REACTIONS OF TELLURIUM CHLORIDE PENTAFLUORIDE, TeF_5Cl, WITH NITROGEN NUCLEOPHILES. PREPARATION AND CHARACTERIZATION OF THE ADDUCTS $(TeF_4)_2 \cdot NR_2Cl$, WHERE R = CH_3, C_2H_5 [†]

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SUMMARY

Reactions of TeF_5Cl with the nitrogen nucleophiles $LiN=C(CF_3)_2$, $[(CH_3)_3Si]_2NH$, and $(CH_3)_3SiNR_2$, where R = CH_3, C_2H_5, result in the reduction of the tellurium to Te(IV) and chlorination of the respective nucleophile. Analogous results are obtained in the reactions of TeF_5Cl with $(CH_3)_3SiCN$, C_6F_5Li, and C_6F_5SLi. In the case of $(CH_3)_3SiNR_2$, the new adducts $(TeF_4)_2 \cdot NR_2Cl$ are obtained in high yield. These compounds have been identified through their infrared, ^{1}H, ^{19}F, and [125]Te NMR, and mass spectra as well as by elemental analysis.

INTRODUCTION

In contrast to the well-documented unreactivity of SF_6, both SF_5Cl and SF_5Br have been shown to react with select nitrogen nucleophiles [1]. These reactions have yet to be explored with the related tellurium systems, even though the first $TeF_5N<$ derivatives resulted from displacement of fluorine in TeF_6 by nitrogen containing groups [2]. We wish to report herein the results of our study of the reactions of TeF_5Cl with

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various nucleophilic reagents including $LiN=C(CF_3)_2$, $(CH_3)_3SiNR_2$ (where $R = CH_3$, C_2H_5), $[(CH_3)_3Si]_2NH$, $(CH_3)_3SiCN$, C_6F_5Li, and C_6F_5SLi.

During the course of our study several reports have appeared which describe the preparation of new multi-substituted SeF_6 and TeF_6 derivatives [3-5]. In all cases, the

$$CF_3SeF_3 \; + \; ClF \; \longrightarrow \; \textit{trans-}CF_3SeF_4Cl \tag{1}$$

$$(C_6H_5)_{4-x}TeF_x \; + \; XeF_2 \; \longrightarrow \; (C_6H_5)_{4-x}TeF_{x+2} \; + \; Xe \tag{2}$$

$$(C_6F_5)_2TeF_2 \; + \; F_2 \; \longrightarrow \; \textit{cis-}(C_6F_5)_2TeF_4 \tag{3}$$
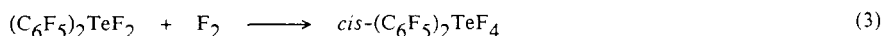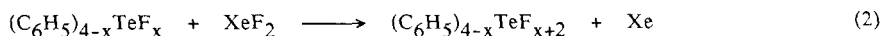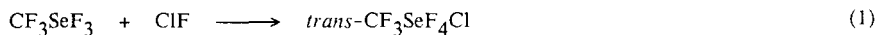
products were generated by an oxidative fluorination, and, with the exception of the phenyltellurium(VI) fluorides [4], the products were found to be unstable with respect to decomposition to selenium tetrafluoride and tellurium tetrafluoride, respectively.

RESULTS AND DISCUSSION

Shreeve and co-workers have found that only select nucleophiles will react with SF_5X ($X = Cl$, Br) in such a way as to preserve both a high coordination number and oxidation state [1,6]. One of these nucleophiles is $LiN=C(CF_3)_2$, which was found to react with SF_5X as shown in equation 4. Because of the strong preference of Te(VI) for

$$SF_5X \; + \; LiN=C(CF_3)_2 \; \xrightarrow[-\text{LiF}]{-196 \text{ to } 25^oC} \; SF_3X=NCF(CF_3)_2 \tag{4}$$
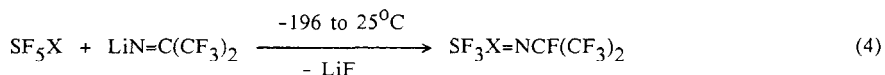
the coordination number six [7], one would not expect to obtain the corresponding five-coordinate product, as it would most likely be unstable with respect to dimerization. Alternatively, one might observe no concomitant (1,3)-fluorine atom shift as in the sulfur system which would then simply yield $TeF_4Cl-N=C(CF_3)_2$ as the product. Unfortunately when $LiN=C(CF_3)_2$ was reacted with TeF_5Cl even under a variety of conditions, we always observed TeF_4 and $ClN=C(CF_3)_2$ as the major products:

$$TeF_5Cl \; + \; LiN=C(CF_3)_2 \; \xrightarrow[-\text{LiF}]{} \; TeF_4 \; + \; ClN=C(CF_3)_2 \tag{5}$$
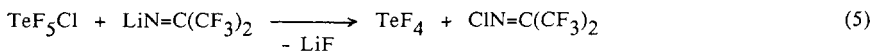
It seems probable that the desired product $TeF_4Cl-N=C(CF_3)_2$ was formed as an intermediate which was unstable towards reductive elimination of $ClN=C(CF_3)_2$.

