STEREOSELECTIVITY IN OCTAHEDRAL PHENYLTELLURIUM(VI) FLUORIDES

BY

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ABSTRACT

The study of the mechanisms of oxidative addition and isomerization reactions in phenyltellurium fluorides is described.

The oxidative fluorination of Ph_2TeX_2 (X = F, Cl) with xenon difluoride leads to the formation of *cis*-Ph_2TeX_4 (phenyl substituents occupy *cis*-position) via a five-coordinate intermediate anion $Ph_2TeX_3^-$, but subsequent isomerization occurs to give the thermodynamically more stable *trans*-Ph_2TeX_4 via a five-coordinate cation $Ph_2TeX_3^+$. In the process of the oxidative fluorination, the first step may involve the formation of $Ph_2TeX_3^-$ by the addition of "F^-" to Ph_2TeX_2. The intermediate $Ph_2TeX_3^-$ has lone pairs of electrons available for the subsequent addition of "F^+" to stabilize the *cis*-configuration. An important feature that arises from this work is the stereoselectivity in oxidative addition and isomerization reactions in which the five-coordinate Te(IV) anion leads to the *cis*-formation while the five-coordinate Te(VI) cation leads to the *trans*-formation.

The oxidative fluorination of Ph_3TeCl with XeF_2 produces *cis*-F_2TePh_3Cl only and this result is consistent with the mechanism proposed: i.e. the initial formation of a five-coordinate anion Ph_3TeFCl^- by the addition of "F^-" to Ph_3TeCl, followed by the addition of "F^+" *trans* to phenyl, produces *cis*-F_2TePh_3Cl. Indeed the formation of the *trans*-isomer, *trans*-F_2TePh_3Cl, has never been observed during the oxidation. Thus stereoselective synthesis of *cis*- and *trans*-F_2TePh_3Cl (phenyl substituents adopt a *mer*-arrangement) was accomplished via five-coordinate cations Ph_3TeFCl^+ and $Ph_3TeF_2^+$. *trans*-F_2TePh_3Cl was found to isomerize to the thermodynamically more stable *cis*-isomer via the five-coordinate cation $Ph_3TeF_2^+$ and thus an intermolecular mechanism is proposed for the isomerization reaction.

The study of the stereoselective fluorine exchange in six-coordinate *mer*-Ph_3TeF_2X (X = F, Cl, or OH) is entirely consistent with the intermolecular mechanism and the results are described.

The preparations and NMR studies of neutral and anionic phenyltin(IV) fluorides, which are isoelectronic with four-, five-, and six-coordinate phenyltellurium fluorides, are presented.

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Meehae Jang

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LIST OF ABBREVIATIONS

ax	axial
bpy	2,2'-bipyridine
DMF	dimethyl formamide
DMSO-d_6	$(CD_3)_2SO$, deuteriated dimethylsulfoxide
eq	equatorial
fac-	facial
fbpy	4-fluoro-2-2'-bipyridine
HMPA	hexamethylphosphoramide
L	unidentate ligand
mer-	meridional
NOE	nuclear Overhauser enhancement
SP	square pyramid
TBP	trigonal bipyramid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane
TPPO	triphenylphosphorous oxide

The ultimate combiner

Fervid Fluorine, though just nine,
Knows her aim in life: combine !
In fact, of things that like to mingle,
None's less likely to stay single.

'Mistress Fluorine'

CHAPTER I

INTRODUCTION

I. INTRODUCTORY REMARKS

The chemistry of octahedral main group molecules - their preparation, characterization, and physical studies - has been rapidly developed in the past few years. In some respects the field has been largely dominated by the preparative chemistry. Consequently a wide range of compounds has been synthesized, but their reaction mechanisms are not well understood.

Most studies have been done on octahedral mono- and di-organo substituted sulfur(VI) compounds (1-4). Relatively little information is available for organo-tellurium(VI) and even less for organo-selenium(VI) compounds (5), however, extensive work has been done on selenium(VI) and tellurium(VI) hexafluorides and their derivatives, and reviews are available in the literature (6,7).

Since the first organotellurium(VI) fluorides were prepared by Passmore and his co-workers (8), several other multi-substituted organotellurium(VI) fluorides have been prepared (9-11), as illustrated in equations [1-4]:

$$(C_2F_5)_2Te \xrightarrow{ClF} \textit{trans}\text{-}(C_2F_5)_2TeF_4 + \textit{trans}\text{-}C_2F_5TeClF_4 + TeClF_5 \qquad [1a]$$

$$(C_2F_5)_2Te_2 \xrightarrow{ClF} \textit{trans}\text{-}C_2F_5TeClF_4 + TeClF_5\ (8) \qquad [1b]$$

$$(C_6H_4CMe_2O)_2Te \xrightarrow{BrF_3} \textit{trans}\text{-}F_2Te(C_6H_4CMe_2O)_2 \qquad [2a]$$

$$\textit{trans}\text{-}F_2Te(C_6H_4CMe_2O)_2 \xrightarrow{\textit{intramolecular}} \textit{cis}\text{-}F_2Te(C_6H_4CMe_2O)_2\ (9) \qquad [2b]$$

$$Ph_{4-X}TeF_X \xrightarrow{XeF_2} Ph_{4-X}TeF_{X+2} + Xe\ (X = 0\text{–}3)\ (10) \qquad [3]$$

$$(C_6F_5)_2TeF_2 \xrightarrow{F_2} cis\text{-}(C_6F_5)_2TeF_4\ (11) \qquad [4]$$

In all cases, the products were generated by oxidative fluorinations using a variety of fluorinating reagents. However, with the exception of the reaction [2], most methods gave only one isomeric product, *i.e. cis-* or *trans*-isomers. In reaction [2], octahedral *trans*-$F_2Te(C_6H_4CMe_2O)_2$ is formed by the oxidative fluorination of $(C_6H_4CMe_2O)_2Te$(IV) with bromine trifluoride, but the *trans*-isomer is rearranged to give the thermodynamically more stable *cis*-isomer by an intramolecular mechanism, and the structure of the *cis*-isomer has been determined by X-ray crystallographic analysis (9).

In reaction [1a], bis(perfluoroethyl) mono-telluride, $(C_2F_5)_2Te$, reacts with ClF at -78 °C in a 1:2 molar ratio to give $(C_2F_5)_2TeF_2$, and at room temperature in a 1:5 ratio to give *trans*-$(C_2F_5)_2TeF_4$ as well as *trans*-$C_2F_5TeClF_4$ and $TeClF_5$. *trans*-$(C_2F_5)_2TeF_4$ was not isolated, but detected by ^{19}F NMR spectroscopy. Similarly, bis(perfluoroethyl) di-telluride in reaction [1b] reacts with ClF step-by-step to form $C_2F_5TeF_3$ and *trans*-$C_2F_5TeClF_4$, respectively.

Klein and Naumann (11) reported the oxidative fluorination of $(C_6F_5)_2TeF_2$ using elemental fluorine, as shown in reaction [4]. The product *cis*-$(C_6F_5)_2TeF_4$, which was detected by ^{19}F NMR spectroscopy at low temperature, was found to be unstable with respect to decomposition to tellurium tetrafluoride when the temperature increased (further discussion will be given in chapter IIIA).

A variety of phenyltellurium(VI) fluorides has been prepared by K. Alam (10) by oxidative fluorinations of phenyltellurium(IV) compounds with xenon difluoride as an oxidizing agent, as described in reaction [3]. The products were characterized mainly by ^{19}F and ^{125}Te NMR spectroscopy and in some cases by elemental analysis and mass spectrometry. The oxidative reactions with xenon difluoride were extremely slow (8 hours-several days) so that the final products invariably contained some impurities, with the desired product in relatively low and varying yields (12).

As discussed above, most synthetic methods are restricted to the formation of one isomer, presumably due to the reaction conditions which might lead to the rearrangement or decomposition of the kinetically favoured isomer. In connection with the problem of isomerization reactions in octahedral main group fluorides, detailed investigation was made on fluorophenyltellurium(VI) compounds. An improved synthesis, in which the reaction is generally complete in 5 minutes with high yield (>95 %) from the minimum of 8 hours by the conventional method (12) and, in particular, the stereoselective syntheses of *cis*- and *trans*-isomers have made it possible to study the reaction mechanisms.

In this thesis, the mechanisms of isomerization and oxidative fluorination reactions in octahedral fluorophenyltellurium(VI) compounds will be discussed. Also some reactions and NMR studies of isoelectronic tin(IV) fluorides will be described.

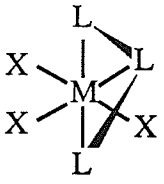
II. MECHANISMS OF STEREOCHEMICAL REARRANGEMENTS

Since an important part of this thesis deals with the mechanisms of stereochemical rearrangements of octahedral metal complexes, the general classification of dynamic processes will be discussed in this section.

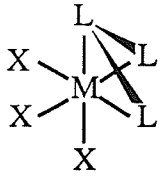
Stereochemical rearrangements of octahedral metal complexes generally follow two main pathways, *i.e. intra-* and *inter*-molecular rearrangements. Before introducing these mechanisms, it is appropriate at this stage to discuss coordination polyhedra and isomer possibilities. In general, two types of isomers may be distinguished for inorganic coordination compounds.

1. Stereoisomers are defined as two or more molecules that have the same molecular formula, the same atom-to-atom bonding sequence, and identical coordination polyhedra, but the atoms have different spatial arrangement. They can be further classified into diasteromers (geometrical isomers) and enantiomers (optical isomers). Optical isomers differ in their direction in which they rotate the plane of polarized light (13,14). Some examples of geometrical isomers of octahedral molecules with unidentate ligands are as follows:

For ML_3X_3 molecules.

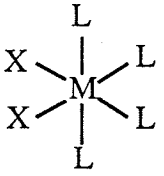


meridional (*mer*-)

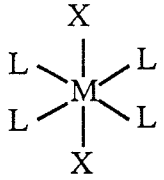


facial (*fac*-)

For ML_4X_2 molecules.



adjacent (*cis*-)



opposite (*trans*-)

On passing to systems with more than two types of ligands, *e.g.* ML_3X_2Y, the number of possible geometrical isomers for both spatial arrangements increases. In this case the geometrical isomers are usually named by the designation *cis* for adjacent positions and *trans* for opposite (180 ° apart) positions with respect to certain ligands.

2. Polytopal isomers have the same constitution but different geometries (polyhedra). The coordination polyhedron of a given molecule may adopt any of several idealized geometries, as in the following examples:

(1) Five-coordination; a trigonal bipyramid (D_{3h}) and square or tetragonal pyramid (C_{4v}).

(2) Six-coordination; a trigonal prism (D_{3h}) and octahedron (O_h).

Polytopal isomers are also possible for higher coordination numbers such as seven-, eight-, nine-, ten-, and twelve-coordinate molecules, and review articles are available in the literature (15).

A. Intermolecular mechanisms

In these mechanisms, rearrangements of complexes proceed by a bond-breaking process; *i.e.* there are changes in coordination number of the metal during the isomerization process. This type of mechanism was first recognized by Werner in 1912 (16) as a possibility of a single bond-dissociation mechanism of octahedral tris(chelate) metal complexes via a five-coordinate intermediate. This is also called a dangling ligand process because only one end of a bidentate ligand is detached. Frequently in the literature (13,14), the isomerization and racemization of octahedral tris(chelate) complexes by the dangling process have been interpreted as an intramolecular mechanism (*vide infra*) unless there is a complete dissociation of the bidentate ligand. However, any type of

rearrangement which involves changes in coordination number of the metal should be classified as the intermolecular mechanism.

Michalak and Martin (17) have reported isomerization reactions in six-coordinate sulfur(VI) fluorides. Bis(chelate) sulfur(IV), $[C_6H_4C(CF_3)_2O]_2S$, is oxidized by BrF_3 to *trans*-$F_2S[C_6H_4C(CF_3)_2O]_2$, but the *trans*-isomer rearranges to give the thermodynamically more stable *cis*-isomer by a dissociative mechanism through a five-coordinate cationic sulfur intermediate, $[C_6H_4C(CF_3)_2O]_2SF^+$:

$$[C_6H_4C(CF_3)_2O]_2S \xrightarrow{BrF_3} \textit{trans}\text{-}F_2S[C_6H_4C(CF_3)_2O]_2 \qquad [5a]$$

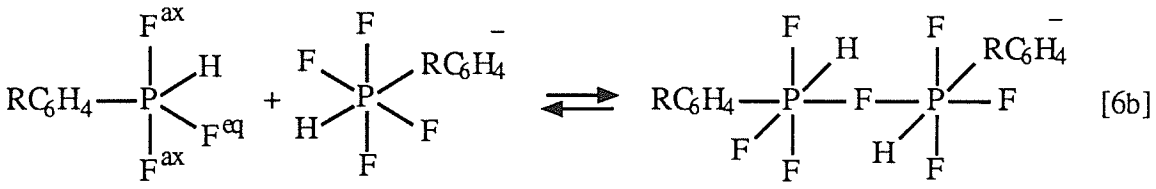
$$\textit{trans}\text{-}F_2S[C_6H_4C(CF_3)_2O]_2 \xrightarrow{\textit{intermolecular}} \textit{cis}\text{-}F_2S[C_6H_4C(CF_3)_2O]_2\ (17) \qquad [5b]$$

Previous NMR studies of ligand exchange in four- and five-coordinate silicon and phosphorus fluorides carried out in our laboratory have shown that intermolecular fluorine exchange is also rapid in systems such as $MeSiF_3$–$MeSiF_4^-$ and SiF_5^-–SiF_6^{2-} (18), $PhPF_3H$–$PhPF_4H^-$ (19), and $PhPF_4$–$PhPF_5^-$ (20) through fluorine-bridged intermediates.

However, stereoselective bond-cleavage is difficult to observe if accompanied by axial-equatorial scrambling of ligands, as illustrated by the $PhPF_3H$–$PhPF_4H^-$ and $PhPF_4$–$PhPF_5^-$ systems. The axial-equatorial fluorine exchange does not slow down even by introducing trifluoromethyl or methyl substituents into the phenyl ring, as observed in the $RC_6H_4PF_3H$–$RC_6H_4PF_4H^-$ system (21):

$$2\,RC_6H_4PF_3H + Et_3N \longrightarrow RC_6H_4PF_2 + Et_3NH^+RC_6H_4PF_4H^- \quad [6a]$$

R = *o*-CF_3, *m*-CF_3, *p*-CF_3, *m*-CH_3



[6b]

Addition of small amounts of triethylamine to $RC_6H_4PF_3H$ produces a six-coordinate $RC_6H_4PF_4H^-$ anion according to equation [6a], and consequently rapid fluorine exchange occurs between five- and six-coordinate phosphorus species, as illustrated in equation [6b]. That the addition of a base may cause fluorine exchange by transferring fluorine between five- and six-coordinate species is similar to the behavior reported for $PhPF_3H$ (19). In the absence of the base, axial-equatorial fluorine exchange in $PhPF_3H$ (19) and $RC_6H_4PF_3H$ (21) has been observed.

The fluorine exchange studies in a six-coordinate *mer*-Ph_3TeF_3 (22) are also consistent with the intermolecular mechanism involving Te-F bond-cleavage. It was demonstrated that the introduction of three phenyl substituents could prevent intramolecular fluorine scrambling, and thus permit study of which fluorines are selectively cleaved. The fact that three phenyl substituents may be required to observe stereoselective bond-cleavage is further supported by several other examples. Therefore, in this thesis, stereoselective fluorine exchange studies in Ph_3TeF_2Cl and Ph_3TeF_2OH, in addition to *mer*-Ph_3TeF_3, will be discussed.

B. Intramolecular mechanisms

Intramolecular rearrangements are defined as processes in which ligand positions in a molecule are permuted without changes in coordination number. Thus, the lack of metal-ligand bond-dissociation is an essential feature. The intramolecular phenomenon can therefore be delineated by the fact that spin-spin coupling is maintained between the nuclei of the metal and ligand that are involved in exchange. Molecules undergoing these rearrangements are also described as stereochemically nonrigid or fluxional. The phenomenon of stereochemical nonrigidity is best characterized for many five-coordinate molecules, and many more experimental data are available for this coordination number than for any other. The origin of the nonrigidity can readily be understood by comparing two polyhedra, *i.e.* trigonal bipyramid and square pyramid. As illustrated in Figure 1, it is relatively easy to convert one polyhedron into the other by small angle deformations and hence to change the axial and equatorial positions for both polyhedra. This mechanism was first suggested by Berry (23) to explain the ^{19}F NMR spectroscopic equivalence of fluorine atoms in phosphorus pentafluoride.

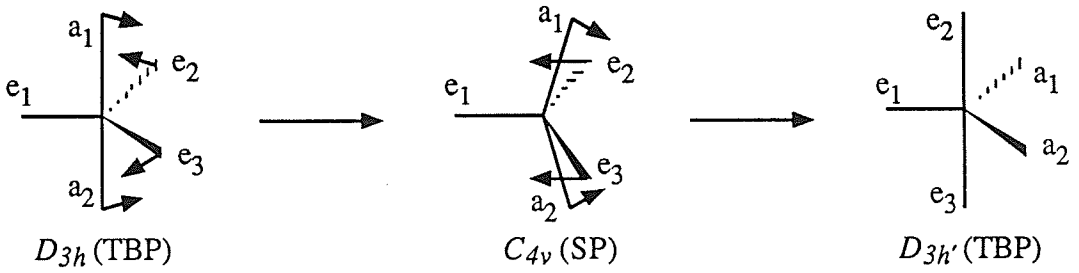


Figure 1. Schematic representation of the Berry intramolecular rearrangement for the trigonal bipyramid involving a square pyramidal intermediate (also known as the pseudoration process).

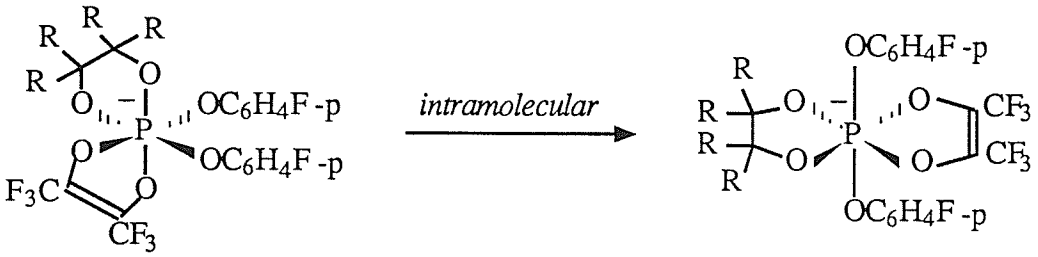
Several different intramolecular mechanisms have been proposed for isomerizations and racemizations of octahedral complexes. They are collectively known as twist mechanisms, *e.g.* the Bailar (trigonal, C_3) twist (24) and the Ray-Dutt (25) or Springer-Sievers (26) (rhombic, C_2) twist. Such distinctions are more meaningful in symmetrically substituted octahedral tris(chelate) complexes. Brady (27) and Serpone & Bickley (13) have concluded that the three twist mechanisms are basically the same, the intermediate being a trigonal prism with the only difference being in the interatomic angles. Therefore, in discussing the twist mechanisms one may consider the same pathway, *i.e.* an ideal octahedral polyhedron converts to the other through an ideal trigonal prismatic polyhedron without regard to the symmetry of the transition state.

The use of mathematical methods was promoted by Muetterties (28) to give a topological representation of polytopal rearrangements. This useful term implies that the rearrangements proceed via intermediates or transition states, *i.e.* polytopal isomers, whose spatial arrangements, as discussed earlier, can be described in terms of idealized polyhedra and the vertices of which correspond to the ligand positions. The polytopal rearrangement can thus represent the intramolecular mechanism for any given coordination number.

Although stereochemical nonrigidity has been presumed for many five-coordinate molecules, barriers to polytopal rearrangement of six-coordinate molecules are expected to be large, since an octahedral arrangement is thought to represent a considerable minimum on the potential energy surface (29,30).

In contrast to the intermolecular mechanism proposed for the *trans-cis* isomerization in octahedral sulfur(VI) fluorides (17), as described in equation [5], studies of six-coordinate derivatives of phosphorus (31) and tellurium (9) have revealed an intramolecular twist mechanism.

In the case of six-coordinate bis(chelate) phosphorus anions (31), the twist mechanism was proposed on the basis of NMR results of the equivalence of the trifluoromethyl groups and the *p*-fluorophenoxy groups, as illustrated in equation [7]. However, since the cleavage of one site of a bidentate ligand should give an average NMR signal for CF_3 groups, the dissociative mechanism must not be ruled out.



cis *trans* [7]

Studies of octahedral fluorophenyltellurium(VI) compounds reveal that the intermolecular mechanism is responsible for isomerization reactions, and thus a thorough discussion will be given later in this thesis comparing it with the twist mechanism proposed for the analogous tellurium(VI) fluorides (9) in the literature.

III. OXIDATIVE ADDITION IN MAIN GROUP COMPOUNDS

Oxidative fluorination reactions of organotellurium(IV) compounds may produce *cis*- or *trans*-isomers of the corresponding organotellurium(VI) fluorides, as described in equations [1-4].

trans-$(C_2F_5)_2TeF_4$, prepared by Passmore *et al.* (8) in reaction [1a], is the first example of the general structure R_2TeX_4 (Figure 2).

cis-R_2TeX_4 *trans*-R_2TeX_4

Figure 2. The two geometrical isomers of R_2TeX_4 (X = halide).

In a similar reaction, only *cis*-$(C_6F_5)_2TeF_4$ was formed (reaction [4]), but it decomposed at 0 °C (11). It is of interest to compare the reaction conditions for the preparations of *trans*-$(C_2F_5)_2TeF_4$ (8) and *cis*-$(C_6F_5)_2TeF_4$ (11).

In the preparation of *trans*-$(C_2F_5)_2TeF_4$, $(C_2F_5)_2Te$ was oxidized to $(C_2F_5)_2TeF_2$ at -78 °C, but further oxidation occurred at room temperature and required a slight excess of ClF rather than stoichiometric amounts of ClF. The formation of *cis*-$(C_6F_5)_2TeF_4$ was detected by ^{19}F NMR at -35 °C, but as the temperature increased to 0 °C, the *cis*-isomer was no longer observed. Furthermore, the oxidative fluorination of Ph_2TeF_2 with XeF_2 in reaction [3] gave only *trans*-Ph_2TeF_4 after constant stirring of the reaction mixture for at least 8 hours at room temperature (10,12).

These observations suggest that the *cis*-isomer is kinetically favoured, but that rearrangement might occur to give the thermodynamically more stable *trans*-isomer.

In addition to these organotellurium(VI) fluorides, oxidative addition reactions of various main group compounds have been accomplished by a variety of oxidizing reagents, the final products being the isomers (*cis* or *trans*) or isomeric mixture, as in the following examples:

$$Ph_2S \xrightarrow[\text{slow}]{\text{large excess } CF_3OF} \textit{trans}\text{-}Ph_2SF_4\ (32) \qquad [8]$$

$$Ph_2S \xrightarrow{F_2} Ph_2SF_2 \xrightarrow{F_2} \textit{cis}\text{- and } \textit{trans}\text{-}Ph_2SF_4\ (33) \qquad [9]$$

$$CF_3SF_3 \xrightarrow[CsF]{Cl_2} \textit{trans}\text{-}CF_3SF_4Cl\ (34) \qquad [10]$$

$$R_fSCl\ [\text{or } (R_f)_2S_2] \xrightarrow{ClF} \textit{trans}\text{-}R_fSF_4Cl\ (35)$$

$$R_f = CF_3,\ C_2F_5,\ \textit{n}\text{-}C_3F_7, \text{ or } \textit{n}\text{-}C_4F_9 \qquad [11]$$

$$(CF_3)_2S \xrightarrow[\text{fluorination}]{\text{electrochemical}} \textit{trans}\text{-}(CF_3)_2SF_4\ (36) \qquad [12]$$

$$(CF_3)_2S \xrightarrow{ClF} \textit{cis}\text{- and } \textit{trans}\text{-}(CF_3)_2SF_4\ (37) \qquad [13]$$

$$R_fR_f'S \xrightarrow{ClF} \textit{cis}\text{- and } \textit{trans}\text{-}R_fR_f'SF_4 \text{ (37,38)}$$

$R_fR_f' = CF_3,CF_3 / CF_3, C_2F_5$ [14]

$$SF_4 \xrightarrow{ClOSO_2CF_3} \textit{cis}\text{- and } \textit{trans}\text{-}SF_4(OSO_2CF_3)Cl \text{ (39,40)} \quad [15]$$

$$SF_4 \xrightarrow{ClOSO_2F} \textit{cis}\text{- and } \textit{trans}\text{-}SF_4(OSO_2F)Cl \text{ (40)} \quad [16]$$

$$(R_fO)_2S{=}NCF_3 \xrightarrow{ClF} \textit{cis}\text{- and } \textit{trans}\text{-}(R_fO)_2SF_4 \text{ (41)}$$

$R_f = CF_3CH_2,\ CF_3CF_2CH_2,\ CF_3CF_2CF_2CH_2$ [17]

$$C_2F_5SeF_3 \xrightarrow{ClF} \textit{trans}\text{-}C_2F_5SeClF_4 \text{ (42)} \quad [18]$$

$$(F_5TeO)_4Te \xrightarrow{XeF_2} \textit{cis}\text{-}(F_5TeO)_4TeF_2 + \textit{trans}\text{-}F_4Te(OTeF_5)_2 + (F_5TeO)_5TeF \text{ (major) (43)} \quad [19]$$

As described in equations [1-19], the oxidative addition reactions of main group compounds may lead to the formation of *cis*- or *trans*-isomers, or isomeric mixtures.

Denney *et al.* (32) have described the oxidative fluorination of Ph_2S using a large excess of CF_3OF, as shown in reaction [8]. The reaction occurred very slowly and only *trans*-Ph_2SF_4 was formed.

On the other hand, fluorination of Ph_2S using elemental fluorine, as reported by Ruppert (33), gave a mixture of *cis*- and *trans*-Ph_2SF_4 (2:1) via isolable Ph_2SF_2, as described in reaction [9]; isomerization was not observed and, furthermore, on adding triethylamine, both isomers were hydrolyzed in $CHCl_3$ to Ph_2SO_2. The mechanism of the hydrolysis reaction was not presented in this paper, but traces of moisture could come from $CHCl_3$ or Et_3N. The *cis-trans* isomerization problem can be clearly seen from these reactions. The fact that only the *trans*-isomer is formed under the reaction conditions given in equation [8] may be attributed to the use of excess CF_3OF and slow reaction, which could provide traces of a Lewis acid such as HF.

This is quite consistent with the results of acid-catalyzed isomerization observed in *cis*- and *trans*-$F_2S[C_6H_4(CF_3)_2O]_2$, as illustrated in equation [5], reported by Michalak and Martin (17). When the stoichiometric amount of a fluorinating reagent BrF_3 was used, the kinetically favoured *trans*-isomer was obtained, but when excess BrF_3 was used, only the *cis*-isomer was obtained. In other words, the formation of a Lewis acid by the use of excess BrF_3 may have led to the impurity-catalyzed isomerization and indeed the isomerization process was observed step-by-step by adding a Lewis acid and further details will be discussed in chapter III.

In the majority of cases of oxidative reactions, *e.g.* reactions [1-19], even when both isomers were isolated or identified spectroscopically, the interconversions between *cis*- and *trans*-isomers have not been observed. Rapid isomerization could interfere with the observation of the kinetically favoured isomer, and this may be the reason that the mechanisms of isomerization and oxidative addition reactions of main group compounds have not been reviewed in the literature and thus not well understood.

The isomer or isomeric mixture listed in reactions [1-19] are the results of the oxidative addition reactions. The problem of *cis-trans* isomerization can also be found in many substitution reactions, as in the following examples:

$$SF_5Cl + Me_2NSiMe_3 \longrightarrow \textit{trans}\text{-}Me_2NSClF_4 + Me_3SiF\ (44) \qquad [20]$$

$$TeF_6 + 2\ MeOH \xrightarrow{NaF} \textit{cis}\text{-}(MeO)_2TeF_4 + 2\ HF\ (45) \qquad [21]$$

$$TeF_5Cl + MeOSiMe_3 \longrightarrow \textit{cis}\text{- and }\textit{trans}\text{-}MeOTeClF_4 + Me_3SiF \qquad [22a]$$

$$TeF_5Cl + MeOH \longrightarrow \textit{cis}\text{- and }\textit{trans}\text{-}MeOTeClF_4 + HF\ (46) \qquad [22b]$$

In conjuction with the mechanistic studies of stereochemical rearrangements in octahedral fluorophenyltellurium(VI) compounds, the proposal of the mechanisms of oxidative addition reactions will be presented in this thesis.

Finally, this thesis will also present NMR studies of analogous tin(IV) fluorides in group IV elements. In particular, the structure of a five-coordiante $Ph_3SnF_2^-$ anion, which was first prepared by Holmes *et al.* (47), is of interest. It is isoelectronic with a five-coordinate $Ph_3TeF_2^+$ cation which undergoes rapid exchange with *mer*-Ph_3TeF_3. However, unlike $Ph_3TeF_2^+$, $Ph_3SnF_2^-$ does not form a stable six-coordinate adduct with fluoride. Furthermore, analogous structures of *mer*-$(C_6F_5)_3AsF_3^-$ and *mer*-$(C_6F_5)_3SbF_3^-$ (counter ions are CsF) in group V elements are known (48). At room temperature, these are in equilibrium with corresponding five-coordinate neutral species, such as $(C_6F_5)_3AsF_2$ and $(C_6F_5)_3SbF_2$, respectively.

It is thus interesting to note that the formation of six-coordination becomes more difficult when the group descends from VI & V to IV, with three bulky phenyl or perfluorophenyl substituents.

CHAPTER II

EXPERIMENTAL

I. CHEMICALS

Xenon difluoride, phosphorus pentafluoride, carbonyl fluoride (PCR Research Chemical Inc.), boron trifluoride, trimethylamine (Matheson), triphenyltellurium chloride, diphenyltellurium dichloride (K & K Laboratories), diphenyltelluride (Strem Chemicals Inc.) were commercial samples and used without further purification.

Triphenyltin chloride and diphenyltin dichloride (Aldrich Chemical Company Inc.) were purified according to the literature method (47) prior to use .

Dichloromethane, acetonitrile, and chloroform solvents (Fisher Certified Grade) were dried over 5 Å molecular sieve. Tetraethylammonium chloride (Eastman) was recrystallized from dry CH_3CN and dried over P_2O_5 (Allied Chemical) in a vacuum desiccator. Pyridine (Fisher Scientific Company) was heated under reflux over potassium hydroxide pellets for 1 hour and distilled at atmospheric pressure with careful exclusion of moisture according to the literature method (49).

Potassium fluoride (Fisher Scientific Company) was dried over P_2O_5 in a vacuum desiccator and heated under vacuum at 100 °C in an oil bath. Sodium fluoride (Fisher Scientific Company) was dried overnight at 150 °C under oil pump vacuum. 18-crown-6 ether (Aldrich) was dried over P_2O_5 in a vacuum desiccator. Hexamethylphosphoramide (J. T. Baker Chemical Co.) was stored over calcium chloride (50).

The following chemicals were all commercial samples and used without further treatment: tetraethylammonium hydroxide (Eastman), hexane, diethyl ether (Fisher Scientific Company), and catechol (BDH). Phosphoryl chloride, pyridine-N-oxide, chlorodiphenylphosphine, hexamethyldisilazane, diphenyliodonium chloride, tetrabutylammonium fluoride, hexafluorobenzene, triphenylphosphine oxide, DMSO-d_6, D_2O, CD_2Cl_2, $CDCl_3$, and CD_3CN were all obtained from Aldrich Chemical Company.

4-Fluoro-2,2'-bipyridine (fbpy) was supplied by Mr. T. Nguyen in this laboratory (51).

All Teflon equipment was dried at 110 °C for several days prior to use. All gases were handled in a standard glass vacuum line using glass reaction tubes fitted with Rotaflo stopcocks and Teflon inserts.

II. INSTRUMENTAL

Fluorine-19 NMR spectra were recorded on Bruker WH90 and AM300 spectrometers at 84.66 MHz and 282.4 MHz, respectively. Fluorine chemical shifts were referenced against C_6F_6 (-162.9 ppm with respect to $CFCl_3$) as an internal reference. The progress of a reaction, involving disappearance of XeF_2 and appearance of fluorinated products and HF (as well as BF_4^- from reaction with glass NMR tubes), was routinely monitored by ^{19}F NMR on a Bruker WH90 spectrometer at 84.66 MHz. Literature values of ^{19}F chemical shifts were converted relative to the $CFCl_3$ scale using the conversion factors (52), for comparison.

Tellurium-125 NMR spectra were recorded on a Bruker AM300 spectrometer at 94.76 MHz using Ph_2Te (692.3 ppm with respect to Me_2Te) as an external reference.

$^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM300 spectrometer with operating frequency of 75.47 MHz using 5 mm ^1H /^{13}C dual probe. Relatively longer acquisition times (up to ~20s) were required to obtain high resolution ^{13}C NMR spectra with digital resolution up to 0.05 Hz/point. Tetramethylsilane (TMS) was used as an internal reference. In some cases, a solvent peak was used as a reference and its chemical shift was calculated with the aid of the values tabulated using TMS as a standard (Table 1).

TABLE 1

Carbon-13 NMR data of some common deuteriated solvents (53)

Deuteriated solvent	C-D Signal Multiplicity	C-D Coupling Constants [Hz]	^{13}C Shift [ppm]
CD_2Cl_2	quintet	27	53.1
$CDCl_3$	triplet	32	77.0 ± 0.5
CD_3CN	septet	21	1.3
	long-range multiplet	1	118.2
C_6D_6	triplet	24	128.0 ± 0.5
Acetone-d_6	septet	20	29.8
	long-range multiplet	<1	206.5

The chemical shift differences in each experiment were within 0.2 ppm and the correction was made against TMS as a reference. Samples of *mer*-Ph_3TeF_3 and a mixture of $Ph_3TeF_2^+PF_6^-$ and $Ph_3TeFCl^+PF_6^-$ were degassed via three freeze-pump-thaw cycles.

Tin-119 NMR spectra were recorded on a Bruker AM300 spectrometer at 111.9 MHz and referenced against external tetramethyltin(IV), Me_4Sn, and recorded with complete proton decoupling.

The proton-decoupled ^{31}P NMR spectra were recorded on a Bruker WH90 spectrometer at 36.44 MHz using 85% H_3PO_4 as an external reference.

All the NMR chemical shifts were reported following the IUPAC convention (54), *i.e.* positive values in high frequency (low field) direction.

Mass spectra were obtained on Finnigan 1015 quadrupole and VG-7070E-HF spectrometers.

III. EXPERIMENTAL DETAILS

A. Fluorination using carbonyl fluoride

1. COF_2 and phenyltellurium(IV) chlorides

Some difficulties were experienced with the preparation of Ph_3TeF according to the literature methods (55,56); synthesis of Ph_3TeF in standard glassware invariably produced large amounts of $Ph_3Te^+BF_4^-$ in high yield (12).

Therefore, an alternative method was tried for the preparation of Ph_3TeF from Ph_3TeCl using carbonyl fluoride as a fluorinating agent in Teflon equipment by using a

method similar to that reported by Shreeve and Gupta for analogous phosphorus compounds (57).

Excess carbonyl fluoride was condensed onto a solution of Ph_3TeCl (150 mg, 0.38 mmol) in dichloromethane (10 mL) cooled to -196 °C in a stoppered reaction tube with a Teflon insert. The reaction mixture was slowly warmed to room temperature and stirred for 6 hours. Removal of volatile materials under vacuum gave a white solid which was identified as Ph_3TeF (>90%) and small amounts of $Ph_3Te^+BF_4^-$ by ^{19}F NMR spectroscopy. Excess COF_2 was added to the solution of Ph_3TeF in CH_2Cl_2, but there was no evidence of oxidative fluorination, as confirmed by ^{19}F NMR spectroscopy. Ph_3TeF was oxidized to *mer*-Ph_3TeF_3 by the addition of stoichiometric amounts of XeF_2.

Excess carbonyl fluoride was added to a Teflon tube containing dichlorodiphenyltellurium(IV) (103 mg, 0.29 mmol) in 10 mL CH_2Cl_2 at -196 °C, the reaction mixture was warmed to room temperature, and stirred for 12 hours. Removal of all volatile materials under vacuum gave a white solid which was identified as a mixture of the new compound, Ph_2TeFCl (78%), with the known compound, Ph_2TeF_2 (12%) (58), as judged by ^{19}F NMR integration, and the unreacted starting compound, Ph_2TeCl_2. A large excess of NaF was added to this mixture with constant stirring for 1 day. The ^{19}F NMR examination of the solution revealed the formation of Ph_2TeF_2 in high yield.

2. COF_2 and phenylmethylchlorosilanes

Excess carbonyl fluoride was condensed onto a solution of $PhMe_2SiCl$ (51.2 mg, 0.30 mmol) in dichloromethane (5 mL) cooled to -196°C. The reaction mixture was warmed to room temperature and stirred for 30 minutes. Removal of volatile materials under vacuum gave a white solid which was identified as $PhMe_2SiF$ by ^{19}F and ^1H NMR

spectroscopy; the proton-coupled ^{19}F NMR spectrum shows a septet at -161.84 ppm having $J(^{1}H\text{-}F) = 7.5$ Hz and with satellites from which $J(^{29}Si\text{-}F) = 276$ Hz. The ^{1}H NMR examination confirmed the presence of phenyl and methyl groups.

Carbonyl fluoride was added to a solution of $Ph_2MeSiCl$ (69.8 mg, 0.30 mmol) in acetonitrile (5 mL) in a manner similar to that above and thus Ph_2MeSiF was produced, as judged by ^{19}F and ^{1}H NMR spectroscopy; the proton-coupled ^{19}F NMR spectrum showed a quartet at -166.43 ppm with $J(^{1}H\text{-}F) = 7$ Hz.

3. Ph_3TeF as a source of fluoride ion

The formation of Ph_3TeF was always accompanied by $Ph_3Te^+BF_4^-$, and thus experiments were performed to see if Ph_3TeF could be a good fluoride donor, giving a stable cation, Ph_3Te^+. Reactions of Ph_3TeF with various phenylsilanes, such as Ph_3SiH, $PhSiCl_3$, Ph_2SiF_2, and $PhSiF_3$, were carried out in an attempt to produce corresponding fluorophenylsilicate anions. Each of the phenylsilanes (0.30 mmol) was dissolved in CH_2Cl_2 and then mixed with a stoichiometric amount of Ph_3TeF in CH_2Cl_2. The fluorine resonances of Ph_2SiF_2 and $PhSiF_3$ were broadened (*e.g.* $\Delta W_{1/2}$ of $PhSiF_3$ = 48 Hz) with loss of $^{29}Si\text{-}F$ coupling when the solutions of Ph_3TeF in CH_2Cl_2 were added to the solutions of Ph_2SiF_2 and $PhSiF_3$ in CH_2Cl_2, respectively.

A slight excess of PF_5 (0.40 mmol) was condensed onto a solution of Ph_3TeF (138 mg, 0.35 mmol) in dichloromethane (10 mL) and stirred for 20 minutes. Evaporation of all volatile materials under vacuum gave a white solid which was identified as a mixture of $Ph_3Te^+PF_6^-$ and $Ph_3Te^+BF_4^-$ in a ratio of 4:1 as determined by ^{19}F NMR integration. $Ph_3Te^+PF_6^-$ was separated from the mixture by using thin layer chromatography (TLC). TLC separations were carried out on silica gel plates using a mixture of CH_2Cl_2 and

CH_3CN (1:1, v:v). Triphenyltellurium(1+) hexafluorophosphate(1-), $Ph_3Te^+PF_6^-$, was identified by ^{19}F, ^{31}P, ^{125}Te, and ^{13}C NMR spectroscopy. A stoichiometric amount of XeF_2 was added to a solution of $Ph_3Te^+PF_6^-$ in CH_2Cl_2. However, the formation of $Ph_3TeF_2^+PF_6^-$ was less than 10% and the rest was fluoride impurities (*e.g.* BF_4^-) in large amounts, as determined by ^{19}F NMR integration.

B. Preparation of fluorophenyltellurium(VI) compounds

A series of fluorophenyltellurium(VI) compounds was first prepared by K. Alam (10,12). However, the reaction conditions consisted of stirring the reaction mixture for periods of 8 hours up to several days. During the prolonged reaction time, impurities were almost always produced along with the desired products. Therefore, the method of oxidative fluorination was modified to improve the yield of the products.

1. Preparation of trifluorotriphenyltellurium(VI), Ph_3TeF_3

a. With catalyst

In a typical reaction, solid XeF_2 (42.0 mg, 0.25 mmol) was added to a stirred solution of Ph_3TeCl (65.0 mg, 0.16 mmol) in dichloromethane (5 mL) in a Teflon bottle. Then Et_4NCl (1.90 mg, 0.01 mmol) was added to the solution with constant stirring. The colorless solution rapidly turned yellow with vigorous xenon gas evolution. When the gas was no longer evolved, the solution became colorless again after 15 minutes. The solution was stirred for another hour and then solvent was slowly evaporated under vacuum to give *mer*-Ph_3TeF_3 in high yield (>95%). The crude product was washed twice with cold acetonitrile to remove BF_4^- if present (in most cases when the reaction

system was clean and dry, further purification was not required), and identified by ^{19}F , ^{125}Te, and ^{13}C NMR spectroscopy.

Each step of oxidative fluorination with the use of the catalyst was monitored by ^{19}F NMR spectroscopy. A three-fold excess of solid Et_4NCl (75.6 mg, 0.46 mmol) was directly added to the solution of Ph_3TeCl (60.0 mg, 0.15 mmol) in $CDCl_3$ (1 mL) into the NMR tube. Solid XeF_2 (38.1 mg, 0.23 mmol) was then added to the solution of Ph_3TeCl and Et_4NCl in $CDCl_3$. Xenon gas evolved for a few minutes. The ^{19}F NMR spectrum was recorded after 5 minutes. The spectrum contained a mixture of *mer*-Ph_3TeF_3 (30%), *cis*-F_2TePh_3Cl (10%), and 60% for the unknown single peak at +49.9 ppm with ^{125}Te-satellites, [$J(^{125}Te\text{-}F)$ = 1892 Hz], as well as small amounts of HF. The ^{19}F NMR integration excluded the area of HF due to its broadness. The solution was then transferred into a large 10 mm NMR tube with additional 1.5 mL $CDCl_3$ for ^{125}Te NMR examination. The ^{125}Te NMR spectrum showed a new resonance at +650.5 ppm with $J(^{125}Te\text{-}F)$ = 1891 Hz. The ^{19}F NMR spectrum was recorded again after the ^{125}Te NMR spectrum was recorded (approximately after 80 minutes). At this stage all of the unknown peak had disappeared to give more *cis*-F_2TePh_3Cl, and eventually *mer*-Ph_3TeF_3 in the presence of HF. The unknown peak was assigned to Ph_3TeFCl_2 based on the NMR results. The reaction of Ph_3TeCl and XeF_2 was repeated using a different molar concentration of Et_4NCl (~1–3 equivalent of Ph_3TeCl), and a similar result was obtained.

mer-Ph_3TeF_3 was prepared alternatively from Ph_3TeF and XeF_2. Solid XeF_2 (22.4 mg, 0.13 mmol) was added to a solution of Ph_3TeF (50.0 mg, 0.13 mmol) and Et_4NCl (1.50 mg, 0.01 mmol) in CH_2Cl_2 (4 mL) in a Teflon bottle. The solution mixture was stirred for 1 hour. Removal of solvent gave *mer*-Ph_3TeF_3 and the crude product was washed with cold acetonitrile and recrystallized from CH_2Cl_2.

b. Without catalyst

Trifluorotriphenyltellurium(VI), Ph_3TeF_3, was prepared according to the method of K. Alam, purified by recrystallization from a mixture of dichloromethane and hexane (2:7, v:v), and washed twice with acetonitrile. The recrystallized sample was dissolved in CH_2Cl_2 and slow evaporation of the solvent afforded colorless, needlelike crystals of *mer*-Ph_3TeF_3.

2. Preparation of difluorotriphenyltellurium(1+) hexafluorophosphate(1-), $Ph_3TeF_2^+PF_6^-$

An excess of PF_5 was condensed onto a solution of purified sample of *mer*-Ph_3TeF_3 (0.48 mmol) in CH_2Cl_2 (4 mL) cooled to -196 °C. The solution was slowly allowed to warm to room temperature and stirred for 30 minutes. Removal of volatile materials under vacuum gave a white solid which was identified as $Ph_3TeF_2^+PF_6^-$ in high yield (> 90%) as confirmed by ^{19}F, ^{125}Te , and ^{13}C NMR spectroscopy.

The formation of $Ph_3TeF_2^+PF_6^-$ was also confirmed by its chemical reactions:

1. Addition of a large excess of NaF to the solution of $Ph_3TeF_2^+PF_6^-$ in CH_2Cl_2, followed by filtration, gave *mer*-Ph_3TeF_3.

2. Addition of a stoichiometric amount of Et_4NCl gave Ph_3TeF_2Cl.

3. Fluorine exchange in the mer-Ph_3TeF_3–$Ph_3TeF_2^+$ system

All Teflon inserts and NMR tubes were dried at 110 °C for several days. The entire glass vacuum manifold was flamed out under vacuum and passivated with PF_5. Gaseous

samples were handled in a standard glass vacuum line with the use of Teflon equipment. Glass NMR tubes were used for NMR experiments without Teflon inserts.

Several variable-temperature experiments were carried out on a mixture of *mer*-Ph_3TeF_3 and $Ph_3TeF_2^+PF_6^-$ with several different concentrations. The typical experimental details are as follows; the freshly prepared sample of $Ph_3TeF_2^+PF_6^-$ (34.0 mg, 0.06 mmol) was dissolved in a deuteriated dichloromethane solvent (1 mL) and its ^{19}F NMR spectrum was recorded. Then a purified sample of *mer*-Ph_3TeF_3 (26.0 mg, 0.06 mmol) was directly added to the solution of $Ph_3TeF_2^+PF_6^-$ in CD_2Cl_2. The mixture was shaken to complete dissolution. After the ^{19}F NMR spectrum of the mixture was recorded at ambient temperature (300 K), the sample was cooled to 280 K and its spectrum was recorded. The low temperature NMR experiments were continued with 10 K temperature decrements until the sample started freezing out at 180 K. The total experimental time required was approximately 4 hours. Even with the careful exclusion of moisture, the hydrolysis product, $P(O)F_2OH$, had already formed after the first variable temperature experiment. The amount of $P(O)F_2OH$ increased gradually, and when the temperature reached 180 K, most of the sample had hydrolyzed to give $P(O)F_2OH$, which hydrolyzed further to give $P(O)F(OH)_2$, so that the concentration information obtained by the ^{19}F NMR integration was not reliable, nor reproducible. Therefore, those results with least impurities were used for the calculations.

4. Preparation of chlorodifluorotriphenyltellurium(VI), Ph_3TeF_2Cl

a. Preparation of *trans*-F_2TePh_3Cl

Difluorotriphenyltellurium(VI) hexafluorophosphate, $Ph_3TeF_2^+PF_6^-$, was prepared

according to the procedure described above. Solid Et_4NCl (86 mg, 0.52 mmol) was then added to a solution of $Ph_3TeF_2^+PF_6^-$ (282 mg, 0.52 mmol) in CH_2Cl_2 with continuous shaking until a clear solution was formed. It was identified as the new compound, *trans*-F_2TePh_3Cl, by ^{19}F and ^{125}Te NMR spectroscopy. After 24 hours in dichloromethane solution, 36% of *trans*-F_2TePh_3Cl had rearranged to *cis*-F_2TePh_3Cl, as well as small amounts of *mer*-Ph_3TeF_3. After 6 days, 77% of *trans*-F_2TePh_3Cl had isomerized, and after one month, all *trans*-F_2TePh_3Cl had disappeared and only *cis*-F_2TePh_3Cl and *mer*-Ph_3TeF_3 remained.

In a separate experiment, excess NaF was added to the solution of *trans*-F_2TePh_3Cl in CH_2Cl_2 as soon as its formation was confirmed by ^{19}F NMR spectroscopy, in an effort to prevent isomerization catalyzed by Lewis acid impurities. However, all of the *trans*-F_2TePh_3Cl had disappeared to give *cis*-F_2TePh_3Cl and *mer*-Ph_3TeF_3 within 24 hours.

b. Preparation of *cis*-F_2TePh_3Cl

cis-F_2TePh_3Cl was prepared according to the method of K. Alam (12) with slight modification; solid XeF_2 (28.8 mg, 0.17 mmol) was added to a stirred suspension of triphenyltellurium(IV) chloride (67.0 mg, 0.17 mmol) in CH_3CN (3 mL) in a Teflon bottle. The reaction mixture was stirred at 0 °C for 8 hours until a slightly yellow solution was formed. The crude product (>90% yield) contained *cis*-F_2TePh_3Cl and *mer*-Ph_3TeF_3 in a 2:3 ratio as determined by ^{19}F NMR integration. *mer*-Ph_3TeF_3 was removed by recrystallization from a mixture of CH_2Cl_2 and hexane (2:7, v:v). Removal of solvent from the remaining solution, followed by washing with cold acetonitrile, gave *cis*-F_2TePh_3Cl. The formation of *cis*-F_2TePh_3Cl was confirmed by ^{19}F and ^{125}Te NMR spectroscopy. *cis*-F_2TePh_3Cl is appreciably soluble in both CH_2Cl_2 and CH_3CN.

c. Preparation of $Ph_3TeFCl^+PF_6^-$

Condensation of PF_5 into a solution of either *cis*- or *trans*-F_2TePh_3Cl (73.5 mg, 0.17 mmol) in CH_2Cl_2 (4 mL) gave the new compound, $Ph_3TeFCl^+PF_6^-$, in high yield (>90%), as confirmed by ^{19}F, ^{125}Te, and ^{13}C NMR spectroscopy. A small amount of $Ph_3TeF_2^+PF_6^-$ was also formed due to the presence of *mer*-Ph_3TeF_3 along with the desired product, $Ph_3TeFCl^+PF_6^-$. The two cations, $Ph_3TeF_2^+PF_6^-$ and $Ph_3TeFCl^+PF_6^-$, were stable in CH_2Cl_2 for at least 1 day, as revealed by ^{19}F NMR spectroscopy, and no intermolecular fluorine exchange was observed between these two cations. However, after 1 day in CH_2Cl_2, these cations slowly produced decomposition with the formation of $P(O)F_2OH$ and $P(O)F(OH)_2$, as confirmed by ^{19}F NMR spectroscopy.

d. Alternative preparation of *cis*-F_2TePh_3Cl

The cation Ph_3TeFCl^+ was also characterized by its chemical reaction with NaF. Excess NaF was added to a solution of $Ph_3TeFCl^+PF_6^-$ in CH_2Cl_2 and kept for 1 day. After the solid was removed by filtration, the ^{19}F NMR spectrum of the solution was recorded; this confirmed the formation of *cis*-F_2TePh_3Cl.

At the end of all the experiments, *mer*-Ph_3TeF_3 was always recovered in ~70% yield from the impure samples of *cis*- and *trans*-F_2TePh_3Cl and the cations, $Ph_3TeF_2^+$ and Ph_3TeFCl^+.

5. Preparation of cis- and trans-Ph_2TeF_4

The preparation of *trans*-tetrafluorodiphenyltellurium(VI), *trans*-Ph_2TeF_4, according to the method of K. Alam (12), required at least 48 hours (up to 7 days) of reaction time. Because of the long reaction time, fluoride impurities were always present and thus only the thermodynamically stable *trans*-isomer was isolated in modest yield (60%) (12).

Therefore, the preparation was modified to improve the yield of the product with the use of catalyst. Each step of oxidative fluorination without catalyst was also monitored by ^{19}F NMR spectroscopy to obtain information about stepwise fluorination.

a. Without catalyst

Solid XeF_2 (120 mg, 0.71 mmol) was added to a solution of Ph_2TeCl_2 (123 mg, 0.35 mmol) in dry CH_2Cl_2 (4 mL) in a Teflon bottle. After the reaction mixture was stirred overnight at room temperature, it was transferred into the NMR tube fitted with a Teflon insert to monitor the reaction by ^{19}F NMR spectroscopy. The solution was still colorless at this stage. The ^{19}F NMR spectrum showed the formation of fluorophenyltellurium(IV) compounds, such as Ph_2TeF_2 and Ph_2TeFCl, as well as large amounts of unreacted XeF_2, indicating no oxidation had yet occurred. Some of the starting compound, *i.e.* Ph_2TeCl_2, presumably remained unreacted (it is not detectable by ^{19}F NMR spectroscopy). After a few hours, the ^{19}F NMR spectrum of the solution was examined; very small amounts of *cis*-Ph_2TeF_4 were detected along with fluorophenyltellurium(IV) compounds in large amounts. The solution turned yellow after constant stirring for another 10 hours. Examination by ^{19}F NMR spectroscopy confirmed that all phenyltellurium(IV) compounds

were oxidized but the desired product, Ph_2TeF_4, was contaminated with other fluorophenyltellurium(VI) compounds and fluoride impurities.

The reaction was repeated under the same condition described above. However, it was carried out in a glass reaction tube instead of a Teflon bottle. It was clear from the color change of the solution, and evolution of xenon gas, that reaction occurred much faster in the glass tube. After stirring for 3 hours, the ^{19}F NMR spectrum in $CDCl_3$ showed that no *cis*-Ph_2TeF_4 was produced under these conditions and, along with other fluorophenyltellurium(VI) compounds, there were fluoride impurities, such as BF_4^-, generated from the reaction of HF and the glass tube. Recrystallization from CH_2Cl_2 and washing two or three times with acetonitrile gave pure *trans*-Ph_2TeF_4, as confirmed by melting point, ^{19}F, ^{125}Te, ^{13}C NMR, and mass spectrometry.

b. With tetraethylammonium chloride

(1) Reaction between Ph_2TeCl_2 and XeF_2. Solid XeF_2 (13.5 mg, 0.08 mmol) was added to a stirred solution of Ph_2TeCl_2 (14.1 mg, 0.04 mmol) in CH_2Cl_2 in a Teflon bottle. Then Et_4NCl (0.66 mg, 0.004 mmol) was added to the solution with continuous stirring. The colorless solution rapidly turned yellow with vigorous gas evolution. When the gas no longer evolved, the solution turned back to colorless again within 10 minutes. The ^{19}F NMR spectrum of the solution in $CDCl_3$ revealed the formation of ~95% *trans*-Ph_2TeF_4 and very small amounts of HF. Evaporation of the solvent gave a white solid. It was washed with cold acetonitrile once and kept in a Teflon bottle. After several days, the ^{13}C NMR spectrum, recorded in CD_2Cl_2, again confirmed the presence of pure *trans*-Ph_2TeF_4. Colorless crystals of *trans*-Ph_2TeF_4 were formed by slow evaporation of dichloromethane solvent. Crystals of *trans*-Ph_2TeF_4 kept in a Teflon bottle are stable indefinitely.

This experiment was repeated in order to record ^{19}F NMR spectra at each stage with slight modification. Solid XeF_2 (40.6 mg, 0.24 mmol) was dissolved in CD_2Cl_2 in a glass NMR tube. The ^{19}F NMR spectrum of the XeF_2 solution in CD_2Cl_2 showed a singlet at -175 ppm with ^{129}Xe-satellites, [$J(^{129}Xe\text{-}F)$ = 5600 Hz], which is in good agreement with a literature value; δF = -175 ppm, $J(^{129}Xe\text{-}F)$ = 5580 Hz in $CDCl_3$ (59). Then solid Et_4NCl (39.7 mg, 0.24 mmol) was added to the solution in the NMR tube and dissolved by shaking. There was no reaction between XeF_2 and Et_4NCl, as judged by ^{19}F NMR spectroscopy, except for the formation of small amounts of HF, which could be formed by the reaction of XeF_2 with traces of moisture in $CDCl_3$ or Et_4NCl. Formation and identification of fluoride impurities will be discussed in detail in section 1-A-4 in chapter IIIA. When solid Ph_2TeCl_2 (41.7 mg, 0.12 mmol) was directly added to the NMR tube, which contained the mixture of XeF_2 and Et_4NCl in CD_2Cl_2, a rapid reaction took place as the solution slowly turned pale yellow. After a few minutes, the rate of gas evolution decreased but the solution stayed yellowish. Further observations by ^{19}F NMR spectroscopy were as follows:

1. All xenon difluoride disappeared and more HF formed. About 50% of fluorophenyltellurium(VI) compounds, such as $Ph_2TeF_2Cl_2$ and Ph_2TeF_3Cl, were formed within 30 minutes, and the rest was fluorophenyltellurium(IV) compounds, such as Ph_2TeF_2 and Ph_2TeFCl.

2. As the concentration of fluorophenyltellurium(IV) compounds was decreased, more fluorophenyltellurium(VI) compounds were formed. It was also observed that $Ph_2TeF_2Cl_2$ was fluorinated to give more Ph_2TeF_3Cl and eventually *trans*-Ph_2TeF_4.

The solution was then kept in a Teflon bottle for a few days without changing any condition. The ^{19}F NMR examination of the solution after 3 days revealed that the solution contained mostly *trans*-Ph_2TeF_4 and trace amounts of Ph_2TeF_3OH. *trans*-

Ph_2TeF_4 was removed by recrystallization from CH_2Cl_2 in an effort to isolate Ph_2TeF_3OH from the mixture. However, the remaining solution did not contain any Ph_2TeF_3OH as judged by ^{19}F NMR spectroscopy; instead, it only contained small amounts of *trans*-Ph_2TeF_4 and BF_4^-.

(2) Reaction between Ph_2Te and XeF_2. Solid xenon difluoride (30.5 mg, 0.18 mmol) was added to a solution of diphenyltelluride(II) in methylene chloride (0.5 mL containing 0.18 mmol Ph_2Te) at room temperature in a Teflon bottle. As the mixture was stirred xenon gas was evolved and the solution became yellowish colored. The reaction was monitored by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of the solution in 50% CD_3CN in CH_2Cl_2 showed that the stoichiometric amount of xenon difluoride used was all consumed within 5 minutes to produce difluorodiphenyltellurium(IV), Ph_2TeF_2, in high yield as determined by ^{19}F NMR integration.

To the solution of difluorodiphenyltellurium(IV) in the NMR tube (0.5 mL CH_2Cl_2 and 0.5 mL CD_3CN containing 0.18 mmol Ph_2TeF_2) an additional equivalent of solid xenon difluoride (30.5 mg, 0.18 mmol) was added. The reactants were mixed by shaking the NMR tube occasionally, but the reaction did not take place even after 40 minutes, as monitored by ^{19}F NMR spectroscopy. The concentration of difluorodiphenyl-tellurium(IV) and xenon difluoride had not changed even after 1 hour. However, when solid Et_4NCl (2.98 mg, 0.018 mmol) was directly added to the solution in the NMR tube, a rapid reaction took place, as judged by xenon gas evolution. The ^{19}F NMR examination of the solution after 5 minutes showed that all the xenon difluoride used was consumed to produce a mixture of *cis- and trans*-Ph_2TeF_4 and *trans*-Ph_2TeF_3OH.

The effect of temperature on this reaction was also studied. Solid XeF_2 (20.3 mg, 0.12 mmol) was added to a solution of Ph_2TeF_2 (38.4 mg, 0.12 mmol) in methylene

chloride with catalytic amounts of Et_4NCl (~ 10% of Ph_2TeF_2). The reaction mixture was stirred at -35 °C for 2 hours, but there was no reaction as judged by the absence of any color change. Xenon gas evolved when the temperature reached at least 15 °C. It was found that below room temperature the reaction was extremely slow.

c. With tetrabutylammonium fluoride

(1) Reaction between Ph_2TeCl_2 and XeF_2. Solid XeF_2 (20.0 mg, 0.12 mmol) was added to a suspension of Ph_2TeCl_2 (21.2 mg, 0.06 mmol) in CH_3CN (2.5 mL) in a Teflon bottle (Ph_2TeCl_2 is insoluble in CH_3CN solvent). The reaction mixture was stirred vigorously for few minutes, but no reaction occurred, as judged by absence of color change. When tetrabutylammonium fluoride (~0.12 mmol) was syringed into the reaction mixture, the solution quickly turned yellow with xenon gas evolution. In addition, it was noticed that no solid particles remained at this stage, probably because undissolved Ph_2TeCl_2 in CH_3CN reacted with XeF_2 rapidly in the presence of Bu_4NF. The solution became colorless (or very faint yellow) in ~30 minutes. The ^{19}F NMR examination of the solution at this stage revealed a mixture of *cis*-Ph_2TeF_3Cl (major) and *trans*-Ph_2TeF_4. On further stirring, the solution mainly produced *trans*-Ph_2TeF_4, as judged by ^{19}F NMR spectroscopy (structural details and yield of the reaction will be discussed in chapter III).

