, the reaction mixture of  $\text{PF}_5$  and  $\text{MePh}_2\text{PF}_2$  was kept in a sealed tube for about one month with the idea of allowing any generated HF, which is generally formed by reaction of highly reactive fluoride compounds with moisture, to react with the glass wall or with any trace of  $\text{MePh}_2\text{PF}_2$ . The  $^{19}\text{F}$  NMR spectrum of this solution displays a doublet of quartets resonance, as recorded in the experimental section, centered at -131.8 ppm. The quartet splitting of each resonance indicates the presence of Me group in this species. However, the presence of phenyl or other substituents can not be derived from the NMR data. This doublet resonance can tentatively be assigned to  $\text{MePh}_2\text{PF}^+$ . One possible way to explain the appearance of the fluorine resonance for this cation after a long time is that all generated HF reacted with the  $\text{MePh}_2\text{PF}_2$  to form  $\text{MePh}_2\text{PF}^+$  and with the glass wall of the NMR tube. A resonance at -149 ppm has been observed in the fluorine spectrum of this solution. As  $\text{FHF}^-$ ,  $\text{BF}_4^-$  and also HF resonate in this area this peak at -149 ppm could not be assigned to a definite counter anion formed by a reaction with HF. In the absence of traces of HF or five-coordinate  $\text{MePh}_2\text{PF}_2$ , direct or impurity catalyzed intermolecular fluorine

exchange in  $\text{MePh}_2\text{PF}^+$  is not expected to occur. The intensity of the fluorine resonance for the corresponding anion  $\text{PF}_6^-$  was found to be double that required for the presumed cationic fluoride (doublet resonance at  $-131.8$  ppm). Any other counter cation for this extra anion could not be identified by the NMR spectroscopic technique. With the available experimental data further speculation about these compounds is useless and in any future extension of this work elemental analysis and conductivity studies may be of great help.

#### 4.5.3 NMR study of catalyzed intermolecular fluorine exchange in $\text{MePh}_2\text{AsF}_2$ :

As discussed in the previous section, the fluorine resonances of  $\text{MePh}_2\text{YF}^+$  could not be observed perhaps because of intermolecular fluorine exchange processes. Usually intermolecular fluorine exchange can be initiated by mixing species with different coordination numbers or by adding a catalyst. Selective intermolecular fluorine exchange in  $\text{mer-Ph}_3\text{TeF}_3$  has been found to be rapid on adding  $\text{Ph}_3\text{TeF}_2^+$  and the mechanism of the exchange process has been investigated by means of NMR in this work. It was of interest to extend the NMR investigation to catalyzed intermolecular fluorine exchange in  $\text{MePh}_2\text{AsF}_2$ .

In this connection, catalyzed intermolecular fluorine exchange in  $\text{MePh}_2\text{AsF}_2$  was found to be rapid on

adding anhydrous HF. Hydrogen fluoride was added as a solution in acetonitrile through a syringe. Several experiments were made at different concentrations of the reactants. Some  $^1\text{H}$  NMR spectra of the methyl proton resonance of  $\text{MePh}_2\text{AsF}_2$  with different amounts of HF (at ambient temperature) are presented in Figure 34. Temperature dependent  $^1\text{H}$  NMR spectra of the exchange system  $\text{MePh}_2\text{AsF}_2\text{-HF}$  were also recorded. Typical temperature dependent  $^1\text{H}$  NMR spectra showing mainly the region of the methyl resonance are given in Figure 35. The spectra shown in Figure 35 are for a solution containing 0.11 mmole of  $\text{MePh}_2\text{AsF}_2$  and  $0.3 \times 10^{-4}$  mmole of HF in a solution of 0.50 mL of acetonitrile.

On adding known amounts of HF to  $\text{MePh}_2\text{AsF}_2$  and recording the  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra, the following observations are made.

(i). The fine structure of methyl resonance in  $^1\text{H}$  NMR spectrum of  $\text{MePh}_2\text{AsF}_2$  is lost and eventually became a broad single peak ( $1/2\Delta \approx 12$  Hz) as HF is added (figure 34).

(ii). The chemical shift of the broad methyl resonance is shifted slightly downfield as HF is added to  $\text{MePh}_2\text{AsF}_2$ . Some proton spectra of  $\text{MePh}_2\text{AsF}_2$  with different amounts of HF are shown in Figure 34.

(iii). The resonance of fluorine in  $\text{MePh}_2\text{AsF}_2$  is lost as HF is added.