The only other nitrogen nucleophile which has been found to react with SF_5X is $(CH_3)_3SiN(CH_3)_2$, which led exclusively to the trans-monosubstituted products $XSF_4N(CH_3)_2$ [1]. On the other hand, molecular orbital calculations have indicated a cis-influence in substituted TeF_6 derivatives [8] as had previously been displayed

chemically [2,9]. Recently, Passmore and co-worker have found that the reaction of TeF_5Cl with CH_3OH or $CH_3OSi(CH_3)_3$ gives a mixture of cis- and trans-$ClTeF_4OCH_3$ in a ratio of 1:6 [10]. They also observed both cis and trans isomers in the hydrolysis of TeF_5Cl [10]. Therefore, it was of interest to carry out reactions between TeF_5Cl and dialkylaminotrimethylsilanes in order to determine both the stereochemistry and degree of substitution of the products. Again we observed reduction of the tellurium in these reactions; however, the adducts $(TeF_4)_2 \cdot NR_2Cl$ ($R = CH_3$, C_2H_5) were formed in essentially quantitative yield but only when TeF_5Cl was used in a molar excess:

$$2\ TeF_5Cl\ +\ (CH_3)_3SiNR_2\ \xrightarrow[-\ FSi(CH_3)_3]{}\ (TeF_4)_2 \cdot NR_2Cl\ +\ ClF \qquad (6)$$
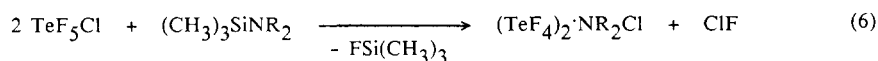
When one equivalent or less of TeF_5Cl was used viscous, dark red oils resulted. In contrast, Passmore has reported a similar reduction of TeF_5Cl by dimethyl amine, but the reaction and the adduct formed, $TeF_4 \cdot HN(CH_3)_2$, were both 1:1 in stoichiometry [10]. It is well known that TeF_4 forms complexes with Lewis bases, but these generally have the formula $TeF_4 \cdot L$. In fact, adducts with the formula $(TeF_4)_2 \cdot L$ have previously been observed only with diamines [11, 12]. Although we cannot totally account for the unexpected stoichiometry of the adducts reported herein, the mass balance of the reactions as well as the spectroscopic and analytical data, which will be presented below, clearly indicate 2:1 adducts.

The adducts $(TeF_4)_2 \cdot NR_2Cl$ were characterized by infrared, ^{1}H, ^{19}F, and [125]Te NMR, and mass spectroscopy as well as by elemental analysis. The infrared spectra were taken on neat films between KCl plates and were rather featureless; however, both C-H and Te-F stretches were apparent. The ^{19}F NMR spectrum of each adduct revealed only a single, broad resonance in the region associated with fluorine bound to tellurium. The fluorine atoms in TeF_4 are known to undergo rapid chemical exchange at room temperature resulting in a single singlet with no observable [125]Te-^{19}F coupling in either the ^{19}F or the [125]Te NMR spectrum [13,14]. In fact, this coupling has only recently been observed in TeF_4 for a spectrum taken at $0^\circ C$ in SO_2Cl_2 [5]. Both the broadness of the resonance and the lack of observed [125]Te-^{19}F coupling point to the reduction of the Te(VI) starting material to Te(IV) in the reactions reported herein.

Each adduct was also examined by [125]Te NMR spectroscopy with each measurement being made on a 50% solution in d_6-acetone. The chlorodimethylamine adduct exhibited a broad singlet at 1246 ppm relative to $(CH_3)_2Te$, while the chlorodiethylamine adduct exhibited a broad singlet at 1194 ppm. Both [125]Te NMR spectra lacked [125]Te-^{19}F coupling, again indicating rapid chemical exchange of fluorines [13,14]. The fact that the chemical shifts observed for the adducts are not in

close proximity to that reported for TeF_4 (559.8 ppm, CH_3CN) [14] bears no great significance because the ^{125}Te resonance is strongly dependent upon the solvent, concentration, and temperature [14,15]. For example, values for the ^{125}Te chemical shift in $TeCl_4$ which differ by almost 600 ppm have been reported for the two solvents $(CH_3)_2CO$ and THF [15]. For comparison we obtained the ^{125}Te NMR spectrum of TeF_4 in d_6-acetone (concentrated solution), and the expected singlet at 1264 ppm provides further evidence that the adducts are Te(IV) species.