Small amounts of fluoride impurities such as SiF_6^{2-} and FHF^- were produced along with *trans*-Ph_2TeF_4.

(2) Reaction of a mixture of Ph_2TeCl_2, Ph_2TeFCl, and Ph_2TeF_2 with XeF_2. The reaction of Ph_2TeCl_2 (30 mg, 0.09 mmol) with excess NaF in CH_3CN produced a mixture of Ph_2TeFCl and Ph_2TeF_2 (also some unreacted Ph_2TeCl_2). The solid

XeF_2 (~30 mg, 0.18 mmol) was added to this mixture. When Bu_4NF (~0.10 mmol) was added, the solution turned yellow, with Xe gas evolution, then back to colorless. Analysis of ^{19}F NMR spectra revealed the formation of Ph_2TeF_3Cl and *trans*-Ph_2TeF_4 and eventually *trans*-Ph_2TeF_4 only.

d. With chlorodiphenyliodide

Solid Ph_2ICl (5.38 mg, 0.02 mmol) was added to a solution of Ph_2TeCl_2 (63.5 mg, 0.18 mmol) in CH_2Cl_2 in a Teflon bottle with constant stirring. After Ph_2ICl had dissolved, solid XeF_2 (59.3 mg, 0.35 mmol) was added to the reaction mixture. The solution became pale yellow after ~4 hours. The ^{19}F NMR spectrum at this stage showed the formation of fluorophenyltellurium(IV) compounds in large amounts. The reaction was complete on further stirring overnight.

e. With water

H_2O (0.90 mL, 0.05 mmol) was syringed into a solution of Ph_2TeCl_2 (17.6 mg, 0.05 mmol) in CD_2Cl_2 (1 mL) in a Teflon bottle. Solid XeF_2 (16.9 mg, 0.10 mmol) was then added to the solution mixture of Ph_2TeCl_2 and H_2O in CD_2Cl_2 with constant stirring. The ^{19}F NMR examination after 3 hours revealed that all XeF_2 used was consumed, but *cis*- and *trans*-Ph_2TeF_4 were not formed. Instead, fluorophenyltellurium(IV) compounds and various fluoride impurities, as well as small amounts of $PhTeF_4Cl$, were present.

For comparison, exactly the same quantities of reactants (*i.e.* Ph_2TeCl_2 and XeF_2) as above were prepared for two other experiments; one with a Et_4NCl catalyst and the other without any catalyst. In the reaction without any catalyst, oxidative fluorination

did not occur even after 3 hours, *i.e.* no formation of Ph_2TeF_4, as examined by ^{19}F NMR spectroscopy. However, the reaction with Et_4NCl produced *trans*-Ph_2TeF_4 (90%) and Ph_2TeF_3OH (10%), as confirmed by ^{19}F NMR integration. Results obtained from the reaction without any catalyst were similar to those of the reaction with water, thereby confirming water itself does not act as a catalyst in oxidative fluorination.

f. Reactions of *trans*-Ph_2TeF_4 with Lewis acids

A 10-fold excess of PF_5 (0.80 mmol) was condensed onto a solution of *trans*-Ph_2TeF_4 (28.6 mg, 0.08 mmol) in CH_2Cl_2 at -196 °C. The reaction mixture was warmed to room temperature with constant stirring. After 20 minutes, excess PF_5 was removed under vacuum. A mixture of some white and pale-yellow oily solid was formed on the bottom of the reaction tube. It was filtered and identified as a mixture of Ph_2TeF_4 and Ph_2Te by mass spectrometry: m/z 360 (M^+, $Ph_2TeF_4^+$); m/z 284 (M^+, Ph_2Te^+), respectively, and the ^{19}F NMR spectrum in excess $CDCl_3$ confirmed that it was *trans*-Ph_2TeF_4. The ^{19}F NMR spectrum of the solution showed only peaks due to PF_6^-. The examination of the solution kept in the glass NMR tube for 3 days revealed the appearance of *trans*-Ph_2TeF_4. Treating with NaF gave more *trans*-Ph_2TeF_4. The reaction was repeated several times with a slight excess of BF_3 or PF_5. However, the formation of a cation $Ph_2TeF_3^+$ was not detected, probably due to rapid fluorine exchange between $Ph_2TeF_3^+$ and *trans*-Ph_2TeF_4 (to be discussed further in section 1-B-2 in chapter IIIA) and the addition of Et_4NCl to the reaction mixture of *trans*-Ph_2TeF_4 with BF_3 or PF_5 in a 1:1 molar ratio always produced nearly pure *trans*-Ph_2TeF_4 with small amounts of fluoride impurities.

C. Hydrolysis of fluorophenyltellurium(VI) compounds

1. Hydrolysis of trans-Ph_2TeF_4

Previous work in our laboratory showed that the hydrolysis of *trans*-Ph_2TeF_4 was very slow; the reaction of *trans*-Ph_2TeF_4 with H_2O in CH_3CN at 25 °C gave a low yield of Ph_2TeF_3OH (20% after 5 days) (60).

The reaction was modified to improve the yield of Ph_2TeF_3OH. A 5-fold excess of tetrapropylammonium hydroxide was added to a solution of *trans*-Ph_2TeF_4 in CH_2Cl_2 and mixed by shaking the reaction tube. All *trans*-Ph_2TeF_4 was hydrolyzed within 2 days and examination by ^{19}F NMR spectroscopy revealed 81% of Ph_2TeF_3OH and 19% of $Ph_2TeF_2(OH)_2$. The assignment of $Ph_2TeF_2(OH)_2$ is made on the basis of ^{19}F and ^{125}Te NMR spectroscopy (details in section 1-B-c in chapter IIIA). This assignment was strongly supported by further hydrolysis reaction of Ph_2TeF_3OH; when more Pr_4NOH was added to the mixture, the ^{19}F NMR spectrum in D_2O showed that the amount of $Ph_2TeF_2(OH)_2$ was largely increased relative to that of Ph_2TeF_3OH.

2. Hydrolysis of mer-Ph_3TeF_3

Crystals of *mer*-Ph_3TeF_3 kept in a Teflon bottle are stable. However, the solution of *mer*-Ph_3TeF_3 in organic solvent in a glass NMR tube was often accompanied by a hydrolysis product, Ph_3TeF_2OH, as well as other fluoride impurities. Ph_3TeF_2OH was also observed as a minor component in samples of *cis*-F_2TePh_3Cl, $Ph_3TeF_2^+PF_6^-$, and Ph_4TeF_2 (60). Crystals of Ph_3TeF_2OH were grown from dichloromethane solution and its solid state structure was determined by X-ray crystallography (60). The results of ^{19}F

NMR and mass spectrometry (m/z 416, M^+; m/z 399, $[M\text{-}OH]^+$; m/z 339, $[M\text{-}Ph]^+$) were consistent with the structure obtained by X-ray analysis. The maximum concentration of Ph_3TeF_2OH in samples of *mer*-Ph_3TeF_3 was estimated to be 19.6% as determined by ^{19}F NMR integration. The solution of Ph_3TeF_2OH often showed broad fluorine resonances in its ^{19}F NMR spectrum, particularly that for fluorine *trans* to phenyl group; however, treatment with NaF or Et_4NCl stopped the exchange process.

The attempted stereoselective synthesis of *cis*- and *trans*-F_2TePh_3OH from the reaction of $Ph_3TeF_2^+PF_6^-$ with tetraalkylammonium hydroxide was not successful: excess PF_5 was condensed onto a solution of the purified sample of *mer*-Ph_3TeF_3 (59.8 mg, 0.14 mmol) in CH_2Cl_2 at -196 °C. When the reaction mixture was warmed to room temperature, some white fumes (probably some PF_5 or POF_3) escaped from the Rotaflo stopcocks (these stopcocks often showed problems of leaking). The reaction mixture was stirred for 20 minutes and the volatile materials were removed under vacuum. The ^{19}F NMR spectrum of the solution showed a slightly broad singlet at -117 ppm with ^{125}Te-satellites, J(Te-F) = 1700 Hz, presumably due to the exchange between $Ph_3TeF_2^+$ and *mer*-Ph_3TeF_3:

1. ^{19}F NMR data of $Ph_3TeF_2^+PF_6^-$; δF^b = -122 ppm and J(Te-F^b) = 1600 Hz.
2. ^{19}F NMR data of Ph_3TeF_3; δF^b = -98 ppm and J(Te-F^b) = 2090 Hz.

Presumably, some *mer*-Ph_3TeF_3 remained unreacted, which may exchange with the cation formed, as implied by the broad averaged ^{19}F NMR resonance. Addition of tetrapropylammonium hydroxide (0.14 mmol) to this solution produced a new small broad peak at -91 ppm in the ^{19}F NMR spectrum. However, mainly because of the large amount of the unreacted *mer*-Ph_3TeF_3, the yield was very low and thus its identity was not confirmed. From the chemical shift correlation observed in some octahedral fluorophenyltellurium(VI) compounds, it is suggested to be the kinetically stable *trans*-F_2TePh_3OH. The ^{19}F NMR examination after 4 days revealed the disappearance of this

peak, and only *mer*-Ph_3TeF_3 was observed. The reaction was not repeated because of difficulties encountered when an old cylinder of gaseous PF_5 in our laboratory was used.

D. Preparation of fluorophenyltin(IV) compounds

1. Fluorotriphenylstannane(IV), Ph_3SnF

Ph_3SnF was prepared most conveniently from Ph_3SnCl and $KF{\cdot}2H_2O$ in CH_2Cl_2 according to the method of Holmes (47), who reported the ^1H NMR spectra of the neutral HMPA adduct, $Ph_3SnF{\cdot}HMPA$, and suggested a five-coordinate structure based on NMR results. Ph_3SnF decomposed at 355 °C (lit. m.p. 350 °C (50) and its mass spectrum showed strong fragments due to Ph_3SnF^+, M^+, and Ph_2SnF^+, $[M\text{-}C_6H_5]^+$ at m/z 351 and m/z 293, respectively.

The ^{19}F NMR spectrum of the $Ph_3SnF{\cdot}HMPA$ adduct in DMSO-d_6 revealed a single resonance at -174.2 ppm with $J(^{119}Sn\text{-}F)$ of 2040 Hz and $J(^{117}Sn\text{-}F)$ of 1949 Hz. The ^{119}Sn NMR spectrum of $Ph_3SnF{\cdot}HMPA$ was recorded in both inert (CD_2Cl_2) and donor (DMSO-d_6) solvents. The shift difference in the two solvents was only 0.6 ppm. NMR results will be discussed in detail in chapter III.

Solid Ph_3SnF (60.0 mg, 0.16 mmol) readily reacted with a solution of phosphoryl chloride, $POCl_3$, (0.20 mmol) in CH_2Cl_2 (2 mL). There was no evidence for the formation of the neutral adduct, $Ph_3SnF{\cdot}POCl_3$, as judged by ^{19}F NMR spectroscopy; instead, $P(O)FCl_2$, $P(O)F_2Cl$, $P(O)F_2(OH)$, and $P(O)F(OH)_2$ were formed. The ^{19}F NMR data of the products are in good agreement with literature values (61). The ^{19}F NMR examination of the mixture in CH_2Cl_2 after 7 days showed the existence of $P(O)F(OH)_2$ only, probably due to the further hydrolysis reaction.

2. *Tetrabutylammonium(1+) difluorotriphenylstannate(1-), $Bu_4N^+Ph_3SnF_2^-$*

a. Preparation of $Bu_4N^+Ph_3SnF_2^-$

$Bu_4N^+Ph_3SnF_2^-$ was prepared according to the method of Holmes (47) with slight modifications. A slight excess of Bu_4NF (0.40 mmol) was added to a suspension of Ph_3SnF (120 mg, 0.33 mmol) in CH_2Cl_2 (4 mL) with continuous shaking until a clear solution formed. Evaporation of dichloromethane solution gave colorless crystals of $Bu_4N^+Ph_3SnF_2^-$. Its melting point (155 °C) agrees well with the literature m.p. value for $Et_4N^+Ph_3SnF_2^-$; 157-158 °C (47), and its mass spectrum of the crystal showed a strong fragment assigned to Ph_3SnF^+ at m/z 370. The compound dissolves appreciably in most organic solvents. The ^{19}F NMR chemical shift and ^{119}Sn-F coupling constant of $Bu_4N^+Ph_3SnF_2^-$ have been measured in both inert (CD_2Cl_2) and donor (CD_3CN, DMSO-d_6) solvents. The recrystallized sample of $Bu_4N^+Ph_3SnF_2^-$ always showed three pairs of satellite peaks due to coupling to ^{119}Sn (8.6%), ^{117}Sn (7.7%), and ^{115}Sn (0.4%) in its ^{19}F NMR spectrum. The ^{119}Sn NMR spectra were also measured in both inert and donor solvents. However, there were no significant changes in the chemical shifts and coupling constants.

b. Attempted preparation of trifluorotriphenylstannate(2-), $Ph_3SnF_3^{2-}$

Various fluorides were used in attempts to prepare $Ph_3SnF_3^{2-}$ from $Ph_3SnF_2^-$. The ^{19}F and ^{119}Sn NMR chemical shifts and coupling constants of the solution in CD_2Cl_2, CD_3CN, or $CDCl_3$ were examined (details in chapter IIIB). Recrystallization of a mixture

of $Ph_3SnF_2^-$ with excess fluoride from various solvents only produced crystals of $Ph_3SnF_2^-$.

A typical experiment, in which an attempt is made to completely eliminate all traces of water, is as follows: the recrystallized sample of $Ph_3SnF_2^-$ is dried under vacuum for several hours. Potassium fluoride is heated at 100 °C in an oil bath for 1 hour. The mixture of KF and 18-crown-6 ether in a 1:1 molar ratio in CH_3CN is stirred until a clear solution forms. Then P_2O_5 is added to the solution with shaking and the solution decanted. The solution of KF (46.5 mg, 0.80 mmol) in 18-crown-6 ether (211 mg, 0.80 mmol) is added to the solution of $Ph_3SnF_2^-$ in acetonitrile (10 mL) under a nitrogen atmosphere. The solution mixture is stirred overnight and its ^{19}F NMR spectrum is examined. The solution typically contains mainly $Ph_3SnF_2^-$, but the formation of SnF_6^{2-} is also observed.

c. Reaction of $Ph_3SnF_2^-$ with catechol

When the solution of $Bu_4N^+Ph_3SnF_2^-$ (56.7 mg, 0.09 mmol) in CH_2Cl_2 (2 mL) was mixed with catechol, C_6H_4–1,2–$(OH)_2$, (9.90 mg, 0.09 mmol), a white solid continuously precipitated out for 10 minutes. The solid was removed by filtration and identified as Ph_3SnF by the method described previously. The ^{19}F NMR spectrum of the solution at room temperature showed a slightly broad peak with satellite peaks due to coupling with ^{119}Sn and ^{117}Sn. Low temperature ^{119}Sn NMR studies suggest a possible formation of six-coordinate complexs, $Bu_4N^+F_2Ph_3Sn$-O-$C_6H_4(OH)^-$.

3. Fluorochlorotriphenylstannate(1-), Ph_3SnFCl^-

Fluorochlorotriphenylstannate(1-), Ph_3SnFCl^-, prepared by the reaction of Ph_3SnF with Et_4NCl in a 1:1 molar ratio according to the method of Holmes (47), did not give satisfactory NMR results. The ^{19}F NMR spectrum showed a very broad peak without any coupling to tin and the ^{119}Sn NMR spectrum did not even show any peak. Addition of 20 fold excess of Et_4NCl to a suspension of Ph_3SnF in CH_3CN gave a well resolved resonance for Ph_3SnFCl^- in the ^{19}F NMR spectrum with $^{117/119}Sn$-coupled satellites. However, at this stage, the formation of $Ph_3SnF_2^-$ also occurred as a result of a redistribution reaction. This was confirmed by ^{119}Sn NMR examination which revealed the formation of $Ph_3SnCl_2^-$, Ph_3SnFCl^-, and very small amounts of $Ph_3SnF_2^-$.

Ph_3SnFCl^- was also formed by the addition of excess Et_4NCl to the solution of $Bu_4N^+Ph_3SnF_2^-$ in CH_2Cl_2. This reaction was repeated many times by varying the concentrations of Et_4NCl and monitoring each time by ^{19}F NMR spectroscopy. All reactions essentially gave identical results, namely a redistribution reaction. No evidence was found for the formation of the six-coordinate dianion, $Ph_3SnF_2Cl^{2-}$.

4. Fluorination of Ph_2SnCl_2

a. Ph_2SnF_2 and $PhSnF_5^{2-}$

Difluorodiphenylstannane(IV), Ph_2SnF_2, was prepared from Ph_2SnCl_2 and $KF{\cdot}2H_2O$ in CH_2Cl_2, according to the literature method (62) with slight modification. Reaction conditions were similar to those described for the synthesis of Ph_3SnF. It decomposed at ~350 °C without melting (lit. m.p.(62); >340 °C). Its mass spectrum

showed a very strong molecular ion, $Ph_2SnF_2^+$, m/z 312, M^+.

Attempts to prepare $Ph_2SnF_3^-$ and $Ph_2SnF_4^{2-}$ by the addition of various fluorides such as KF, NaF, Bu_4NF, CsF, and K^+FHF^- to the suspension of Ph_2SnF_2 in CH_2Cl_2 or CH_3CN at varing temperatures (~10 °C–35 °C) were all unsuccessful, mainly due to the extreme insolubility of Ph_2SnF_2. Even after prolonged stirring of the reaction mixture in CH_3CN or CH_2Cl_2 for 7 days, most reactants remained insoluble. The ^{19}F NMR spectrum of the filtrate showed an extremely broad peak, barely distinguishable from the baseline, and thus revealed that Ph_2SnF_2 did not unergo complexation with F^- at this stage.

After further stirring of the reaction mixture of Ph_2SnF_2 and excess fluoride in CH_3CN for about a month at room temperature, the ^{19}F NMR spectrum of the solution revealed the formation of $PhSnF_5^{2-}$ and $Ph_3SnF_2^-$ as a result of redistribution and fluoride addition reactions. The formation of $PhSnF_5^{2-}$ was confirmed by its ^{19}F NMR spectrum as well as by low temperature ^{119}Sn NMR spectroscopy at 260 K. By removing crystals of $Ph_3SnF_2^-$ by recrystallization from CH_2Cl_2 solution, the concentration of $PhSnF_5^{2-}$ was increased; however, an attempt to isolate $PhSnF_5^{2-}$ was not successful because fluoride impurities such as SiF_6^{2-} and BF_4^- increased during the recrystallization process.

b. Reaction of Ph_2SnCl_2 with XeF_2

When solid XeF_2 (15.2 mg, 0.09 mmol) was slowly added to a solution of Ph_2SnCl_2 (30.9 mg, 0.09 mmol) and Et_4NCl (1.49 mg) in CH_2Cl_2 (4 mL) with constant stirring, an exothermic reaction occurred and the solution became dark green colored for about 2 to 3 minutes, and then eventually a white solid, which was insoluble in common organic solvents, formed. It dissolved in excess DMSO and its ^{19}F NMR spectrum was identical

with that of the known species, $SnF_5(DMSO)^-$, reported by Dean and Evans (63). Addition of excess Bu_4NF to the white solid gave a mixture of SnF_6^{2-} (54%), $ClSnF_5^{2-}$ (38%), *cis*-$Cl_2SnF_4^{2-}$ (7%), and *trans*-$Cl_2SnF_4^{2-}$ (1%), as examined by ^{19}F NMR spectroscopy. The ^{19}F NMR data agree well with literature values (63).

5. Fluorination with $Bu_4N^+Ph_3SnF_2^-$

a. Preparation of $PhSnF_5^{2-}$

The recrystallized sample of $Bu_4N^+Ph_3SnF_2^-$ (409 mg, 0.65 mmol) was added to a solution of Ph_2SnCl_2 (107 mg, 0.31 mmol) in CH_2Cl_2 (4 mL). The reactants were mixed by shaking the reaction tube. After shaking the reaction mixture for 2 minutes a white precipitate formed, which was insoluble in common organic solvents. The white precipitate was filtered out and weighed (~500 mg). The identity of this solid is not clear, but it had the following properties: it started melting at ~315 °C but decomposed to a dark brown oil at ~400 °C. Its mass spectrum showed fragment ions m/z 293 and m/z 351 for ^{120}Sn, assigned to Ph_2SnF^+ and Ph_3Sn^+, respectively. From the m.p., mass spectrum, and its solubility, the solid is suspected to be a mixture of Ph_2SnF_2 and Ph_3SnF. Furthermore, the ^{19}F NMR spectrum of the filtrate did not exhibit any resonance.

Bu_4NF was added to the precipitate in CH_2Cl_2 until a colorless solution was formed. Examination of the ^{19}F NMR spectrum revealed the formation of $PhSnF_5^{2-}$ as well as $Ph_3SnF_2^-$. Crystals of $Ph_3SnF_2^-$ were obtained by recrystallization from dichloromethane solution.

b. Preparation of Ph_2TeFCl and Ph_2TeF_2

The solution of $Bu_4N^+Ph_3SnF_2^-$ (81.9 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was mixed with a solution of Ph_2TeCl_2 (21.2 mg, 0.06 mmol) in CH_2Cl_2 (2 mL). The solution mixture turned cloudy and a white precipitate formed within a few minutes. The precipitate was filtered out and weighed (~30 mg). It was identified as Ph_3SnF by melting point (decomp. <350 °C) and its chemical reaction. Addition of excess Bu_4NF in $CHCl_3$ to the precipitate gave $Bu_4N^+Ph_3SnF_2^-$, as confirmed by ^{19}F NMR spectroscopy. Examination of the ^{19}F NMR spectra of the filtrate revealed the formation of a mixture of Ph_2TeF_2 and Ph_2TeFCl, as well as some unreacted Ph_2TeCl_2 (<10%), as judged by ^{125}Te NMR spectroscopy. However, Ph_2TeF_2 was formed in high yield when an excess of $Bu_4N^+Ph_3SnF_2^-$ was added to this mixture, as judged by ^{19}F and ^{125}Te NMR spectroscopy.

When the solutions of $Bu_4N^+Ph_3SnF_2^-$ and Ph_2TeCl_2 in CH_2Cl_2 were mixed in a 1:1 molar ratio, the ^{19}F NMR spectrum revealed similar products, *i.e.* the formation of Ph_2TeF_2 and Ph_2TeFCl.

c. Preparation of $Bu_4N^+Ph_2PF_4^-$

The starting compound, Ph_2PF_3, was prepared most conveniently from diphenylchlorophosphine and XeF_2 in CH_2Cl_2, according to the method developed in our laboratory (64), and identified by ^{19}F NMR spectroscopy (65). Crystals of $Bu_4N^+Ph_3SnF_2^-$ (252 mg, 0.40 mmol) were added to a solution of Ph_2PF_3 (84.7 mg, 0.35 mmol) in CH_2Cl_2. A white precipitate formed in the solution mixture. It was filtered out and identified as Ph_3SnF by its chemical reaction as described previously. Examination of

the ^{19}F NMR spectrum of the solution confirmed the formation of *trans*-$Ph_2PF_4^-$. The ^{19}F NMR data obtained for *trans*-$Ph_2PF_4^-$(counter ion Bu_4N^+) were close to those of *trans*-$Ph_2PF_4^-$(counter ion Cs^+) reported by Schmutzler *et al.* (66).

d. Preparation of $P(O)FCl_2$ and $P(O)F_2Cl$

A slight excess of $POCl_3$ was added to a solution of $Bu_4N^+Ph_3SnF_2^-$ in CH_2Cl_2. The ^{19}F NMR spectrum of the solution confirmed the formation of $P(O)FCl_2$ and $P(O)F_2Cl$ (61), as well as small amounts of $P(O)F_2OH$. They were all hydrolyzed to give $P(O)F(OH)_2$ in solution in the glass tube, as described previously in the reaction of Ph_3SnF with $POCl_3$.

e. Reactions of $Ph_3SnF_2^-$ with Ph_3TeCl and Ph_3PF_2

Crystals of $Bu_4N^+Ph_3SnF_2^-$ were added to a solution of Ph_3TeCl or Ph_3PF_2 in a 1:1 molar ratio in CH_2Cl_2, respectively. The ^{19}F NMR spectrum of the mixture of Ph_3TeCl and $Bu_4N^+Ph_3SnF_2^-$ in CD_2Cl_2 showed that the ^{19}F NMR resonance of $Ph_3SnF_2^-$ was slightly broadened, but no other peak was observed at room temperature.

However, the mixture of Ph_3PF_2 and $Bu_4N^+Ph_3SnF_2^-$ showed multiplet ^{19}F NMR resonances due to uncomplexed species. In other words, there is no interaction between two five-coordinate species Ph_3PF_2 and $Ph_3SnF_2^-$.

CHAPTER III

RESULTS AND DISCUSSION

A. fluorophenyltellurium(VI) compounds

I. OXIDATIVE FLUORINATION

Structures of fluorophenyltellurium compounds were determined mainly by ^{19}F and ^{125}Te NMR spectroscopy. In particular, the reaction progress was monitored by ^{19}F NMR as often as possible.

Fluorine occurs in 100% abundance as the isotope ^{19}F which has a nuclear spin of 1/2 (NMR properties of some spin-1/2 nuclei are given in Table 2); therefore, fluorinated tellurium compounds are ideally suited to a study by NMR spectroscopy.

There are two magnetically active (I=1/2) tellurium isotopes, ^{123}Te (0.87%) and ^{125}Te (6.99%), but attention is usually confined to ^{125}Te nucleus owing to its greater sensitivity to NMR detection. Although there is no problem in observing ^{123}Te resonances, the low natural abundance makes the measurement of ^{123}Te resonances unfavorable (see Table 2).

Both ^{123}Te and ^{125}Te nuclei are observed to be coupled to fluorine-19 nucleus in ^{19}F NMR spectra, but they appear as satellite peaks. The appearance of tellurium-coupled satellites in ^{19}F NMR spectra provides a means for studying stereochemical rearrangements and Te-F bond lability.

A. Synthesis of fluorophenyltellurium(IV) compounds

The preparation of fluorophenyltellurium(IV) compounds by the method of Emeleus and Heal (55), who had prepared the first organotellurium(IV) fluorides, did not give a satisfactory yield of the products and also created some experimental difficulties. Furthermore, even with the modified method (56), the preparation of Ph_3TeF required several experimental procedures and produced an impure product in high yield (12).

TABLE 2

NMR properties of some spin-1/2 nuclei (78)

Isotope	Natural Abundance N / %	Magnetic moment μ / μN	Magnetogyric ratio g / 107 rad T^{-1} S^{-1}	NMR frequency MHz	Standard	Receptivity D^P	Receptivity D^C
^{1}H	99.985	4.8371	26.7510	100.000	Me_4Si	1.00	5.7×10^{3}
^{13}C	1.108	1.2162	6.7263	25.145	Me_4Si	1.8×10^{-4}	1.00
^{19}F	100	4.5506	25.1665	94.094	CCl_3F	0.8328	4.7×10^{3}
^{29}Si	4.70	-0.9609	-5.3141	19.8672	Me_4Si	3.7×10^{-4}	2.09
^{31}P	100	1.9581	10.829	40.4807	H_3PO_4	0.0663	3.8×10^{2}
^{77}Se	7.58	0.9223	5.101	19.0915	Me_2Se	5.3×10^{-4}	2.98
^{119}Sn	8.58	-1.803	-9.971	37.291	Me_4Sn	4.5×10^{-3}	25.2
^{125}Te	6.99	-1.528	-8.453	31.550	Me_2Te	2.21×10^{-3}	12.5
^{129}Xe	26.44	-1.338	-7.400	27.661	$XeOF_4$	5.6×10^{-3}	31.8

D^p is the receptivity relative to that of ^{1}H and **D^c** is the receptivity relative to that of ^{13}C.

Thus, a convenient high yield synthesis of some fluorophenyltellurium(IV) compounds will be discussed in this section. A new compound, Ph_2TeFCl, is also prepared in this manner.

1. Fluorination with COF_2

Previous studies by Shreeve and her co-workers have shown that carbonyl fluoride, COF_2, is a useful reagent for displacing either hydrogen by fluorine atom from P-H, N-H, and C-H bonds (57), or oxygen by fluorine atom from the oxides of V, Nb, Ta, Cr, Mo, W, B, Si, Ge, Sn, P, Se, Te, I, and U (67).

Since COF_2 has been demonstrated to be a highly versatile reagent for introducing fluorine into a variety of different molecules containing main group elements as well as transition metal oxides, it might also be used for the formation of Te-F bond from tellurium(IV) chlorides. The preparation of fluorophenyltellurium(IV) compounds has not been achieved with a fluorinating agent as mild as carbonyl fluoride. In particular, the preparation of Ph_3TeF according to the literature methods (55,56) in an ordinary glass reaction tube always produced the impure product, $Ph_3Te^+BF_4^-$, in high yield (>70%) with some experimental difficulties to isolate Ph_3TeF even in small amounts (12).

Chlorotriphenyltellurium(IV), Ph_3TeCl, reacts with carbonyl fluoride in a suitable solvent to yield fluorotriphenyltellurium(IV) according to equation [23]:

$$2\,Ph_3TeCl + COF_2 \longrightarrow 2\,Ph_3TeF + COCl_2\,(COFCl) \qquad [23]$$

The formation of Ph_3TeF is confirmed by ^{19}F and ^{125}Te NMR spectroscopy, but Te-F coupling has not been observed; δF = -137 ppm and $\delta^{125}Te$ = 753 ppm. The by-products, such as COFCl and $COCl_2$, or excess COF_2 can be detected by ^{19}F or ^{13}C NMR spectroscopy. Oxidative fluorination did not occur on addition of excess carbonyl fluoride to Ph_3TeF, as illustrated in equation [24]:

$$Ph_3TeF + \text{excess } COF_2 \xrightarrow{\sim\sim} Ph_3TeF_3 \qquad [24]$$

Ph_3TeF is oxidized to give *mer*-Ph_3TeF_3 by the addition of a stoichiometric amount of XeF_2.

In solution (CH_2Cl_2 or $CHCl_3$), Ph_3TeF reacts rapidly with glass to form $Ph_3Te^+BF_4^-$. The solution of Ph_3TeF in $CHCl_3$ after several weeks produced $Ph_3Te^+BF_4^-$ in almost quantitative yield and, furthermore, the solution did not contain any trace of Ph_3TeF, as examined by ^{19}F NMR spectroscopy. It is thus necessary to minimize the contact of Ph_3TeF and its solution with glass. Crystals of fluorotriphenyl-tellurium(IV), Ph_3TeF, can be stored in a Teflon bottle to prevent the reaction with glass. However, even with the use of Teflon equipment, our Ph_3TeF was always contaminated with small amounts of $Ph_3Te^+BF_4^-$; it could have been produced by using glass equipment (glass vacuum manifold, NMR tubes, or glass pipet), and which, in turn, might catalyze rapid intermolecular fluorine exchange in Ph_3TeF, as illustrated in equation [25]:

$$Ph_3TeF + Ph_3Te^+BF_4^- \rightleftharpoons [Ph_3Te\text{-}F\text{-}TePh_3]^+BF_4^- \quad [25]$$

On the basis of NMR analysis, it was suggested by McWhinnie and Mallaki (56) that fluorotriphenyltellurium(IV), Ph_3TeF, could be an ionic species since neither ^{19}F nor ^{125}Te NMR spectra revealed the presence of Te-F coupling, each giving a single peak in chloroform or dichloromethane solution, which is quite consistent with formation of an ionic compound.

However, it does not eliminate the possibility of formation of covalent Ph_3TeF because if the exchange process is too rapid in solution on the NMR time scale, as shown in equation [25], then Te-F coupling may not be observed. In fact, examination of the ^{19}F NMR spectrum of Ph_3TeF in dichloromethane solution revealed that, as the concentration of $Ph_3Te^+BF_4^-$ increases, the half height width of fluorine resonance of Ph_3TeF becomes larger, *i.e.* the rate of the intermolecular fluorine exchange becomes faster as the amount of $Ph_3Te^+BF_4^-$ increases. This is illustrated in Table 3.

The attempted separation of Ph_3TeF from the mixture by recrystallization or TLC technique resulted in the formation of $Ph_3Te^+BF_4^-$. Triphenyltellurium(1+) tetrafluoroborate(1-), $Ph_3Te^+BF_4^-$, can easily be separated from the mixture by TLC technique using acetonitrile as solvent.

Carbonyl fluoride also reacts with Ph_2TeCl_2 to give the new compound, fluorochlorodiphenyltellurium(IV), Ph_2TeFCl, in ~80% yield, as described in equation [26]:

$$Ph_2TeCl_2 + COF_2 \longrightarrow Ph_2TeFCl + COFCl \quad [26]$$

TABLE 3

Analysis of ^{19}F NMR spectrum of Ph_3TeF in CD_2Cl_2[a]

Intensity (%) ^{19}F NMR peak ratio		Half height width of Ph_3TeF peak
Ph_3TeF[b]	$Ph_3Te^+BF_4^-$	$\Delta W1/2$ (Hz)
67.2	32.8	20
39.2	60.8	40
35.8	64.2	50

[a] Values are taken from the three different samples.

[b] Exchange broadened resonances of Ph_3TeF, probably exchanging with $Ph_3Te^+BF_4^-$.

Ph_2TeF_2 was also formed as a minor component in this reaction. The formation of Ph_2TeFCl was confirmed by a singlet ^{19}F NMR resonance with ^{125}Te-coupled satellites and a doublet in the ^{125}Te NMR spectrum. The yield of the reaction and NMR data are given in Table 4. Addition of a large excess of NaF to the mixture in CH_2Cl_2, followed by filtration of excess NaF, gave mainly Ph_2TeF_2, as confirmed by ^{19}F NMR spectroscopy.

Naumann and Herberg (68) reported oxidative fluorination of $(CF_3)_2Te$ by ClF. Addition of 1 equivalent of ClF to the solution of $(CF_3)_2Te$ in CH_3CN at -78 °C gave a mixture of $(CF_3)_2TeF_2$, $(CF_3)_2TeFCl$, and $(CF_3)_2TeCl_2$, and eventually $(CF_3)_2TeF_2$ was formed on addition of one more equivalent of ClF. Difluorobis(perfluoromethyl)-tellurium(IV), $(CF_3)_2TeF_2$, was also prepared by Gombler (69); the reported ^{19}F NMR data are identical with those reported by Naumann and Herberg.

It should be noted that replacement of fluorine by chlorine from R_2TeF_2 ($R=C_6H_5$ and CF_3) results in a downfield shift of ^{19}F NMR resonances:

$$Ph_2TeF_2\ (\delta\ -124.6\ ppm) \longrightarrow Ph_2TeFCl\ (\delta\ -108.7\ ppm)$$

$$(CF_3)_2TeF_2\ (\delta\ -125.3\ ppm) \longrightarrow (CF_3)_2TeFCl\ (\delta\ -104\ ppm)$$

The Te-F coupling constant of $(CF_3)_2TeFCl$ is not available in the references cited above (68,69) for comparison, but the magnitude of the Te-F coupling constant of Ph_2TeFCl falls within the range expected for Te(IV) fluorides.

TABLE 4

The ^{19}F and ^{125}Te NMR data of fluorophenyltellurium(IV) compounds and their yields[a] from reaction [26]

Compound	δF	δ(^{125}Te)	J(^{125}Te-F)	% Yield
Ph_2TeCl_2		916		10
Ph_2TeF_2[b]	-128 (-124.6)	1120	545 (566.2)	12
Ph_2TeFCl[c]	-108 (-108.7)	1068	585 (584.0)	78

[a] Chemical shifts in ppm, coupling constants in Hz, and solvent is CD_2Cl_2: values in parentheses were obtained in CD_3CN solvent.

[b] Lit. value (58); δF = -126.7 ppm, J(^{125}Te-F) = 540 Hz.

[c] This work.

2. *Fluorination with Ph_3TeF*

Since Ph_3TeF shows such a strong tendency to lose its fluorine in contact with glass to form $Ph_3Te^+BF_4^-$, it could be used as a fluoride ion donor.

Phosphorus pentafluoride, PF_5, is a Lewis acid whose acceptor properties are known to be comparable to those of BF_3 (70), and thus the reaction of PF_5 with Ph_3TeF is expected to yield an ionic species $Ph_3Te^+PF_6^-$ which should be almost as stable as $Ph_3Te^+BF_4^-$. The reaction of Ph_3TeF with PF_5 in CH_2Cl_2 produced a stable white solid which was identified as triphenyltellurium(1+) hexafluorophosphate(1-), $Ph_3Te^+PF_6^-$. This salt was purified by TLC on a silica gel plate from a mixture of CH_2Cl_2:CH_3CN (1:1, v:v). The solution of $Ph_3Te^+PF_6^-$ in CD_3CN exhibits a doublet ^{19}F resonance at -71.1 ppm with $J(^{31}P\text{-}F)$ = 720 Hz and a singlet ^{125}Te resonance at +769 ppm. The ^{19}F NMR parameters of hexafluorophosphate(1-) anion, PF_6^-, are relatively insensitive to the cation. The ^{13}C NMR examination of $Ph_3Te^+PF_6^-$ revealed the equivalence of the three phenyl substituents (Table 5).

The attempted preparation of five-coordinate fluorophenylsilicate anions from the corresponding phenylsilanes and Ph_3TeF was unsuccessful. However, the addition of Ph_3TeF to phenylsilanes caused significant line broadening with loss of ^{29}Si-F coupling in their ^{19}F NMR spectra, most likely due to the rapid exchange between four- and five-coordinate silicon species, *e.g.* equation [27]:

$$PhSiF_3 + Ph_3TeF \rightleftharpoons Ph_3Te^+PhSiF_4^- \qquad [27a]$$

$$PhSiF_3 + PhSiF_4^- \rightleftharpoons F_3PhSi\text{-}F\text{-}SiPhF_3^- \qquad [27b]$$

TABLE 5

The carbon-13 NMR data of $Ph_3Te^+PF_6^-$ in CD_2Cl_2

Position of carbons	$\delta(^{13}C)$ in ppm	$J(^{125}Te\text{-}^{13}C)$ in Hz
ipso (C-1)	123.18	240.10
ortho (C-2)	135.55	34.51
meta (C-3)	132.18	29.76
para (C-4)	133.94	28.76

As illustrated in Figure 3, the addition of Ph_3TeF to the solution of $PhSiF_3$ resulted in considerable line broadening ($\Delta W_{1/2}$ = 48 Hz) with loss of ^{29}Si-F coupling. In addition, the ^{19}F NMR spectrum of the mixture did not show a resonance due to Ph_3TeF species. Similar fluorine exchange between four- and five-coordinate silicon species occurs in the $MeSiF_3$–$MeSiF_4^-$ system through a fluorine-bridged intermediate (18).

Klanberg and Muetterties reported the preparation of five-coordinate fluorophenylsilicate anions with tetraalkylammonium as cations and studied their dynamic properties by temperature-dependent ^1H and ^{19}F NMR spectroscopy (71). Tetrafluorophenylsilicate(1-) anion, $PhSiF_4^-$, was shown to have fluorine equivalence throughout a wide temperature range in ^{19}F NMR spectra. Intramolecular ligand exchange has been proposed for $PhSiF_4^-$ to explain the observed equivalence of the ^{19}F NMR signal and retention of ^{29}Si-F coupling, as found in SiF_5^- (71) and $MeSiF_4^-$ (72). To date, low temperature spectra with providing evidence for non-equivalent fluorines have not been observed, although SiF_5^- and $PhSiF_4^-$ are found to be nearly trigonal bipyramidal in the solid state, as determined by X-ray crystallography (73,74).

3. Fluorination with $Bu_4N^+Ph_3SnF_2^-$

Tetraalkylammonium difluorotriphenylstannates, $R_4N^+Ph_3SnF_2^-$, have been prepared by Holmes and co-workers (47).

This work found that $Ph_3SnF_2^-$ is an excellent source of fluoride ion because of the formation of an insoluble white solid Ph_3SnF as it donates a fluoride ion according to equation [28]:

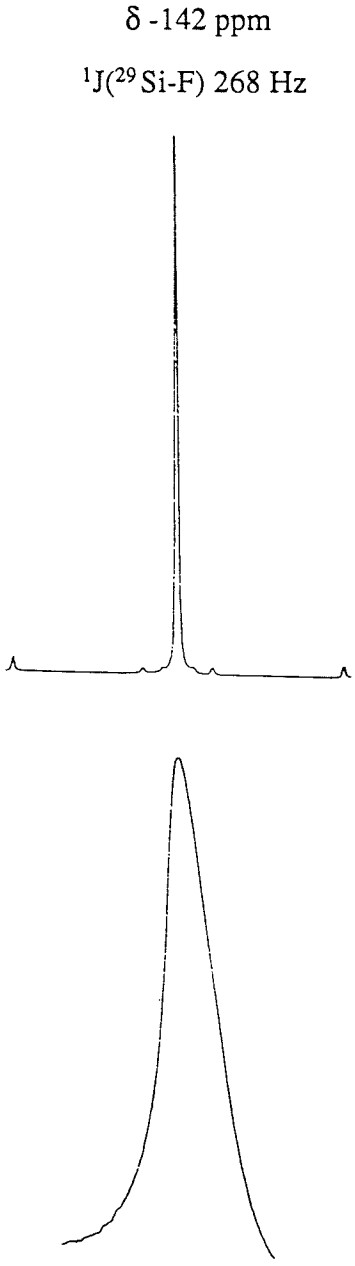


Figure 3. ^{19}F NMR spectrum of $PhSiF_3$ in CD_2Cl_2 (top) and a mixture of $PhSiF_3$ and Ph_3TeF (1:1) in CD_2Cl_2 at room temperature (bottom): addition of Ph_3TeF caused a significant line broadening with loss of ^{29}Si-satellites: $\Delta W_{1/2}$ increases from 2 Hz (top) to 48 Hz (bottom).

$$Ph_3SnF_2^- + A \longrightarrow Ph_3SnF\downarrow + AF^- \qquad [28]$$

Ph_2TeCl_2 reacts with $Ph_3SnF_2^-$, as judged by the immediate precipitation of Ph_3SnF, to produce a mixture of Ph_2TeF_2 and Ph_2TeFCl:

$$Ph_2TeCl_2 \xrightarrow[CH_2Cl_2]{Ph_3SnF_2^-} Ph_2TeF_2 + Ph_2TeFCl + Ph_3SnF\downarrow + Cl^- \qquad [29]$$

Addition of a large excess of $Ph_3SnF_2^-$ produces Ph_2TeF_2 in high yield.

Fluorophenyltellurium(IV) compounds were characterized by ^{19}F NMR spectroscopy. The white precipitate was confirmed to be Ph_3SnF by its m.p. (decomp. <350 °C) and chemical reaction with Bu_4NF to form $Bu_4N^+Ph_3SnF_2^-$ (further details will be discussed in chapter IIIB).

However, the insoluble Ph_3SnF did not precipitate out in the following 1:1 reaction mixtures: (1) $Ph_3SnF_2^-$ and Ph_3TeCl, and (2) $Ph_3SnF_2^-$ and Ph_3PF_2. The ^{19}F NMR spectrum of the first mixture in CD_2Cl_2 revealed that there is slow fluorine exchange at room temperature, as shown by a slightly broad ^{19}F NMR peak of $Ph_3SnF_2^-$, but no other peak was observed to indicate the formation of Te-F bond.

The ^{19}F NMR spectrum of the mixture of $Ph_3SnF_2^-$ and Ph_3PF_2 showed multiplets due to individual species and no exchange was observed.

4. Fluoride impurities

As discussed in the previous section I-A-2, there is a noticeable broadening of the ^{19}F NMR resonance of Ph_3TeF as the formation of fluoride impurities (*e.g.* BF_4^-) increased (Table 3). Presumably, Lewis acid fluorides (*e.g.* BF_3) might be responsible for the line broadening by causing fluorine exchange in Ph_3TeF, as shown in equation [25].

These fluoride impurities are found to be responsible for isomerization and fluorine exchange in octahedral fluorophenyltellurium(VI) compounds. Thus it is appropriate to discuss the formation and identification of all the possible fluoride impurities prior to the discussion of octahedral Te(VI) compounds. ^{19}F NMR spectroscopy can be used to conveniently monitor the presence of these impurities.

a. The source of a Lewis acid HF

1. An early study (75) in our laboratory has shown that xenon difluoride decomposes slowly in CH_3CN solution and as a result a large amount of HF is produced. H_2O might react with fluorine-containing compounds (*e.g.* XeF_2) to liberate HF. In general, H_2O and HF impurities are invariably present in solutions containing reactive fluorides:

$$XeF_2 + H_2O \longrightarrow 2\,HF + Xe + 1/2\,O_2 \qquad [30]$$

2. When PF_5 is used in the reaction, a trace of moisture reacts with PF_5 to liberate HF, as illustrated in equation [31]:

$$PF_5 + H_2O \longrightarrow P(O)F_3 + 2\,HF \xrightarrow{H_2O} P(O)F_2(OH) + HF \xrightarrow{H_2O} P(O)F(OH)_2 + HF \qquad [31]$$

The formation of the hydrolysis products of PF_5 can be identified by ^{19}F NMR spectroscopy (Table 6).

b. The source of SiF_4 and BF_3

Lewis acids such SiF_4 and BF_3 are produced by the reaction of HF with glass (SiO_2 or B_2O_3, etc.):

$$6\,HF + B_2O_3 \longrightarrow 2\,BF_3 + 3\,H_2O \qquad [32a]$$

$$4\,HF + SiO_2 \longrightarrow SiF_4 + 2\,H_2O \qquad [32b]$$

TABLE 6

^{19}F NMR data of some fluorine-containing compounds

Compound	Chemical shift [ppm]	Coupling constant [Hz]	Reference
$P(O)F_3$	-93.2	1062	61
$P(O)F_2(OH)$	-85.6	980	†
$P(O)F(OH)_2$	-74	956	†
$P(O)FCl_2$	-8	1180	†
$P(O)F_2Cl$	-47	1137	76
PF_5	-76	930	61
PF_6^-	-71.1	720	†
BF_3	-126 ~ -131	10 (^{11}B-F)	77
BF_4^-	-145 ~ -150		†
SiF_4	-160 ~ -170	178 (Si-F)	77
SiF_6^{2-}	-127	110 (Si-F)	†
FHF^-	-149.4		77

† This work.

A typical example for the formation of these Lewis acids in glass apparatus is illustrated in the following observation: when the solution of a mixture of Ph_3PF_2 and fbpy (1:1 molar ratio) in CH_2Cl_2 is kept in a glass reaction tube for several days, the ^{19}F NMR examination revealed the presence of SiF_4(fbpy) only. No trace of Ph_3PF_2 or any other phosphorus fluoride was found. Presumably, HF was produced by the reaction of Ph_3PF_2 with moisture, which then further reacted with glass to form a Lewis acid SiF_4, equation [32b] above, and subsequently SiF_4 formed 1:1 adduct with a bidentate ligand fbpy to produce a stable six-coordinate species, SiF_4(fbpy). This complex was prepared by the reaction of SiF_4 and fbpy by Nguyen (51), and the ^{19}F and ^1H NMR spectra of SiF_4(fbpy), which was formed by the reaction of the glass tube with Ph_3PF_2 as described above, were identical with those of the authentic sample (51).

These Lewis acid fluorides (*e.g.* HF, SiF_4, and BF_3) are very reactive species, and thus they do not persist as free species. These Lewis acids react with fluorine-containing compounds to produce fluoride anions such as FHF^-, SiF_6^{2-}, and BF_4^- which can be identified by ^{19}F NMR spectroscopy (Table 6). An example can be found from the reagent tetrafluorobutylammonium fluoride: the solution of Bu_4NF stored in THF invariably contains fluoride impurities such as SiF_6^{2-} and BF_4^-, as identified by ^{19}F NMR (a typical ^{19}F NMR spectrum with these fluoride impurities will be shown in chapter IIIB).

B. Synthesis of fluorophenyltellurium(VI) compounds

A series of fluorophenyltellurium(VI) compounds was prepared by K. Alam (10,12). However, oxidative fluorination with xenon difluoride is a slow process yielding the products in low yield. Hence a modified method was required to improve the reactions.

In this section, an alternative to the conventional method of oxidative fluorination will be discussed; the modified method also allows stepwise fluorination to be observed.

1. Improved synthesis of mer-Ph_3TeF_3

Fluorotriphenyltellurium(IV), Ph_3TeF, reacts with xenon difluoride at ambient temperature to yield trifluorotriphenyltellurium(VI), *mer*-Ph_3TeF_3 (12):

$$Ph_3TeF + XeF_2 \xrightarrow[CH_2Cl_2]{25\ ^\circ C} \textit{mer}\text{-}Ph_3TeF_3 + Xe \qquad [33]$$

Trifluorotriphenyltellurium(VI), *mer*-Ph_3TeF_3, can also be prepared from the reaction of Ph_3TeCl with a stoichiometric amount of XeF_2, as outlined in equation [34]:

$$2\ Ph_3TeCl + 3\ XeF_2 \xrightarrow[CH_2Cl_2]{25\ ^\circ C} 2\ \textit{mer}\text{-}Ph_3TeF_3 + Cl_2 + 3\ Xe \qquad [34]$$

The assignment of the ^{19}F and ^{125}Te NMR resonances summarized in Table 7 follows directly from the multiplet patterns: *mer*-Ph_3TeF_3 is characterized by a triplet and doublet ^{19}F NMR resonances (relative intensities = 1:2), each with ^{125}Te-coupled satellites, as shown in Figure 4. Its ^{125}Te NMR spectrum shows a doublet of triplets, as shown in Figure 5.

TABLE 7

NMR data of Ph_3TeF_3 and its derivatives

Compound	Fluorine spin system	Chemical shift [ppm]			Coupling constant [Hz]		
		$\delta(F^a)$	$\delta(F^b)$	$\delta(^{125}Te)$	$J(F^aF^b)$	$J(TeF^a)$	$J(TeF^b)$
mer-Ph_3TeF_3	ab_2	-3.3	-97.9	787	39.5	2852	2090
cis-F_2TePh_3Cl	ab	1.1	-86.2	778	45	2578	1900
trans-F_2TePh_3Cl	b_2		-99	783		1802	
$Ph_3TeF_2^+PF_6^-$	b_2		-122	894			1600
$Ph_3TeFCl^+PF_6^-$	b		-90	890			1400
Ph_3TeFCl_2	a	49.7		645		1903	
cis-F_2TePh_3OH	ab	-3	-76		69	2500	21

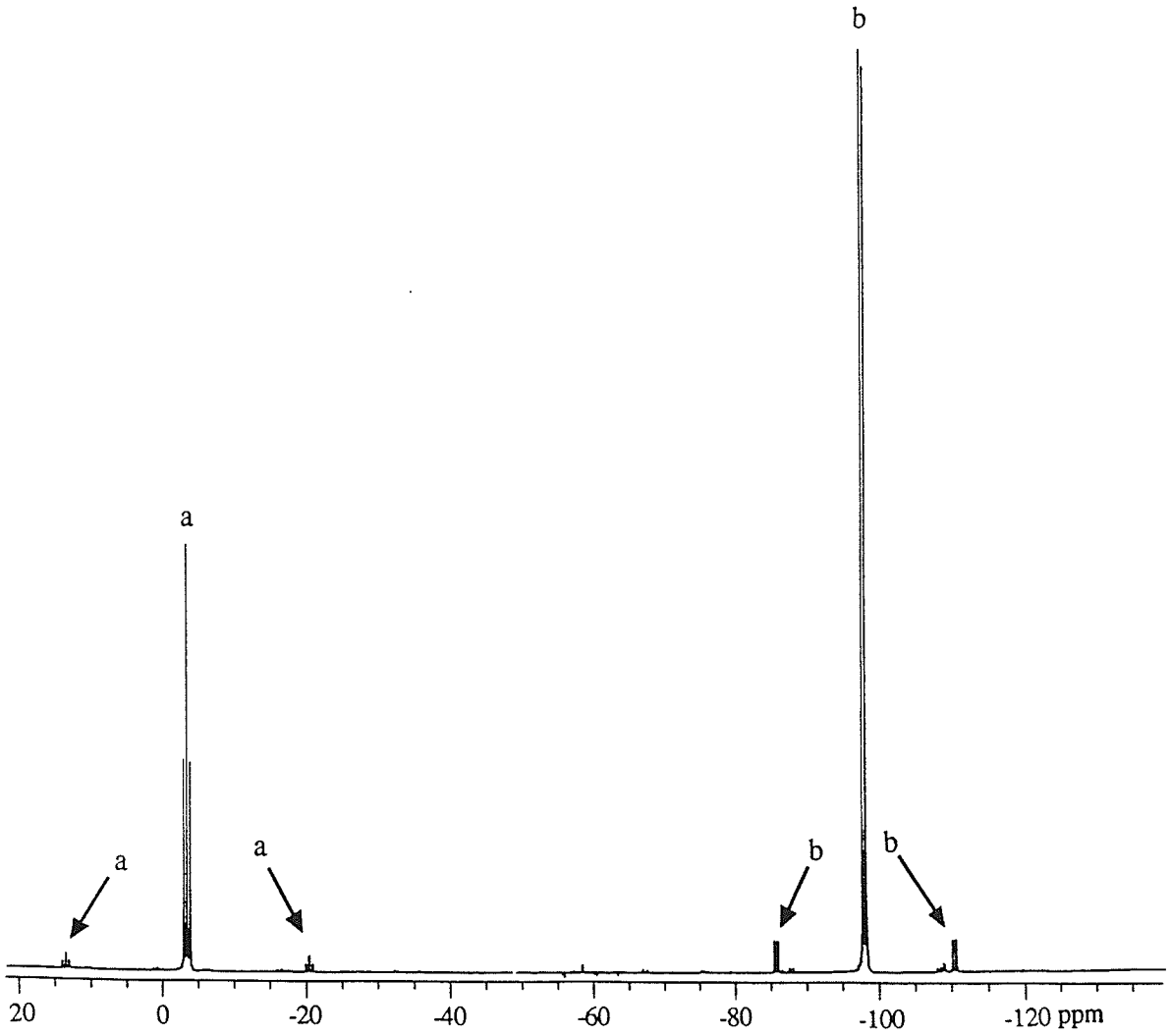


Figure 4. The ^{19}F NMR spectrum of *mer*-$Ph_3TeF^aF_2^b$ in CD_2Cl_2 showing triplet F^a (peaks a) and doublet F^b (peaks b) resonances.

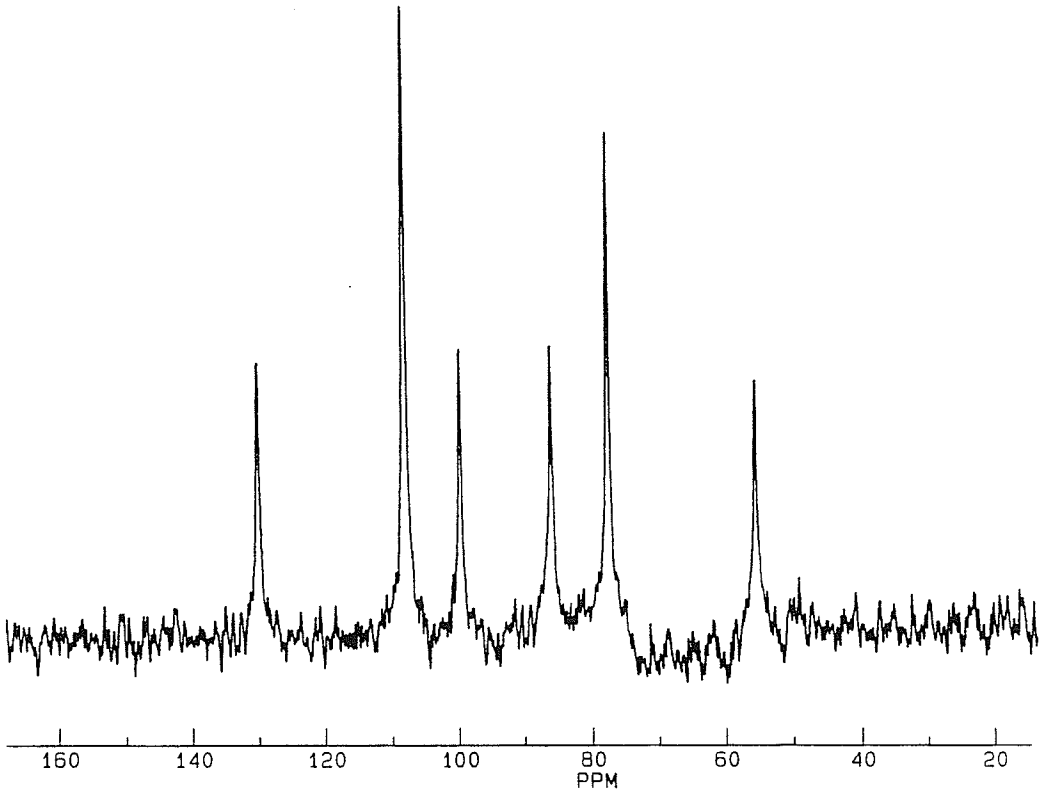
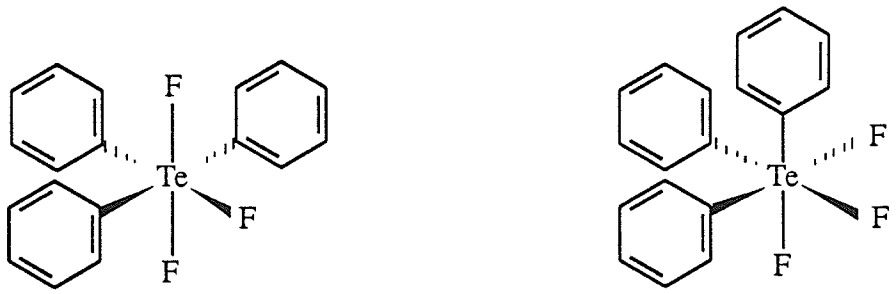


Figure 5. The ^{125}Te NMR spectrum of *mer*-Ph_3TeF_3 in CD_2Cl_2 showing doublet of triplets. The chemical shift is measured relative to Ph_2Te. The converted values relative to Me_2Te are summarized in Table 7.

Although these data alone rigorously establish the stereochemical arrangement of the substituents about the central Te atom in solution, the conclusion that they are in fact in *mer*-position is strongly supported by ^{13}C NMR results which will be discussed shortly. Furthermore, X-ray crystallographic determination of Ph_3TeF_3 (22) revealed that it is the *mer*-isomer. Evidence for the formation of the *fac*-isomer has not been obtained.

The favorable *mer*-arrangement over the *fac*-structure of three phenyl substituents in molecules of Ph_3TeF_3 is probably due to the steric repulsion between bulky phenyl substituents, as illustrated in Figure 6:



mer-Ph_3TeF_3 *fac*-Ph_3TeF_3

Figure 6. The two possible geometrical isomers of Ph_3TeF_3.

The prediction that the *fac*-arrangement may not be favoured due to steric crowding is reasonable because even with the *mer*-structure, the bulky phenyl groups are rotated with respect to each other as a result of intramolecular steric repulsion, as examined by X-ray crystallography (22).

It is of interest to compare the structure of *mer*-Ph_3TeF_3 with the isoelectronic and isostructural trifluorotris(perfluorophenyl)arsenic and -antimony anions (48), as in the following examples:

mer-$(C_6F_5)_3AsF_3^-$ *mer*-$(C_6F_5)_3SbF_3^-$

Figure 7. Structures of $(C_6F_5)_3AsF_3^-$ and $(C_6F_5)_3SbF_3^-$ (counter ions are Cs^+) (48).

These anions are formed by the reaction of $(C_6F_5)_3AsF_2$ or $(C_6F_5)_3SbF_2$ with slight excess of CsF, and their structural assignments are given on the basis of ^{19}F NMR spectroscopy.

Oxidative fluorination under the conditions given in equations [33] & [34] is extremely slow (~8-48 hours) so that the products invariably contain large amounts of impurities which interfere with the ^{19}F NMR resonances. Furthermore, traces of these Lewis acid impurities, such as HF and BF_3,. might catalyze intermolecular fluorine exchange in the system, *e.g.* equation [35].

$$Ph_3TeF_3 + BF_3 \rightleftharpoons Ph_3TeF_2^+BF_4^- \qquad [35a]$$

$$Ph_3TeF_3 + Ph_3TeF_2^+ \rightleftharpoons F_2Ph_3Te\text{-}F\text{-}TePh_3F_2^+ \qquad [35b]$$

In the presence of fluoride impurities, fluorine resonances become broader with loss of Te-F^a coupling, and often an extremely broad F^a peak is observed, barely distinguishable from the baseline. The absence of ^{125}Te-F^a coupling in the ^{19}F NMR spectrum of *mer*-Ph_3TeF_3 eliminates an *intramolecular* process from consideration. The fine multiplet structure reappears after the addition of NaF to the exchanging sample. Purification is usually necessary to obtain products of sufficient purity for a meaningful NMR investigation, otherwise fluorine exchange would mislead interpretation of the results. Crystallization of *mer*-Ph_3TeF_3 from a mixture of CH_2Cl_2:hexane (2:7, v:v) affords colorless crystals; if protected from moisture, the crystals of *mer*-Ph_3TeF_3 could be kept for months at room temperature in a Teflon bottle without changes in the ^{19}F NMR spectra. The X-ray crystallographic structure determination (22) revealed that molecules of *mer*-Ph_3TeF_3 have slightly distorted octahedral geometry about the central Te atom with three phenyls and three fluorines in *mer*-positions, which is consistent with the solution structure determined from its NMR spectrum. It is of interest to note that the Te-F^a bond (1.954 Å) is significantly longer than the Te-F^b bond (1.915 Å) which might be an important factor for the selective cleavage of the Te-F^a bond.