(iv). On lowering the temperature of the system

$\text{MePh}_2\text{AsF}_2\text{-HF}$ , the methyl protons with triplet splitting due to coupling with two equivalent fluorines reappear at  $-33^\circ\text{C}$  (Figure 35). The spectra were reproduced at each temperature by warming the solution.

(v). An impurity peak labelled as "a" in Figures 34 and 35 appears in the proton spectrum as HF is added to  $\text{MePh}_2\text{AsF}_2$ . This peak, however, did not change very much with temperature or added HF with respect to chemical shift or intensity.

(vi). Another broad impurity (?) peak appears on letting the solution containing  $\text{MePh}_2\text{AsF}_2$  and HF stand for about 2 h. This peak is labelled as "b" in the spectra shown in Figure 35. This peak (b) became sharper and shifted towards lowfield at  $-33^\circ\text{C}$ . This peak was also not identified.

As the impurity peaks described above were not characterized and they overlapped considerably with the line shape of broad methyl protons resonance, quantitative analysis of the exchange process was not undertaken. Only a tentative explanation of the experimental results may be made. In the first place, HF may abstract a fluorine from  $\text{MePh}_2\text{PF}_2$  to form  $\text{MePh}_2\text{PF}^+$ . However, the corresponding counter anion was not confirmed. The tentative mechanism of rapid intermolecular fluorine exchange in  $\text{MePh}_2\text{AsF}_2$  is then as shown in equation [66] with a fluorine bridged intermediate:

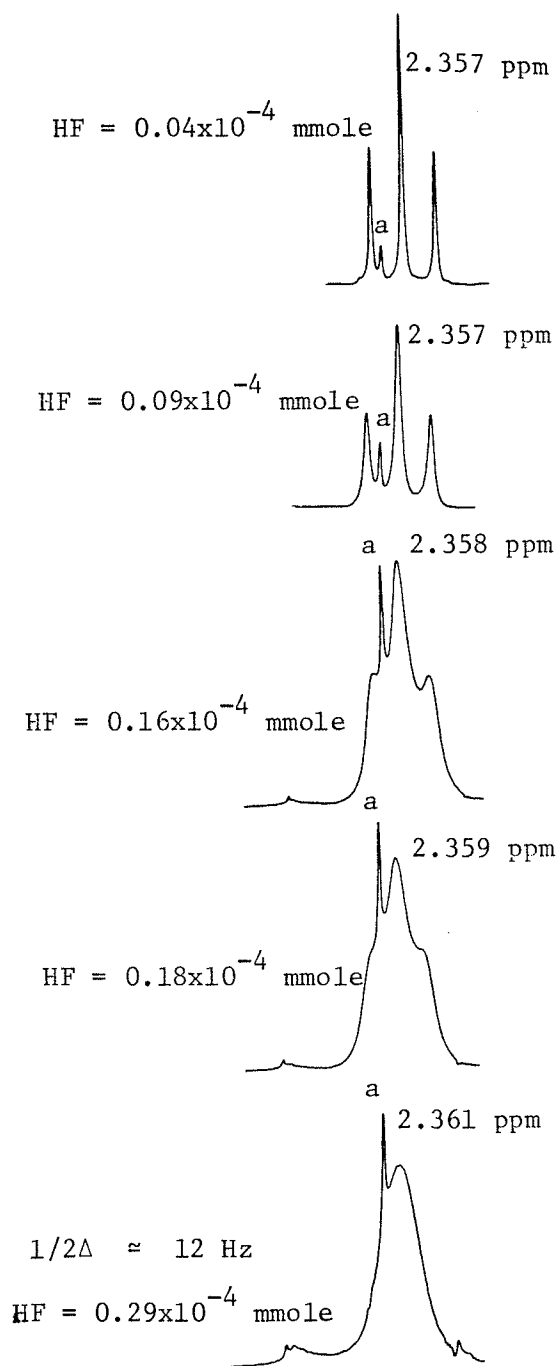


Figure 34.  $^1\text{H}$  NMR spectra of the methyl region of  $\text{MePh}_2\text{AsF}_2$  (0.12 mmole) in presence of different amounts of anhydrous hydrogen fluoride. Peak a is discussed in the text.