The electron impact mass spectrum of each adduct $(TeF_4)_2 \cdot NR_2Cl$ gave primarily ions associated with the respective chloroamine. On the other hand, the chemical ionization mass spectra provided further evidence for the proposed stoichiometries. Tellurium has eight naturally occurring isotopes, and thus the appearance of isotopic envelopes can be used to confirm the presence and number of tellurium atoms. For example, a portion of the chemical ionization mass spectrum of $(TeF_4)_2 \cdot N(C_2H_5)_2Cl$ with several complex patterns corresponding to $^{130}Te_2F_7N(C_2H_5)^{35}Cl^+$ at 471 m/z, $^{130}Te_2F_8^{35}Cl^+$ at 461 m/z, and $^{130}Te_2F_6N(C_2H_5)(C_2H_4)^+$ at 445 m/z has been reproduced along with a computer simulation in Figure 1a. For comparison the highest mass fragment obtained from the chemical ionization mass spectrum of TeF_4, namely $^{130}Te_2F_7^+$ at 393 m/z, is shown in Figure 1b along with the calculated isotopic distribution.

As a test of adduct formation chlorodimethylamine was prepared in toluene and reacted with TeF_4. The resulting red oil had the same properties as those described above in reactions where TeF_5Cl was not used in excess. Greenwood _et al._ have previously prepared pentafluorotellurate salts by reacting 1:1 adducts of TeF_4 with hydrogen fluoride as shown in equation 7 [12]. Correspondingly, the adduct

$$TeF_4 \cdot NC_5H_5 + HF \longrightarrow [C_5H_5NH^+][TeF_5^-] \qquad (7)$$
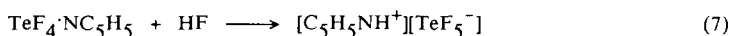
$(TeF_4)_2 \cdot N(CH_3)_2Cl$ was dissolved in anhydrous HF; however, when the HF was removed to a NaF scrubber, no reaction had taken place as determined by mass balance. This lack of reactivity with HF may be due to the reduced basicity of the chloroamine. In a final attempt to prepare one of the initially desired Te(VI) amino derivative, we attempted the oxidation of $[(CH_3)_2N]_2TeF_2$ [16] with ClF. Unfortunately our attempts resulted in only black oily residues which contained no fluorine.

The vast majority of $TeF_5N<$ derivatives have been previously prepared from $TeF_5NHSi(CH_3)_3$ which itself is prepared from TeF_6 and hexamethyldisilazane [17]. The reaction of TeF_5Cl with hexamethyldisilazane failed to give the desired product $TeF_4Cl-NHSi(CH_3)_3$ but gave instead TeF_4, $FSi(CH_3)_3$, $FSi(CH_3)_2CH_2Cl$, and N_2 as
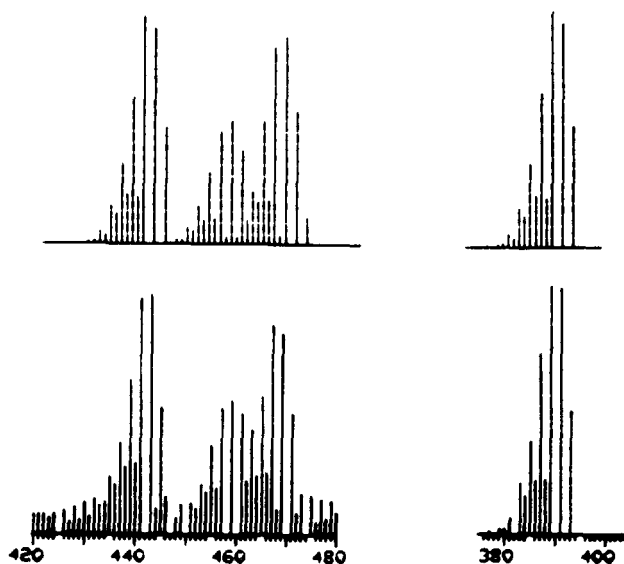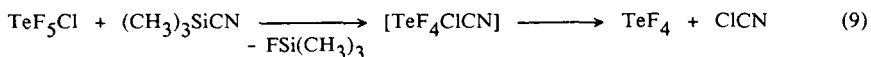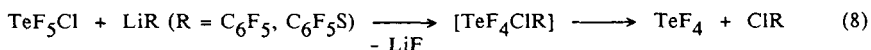
Fig. 1. (a) The CI-Mass Spectrum of $(TeF_4)_2 \cdot N(C_2H_5)_2Cl$ (bottom) and Computer Simulation (top). (b) The CI-Mass Spectrum of TeF_4 (bottom) and Computer Simulation (top).