Oxidative fluorination with XeF_2 is such a slow process that often the impurities have been the dominant by-products (12), which could cause ligand exchange in the system. When the system undergoes impurity-catalyzed exchange, it is difficult to make detailed mechanistic interpretations based on product and isomer distribution. Therefore, an alternative synthesis was necessary to improve the reactions with XeF_2. Oxidative fluorination is very fast when a catalyst, tetraethylammonium chloride, is used, as described in equation [36]:

$$Ph_3TeF + XeF_2 \xrightarrow[5\text{-}10\ min.]{Et_4NCl} \textit{mer}\text{-}Ph_3TeF_3 + Xe \qquad [36]$$

When the reaction system (*e.g.* reactants, solvents, and Teflon equipment) is clean and dry, an additional purification step is usually unnecessary and evaporation of dichloromethane solution under vacuum gives pure *mer*-Ph_3TeF_3 in high yield (>95%).

In the oxidative fluorination process in reaction [36], the following route is suggested: the formation of an unobserved intermediate anion, Ph_3TeFCl^-, followed by attack of "F^+" at tellurium, *trans* to the phenyl substituent, leads to the formation of *cis*-F_2TePh_3Cl. The *trans* isomer, *trans*-F_2TePh_3Cl (to be discussed in section II), has never been detected by ^{19}F NMR spectroscopy during the course of the oxidative reaction. In the presence of fluoride impurities (*e.g.* FHF^- or BF_4^-), a further fluorination reaction occurs to give *mer*-Ph_3TeF_3 (mechanisms and structural details will be discussed further in section I-C).

Using the catalyst, Et_4NCl, it was possible to detect stepwise fluorination in the oxidative reaction of Ph_3TeCl with XeF_2, as illustrated in equation [37]:

$$Ph_3TeCl \xrightarrow[XeF_2]{Cl^-} Ph_3TeFCl_2 \longrightarrow Ph_3TeF_2Cl \longrightarrow \textit{mer}\text{-}Ph_3TeF_3 \qquad [37]$$

The reaction progress was monitored by ^{19}F and ^{125}Te NMR spectroscopy. The

products obtained in each step of reaction [37] are consistent with the expected products if the mechanism proposed above is followed and, again, the detailed mechanistic approach will be given in section I-C-2.

The mixed-halo phenyltellurium(VI) compounds, *mer*-Ph_3TeFCl_2 and *mer*-Ph_3TeF_2Cl (phenyl substituents have *mer*-arrangement), were identified by ^{19}F and ^{125}Te NMR spectroscopy. *mer*-Ph_3TeF_2Cl exists in two geometrical isomers, *i.e. cis*- and *trans*-F_2TePh_3Cl, with respect to fluorines (details in section II). However, in the oxidation above (equation [37]), only the *cis*-isomer is formed.

The following spectra illustrate the reaction progress in equation [37]:

1. The ^{19}F NMR spectrum of the mixture of fluorophenyltellurium(VI) compounds in $CDCl_3$ was recorded after 5 minutes of reaction time (for NMR data see Table 7), as shown in Figure 8 The first Te(VI) species to appear in the fluorination process in reaction [37] contains fluorine in a single magnetic environment as it exhibits only a single ^{19}F NMR resonance at +49.7 ppm with ^{125}Te-satellites (peaks c), J(Te-F) = 1903 Hz.

2. The ^{125}Te NMR spectrum (Figure 9), recorded subsequently after the ^{19}F NMR spectrum was examined (recording time; ~3 hour), revealed a doublet (peaks c) with the same magnitude of the Te-F coupling as in the ^{19}F NMR spectrum in Figure 8.

3. The ^{125}Te NMR spectrum was recorded again in order to monitor the reaction progress. As illustrated in Figure 10, amounts of *mer*-Ph_3TeF_3 and *cis*-F_2TePh_3Cl were increased relative to those of Ph_3TeFCl_2. Presumably, Ph_3TeFCl_2 further reacted with fluorides (e.g. HF, the broad peak shown in Figure 8) to give *cis*-F_2TePh_3Cl, and eventually to give *mer*-Ph_3TeF_3. In other words, the ^{19}F NMR resonances of Ph_3TeFCl_2 decrease as formation of *cis*-F_2TePh_3Cl increases, which exhibits two distinctive doublets in the ^{19}F NMR spectrum due to two non-equivalent fluorines (peaks b), as illustrated in Figure 11.

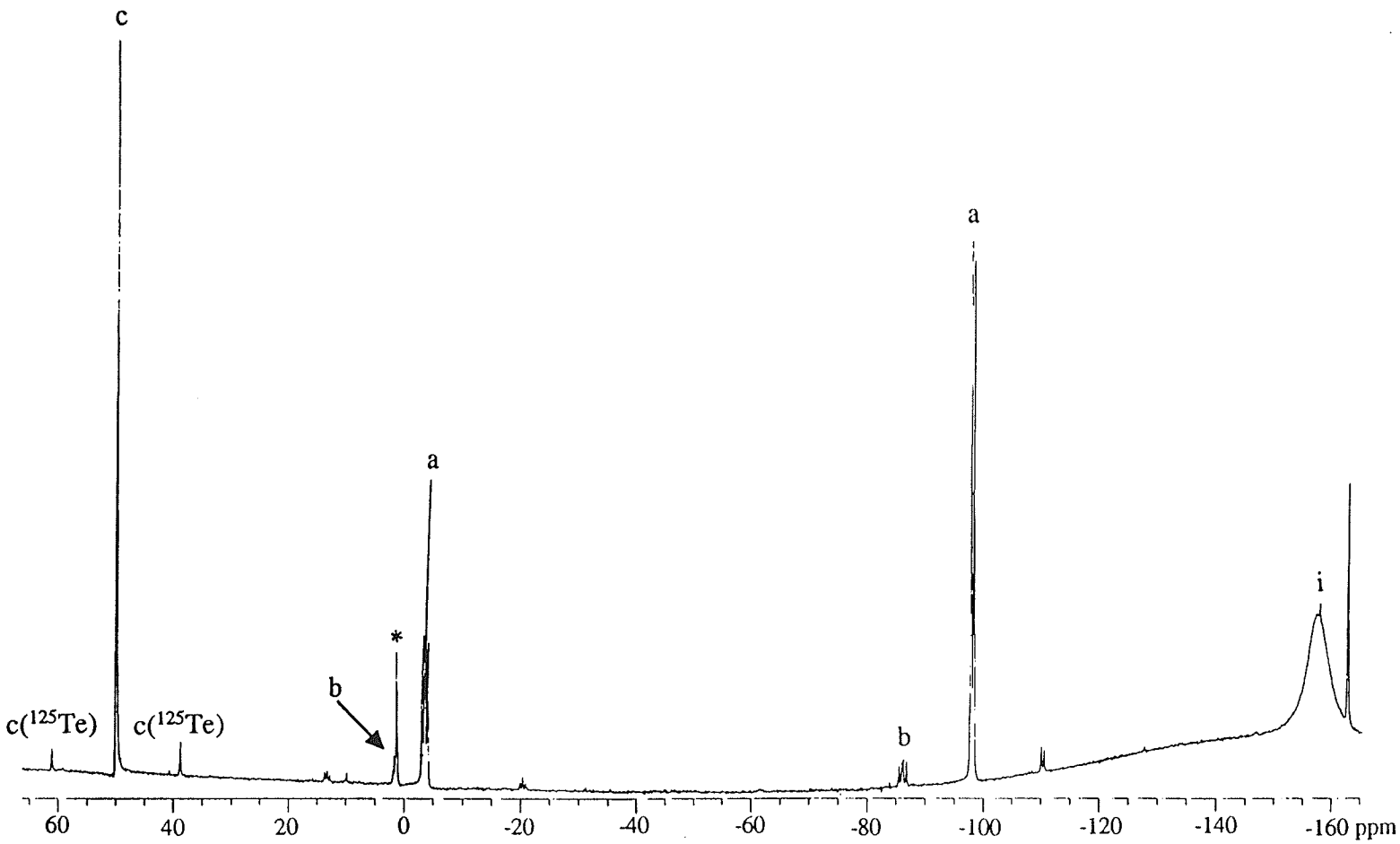


Figure 8. The ^{19}F NMR spectrum of a mixture of *mer*-Ph_3TeF_3 (peaks a), *cis*-F_2TePh_3Cl (peaks b), Ph_3TeFCl_2 (peaks c), and an unknown species (singlet marked with *); ~20 mg/mL in $CDCl_3$. The broad peak at ~-160 ppm (marked with i) is fluoride impurity (*e.g.* HF).

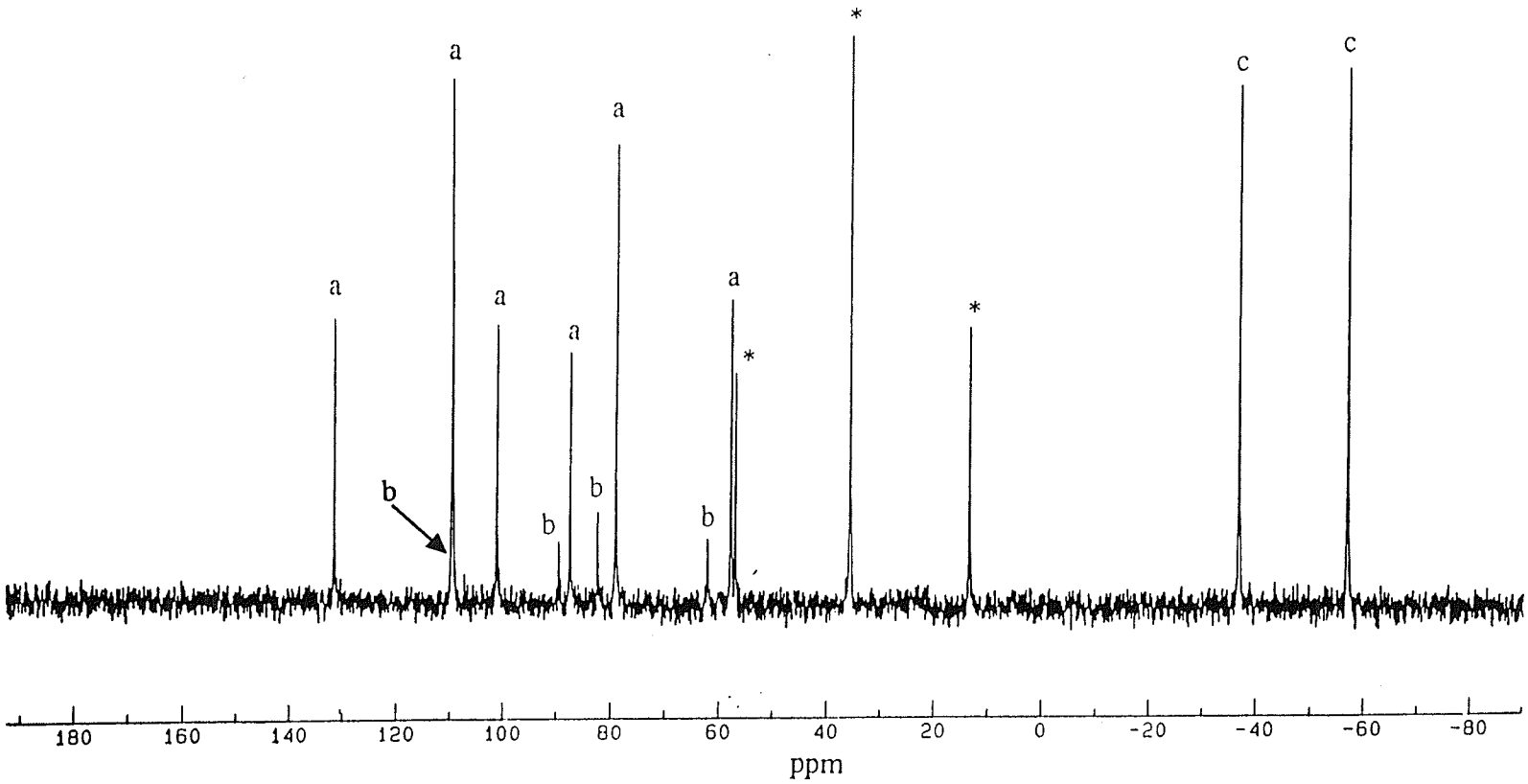


Figure 9. The ^{125}Te NMR spectrum of a mixture of *mer*-Ph_3TeF_3 (peaks a), *cis*-F_2TePh_3Cl (peaks b), Ph_3TeFCl_2 (peaks c), and an unknown species (triplet marked with *); 200 mg/mL in $CDCl_3$. The ratio of *mer*-Ph_3TeF_3 to Ph_3TeFCl_2 is approximately 2:1. The unknown species contains two equivalent fluorines, as determined by ^{19}F and ^{125}Te NMR spectroscopy. The chemical shift is measured relative to Ph_2Te. The converted values relative to Me_2Te are reported in Table 7.

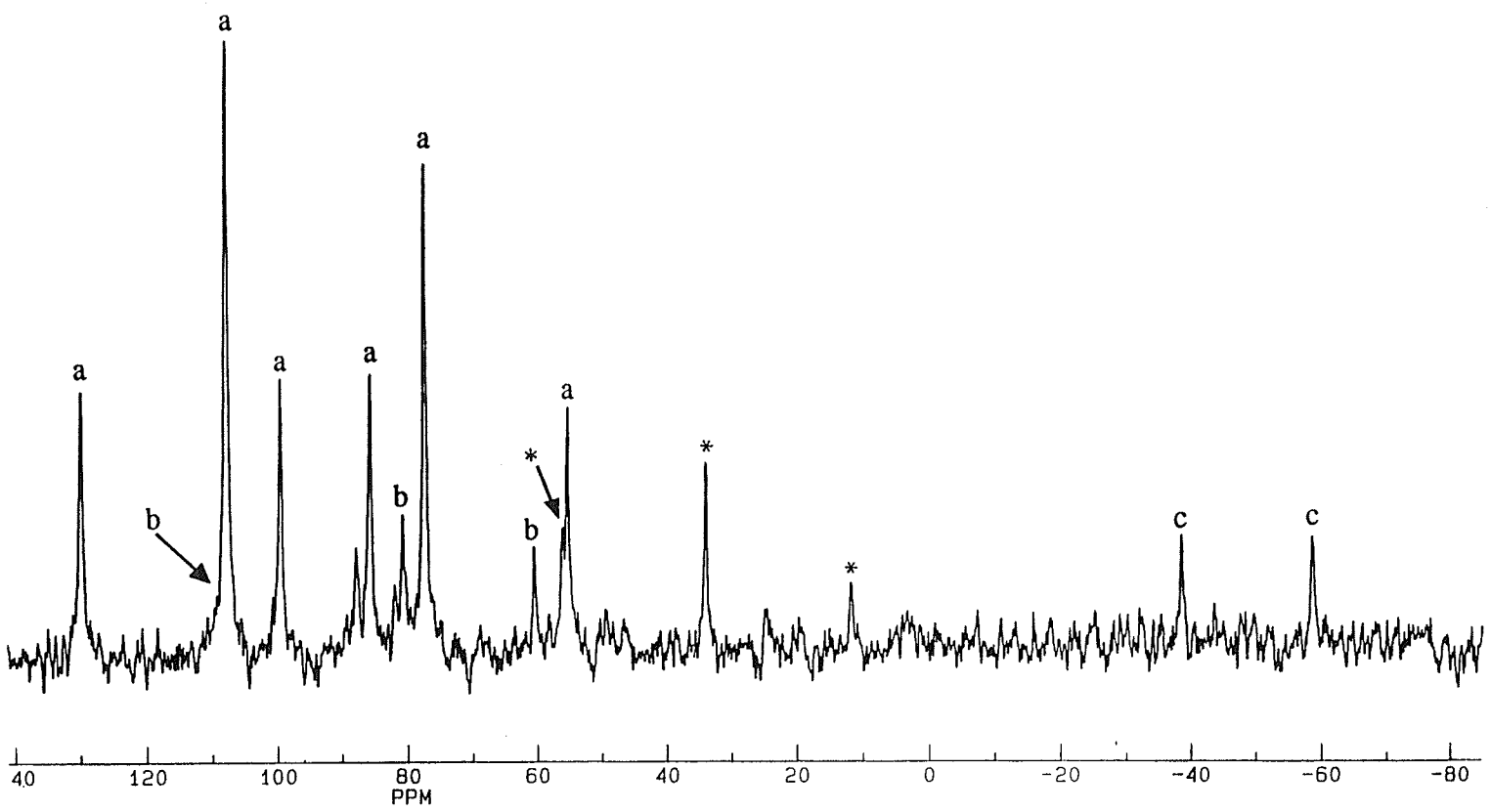


Figure 10. The ^{125}Te NMR spectrum of the same mixture as shown in Figure 9, recorded after 3 hours in $CDCl_3$; the amount of Ph_3TeFCl_2 (peaks c) decreased relative to the formation of *mer*-Ph_3TeF_3 (peaks a) and *cis*-F_2TePh_3Cl (peaks b). The chemical shift is measured relative to Ph_2Te. The converted values relative to Me_2Te are reported in Table 7.

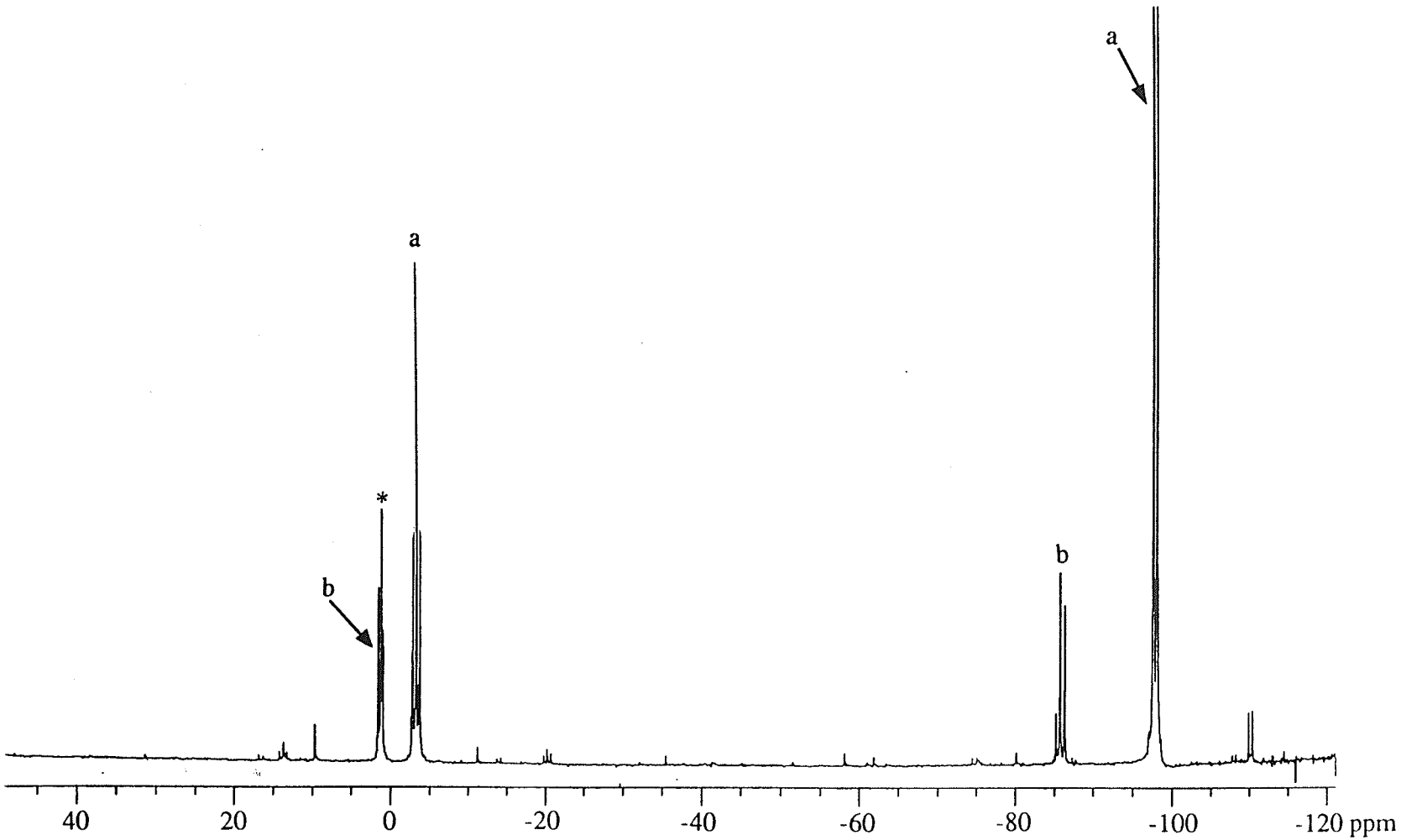


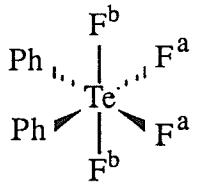
Figure 11. The ^{19}F NMR spectrum of the mixture of *mer*-Ph_3TeF_3 (peaks a), *cis*-F_2TePh_3Cl (peaks b), Ph_3TeFCl_2 (peaks c), and an unknown species (singlet marked with ∗); 200 mg/mL in $CDCl_3$. The chemical shift is measured relative to Ph_2Te. The converted values relative to Me_2Te are reported in Table 7.

The magnitude of $J(^{125}Te\text{-}F)$ of Ph_3TeFCl_2 (~1900 Hz) is consistent with that of $J(^{125}Te\text{-}F)$ found in many other six-coordinate tellurium compounds. In addition, a significant downfield shift (~50 ppm) of $\delta F(Ph_3TeFCl_2)$ compared with $\delta F(mer\text{-}Ph_3TeF_3)$ in ^{19}F NMR is also consistent with the similar chemical shift effect observed in other phenyltellurium(VI) compounds when fluorine is replaced by chlorine.

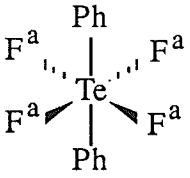
All attempts to separate Ph_3TeFCl_2 failed due to its facile fluorination by HF to give *mer*-Ph_3TeF_3.

2. Synthesis of cis- and trans-Ph_2TeX_4 (X = F, Cl)

Tetrafluorodiphenyltellurium(VI), Ph_2TeF_4, can exist as two geometrical isomers with respect to phenyl substituents, *i.e.* *cis*- and *trans*-Ph_2TeF_4, as illustrated in Figure 12:



cis-12a

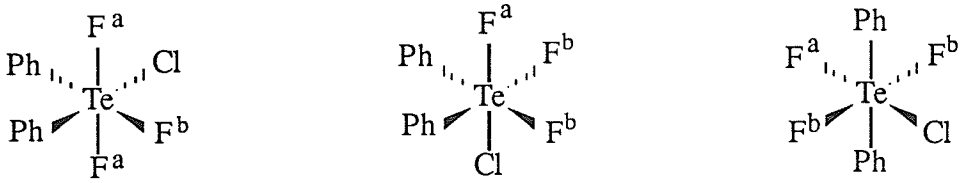


trans-12b

Figure 12. The two geometrical isomers of Ph_2TeF_4.

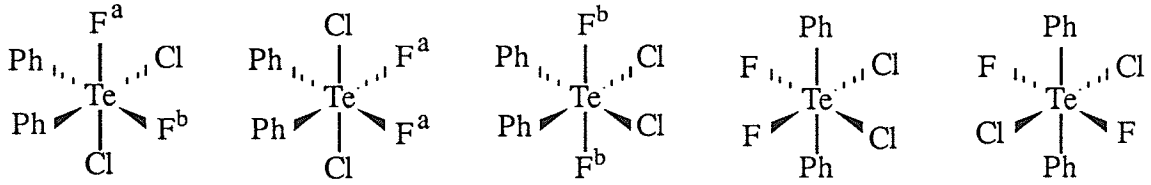
However, for Ph_2TeX_4 with mixed-halo ligands (X = F/Cl), the number of possible geometrical isomers increases, as illustrated in Figure 13 for Ph_2TeF_3Cl and Figure 14 for

$Ph_2TeF_2Cl_2$. *cis*- and *trans*-isomers are designated with respect to phenyl substituents.



cis-13a *cis*-13b *trans*-13c

Figure 13. The three possible geometrical isomers of Ph_2TeF_3Cl.



cis-14a *cis*-14b *cis*-14c *trans*-14d *trans*-14e

Figure 14. All possible geometrical isomers of $Ph_2TeF_2Cl_2$.

The preparation of *cis*- and *trans*-Ph_2TeX_4 and an impurity-catalyzed *cis-trans* isomerization will be discussed in this section.

a. Improved synthesis of *trans*-Ph_2TeF_4. Oxidative fluorination of Ph_2TeF_2 with a stoichiometric amount of XeF_2 gives the thermodynamically stable isomer, *trans*-Ph_2TeF_4, which was first prepared by K. Alam (10,12):

$$Ph_2TeF_2 + XeF_2 \xrightarrow[CH_2Cl_2]{\text{48 hours}} \textit{trans}\text{-}Ph_2TeF_4 \qquad [38]$$

trans-Ph_2TeF_4 is characterized by a singlet ^{19}F NMR spectrum with a pair of doublet satellites coupling to ^{125}Te and ^{123}Te (Figure 15), and by a quintet ^{125}Te NMR spectrum with the same Te-F coupling (Figure 16). NMR data are summarized in Table 8.

The reactions with XeF_2 are extremely sluggish so that it required at least 48 hours to complete the oxidation with about 60% yield of *trans*-Ph_2TeF_4 (the rest being fluoride impurities such as BF_4^- and HF) (12).

Diphenyltelluride(II), Ph_2Te, also reacts with XeF_2 step-by-step to give the *trans*-isomer, as illustrated in equation [39]:

$$Ph_2Te \xrightarrow[\text{Fast}]{XeF_2} Ph_2TeF_2 \xrightarrow[\text{Slow}]{XeF_2} \textit{trans}\text{-}Ph_2TeF_4 \qquad [39]$$

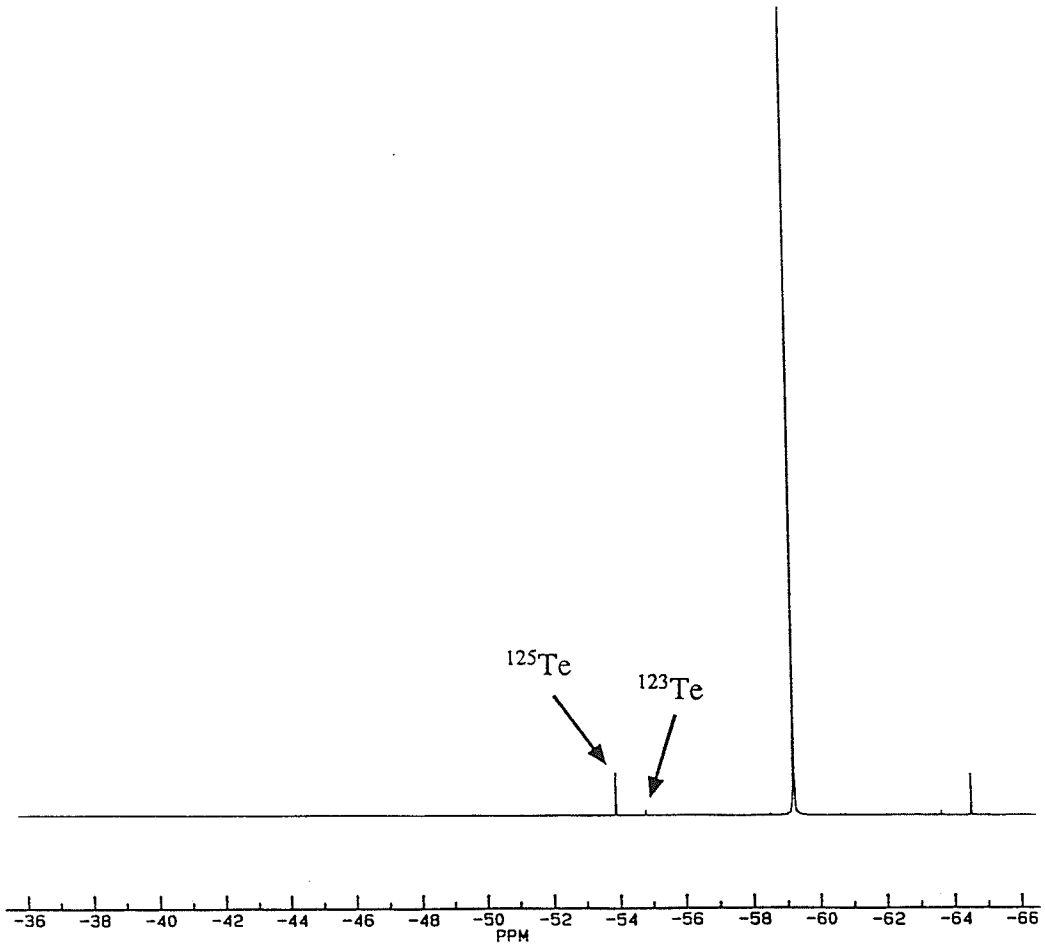


Figure 15. The ^{19}F NMR spectrum of *trans*-Ph_2TeF_4; ~15mg/mL CD_3CN.

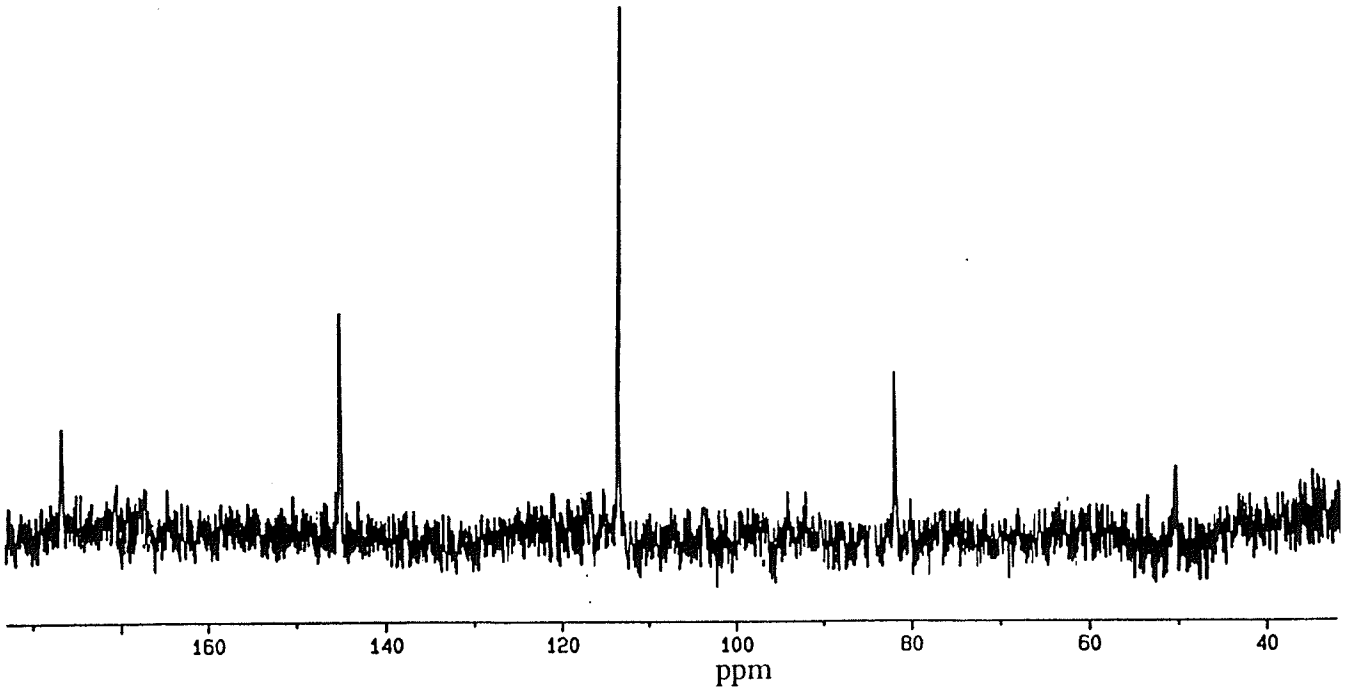


Figure 16. The ^{125}Te NMR spectrum of *trans*-Ph_2TeF_4; ~80 mg/mL in $CDCl_3$. The chemical shift is measured relative to Ph_2Te. The converted values relative to Me_2Te are reported in Table 8.

TABLE 8

NMR data of Ph_2TeX_4 (X = F/Cl, or OH)

Compound	Fluorine spin system	Chemical shift [ppm]			Coupling constant [Hz]			
		$\delta(F^a)$	$\delta(F^b)$	$\delta(^{125}Te)$	$J(F^aF^b)$	$J(TeF^a)$	$J(TeF^b)$	Solvent
cis-Ph_2TeF_4 12a	a_2b_2	-32.7	-75.9		87.3	2884	2675	CD_3CN
cis-$Ph_2TeF_2Cl_2$ 14a	ab	+63	-43		97.7	2500	2220	CD_3CN
cis-Ph_2TeF_3Cl 13a	ab_2	-19.9	-48.9		88.9	2830	2418	CD_3CN
trans-Ph_2TeF_4 12b	a_4	-56.7		806		2997		CD_3CN
trans-Ph_2TeF_3Cl 13c	ab_2	+37	-50.2		88.8	2830	2375	CD_2Cl_2
trans-Ph_2TeF_3OH	ab_2	-32.5	-61.5	799	35	2925	2700	$CDCl_3$
trans-$Ph_2TeF_2(OH)_2$	b_2		-45	768			2700	D_2O

The oxidative fluorination of $Ph_2Te(II)$ with a stoichiometric amount of XeF_2 (equation [39]) was complete within ~5 minutes to give Ph_2TeF_2 in high yield. The ^{19}F NMR spectrum revealed the formation of Ph_2TeF_2 only, without being accompanied by any other peak, e.g. XeF_2, BF_4^-. However, the further oxidative fluorination of Ph_2TeF_2 with an additional equivalent of XeF_2 did not occur even after 1 hour. The ^{19}F NMR spectrum at this stage revealed a mixture of Ph_2TeF_2 with a large amount of XeF_2 (also small amounts of HF were produced). When catalytic amounts of tetraethylammonium chloride, Et_4NCl, were added to this reaction mixture, the oxidative reaction was very fast (~5–10 minutes) to give *trans*-Ph_2TeF_4 in high yield (~95%) (Table 8). A small broad peak (< 5%) was detected in the HF region (δ = ~-159 – -161 ppm) in the ^{19}F NMR spectrum.

In general, it was found that when the catalyst, tetraethylammonium chloride, is employed in the reaction of Ph_2TeCl_2 with XeF_2, the oxidation is complete within 30 minutes to give *trans*-Ph_2TeF_4 in high yield (>95%) according to equation [40]:

$$Ph_2TeCl_2 + 2\,XeF_2 \xrightarrow[30\ min.]{Et_4NCl} \textit{trans}\text{-}Ph_2TeF_4 \qquad [40]$$

The % yield for typical reaction conditions are summarized in Table 9.

TABLE 9

Reactions conditions and yield of *cis*- and *trans*-Ph_2TeX_4 (X = F, Cl)

Molar ratio of reactants	Reaction conditions	*cis*-Ph_2TeX_4	*trans*-Ph_2TeX_4
$Ph_2Te:XeF_2:Et_4NCl$ (1:2:0.1)	10 minutes, CD_3CN, NMR tube	Ph_2TeF_4 12a (14%)	Ph_2TeF_4 12b (40%)
$Ph_2TeCl_2:XeF_2$ (1:2), no R_4NX	3 hours, $CDCl_3$, glass tube	Ph_2TeF_4 12a (0%)	Ph_2TeF_4 12b (49%)
$Ph_2TeCl_2:XeF_2:Et_4NCl$ (1:2:0.1)	30 minutes, CD_3CN, Teflon bottle	Ph_2TeF_4 12a (<4%)	Ph_2TeF_4 12b (~95%)
$Ph_2TeCl_2:XeF_2:Et_4NCl$ (1:2:2)	30 minutes, CD_2Cl_2, Teflon bottle	$Ph_2TeF_2Cl_2$ 14a (82%)	Ph_2TeF_3Cl 13c (18%)
$Ph_2TeCl_2:XeF_2:Bu_4NF$ (1:2:1)	30 minutes, CD_3CN, Teflon bottle	Ph_2TeF_3Cl 13a (84%)	Ph_2TeF_4 12a (16%)

Addition of tetrabutylammonium fluoride, Bu_4NF, also accelerates the oxidative reaction of Ph_2TeCl_2 with XeF_2, and the detailed reaction pathway and products will be discussed shortly.

When the catalyst R_4NX is used, the completion of oxidation is indicated by the distinct color change of the solution from colorless to yellowish and back to colorless, which occurs within several minutes. Small amounts of fluoride impurities such as FHF^- or SiF_6^{2-} can be removed by recrystallization of the product. It should be pointed out that the reagent Bu_4NF contains SiF_6^{2-} and BF_4^-, as confirmed by ^{19}F NMR spectroscopy. Crystals of *trans*-Ph_2TeF_4 are easily obtained by slow evaporation of solvent from its dichloromethane solution and are indefinitely stable if kept in a Teflon bottle.

When the reaction was carried out in a glass reaction tube, the colorless solution turned dark-yellow within 30 minutes, but the solution did not turn clear; instead it remained yellow. The NMR examination of the solution after ~3 hours confirmed that the oxidation was complete, but the yield was relatively low (see Table 9) and also large amounts of fluoride impurities were produced. Recrystallization of the crude mixture from CH_2Cl_2, followed by washing with acetonitrile, gives pure *trans*-Ph_2TeF_4.

The fact that the oxidative reaction occurs much faster in the glass reaction tube than in Teflon implies that Lewis acid catalysts might be required in the oxidative reaction. Furthermore, the fact that the conventional method (12) had required ~48 hours or more to complete the oxidation suggests the possible formation of Lewis acids during that period.

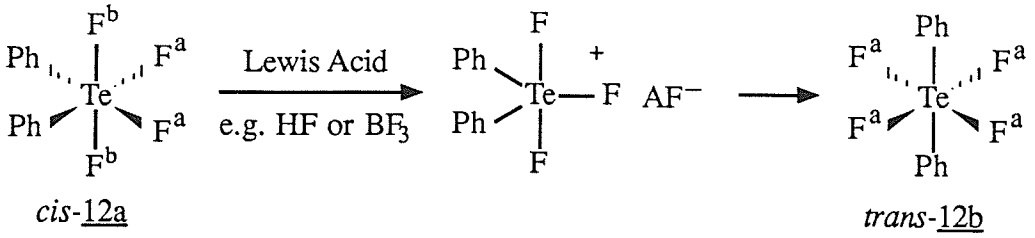
Therefore, from these observations, it may be inferred that the oxidative reaction may not occur under anhydrous conditions, *i.e.* it requires a catalyst. Indeed, this was clearly observed in the following experiment: when the reaction was carried out in dry solvent (CH_2Cl_2 or CH_3CN) in a Teflon reaction bottle, there was no sign of oxidative reaction even after ~14 hours, as judged by the color change. However, when the

reaction mixture was transferred into a glass NMR tube to monitor a reaction progress, xenon gas was vigorously evolved and the solution turned yellow.

The thermodynamically stable isomer, *trans*-Ph_2TeF_4, was identified by ^{19}F and ^{125}Te NMR (Table 8), and mass spectrometry (10). The carbon-13 NMR examination of *trans*-Ph_2TeF_4, which will be discussed shortly, confirms the *trans*-geometry.

b. Synthesis of *cis*-Ph_2TeX_4 (X = F/Cl). The formation of small amounts of the kinetically favoured isomer, *cis*-Ph_2TeF_4, was often observed along with the *trans*-isomer in the reaction of Ph_2TeF_2 with XeF_2 (79). *cis*-Ph_2TeF_4 is characterized by two triplets of equal intensity with Te-coupled satellites in the ^{19}F NMR spectrum (Table 8).

When Ph_2TeCl_2 and a stoichiometric amount of XeF_2 were placed in a Teflon reaction bottle without a catalyst, the oxidation was very slow which, as discussed previously, was indicated by the color change and the presence of unreacted XeF_2 in the ^{19}F NMR spectrum. When the solution was examined by ^{19}F NMR after ~14 hours, small amounts of *cis*-Ph_2TeF_4 were formed without being accompanied by the *trans*-isomer. However, after all the XeF_2 used was consumed (after several hours), the solution contained mainly the *trans*-isomer. The fact that the amount of the *cis*-isomer varies with experimental conditions (reaction tube and time) indicates that fluoride impurities, which may be generated in the glass reaction tube during the prolonged reaction period with XeF_2, might catalyze the isomerization of *cis*- to *trans*-Ph_2TeF_4. Presumably the kinetically favoured *cis*-isomer is converted to the thermodynamically more stable *trans*-isomer in the presence of Lewis acid impurities via an unobserved five-coordinate cation, $Ph_2TeF_3^+$, as illustrated in equation [41]:



cis-12a *trans*-12b [41]

The impurity-catalyzed isomerization is supported by the following experiment, as monitored by ^{19}F NMR: when the reaction of Ph_2TeCl_2 with XeF_2 was carried out in a Teflon bottle, the formation of *cis*-Ph_2TeF_4 (~19%) was observed along with the *trans*-isomer, this yield being obtained after all the XeF_2 had been consumed. However, *cis*-Ph_2TeF_4, which was formed first, isomerized to give the *trans*-isomer. When the same reactants were placed in an ordinary glass reaction tube, only the *trans*-isomer was produced within 3 hours (Table 9). A large amount of BF_4^- was observed in this reaction, indicating the presence of Lewis acid fluorides, which might react with the *cis*-isomer to give the cation, and the subsequent addition of fluoride to the cation produces the thermodynamically stable *trans*-isomer.

The attempted preparation of *cis*-Ph_2TeF_4 via $Ph_2TeF_3^+$ (i.e. the reverse reaction in equation [41]) always resulted in the regeneration of *trans*-Ph_2TeF_4.

In order to prepare the $Ph_2TeF_3^+$ cation, a slight excess of a strong Lewis acid such as PF_5 or BF_3 was added to the solution of *trans*-Ph_2TeF_4 in CD_2Cl_2. However, addition of the Lewis acid caused only a slight broadening of the ^{19}F NMR resonances of *trans*-Ph_2TeF_4, as illustrated in Figures 17.1–17.2 for the reaction of *trans*-Ph_2TeF_4 with BF_3. Addition of 1 equivalent of Et_4NCl, in an effort to produce *cis*-Ph_2TeF_3Cl 13a, immediately regenerated sharp resonances of *trans*-Ph_2TeF_4 with some boron fluorides, as illustrated in Figure 17.3.

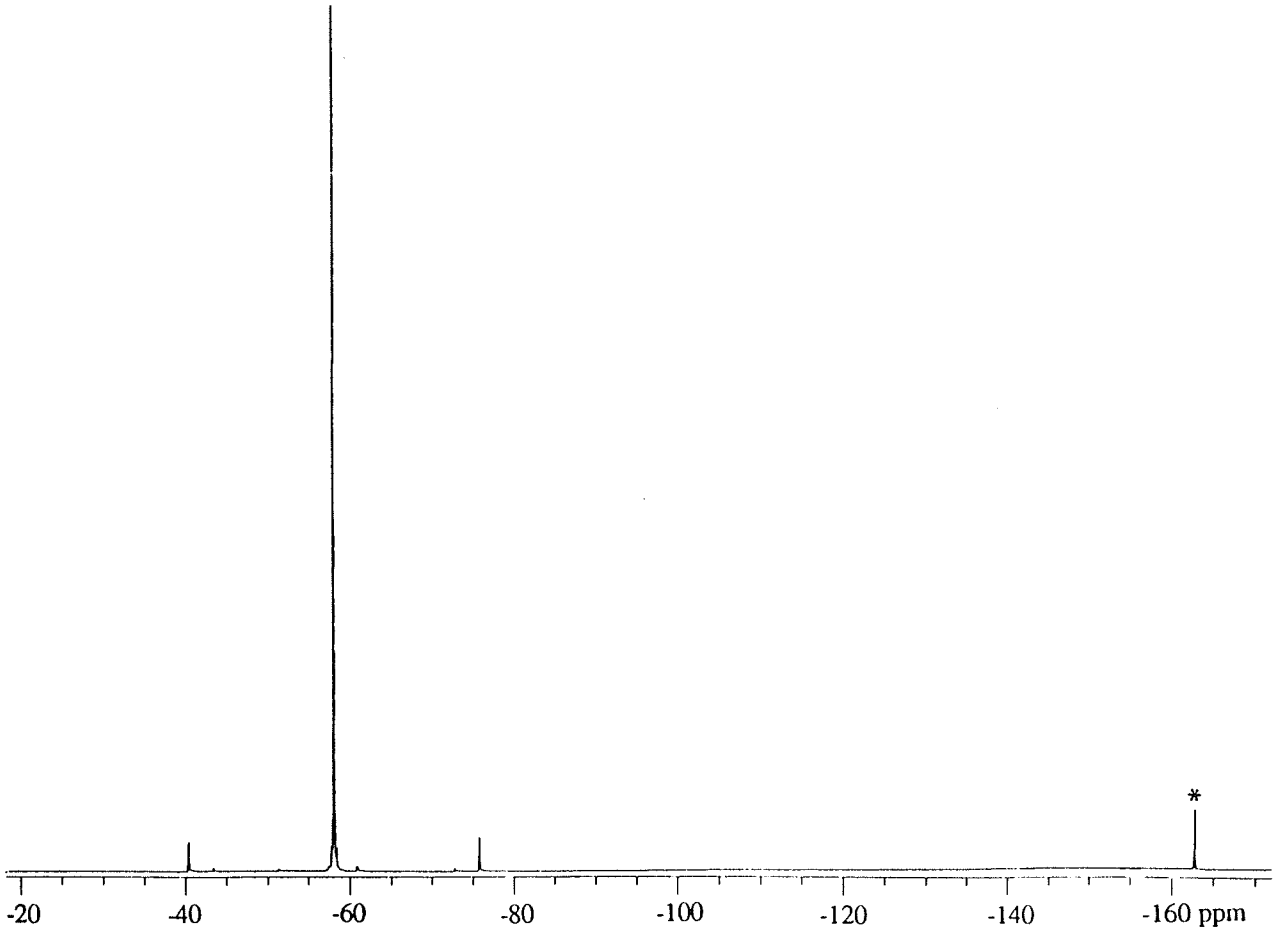


Figure 17.1 The ^{19}F NMR spectrum of *trans*-Ph_2TeF_4 in CD_2Cl_2. A reference (C_6F_6) peak is marked with ∗.

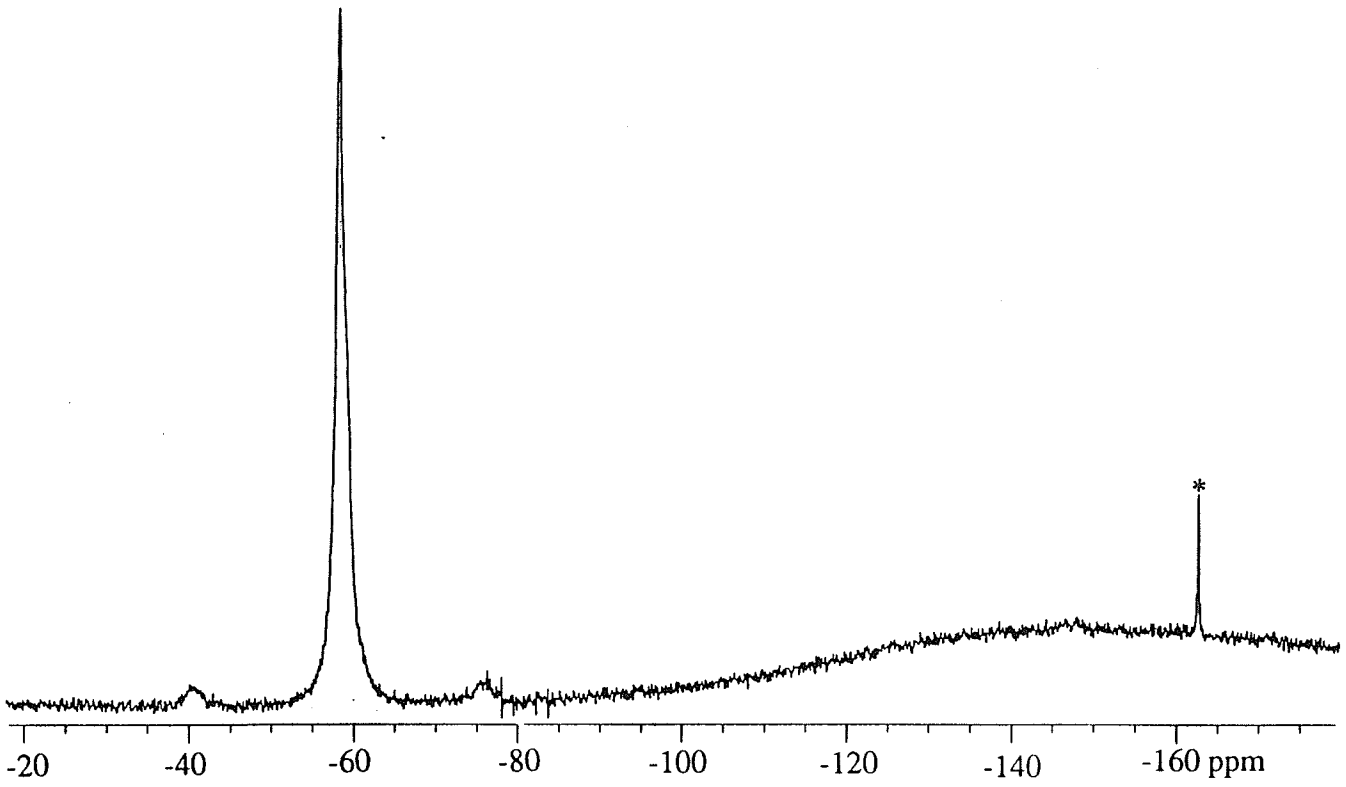


Figure 17.2 The exchanging ^{19}F NMR spectrum of *trans*-Ph_2TeF_4 when BF_3 was added to *trans*-Ph_2TeF_4 in CD_2Cl_2. A reference (C_6F_6) peak is marked with *.

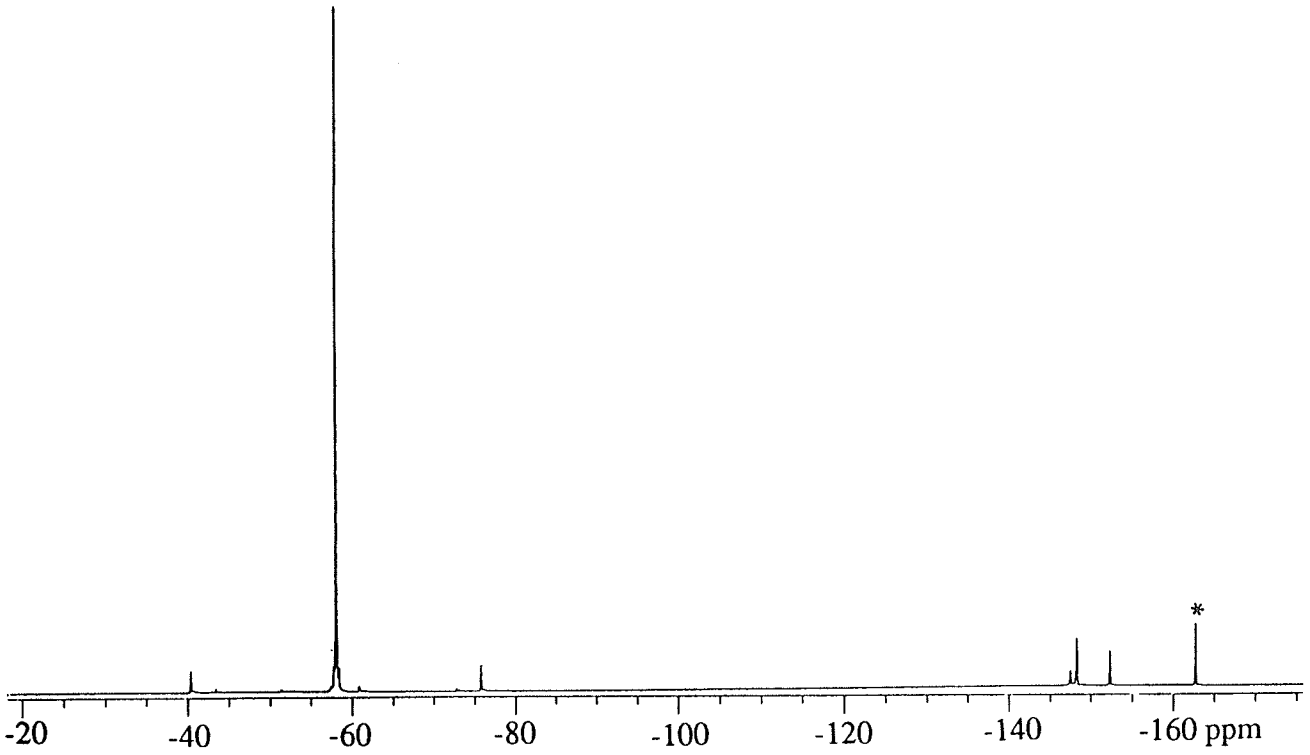


Figure 17.3 The ^{19}F NMR spectrum of *trans*-Ph_2TeF_4, obtained after Et_4NCl was added to the exchanging sample shown in the previous spectrum (Figure 17.2) in CD_2Cl_2. A reference (C_6F_6) peak is marked with *.

On the other hand, when a large excess of PF_5 was added to *trans*-Ph_2TeF_4, the ^{19}F NMR spectrum of the solution in CD_2Cl_2 showed only a doublet assigned to PF_6^-, and peaks due to *trans*-Ph_2TeF_4 disappeared, as shown in Figures 18.1–18.2. Similarly, addition of NaF, in an effort to produce *cis*-Ph_2TeF_4, to this solution regenerated *trans*-Ph_2TeF_4 (Figure 18.3). The formation of PF_6^- ion, the disappearance of *trans*-Ph_2TeF_4 in the ^{19}F NMR spectrum by the reaction of *trans*-Ph_2TeF_4 with PF_5 (Figure 18.2), and regeneration of *trans*-Ph_2TeF_4 by the addition of NaF, suggest that the counter ion must be $Ph_2TeF_3^+$ but was not detected by NMR. This may be due to rapid exchange between the $Ph_2TeF_3^+$ cation and *trans*-Ph_2TeF_4. An alternative mechanism accounting for rapid exchange could be an intramolecular pseudo-rotation between axial and equatorial fluorines in $Ph_2TeF_3^+$, as proposed for many fluxional five-coordinate fluorides (see chapter I).

These observations can be summarized as follows: it is extremely difficult to remove fluorine from the *trans*-isomer to generate the five-coordinate $Ph_2TeF_3^+$ cation, and even when the cation is formed, the *trans*-isomer is regenerated immediately in the presence of fluoride. In other words, the formation of the $Ph_2TeF_3^+$ cation produces the *trans*-isomer which is the thermodynamically stable product.

The role of Ph_2ICl as a catalyst was also examined. When a catalytic amount of Ph_2ICl was added to a reaction mixture of Ph_2TeCl_2 and 2 equivalents of XeF_2, there was no immediate reaction, as judged by absence of a color change. In general, under these conditions, reaction proceeds at about the same rate as in the absence of any catalyst. However, when Ph_2ICl was used, the product (*trans*-Ph_2TeF_4) was contaminated with more fluoride impurities than the product obtained without a catalyst.

Studies so far have shown that *cis*-Ph_2TeF_4 12a is the kinetically favoured isomer in the oxidative fluorination of Ph_2TeX_2 (X=F/Cl) with XeF_2, but using a catalyst, such as Et_4NCl or Bu_4NF, only the *trans*-isomer 12b is isolated.

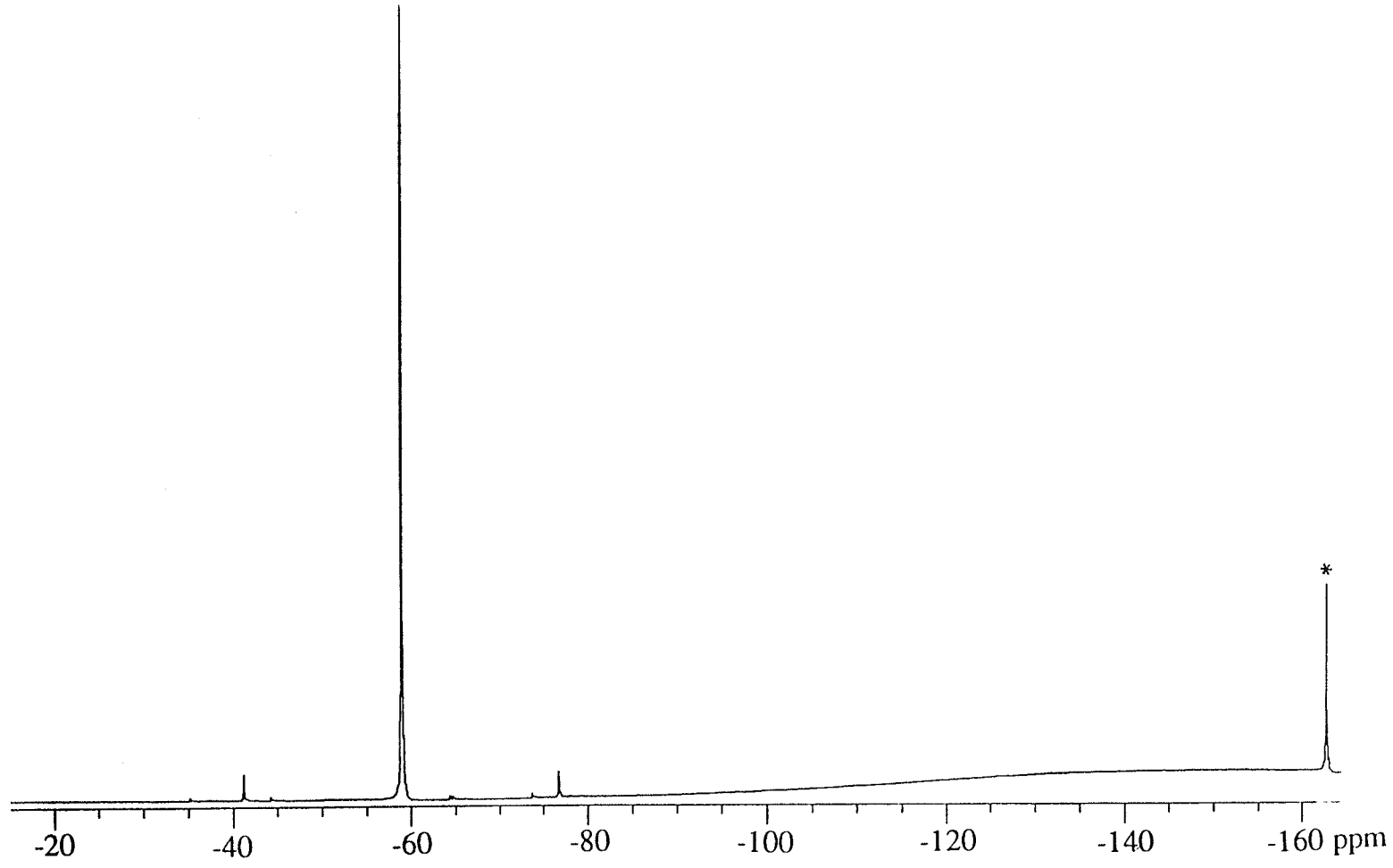


Figure 18.1 The ^{19}F NMR spectrum of *trans*-Ph_2TeF_4 in CD_2Cl_2 (used for the reaction with PF_5).

A reference (C_6F_6) peak is marked with *.