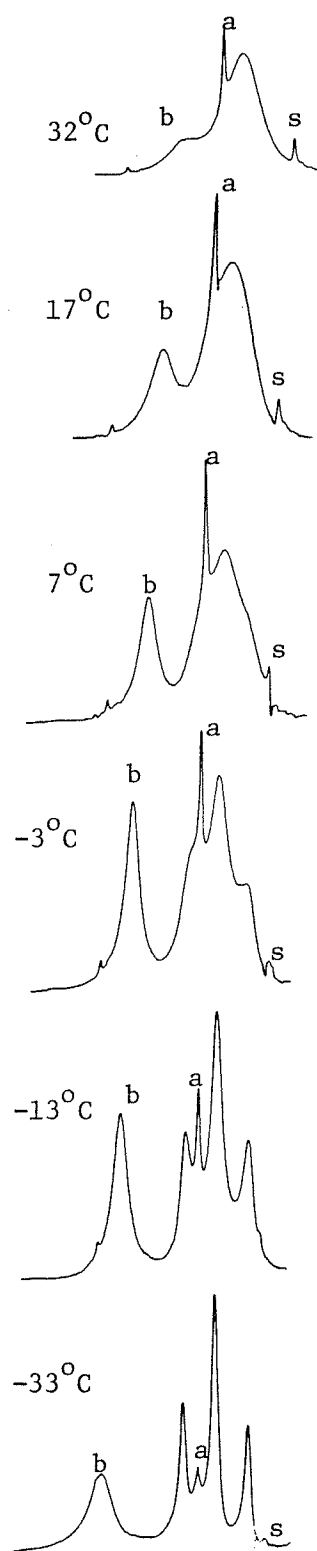
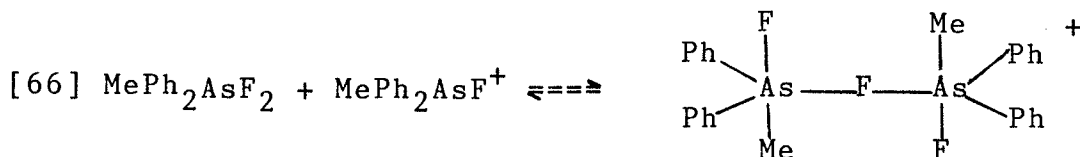


Figure 35. Temperature dependent  $^1\text{H}$  NMR spectrum of the methyl region of the system  $\text{MePh}_2\text{AsF}_2\text{-HF}$ . Peaks a and b are discussed in the text. s is the satellite caused by  $^{13}\text{C}$  isotope from solvent acetonitrile.





Faster exchange and shifting of the broad resonance of the methyl region to higher field with a higher concentration of HF (Figure 34) supports the formation of the intermediate shown in equation [66].

The addition of tetrabutylammonium fluoride to  $\text{MePh}_2\text{AsF}_2$  did not cause fluorine exchange. As fluoride is a good coordinating ligand, this result suggests that coordination to  $\text{MePh}_2\text{AsF}_2$  by any impurity catalyst in the exchange system  $\text{MePh}_2\text{AsF}_2\text{-HF}$  has not occurred. Thus, rapid fluorine exchange between a six-coordinate species and five-coordinate  $\text{MePh}_2\text{AsF}_2$  in the exchange system  $\text{MePh}_2\text{AsF}_2\text{-HF}$  can be safely eliminated. In any future extension of this work line shape analysis of the methyl proton resonance after the characterization of the mentioned impurities would be of help to obtain the activation parameters and confirmation of the proposed mechanism.

## 5. CONCLUSIONS

As proposed for this project (chapter 2), reactions of a series of phenyltellurium compounds, Te(I,II and IV), with  $\text{XeF}_2$  have been investigated and a variety of phenyltellurium(VI) fluorides (Table V) containing one to four phenyl ligands have been prepared. These results clearly demonstrate that phenyl ligands stabilize Te(VI) fluoride derivatives.

The rate of oxidation of Te(I), Te(II) and Te(IV) compounds by  $\text{XeF}_2$  is seen to be dependent upon the type of starting phenyltellurium compound. Thus,  $\text{PhTeF}_5$  is obtained from  $\text{Ph}_2\text{Te}_2$  in a few hours whereas oxidation of  $\text{Ph}_2\text{TeF}_2$  to trans- $\text{Ph}_2\text{TeF}_4$  with a large excess of  $\text{XeF}_2$  takes 2 days. Only one isomeric form is the major product in all the reactions investigated in this project.