major products. The silane $FSi(CH_3)_2CH_2Cl$ most likely resulted from free radical chlorination of $FSi(CH_3)_3$ by a chloroamine intermediate such as $(CH_3)_3SiNHCl$. This silane has been previously prepared by the gas phase chlorination of $ClSi(CH_3)_3$ followed by metathesis with KHF_2 to give the fluorosilane [18].

Tellurium chloride pentafluoride was reacted with a variety of other nucleophiles as shown in Table 1, and in each case reduction to Te(IV) was observed. The observed reaction products indicate that the desired disubstituted Te(VI) products may have been formed as intermediates which undergo reductive elimination as shown in equations 8 and 9. Shreeve and co-workers have reported related results from the reactions of

$$TeF_5Cl + LiR \ (R = C_6F_5, C_6F_5S) \xrightarrow[- \ LiF]{} [TeF_4ClR] \longrightarrow TeF_4 + ClR \qquad (8)$$

$$TeF_5Cl + (CH_3)_3SiCN \xrightarrow[- \ FSi(CH_3)_3]{} [TeF_4ClCN] \longrightarrow TeF_4 + ClCN \qquad (9)$$

SF_5Cl with C_6F_5Li, C_6F_5SLi, CH_3SLi [6a], and $(CH_3)_3SiCN$ [6b]; however, they were successful in obtaining the highly substituted S(VI) derivative $CF_3SF_2(CN)_2Cl$ from the reaction of CF_3SF_4Cl with $(CH_3)_3SiCN$ [6b].

TABLE 1

Reactions of TeF$_5$Cl with nucleophiles

Reaction	Conditions and Comments	Products
TeF$_5$Cl LiN=C(CF$_3$)$_2$	(8.0 mmol) (6.0 mmol) Pyrex vessel, Freon 11 solvent. Warmed to -65°C in thermostatted bath for three days.	a) 1.3 g solid LiF and TeF$_4$ b) ClN=C(CF$_3$)$_2$ (^{19}F NMR, IR, MS)
TeF$_5$Cl (Me$_3$Si)$_2$NH	(30.0 mmol) (20.0 mmol) S. S. Parr Autoclave, allowed to warm slowly from -78°C to r.t. over two days.	a) noncondensibles b) 1.05 g ClCH$_2$SiMe$_2$F, 2.95 g FSiMe$_3$ (IR, ^{19}F and ^{1}H NMR, MS) c) 5.93 g TeF$_4$ (^{19}F NMR)
TeF$_5$Cl Me$_3$SiCN	(5.77mmol) (5.04mmol) FEP vessel, Me$_3$SiCN added in two aliquots, -55°C to r.t. overnight.	a) 0.95 g volatiles. ClCN, FSiMe$_3$, and TeF$_5$Cl (IR) b) 0.55 g off white solid – TeF$_4$ (^{19}F NMR)
TeF$_5$Cl C$_6$F$_5$Li	(5.0 mmol) (5.0 mmol) Pyrex vessel, diethyl ether solvent. Held at -78°C overnight.	a) volatiles Et$_2$O, trace C$_6$F$_5$H, C$_6$F$_5$Cl (IR, ^{19}F NMR, MS) b) 1.15 g off white solid – TeF$_4$ (^{19}F NMR) and LiF
TeF$_5$Cl C$_6$F$_5$SLi	(5.0 mmol) (5.0 mmol) Pyrex vessel, diethyl ether solvent. Held at -78°C overnight.	a) volatiles Et$_2$O, C$_6$F$_5$SCl, C$_6$F$_5$SSC$_6$F$_5$ (IR, ^{19}F NMR, MS) b) 1.77g off white solid – TeF$_4$ (^{19}F NMR) and LiF