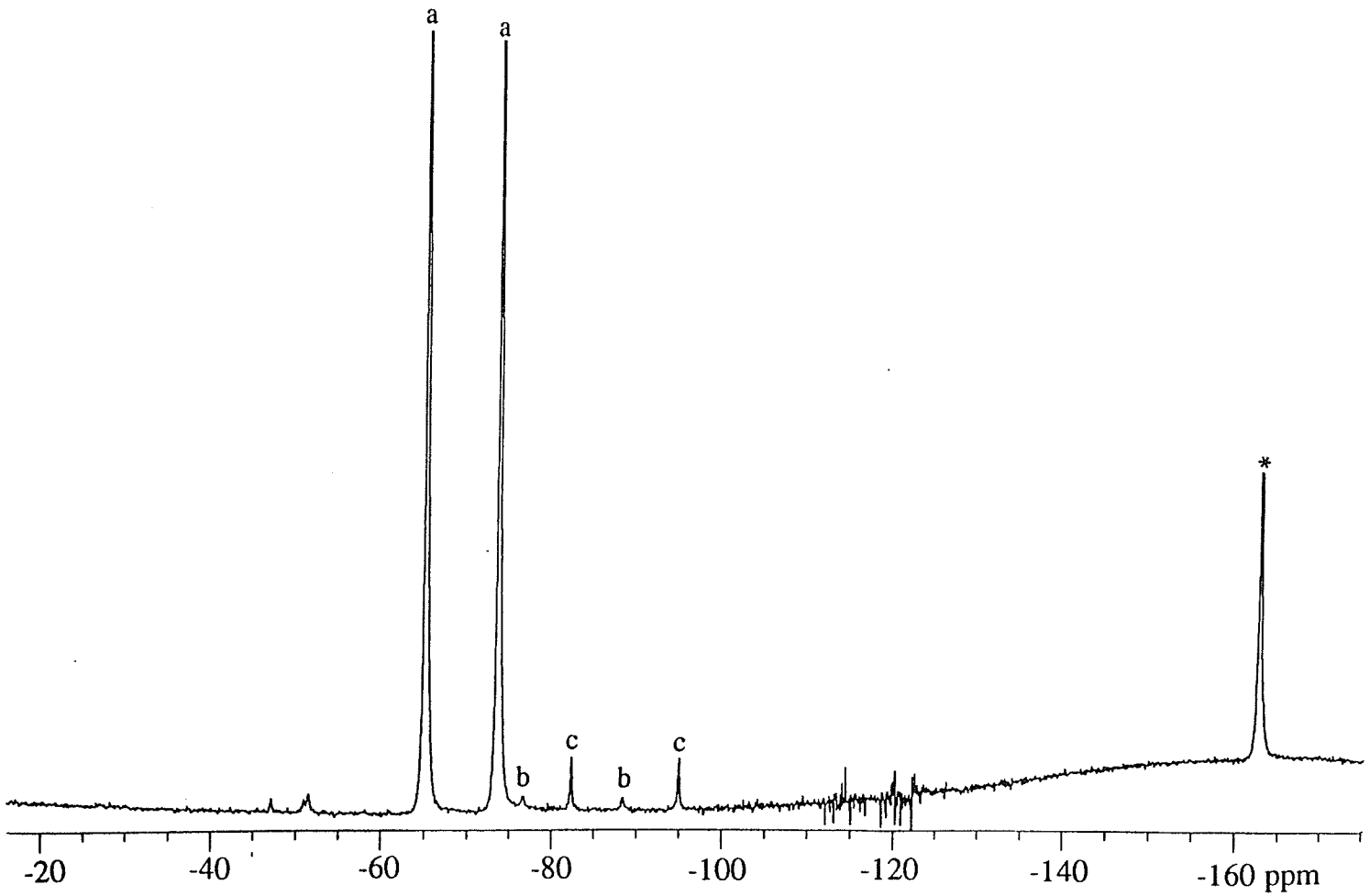


Figure 18.2 The ^{19}F NMR spectrum of the solution, obtained after a large excess of PF_5 was added to the previous sample shown in Figure 18.1 in CD_2Cl_2; PF_6^- (peaks a), $POF(OH)_2$ (peaks b), and $POF_2(OH)$ (peaks c). A reference (C_6F_6) peak is marked with *.

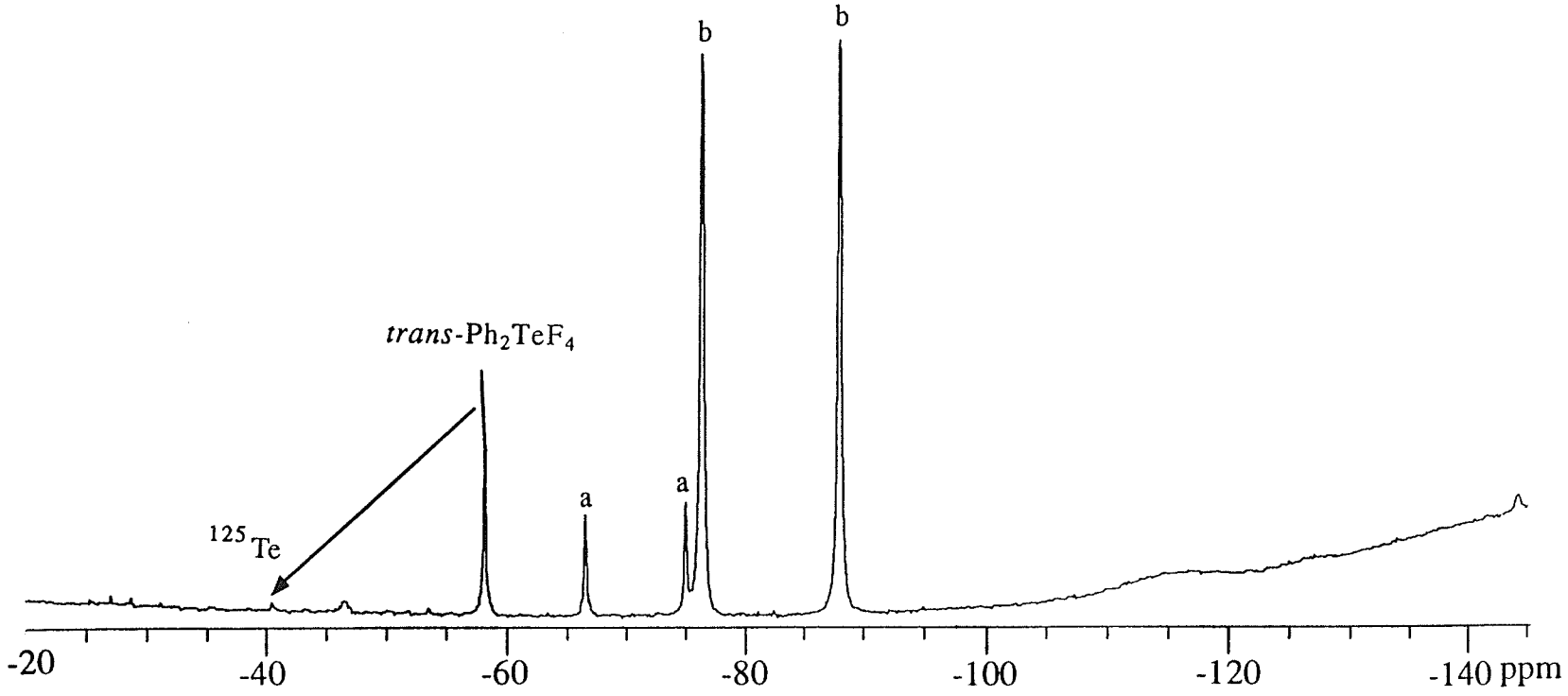


Figure 18.3 The ^{19}F NMR spectrum of *trans*-Ph_2TeF_4, obtained after NaF was added to the previous solution shown in Figure 18.2 in CD_2Cl_2; PF_6^- (peaks a), $POF(OH)_2$ (peaks b). A reference (C_6F_6) peak is not included.

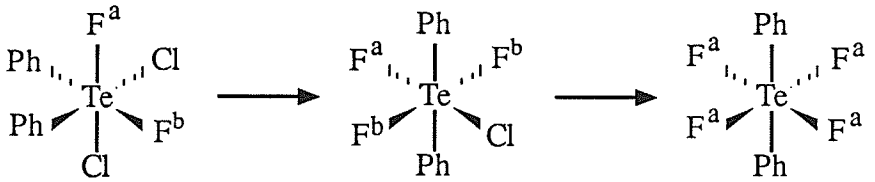
The following experiment will demonstrate that the *cis*-phenyl-configuration is kinetically favoured and that, by using a catalyst, the *cis*-isomer can be formed initially but it then isomerizes to the *trans*-isomer.

(1) With tetraethylammonium chloride.

1. A mixture of XeF_2 and Et_4NCl in a 1:1 molar ratio was dissolved in CH_2Cl_2. ^{19}F NMR examination of the solution revealed that there was no direct interaction between two species, except for the formation of small amounts of HF, shown by a peak at ~-162 ppm in the ^{19}F NMR spectrum.

2. A stoichiometric amount of Ph_2TeCl_2 was added to the 1:1 mixture of XeF_2 and Et_4NCl in CH_2Cl_2 prepared above. As illustrated in Figure 19, the ^{19}F NMR spectrum of the solution in CD_2Cl_2/CH_2Cl_2 (1/1, v/v) exhibited two doublets (84%) and a triplet and doublet (16%) with ^{125}Te-coupled satellites. The large ^{125}Te-F coupling constants (>2000 Hz, see Table 8) indicate that these species are octahedral Te(VI) fluorides. The doublet resonances (ab fluorine spin system) gradually disappeared to give the triplet and doublet resonances (ab_2 fluorine spin system), and eventually to a single resonance due to *trans*-Ph_2TeF_4 12b according to equation [42]:

$$Ph_2TeCl_2 + 2\,XeF_2 \xrightarrow[CH_2Cl_2]{Et_4NCl}$$



cis-14a *trans*-13c *trans*-12b [42]

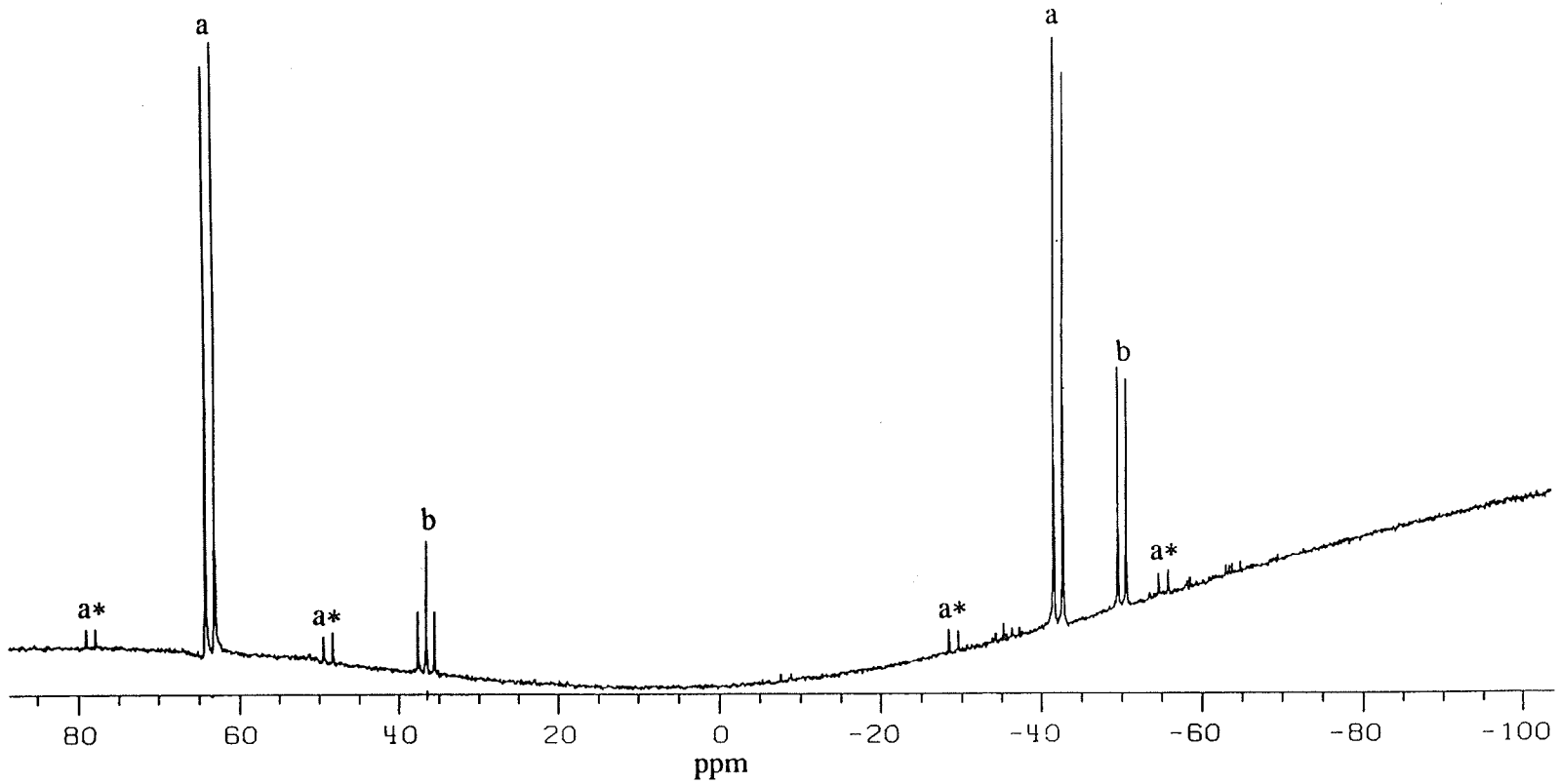


Figure 19. The ^{19}F NMR spectrum of *cis*-$Ph_2TeF_2Cl_2$ 14a (peaks a) and *trans*-Ph_2TeF_3Cl 12c (peaks b) (relative ratio; 4.6:1) in CD_2Cl_2/CH_2Cl_2 (1/1). ^{125}Te-coupled satellites are marked with *. The extremely broad baseline is due to Teflon.

After constant stirring of the reaction mixture for 1 hour, the solution contained mostly *trans*-Ph_2TeF_4 12b, as judged by ^{19}F NMR spectroscopy; the ^{19}F NMR spectrum of the final product showed a triplet and doublet in small amounts in addition to *trans*-Ph_2TeF_4. The structural assignment of *cis*-$Ph_2TeF_2Cl_2$ 14a is made on the basis of ^{19}F NMR spectroscopy; the fact that two doublets eventually converted to a singlet due to *trans*-Ph_2TeF_4 indicates that two phenyl substituents are retained during the process of the oxidative addition reaction, and if this is the case, there is only one possible structure, *cis*-14a, which has non-equivalent fluorines (Table 8). The structural assignment of *trans*-Ph_2TeF_3Cl 13c is also made on the basis of the ^{19}F NMR spectrum, *i.e.* a triplet and doublet ^{19}F NMR resonances (ab_2 fluorine spin system) with relative intensities of 1:2. Furthermore, it is distinguished from *cis*-Ph_2TeF_3Cl 13a (*vide infra*, equation [43]) and also from the known species *trans*-Ph_2TeF_3OH, which will be discussed shortly.

These observations confirm that in the oxidative fluorination of Ph_2TeCl_2 with XeF_2, *cis*-phenyl geometry is kinetically favoured, and then further reaction gives *trans*-13c through a five-coordinate cation and, finally, thermodynamically stable *trans*-12b. NMR data are presented in Table 8 and mechanistic details will be discussed in section I-C.

(2) With tetrabutylammonium fluoride.

1. A mixture of Ph_2TeCl_2 and 2 equivalents of XeF_2 was dissolved in CH_3CN, but there was no immediate reaction, as judged by ^{19}F NMR spectroscopy. Addition of ~1 equivalent of Bu_4NF produced a mixture of *cis*-Ph_2TeF_3Cl 13a (~84%) and *trans*-Ph_2TeF_4 12b (~16%) within ~30 minutes (Table 9), as examined by ^{19}F NMR spectroscopy (Figure 20):

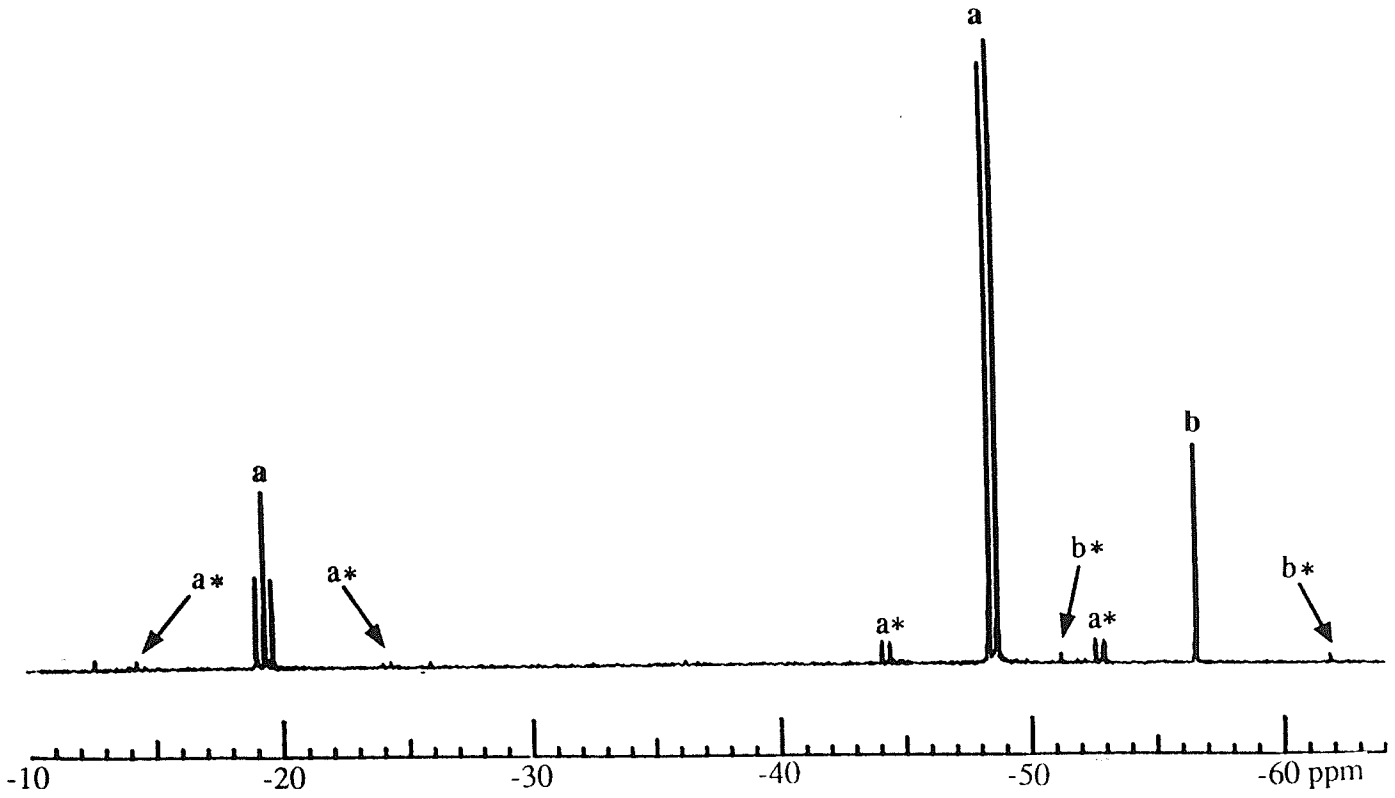
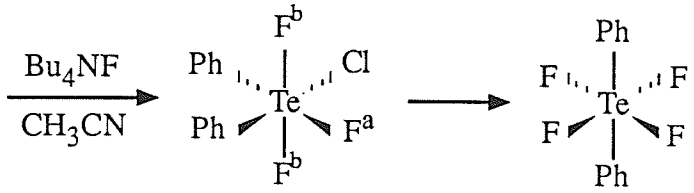


Figure 20. The ^{19}F NMR spectrum of *cis*-Ph_2TeF_3Cl 13a (peaks a) and *trans*-Ph_2TeF_4 12b (peaks b) (relative ratio; 5.3:1) in 0.5 mL CD_3CN in CH_3CN. ^{125}Te-coupled satellites are marked with *.

$Ph_2TeCl_2 + 2\,XeF_2$



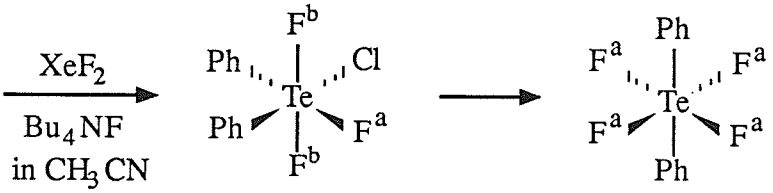
[43]

cis-13a *trans*-12b

After constant stirring overnight, the ^{19}F NMR spectrum showed that *trans*-Ph_2TeF_4 was the only Te product, with small amounts of fluoride impurities, such as SiF_6^{2-} and FHF^-, which have come from the solution of Bu_4NF in THF.

2. A similar result was obtained when a mixture of Ph_2TeCl_2, Ph_2TeFCl, and Ph_2TeF_2 reacted with XeF_2 in the presence of Bu_4NF according to equation [44]:

$Ph_2TeCl_2 + Ph_2TeFCl + Ph_2TeF_2$



[44]

cis-13a *trans*-12b

The initial product *cis*-13a, in equations [43] and [44], contains three fluorines, *i.e.* *cis*-Ph_2TeF_3Cl, presumably because Bu_4NF was used instead of Et_4NCl. When Et_4NCl was used as a catalyst, *cis*-$Ph_2TeF_2Cl_2$ 14a was produced (*i.e.* *cis*-phenyl-structure with two fluorines, see equation [42]). The mechanistic details will be discussed later in section I-C.

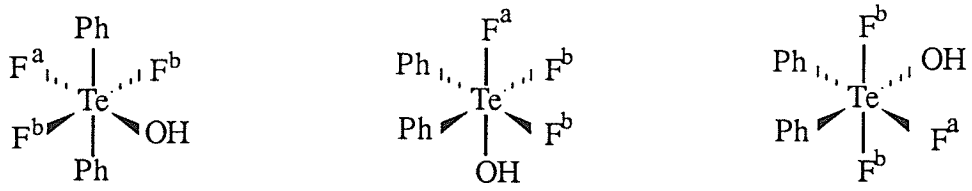
The structural assignment of 13a is based on NMR results. Triplet and doublet ^{19}F NMR resonances indicate an ab_2 fluorine spin system, and for a *cis*-structure there are two possible geometrical isomers, *i.e.* *cis*-13a and *cis*-13b, as shown in Figure 13.

The ^{19}F NMR parameters of *cis*-Ph_2TeF_3Cl 13a are expected to be very similar to those of *cis*-Ph_2TeF_4 12a, and by comparison, *cis*-13a is suggested to be the correct structure for the reaction product because a triplet (F^a) appears at lowfield and a doublet (F^b) at high field, at similar positions to those for the triplets in *cis*-12a (see Table 8). However, since both *cis*-13a and *cis*-13b have ab_2 fluorine spin systems, it cannot be stated with certainty that *cis*-13a is the correct isomer. However, it should be emphasized that the phenyl substituents in both isomers are *cis* to each other.

c. Hydrolysis of *trans*-Ph_2TeF_4. Previous studies in our laboratory (60) have shown that *trans*-Ph_2TeF_4 hydrolyzed very slowly in the presence of excess H_2O, and the product Ph_2TeF_3OH was formed in 20% yield after 5 days according to equation [45]:

$$\textit{trans}\text{-}Ph_2TeF_4 + H_2O \xrightarrow[CH_3CN]{25\ ^\circ C} Ph_2TeF_3OH + HF \qquad [45]$$

Three isomeric structures are possible for Ph_2TeF_3OH, and each of the three isomers is expected to have an ab_2 fluorine spin system in its ^{19}F NMR spectrum:



21a 21b 21c

Figure 21. The three possible geometrical isomers of Ph_2TeF_3OH.

Experimentally, only one ab_2 ^{19}F NMR spectrum was observed (Table 8), and thus it could not be established which isomer is the hydrolysis product.

The experiment was modified to improve the yield of the reaction. The hydrolysis of *trans*-Ph_2TeF_4 was carried out in dichloromethane solution at 25 °C in the presence of a 5-fold excess of tetrapropylammonium hydroxide, Pr_4NOH. After 2 days, all of the *trans*-Ph_2TeF_4 had hydrolyzed, as judged by ^{19}F NMR spectroscopy, and gave a 4:1 mixture of the hydrolysis products, Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$. The structural assignment for $Ph_2TeF_2(OH)_2$ is made on the basis of ^{19}F, ^{125}Te, and ^{13}C NMR spectroscopy. Figure 22 illustrates the ^{19}F NMR spectrum of the 4:1 mixture of Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$ in $CDCl_3$. When excess Pr_4NOH was added to this mixture, some of Ph_2TeF_3OH further hydrolyzed to give $Ph_2TeF_2(OH)_2$. The product then consisted of a 2:3 mixture of Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$, as determined by ^{19}F NMR integration, which is illustrated in Figure 23.

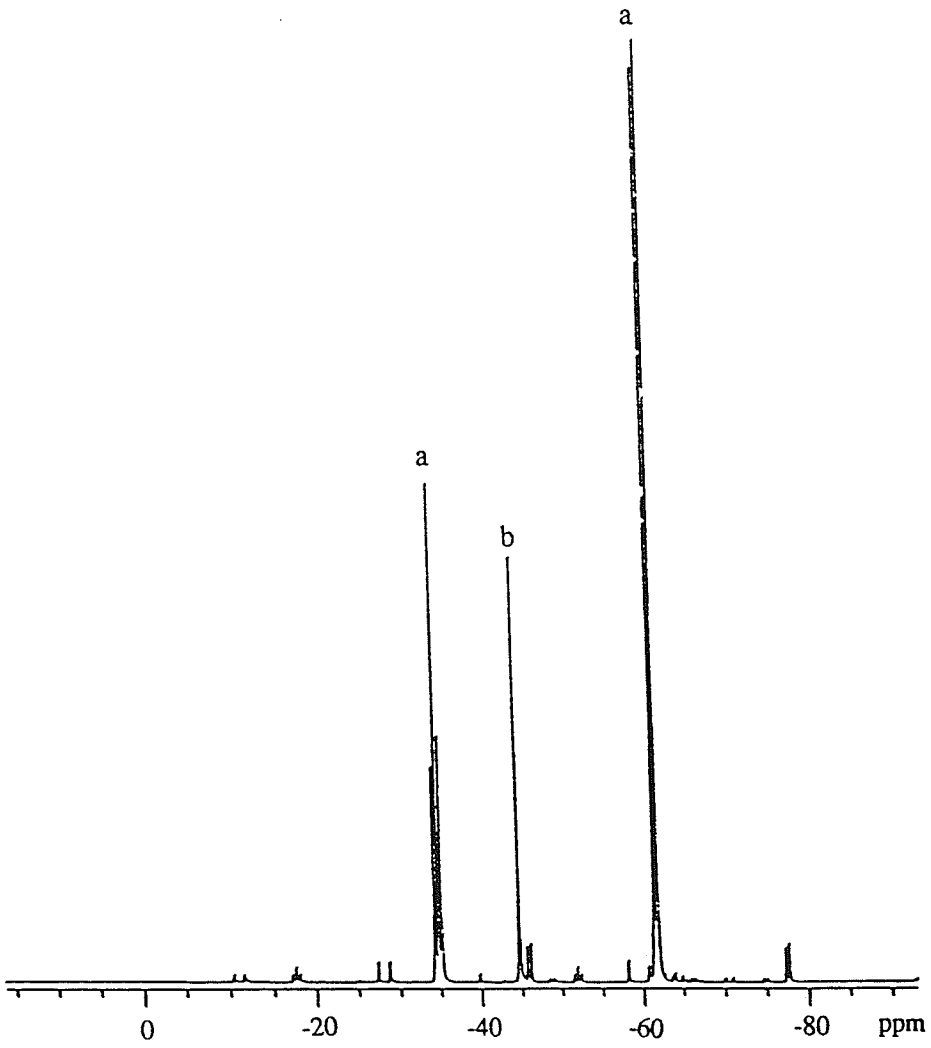


Figure 22.1 The ^{19}F NMR spectrum of a 4:1 mixture of Ph_2TeF_3OH (peaks a) and $Ph_2TeF_2(OH)_2$ (peaks b) in $CDCl_3$. $Ph_2TeF_2(OH)_2$ consists of a singlet ^{19}F NMR resonance due to equivalent fluorines.

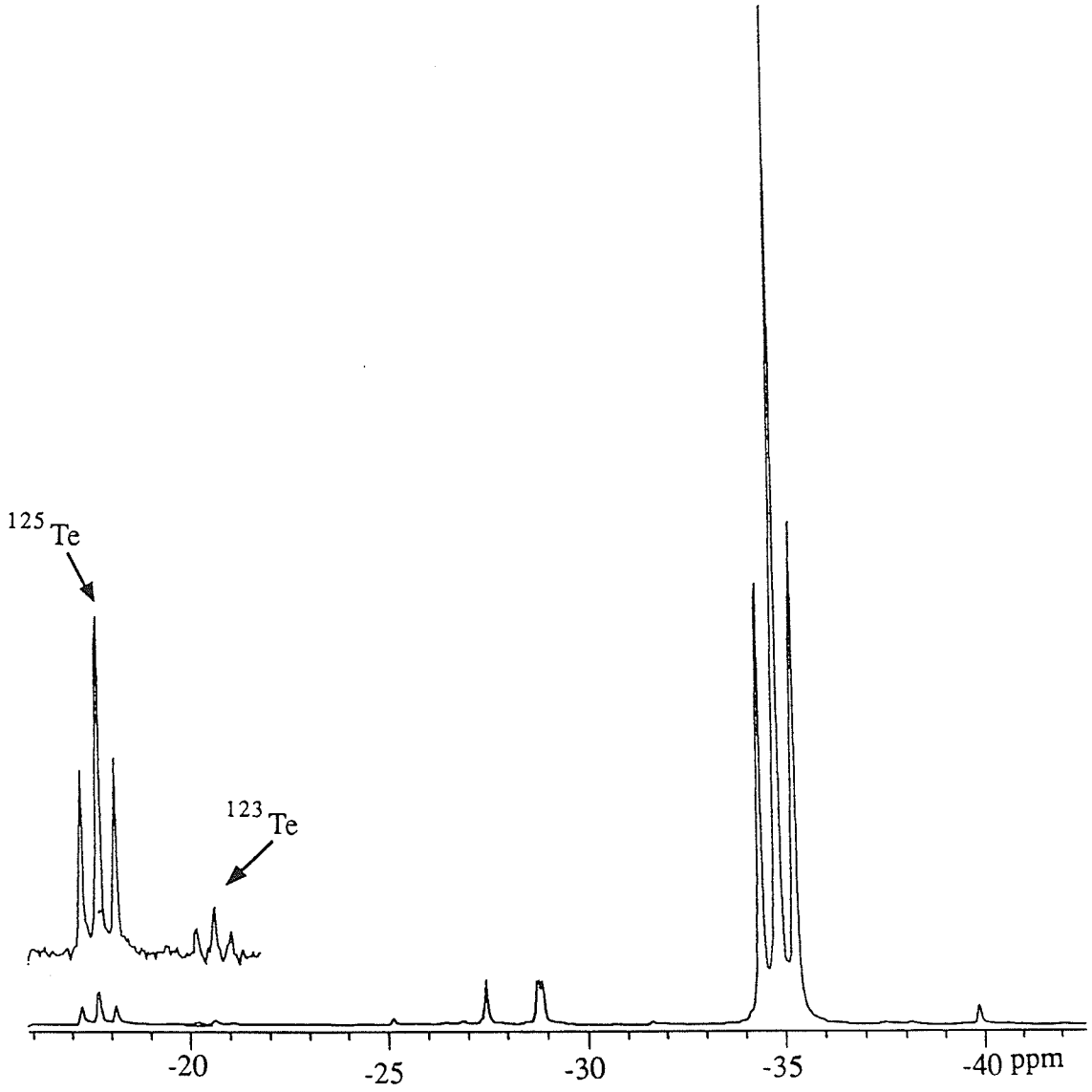


Figure 22.2 ~15-40 ppm expanded ^{19}F NMR spectrum of $Ph_2TeF^aF_2{}^bOH$ showing the F^a triplet resonance with $^{125/123}Te$-coupled satellites on its low field side.

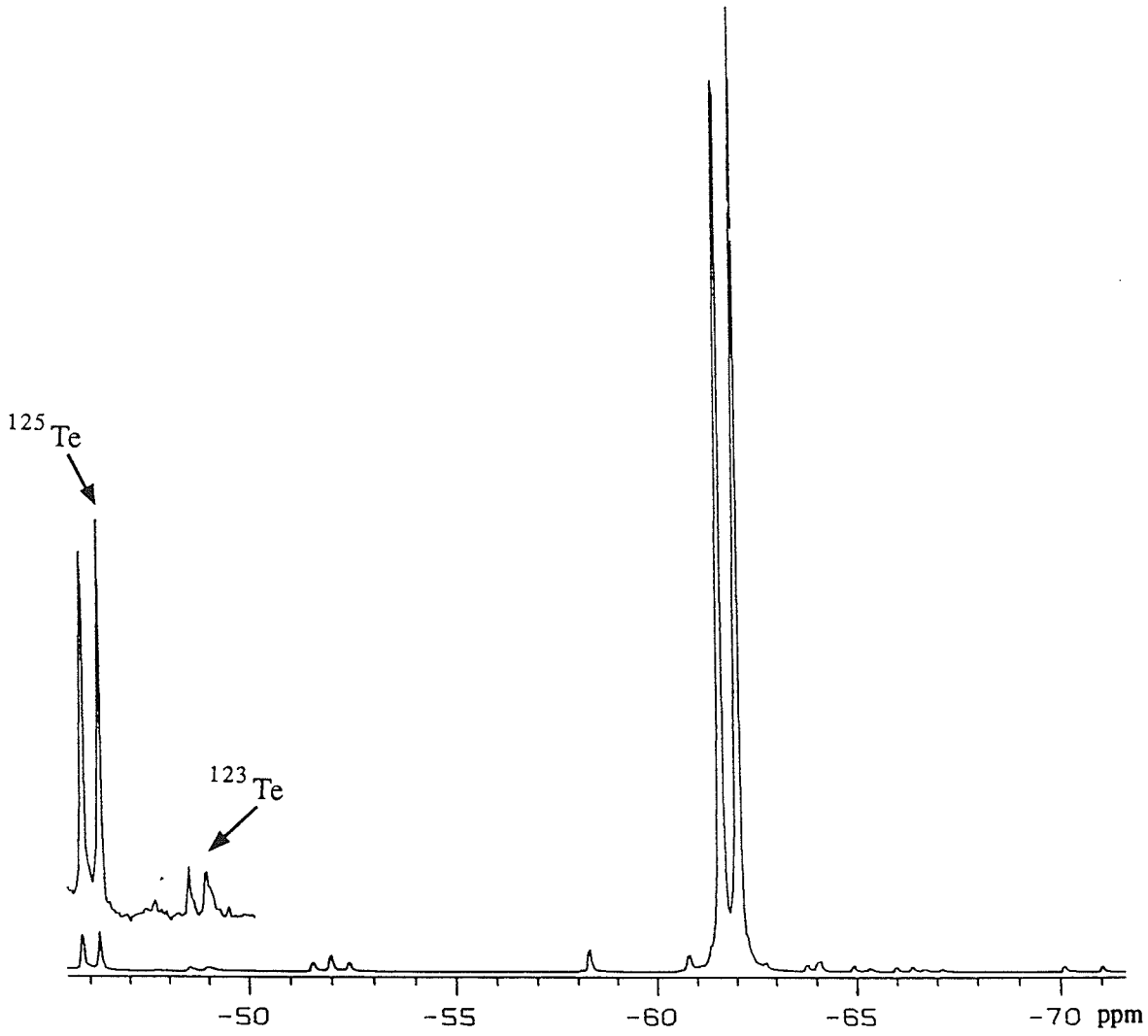


Figure 22.3 ~45-75 ppm expanded ^{19}F NMR spectrum of $Ph_2TeF^aF_2^bOH$ showing the F^b doublet resonance with $^{125/123}Te$-coupled satellites on its low field side.

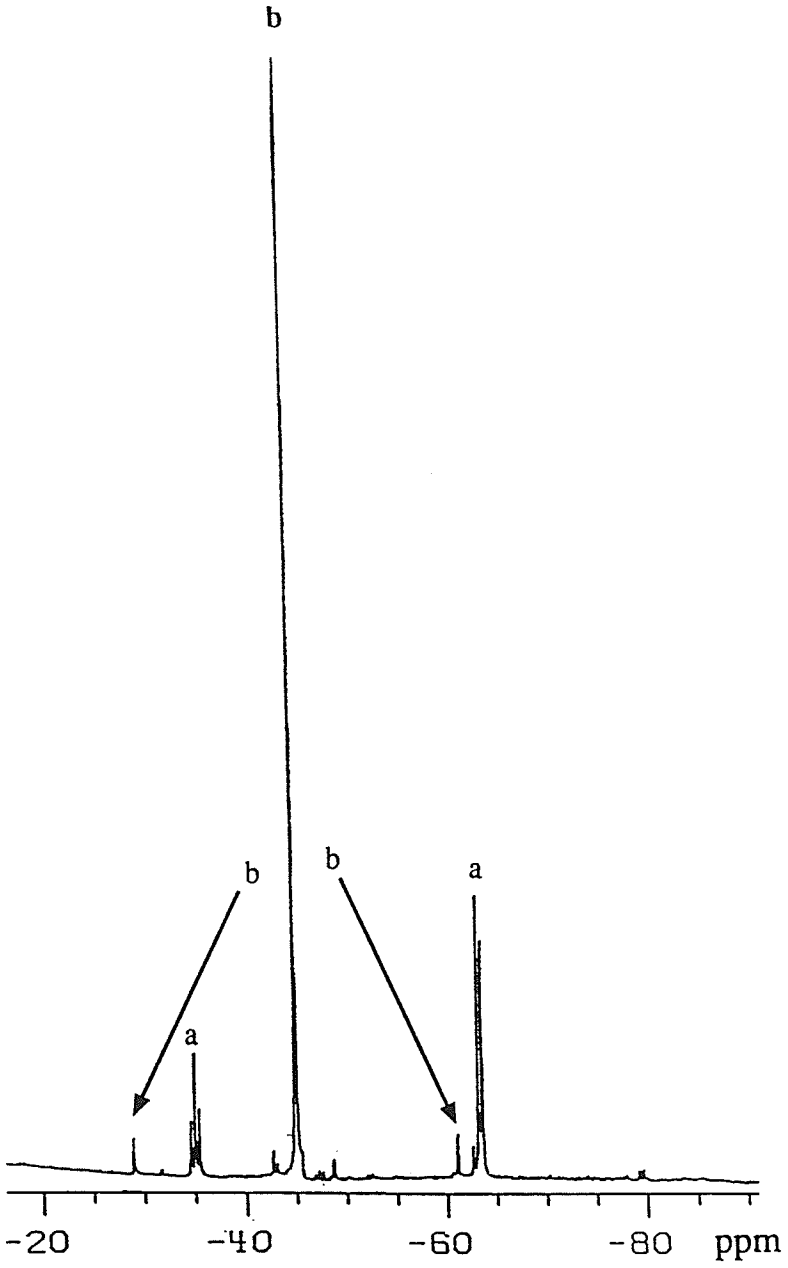


Figure 23. The ^{19}F NMR spectrum of a 2:3 mixture of Ph_2TeF_3OH (a triplet and doublet marked with a) and $Ph_2TeF_2(OH)_2$ (a singlet marked with b) in $CDCl_3/D_2O$ (1:1).

A doublet of triplets ^{125}Te NMR spectrum of Ph_2TeF_3OH, shown in Figure 24, still does not establish the geometry (for the ^{19}F and ^{125}Te NMR data of the hydrolysis products, see Table 8). However, the results of ^{13}C NMR spectroscopy, which will be discussed shortly, indicate that the two phenyl substituents are equivalent. Therefore, its structure could be either 21a or 21b, but not 21c, because structure 21c consists of non-equivalent phenyl substituents.

In the presence of excess R_4NOH, the hydrolysis products, Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$, are stable for about two days, but they eventually decompose to give an unidentified white solid, extremely insoluble in most organic solvents (m.p. >350 °C, dec).

So far the improved synthesis of Ph_2TeF_3OH has been discussed. In addition, this species was often observed as a minor component in the preparation of *trans*-Ph_2TeF_4 by the oxidative fluorination of Ph_2TeX_2 (X = F/Cl) with XeF_2. Recrystallization of the mixture of *trans*-Ph_2TeF_4 and Ph_2TeF_3OH from CH_2Cl_2 gave colorless crystals of *trans*-Ph_2TeF_4. The remaining solution was examined, but it did not contain any ^{19}F NMR resonance.

The hydrolysis product, $Ph_2TeF_2(OH)_2$, contains two equivalent fluorines, as judged by the singlet ^{19}F NMR resonance with ^{125}Te-coupled satellites (Figure 23) and a triplet ^{125}Te NMR resonance at 768 ppm with the same magnitude of $J(^{125}Te\text{-}F)$ obtained in the ^{19}F NMR spectrum. The ^{125}Te NMR spectrum of the mixture of Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$ is shown in Figure 25.

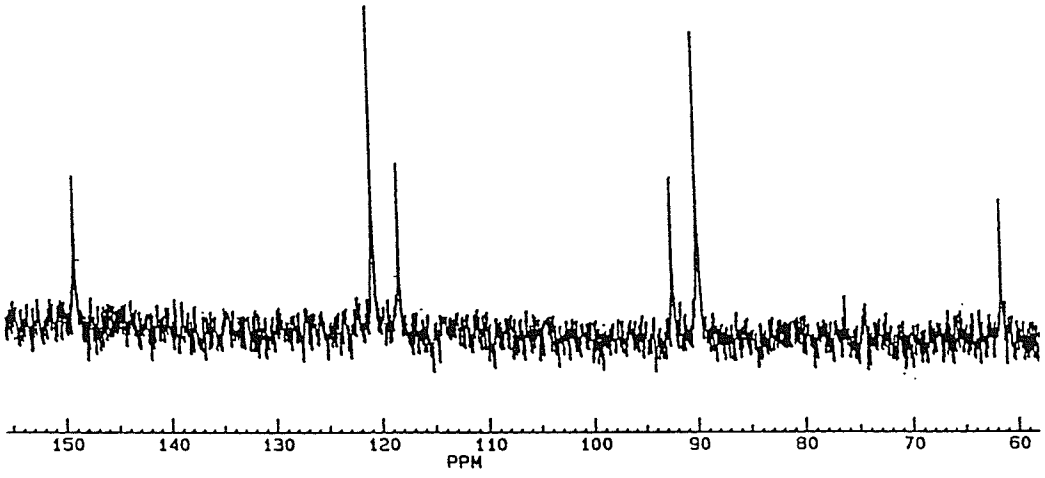


Figure 24. The ^{125}Te NMR spectrum of $Ph_2TeF^aF_2{}^bOH$ in CD_3CN showing doublet of triplets.

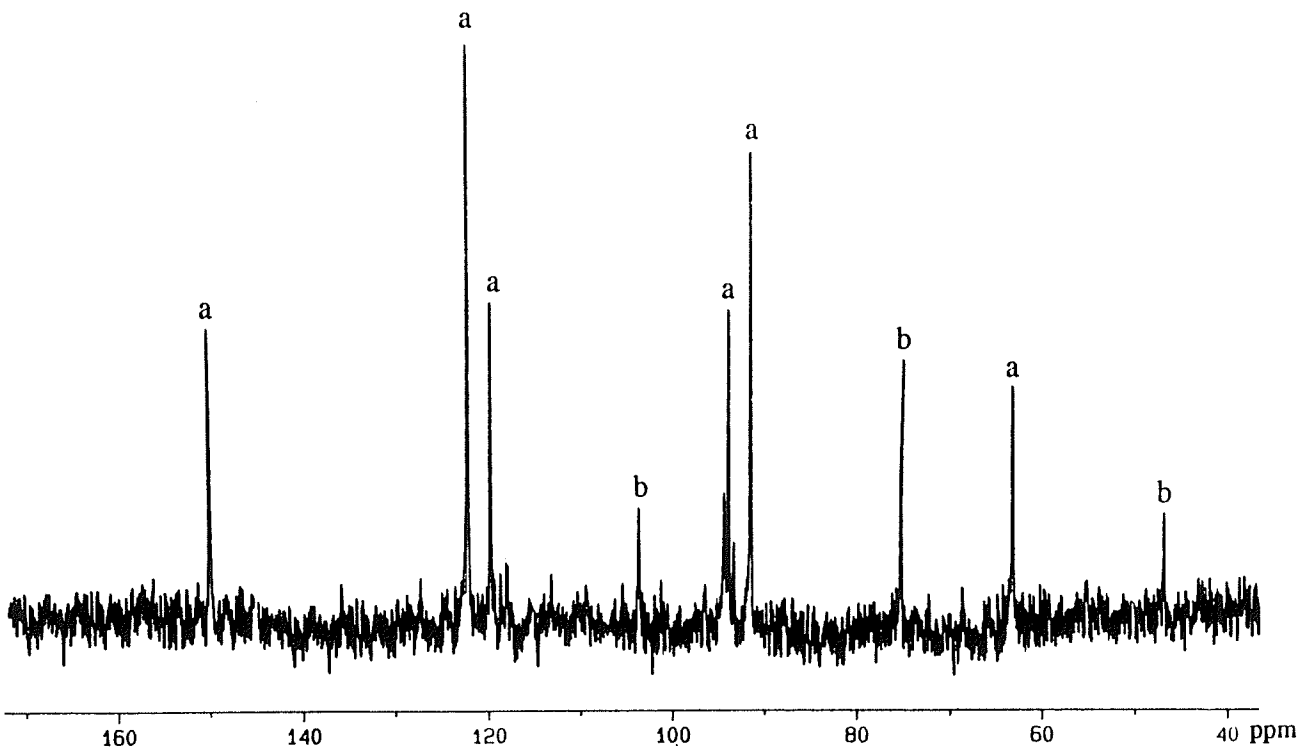
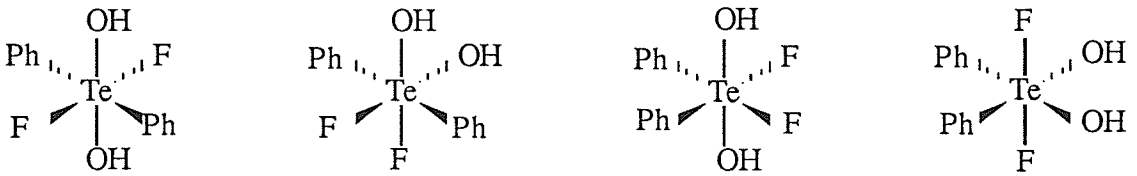


Figure 25. The ^{125}Te NMR spectrum of a mixture of Ph_2TeF_3OH (doublet of triplets marked with a) and $Ph_2TeF_2(OH)_2$ (triplet marked with b) in $CDCl_3$. The chemical shift is measured relative to Ph_2Te. For the converted values relative to Me_2Te, see Table 8.

For $Ph_2TeF_2(OH)_2$, which contains two equivalent fluorines, as judged by ^{19}F and ^{125}Te NMR spectroscopy, there are four possible geometrical isomers, as illustrated in Figure 26;



trans-26a *trans*-26b *cis*-26c *cis*-26d

Figure 26. The four possible geometrical isomers of $Ph_2TeF_2(OH)_2$. All have equivalent phenyl and fluorine substituents (*cis* and *trans* denote the orientation of the phenyl substituents).

They are not distinguishable in solution by NMR spectroscopy, and thus it remains undecided which isomer is the hydrolysis product obtained.

However, the phenyl substituents of the thermodynamically stable hydrolysis products should be *trans* to each other, *i.e.* *trans*-21a for Ph_2TeF_3OH and *trans*-26a or *trans*-26b for $Ph_2TeF_2(OH)_2$, since the thermodynamically stable isomers of Ph_2TeX_4 (X = F/Cl) favour the *trans*-configuration for the phenyl substituents. The structures of *trans*-26a and *trans*-26b could not be distinguished by NMR spectroscopy.

Furthermore, the formation of Ph_2TeF_3OH (equation [45]) probably involves the following mechanism:

$$Ph_2TeF_3^+ + H_2O \longrightarrow Ph_2TeF_3OH + H^+ \qquad [46]$$

As discussed previously, the $Ph_2TeF_3^+$ cation always generates the *trans*-geometry with the incoming ligand and thus Ph_2TeF_3OH is probably the *trans*-isomer.

C. Mechanisms of oxidative fluorination

There appears to be no simple generalization about the mechanisms of oxidative fluorination reactions of main group compounds in the literature. It may be partially due to the difficulty of handling the oxidizing agent, which makes it difficult to observe the reaction progress, including intermediate and isomerization processes.

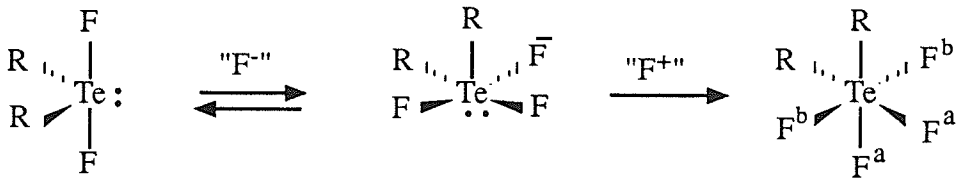
1. The proposed mechanism

The formation of fluoride impurities always occurs in the reaction of Ph_2TeF_2 with XeF_2, mainly due to the slowness of the oxidative reaction. These fluoride impurities are capable of catalyzing isomerization, which interferes with the observation of the kinetically favoured products. In other words, interpretation of the mechanisms of oxidative reactions can be greatly complicated by the presence of impurities, by isomerization reactions, and by the the existence of more than one isomeric product.

However, it was shown that these fluoride impurities were indeed required to catalyze the oxidation, *e.g.* for reaction in a glass tube (Table 9). This observation, although it is less direct evidence, indicates that the formation of ionic intermediates may be a prerequisite to the oxidation process, *i.e.* the inability to form an ionic intermediate

may be responsible for the slowness of the oxidation.

More importantly, the oxidative reaction proceeds very rapidly on addition of catalytic amounts of tetraalkylammonium halide, R_4NX (X = F, Cl), which constitutes evidence that the reaction involves an ionic intermediate. In addition, the reaction of $(C_6H_5)_2TeF_2$ with XeF_2 gives the kinetically favoured product, *cis*-$(C_6H_5)_2TeF_4$, and the analogous reaction of $(C_6F_5)_2TeF_2$ with F_2 gives *cis*-$(C_6F_5)_2TeF_4$ (11), *i.e.* in the oxidative fluorination of R_2TeF_2 (R = C_6H_5 or C_6F_5) the following mechanism is proposed:



[47]

intermediate tellurate(IV) anion

kinetically favoured *cis*-R_2TeF_4

a. The source of fluoride anion (F^-)

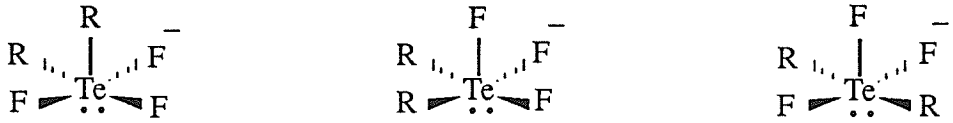
In the first step of reaction [47], various fluoride impurities, such as HF, FHF^-, BF_4^-, SiF_5^-, SiF_6^{2-} or R_4NF, may serve as a source of fluoride anion (F^-). This is certainly reasonable, because these species have been observed in almost every reaction, *e.g.* during or after the oxidative fluorination. This could be the reason why the oxidative reaction is very slow in a Teflon reaction bottle (Table 9), because the formation of fluoride impurities indicated above is not likely to occur under such conditions. However, it was observed that even with a Teflon reaction bottle, small amounts of

fluoride impurities were found, presumably due to the use of glass pipet or glass vacuum manifold that was used for evaporation of solvent.

Furthermore, the oxidation occurs much faster in a glass reaction tube (Table 9) because fluoride impurities are easily generated by reaction of HF with glass (see section I-A-4).

b. The intermediate tellurate(IV) anion

Once the fluoride ions are present in solutions of R_2TeF_2 (R = C_6H_5, C_6F_5) in common organic solvents, the intermediate tellurate(IV) anion may be formed, and an equilibrium is established between R_2TeF_2 and $R_2TeF_3^-$. The square pyramidal structure of $R_2TeF_3^-$ can exist as three possible geometrical isomers:



27a 27b 27c

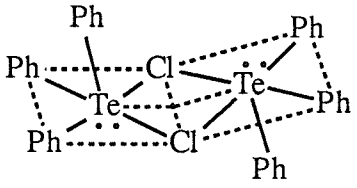
Figure 27. The three possible geometrical isomers of *cis*-$R_2TeF_3^-$ (R = C_6H_5, C_6F_5).

The intermediate structure should prefer either 27a or 27b, i.e. *cis*-R groups, to give kinetically favoured *cis*-R_2TeF_4. In other words, if the intermediate prefers structure 27c, then the *trans*-isomer, *trans*-R_2TeF_4, is expected to be the kinetically favoured product. However, our results and Naumann's results (11) have shown that the *cis*-

isomer is the kinetically favoured product.

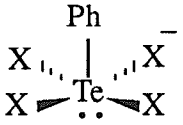
In the mechnism proposed in equation [47], the intermediate 27a in which R is *trans* to the lone pair, rather than 27a, is suggested on the basis of the structures known in the literature, as in the following examples:

1. A dimeric structure of Ph_3TeCl, as determined by X-ray crystallography (80). Ph_3TeCl increases the coordination number of the central atom by dimerization. $[Ph_3TeCl]_2$ is a chloride-bridged dimer with 5-coordinate square pyramidal geometry about Te and a phenyl group *trans* to the lone pair:

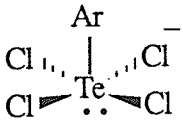


2. Square pyramidal structures of tellurate(IV) anions:

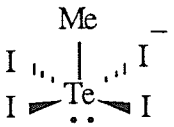
(1) Tetrahalophenyl tellurates(IV) of the type, $Ph_3Te^+PhTeX_4^-$ (X = Cl, Br, I) with a phenyl group *trans* to the lone pair (81):



(2) Tetrachloroaryl tellurates(IV) of the type, $Y^+ArTeCl_4^-$ (Y = $MePh_3P$, Ph_3Te, C_7H_7, and Me_4N), with an aryl group trans to the lone pair (82):

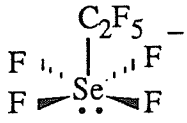


(3) Tetraiodomethyl tellurates(IV), $Me_3Te^+MeTeI_4^-$, with a methyl group *trans* to the lone pair (83):



Although some literature information is available about tetrahaloorgano tellurates(IV), as in the above examples, and even more for pentahalo tellurates(IV) (84), there is no information on penta-coordinate halo anionic species of tellurium(IV) with two or more organic groups. Presumably with bulky substituents, a tetra-coordinate structure is favoured over the more crowded square pyramid.

3. A penta-coordinate structure of selenium(IV) (also a group VI element), $Cs^+C_2F_5SeF_4^-$ (85):



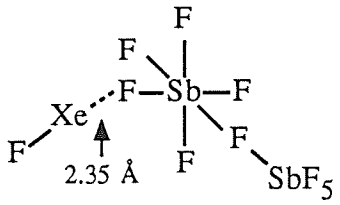
c. The source of fluorine cation ("F^+")

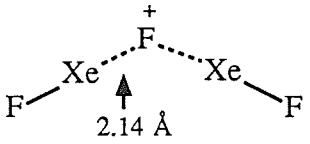
The second step in reaction [47] requires a source of fluorine cation ("F^+"), which then attacks at tellurium, *trans* to the R group of the intermediate 27a, to form the kinetically favoured product, *cis*-R_2TeF_4. The observation of fluoride anions (*e.g.* BF_4^-, FHF^-) in the oxidative reaction suggests the possible existence of fluorine cations (*e.g.* XeF^+, F-Xe-F-Xe-F^+, $Ph_2TeF_3^+$) as their counter ions, any of which could serve as a source of "F^+".

There is sufficient structural evidence in the literature to suggest that the important reactive species in oxidative fluorinations are XeF^+ or $Xe_2F_3^+$:

1. A variety of adducts of XeF_2 with pentafluorides such as SbF_5, AsF_5, TaF_5, NbF_5, PtF_5, RuF_5, IrF_5, and OsF_5 have been prepared, the majority having 2:1, 1:1, or 1:2 stoichiometries (86–93), *e.g.* $XeF_2 \cdot 2SbF_5$, $2XeF_2 \cdot AsF_5$, and $XeF_2 \cdot RuF_5$. X-ray crystallographic studies of $XeF_2 \cdot 2SbF_5$, $XeF_2 \cdot RuF_5$, and $2XeF_2 \cdot AsF_5$ have shown that these adducts are actually $XeF^+Sb_2F_{11}^-$, $XeF^+RuF_6^-$, and $Xe_2F_3^+AsF_6^-$, respectively (94–96). In general, adducts of XeF_2 with pentafluorides can be written as $XeF^+MF_6^-$, $XeF^+ M_2F_{11}^-$, and $Xe_2F_3^+MF_6^-$.

In the $XeF_2 \cdot 2SbF_5$ compound (94), the structure consists of essentially XeF^+ and $Sb_2F_{11}^-$ ions, which have a rather short anion-cation contact, indicating a rather strong fluorine-bridge F-Xe···F-Sb with presumably considerable covalent character. However, the results of Raman studies (92) indicate that in the V-shaped $Xe_2F_3^+$ ion, the bridging Xe···F bonds are longer and weaker than the terminal Xe-F bonds:





Therefore, in the oxidation of Te(IV) compounds with XeF_2, it may be more reasonable to expect that a Lewis acid such HF or BF_3 interacts with 2 equivalents of XeF_2 to form $Xe_2F_3^+$, which can serve as a source of "F^+", as described in equation [48]:

$$2\ XeF_2 + A\ (HF \text{ or } BF_3) \rightleftharpoons F\text{-}Xe\text{-}F\text{-}Xe\text{-}F^+AF^- \qquad [48]$$

The ^{129}Xe NMR spectrum of the $Xe_2F_3^+$ cation has been obtained in BrF_5 solvent at -60 °C (97), in which $J^{129}Xe\text{-}F^b$(bridging) = 4828 Hz, $J^{129}Xe\text{-}F^t$(terminal) = 6662 Hz. However, no NMR evidence has been found for the existence of the $Xe_2F_3^+$ ion in the oxidative fluorination of Te(IV) compounds with XeF_2 in this work. This is not surprising since it is a very reactive species, which may instantaneously react with the intermediate tellurate(IV) anion to form the stable six-coordinate Te(VI) compound, as shown in equation [47]. Furthermore, the broad peak often observed during the oxidative reaction in the region of fluoride impurities (HF or BF_3), in the ^{19}F NMR spectrum, indicates the possibility of fluorine exchange, as illustrated in equation [48].

Stein *et. al.* (98) have prepared $XeF^+Sb_2F_{11}^-$ by the reaction of a mixture of xenon, fluorine, and antimony pentafluoride, and during the course of their work they observed a yellow color characteristic of monofluoroxenon cation, XeF^+. The characteristic yellow color has always been observed during oxidative fluorination of Te(IV) compounds with XeF_2. The yellow color disappeared after several minutes.

Furthermore, there has been an example in the literature where $XeF^+MF_6^-$ (M = As, Sb) compounds were used to donate fluorine cation ("F^+") to $(CF_3)_2S$ to give $(CF_3)_2SF^+MF_6^-$ (99).

2. Recently, Schrobilgen has prepared the acetonitrile and perfluoroacetonitrile adducts of monofluoroxenon cation, *i.e.* $CH_3CN{-}XeF^+$ (100) and $CF_3CN{-}XeF^+$ (101). Their ^{19}F NMR spectra were examined in BrF_5 solvent at -58 to -68 °C.

In summary, aside from an early study of XeF_2 in HF (102), in which the addition of traces of Lewis acids considerably increases the reactivity of xenon difluoride via an ionization step, there are many examples of fluoroxenon cations in the literature, as discussed above. Furthermore, sources of positive fluorine have been reviewed by Cartwright and Woolf (103).

d. Oxidative reactions of R_2TeF_2 (R = C_6H_5 or C_6F_5)

In the previous sections, the mechanism of the oxidative fluorination of R_2TeF_2 has been discussed, and therefore, the results will be examined in this section.