$^{125}\text{Te}$  NMR data of the product phenyltellurium(VI) fluorides are obtained.  $^{19}\text{F}$  NMR and  $^{125}\text{Te}$  NMR spectra have clearly established the geometry of  $\text{PhTeF}_5$ , trans- $\text{Ph}_2\text{TeF}_4$ ,  $\text{Ph}_3\text{TeF}_2\text{Cl}$  and mer- $\text{Ph}_3\text{TeF}_3$ . A structure assignment of  $\text{Ph}_4\text{TeF}_2$  will probably have to wait for X-ray studies. Empirical correlations of fluorine-fluorine coupling constants and fluorine chemical shifts in the phenyltellurium(VI) fluorides clearly characterized the trace amount of cis- $\text{Ph}_2\text{TeF}_4$  formed in the reaction of  $\text{XeF}_2$  and  $\text{Ph}_2\text{TeF}_2$ , which otherwise was not identified.

The reaction of mer- $\text{Ph}_3\text{TeF}_3$  with  $\text{PF}_5$  has been reproduced several times under identical reaction conditions and each time the novel ionic compound  $\text{Ph}_3\text{TeF}_2^+\text{PF}_6^-$  was obtained. The compound was characterized by chemical reactions and NMR spectra.

Fluorine exchange in the system  $\text{Ph}_3\text{TeF}_3$ - $\text{Ph}_3\text{TeF}_2^+$  has been investigated by means of NMR and the mechanism of the exchange process has been unequivocally established. Thus, in this exchange system it is only the  $\text{F}^a$  fluorine of  $\text{Ph}_3\text{TeF}^a\text{F}^b_2$  which is involved in the exchange process and occupies the bridging position in the intermediate.

Substituted phenyltellurium(VI) fluorides are formed in the reactions of  $\text{PhTeF}_5$ , trans- $\text{Ph}_2\text{TeF}_4$  and mer- $\text{Ph}_3\text{TeF}_3$  with  $\text{MeOH}$ ,  $\text{Me}_2\text{NH}$ ,  $\text{H}_2\text{O}$ , and  $\text{X-SiMe}_3$  ( $\text{X} = \text{MeO}$ ,  $\text{Me}_2\text{N}$ ,  $\text{Et}_2\text{N}$ ). The rate at which a nucleophile reacts with a given type of phenyltellurium(VI) fluoride is found to decrease as the number of phenyl ligands in the starting tellurium(VI) compound increase. Since these reactions result in the replacement of fluorine, the rate differences could be a reflection of different Te-F bond lengths.

The structures of the substituted products  $\text{PhTeF}_4\text{X}$  ( $\text{X} = \text{HO}$ ,  $\text{MeO}$ ,  $\text{Me}_2\text{N}$ ,  $\text{Et}_2\text{N}$ ) are unambiguously established from their  $^{19}\text{F}$  NMR spectra and possible assignments of fluorine resonances in the observed  $\text{abc}_2$  spin systems are made on the basis of calculated chemical shifts. The structures of  $\text{Ph}_3\text{TeF}_2\text{X}$  ( $\text{X} = \text{MeO}$ ,  $\text{Me}_2\text{N}$ ,  $\text{Et}_2\text{N}$ ) are also

established from the observed ab spin system in  $^{19}\text{F}$  NMR spectra. The structures of  $\text{Ph}_2\text{TeF}_3\text{X}$  ( $\text{X} = \text{MeO}, \text{Me}_2\text{N}, \text{Et}_2\text{N}$ ) could not be determined from the available NMR data and clearly X-ray diffraction studies are required to determine these structures.

In summary, considerable effort has been made to follow the oxidative fluorinations of phenyltellurium compounds with xenon difluoride and reactions of the resulting phenyltellurium(VI) fluorides with various nucleophiles and the fluoride acceptor  $\text{PF}_5$ . Structures have been determined by NMR studies for many products obtained in the above reactions, but it is clear that some products obtained in this work require crystallographic studies to determine their structures. No attempt has been made in this thesis to use stronger fluoride acceptors like  $\text{AsF}_5$  and  $\text{SbF}_5$  to prepare ionic compounds and it may very well be that quite stable fluoro cations of phenyltellurium(VI) fluorides would be prepared if the fluoride acceptor was changed and if alternative phenyltellurium(VI) fluorides were used as the fluoride donors.

It is clear then that reactions of phenyltellurium compounds with xenon difluoride and reactions of phenyltellurium(VI) fluorides with various nucleophiles and fluoride acceptor constitute an area of study which is rich in potential for the formation of novel compounds and a variety of structural types. Extension of the work

described in this thesis would contribute greatly to the present very incomplete understanding of reactions and mechanisms of organotellurium(VI) fluorides.

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