We recently learned that Sladky and co-workers have been able to prepare a variety of disubstituted TeF$_6$ derivatives of the type *cis*-ROTeF$_4$NR'R" from the replacement of an F atom in TeF$_5$OR by nitrogen containing groups [22]. Sladky attributes their success to the stabilization of the labile Te(VI)-N bond by the preformed Te(VI)-O bond. Our study, as well as the results of Lawlor and Passmore [10], clearly indicate that the chlorine atom in TeF$_5$Cl is not sufficient to stabilize a labile Te(VI)-N bond.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer, either on gases, pressure 1-10 torr, or on capillary films between KCl windows. Mass spectra were obtained on a Hewlett-Packard 5985A GC/MS system using either a controlled gas inlet or solid inlet probe. Only the most important ions are reported. The mass numbers are given for ^{130}Te and ^{35}Cl where applicable; the intensities include all isotopes. The ^{1}H and ^{19}F NMR spectra were recorded on either a Varian EM360L or a Nicolet NIC 200 FT nuclear magnetic resonance spectrometer. The ^{125}Te NMR spectra were taken on the Nicolet NIC 200 FT NMR spectrometer at 63.2 MHz and referenced to external $(HO)_6Te$ (1M in D_2O). The equation $(CH_3)_2Te = (HO)_6Te + 712$ was then used to convert the ^{125}Te chemical shifts with respect to neat $(CH_3)_2Te$. Elemental Analyses were obtained from Galbraith Laboratories, Inc. in Knoxville, Tennessee.

The compounds TeF_5Cl [20], $LiN=C(CF_3)_2$ [21], C_6F_5Li [6a], C_6F_5SLi [6a], and $[(CH_3)_2N]_2TeF_2$ [16] were prepared by literature methods. All other reagents were taken from laboratory stock and purified, where necessary, before use.

Preparation of $(TeF_4)_2 \cdot NR_2Cl$

In a typical reaction, TeF_5Cl (6.6 mmol) was condensed into an FEP tube reactor followed by dry CCl_3F (5.56 g). The dialkylaminotrimethylsilane (3.5 mmol total) was then added in three aliquots of approximately 1.1-1.2 mmol each with the reaction mixture being allowed to stand at -78°C for one day between aliquots. The reaction mixture was then allowed to warm slowly to room temperature whereupon the white solid which had formed turned to a pale yellow oil. The solvent, any unreacted starting materials and by-products were then removed to a -196°C trap under dynamic vacuum until there was no change in the weight of the oil which remained in the reactor.

$(TeF_4)_2 \cdot N(CH_3)_2Cl$ (nc) 90% yield; IR (capillary film): 3160 (w), 3040 (w), 1457 (m), 625 (s), 500 (vsb) cm^{-1}; ^{1}H NMR (TMS): 2.47 (s); ^{19}F NMR (d_6-acetone): -48.0 (s); ^{125}Te NMR (d_6-acetone): 1246 (bs); mass spectrum (70 eV): major m/z = 79 $[ClN(CH_3)_2^+$, 65%], 78 $[ClN(CH_3)CH_2^+$, 100%], 43 $[N(CH_3)CH_2^+$, 17%], 42 $[N(CH_2)CH_2^+$, 30%]; chemical ionization mass spectrum (methane): major m/z = 393 $(Te_2F_7^+$, 61%), 230 $[TeF_3N(CH_3)CH_2^+$, 100%], 207 $(TeF_4H^+$, 22%), 187 $(TeF_3^+$, 80%). Anal. Calcd for $C_2H_6NClF_8Te_2$: C, 4.94; H, 1.24; N, 2,88. Found: C, 5.30, H, 1.54; N, 2.89.

$(TeF_4)_2 \cdot N(C_2H_5)_2Cl$ (nc) 78% yield; IR (capillary film): 3120 (w), 3010 (w), 1455 (w), 620 (s), 490 (vsb) cm^{-1}; ^{1}H NMR (CDCl$_3$): 2.96 (q, CH$_2$), 1.25 (t, CH$_3$); ^{19}F NMR (d_6-acetone): -38.6; ^{125}Te NMR (d_6-acetone): 1194 (bs); mass spectrum (70 eV): major m/z = 107 $[ClN(C_2H_5)_2^+$, 18%], 92 $[ClN(C_2H_5)CH_2^+$, 38%], 64 $(ClC_2H_5^+$, 45%), 56 $(NC_3H_6^+$, 100%); chemical ionization mass spectrum (methane): major m/z = 471

$[Te_2F_7N(C_2H_5)Cl^+, 77\%]$, 461 $(Te_2F_8NCl^+, 53\%)$, 445 $[Te_2F_6(C_2H_5)C_2H_4^+, 100\%]$, 239 $[TeF_2(C_2H_5)C_2H_4^+, 59\%]$, 211 $(TeF_2C_2H_5^+, 18\%)$. Anal. Calcd for $C_4H_{10}NClF_8Te_2$: C, 9.33; H, 1.94; N, 2.72. Found: C, 9.60; H, 2.22; N, 2.85.

ACKNOWLEDGMENTS

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