The oxidative fluorinations of $(C_6H_5)_2TeF_2$ and $(C_6F_5)_2TeF_2$ give the kinetically favoured products, *cis*-$(C_6H_5)_2TeF_4$ and *cis*-$(C_6F_5)_2TeF_4$ (11), respectively, according to equation [49]:

$$(C_6H_5)_2TeF_2 \xrightarrow[CH_3CN,\ 25\ ^\circ C]{XeF_2} cis\text{-}(C_6H_5)_2TeF_4 \qquad [49a]$$

$$(C_6F_5)_2TeF_2 \xrightarrow[CH_3CN,\ -35\ ^\circ C]{F_2} cis\text{-}(C_6F_5)_2TeF_4\ (11) \qquad [49b]$$

These reactions can be compared by making use of the NMR parameters given in Table 10. The starting compounds, $(C_6H_5)_2TeF_2$ and $(C_6F_5)_2TeF_2$, were prepared by oxidative fluorinations of $(C_6H_5)_2Te$ and $(C_6F_5)_2Te$ (11), respectively.

As discussed in detail in the previous section B-2, *cis*-$(C_6H_5)_2TeF_4$ was found to undergo impurity-catalyzed isomerization to give the thermodynamically more stable *trans*-$(C_6H_5)_2TeF_4$.

Klein and Naumann (11) have reported that the reaction of $(C_6F_5)_2TeF_2$ with F_2 (equation [49b]) produced *cis*-$(C_6F_5)_2TeF_4$, which is characterized by two triplets of equal intensity in the ^{19}F NMR spectrum at -35 °C. However, as the temperature increased to 0 °C, these resonances disappeared to give a sharp singlet with satellites due to ^{125}Te-F coupling and this new resonance was assigned to TeF_4. This result was ascribed to reduction of Te(VI) (in $(C_6F_5)_2TeF_4$) to Te(IV).

For tellurium tetrafluoride, which has pseudo trigonal bipyramidal configuration with C_{2v} symmetry, Te-F coupling has never been observed due to rapid Te-F exchange. In an early study, Muetterties and Phillips (104) could not observe Te-F coupling for TeF_4, even at -100 °C in toluene (lowest melting solvent for TeF_4) because of rapid exchange. The reported ^{19}F chemical shift of TeF_4 (104) is -27.1 ppm.

TABLE 10

NMR data of R_2TeF_2 and *cis*- and *trans*-R_2TeF_4 (R=C_6H_5 and C_6F_5)[a]

This work			Klein and Naumann (11)		
$(C_6H_5)_2TeF_2$	δF	-124.6	$(C_6F_5)_2TeF_2$	δF	-102.5
	J(TeF)	566		J(TeF)	403
cis-$(C_6H_5)_2TeF_4$	δF^a	-32.7	*cis*-$(C_6F_5)_2TeF_4$	δF^a	-21.3
	δF^b	-75.9		δF^b	-39.4
	$J(F^aF^b)$	87.3		$J(F^aF^b)$	100.9
	$J(TeF^a)$	2884		$J(TeF^a)$	–
	$J(TeF^b)$	2675		$J(TeF^b)$	–
trans-$(C_6H_5)_2TeF_4$	δF	-56.7	*trans*-$(C_6F_5)_2TeF_4$[b]	δF	-24.7
	J(TeF)	2997		J(TeF)	3540

[a] Chemical shift in ppm, coupling constant in Hz, and solvent is CD_3CN.

[b] The decomposition product of *cis*-$(C_6F_5)_2TeF_4$ was originally assigned as TeF_4(11), but this is probably incorrect (see text).

Birchall *et al.* (105) have accurately measured the ^{125}Te chemical shift of TeF_4 for the first time, $\delta^{125}Te = 1270$ ppm, but also failed to observe Te-F coupling.

Furthermore, Thrasher *et al.* (106) have obtained the ^{19}F NMR spectrum of TeF_4, which contained a broad single resonance and no evidence for Te-F coupling.

Therefore, the decomposition product of *cis*-$(C_6F_5)_2TeF_4$ at 0 °C, reported by Naumann (11), may not necessarily be TeF_4, because even at -100 °C Te-F coupling in TeF_4 has not been observed. In particular, the magnitude of the coupling constant of the decomposition product, J(Te-F) = 3540 Hz (Table 10), is far from those reported for other Te(IV) species, *e.g.* $(C_6H_5)_2TeFCl$ (584 Hz), $(C_6H_5)_2TeF_2$ (566 Hz), $(C_6F_5)_2TeF_2$ (403 Hz), and for the analogous species Ph_2SeF_2 ($J^{77}Se$-F = 581 Hz) (58). Values over ~1000 Hz cannot be found in the literature for organotellurium(IV) fluorides, or for analogous compounds of other group VI elements.

On the other hand, the large coupling constant (3540 Hz) of the decomposition product falls within the range of those reported for other Te(VI) species, *e.g.* for TeF_6, $\delta F = -57.9$ ppm and J(Te-F) = 3688 Hz (104). The values for fluorophenyltellurium(VI) compounds listed in Tables 6 & 8, and for other known Te(VI) fluorides (too extensive to report) indicate that the decomposition product could be a Te(VI) species.

The fact that the decomposition product showed a sharp ^{19}F NMR resonance and a large Te-F coupling constant suggests formation of *trans*-$(C_6F_5)_2TeF_4$ rather than TeF_4. Aside from the NMR data, this is certainly reasonable because *cis*-$(C_6H_5)_2TeF_4$ isomerizes to the thermodynamically more stable *trans*-$(C_6H_5)_2TeF_4$ in the presence of a Lewis acid, such as BF_3 or HF. The fact that the preparation of *cis*-$(C_6F_5)_2TeF_4$ was carried out in an ordinary glass reaction vessel indicates the possible formation of Lewis acids, which can readily catalyze isomerization.

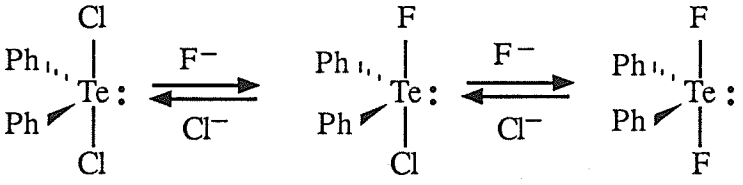
In conclusion, this thesis proposes that the mechanism of oxidative fluorination of R_2TeF_2 involves the tellurium(IV) anionic intermediate, and the attack of "F^+" at tellurium, *trans* to phenyl, of that intermediate gives the kinetically favoured product, *cis*-R_2TeF_4, which is converted to its *trans*-isomer by an impurity-catalyzed isomerization.

2. Oxidative fluorinations of phenyltellurium(IV) compounds with xenon difluoride

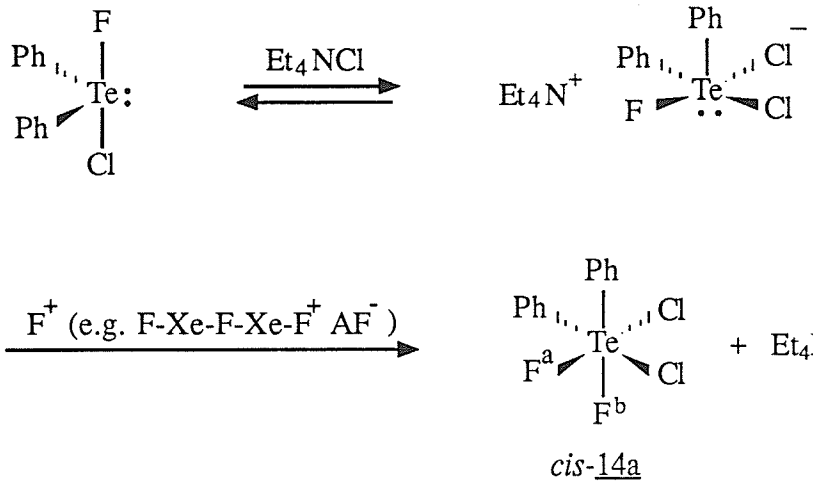
In the previous section B, the results of oxidative fluorinations of phenyltellurium(IV) compounds with xenon difluoride were presented. In this section, the mechanisms of oxidation will be discussed for the reactions described in section B.

a. Oxidation of Ph_2TeCl_2

(1) With tetraethylammonium chloride. In the reaction of Ph_2TeCl_2 with 2 equivalents of XeF_2 in the presence of tetraethylammonium chloride, the first isomeric form to appear is *cis*-$Ph_2TeF_2Cl_2$ 14a (Table 8), as illustrated in equation [42]. The following mechanism is suggested:



[50a]



cis-14a

Although the starting compound is Ph_2TeCl_2, Et_4NCl must react with Ph_2TeFCl, presumably because the initial isomeric form (*cis*-14a) contains two non-equivalent fluorines according to equation [50b]. It has been shown in the reaction of Ph_2TeCl_2 with XeF_2 without catalyst (experimental section B-5) that a mixture of Ph_2TeFCl and Ph_2TeF_2 (as well as unreacted Ph_2TeCl_2) was formed before oxidation occurred. Furthermore, in the reaction of Ph_2TeCl_2 with R_4NF, NaF, or $Ph_3SnF_2^-$, equilibrium is established between these species, as described in equation [50a].

For the intermediate *cis*-$Ph_2TeFCl_2^-$ in equation [50b], there are two possible geometrical isomers of the square pyramidal species with lone pairs *trans* to phenyl groups:

28a 28b

Figure 28. The two possible geometrical isomers of *cis*-$Ph_2TeFCl_2^-$.

The structure 28a must be the possible intermediate, because only 28a can produce *cis*-14a which gives an ab fluorine spin system in its ^{19}F NMR spectrum.

In solution, equilibrium favours Ph_2TeFCl in equation [50a] and, furthermore, formation of tellurate(IV) anionic species with two R groups has not been reported in the literature: *i.e.* $PhTeCl_3$ forms an ionic adduct $R_4N^+PhTeCl_4^-$ (colorless crystals) with R_4NCl (82). However, Ph_2TeCl_2 does not form an adduct with the same chloride.

The following experiments were conducted in an effort to observe the formation of the intermediate:

1. A 1–3 molar ratio of Et_4NCl was added to a mixture of Ph_2TeFCl and Ph_2TeF_2 in $CDCl_3$, and their ^{19}F NMR spectra were examined at room temperature, with the following results:

Ph_2TeF_2	no Cl^-	1 Cl^-	2 Cl^-	3 Cl^-
δ [ppm]	-127.5	-126.5	-126.7	-125.7
J(^{125}Te-F) [Hz]	555	565	588	608
Ph_2TeFCl	no Cl^-	1 Cl^-	2 Cl^-	3 Cl^-
δ [ppm]	-109	-110	-111	-111.8
J(^{125}Te-F) [Hz]	595	575	563	547

Although the chemical shift values differ only by 2 ppm between Ph_2TeX_2 and the mixture of Ph_2TeX_2 and 3 equivalents of Et_4NCl, the changes in coupling constant values indicate that J is a more sensitive parameter for adduct formation. This trend has also been observed for NMR parameters between Te(IV) and Te(VI) fluorides.

2. Similar results were obtained in the ^{19}F NMR spectra of a mixture of Ph_2TeF_2 and Ph_2TeFCl with a strong donor molecule, DMSO, in CD_3CN/CH_2Cl_2 (1:1), as follows:

Ph_2TeF_2	no DMSO	1 DMSO
δ [ppm]	-125	-124.9
J(^{125}Te-F) [Hz]	625	629.5
Ph_2TeFCl	no DMSO	1 DMSO
δ [ppm]	-112	-112.7
J(^{125}Te-F) [Hz]	545	536.7

The changes in chemical shifts and coupling constants follow the same direction that was observed in the chloride adduct described above.

3. Variable low temperature ^{19}F NMR spectra were obtained for a mixture of Ph_2TeF_2 and Bu_4NF (~ 1:2 ratio) in CD_3CN from 300 K down to 235 K (the freezing point of CH_3CN), with the following results:

^{19}F NMR data of a mixture of Ph_2TeF_2 and Bu_4NF in CD_3CN at variable temperatures		
Temperature (K)	δ [ppm]	J(^{125}Te-F) [Hz]
300	-124.7	562.0
270	-125.7	560.2*
250	-126.2	567.3
240	-126.5	570.9
235	-126.7	573.5

* The coupling constant obtained at 270 K was slightly decreased in contrast to the other values.

As before, the coupling constants are more sensitive to change than the chemical shifts. It is noted that with fluoride addition, ^{19}F chemical shifts in Ph_2TeF_2 move towards higher field in contrast to chloride addition, which moves δF to lower field. However, even at 235 K, the ab_2 ^{19}F NMR spectrum expected for $Ph_2TeF_3^-$ was not obtained.

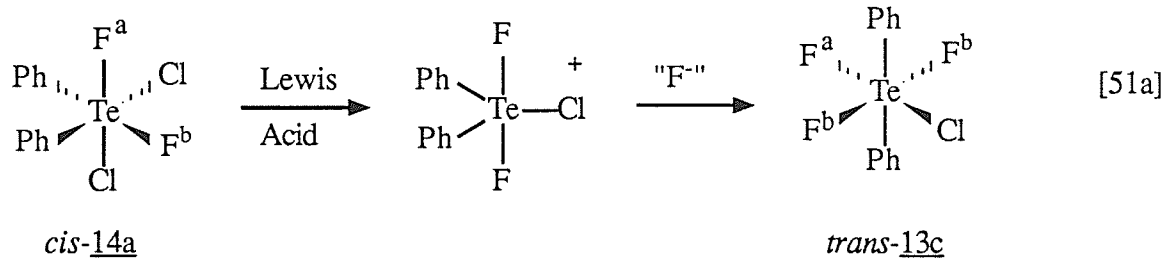
Morris and Moss (107) have reported ^{19}F NMR studies of $Bu_4N^+TeF_5^-$ in CH_2Cl_2. On addition of Bu_4NF to TeF_4, there was evidence (a broad single peak) of fast exchange between free F^- and TeF_5^-, but at 223 K the exchange slowed and an ab_4 fluorine NMR spectrum was obtained, thereby confirming the square pyramidal structure. The crystal structure of $KTeF_5$ has been determined by X-ray diffraction methods (108,109); the structure contains isolated TeF_5^- ions which approximate to a square pyramid.

Stoichiometric amounts of XeF_2 were added to the mixtures described above, *i.e.* the mixture of Et_4NCl and Ph_2TeX_2 (X = F, Cl), the mixture of DMSO and Ph_2TeX_2, and the mixture of F^- and Ph_2TeF_2. However, only the DMSO adduct did not undergo oxidative fluorination with XeF_2 while the others produced Te(VI) fluorides almost instantaneously. The ^{19}F NMR spectrum of the mixture of the DMSO adduct and XeF_2 revealed that all XeF_2 was used, but no oxidation of Te(IV) fluorides occurred. However, the ^{19}F NMR spectrum of this mixture exhibited a new peak at ~-170 ppm (HF region), probably formed by the reaction of XeF_2 with moisture that was present in DMSO.

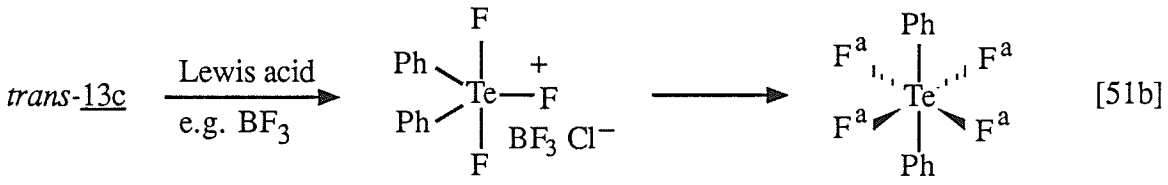
All these results are consistent with a requirement that the intermediate for the oxidation from Te(IV) to Te(VI) involves the addition of halide ion to Te(IV) to give a tellurate(IV) anion, *i.e.* $Ph_2TeX_2 + X^- \longrightarrow Ph_2TeX_3^-$, since only under this condition does the oxidation proceed.

The first isomeric form (*cis*-14a) to appear in the oxidation, as shown in equation [50b], undergoes stepwise fluorination to give *trans*-Ph_2TeF_3Cl 13c, *i.e.* the concentration of *cis*-14a decreases with concomitant formation of *trans*-13c and

eventually *trans*-Ph_2TeF_4 12b. The following route is suggested for the fluorination, as illustrated in equation [51]:



cis-14a *trans*-13c [51a]

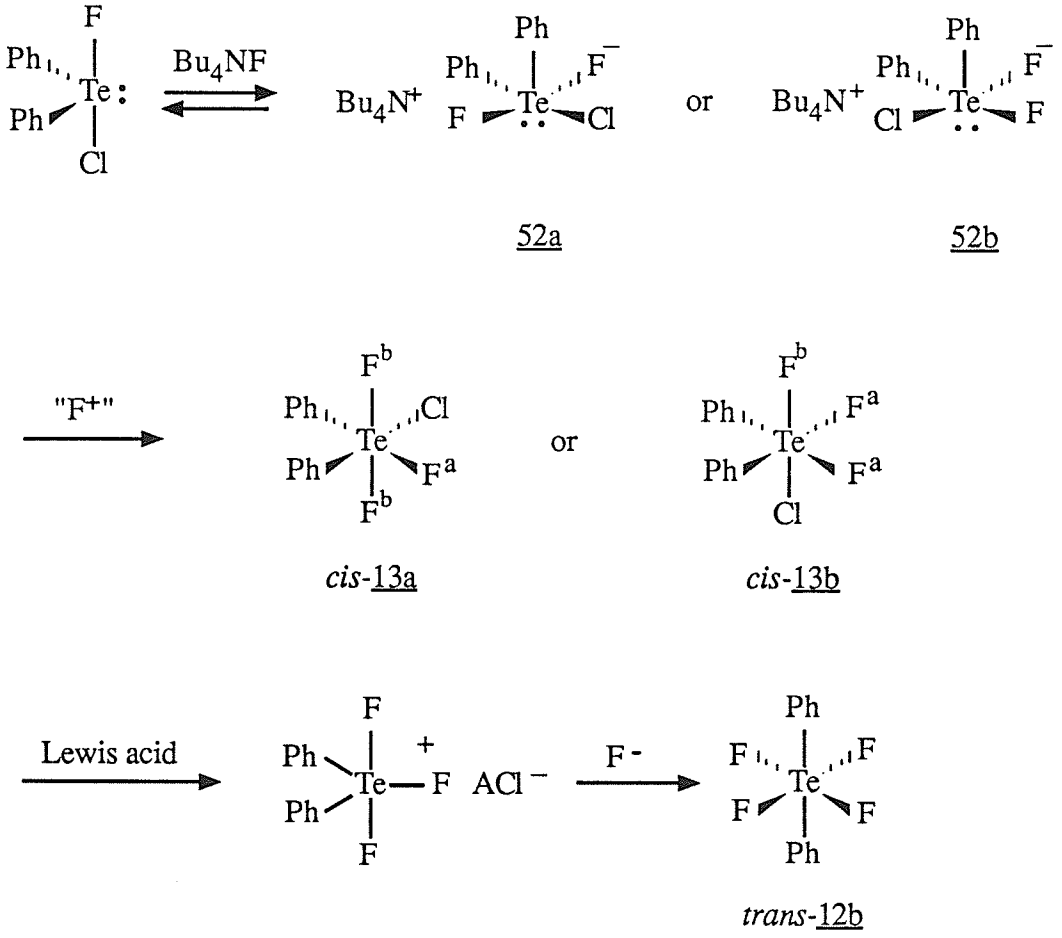


[51b]

It was discussed earlier that when the $Ph_2TeF_3^+$ cation is the intermediate, only the *trans*-geometry product, *i.e.* the thermodynamically stable isomer, is formed. It seems that the *trans*-geometry is also favoured for the product when the mixed-halo cation $Ph_2TeF_2Cl^+$ is the intermediate, as described in equation [51a]. The formation of kinetically favoured *cis*-Ph_2TeF_3Cl 13a, to be discussed shortly, has never been observed in this process. *trans*-Ph_2TeF_3Cl, 13c, in equation [51a], is then further fluorinated to give *trans*-Ph_2TeF_4 12b, via the $Ph_2TeF_3^+$ cation, as described in equation [51b]. A small amount of *trans*-Ph_2TeF_3Cl 13c is often observed as a final product along with *trans*-Ph_2TeF_4.

(2) With tetrabutylammonium fluoride. The oxidative fluorination of Ph_2TeCl_2 with XeF_2, when Bu_4NF is used as a catalyst, initially gives kinetically favoured *cis*-Ph_2TeF_3Cl 13a in large amount (Table 9), which is subsequently fluorinated to give *trans*-12b, as illustrated in equation [19], and the stoichiometry of the reaction is shown in equation [43].

For this reaction, after equilibrium is established between Ph_2TeCl_2, Ph_2TeFCl, and Ph_2TeF_2 as described in equation [50a], the following mechanism is suggested:



[52]

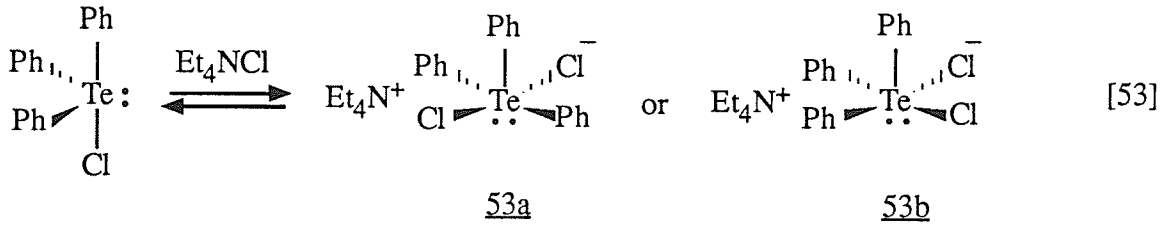
This mechanism should be compared to that in equation [49]. The initial formation of *cis*-Ph_2TeF_3Cl may be attributed to the use of Bu_4NF rather than Et_4NCl. The intermediate anion, $Ph_2TeF_2Cl^-$, contains two fluorines and thus can exist as two geometrical isomers, as illustrated in equation [52]. The attack of "F^+" then produces *cis*-13a or *cis*-13b, accordingly. The appearance of an ab_2 (or a_2b) fluorine spin system in the ^{19}F NMR spectrum does not identify the geometry. However, as discussed in section B-2-b(2), by comparing the ^{19}F NMR spectrum with that of *cis*-Ph_2TeF_4 (a_2b_2 fluorine spin system), *cis*-13a is suggested as the possible geometry. This suggests that it originated from the intermediate anion 52a, *i.e.* the structure of $Ph_2TeF_2Cl^-$ with fluorines *trans* to each other. *cis*-Ph_2TeF_3Cl 13a is then eventually fluorinated to *trans*-Ph_2TeF_4 12b via the $Ph_2TeF_3^+$ cation.

It is important to note that formation of the *trans* isomer, *trans*-Ph_2TeF_3Cl 13c, was not detected in this reaction. This again confirms that the *cis*-configuration is kinetically favoured and that formation of the intermediate $Ph_2TeF_3^+$ cation generates the thermodynamically stable *trans*-12b only.

b. Oxidation of Ph_3TeCl

The results of oxidative fluorinations of Ph_3TeX (X = F, Cl) with XeF_2 were discussed in section B-1. In this section, the mechanism of oxidation will be discussed. Th oxidative fluorination of Ph_3TeCl with XeF_2 in the presence of equimolar of Et_4NCl allows one to detect stepwise fluorination, as described in equation [37]. A similar mechanism to that described in section a can be applied to this reaction, since the product of each step is consistent with this mechanism.

1. The first step involves the formation of a tellurate(IV) anion, as illustrated in equation [53]:

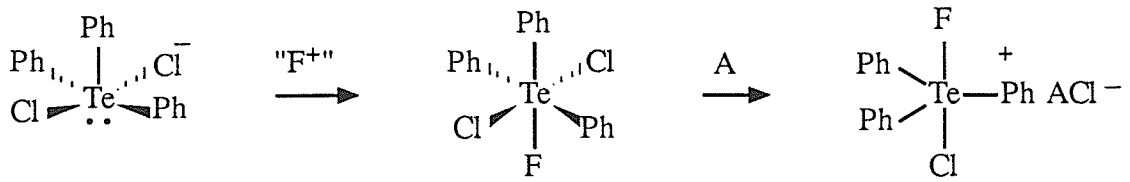


[53]

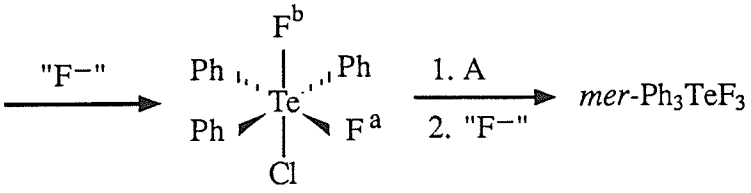
53a 53b

As with two phenyl groups, if the intermediate is expected to have one phenyl group *trans* to the lone pair, there are two possible structures 53a and 53b. Of the two intermediate structures 53a and 53b above, structure 53a is sterically less crowded than structure 53b. This is consistent with formation of *mer*-structures, such as *mer*-Ph_3TeF_3 and *mer*-Ph_3TeF_2Cl only, in the oxidative fluorination. In other words, the thermodynamic stability of *mer*- over the *fac*-structure is not only a consequence of the octahedral species but also determined by the structure of the intermediate anion as well.

2. The attack of "F^+" at tellurium, *trans* to the phenyl group, of the intermediate Te(IV) anion produces Ph_3TeFCl_2, which is subsequently fluorinated to give *cis*-F_2TePh_3Cl, and eventually *mer*-Ph_3TeF_3, as illustrated in equation [54]:



54a

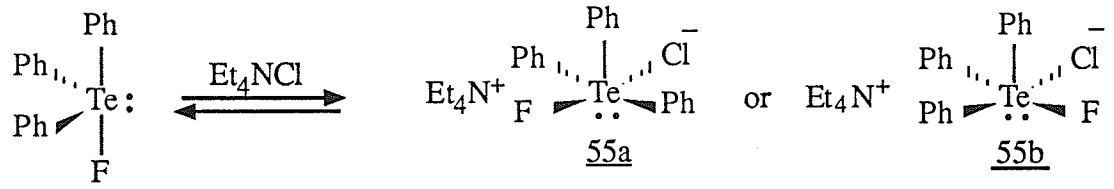


[54]

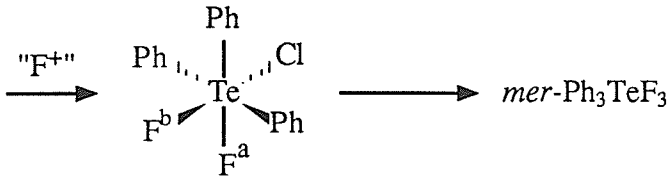
54b

Each step was confirmed by ^{19}F and ^{125}Te NMR spectroscopy (NMR spectra are given in Figures 8-11) and the NMR data are given in Table 7. From the Ph_3TeFCl^+ cation, *cis*-F_2TePh_3Cl 54b is generated; the details of the reaction will be discussed in section II-A-2.

The reaction of Ph_3TeF with XeF_2 in the presence of Et_4NCl also gives *cis*-F_2TePh_3Cl 54b and eventually *mer*-Ph_3TeF_3, and this is also consistent with the proposed mechanism, as illustrated in equation [55]:



55a or 55b



mer-Ph_3TeF_3 [55]

55c

In this mechanism, the tellurate(IV) anion, Ph_3TeFCl^-, can exist as two geometrical isomers, *i.e.* 55a and 55b. However, structure 55b, as discussed above for structures 53a and 53b, is expected to be unfavourable. Thus, addition of "F^+" to Ph_3TeFCl^- 55a gives *cis*-F_2TePh_3Cl. If the proposed mechanism is followed, only *cis*-F_2TePh_3Cl 55c can be formed in the oxidative fluorination of Ph_3TeX (X= F, Cl) with XeF_2, and indeed no trace of *trans*-F_2TePh_3Cl has been observed for this oxidative reaction.

3. Oxidative fluorination of tellurane

So far, the mechanisms of oxidative fluorinations of phenyltellurium(IV) compounds using XeF_2 as an oxidizing agent have been discussed. In this section, the application of the proposed mechanism to an analogous reaction in the literature will be discussed.

As already discussed, the oxidative fluorination of Ph_2TeF_2 with XeF_2 produces kinetically favoured *cis*-Ph_2TeF_4 according to the mechanism illustrated in equation [47] through an anionic intermediate. However, the analogous reaction of tellurane with BrF_3, reported by Martin *et al.* (9), produces a kinetically favoured *trans*-pertellurane rather than a *cis*-pertellurane (tellurane and pertellurane indicate Te(IV) and Te(VI) compounds, respectively, and the details for the nomenclature and reactions will be

discussed further in section II-B). This result may be explained by the structure of the intermediate in the oxidative reaction (*vide infra*).

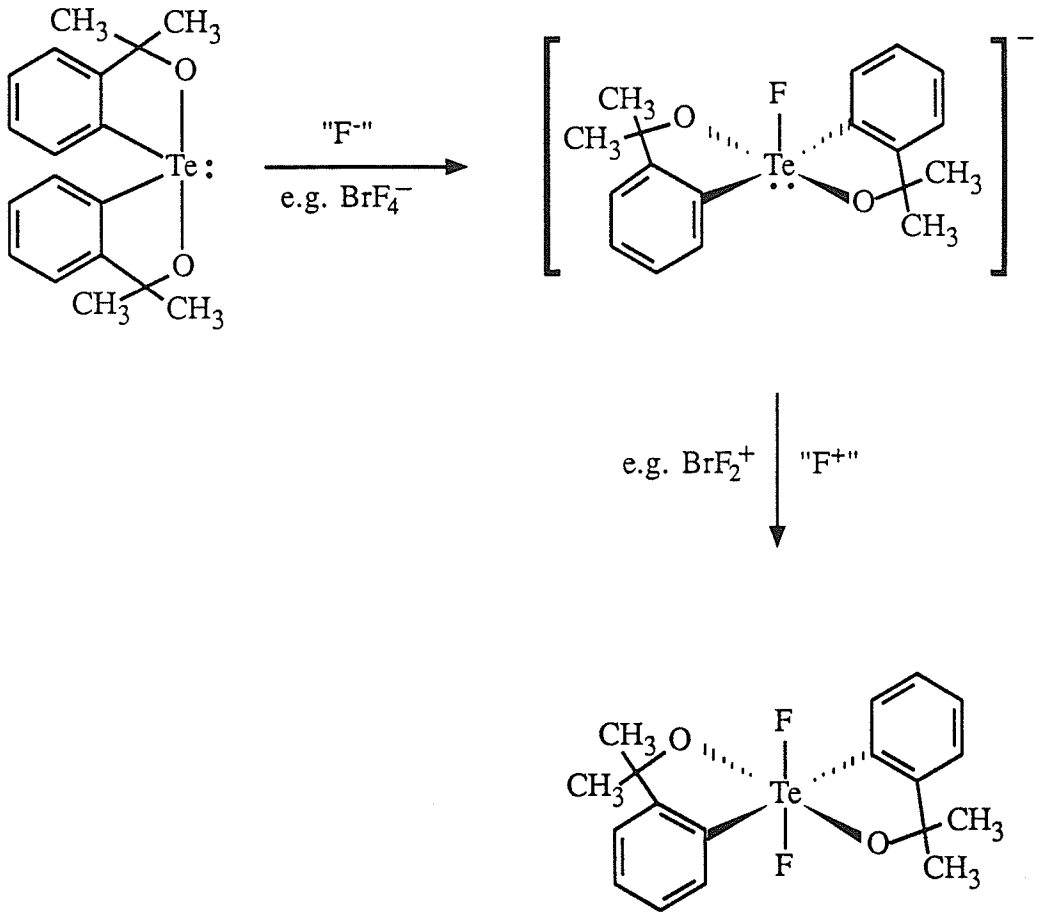
In this reaction, the following mechanism is proposed, as illustrated in equation [56].

1. The first step involves the addition of fluoride anion (F^-) to tellurane to form a five-coordinate square pyramidal tellurate(IV) anion; the source of fluoride ion could be BrF_4^-.

A square pyramidal geometry of a five-coordinate compound containing non-bonding electron pairs has been discussed in the previous sections. The appearance of a square pyramidal geometry for a main group element such as P, Si, or Ge requires the presence of two unsaturated five-membered rings with atoms in any one ring attached directly to the central atom, or the presence of a more strained four-membered ring, and many examples have been reviewed by Holmes (110) and Littlefield & Doak (111). In particular, square pyramidal structures of the related five-coordinate P and Si catecholyl derivatives, $FP(OC_6H_4O)_2$ (112) and $FSi(OC_6H_6O)_2^-$ (113), show that fluorine is in an axial site in each case. These and other examples are shown in Figure 29.

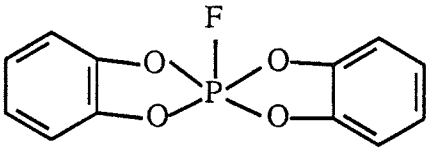
As shown by these examples, bidentate or bulky ligands may occupy the equatorial site while fluorine occupies the axial site of the square pyramid.

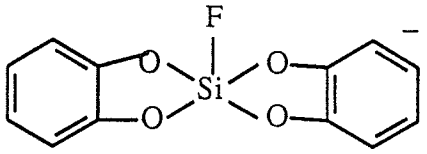
Therefore, it is reasonable to expect that the bidentate ligands of the intermediate Te(IV) anion in equation [56] occupy the plane while fluorine occupies the axial position, *trans* to the lone pair. The detailed orientation of the bidentate ligands of *cis*-pertellurane has been determined by X-ray crystallography (9).

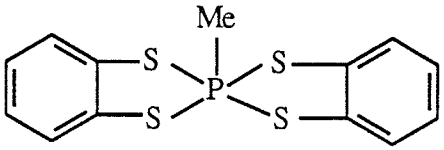


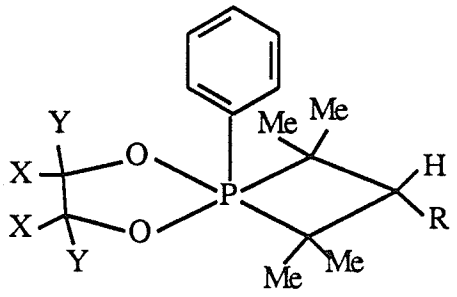
[56]

trans-pertellurane



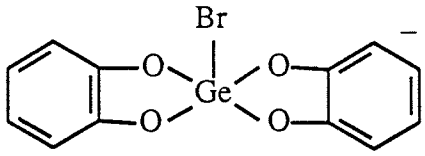


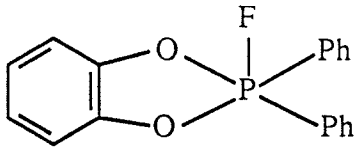


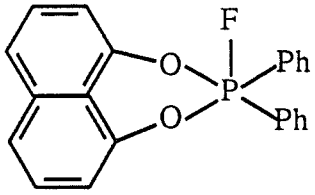


X	Y	R
CF_3	Br	H
H	H	Me

Figure 29. Examples of square pyramidal structures of five-coordinate main group compounds (110-113) (continued on the following page).







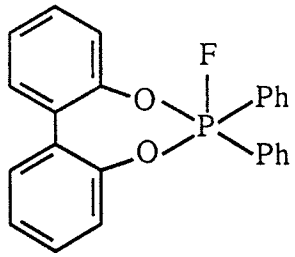


Figure 29. (continued).

2. The second step of the mechanism involves the attack of fluorine cation ("F^+"), *e.g.* BrF_2^+, which is added to tellurium, *trans* to fluorine, and as a result, the kinetically favoured *trans*-isomer is formed, as illustrated in equation [56].

D. ^{13}C NMR studies of fluorophenyltellurium(VI) compounds

Structural assignments and fluorine exchange studies of some fluorophenyl-tellurium(VI) compounds have been carried out using ^{19}F and ^{125}Te NMR spectroscopy. In particular, ^{19}F NMR spectroscopy has proved to be quite useful for studying fast reactions, such as isomerization of *trans- to cis*-F_2TePh_3Cl.

Carbon-13 NMR studies of fluorophenyltellurium(VI) compounds, particularly the heteronuclear couplings between carbon and fluorine, provide a detailed assignment of phenyl substituents about the central Te atom, thereby leading to an unambiguous identification among several possible geometrical isomers for a given molecule. The ^{13}C NMR studies are particularly useful when assignments of ^{19}F NMR resonances are obscured by rapid fluorine exchange in the system.

The only stable carbon isotope with a nuclear spin, ^{13}C, has a natural isotopic abundance of only 1.1%, and its magnetic moment is merely a quarter of the proton magnetic moment (Table 2). Both its low natural abundance and its small magnetic moment make carbon-13 a very insensitive NMR probe compared with proton or fluorine probe. However, the proton spin-decoupling method has been applied throughout the ^{13}C measurements to obtain simple spectra that lack all proton-carbon splittings. The decoupling experiment increases the sensitivity of ^{13}C NMR measurements because the intensities of all multiplet lines in a coupled spectrum are accumulated in one singlet signal in the decoupled spectrum. The sensitivity enhancement of proton-decoupled ^{13}C NMR is

not only a consequence of the multiplet's collapse, but also of nuclear Overhauser enhancement (NOE). The latter effect is particularly useful for assigning the signals due to quarternary carbons, *i.e.* ipso carbons (C_1), since the intensities of these signals, which lack Overhauser enhancement, are weaker. Further information about NOE can be obtained from several reviews on carbon-13 NMR spectroscopy (114–117).

1. The carbon-13 NMR spectrum of mer-Ph_3TeF_3

Before analyzing the spectra, it is necessary to introduce the numbering scheme for the carbon atoms of the phenyl substituents of *mer*-Ph_3TeF_3 is illustrated in Figure 30:

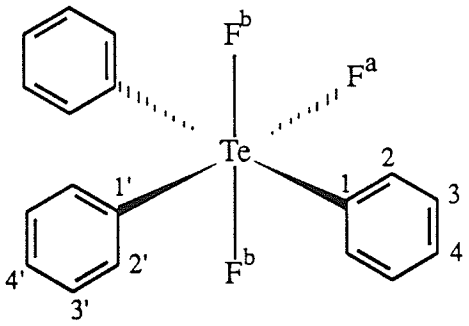


Figure 30. Carbon atom numbering scheme of phenyl groups in *mer*-Ph_3TeF_3.

The two phenyl substituents that are *trans* to each other are equally numbered since they are magnetically equivalent. Each carbon can also be differentiated by the use of names such as ortho (C_2), meta (C_3), and para (C_4). The carbon directly attached to the Te atom (C_1) is called the ipso carbon.

The carbon-13 NMR spectra of *mer*-Ph_3TeF_3 are shown in Figures 31.1–31.3, and NMR data are collected in Table 11.

The assignments were made based on the integrated peak intensity:

1. The assignments for the two sets of non-equivalent phenyl substituents are straightforward from the intensity information, as clearly pictured in Figures 31.2 and 31.2. The intensities of ^{13}C resonances of the phenyl substituent, *trans* to F^a (C_1-C_4'), are much weaker (about half) than those of the two equivalent phenyl substituents that are *trans* to each other (*i.e.* C_1-C_4).

2. The ipso carbon (*i.e.* C_1 and C_1') has the smallest intensity because it lacks the NOE effect and also is the most deshielded, as shown in Figure 31.1. The C_1' peak intensities are about half of C_1, as shown in Figures 31.1 and 31.3.

3. The chemical shifts of C_2 and C_3 (also C_2' and C_3') are tentatively assigned. These assignments are based on the magnitude of coupling constants; $J(C_2\text{-}^{125}Te) < J(C_3\text{-}^{125}Te)$. This trend was made by comparing with J(C-F) (more details in the following sections).

4. The chemical shift of the para carbon (C_4 and C_4') is assigned based on the integrated peak intensity; it has only one carbon and, thus, its resonance intensity is only half that of the ortho and meta carbons.

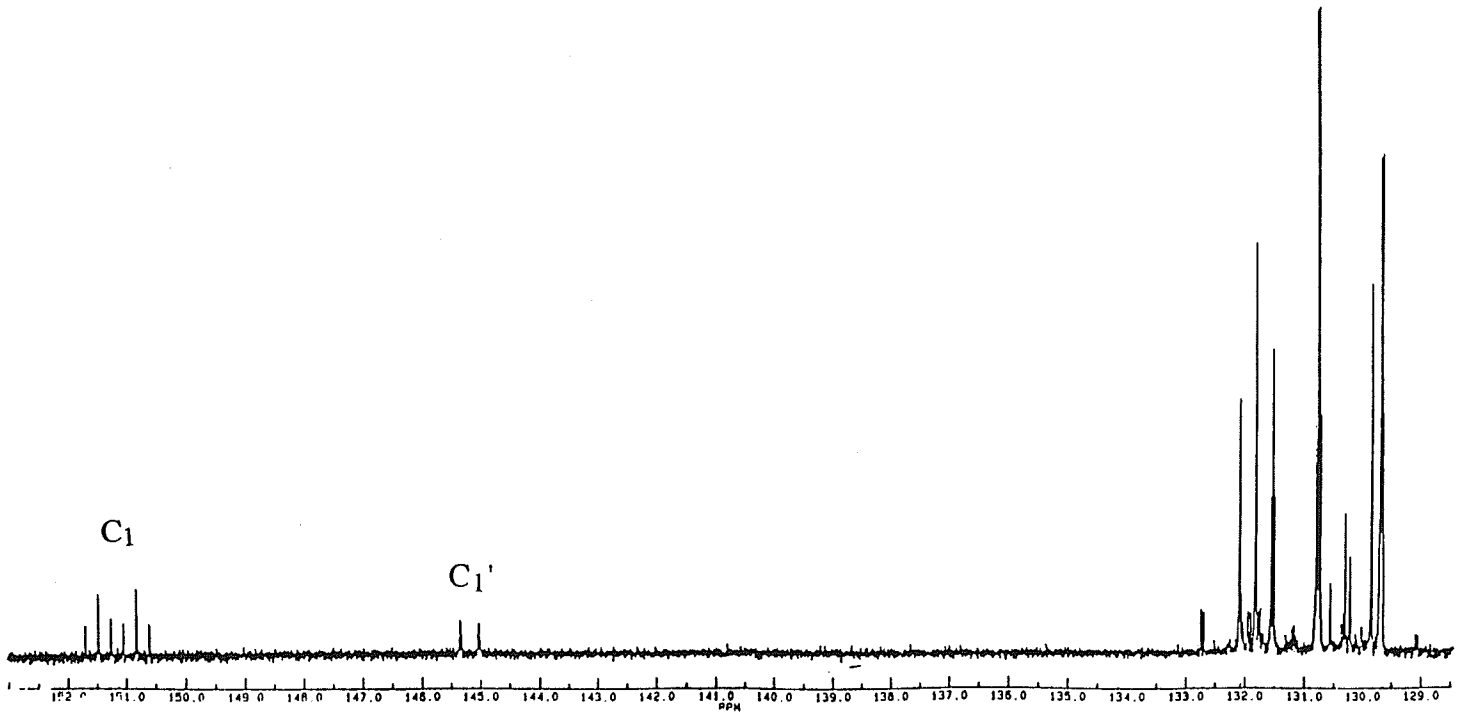


Figure 31.1 The $^{13}C\{^{1}H\}$ NMR spectrum of *mer*-Ph_3TeF_3, 100 mg/mL CD_2Cl_2; full spectrum.

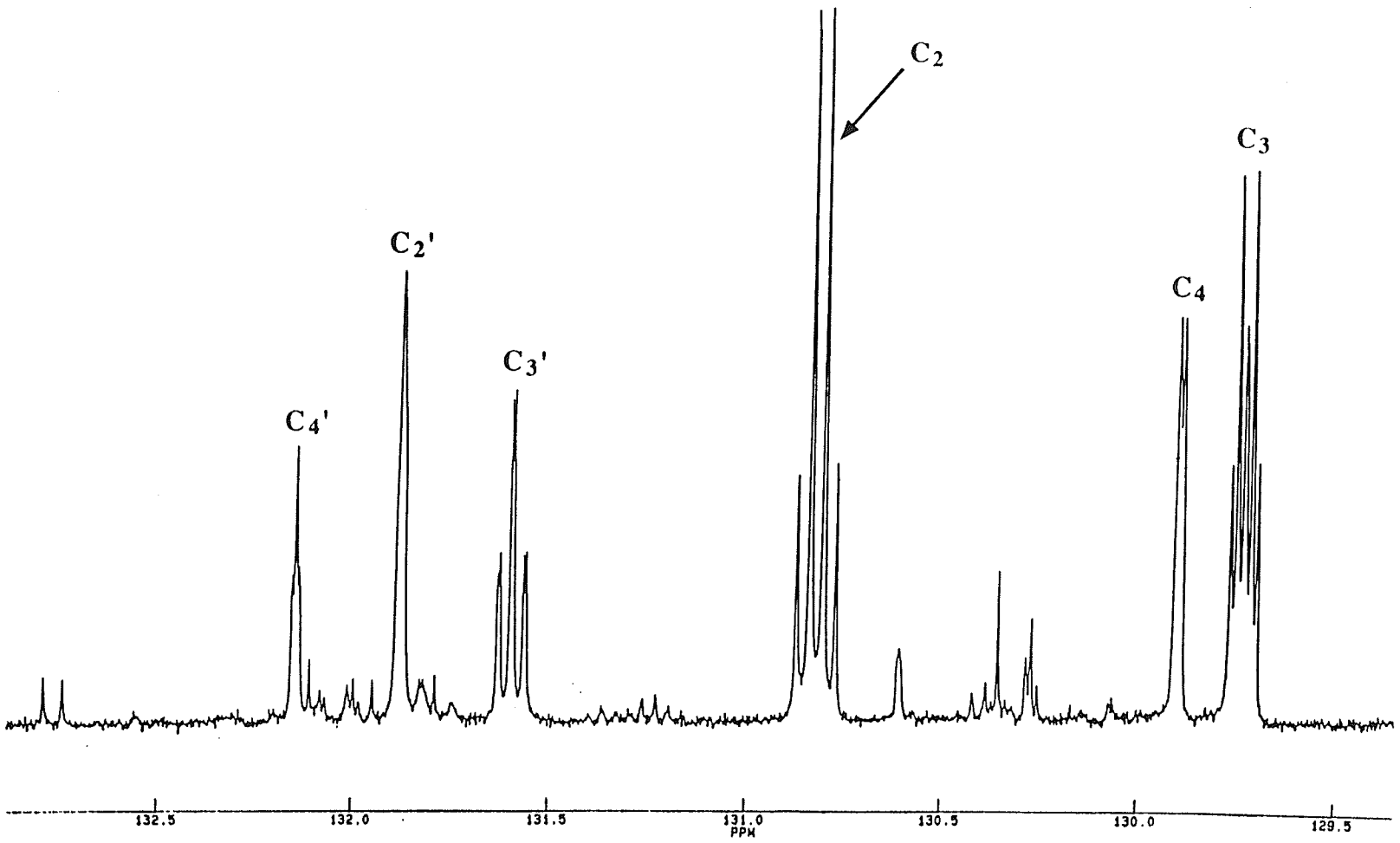


Figure 31.2 ~133-129 ppm expanded spectrum of *mer*-Ph_3TeF_3; ortho- (C_2, C_2'), meta- (C_3, C_3'), and para-carbon (C_4, C_4') resonances.

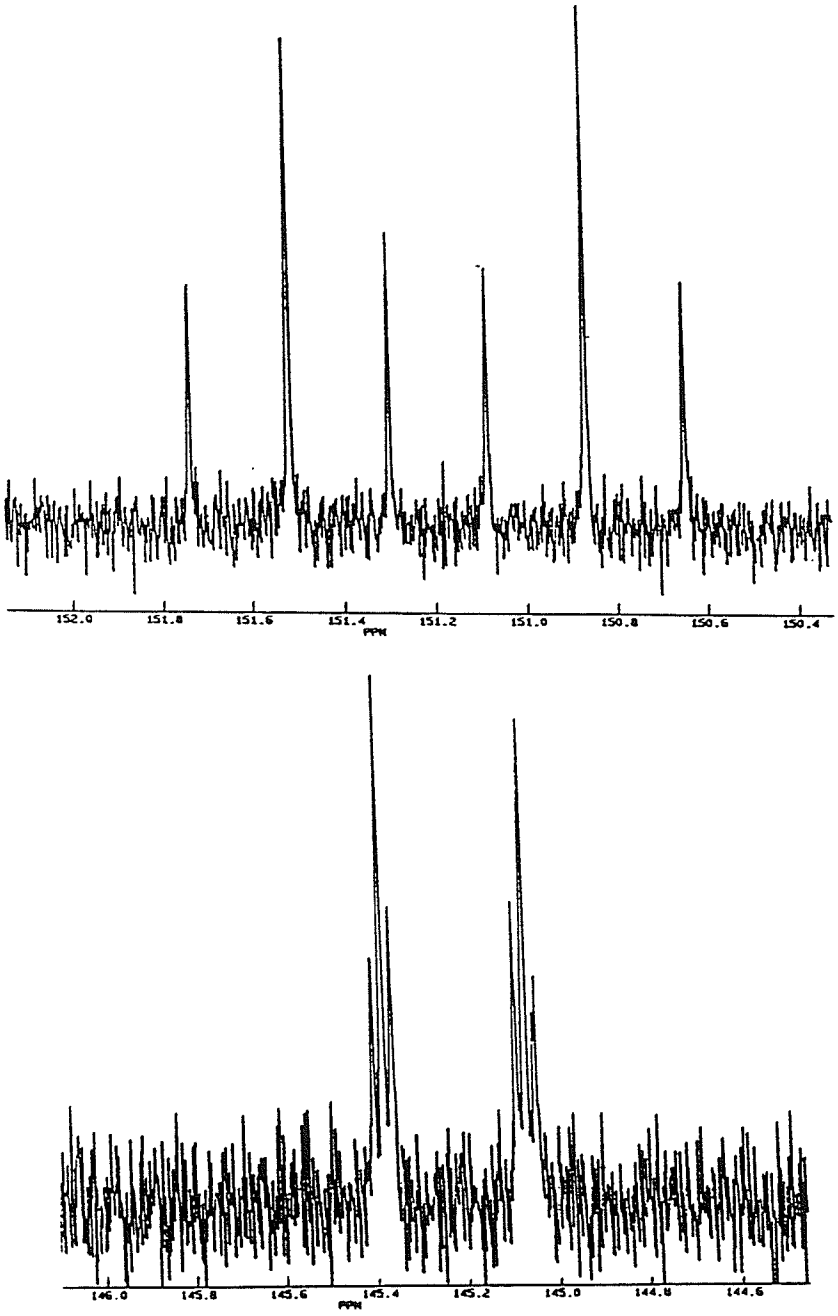


Figure 31.3 Expanded spectrum of *mer*-Ph_3TeF_3 showing the ipso-carbon resonances; C_1-resonance (top) and C_1' resonance (bottom).

TABLE 11

Carbon-13 NMR data for *mer* -Ph_3TeF_3 *

	two phenyl ligands trans to each other				phenyl ligand trans to F^a			
	C_1	C_2	C_3	C_4	C_1'	C_2'	C_3'	C_4'
δC [ppm]	151.19	130.83	129.74	129.90	145.22	131.88	131.59	132.15
$J(CF^a)$ [Hz]	49.13	2.50	2.75	0.89	23.70	†	0.44	≠
$J(CF^b)$ [Hz]	16.48	2.50	1.23	≠	1.69	†	2.51	0.65
$J(CTe)$ [Hz]	‡	63.08	94.62	25.07	‡	†	35.58	-

* The solvent used was CD_2Cl_2. ‡ Tellurium satellites too weak to be identified (no NOE effect).

† Assignment difficult due to overlapping multiplicities. ≠ Assignment uncertain.

2. The carbon-13 NMR spectrum of a mixture of $Ph_3TeF_2^+$ and Ph_3TeFCl^+

The preparation and characterization of five-coordinate cations $Ph_3TeF_2^+$ and Ph_3TeFCl^+ will be discussed in the following section II; these cations are suggested to have a trigonal bipyramidal geometry on the basis of ^{19}F and ^{125}Te NMR spectroscopy. Carbon-13 NMR spectroscopy is particularly useful for confirming the trigonal bipyramidal geometry of these cations since it reveals the equivalence of the phenyl groups in both species.

The carbon-13 NMR spectra of a mixture of cations, $Ph_3TeF_2^+$ and Ph_3TeFCl^+, are given in Figures 32.1–32.3, and NMR data are collected in Table 12. The same numbering system that was used for *mer*-Ph_3TeF_3 is applied to the cations, except that all phenyl substituents in both cations are equivalent. For phenyl substituents of $Ph_3TeF_2^+$, C_1-C_4 is used while C_1'-C_4' is used for Ph_3TeFCl^+ in order to distinguish the two cations.

It is straightforward to assign the two sets of phenyl resonances for $Ph_3TeF_2^+$ and Ph_3TeFCl^+ from the multiplicity pattern arising from heteronuclear coupling between carbon and fluorine; *i.e.* triplet ^{13}C NMR resonances for $Ph_3TeF_2^+$ cation, and doublet ^{13}C resonances for Ph_3TeFCl^+ cation. Similarly, the assignments of the carbon resonances for the cations can be made on the basis of the integrated peak intensity, as illustrated for the ^{13}C NMR spectrum of *mer*-Ph_3TeF_3 previously.

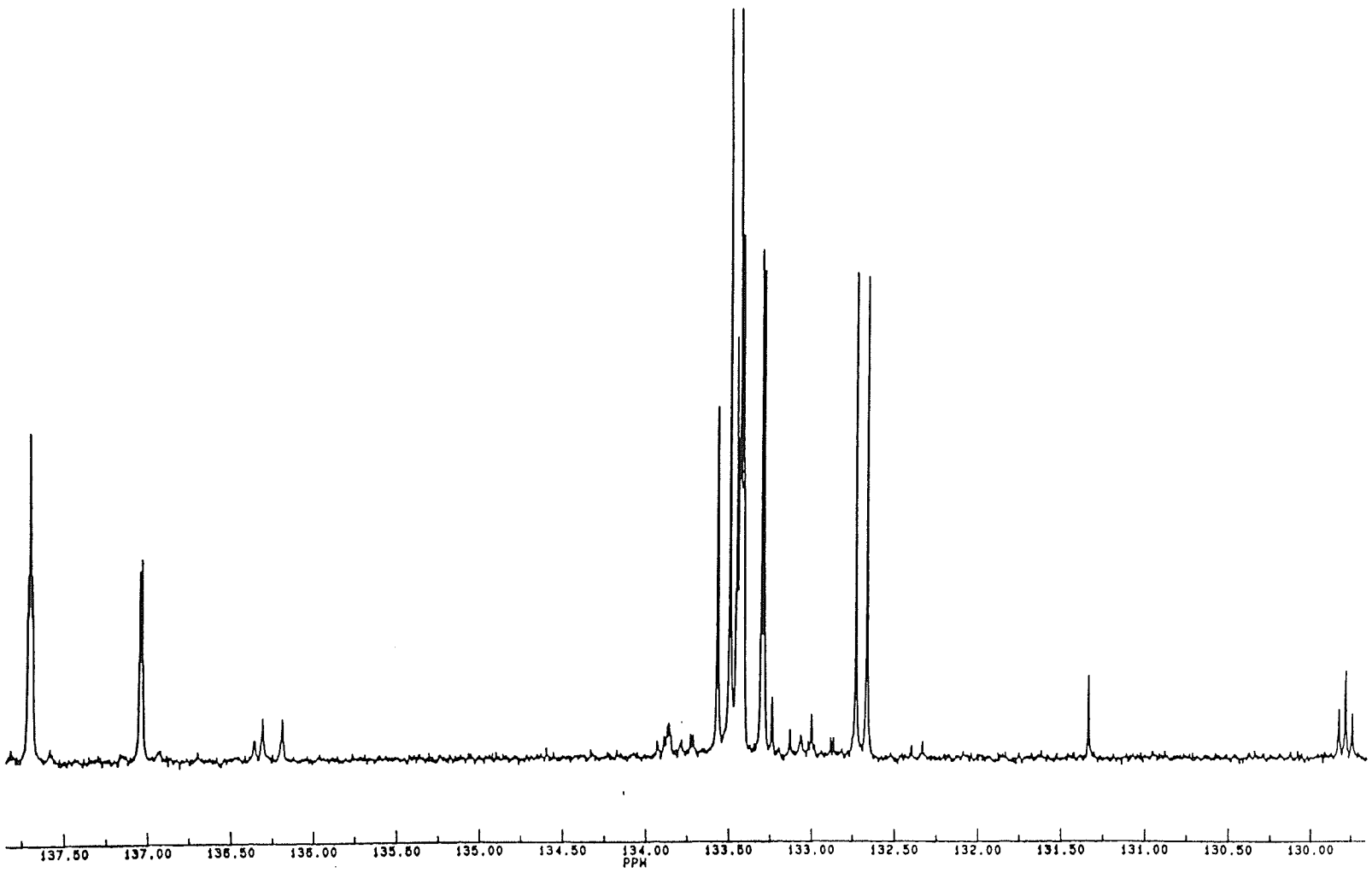


Figure 32.1 The $^{13}C\{^{1}H\}$ NMR spectrum of a mixture of $Ph_3TeF_2^+PF_6^-$ and $Ph_3TeFCl^+PF_6^-$; 100 mg/mL CD_2Cl_2, full spectrum.

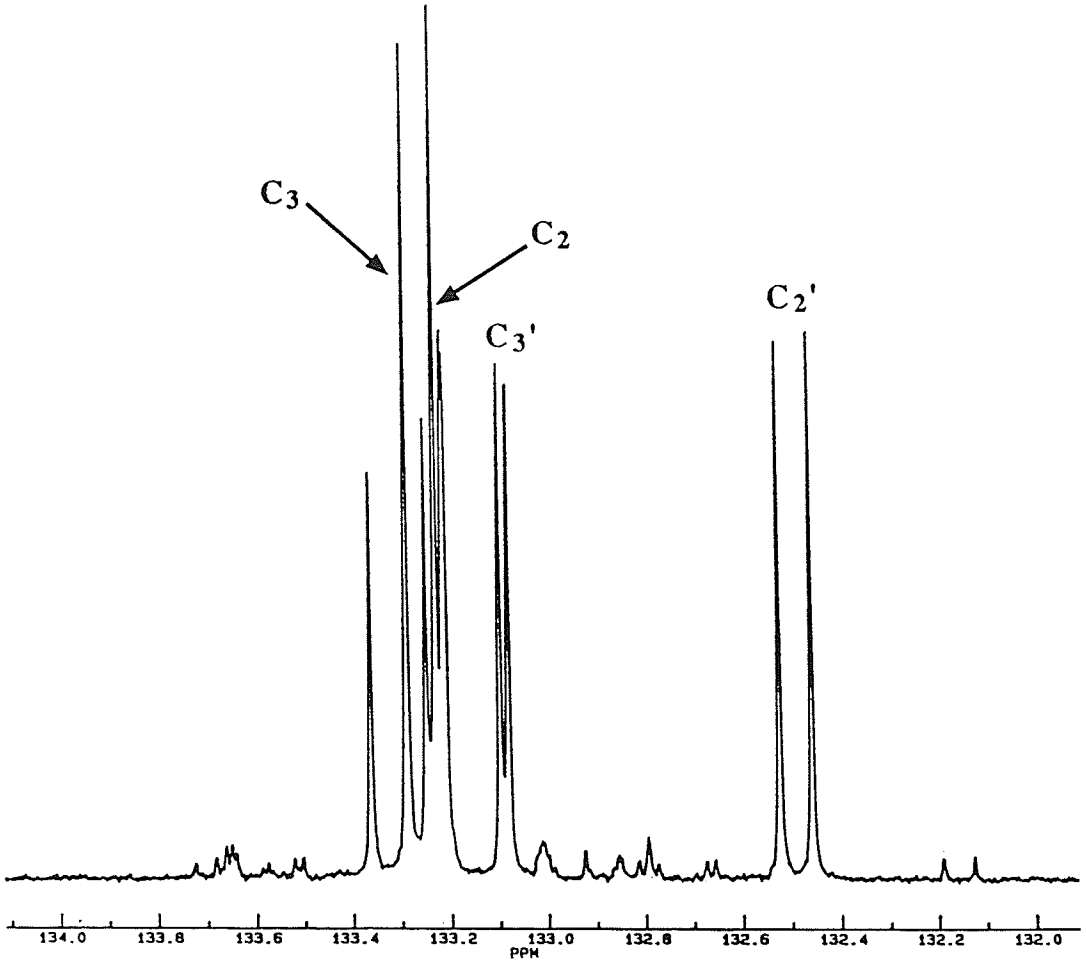


Figure 32.2 Expanded spectrum of the mixture of $Ph_3TeF_2^+PF_6^-$ and $Ph_3TeFCl^+PF_6^-$; ortho- (C_2, C_2') and meta-carbon (C_3, C_3') resonances.

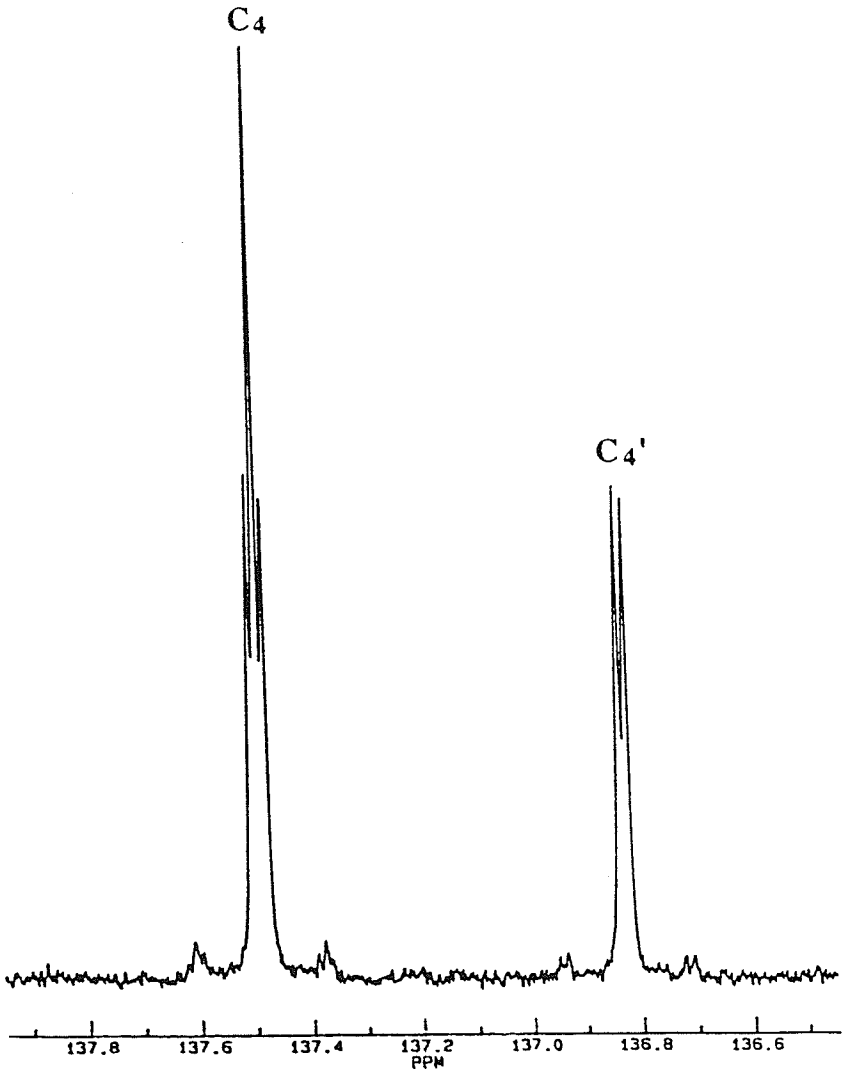


Figure 32.3 Expanded spectrum of a mixture of $Ph_3TeF_2^+PF_6^-$ and $Ph_3TeFCl^+PF_6^-$; para-carbon (C_4, C_4') resonances.

TABLE 12

Carbon-13 NMR data of $Ph_3TeF_2^+ PF_6^-$ and $Ph_3TeFCl^+ PF_6^-$ *

	$Ph_3TeF_2^+ PF_6^-$				$Ph_3TeFCl^+ PF_6^-$			
	C_1	C_2	C_3	C_4	C_1'	C_2'	C_3'	C_4'
δc [ppm]	125.59	133.29	133.23	137.49	132.16	132.49	133.09	136.83
J(CF) [Hz]	3.10	5.60	1.50	0.98	4.91	4.95	1.32	1.06
J(CTe) [Hz]	-	54.72	65.58	17.51	-	50.19	63.85	16.98

* Solvent used was CD_2Cl_2.

Compared to the large downfield shift of the ipso carbon resonances observed in *mer*-Ph_3TeF_3, a smaller downfield shift was observed for the ipso carbon resonance of the cation $Ph_3TeF_2^+$. It is of interest to note that a similar effect on the chemical shift of ipso carbons has been found in a variety of phenyl-substituted 3-, 4-, and 5-coordinate boron, silicon, and phosphorus fluorides prepared in our laboratory[1]; *i.e.* when the coordination number increases there is a large downfield shift of the resonance of the ipso carbon of the phenyl substituents. Examples are given in Table 13. This effect may be a useful criterion of adduct formation, since it also applies to non-fluorinated species and thus serves as a diagnostic tool.

The chemical shifts of C_2 and C_3 (also C_2' and C_3') are tentatively assigned. As shown in Table 12, $J(C_2\text{-Te})$ is smaller than $J(C_3\text{-Te})$ while $^2J(C_2\text{-F})$ is larger $^3J(C_3\text{-F})$.

3. The Carbon-13 NMR spectrum of trans-Ph_2TeF_4

The ^{13}C NMR spectrum of *trans*-Ph_2TeF_4 is relatively simple since phenyl substituents and fluorines, are equivalent; carbon nuclei in the phenyl substituents are coupled to four equivalent fluorines, thus giving a quintet resonance for each carbon. This is illustrated in Figures 33.1–33.3, and NMR data are presented in Table 14, with carbon atom numbering scheme shown.

Assignments are made based on the integrated peak intensities: C_1 has the smallest resonance intensity. The intensity of the C_4-resonance is about half of C_2 and C_3 resonance intensities. Again, tentative assignments of C_2 and C_3 resonances are made based on the magnitude of J(C-Te).

---

[1] C. Wang, A. F. Janzen, and M. Jang. Unpublished results.

TABLE 13

Carbon-13 NMR chemical shifts of ipso carbons (in ppm) of some phenyl-boron, -silicon, -phosphorus, and -tellurium fluorides*

Compound	Ipso carbon (C_1) shift
$C_6H_5BF_2$	124.8
$C_6H_5BF_3^-$	150.1
$C_6H_5SiF_3$	120.8
$C_6H_5SiF_4^-$	141.1
$C_6H_5PF_4$	125.9
$C_6H_5PF_5^-$	151.6
$(C_6H_5)_3TeF_2^+$	129.6
mer-$(C_6H_5)_3TeF_3$	151.2[1]
	145.2[2]

* Values for B, Si, and P are from C. Wang (unpublished data).

[1] δC_1 of two phenyl groups *trans* to each other.

[2] δC_1 of one phenyl group *trans* to F^a ligand.

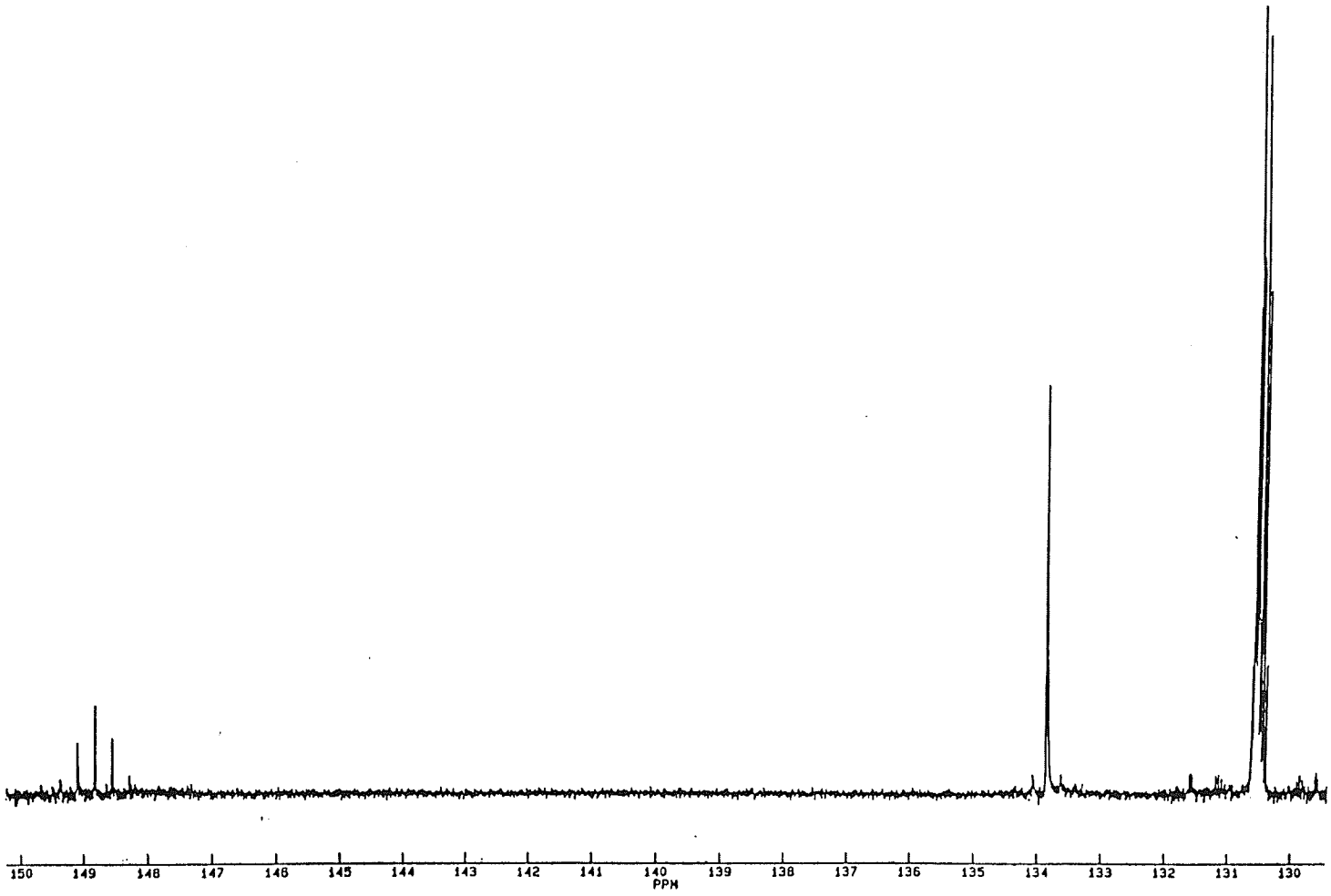


Figure 33.1 The $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-Ph_2TeF_4; 100 mg/mL CD_2Cl_2, full spectrum.

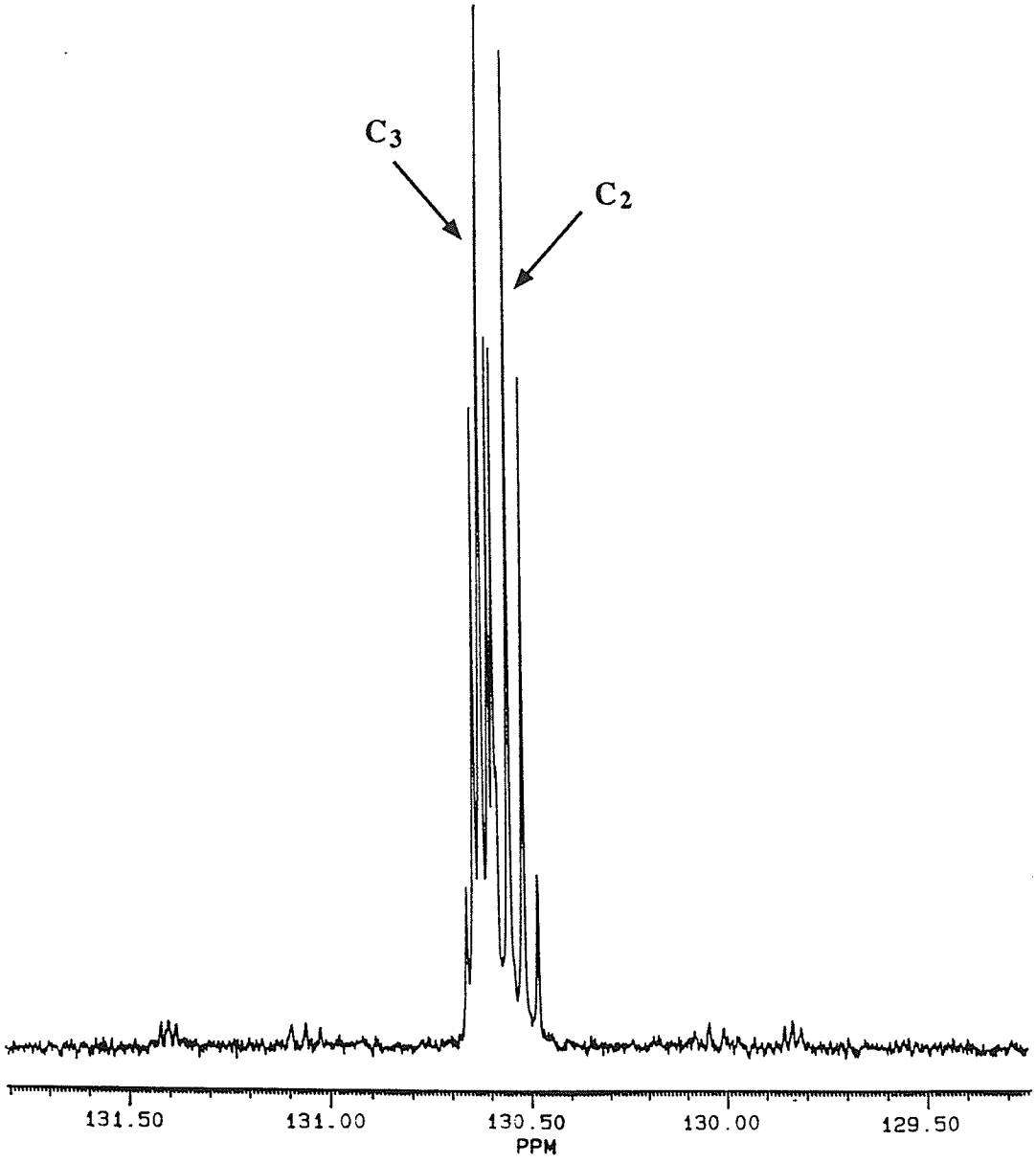


Figure 33.2 Expanded spectrum of *trans*-Ph_2TeF_4; ortho- (C_2) and meta-carbon (C_3) resonances.

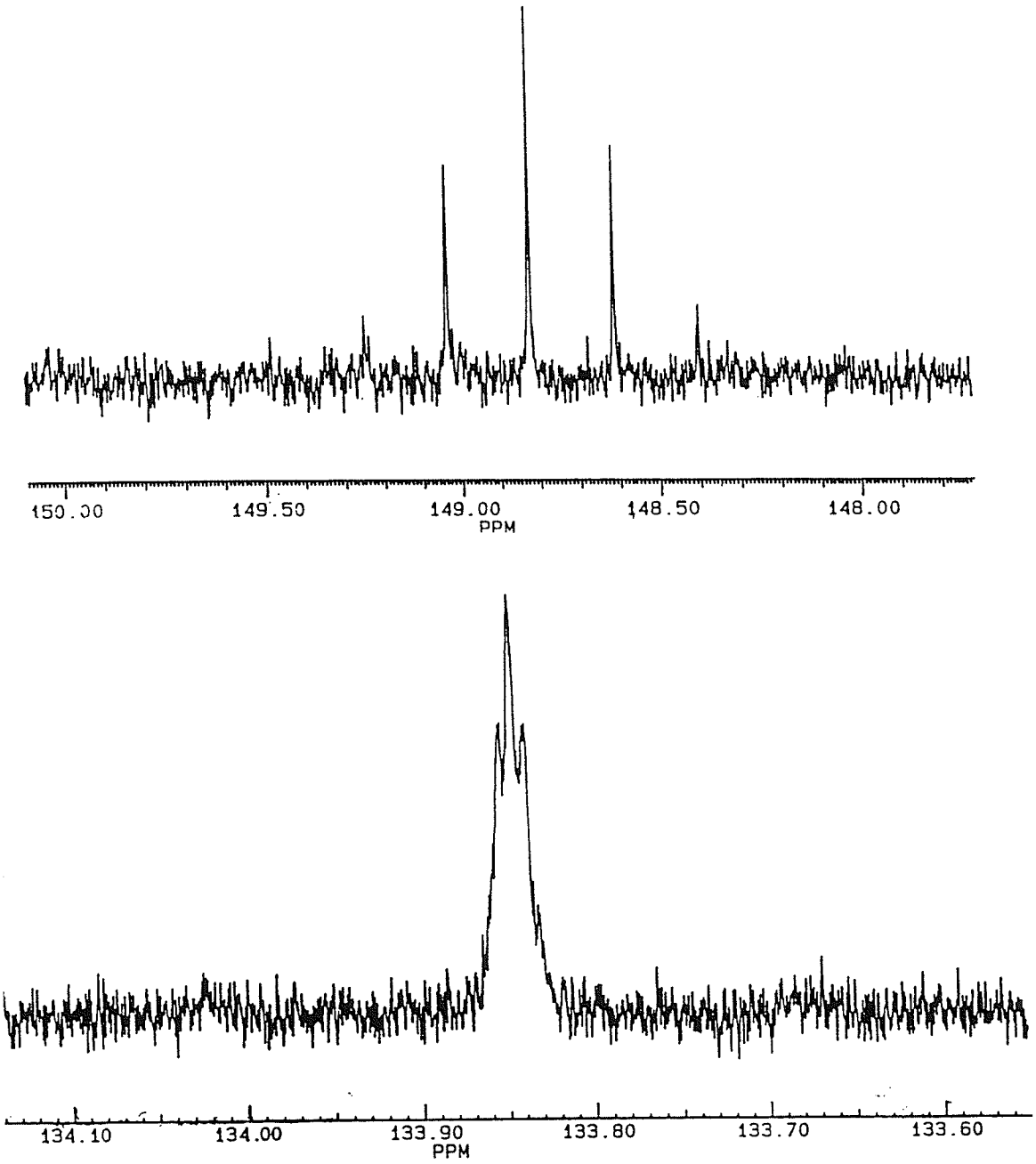
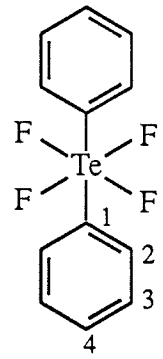


Figure 33.3 Expanded spectrum of *trans*-Ph_2TeF_4; ipso- (top) and para-carbon (bottom) resonances. Resolution enhanced: digital resolution = 1.5 Hz/point.



The structure of *trans*-Ph_2TeF_4 with atom numbering scheme.

TABLE 14

Carbon-13 NMR data of *trans* -Ph_2TeF_4*

	C_1	C_2	C_3	C_4
δC [ppm]	148.80	130.55	130.60	133.85
JCF [Hz]	16.0	2.69	1.46	0.53
JCTe [Hz]	†	71.0	109.8	25.60

* Solvent used was CD_2Cl_2. † ^{125}Te-satellites were not detected due to the low intensity of ipso carbon (no NOE effect).

4. Carbon-13 NMR spectra of Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$

The ^{13}C NMR spectrum of a mixture of the hydrolysis products, Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$, was recorded several times. The assignments of the ortho, meta, and para resonances were not certain because of the complexity of the spectrum resulting from the two very similar compounds. However, ipso carbon resonances were clearly distinguished since they showed a significant downfield shift from others as expected (see Table 13). It was clear from the pattern of the ipso carbon resonances that the phenyl substituents are equivalent in both species; the C_1-resonance of Ph_2TeF_3OH is a doublet of triplets (a pair of equivalent fluorines and one non-equivalent fluorine), and a triplet C_1-resonance for $Ph_2TeF_2(OH)_2$ (two equivalent fluorines). The ^{13}C NMR spectra of ipso carbon resonances are presented in Figure 34 and Figure 35 for Ph_2TeF_3OH and $Ph_2TeF_2(OH)_2$, respectively, together with their NMR data.

II. STEREOSELECTIVE SYNTHESIS AND ISOMERIZATION

Oxidative fluorinations of phenyltellurium(IV) compounds with XeF_2 lead to final products such as *cis*-F_2TePh_3Cl and *trans*-Ph_2TeF_4 which, as discussed previously, are the thermodynamically stable ones. Since isomerization of the initially formed product, the kinetically favoured isomer, may occur, the nature of the final product does not necessarily give an indication as to the initial product of the reaction. Hence stereoselective synthesis of the kinetically favoured isomer might be essential to investigate the mechanism of the isomerization reaction.

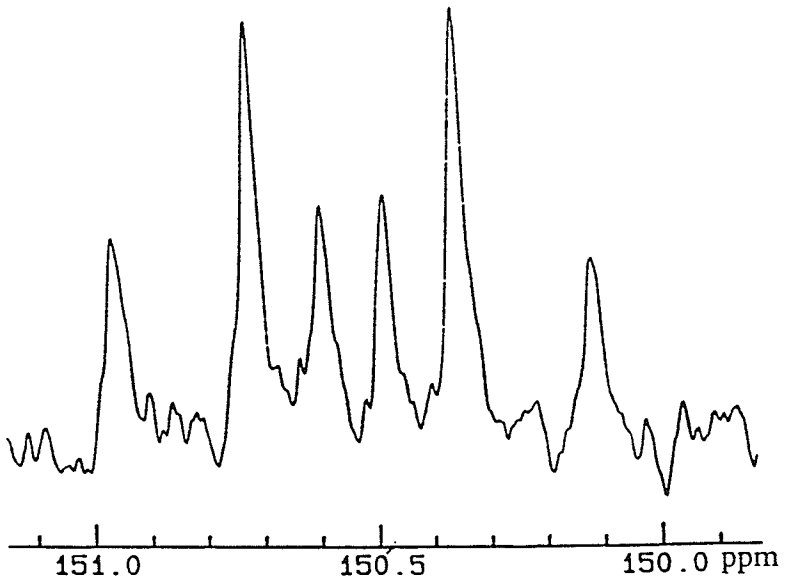


Figure 34. The ^{13}C NMR spectrum of Ph_2TeF_3OH in $CDCl_3$ showing the ipso-carbon resonance of phenyl substituents in Ph_2TeF_3OH; $\delta(C_1)$ = + 150.54 ppm, $J(C_1\text{-}F^a)$ = 28.03 Hz, $J(C_1\text{-}F^b)$ = 18.26 Hz.

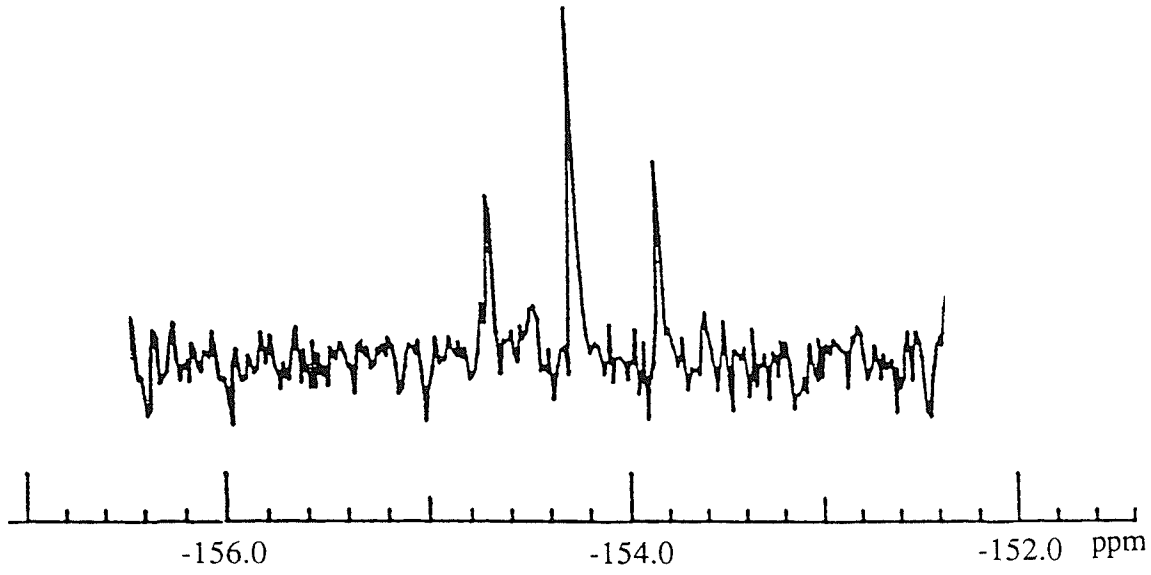


Figure 35. The ^{13}C NMR spectrum of $Ph_2TeF_2(OH)_2$ in $CDCl_3$ showing the ipso-carbon resonance; $\delta(C_1)$ = + 154.24 ppm, $J(C_1\text{-}F)$ = 32.08 Hz.

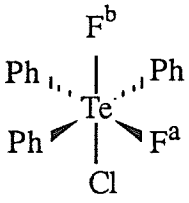
cis- and *trans*-F_2TePh_3Cl have been prepared via five-coordinate cations $Ph_3TeF_2^+$ and Ph_3TeFCl^+, respectively, and were used to show that the kinetically favoured *trans*-isomer isomerizes to its *cis*-isomer by an *intermolecular* mechanism, as determined by NMR spectroscopy.

The preparation of *cis*- and *trans*-Ph_2TeF_4 was described in the previous section. The isomerization of the kinetically favoured *cis*-isomer to the thermodynamically favoured *trans*-isomer is catalyzed by Lewis acid impurities and thus a similar mechanism is suggested.

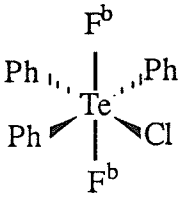
Our results of intermolecular mechanism will be compared with a recent report of an *intramolecular* isomerization mechanism suggested for analogous tellurium compounds.

A. Synthesis of *mer*-Ph_3TeF_2Cl

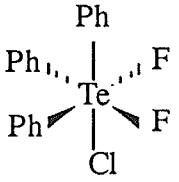
There are three possible geometrical isomers of difluorochlorotriphenyltellurium(VI), Ph_3TeF_2Cl (*cis* and *trans* with respect to two fluorines), as illustrated in Figure 36:



cis-36a



trans-36b



cis-36c

Figure 36. The three possible geometrical isomers of Ph_3TeF_2Cl with *mer*- and *fac*-arrangement of phenyl substituents.

When three phenyl substituents retain their *mer* arrangement, Ph_3TeF_2Cl can exist as two geometrical isomers with respect to two fluorines, *i.e.* *cis*-36a and *trans*-36b. When phenyl substituents have the *fac*-arrangement, only one isomer is possible, *cis*-36c.

The oxidative fluorination of Ph_3TeCl with 1 equivalent of xenon difluoride, according to the method of K. Alam (12), only gives the thermodynamically stable *cis*-isomer 36a:

$$Ph_3TeCl + XeF_2 \xrightarrow[CH_3CN]{0\ ^\circ C,\ 8\ hrs.} cis\text{-}F_2TePh_3Cl\ \underline{36a} + Xe \qquad [57]$$

cis-F_2TePh_3Cl 36a has non-equivalent fluorines (F^a and F^b) and the ab ^{19}F NMR spectrum (Table 7) establishes the geometry as the *cis*-isomer. In addition, a doublet of doublets ^{125}Te NMR spectrum of *cis*-F_2TePh_3Cl confirms the presence of two non-equivalent fluorines. Furthermore, *cis*-F_2TePh_3Cl was characterized by elemental analysis and mass spectrometry (10). Evidence for the formation of the kinetically favoured isomer, *trans*-F_2TePh_3Cl 36b, had not been obtained under the conditions given in equation [57]. As discussed in section C-2-b, the formation of the *cis*-isomer only is predicted in the oxidative fluorination of Ph_3TeCl with XeF_2, according to the proposed mechanism.

Therefore, the preparation of the *trans* isomer, *trans*-F_2TePh_3Cl 36b, via a five-coordinate cation, will be presented in this section. *cis*-F_2TePh_3Cl can also be prepared by a similar method.

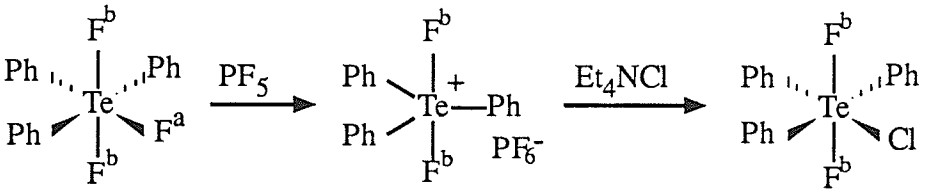
1. Stereoselective synthesis of trans-F_2TePh_3Cl

trans-F_2TePh_3Cl 36b, can be prepared in two-stages:

1. The preparation of the $Ph_3TeF_2^+$ cation by adding a Lewis acid, PF_5, to the solution of *mer*-Ph_3TeF_3 in CH_2Cl_2.

2. The subsequent addition of chloride ion to the $Ph_3TeF_2^+$ cation prepared above.

The reactions are described in equation [58]:



[58]

trans-36b

The formation of the five coordinate cation $Ph_3TeF_2^+$, *i.e.* the first step in reaction [58], was confirmed by ^{19}F, ^{125}Te, and ^{13}C NMR spectroscopy; this suggests that it has trigonal bipyramidal geometry. The equivalence of the fluorines is confirmed by singlet ^{19}F and triplet ^{125}Te NMR resonances, shown in Figures 37 and 38, respectively (see Table 7 for NMR data), and the equivalence of the phenyl substituents is shown by ^{13}C NMR resonances (section D-2).

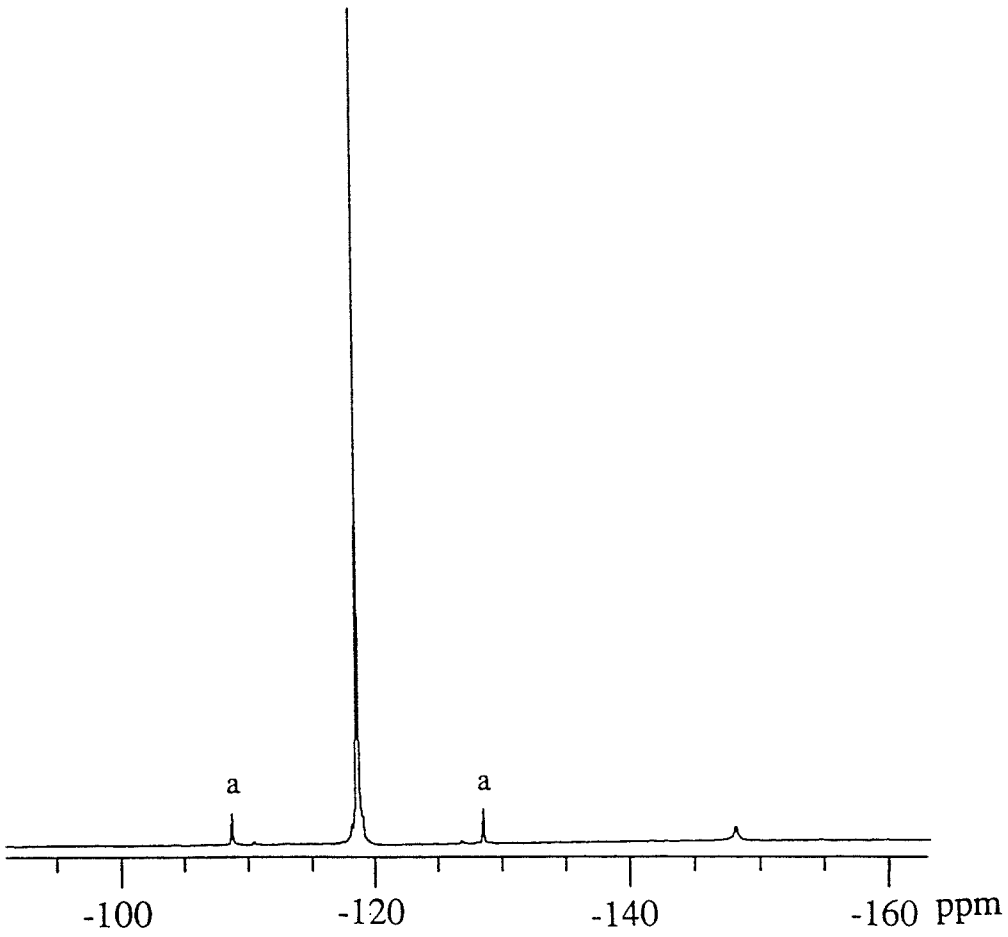


Figure 37. The ^{19}F NMR spectrum of $Ph_3TeF_2^+PF_6^-$ in CD_2Cl_2: ^{125}Te-satellites are marked with a. Peaks due to PF_6^- ion are not included.

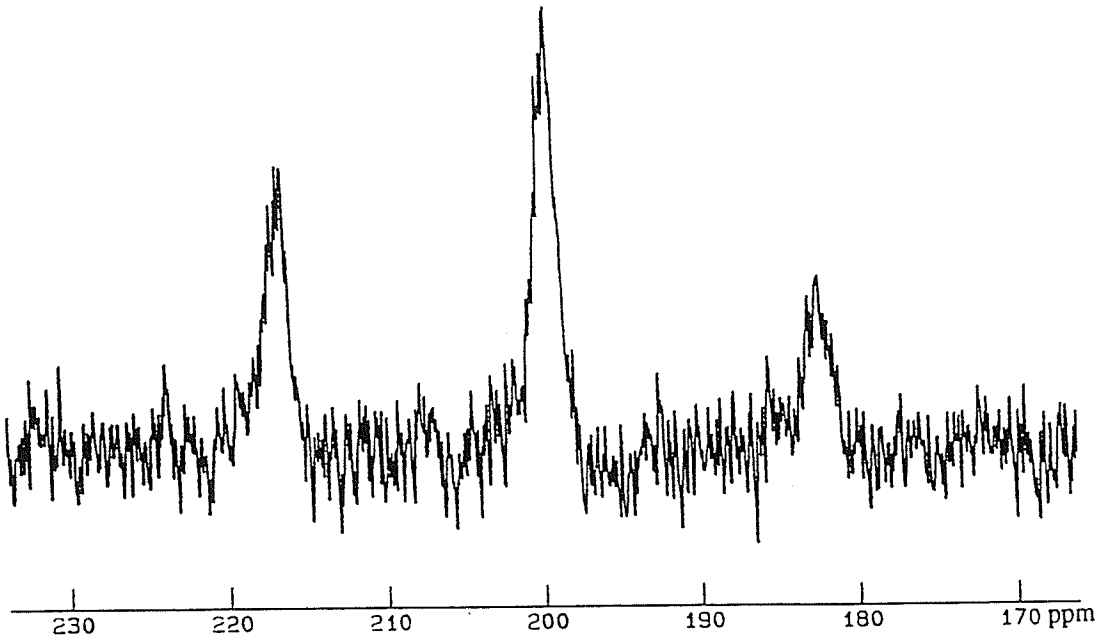


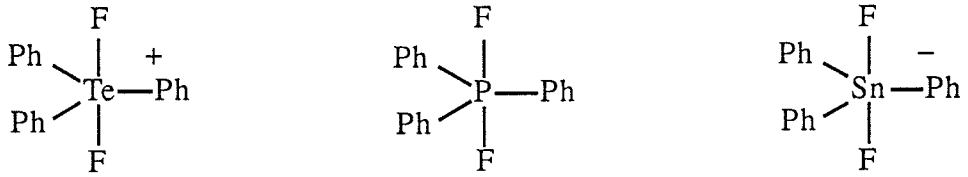
Figure 38. The ^{125}Te NMR spectrum of $Ph_3TeF_2^+PF_6^-$ in CD_2Cl_2. The chemical shift is measured relative to Ph_2Te. For the converted chemical shift relative to Me_2Te, see Table 7.

Furthermore, chemical reactions of $Ph_3TeF_2^+$ with NaF and R_4NCl confirm its identity, as illustrated in equation [59]:

$$Ph_3TeF_2^+ \xrightarrow{NaF} \textit{mer}\text{-}Ph_3TeF_3 \qquad [59a]$$

$$Ph_3TeF_2^+ \xrightarrow{R_4NCl} Ph_3TeF_2Cl \qquad [59b]$$

The analogous trigonal bipyramidal geometry can be observed in a series of isoelectronic and isostructural species, as in the following examples:



$Ph_3TeF_2^+PF_6^-$ Ph_3PF_2 $R_4N^+Ph_3SnF_2^-$

Figure 39. Trigonal bipyramidal geometry of difluorotriphenyl -tellurium(VI)(1+), -phosphorus(V), and -tin(IV)(1-).

Difluorotriphenylphosphorane(V), Ph_3PF_2, has been prepared by several different methods in the literature (57,65,118), and its trigonal bipyramidal structure is well

established. Holmes and his co-workers (47) have suggested a trigonal bipyramidal geometry for the $Ph_3SnF_2^-$ anion (also for Ph_3SnFCl^-) on the basis of ^1H NMR analysis which indicates that the three phenyl substituents occupy the equatorial plane. Our additional spectroscopic studies on these complexes confirm the suggested structure and the details will be given in chapter IIIB.

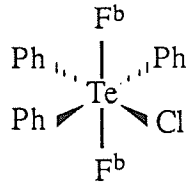
The addition of chloride ion to the solution of $Ph_3TeF_2^+PF_6^-$ in CH_2Cl_2, *i.e.* the second step in reaction [58], gives *trans*-F_2TePh_3Cl 36b. The structure of the *trans*-isomer 36b was confirmed by ^{19}F and ^{125}Te NMR spectroscopy. The solution of *trans*-F_2TePh_3Cl in CD_2Cl_2 exhibits a singlet ^{19}F resonance with ^{125}Te-satellites, as illustrated in Figure 40, and a triplet ^{125}Te resonance with the same J(Te-F) magnitude obtained in the ^{19}F NMR spectrum, as illustrated in Figure 41. NMR data are summarized in Table 7. It was found that δF^b and J(Te-F^b) of *trans*-36b are very similar to corresponding values for *trans* fluorines (F^b) in *mer*-Ph_3TeF_3. The ^{125}Te NMR chemical shift is also within the range normally observed for octahedral fluorophenyltellurium(VI) compounds.

The stereochemical preference for the *mer*-arrangement of phenyl substituents in *trans*-F_2TePh_3Cl is presumably determined by the presence of three phenyl substituents for a planar arrangement in the following molecules:

1. *mer*-Ph_3TeF_3, *cis*-F_2TePh_3Cl, and *cis*-F_2TePh_3OH have the phenyl substituents in a *mer*-arrangement about the central Te atom in octahedral geometry. The structures in solution are consistent with the solid state structures determined by X-ray crystallography for *mer*-Ph_3TeF_3 (22) and *cis*-F_2TePh_3OH (60).

2. The $Ph_3TeF_2^+$ cation (Figure 39) and a mixed-halo cation Ph_3TeFCl^+, to be discussed later, have trigonal bipyramidal geometry with phenyl substituents in the equatorial plane, as indicated by NMR spectroscopy.

trans-F_2TePh_3Cl



δF^b = -99 ppm and J(Te-F^b) = 1800 Hz

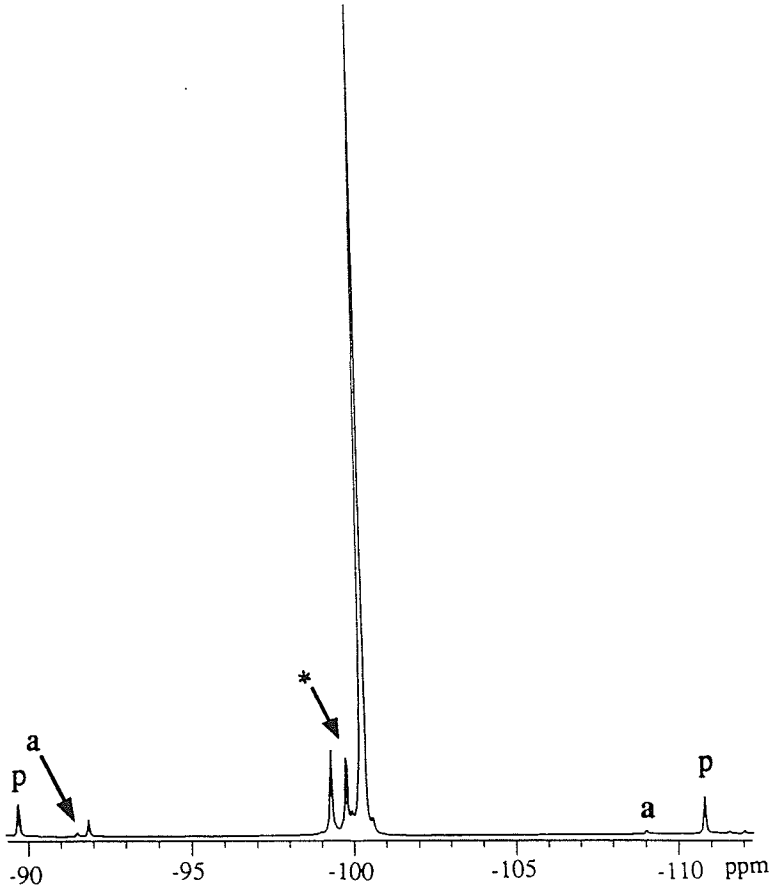
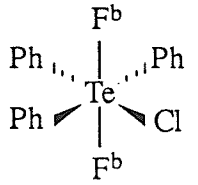


Figure 40. The ^{19}F NMR spectrum of *trans*-F_2TePh_3Cl in CD_2Cl_2 (0.14 mmol/mL): $^{125/123}Te$-coupled satellites are marked with p and a, respectively. A small amount of *cis*-F_2TePh_3Cl is also present (one of its doublets is shown and marked with an asterisk).

trans-F_2TePh_3Cl



$\delta^{125}Te$ = + 783 ppm

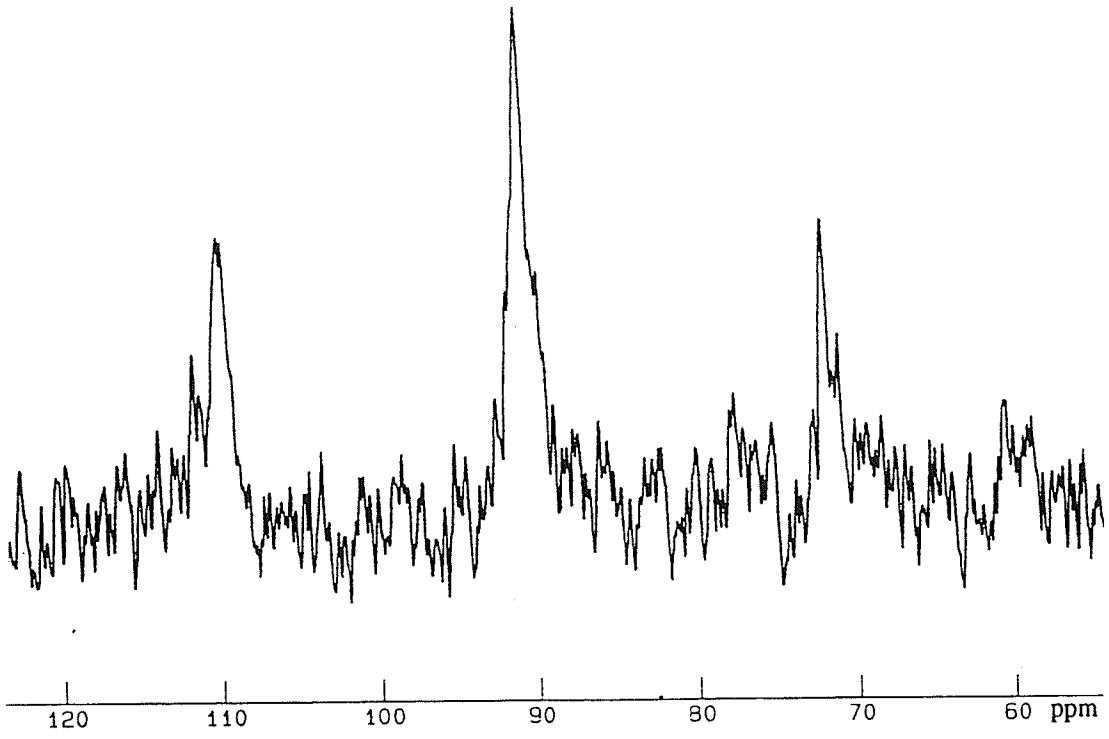
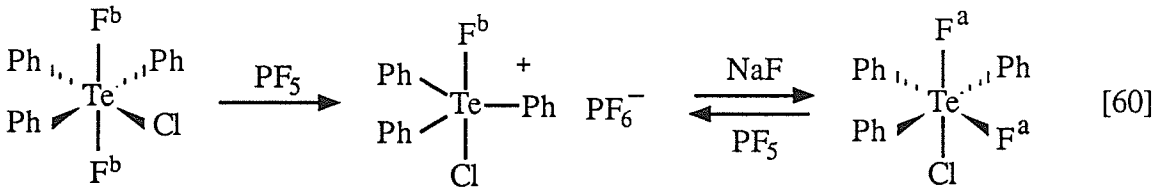


Figure 41. The ^{125}Te NMR spectrum of *trans*-F_2TePh_3Cl in CD_2Cl_2 (0.14 mmol/mL). The chemical shift is measured relative to Ph_2Te. The converted value of $\delta^{125}Te$ relative to Me_2Te is +783 ppm (Table 7).

3. The isoelectronic species, $Ph_3SnF_2^-$ (Figure 39) and Ph_3SnFCl^-, as stated above, have trigonal bipyramidal geometry with phenyl substituents in the equatorial plane.

2. Stereoselective synthesis of cis-F_2TePh_3Cl

Reactions of Ph_3TeCl with XeF_2 in a suitable solvent produce the thermodynamically stable *cis*-F_2TePh_3Cl only, as described in equation [57]. Furthermore, *cis*-F_2TePh_3Cl has been prepared in two stages in a similar manner to that described for the synthesis of the *trans*-isomer; *i.e.* the reaction of *trans*-F_2TePh_3Cl, which was prepared according to equation [58], with the Lewis acid, PF_5, to give the cation Ph_3TeFCl^+. The fluoride ion was then added at the equatorial plane of Ph_3TeFCl^+ to give the *cis*-isomer, as illustrated in equation [60]:



[60]

trans-36b *cis*-36a

Each reaction step in equation [60] was verified by NMR spectroscopy. The mixed-halo cation Ph_3TeFCl^+ has a trigonal bipyramidal geometry similar to that of $Ph_3TeF_2^+$, as confirmed by NMR studies; fluorochlorotriphenyltellurium(1+), Ph_3TeFCl^+, contains

fluorine in a single magnetic environment as it exhibits a singlet ^{19}F NMR spectrum with ^{125}Te-coupled satellites and a doublet ^{125}Te NMR spectrum. The ^{19}F NMR spectrum of the cation Ph_3TeFCl^+ is illustrated in Figure 42 and NMR data are presented in Table 7. The formation of the cations $Ph_3TeF_2^+$ and Ph_3TeFCl^+ from octahedral *mer*-Ph_3TeF_3, *trans*-F_2TePh_3Cl or *cis*-F_2TePh_3Cl results in an upfield shift of 100 to 120 ppm in the ^{125}Te NMR spectrum and a decrease of the magnitude of $J(^{125}Te\text{-}F^b)$ by about 200-700 Hz.

The equivalence of the phenyl substituents in the Ph_3TeFCl^+ cation, as revealed by ^{13}C NMR spectroscopy (section D-2), supports the trigonal bipyramidal geometry of Ph_3TeFCl^+.

The addition of NaF to Ph_3TeFCl^+, *i.e.* the second step in reaction [60], gave *cis*-F_2TePh_3Cl, whose structure has already been discussed (section B-1). The Ph_3TeFCl^+ cation can also be formed by the reaction of *cis*-F_2TePh_3Cl with PF_5, the reverse reaction of the second step in equation [60].

B. Isomerization by an *intermolecular* mechanism

The isolation of the thermodynamically stable isomer only, *i.e.* *cis*-F_2TePh_3Cl, in the oxidative fluorination of Ph_3TeCl with XeF_2 is expected if the reaction follows the proposed mechanism (section C-2-b). The kinetically favoured *trans*-isomer, *trans*-F_2TePh_3Cl 36b, must then be prepared from *mer*-Ph_3TeF_3 via the five-coordinate cation $Ph_3TeF_2^+$, as illustrated in equation [58], However, it was observed that the *trans*-isomer is gradually converted to its *cis*-isomer in solution, as monitored by ^{19}F NMR spectroscopy of a solution containing 100% *trans*-F_2TePh_3Cl in CD_2Cl_2.

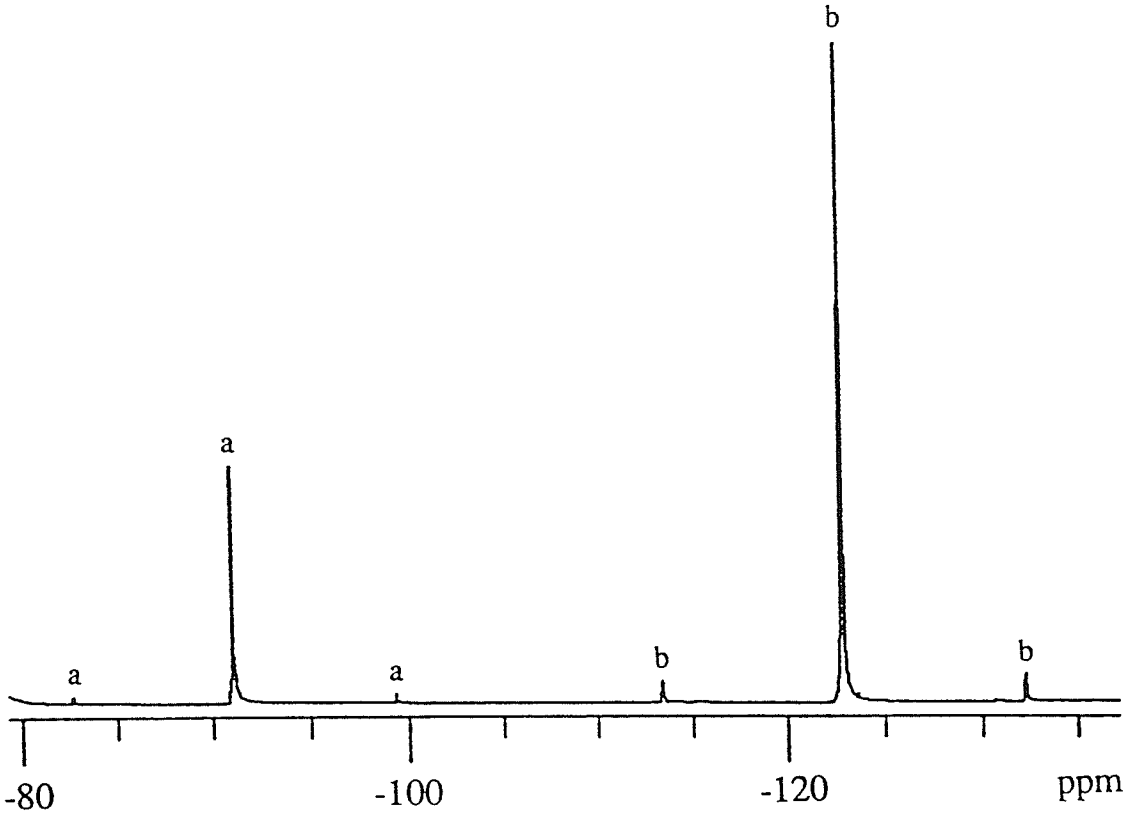
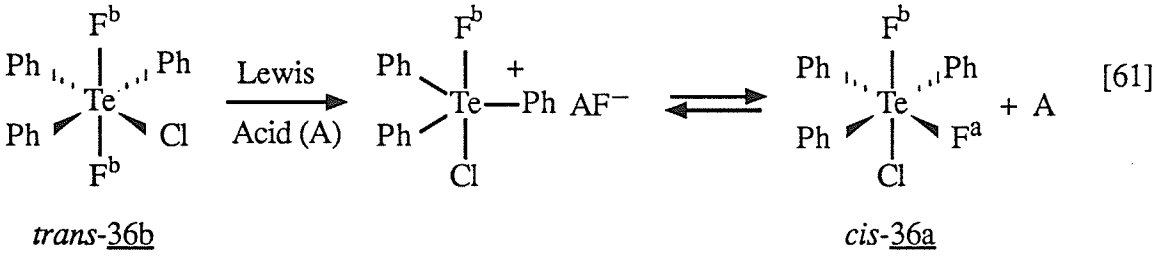


Figure 42. The ^{19}F NMR spectrum of $Ph_3TeFCl^+PF_6^-$ (peaks a) and $Ph_3TeF_2^+PF_6^-$ (peaks b) in CD_2Cl_2. ^{125}Te-coupled satellites are shown. Peaks due to PF_6^- ion are not included.

The isomerization process was monitored by measuring the relative areas of the fluorine resonances of both *cis*- and *trans*-isomers in the ^{19}F NMR spectra. After a few hours in dichloromethane solution, *cis*-F_2TePh_3Cl began to form in the sample that had originally contained 100% *trans*-F_2TePh_3Cl. It was estimated that only 64% of the *trans*-isomer remained after 24 hours and the rest was mainly *cis*-F_2TePh_3Cl, along with small amounts of *mer*-Ph_3TeF_3. The detection of *mer*-Ph_3TeF_3 is of particular importance because it implies the presence of fluoride impurities. In fact, NMR examination at this stage directly confirmed the presence of small amounts of fluoride impurities, such as $P(O)F_2OH$, $P(O)F(OH)_2$, and BF_4^-, which may originate from the reaction of PF_5 and HF with moisture and glass NMR tubes. After one month in solution, all *trans*-F_2TePh_3Cl had disappeared and only *cis*-F_2TePh_3Cl and *mer*-Ph_3TeF_3 remained. The repeated observations of the isomerization process were consistent with the results described above.

These observations, particularly the presence of Lewis acid impurities, suggest that the intermolecular isomerization mechanism involves Te-F bond-cleavage, as illustrated in equation [61]:



[61]

trans-36b *cis*-36a

Therefore, the following experiment was designed to perform the step-by-step isomerization of *trans*- to *cis*-F_2TePh_3Cl, according to equation [61], with verification by NMR spectroscopy at each stage:

1. The preparation of $Ph_3TeFCl^+PF_6^-$ by the reaction of *trans*-F_2TePh_3Cl with a Lewis acid PF_5.

2. The subsequent addition of fluoride ion to the solution of $Ph_3TeFCl^+PF_6^-$ in CH_2Cl_2 to give the *cis*-isomer 36a.

It required a total of ~1 hour to add PF_5 to *trans*-F_2TePh_3Cl, remove excess PF_5, record the NMR spectrum of the cation Ph_3TeFCl^+, add NaF, filter off excess solid NaF, and finally record the NMR spectrum of *cis*-F_2TePh_3Cl. The chemical reactions during this time occurred instantaneously, and thus it is concluded that the intermolecular mechanism involving Te-F bond-cleavage is responsible for the isomerization of octahedral fluorophenyltellurium(VI) compounds.

In contrast to our proposed *intermolecular* mechanism, Martin and his co-workers (9) have proposed an *intramolecular* mechanism for the *trans-cis* isomerization of analogous octahedral organotellurium(VI) fluorides.

The indicated nomenclature, originally proposed by Musher (119), is suggested to be more suitable for the analysis of the stereochemical problems compared to the conventional nomenclature and was recently adopted by Martin to describe his permutational isomerization work. For example, the following hypothetical molecules are called tellurane and pertellurane to represent tetra- and hexa-valent tellurium compounds, respectively (119), as briefly discussed in the section C-2-c:

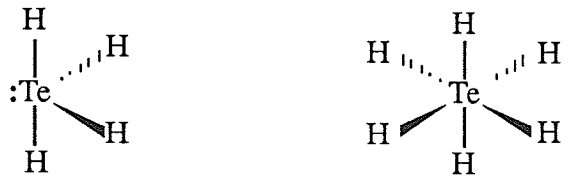


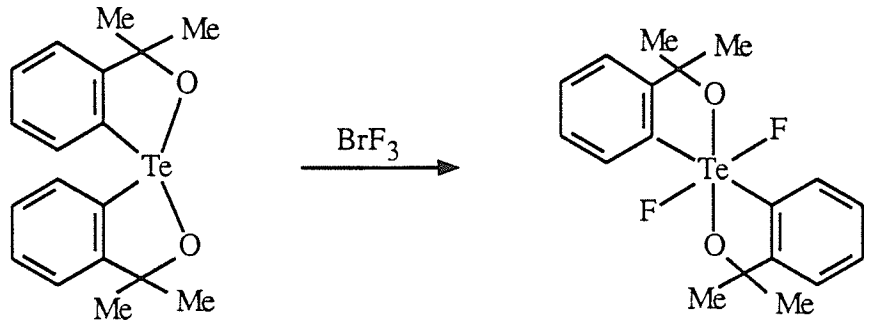
Figure 43. A suggested nomenclature for Te(IV) and Te(VI), respectively (119).

A similar nomenclature may be applied to the sulfur and selenium analogues, *i.e.* sulfurane and persulfurane; selenane and perselenane.

Martin and his co-workers (9) have synthesized an octahedral *trans*-pertellurane, $F_2Te(C_6H_4CMe_2O)_2$, by the oxidative fluorination of the tellurane, $(C_6H_4CMe_2O)_2Te$, with bromine trifluoride, as outlined in equation [62].

The kinetically favoured *trans*-pertellurane was almost completely converted (90%) to the thermodynamically stable *cis*-pertellurane after 3 days in quinoline and 1,2-dichloroethane at 60 °C and an *intramolecular*, non-dissociative mechanism was proposed for the isomerization, as illustrated in equation [63].

They argued that, by using a basic medium, such as quinoline, that lacks a strong Lewis acid necessary for catalysis of the bond-breaking process, the isomerization required heating at 60 °C for about 3 days to reach the equilibrium ratio of 9 to 1. On the other hand, they found that the *trans*-pertellurane isomerizes rapidly at room temperature in the presence of catalytic amounts of a Lewis acid, such as sulfur trioxide or antimony pentafluoride, to give the more stable *cis*-pertellurane. In other words, in the absence of acid catalysts, the isomerization does not occur under mild conditions, but requires heating of the solution.

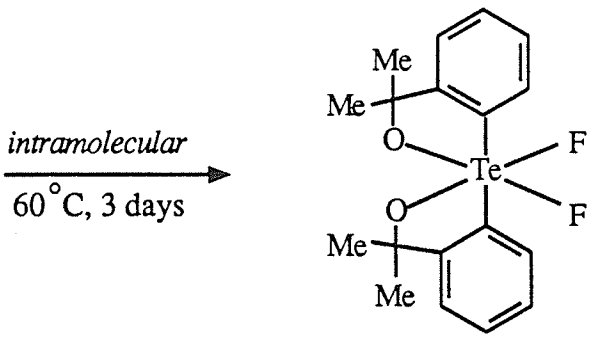


[62]

tellurane

trans-pertellurane

trans- pertellurane



[63]

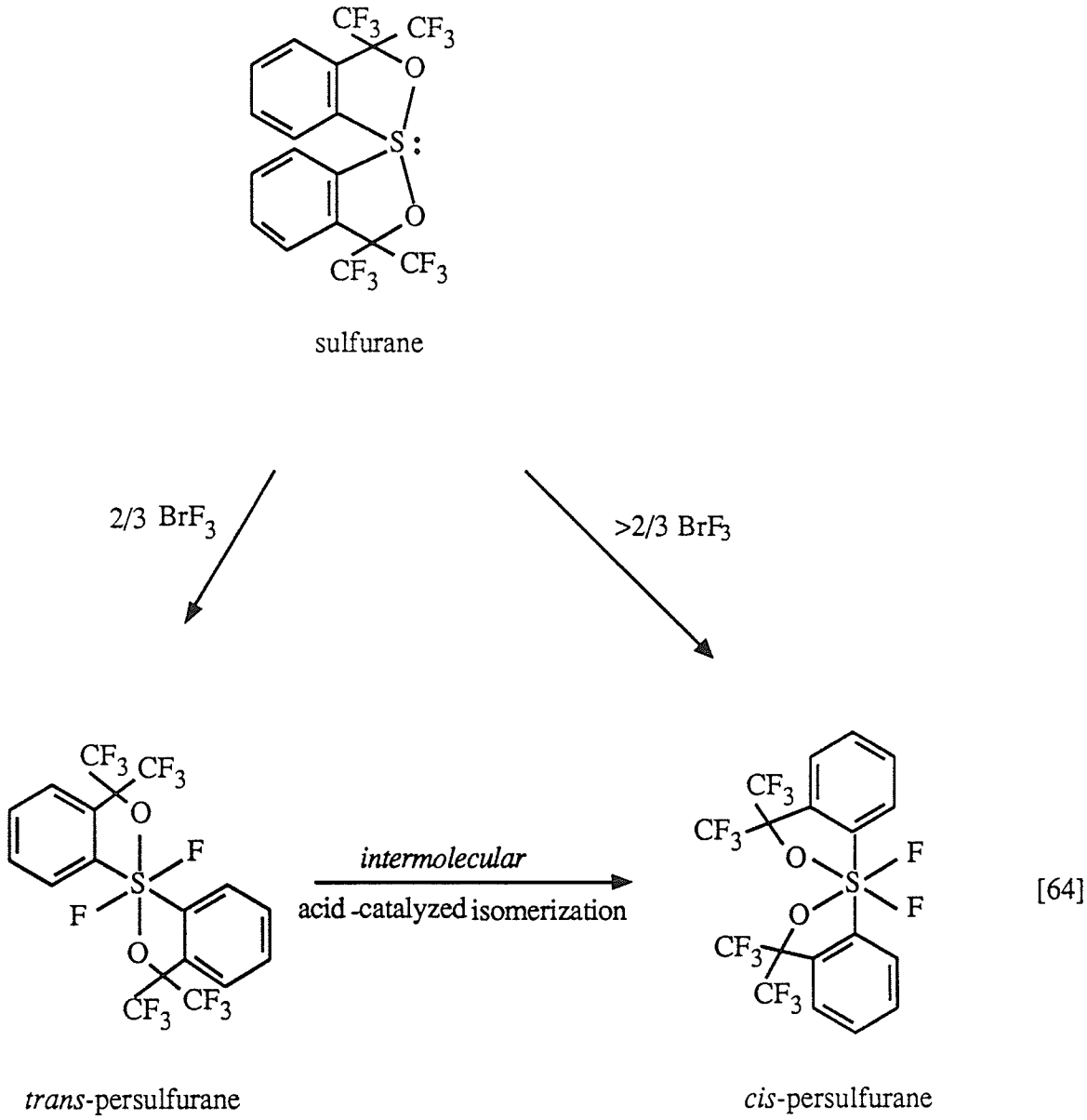
cis-pertellurane

However, during that period, Lewis acid impurities are likely to be produced since complete removal of moisture from solvents or even from glassware is extremely difficult. Our studies reveal that traces of Lewis acids can be easily generated in solution by the reaction of fluorinated compounds with moisture, and with glass.

Hence these results suggest that the *intermolecular* mechanism is responsible for the low energy pathway for isomerization of *trans*- to *cis*-pertellurane.

The same group has reported the synthesis of the isoelectronic and isostructural *cis*- and *trans*-persulfurane, and isomerization of the *trans* to the *cis*-isomer . Martin and Michalak oxidatively fluorinated a sulfurane, $[C_6H_4(CF_3)_2O]_2S$, with bromine trifluoride in varying amounts (17,120,121); if the ratio of BrF_3 and sulfurane was equal to 2/3 (*i.e.* a stoichiometric amount of BrF_3 was used), the kinetically favoured *trans*-persulfurane, $F_2S[C_6H_4C(CF_3)_2O]_2$, was obtained. However, if the ratio was greater than 2/3 (*i.e.* excess BrF_3 was used), then the thermodynamically more stable *cis*-persulfurane resulted, as illustrated in equation [64].

The fact that the oxidative fluorination of sulfurane with excess BrF_3 gives the thermodynamically stable *cis*-isomer only is quite consistent with our results of oxidative fluorinations with XeF_2, which also produce the thermodynamically stable isomers. In both examples, a common factor, which may be responsible for the isomerization, is the presence of Lewis acid fluorides. Michalak and Martin (17) have suggested that the isolation of the thermodynamically stable *cis*-isomer, rather than the kinetically stable *trans*-isomer, in the fluorinations of sulfurane with excess BrF_3, could be attributed to acid-catalyzed isomerization by excess Lewis acid (bromine trifluoride) or, perhaps, by traces of HF. This is consistent with our results that the rapid isomerization of *cis*- to *trans*-Ph_2TeF_4 is also catalyzed by Lewis acid impurities generated during prolonged reactions with XeF_2.


CF3 CF3
O
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CF3 CF3
sulfurane
2/3 BrF3
>2/3 BrF3
CF3 CF3
O
F
S
F
O
CF3 CF3
trans-persulfurane
intermolecular
acid -catalyzed isomerization
CF3
CF3
O
F
S
F
O
CF3
CF3
cis-persulfurane

[64]

In the case of persulfurane, Michalak and Martin (17) found that the addition of catalytic amounts of a Lewis acid, antimony pentafluoride, to the *trans*-isomer catalyzed the isomerization to give the thermodynamically stable *cis*-isomer. Furthermore, they have prepared the five-coordinate intermediate cation by the reaction of *trans*-persulfurane with PF_5 and characterized the product by ^{19}F NMR spectroscopy as persulfonium(1+) hexafluoro-phosphate(1-), $[(C_6H_4C(CF_3)_2O]_2SF^+PF_6^-$ (120).

However, the expected intermediate cation, $Ph_2TeF_3^+$, in the isomerization of *cis*- to *trans*-Ph_2TeF_4, as shown in equation [41], has not been isolated, nor detected by NMR spectroscopy, probably due to the rapid exchange (section B-2-b). An attempted reaction of *trans*-Ph_2TeF_4 with Lewis acid PF_5 or BF_3, in an effort to prepare *cis*-Ph_2TeF_4 via the $Ph_2TeF_3^+$ cation, only resulted in the regeneration of the *trans*-isomer.

Furthermore, it should be pointed out that there is no evidence of *intramolecular* scrambling of fluorine ligands in the purified samples of any fluorophenyltellurium(VI) compound, as judged by NMR spectroscopy.

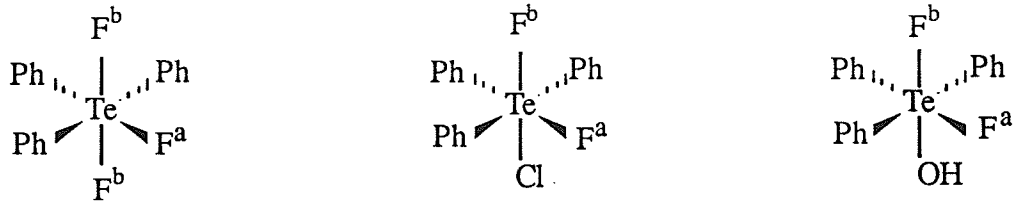
In conclusion, on the basis of our experimental evidence, and also by the fact that isomerization in pertellurane and persulfurane is catalyzed by Lewis acids such as SbF_5 and SO_3, as discussed above, it is proposed that the *intermolecular* process is the lowest energy pathway for isomerization of octahedral Te(VI) fluorides, in contrast to the *intramolecular* process proposed by Martin *et al.* (9).

III. STEREOSELECTIVE FLUORINE EXCHANGE

Octahedral fluorophenyltellurium(VI) compounds exhibit narrow multiplet NMR resonances, characteristic of rigid compounds, in solution. However, occasionally their ^{19}F NMR resonances become broad with loss of Te-F coupling, indicative of intermolecular exchange. Lewis acid impurities may generate five-coordinate Te(VI) species that, in turn, catalyze fluorine exchange in octahedral fluorophenyltellurium(VI) species.

Previous studies in our laboratory (22) have shown that fluorine exchange can be initiated in octahedral *mer*-Ph_3TeF_3 by adding a five-coordinate $Ph_3TeF_2^+$ cation, which leads to the stereoselective exchange of F^a.

Furthermore, my work reveals that stereoselective Te-F^a bond-cleavage is observed in octahedral fluorophenyltellurium(VI) compounds of the type, *mer*-$Ph_3TeF^aF^bX$ (X=F, Cl, and OH), as in the following examples (Figure 44):



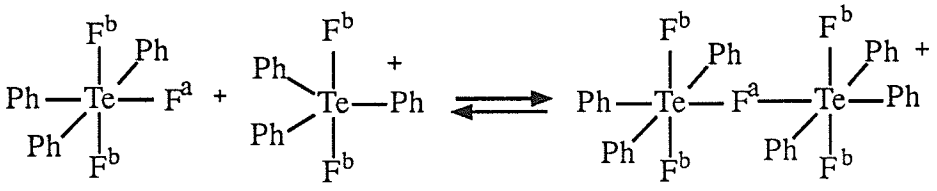
mer-Ph_3TeF_3 *cis*-F_2TePh_3Cl *cis*-F_2TePh_3OH

Figure 44. Three examples in which stereoselective cleavage of a Te-F^a bond occurs. All have three phenyl substituents in a *mer*-arrangement.

It should be noted that phenyl groups of fluorophenyltellurium(VI) compounds are not involved in any type of ligand exchange in solution since they exhibit multiplet ^{13}C resonances with $^{n}J(C\text{-}F)$ coupling (n=3-6), as discussed in section I-D.

A. Stereoselective fluorine exchange in *mer*-Ph_3TeF_3

The fluorine exchange studies were performed on an equimolar mixture of six-coordinate *mer*-Ph_3TeF_3 and five-coordinate $Ph_3TeF_2^+$ cation at room temperature (22). The preliminary results have demonstrated that intermolecular exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system is rapid on the NMR time scale and involves the cleavage of the Te-F^a bond, but not the Te-F^b bonds, as illustrated in equation [65]:



[65]

F^a-bridged intermediate

The mechanism of the rapid exchange between five- and six-coordinate phenyltellurium(VI) fluorides through a fluorine-bridged intermediate in which only the F^a ligand occupies the bridging position is suggested based on the following observations:

1. The loss of F^a-F^b and Te-F^a coupling but retention of Te-F^b coupling, *i.e.* the Te-F^a bond is cleaved while the Te-F^b bonds are retained during the exchange process.

2. The observed chemical shifts and coupling constants of F^b ligands of the mixture are the weighted averages of F^b ligands in *mer*-Ph_3TeF_3 and $Ph_3TeF_2^+$.

3. The F^a chemical shift of the mixture moves significantly to higher field compared to that of *mer*-Ph_3TeF_3.

So far, the exchanging behavior of the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system at room temperature has been discussed. Since it is now possible to prepare the five-coordinate $Ph_3TeF_2^+$ cation in sufficient concentration that NMR spectroscopy can be used to detect it, the dynamic NMR (DNMR) experiment was carried out on the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system at variable temperatures, in an effort to obtain thermodynamic parameters, and the results will be presented in this section.

Applications of the DNMR technique to the study of processes that involve bond-formation and bond-cleavage have been found extremely useful, particularly to detect fast reactions (chemical equilibrium) that are not observable by classical chemical techniques. The theory of DNMR processes has been developed by both classical procedures (the Bloch equations) and quantum mechanics (density matrices). Detailed descriptions of the development of the theory and techniques of DNMR can be found in some excellent reviews (122,123), and particularly to organic and inorganic compounds (124). The DNMR technique essentially measures the mean life time, τ, of a process, the inverse of which is the rate constant. Direct comparison between calculated (by computer simulation) and the experimental spectra at given temperatures is possible. From a series of rate constants at different temperatures, activation parameters for the exchange reaction may be calculated. In addition to kinetic information, thermodynamic parameters can be evaluated from the DNMR technique. When two species undergo rapid exchange on the NMR time scale, the chemical shift observed is a mole fraction weighted average of two resonances (125), as illustrated in equation [66]:

when $A + B \rightleftharpoons [AB]$

then, $\delta obs = X_A\delta_A + X_{AB}\delta_{AB}$

$= \{[A]/[A]+[AB]\}\delta_A + \{[AB]/[A]+[AB]\}\delta_{AB}$ [66]

(X represents the mole fraction of the given substance)

From the observed chemical shift (δobs), the concentration of the intermediate, [AB], can be calculated and, therefore, the equilibrium constant can be evaluated for a given reaction at different temperatures.

The evaluation of equilibrium constants as a function of temperature offers the possibility of calculating thermodynamic parameters, *e.g,*

$$\frac{d\ln K}{d(1/T)} = - \frac{\Delta H}{R} \qquad [67]$$

During many trials of DNMR experiments to obtain the most reliable data, certain unavoidable difficulties were encountered when handling very unstable compounds, such as the $Ph_3TeF_2^+$ cation, and various impurities that accompanied the fast exchange reactions. Difluorotriphenyltellurium(1+) cation, $Ph_3TeF_2^+$, readily decomposes in solution, in contrast to the hexafluorophosphate anion, PF_6^-, which is of high stability, even toward aqueous alkali (126). Unless kept rigorously anhydrous, the $Ph_3TeF_2^+$ cation was found to attack glass gradually and thus should preferably be stored in a Teflon bottle. Therefore, the most serious disadvantage of using $Ph_3TeF_2^+$ cation in this exchange study is that, after standing for a few minutes in solution in glass NMR tubes for

routine ^{19}F NMR analysis, the $Ph_3TeF_2^+$ cation already starts to decompose, generating impurities such as BF_4^-.

Even though efforts were made to eliminate these difficulties, they could only be minimized and thus only a qualitative description of the dynamic behavior will be given.

Variable temperature 84.7 MHz ^{19}F NMR experiments on a mixture of *mer*-Ph_3TeF_3 (1 mmol) and $Ph_3TeF_2^+PF_6^-$ (1 mmol) were carried out in CD_2Cl_2 solution from 300 K down to 180 K. Figure 45 illustrates the temperature-dependent ^{19}F NMR spectra observed in the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system. Changes in chemical shifts and coupling constants are similar to those reported previously (22). At room temperature, the averaged chemical shift of F^a appeared at -58 ppm but as the temperature decreased, it moves to downfield. Eventually at 180 K, the chemical shift of the F^a resonance appeared at -3 ppm, which is the same as that of *mer*-Ph_3TeF_3 when there is no exchange. But even at this temperature, Te-F coupling was not observed. Unfortunately, below this temperature (< 180 K), the rest of the spectrum started to broaden, perhaps the result of increased viscosity, precipitation of impurities, or other problems.

As shown in Figure 45, despite purification of all starting materials and solvents, the mixture was contaminated with small but detrimental amounts of fluoride impurities, such as $P(O)F(OH)_2$, $P(O)F_2(OH)$ and BF_4^- which were difficult to remove. In particular, $P(O)F_2(OH)$ gradually increased during the variable temperature NMR experiment. Because of these problems, only rough equilibrium constants can be calculated from exchanging NMR spectra.

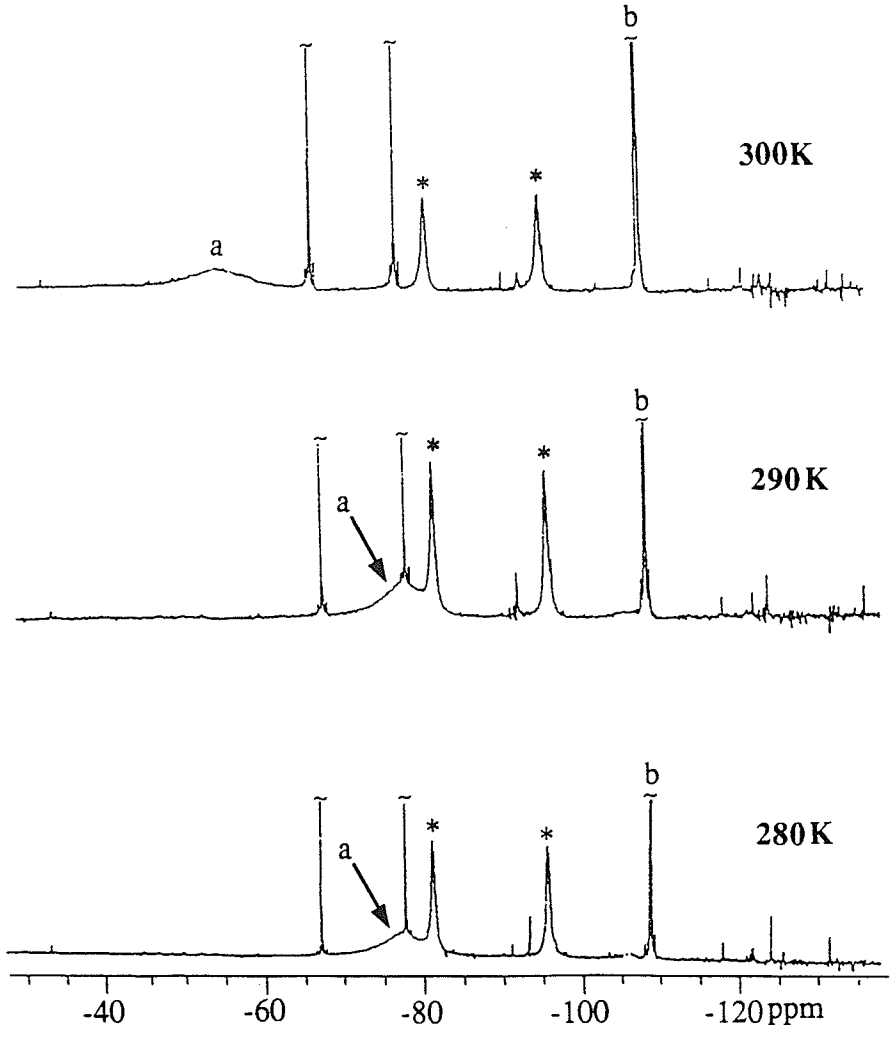


Figure 45. Temperature-dependent ^{19}F NMR spectra of a mixture of *mer*-Ph_3TeF_3 and $Ph_3TeF_2^+PF_6^-$(1:1) in CD_2Cl_2 (84.7 MHz): apparent variations of F^a (marked with a) in chemical shift are significant (see text). The peak marked with b is the average chemical shift of *mer*-$Ph_3TeF^aF_2^b$ and $Ph_3TeF_2^b$. The peak indicated by * is $P(O)F_2(OH)$ present as an impurity. The unmarked doublets are due to PF_6^- (continued on the following page).

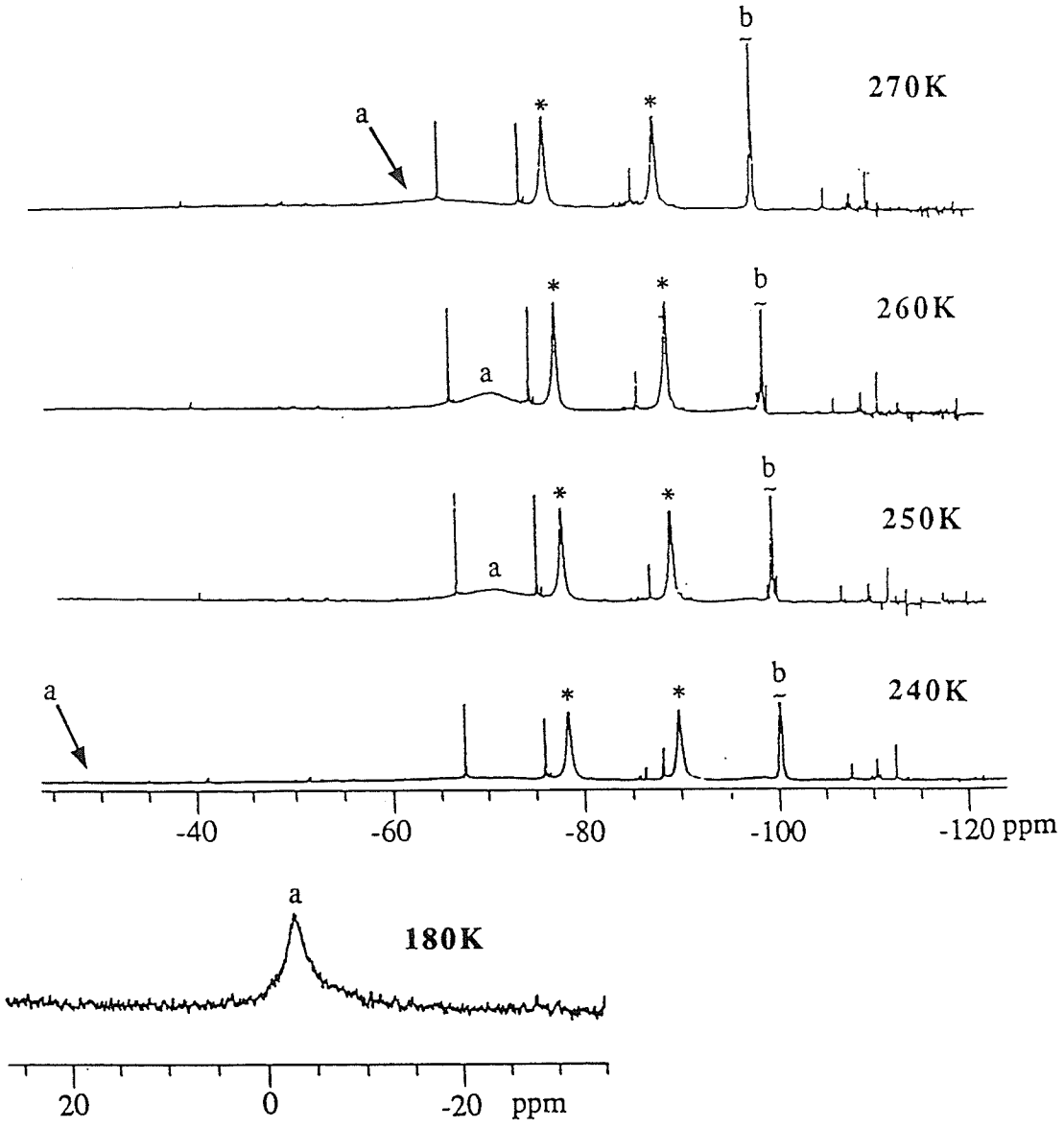


Figure 45. (continued). At 180 K, the rest of the spectrum is unchanged.

The values of ΔH are customarily obtained from a linear plot of lnK versus T^{-1} which has a slope of $-\Delta H/R$, as shown in equation [67], when K is known from at least two different temperatures.

The reaction enthalpy (ΔH) of the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system was calculated to be -14.2 $kJmol^{-1}$ (see APPENDIX). The value of ΔH of -14.2 $kJmol^{-1}$ extracted from exchanging broadened NMR spectra should be regarded with considerable caution since the method used was very approximate.

B. Stereoselective fluorine exchange in *cis*-F_2TePh_3Cl

Results of oxidative fluorination with XeF_2 have shown that *trans*-F_2TePh_3Cl is the kinetically favoured isomer and *cis*-F_2TePh_3Cl is the thermodynamically favoured one (see section II). Both isomers give sharp NMR resonances in solution, with Te-F coupling, characteristic of rigid molecules. However, the *trans*-isomer rearranges to give the *cis*-isomer in the presence of fluoride impurities through the intermediacy of a cation, as illustrated in equation [61]. That intermediate cation, Ph_3TeFCl^+, has been prepared to analyze the isomerization mechanism, which was determined to be an *intermolecular* process involving Te-F bond-cleavage. Since *trans*-F_2TePh_3Cl in the presence of Lewis acid impurities produces the Ph_3TeFCl^+ cation which, in turn, catalyzes isomerization, the possibility that traces of fluoride impurities might catalyze fluorine exchange in the thermodynamically stable *cis*-F_2TePh_3Cl should also be emphasized. This is reasonable because it is the five-coordinate $Ph_3TeF_2^+$cation which causes fluorine exchange in octahedral *mer*-Ph_3TeF_3. It should be remembered that the Ph_3TeFCl^+ cation can also be formed from *cis*-F_2TePh_3Cl as well as from *trans*-F_2TePh_3Cl, as described in equation [60].

As discussed above, molecules of *cis*-F_2TePh_3Cl are rigid in solution on the NMR time scale. However, when the solution stands for several days in a glass NMR tube, evidence of intermolecular fluorine exchange is found, *i.e.* the ^{19}F NMR peaks become broad with loss of F^a-F^b and Te-F^b coupling, as found previously for solutions of *mer*-Ph_3TeF_3. But treating solutions of *cis*-F_2TePh_3Cl with small amounts of NaF or R_4NCl stopped all fluorine exchange, presumably because any five-coordinate Te(VI) cation was converted to a stable six-coordinate Te(VI) compound.

The dynamic NMR experiment was performed on octahedral *cis*-F_2TePh_3Cl by adding to the solution known amounts of the five-coordinate Te(VI) cation, Ph_3TeFCl^+, prepared according to equation [60]; during reactions of PF_5 with *cis*-F_2TePh_3Cl for the preparation of the Ph_3TeFCl^+ cation, some *mer*-Ph_3TeF_3 was present and, consequently, both $Ph_3TeF_2^+$ and Ph_3TeFCl^+ were formed in solution. However, it should be noted that there is no intermolecular exchange between the two cations.

Because of interference of the peaks due to $Ph_3TeF_2^+$ and *mer*-Ph_3TeF_3, the exchange broadened ^{19}F NMR spectra for the *cis*-F_2TePh_3Cl-Ph_3TeFCl^+ system obtained at variable temperatures will not be presented.

When approximately 1 equivalent of the Ph_3TeFCl^+ cation was added to the solution of *cis*-F_2TePh_3Cl in CD_2Cl_2, the following results were observed in the ^{19}F NMR spectrum at room temperature:

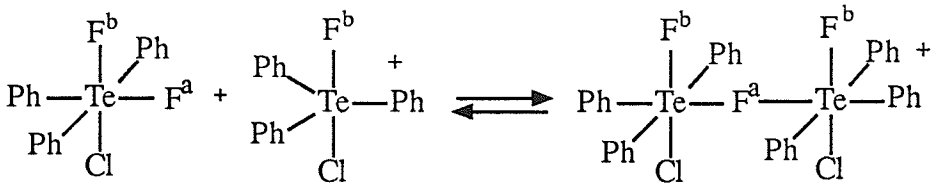
1. As Ph_3TeFCl^+ is added to *cis*-F_2TePh_3Cl, the F^a-F^b coupling is lost but the Te-F^b coupling is retained.

2. The averaged chemical shift of F^b moves to slightly higher field (~-88 ppm); δF^b(*cis*-F_2TePh_3Cl) = -86.7 ppm, δF^b(Ph_3TeFCl^+) = -90 ppm.

3. The F^a peak at +1.1 ppm in *cis*-F_2TePh_3Cl (Table 7) moves to significantly high field (~-82 ppm) and the Te-F^a coupling is lost.

As the temperature is lowered, the F^a peak moves to lower field (*e.g.* at -280 K, δF^b = -44 ppm), but there is little change in the chemical shift of the F^b peak throughout the experiment, presumably because of the small chemical shift differences in the two species. Finally at 190 K, all the fluorine exchange stopped and multiplets reappeared.

These results are very similar to those observed in the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system. Although the thermodynamic data could not be evaluated from this dynamic NMR experiment, it was possible to demonstrate that rapid intermolecular fluorine exchange can be initiated in six-coordinate *cis*-F_2TePh_3Cl on addition of five-coordinate $Ph_3TeFCl^+PF_6^-$, by a mechanism involving a fluorine-bridged intermediate in which F^a occupies the bridging position, as shown in equation [68].



F^a-bridged intermediate

[68]

C. Stereoselective fluorine exchange in *cis*-F_2TePh_3OH

The solid state structure of molecules of Ph_3TeF_2OH has been determined by X-ray crystallography (60), but a good method of preparation has not been established. It was often observed as a minor product in samples of *mer*-Ph_3TeF_3, *cis*-F_2TePh_3Cl, $Ph_3TeF_2^+PF_6^-$, and Ph_4TeF_2. Colourless crystals of Ph_3TeF_2OH were grown from dichloromethane solution of an impure sample of *mer*-Ph_3TeF_3 (60), and its crystal

structure revealed that it to be the *cis*-isomer, with phenyl substituents in the *mer*-arrangement (see Figure 46).

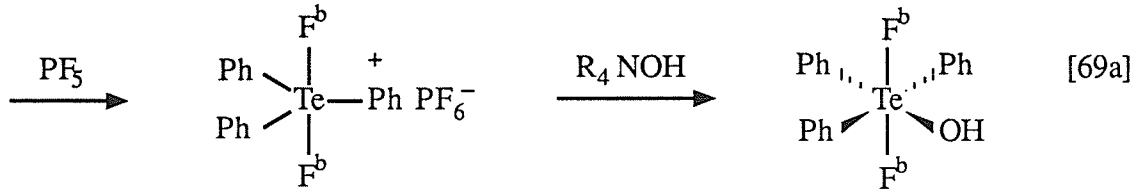
cis-46a *trans*-46b

Figure 46. The two possible geometrical isomers of *mer*-Ph_3TeF_2OH.

As shown in Figure 46, *mer*-Ph_3TeF_2OH can exist as two geometrical isomers with respect to fluorines, i.e. *cis*- and *trans*-F_2TePh_3OH.

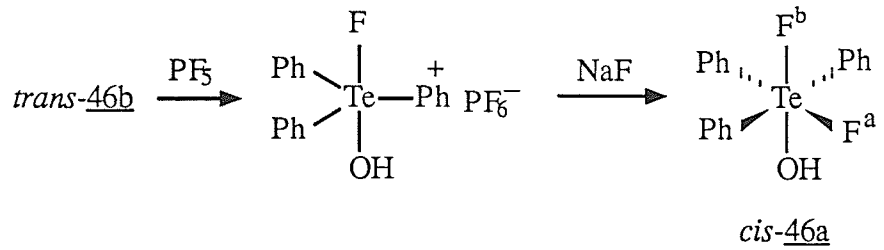
An attempted synthesis of *cis*-46a and *trans*-46b via five-coordinate cations, $Ph_3TeF_2^+$ and Ph_3TeFOH^+, respectively, was not successful, as illustrated in equation [69]:

mer-Ph_3TeF_3



[69a]

trans-46b



cis-46a

[69b]

In the reaction [69a], *mer*-Ph_3TeF_3 formed in large amounts, although a small broad peak at -90 ppm also appeared in the ^{19}F NMR spectrum, which might be due to the kinetically favoured isomer, *trans*-F_2TePh_3OH 46b, but its identity was not confirmed.

Perhaps the use of PF_5 was inappropriate for the synthesis of the hydrolysis product because the reaction of PF_5 with moisture, commonly present in R_4NOH, could generate fluoride impurities, which would then further react with the $Ph_3TeF_2^+$ cation to produce *mer*-Ph_3TeF_3. Fluoride impurities, such as $P(O)F_2OH$ and $P(O)F(OH)_2$, were detected by ^{19}F NMR spectroscopy.

The thermodynamically stable *cis*-isomer, *cis*-F_2TePh_3OH 46a, shows two doublets of equal intensity (ab fluorine spin system) in the ^{19}F NMR spectrum, which is consistent with the solid state structures determined by X-ray crystallography (60). The ^{19}F NMR spectrum of *cis*-F_2TePh_3OH will be shown shortly and its NMR data are presented in Table 7.

Since *cis*-F_2TePh_3OH has non-equivalent fluorines, F^a and F^b, the selective bond-cleavage may be studied by comparison with the two previous examples of the stereoselective fluorine exchange found in the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ and *cis*-F_2TePh_3Cl-Ph_3TeFCl^+ systems. Furthermore, the X-ray crystal structure of *cis*-F_2TePh_3OH (60) revealed that the Te-F^a bond (2.011 Å) is significantly longer than the

Te-F^b bond (1.951 Å) which, as found in *mer*-Ph_3TeF_3 (22), might be an important feature for selective bond-cleavage.

Under certain conditions, no intra- or intermolecular fluorine exchange can be observed by ^{19}F NMR and thus *cis*-F_2TePh_3OH is a rigid molecule in solution. Recrystallizing *cis*-F_2TePh_3OH from CH_2Cl_2, or treating the solution of *cis*-F_2TePh_3OH with NaF, stops all fluorine exchange. The fact that treatment with NaF or R_4NCl stopped all fluorine exchange in the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ and *cis*-F_2TePh_3Cl-Ph_3TeFCl^+ systems, and also in the exchanging sample of *cis*-F_2TePh_3OH, indicates that any five-coordinate Te(VI) cation, which initiates the exchange in the system, was converted to a stable six-coordinate Te(VI) compound.

Intermolecular fluorine exchange in *cis*-F_2TePh_3OH was observed, after its solution had stood in a glass NMR tube for several days, as judged by ^{19}F NMR spectroscopy; the exchange leads to loss of F^a-F^b and the Te-F^a couplings but retention of Te-F^b coupling, as shown in Figure 47, and these results demonstrate that Te-F^a bond in *cis*-F_2TePh_3OH is cleaved during the exchange process.

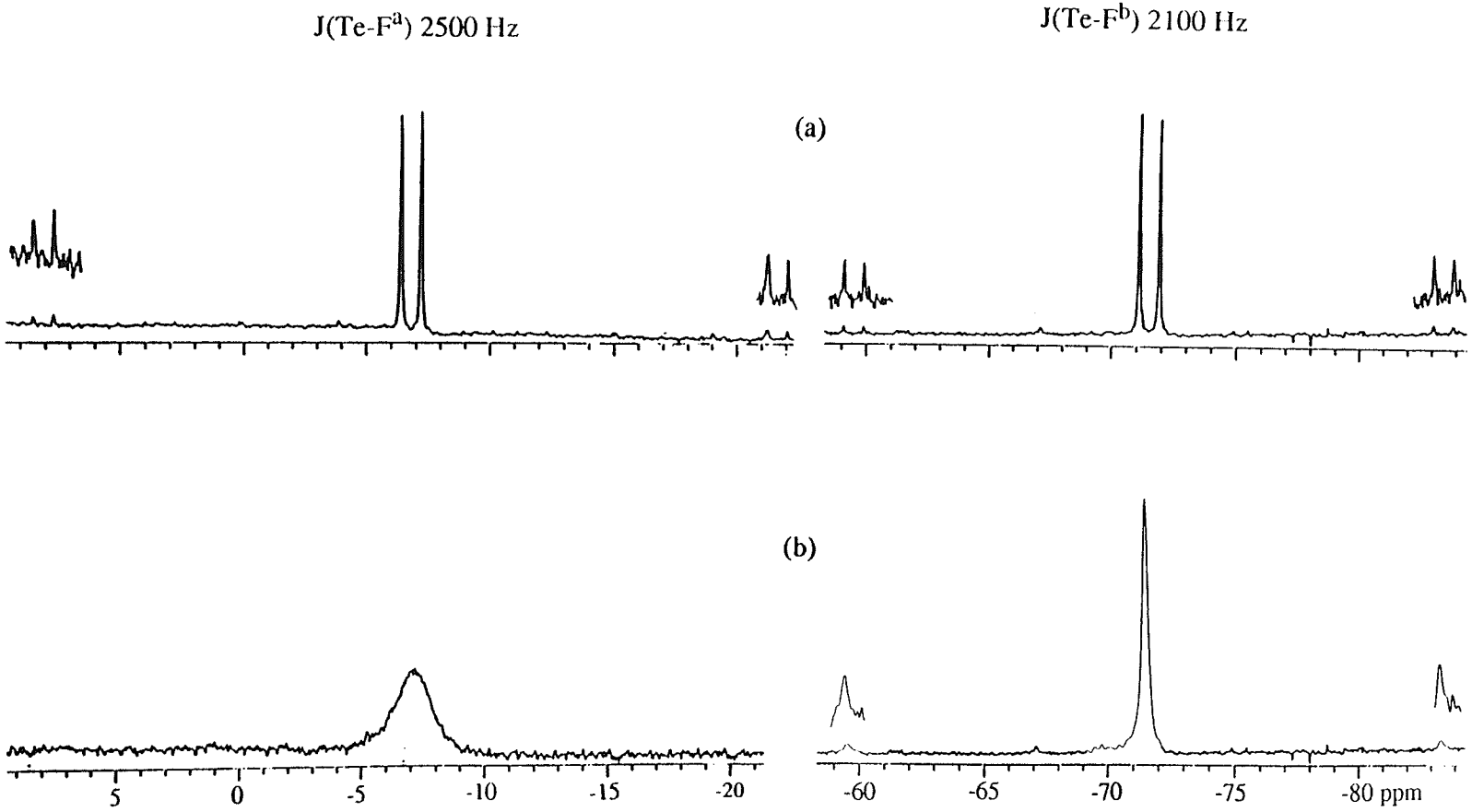
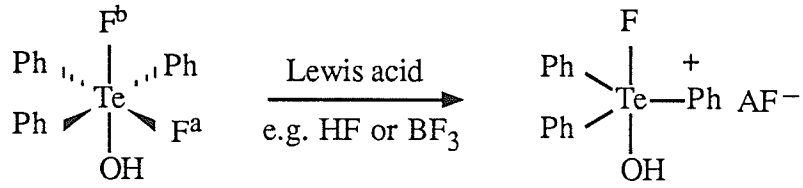


Figure 47. The 84.7 MHz ^{19}F NMR spectra of *cis*-F_2TePh_3OH in CD_2Cl_2 at room temperature: (a) in the absence of fluorine exchange (fresh solution) (b) with exchange, showing loss of F^a-F^b and Te-F^a couplings but retention of Te-F^b coupling (solution has stood in glass tube for several days).

This behavior resembles that observed in the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ and *cis*-F_2TePh_3Cl-Ph_3TeFCl^+ systems and thus a similar mechanism may be proposed:

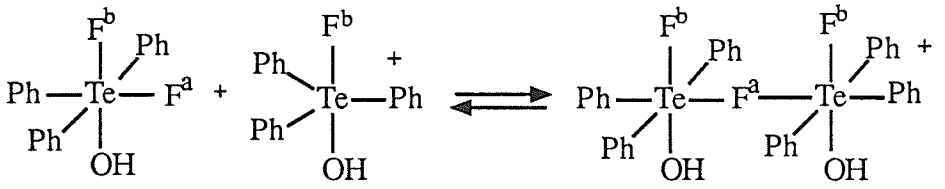
1. The initial formation of the five-coordinate cation Ph_3TeFOH^+ in the presence of Lewis acid impurities, as described in equation [70]:



[70]

Although the Ph_3TeFOH^+ cation could not be observed directly, a Lewis acid, such as HF, or silicon or boron fluorides, may be produced, which then reacts with *cis*-F_2TePh_3OH to give the cation. Furthermore, the fact that the treatment of an exchanging sample of *cis*-F_2TePh_3OH with NaF stopped all fluorine exchange and regenerated *cis*-F_2TePh_3OH indicates the presence of a five-coordinate Te(VI) cation, which is converted to a stable six-coordinate Te(VI) species by the addition of NaF.

2. As the five-coordinate Te(VI) cation, Ph_3TeFOH^+, is formed, rapid exchange occurs between five- and six-coordinate Te(VI) species, involving a fluorine-bridged intermediate in which F^a occupies the bridging position, as described in equation [71]:



[71]

F^a-bridged intermediate

D. Conclusion

Stereoselective Te-F^a bond-cleavage was observed in octahedral fluorotriphenyl-tellurium(VI) compounds of the type, *mer*-$Ph_3TeF^aF^bX$ (X = F, Cl, or OH). For *mer*-Ph_3TeF_3 and *cis*-F_2TePh_3Cl, on addition of the corresponding five-coordinate Te(VI) species it was possible to demonstrate by the DNMR technique that the exchange involves the cleavage of Te-F^a bonds.

The observation of stereoselective fluorine exchange was made possible by the presence of three phenyl groups in a *mer*-arrangement which prevents intramolecular scrambling of the fluorine ligands.

The stereoselective exchange of F^a ligands is favoured by the following factors:

1. Significantly longer Te-F^a bonds compared to Te-F^b bonds, as determined by X-ray crystallography for *mer*-Ph_3TeF_3 (22) and *cis*-F_2TePh_3OH (60).

2. A F^a-bridged intermediate which minimizes the steric interaction among six phenyl substituents.

RESULTS AND DISCUSSION

B. fluorophenyltin(IV) compounds

I. INTRODUCTION

Tin can exist in two oxidation states, tin(II) and tin(IV), and has been shown to form a wide variety of structural types in which the tin atom is two-, three-, four-, five-, six-, seven-, and eight-coordinated in neutral, cationic, and anionic species. Intermolecular association gives dimers and oligomers in one-, two-, and three-dimensional polymeric arrays (128-131). Examples of seven-coordinate tin(IV) complexes are $MeSn(NO_3)_3$ (129) and $R_2Sn(NCS)_2$·terpyridyl (130). For the former, X-ray analysis (129) revealed that the molecules have approximately pentagonal bipyramidal geometry.

The ability of tin(IV) to form six-coordinate complexes has been known for some time. The octahedral arrangement in the hexachlorostannate anion ($SnCl_6^{2-}$) was confirmed by X-ray studies over 60 years ago (132). Since that time studies have shown that the tin(IV) tetrahalides coordinate with an enormous range of monodentate ligands to form six-coordinate adducts of the type $SnX_4 \cdot L_2$ (128,133,134). There is a general tendency that the acceptor strength of tin(IV) decreases when halogens are replaced by less electronegative organic groups (135). However, six-coordination in organotin(IV) halides is still widely observed for mono- and di-organotin(IV) halides, though less widely for triorganotin(IV) halides. Most of the known organoammonium stannate salts are bromo/chloro/iodo or mixed-halo species, *e.g.* $[C_5H_5NH_2]_2[Me_2SnCl_4]$ (136); there are very few reports of six-coordinate halogenoorganostannates containing fluorine(s) that exist in the solid state as discrete units, *i.e.* $[R_nSnX_{6-n}]$.

In this section, the preparations and NMR (^{19}F, ^{13}C, and ^{119}Sn) studies of some fluorophenylstannate(IV) complexes will be discussed. In particular, evidence will be presented for the existence of six-coordinate fluorophenylstannates(IV). Fluorophenylstannate(IV) anions are isoelectronic with the corresponding, electrically neutral fluorophenyltellurium(VI) compounds, and thus determination of their structures

in solution by NMR spectroscopy is of particular interest with respect to organo-tellurium(VI) chemistry.

Before discussing the results of this work, it is appropriate to introduce the general aspects of tin NMR spectroscopy. Elemental tin contains ten naturally occurring isotopes, and only three of these have non-zero nuclear magnetic moments, *i.e.* ^{115}Sn, ^{117}Sn, and ^{119}Sn (Table 15) (137). Each of the three magnetic tin isotopes has a nuclear spin of 1/2 and all these isotopes have approximately equal nuclear magnetic moments. However, tin-NMR investigations are generally measured for ^{119}Sn nuclei because of the high natural abundance and the greater sensitivity to NMR detection (see Table 15), although there is no problem observing all three isotopes of tin-satellites in ^{19}F NMR spectra. The application of ^{119}Sn NMR spectroscopy to the study of the structure of organotin(IV) derivatives has been developed, and one of its most notable features is the dependence of ^{119}Sn chemical shifts on the coordination number of tin; excellent surveys of ^{119}Sn NMR spectroscopy are available in the literature (138-142). The significant shift of the tin-119 resonances to high field in going from tetrahedral to trigonal bipyramidal or octahedral symmetry is particularly convenient for studying even weak donor-acceptor interactions in solution. There are, of course, other factors to be considered besides the coordination number, *e.g.* substituent effects. However, the detailed discussion is beyond the scope of this thesis and further information may be obtained from the literature (137). It should be noted that published data have been concerned with organotin species containing mainly neutral oxygen or nitrogen donors, there being very few compounds involving fluorine.

TABLE 15

Nuclear magnetic moments and natural abundance of tin isotopes (137)

Isotope	Nuclear magnetic moment, μ (nuclear magnetons)	Natural abundance (%)	Relative NMR* sensitivity
^{112}Sn	-	1.01	-
^{114}Sn	-	0.68	-
^{115}Sn	-0.9132	0.35	3.5×10^{-2}
^{116}Sn	-	14.28	-
^{117}Sn	-0.9949	7.61	4.5×10^{-2}
^{118}Sn	-	23.84	-
^{119}Sn	-1.0409	8.58	5.2×10^{-2}
^{120}Sn	-	32.75	-
^{122}Sn	-	4.74	-
^{124}Sn	-	6.01	-

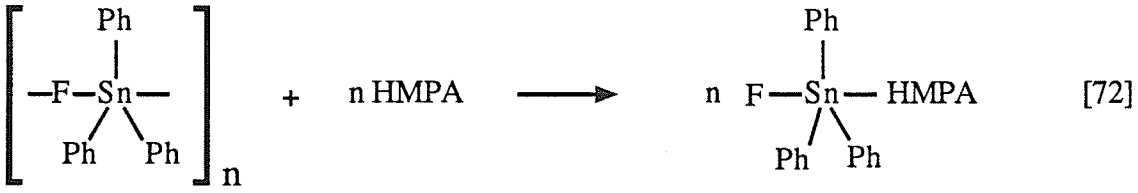
* Relative NMR sensitivity to that of ^{1}H.

The structures of a series of fluorophenylstannate(IV) complexes will be discussed with reference to NMR spectroscopy. As discussed above, the appearance of tin-coupled satellites in the ^{19}F NMR spectra has been very useful in assigning structures of tin compounds containing fluorine(s). In particular, direct isomeric identification is possible on the basis of Sn-F chemical shifts and coupling constant values.

II. FLUOROTRIPHENYLSTANNANE(IV), Ph_3SnF

A. Reaction with Lewis bases

Synthesis and I.R. studies of fluorotriphenylstannane(IV), Ph_3SnF, have been reported in the literature (50,143-145). However, because of its insolubility due to its polymeric linear trigonal bipyramidal bridged-fluorine structure, like that of trimethyltin fluoride which was revealed by an X-ray study (146), solution NMR studies have not been carried out in common organic solvents. Holmes and his co-workers (47) have reported ^1H NMR spectra of Ph_3SnF in hexamethylphosphoramide (HMPA), for which the powerful donor molecule HMPA caused depolymerization by the reaction [72]:



[72]

i.e. the neutral adduct, $Ph_3SnF{\cdot}HMPA$, is a monomeric five-coordinate structure with a base molecule occupying an axial position *trans* to F.

The same group has also produced seven anions in salts of the type $R_4N^+Ph_3SnX_2^-$ (X = halide or mixed-halide) which, they suggested, have a trigonal bipyramidal structure with phenyl substituents in the equatorial plane, on the basis of ^1H NMR spectroscopy.

We have repeated the synthesis of three of these (see below) in order to examine their ^{19}F, ^{119}Sn, and ^{13}C NMR spectra. In particular, the reaction of $Ph_3SnF_2^-$ with catechol suggests a possible formation of six-coordination in tin(IV), as evidenced by ^{119}Sn NMR spectroscopy, and it should be recalled that examples of six-coordinate complexes of Ph_3SnF with Lewis bases could not be found in the literature.

Fluorotriphenylstannane(IV), Ph_3SnF, was most conveniently prepared according to the method of Holmes (47), and identified by melting point (50,143), mass spectrometry, and chemical reactions with various Lewis bases. Like many other organotin(IV) fluorides, Ph_3SnF decomposes at high temperature without melting; *e.g.* Me_3SnF >360 °C (146) and Me_2SnF_2 ~400 °C (147). Characterization of Ph_3SnF by mass spectrometry was relatively simple because of the ten tin isotopes of the fragment ions (Table 15); primary cleavage of Sn-C and Sn-F bonds occurred before other fragmentation reactions.

1. Ph_3SnF with HMPA or DMSO

Ph_3SnF neither dissolves appreciably in, nor reacts with, the following solvents or molecules: CH_3CN, DMF, pyridine, bpy, fbpy, pyridine-N-oxide, triphenylphosphorus oxide (TPPO). An equimolar mixture of Ph_3SnF and HMPA, prepared by the method of Holmes (47), did not give any detectable resonance in the ^{19}F and ^{119}Sn NMR spectra. Only the treatment of Ph_3SnF with a large excess (~5 fold) of a strong donor molecule such

as HMPA or DMSO produced satisfactory NMR results. The ^{19}F and ^{119}Sn NMR spectra of the neutral HMPA adduct, $Ph_3SnF{\cdot}HMPA$, are shown in Figures 48 and 49, respectively and the NMR data are presented in Table 16.

2. Ph_3SnF with $POCl_3$

The reaction of Ph_3SnF with $POCl_3$ resulted in successive fluorinations of $POCl_3$, as described in equation [73].

$$Ph_3SnF + 2\,POCl_3 \xrightarrow{CH_2Cl_2} P(O)FCl_2 + P(O)F_2Cl + Ph_3SnCl \qquad [73]$$

Some hydrolysis products, such as $P(O)F_2(OH)$ and $P(O)F(OH)_2$, were also produced in the reaction. The formation of Ph_3SnCl was detected by its ^{119}Sn NMR spectrum, *i.e.* a singlet ^{119}Sn resonance at -44 ppm (lit. value (137); -44.7 ppm). When the dichloromethane solution stood in a glass reaction tube for 7 more days, further hydrolysis occurred to give the $P(O)F(OH)_2$ species only, as confirmed by ^{19}F NMR spectroscopy. The ^{19}F NMR data of all the phosphorus compounds agree well with the literature values (61). The reaction of $Ph_3SnF_2^-$ with $POCl_3$ also gave the same products, as confirmed by ^{19}F NMR spectroscopy.

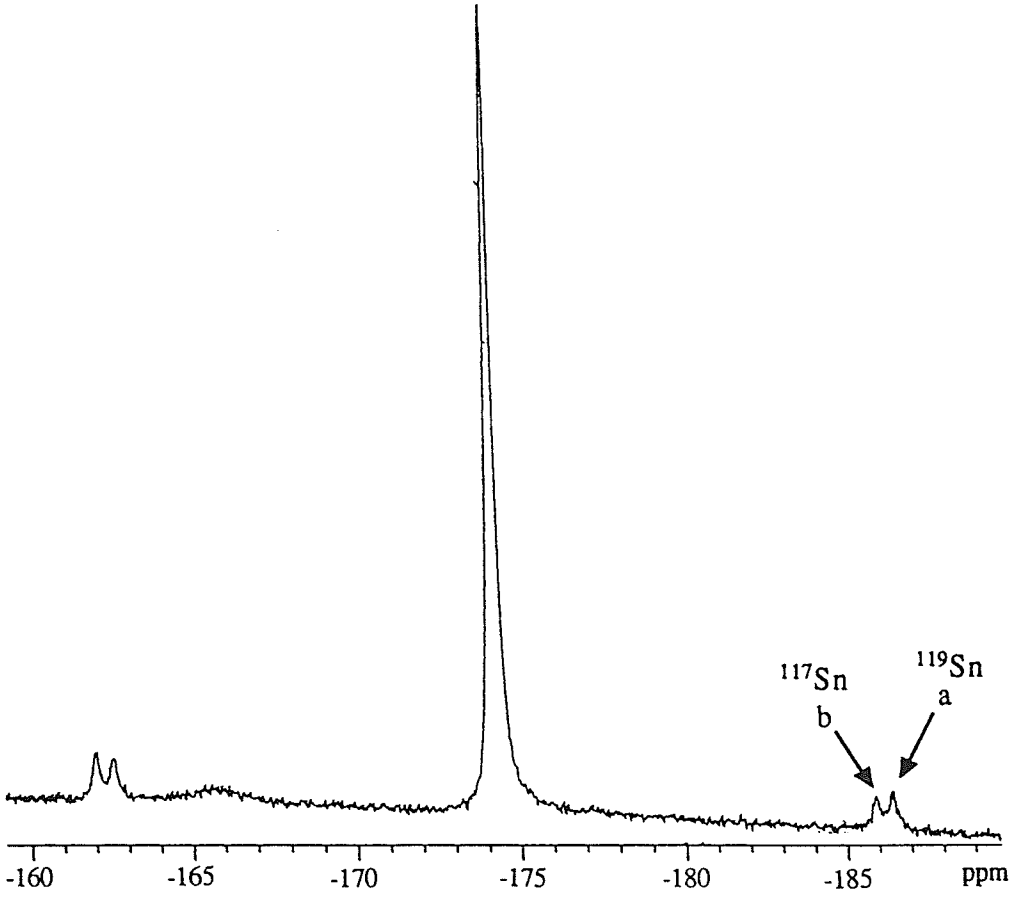


Figure 48. The ^{19}F NMR spectrum of Ph_3SnF in excess HMPA (~5 fold); in DMSO-d_6. $^{119/117}Sn$-coupled satellites are shown (marked with a and b, respectively).

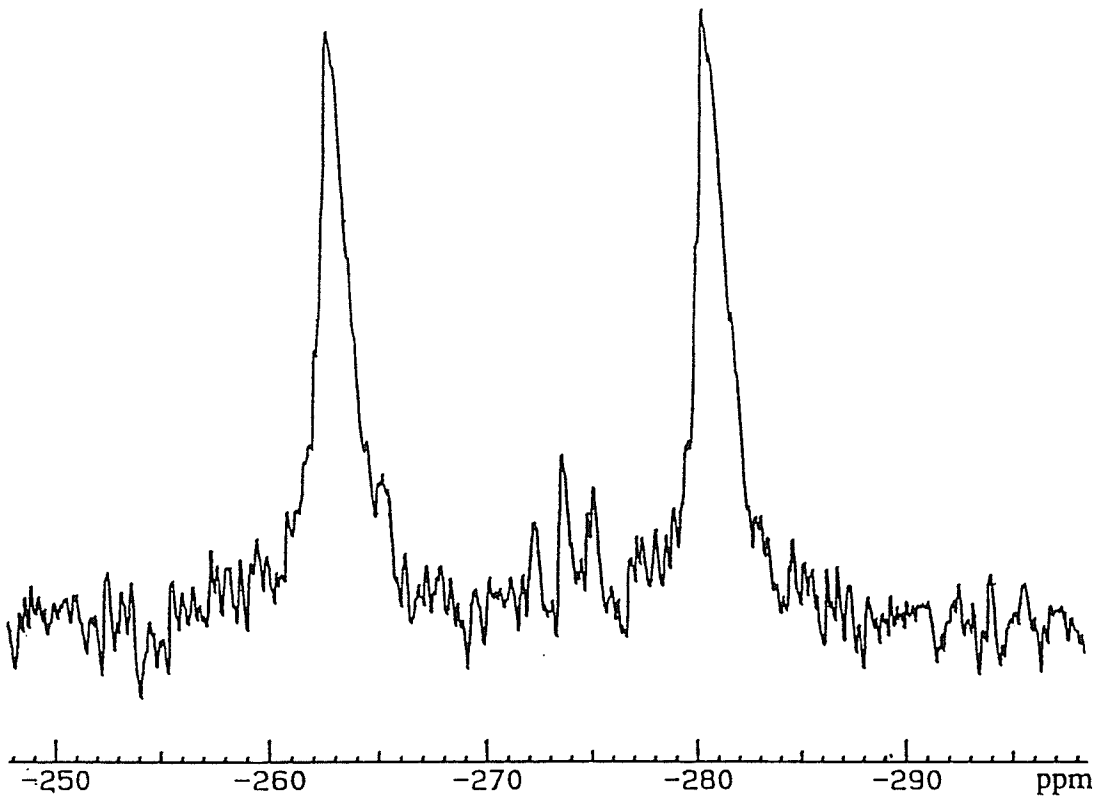


Figure 49. The ^{119}Sn NMR spectrum of Ph_3SnF in excess HMPA in $CDCl_3$.

TABLE 16

The ^{19}F and ^{119}Sn NMR data of five-coordinate neutral and anionic adducts of Ph_3SnF

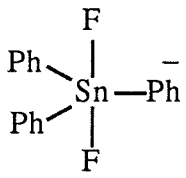
Compound	δF [ppm]	$\delta^{119}Sn$ [ppm]	$J(^{119}Sn\text{-}F)$[a] [Hz]	Solvent
$Ph_3SnF{\cdot}HMPA$	-174.2	-272	2040	$CDCl_3$
$Ph_3SnF{\cdot}DMSO$	-178.2	-271	2090	DMSO-d_6
$Ph_3SnF_2^-$[b]	-160.0	-345	1950	CD_2Cl_2
Ph_3SnFCl^- [c]	-159.0	-293	1916	$CDCl_3$

[a] The values of $J(^{117}Sn\text{-}F)$ are not given because the ratio of $^nJ(^{119}Sn\text{-}F)/^nJ(^{117}Sn\text{-}F)$ is equal to that of $\gamma(^{119}Sn)/\gamma(^{117}Sn) = 1.0465$.

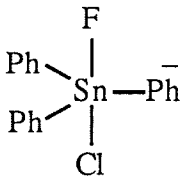
[b] Counter ion is Bu_4N^+. [c] Counter ion is Et_4N^+.

III. FLUOROPHENYLSTANNATE(1-) ANIONS; $Ph_3SnF_2^-$ and Ph_3SnFCl^-

Previous ^1H NMR studies of these complexes have shown them to have the structures illustrated in Figure 50 (47):



difluorotriphenylstannate(1-)



fluorochlorotriphenylstannate(1-)

Figure 50. Trigonal bipyramidal structures of $Ph_3SnF_2^-$ and Ph_3SnFCl^-(47). (counter ions are Et_4N^+).

Further evidence from our NMR results (^{19}F, ^{119}Sn, and ^{13}C) of these complexes confirmed the trigonal bipyramidal structures originally suggested by Holmes (47). Singlet ^{19}F with tin-coupled satellites and triplet ^{119}Sn resonances, shown in Figures 51 and 52, respectively, indicate that the two fluorines in $Ph_3SnF_2^-$ are equivalent. Further evidence for the trigonal bipyramidal geometry of $Ph_3SnF_2^-$, in which three phenyl substituents occupy the equatorial plane, was obtained from ^{13}C NMR studies. The ^{13}C NMR spectrum is given in Figure 53 and NMR data are given in Table 17.

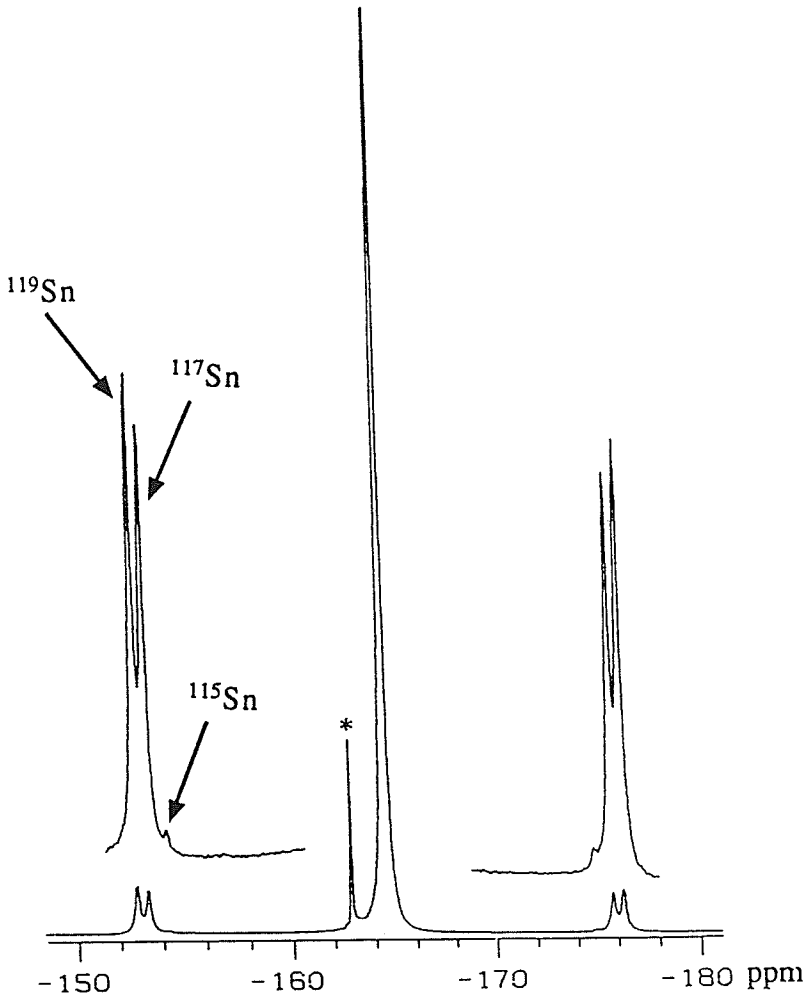


Figure 51. The ^{19}F NMR spectrum of $Bu_4N^+Ph_3SnF_2^-$ in $CDCl_3$. The reference (C_6F_6) peak is marked with asterisk. All three Sn-satellites are shown.

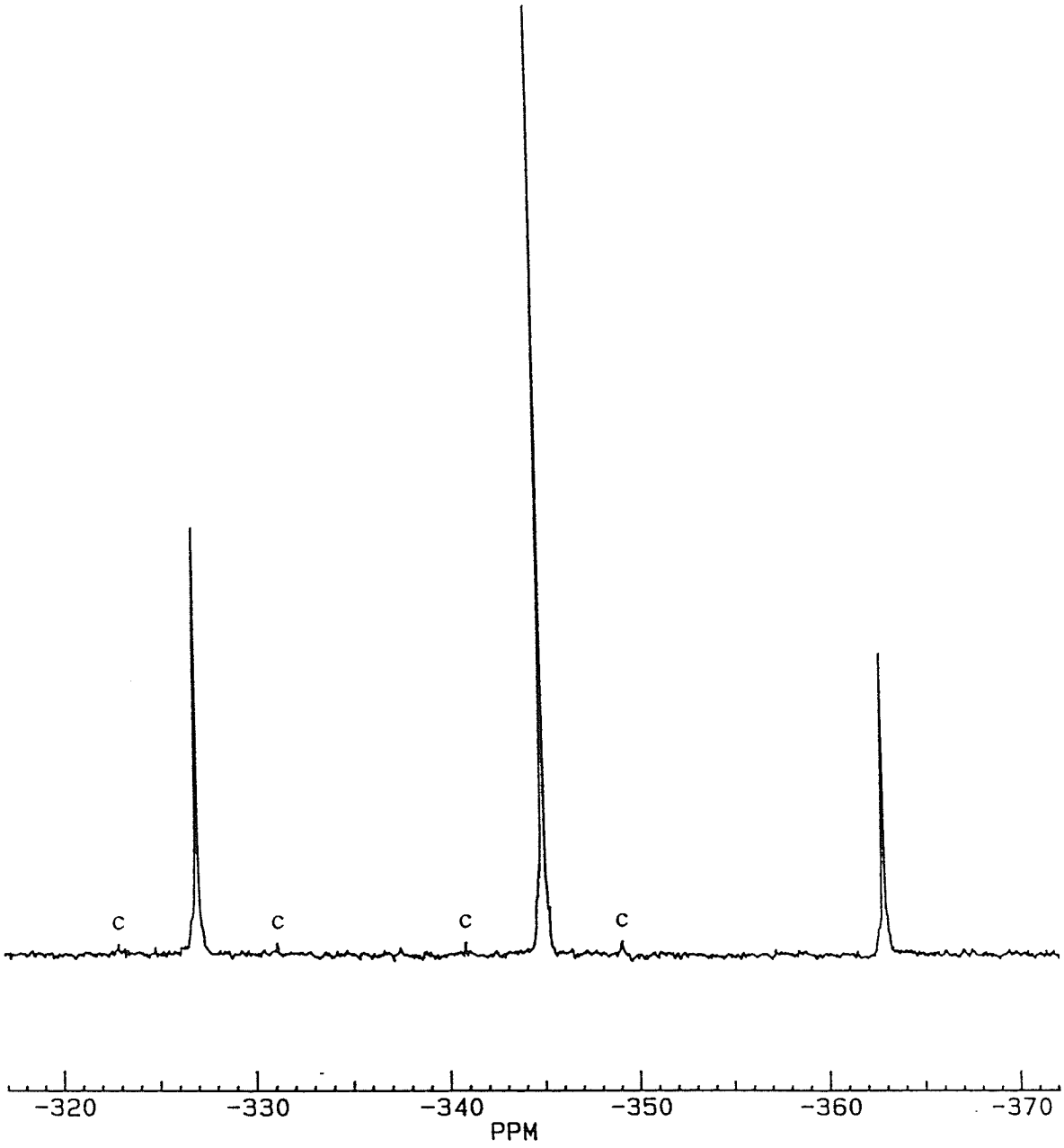


Figure 52. The ^{119}Sn NMR spectrum of $Bu_4N^+Ph_3SnF_2^-$ in $CDCl_3$: ^{13}C-satellites are marked with c.

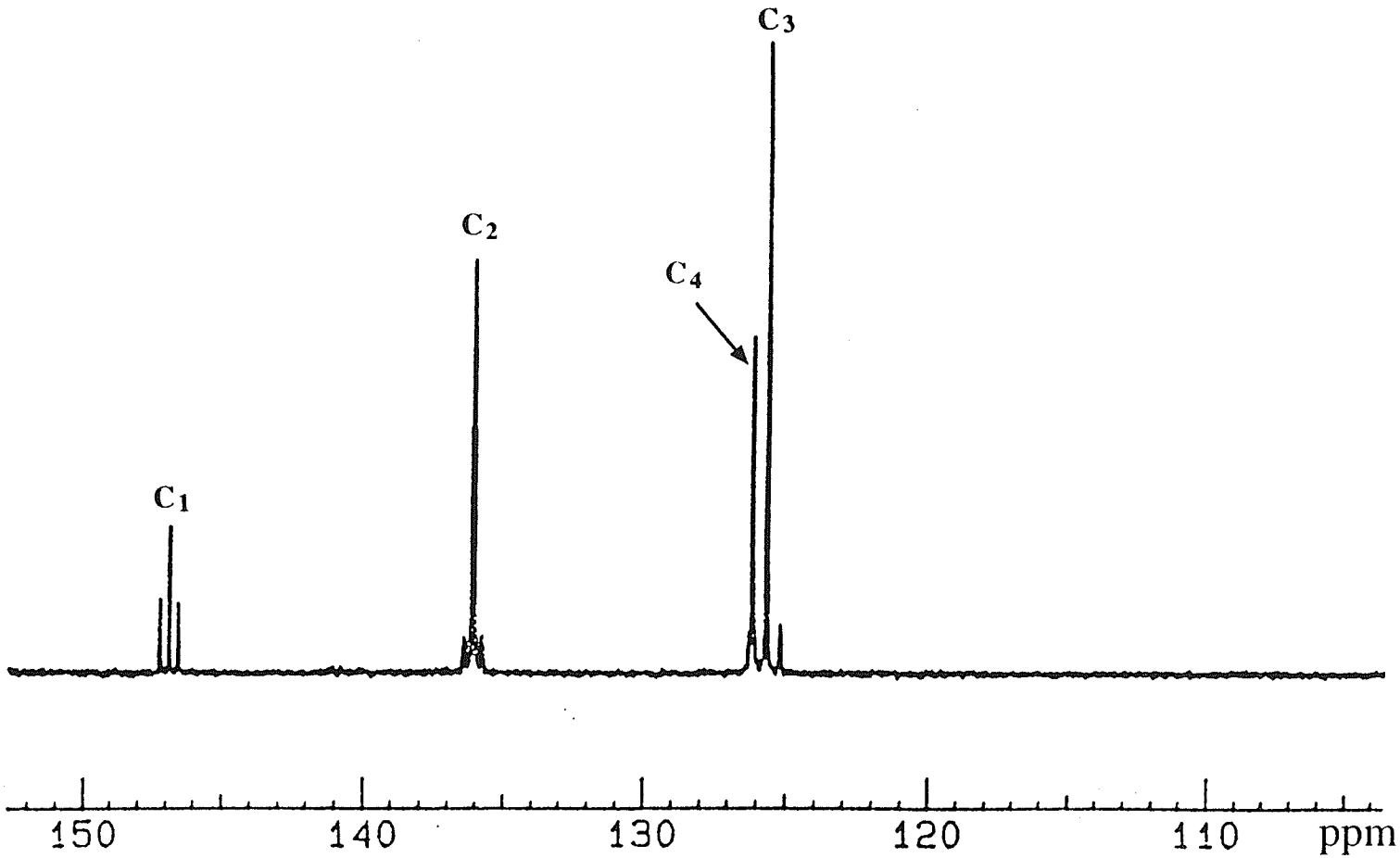
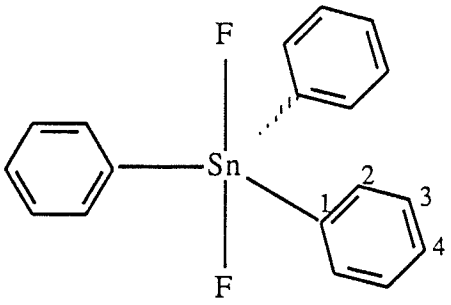


Figure 53. The $^{13}C\{^1H\}$ spectrum of $Ph_3SnF_2^-$ in $CDCl_3$ (120 mg/mL). Peaks due to Bu_4N^+ are not included.



The structure of $Ph_3SnF_2^-$ with atom numbering scheme:
all three phenyl groups are equivalent.

TABLE 17

Carbon-13 NMR data of $Bu_4N^+Ph_3SnF_2^-$ in $CDCl_3$ [a]

	C_1	C_2	C_3	C_4
δC [ppm]	146.86	136.07	125.62	126.13
JCF [Hz]	24.90	3.02	2.0	-
JCSn [Hz]	920[b]	47.54	70.94	15.09

a ^{13}C NMR data for the counter ion Bu_4N^+ are not included.

b The value of $J(C_1Sn)$ obtained from ^{119}Sn NMR spectrum was ~920 Hz.

The equivalence of three phenyl substituents was demonstrated by the appearance of four sets of peaks corresponding to C_1 to C_4, each of which was a triplet except for the para carbon (C_4), which was not resolved, probably due to very small coupling.

Assignments for the ipso (C_1) and para (C_4) resonances are made on the basis of peak intensities. The ipso carbon has the smallest intensity because it lacks the NOE effect. The para carbon resonances have weaker intensities than those of ortho (C_2) and meta (C_3) resonances.

Assignments for C_2 and C_3 are tentatively made by comparison with the literature data. Holecek *et al.* (148) reported carbon-13 NMR data for 24 complexes of four- and five-coordinate triphenyltin(IV), two of them being five-coordinate anionic complexes. They assigned the chemical shifts of C_2 and C_3 on the basis of proton-coupled spectra. All 24 complexes revealed that $^3J(^{119}Sn\text{-}C)$ of meta carbons (C_3) is significantly larger than $^2J(^{119}Sn\text{-}C)$ of ortho carbons (C_2). For comparison, ^{13}C NMR data of $Ph_3SnCl_2^-$ and $Ph_3SnBr_2^-$ are given in Table 18.

A recent X-ray structural determination by Tari and Secco[2] gave conclusive evidence for the trigonal bipyramidal geometry of $Bu_4N^+Ph_3SnF_2^-$ in the solid state.

Holmes *et al.* (47) reported the formation of tetraalkylammonium(1+) fluorochlorotriphenylstannate(1-), $Et_4N^+Ph_3SnFCl^-$, from Ph_3SnF and Et_4NCl (1:1 molar ratio) in CH_3CN, and identified it in solution by ^1H NMR spectroscopy. In this reaction, only 40% of Ph_3SnF used reacted with Et_4NCl to give $Et_4N^+Ph_3SnFCl^-$ and the rest remained insoluble even after prolonged stirring of the reaction mixture. Attempts to isolate Ph_3SnFCl^- by recrystallization resulted in the formation of Ph_3SnF.

---

[2] L. Tari and A. S. Secco. Unpublished results.

TABLE 18

Carbon-13 NMR chemical shifts ($\delta^{13}C$) and coupling constants ($J^{119}Sn\text{-}C$) of $R_4N^+Ph_3SnX_2^-$ (X = F, Cl, and Br) (148)

	$\delta(^{13}C)$ of phenyl groups of Ph_3Sn [ppm]			
Compound	*ipso*	*ortho*	*meta*	*para*
$Ph_3SnF_2^-$ 1[a]	146.86	136.07	125.62	126.13
$Ph_3SnCl_2^-$ 2[b]	147.49	135.84	126.68	127.22
$Ph_3SnBr_2^-$ 3[b]	144.51	136.13	128.33	128.92
	^nJ ($^{119}Sn\text{-}^{13}C$) [Hz]			
Compound	*n = 1*	*n = 2*	*n = 3*	*n = 4*
$Ph_3SnF_2^-$ 1[a]	920	47.5	70.9	15.1
$Ph_3SnCl_2^-$ 2[b]	847	50.0	73.2	14.6
$Ph_3SnBr_2^-$ 3[b]	798	47.6	70.8	16.0

[a] This work (counter ion is Bu_4N^+).

[b] Counter ions are Et_4N^+.

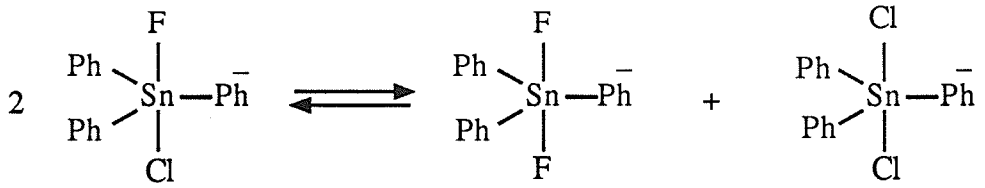
I have confirmed the ^{1}H NMR result for $Et_4N^+Ph_3SnFCl^-$, but found rapid fluorine exchange when the 1:1 mixture of Ph_3SnF and Cl^-, prepared according to the method of Holmes, was examined by ^{19}F and ^{119}Sn NMR spectroscopy.

The ^{19}F NMR spectrum of the solution only exhibited a very broad peak without ^{119}Sn-coupled satellites. Furthermore, no resonance was detected in the ^{119}Sn NMR spectrum. It required a 20 fold excess of Cl^- to stop exchange in Ph_3SnFCl^-, whose solution in $CDCl_3$ showed a singlet ^{19}F with $^{117/119}Sn$-satellites and a doublet ^{119}Sn NMR resonance (the ^{19}F and ^{119}Sn NMR data of non-exchanging Ph_3SnFCl^- are given in Table 16 and the spectra will be presented shortly). Presumably, excess Cl^- converts any remaining four-coordinate tin species in solution to five-coordinate species, thereby preventing fluorine exchange via an intermediate, such as $ClPh_3Sn\text{-}F\text{-}SnPh_3F$.

Similarly, Ph_3SnF required a five-fold excess of a base, such as HMPA or DMSO, to form stable adducts, i.e. $Ph_3SnF{\cdot}HMPA$ or $Ph_3SnF{\cdot}DMSO$, as discussed in the previous section II-A-1.

Unlike Ph_3SnFCl^- and $Ph_3SnF{\cdot}L$ (L = HMPA, DMSO), $Ph_3SnF_2^-$ does not show any fluorine exchange, presumably because $Ph_3SnF_2^-$ is stable and can be isolated as the $Bu_4N^+Ph_3SnF_2^-$ salt. Therefore, any four-coordinate tin species, particularly the insoluble Ph_3SnF, can be completely eliminated by recrystallization.

When excess Cl^- was added to Ph_3SnFCl^- to stop exchange, a redistribution reaction, as shown in equation [74], was detected by ^{19}F and ^{119}Sn NMR spectroscopy.



[74]

Figure 54 illustrates the ^{19}F NMR spectrum of the mixture of Ph_3SnFCl^- and $Ph_3SnF_2^-$ resulting from the redistribution reaction. Most crystals of $Ph_3SnF_2^-$ were removed from the mixture by recrystallization, leaving mainly Ph_3SnFCl^- and $Ph_3SnCl_2^-$ in solution, as shown by the ^{119}Sn NMR spectrum in Figure 55. Attempts to produce a six-coordinate complex $Ph_3SnF_2Cl^{2-}$ by the reaction of $Ph_3SnF_2^-$ with excess Cl^- resulted in a partial substitution reaction to give Ph_3SnFCl^- according to equation [75].

$$Ph_3SnF_2^- + Cl^- \rightleftharpoons Ph_3SnFCl^- + F^- \qquad [75]$$

The ^{119}Sn NMR spectrum of this mixture revealed the presence of Ph_3SnFCl^- as well as $Ph_3SnF_2^-$, as shown in Figure 56.

So far, the formation of five-coordinate neutral and anionic complexes from Ph_3SnF, and their structural properties as evidenced by NMR, have been discussed. Except for $Bu_4N^+Ph_3SnF_2^-$, these complexes are too unstable to be isolated as solids. No evidence has been found for the formation of six-coordinate stannates in solution. As discussed above, addition of excess Cl^- in an effort to produce six-coordinate species resulted in the redistribution reaction. Various fluorides (see experimental section) were used in attempts to synthesize the six-coordinate dianion, $Ph_3SnF_3^{2-}$, using methods similar to those for the synthesis of the five-coordinate complexes from the same reagents. However, NMR examination of the products did not confirm the presence of six-coordinate complexes. Even when a large excess of fluoride ion is added to Ph_3SnF, a second fluoride ion is not added to give six-coordinate anion, $Ph_3SnF_3^{2-}$, the product only corresponding to $Ph_3SnF_2^-$.

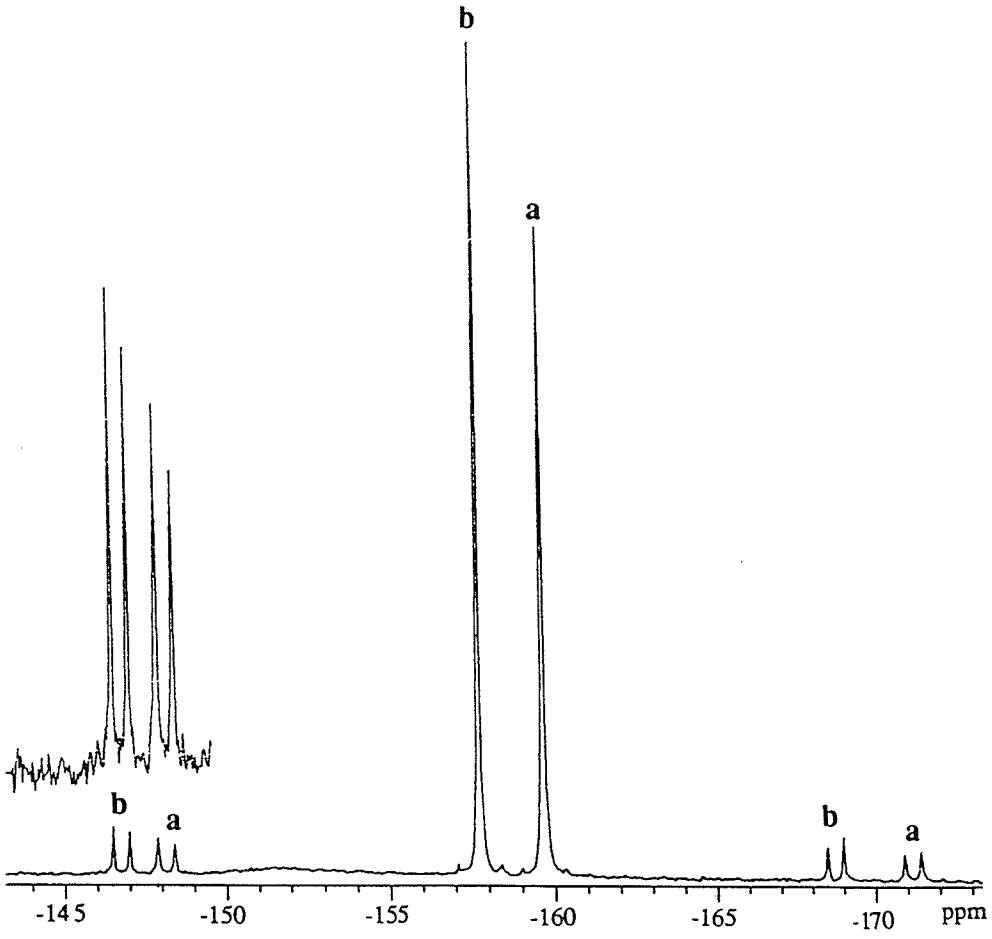


Figure 54. The ^{19}F NMR spectrum of $Ph_3SnF_2^-$ (peaks a) and Ph_3SnFCl^- (peaks b) in $CDCl_3$ ($Ph_3SnCl_2^-$, resulting from a redistribution reaction, is detected by its ^{119}Sn NMR spectrum); see text, for details.

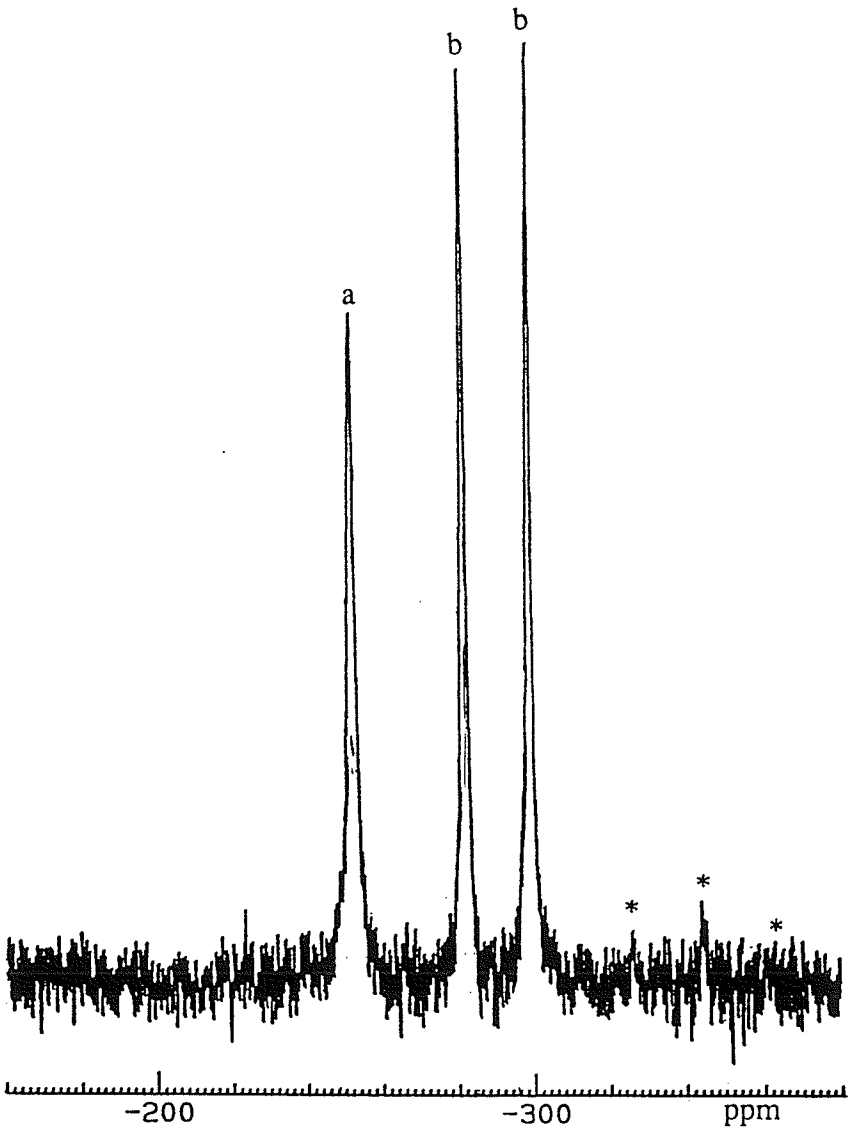


Figure 55. The ^{119}Sn NMR spectrum of a mixture of $Ph_3SnCl_2^-$ (singlet marked with a), Ph_3SnFCl^- (doublet marked with b), and small amounts of $Ph_3SnF_2^-$ resulting from a redistribution reaction (most crystals of $Ph_3SnF_2^-$ were removed at this stage). Peaks due to $Ph_3SnF_2^-$ (triplet) are marked with c.

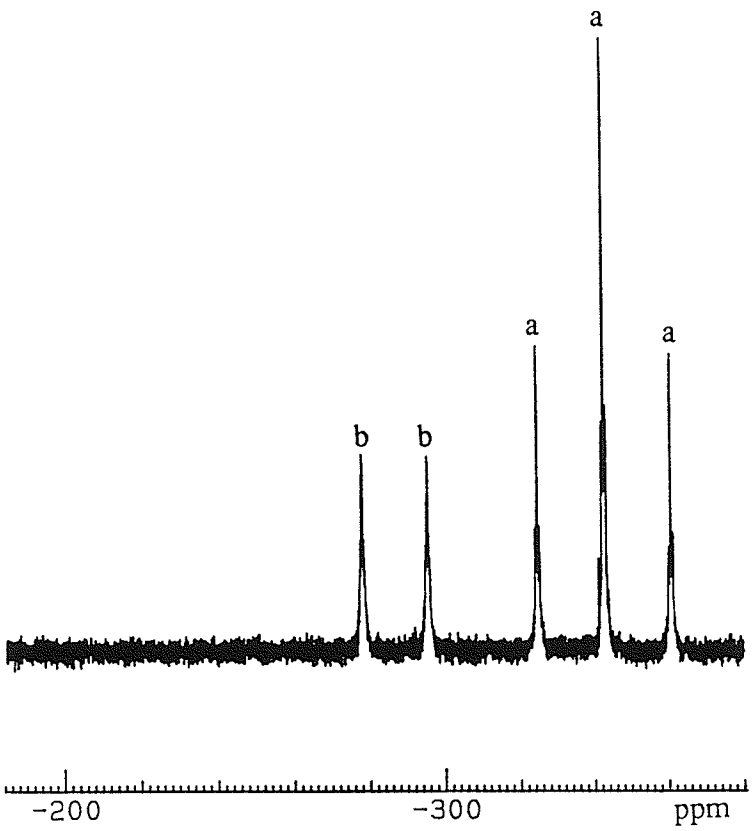


Figure 56. The ^{119}Sn NMR spectrum of a mixture of $Ph_3SnF_2^-$ (triplet marked with a) and Ph_3SnFCl^- (doublet marked with b) in CD_2Cl_2 resulting from a redistribution reaction.

In contrast to Ph_3SnF, many other stannanes readily form six-coordinate species by coordination of two donor molecules (see the previous section I). Indeed SnF_4 reacts with some nucleophiles (*e.g.* pyridine) to produce only six-coordinate complexes; *i.e.* it has a reactivity quite different from that of Ph_3SnF, which produces only five-coordinate compounds upon treatment with an excess of the nucleophile. The reluctance of Ph_3SnF and $Ph_3SnF_2^-$ to form six-coordinate compounds is not due to an intrinsically weak Lewis acidity at tin, or the presence of bulky phenyl groups.

Studies have shown that the acceptor strength of tin declines when the halogen in SnX_4 is replaced by an organic group (135). Reported examples of six-coordinate tin complexes with bulky organic substituents are $Ph_3SnCl_3^{2-}$ (149) and n-$BuSnCl_3$·bpy (150). However, the elemental analysis reported for $Ph_3SnCl_3^{2-}$ (149) is in closer agreement with that calculated for $Ph_3SnCl_2^-$; Nicholson *et al.* (149) also reported ^{13}C NMR spectra of several five-coordinate tin complexes including $Ph_3SnCl_2^-$, but could not obtain a ^{13}C NMR spectrum, characteristic of six-coordinate $Ph_3SnCl_3^{2-}$.

Similarly, the formation of six-coordinate $Ph_3SnF_3^{2-}$ was not detected by NMR spectroscopy. The addition of various fluorides (Bu_4NF, KF/crown-ether, K^+FHF^-, CsF, and NaF) to the solution of recrystallized $Bu_4N^+Ph_3SnF_2^-$ in non-coordinating solvents resulted in ^{19}F NMR spectra that showed only a singlet ^{19}F resonance with tin-coupled satellites due to equivalent fluorines and which did not exhibit a ^{19}F NMR resonance characteristic of *mer*-$Ph_3SnF_3^{2-}$. However, there were large differences in ^{19}F chemical shifts and ^{119}Sn-F coupling constants when additional fluoride was added. It is hard to imagine that solvent systems could account for such differences without specific interactions with $Ph_3SnF_2^-$.

Furthermore, the fluorine-19 NMR spectra of $Ph_3SnF_2^-$ in both inert and donor solvents have been examined, and the data are given in Table 19.

TABLE 19

The ^{19}F NMR data of $Bu_4N^+Ph_3SnF_2^-$ in inert and donor solvents

Solvent	δF in ppm	J(^{119}Sn-F) in Hz
$CDCl_3$	-160.6	1944
CD_2Cl_2	-160.0	1950
CD_3CN	-160.8	2000
DMSO-d_6	-163.3	2023
HMPA in CD_3CN	-164.0	2010
HMPA in CD_2Cl_2	-163.8	2000
HMPA in DMSO-d_6	-167.0	2040

The values obtained in non-polar solvents, *e.g.* CD_2Cl_2, were significantly different from the values obtained in polar solvents, *e.g.* DMSO-d_6. This suggests that there might be an interaction between solvent molecules and $Ph_3SnF_2^-$ in polar-coordinating solvents. Base solvent can occupy the sixth site of the octahedron and it could compete with the incoming fluoride ligand. This may not be unreasonable because in fact octahedral fluorostannate complexes of the type, $SnF_5 \cdot B^-$ (B represents various solvents or bases), are known and their structures were examined by ^{19}F NMR spectroscopy (134). The NMR study confirmed the presence of a $SnF_5 \cdot B^-$ species, indicating that a molecule of solvent (B) occupied the sixth position in the octahedron.

In the following section, some NMR evidence to support the formation of six-coordinate fluorophenylstannates and their octahedral symmetry will be discussed.

IV. OCTAHEDRAL FLUOROPHENYLSTANNATES

A. Pentafluorophenylstannate(2-), $PhSnF_5^{2-}$

A six-coordinate pentafluorophenylstannate(2-), $PhSnF_5^{2-}$, was formed by the reaction of Ph_2SnF_2 with excess fluoride, or Ph_2SnCl_2 and $Ph_3SnF_2^-$ with excess fluoride. $Ph_3SnF_2^-$ in the latter method was used as fluorinating agent.

The starting compound Ph_2SnF_2 was prepared by a similar method to that used for Ph_3SnF and was identified by m.p.(62) and mass spectrometry. Like the other organotin(IV) fluorides, Ph_2SnF_2 is insoluble in common organic solvents and it decomposes at ~350 °C. The high decomposition temperature, low volatility, and low solubility of Ph_2SnF_2 are indicative of a polymeric structure, like that of Ph_3SnF. For

compounds of the general formula R_2SnX_2, where X has donor properties, the possibility of tin achieving coordination number six by autocomplex polymer formation arises, as shown by the X-ray analysis of Me_2SnF_2 (147); *i.e.* in Ph_2SnF_2 the tin atoms are in an octahedral environment with four equatorial bridging fluorine atoms and with phenyl groups above and below the tin to complete the octahedron. The octahedral coordination in Ph_2SnF_2 should be compared with trigonal bipyramidal coordination in Ph_3SnF, which has only one bridging fluorine. The strong self-coordination of Ph_2SnF_2 inhibits reactions with Lewis bases and thus the formation of discrete complexes. Ph_2SnF_2 did not dissolve in HMPA, DMSO, or any other Lewis base under various conditions (*i.e.* longer reaction time, higher temperature). After the reaction mixture of Ph_2SnF_2 and a large excess of Bu_4NF in CH_2Cl_2 had been stirred for nearly for a month, the unreacted solid Ph_2SnF_2 (~40% by weight) was filtered off and the filtrate was examined by ^{19}F and ^{119}Sn NMR spectroscopy. The solution contained a mixture of $Ph_3SnF_2^-$ and $PhSnF_5^{2-}$ as a result of redistribution and fluoride addition reactions.

The formation of $[Bu_4N]_2[PhSnF_5]$ was observed by NMR spectroscopy. The ^{19}F NMR spectrum shows a typical ab_4 fluorine spin system; *i.e.* quintet and doublet ^{19}F NMR resonances in a ratio of 1:4 with $^{117/119}Sn$-satellites. In other words, there are four equivalent and one unique fluorine atoms in the $PhSnF_5^{2-}$ dianion, and thus the structure of the ion must be octahedral, as shown in Figure 57.

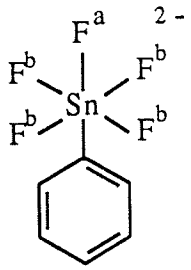


Figure 57. The octahedral structure of $PhSnF_5^{2-}$.

The ^{19}F NMR spectrum of $PhSnF_5^{2-}$ is shown in Figure 58 (NMR data are summarized in Table 20).

The ^{119}Sn NMR spectrum of the mixture exhibited the resonance of $Ph_3SnF_2^-$ only because of the small quantity of $PhSnF_5^{2-}$ present in the mixture. However, the following preparation method produces $PhSnF_5^{2-}$ more efficiently. The reaction of Ph_2SnCl_2 with $Ph_3SnF_2^-$ gives a mixture of insoluble phenyltin(IV) fluorides, as illustrated in equation [76].

$$2\ Bu_4N^+Ph_3SnF_2^- + Ph_2SnCl_2 \longrightarrow Ph_2SnF_2 + 2\ Ph_3SnF + 2\ Bu_4NCl \qquad [76]$$

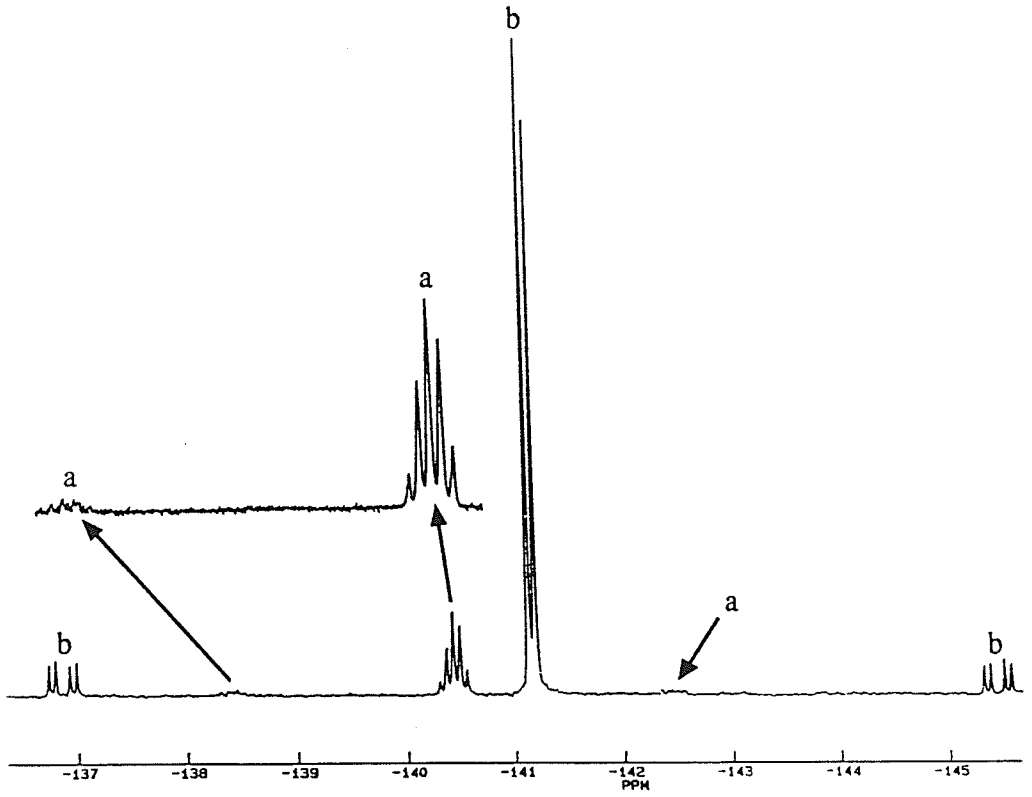


Figure 58. The ^{19}F NMR spectrum of $[PhSnF^{a}F_{4}^{b}]^{2-}$ showing a quintet (peaks a) and doublet (peaks b) in CD_2Cl_2 obtained at 282.4 MHz.

TABLE 20

The ^{19}F and ^{119}Sn NMR data of six-coordinate fluorophenylstannates

Compound	δF [ppm]	$\delta^{119}Sn$ [ppm]	J(^{119}Sn-F) [Hz]	Solvent
$[Bu_4N][PhSnF_5]$	δF^a -140.4 δF^b -141.2	-406	J(Sn-F^a) 1107 J(Sn-F^b) 2484 J(F^a-F^b) 17.89	CD_2Cl_2
F_2Ph_3Sn-O-$C_6H_4OH^-$	–	-321	1862	CD_2Cl_2

The addition of excess fluoride to the mixture then produces fluorophenylstannate complexes, such as $PhSnF_5^{2-}$, $Ph_3SnF_2^-$, and Ph_3SnFCl^-, presumably as a result of redistribution and fluoride addition reactions, as discussed previously. It is not clear how such an instantaneous reaction could occur between Ph_2SnF_2 and F^- under this condition. The formation of all fluorophenylstannate complexes was also detected by the ^{119}Sn NMR spectrum; $\delta^{119}Sn$ ($PhSnF_5^{2-}$) = -406 ppm. Colton (151) has reported ^{119}Sn chemical shifts of five- and six-coordinate phenyltin(IV) halides in dichloromethane solution:

$$\delta^{119}Sn\ (PhSnCl_4^-) = -260\ ppm \longrightarrow \delta^{119}Sn\ (PhSnCl_5^{2-}) = -550\ ppm$$

$$\delta^{119}Sn\ (PhSnBr_4^-) = -637\ ppm \longrightarrow \delta^{119}Sn\ (PhSnBr_5^{2-}) = -1007\ ppm$$

Since NMR data for $PhSnF_4^-$ are not available, direct comparison is not possible. However, the ^{119}Sn chemical shift of the six-coordinate complex $PhSnF_5^{2-}$ appeared at higher field compared to that of the five-coordinate complex $Ph_3SnF_2^-$. Furthermore, there is consistency in the change in ^{119}Sn chemical shifts to higher field on going from fluorine to chlorine, and to bromine in the same group VI

Crystals of $Bu_4N^+Ph_3SnF_2^-$ could be removed by slow evaporation of dichloromethane solution to separate $PhSnF_5^{2-}$ from the mixture. However, the fluoride impurities, such as SiF_6^{2-} and BF_4^-, generated during the recrystallization process, made it difficult to crystallize $[Bu_4N]_2[PhSnF_5]$. A typical ^{19}F NMR spectrum of $PhSnF_5^{2-}$ exhibits the presence of the fluoride impurities, as shown in Figure 59.

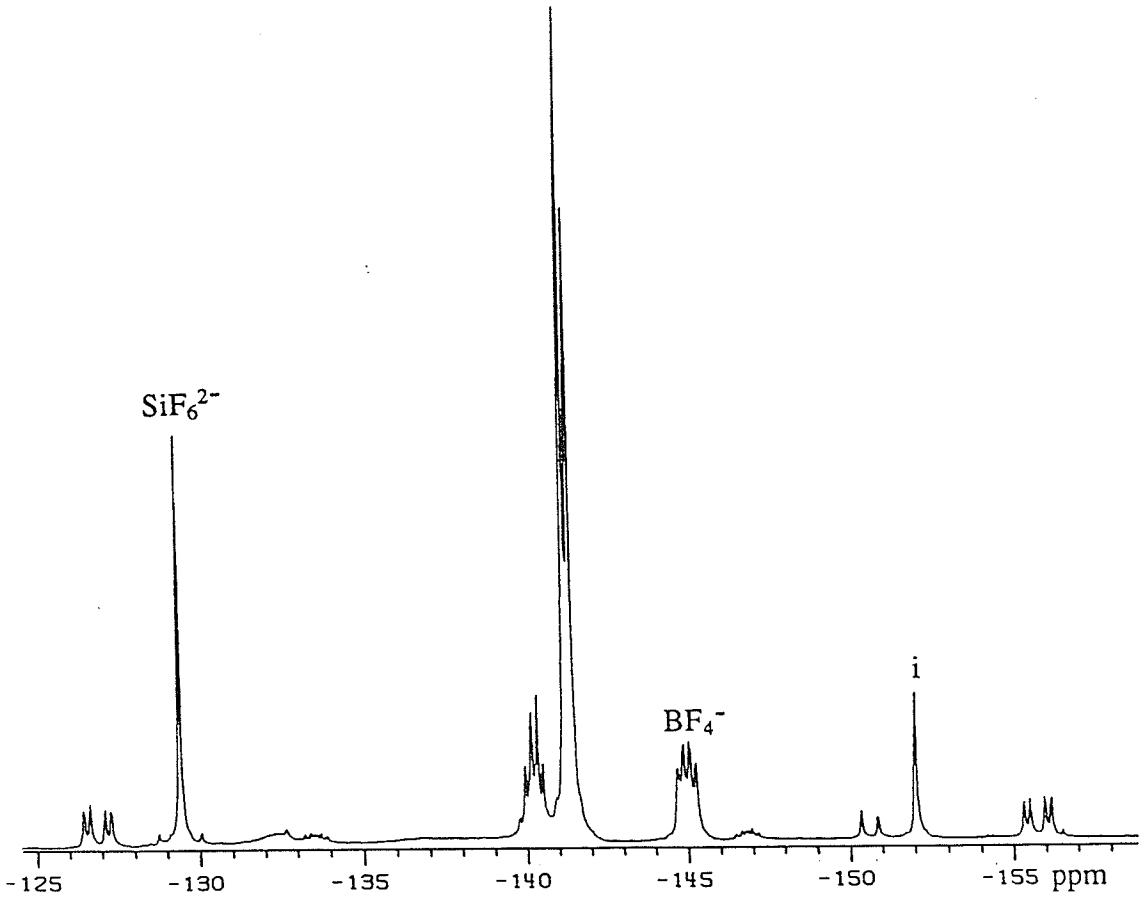


Figure 59. A typical ^{19}F NMR spectrum of $[PhSnF^aF_4{}^b]^{2-}$ (quintet marked with a and doublet marked with b) with fluoride impurities (SiF_6^{2-}, BF_4^- and the unknown marked with i) in $CDCl_3$.

B. Possible formation of six-coordinate $F_2Ph_3Sn\text{-}O\text{-}C_6H_4OH^-$

Reactions of $Ph_3SnF_2^-$ with various symmetrical ligands, such as bpy, fbpy, $CF_3C(O)CH_2C(O)CH_3$, $CF_3C(O)CH_2C(O)CF_3$, and $C_6H_4(OH)_2$, were performed in an effort to produce six-coordinate complexes of the type, $Ph_3SnF{\cdot}LL$ (LL = bidentate ligand). Direct reaction between Ph_3SnF and bidentate ligand (LL) to form $Ph_3SnF{\cdot}LL$ was not successful mainly due to the extreme insolubility of Ph_3SnF.

There was no interaction between $Ph_3SnF_2^-$ and bpy or fbpy, as judged by NMR spectroscopy. The ^{119}Sn NMR spectra of $Ph_3SnF_2^-$ in solution with 1-5 equivalents of bpy show only a triplet at -342 ± 4 ppm characteristic of a five-coordinate complex, *i.e.* $Ph_3SnF_2^-$. An equimolar mixture of $Ph_3SnF_2^-$ and fbpy yielded two ^{19}F NMR resonances, one due to $Ph_3SnF_2^-$ and the other to the free fbpy ligand, which shows a singlet fluorine resonance at -103.2 ppm (51) in $CDCl_3$.

Unlike the other bidentate ligands discussed above, catechol, $C_6H_4(OH)_2$, reacts with $Ph_3SnF_2^-$ readily, as judged by the immediate precipitation of Ph_3SnF, which may result in a six-coordinate complex anion, $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$. The stoichiometry of the reaction is not clear. The presence of $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$ in solution may be suggested by low temperature ^{119}Sn NMR spectroscopy. The ^{119}Sn NMR spectrum at room temperature shows a broad triplet ($\Delta W_{1/2}$ = ~100 Hz) at -326 ppm ($J^{119}Sn\text{-}F$ = 1915 Hz), indicative of an exchanging process (Figure 60). Perhaps $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$ might be exchanging with $FPh_3Sn\text{-}O_2C_6H_4$, as illustrated in equation [77].

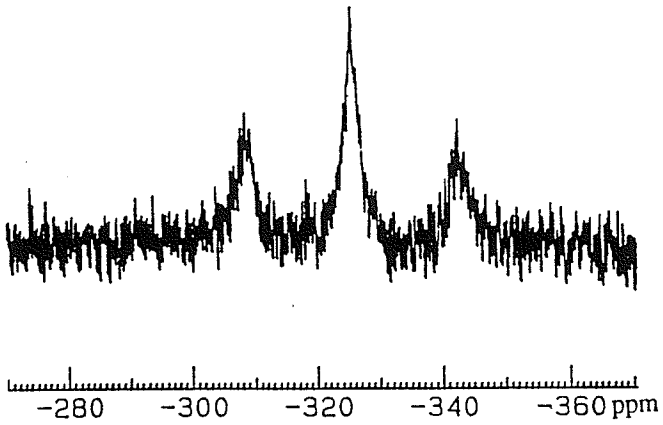
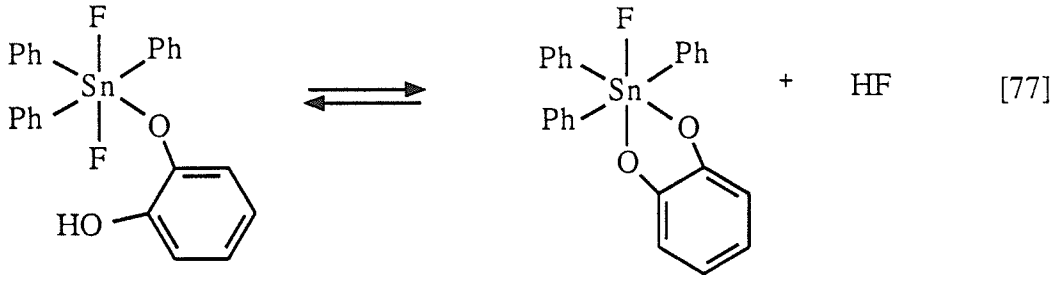


Figure 60. The ^{119}Sn NMR spectrum of an equimolar mixture of $Ph_3SnF_2^-$ and catechol in CD_2Cl_2 at room temperature.



[77]

On cooling the solution to 260 K, a sharp triplet ^{119}Sn NMR resonance appeared at -321 ppm with J(^{119}Sn-F) = 1862 Hz (Figure 61). The NMR data are summarized in Table 20. The ^{119}Sn chemical shift and ^{119}Sn-F coupling constant values obtained for $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$, are quite different from those of pure $Ph_3SnF_2^-$ (Table 16). In CD_2Cl_2 solvent, $\Delta\delta$ = 24 ppm and ΔJ = 88 Hz, which is an indication of the change in the coordination number of tin.

Evidence that three phenyl substituents are retained in the complex formation of $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$ was obtained from the following ^{119}Sn NMR experiment. The triplet resonance at -326 ppm (J = 1915 Hz) in Figure 60 is shifted to higher field, *i.e.* towards $Ph_3SnF_2^-$, in the presence of added pure $Ph_3SnF_2^-$, δ^{119}Sn = -334 ppm and J(^{119}Sn-F) = 1946 Hz, Figure 62.

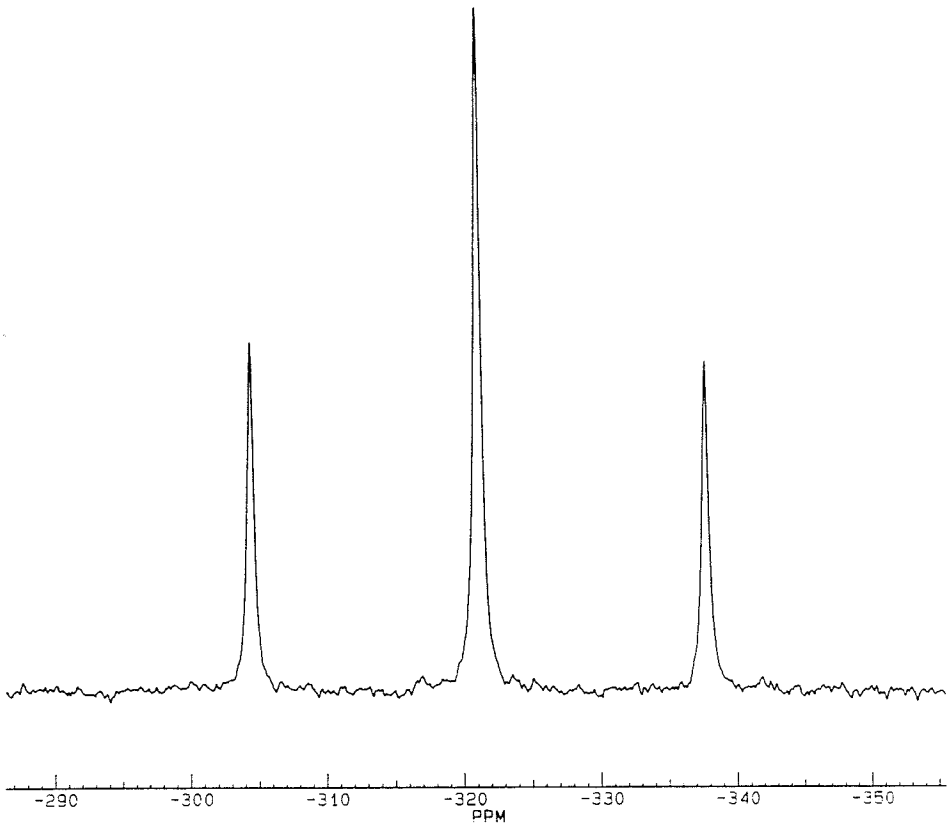


Figure 61. The ^{119}Sn NMR spectrum of an equimolar mixture of $Ph_3SnF_2^-$ and catechol in CD_2Cl_2 at 260 K.

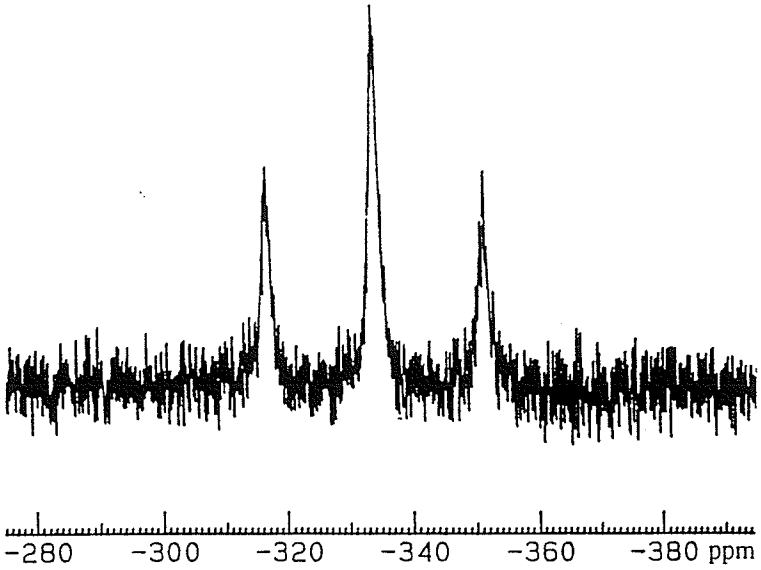


Figure 62. The ^{119}Sn NMR spectrum obtained after the addition of $Ph_3SnF_2^-$ to the mixture shown in Figure 60: note the changes in chemical shift.

A steric preference for the *mer*-geometry of $F_2Ph_3Sn\text{-}O\text{-}C_6H_4(OH)^-$ over the *fac* can be found in *mer*-Ph_3SnO_3 geometry (152). The X-ray crystal structure of triphenyltin acetate, $Ph_3Sn\text{-}O\text{-}C(O)CH_3$, revealed a distorted, six-coordinate *mer*-Ph_3SnO_3 geometry. The structure of triphenyltin acetate consists of polymeric chains in which planar triphenyltin units are bridged by carboxylate groups. Figure 63 shows part of the structure.

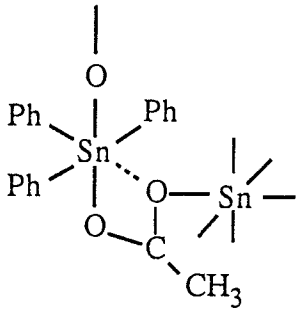


Figure 63. *mer*-Ph_3SnO_3 geometry of a polymeric triphenyltin acetate (by X-ray crystallography) (152).

CONCLUSIONS

The mechanisms of oxidative addition and isomerization reactions in octahedral phenyltellurium(VI) fluorides have been studied, and two mechanistic pathways are proposed and demonstrated for *cis*- and *trans*-Ph_2TeX_4 (X = F, Cl) and *cis*- and *trans*-F_2TePh_3Cl.

Oxidative fluorinations of Ph_2TeX_2 (X = F, Cl) with XeF_2 produced *cis*-Ph_2TeX_4 (X = F, Cl) via ionic intermediates. Evidence has been presented to support the following mechanism: initial formation of a five-coordinate anionic intermediate *cis*-$Ph_2TeX_3^-$ (phenyl substituents occupy *cis*-position), followed by the addition of "F^+" at tellurium, *trans* to phenyl, which leads to the formation of *cis*-Ph_2TeX_4. Unfortunately, isolation and characterization of the intermediate could not be achieved, probably because of rapid equilibration. Mechanistic conclusions have been drawn on the basis of the available evidence. Both experimental data, and the literature dealing with these systems, are consistent with the mechanism proposed for this process. The kinetically favoured *cis*-Ph_2TeX_4 isomerizes to the thermodynamically more stable *trans*-Ph_2TeX_4 via the five-coordinate cation $Ph_2TeX_3^+$ in a reaction catalyzed by Lewis acid fluorides.

In the oxidative fluorination of Ph_3TeCl with XeF_2, only *cis*-F_2TePh_3Cl was produced, which is consistent with the proposed mechanism; the formation of *trans*-F_2TePh_3Cl was not detected by NMR during the course of the oxidative reaction. Therefore, *cis*- and *trans*-F_2TePh_3Cl were prepared from *mer*-Ph_3TeF_3 via five-coordinate cations Ph_3TeFCl^+ and $Ph_3TeF_2^+$, as confirmed by ^{19}F and ^{125}Te NMR spectroscopy, and the mechanism of isomerization reactions was studied. *trans*-F_2TePh_3Cl was found to isomerize to the thermodynamically more stable *cis*-isomer in a reaction catalyzed by Lewis acid fluorides. For this isomerization, it was concluded that

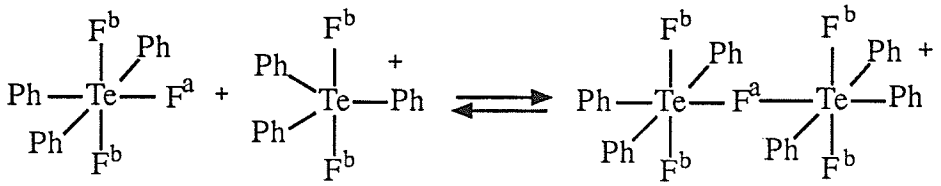
an intermolecular route involving Te-F bond-cleavage is responsible.

The solutions of octahedral phenyltellurium(VI) fluorides exhibit NMR resonances characteristic of rigid molecules, as confirmed by ^{19}F, ^{125}Te, and ^{13}C NMR spectroscopy. The NMR studies confirmed that there is no intramolecular scrambling of ligands in purified samples. However, intermolecular fluorine exchange was initiated in *mer*-Ph_3TeF_3, *cis*-F_2TePh_3Cl, and *cis*-F_2TePh_3OH (the three phenyl substituents adopt a *mer*-arrangement) by adding the corresponding five-coordinate cations, as follows. For *mer*-Ph_3TeF_3 and *cis*-F_2TePh_3Cl, the five-coordinate cations $Ph_3TeF_2^+$ and Ph_3TeFCl^+ were prepared to study the exchange processes by variable temperature NMR spectroscopy. For *cis*-F_2TePh_3OH, the five-coordinate cation Ph_3TeFOH^+ could not be prepared, but evidence that it is required in the stereoselective fluorine exchange was presented. In all cases, for three phenyl substituents in a *mer*-arrangement, stereoselective fluorine (F^a ligand) exchange was observed between five- and six-coordinate Te(VI) fluorides via fluorine-bridged intermediates.

In summary, the major significance of this study is the stereoselectivity of oxidative addition and isomerization reactions observed for phenyltellurium fluorides. Oxidative fluorination of diphenyltellurium(IV) difluoride occurs by addition of "F^+" at tellurium in a first formed five-coordinate Te(IV) anionic intermediate to give a *cis*-phenyl octahedral isomer, which subsequently isomerizes via five-coordinate Te(VI) cationic intermediate to the *trans*-phenyl isomer.

APPENDIX

Evaluation of thermodynamic parameters for the mer-Ph_3TeF_3-$Ph_3TeF_2^+$ system



[A] [B] [AB]

1. Evaluation of equilibrium constants (K_T)

$$K_T = \frac{[AB]}{[A] + [B]} \qquad [A1]$$

From equation [66], for F^a

$$\delta_{obs} = X_A\delta_A(F^a) + X_{AB}\delta_{AB}(F^a)$$

$$= \frac{[A]}{[A] + [AB]}\delta_A(F^a) + \frac{[AB]}{[A] + [AB]}\delta_{AB}(F^a)$$

$$= \frac{1}{[A] + [AB]}\{[A]\delta_A(F^a) + [AB]\delta_{AB}(F^a)\}$$

expanding this equation,

$$[A]\delta_{obs}(F^a) + [AB]\delta_{obs}(F^a) = [A]\delta_A(F^a) + [AB]\delta_{AB}(F^a)$$

adding $-[AB]\delta_A(F^a)$ to both sides,

$$[A]\delta_{obs}(F^a) + [AB]\delta_{obs}(F^a) - [AB]\delta_A(F^a) = [A]\delta_A(F^a) + [AB]\delta_{AB}(F^a) - [AB]\delta_A(F^a)$$

$$[A]\{\delta_{obs}(F^a) - \delta_A(F^a)\} + [AB]\{\delta_{obs}(F^a) - \delta_A(F^a)\} = [AB]\{\delta_{AB}(F^a) - \delta_A(F^a)\}$$

$$([A] + [AB])\{\delta_{obs}(F^a) - \delta_A(F^a)\} = [AB]\{\delta_{AB}(F^a) - \delta_A(F^a)\}$$

Let $[A] + [AB] = [A^0]$,

$$\text{then} \qquad [AB] = \frac{[A^0]\{\delta_{obs}(F^a) - \delta_A(F^a)\}}{\delta_{AB}(F^a) - \delta_A(F^a)} \qquad [A2]$$

2. Evaluation of ΔH

(1) at 300 K;

$\delta_A(F^a) = -3$ ppm and $\delta_{obs}(F^a) = -58$ ppm

$[A^0] = [A] + [AB] = 1.01 \times 10^{-3}$ M and $[B^0] = [B] + [AB] = 1.06 \times 10^{-3}$ M

(concentrations were obtained from ^{19}F NMR integration relative to C_6F_6 reference)

δ_{AB} is assumed to be -132 ppm

Now, the concentration of the intermediate can be calculated by using equation [A2],

$$[AB] = \frac{1.01 \times 10^{-3}\,(-58 + 3)}{-132 + 3} = 4.3 \times 10^{-4}$$

and $[A^0] = [A] + [AB]$, thus $[A] = [A^0] - [AB] = 5.8 \times 10^{-4}$

Similarly, $[B] = 6.3 \times 10^{-4}$

$$K_{300} = \frac{4.3 \times 10^{-4}}{(5.8 \times 10^{-4})(6.3 \times 10^{-4})} = 1.2 \times 10^{3}$$

(1) at 280 K;

$\delta_{obs}(F^a) = -76$ ppm and $\delta_{AB} = -132$ ppm

$[A^0] = 8.3 \times 10^{-4}$ M, $[B^0] = 1.2 \times 10^{-3}$ mmol,

$$[AB] = \frac{8.3 \times 10^{-4}(-76 + 3)}{-132 + 3} = 4.7 \times 10^{-4}$$

$[A] = 3.6 \times 10^{-4}$ and $[B] = 7.3 \times 10^{-4}$

$$\text{Thus, } K_{280} = \frac{(3.6 \times 10^{-4})(7.3 \times 10^{-4})}{4.7 \times 10^{-4}} = 1.8 \times 10^{3}$$

(below 270 K, impurities were dominant, thus equilibrium constants could not be calculated).

Table. Values of equilibrium constants for the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system at two different temperatures.

T (K)	Keq	lnK	$10^3/T$
300	1.2×10^3	7.09	3.33
280	1.8×10^3	7.50	3.57

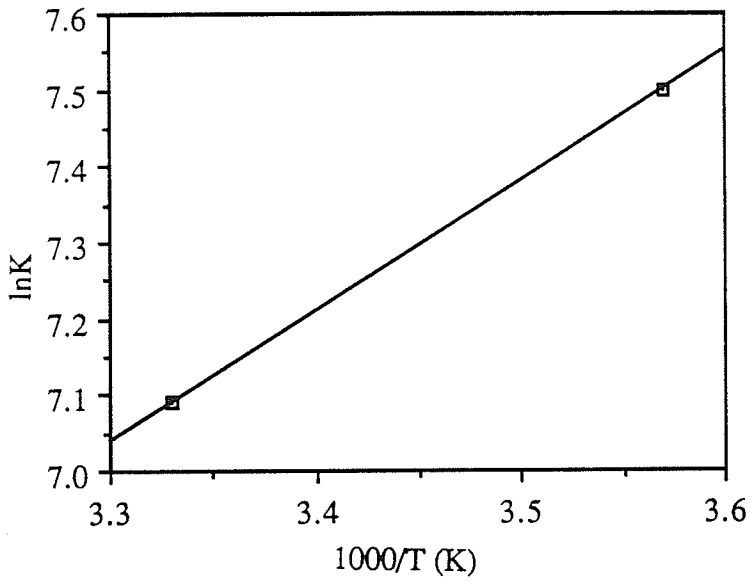


Figure. Plot of lnK vs. 1000/T (K)

From the graph, slope = $1.7083 \times 10^3 = -\Delta H/R$ ($R = 8.31431\ JK^{-1}mol^{-1}$) therefore, the reaction enthalpy, ΔH, for the *mer*-Ph_3TeF_3-$Ph_3TeF_2^+$ system is calculated to be $-14.2\ kJmol^{-1}$.

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