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AN ABSTRACT OF THE THESIS OF Joseph Onuorah Udeaja for the
Master of Science in Chemistry presented July 28, 1986.

Title: The Chemistry of Novel Chromium(IV) Systems
and Fluorinated Hypochlorites.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

Gary L. Gard, Chairman

Carole R. Gatz

Morris B. Silverman

Chromium(IV) has been of interest for some time because of its role as an intermediate in chromic oxidation reactions. Since there are not a great number of stable tetravalent chromium complexes known, and the use of such species as oxidizing agents has not been widely explored, the preparation, isolation and characterization of new stable tetravalent chromium species may allow chemists the opportunity to more fully

understand the role which tetravalent chromium plays in oxidation reactions. The present study thus involves the synthesis of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ and other Cr(IV) derivatives and the use of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ in oxidative reactions with selected fluorinated alcohols. Interestingly, the reaction of fluorinated alcohols with $\text{Cr}(\text{OC}_4\text{H}_9)_4$ or $\text{Cr}(\text{NEt}_2)_3$ was found to be a useful method for preparing similar products.

The reaction of fluorinated hypochlorites, CF_3OCl and $(\text{CF}_3)_3\text{COCl}$, have been extensively studied; both the oxidative displacement and addition reactions of F-tert-butyl hypochlorite with transition and post-transition metal chlorides have been studied by Dr. Gard's group at Portland State University and Dr. Shreeve's group at University of Idaho. We have now extended the chemistry of fluorinated hypochlorite to include the heptafluoroisopropyl hypochlorite, $i\text{-C}_3\text{F}_7\text{OCl}$, and we report the preparation of a new fluorinated hypochlorite, perfluoro-tertiary-amyl hypochlorite, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$, which is an important addition to the fluorinated hypochlorite chemistry studied in Dr. Gard's laboratory at Portland State University.

Analytical data, infrared and nmr spectra are presented in order to support the proposed structures of the new compounds formed.

THE CHEMISTRY OF
NOVEL CHROMIUM(IV) SYSTEMS
AND
FLUORINATED HYPOCHLORITES

by
JOSEPH ONUORAH UDEAJA

A thesis submitted in partial fulfillment of the
requirements for the degree of

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in
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1986

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of
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CHAPTER I

INTRODUCTION

A. CHROMIUM IV COMPOUNDS

For a number of years, Dr. Gard's research group at Portland State University has been studying the synthesis and properties of chromium in its high valent states of +4, +5, and +6(1,2,3). For example, in the +6 state the following new oxidants are known, see Table I. (4)

With Cr^{+5} the following systems have been studied, see Table II.

Interesting structural studies have also been carried out in conjunction with Dr. Kenneth Hedberg's group at Oregon State University and Dr. Roger Willet's group at Washington State University. In particular, the structures of CrOF_3 and CrF_5 have been elucidated and reported (5,6,7).

It thus became of interest to expand our studies of high valent chromium compounds to include the +4 oxidation state. It is interesting to note that the +4 oxidation state has been relatively uncommon for chromium. Some of the known compounds in this group include:

TABLE I

KNOWN CHROMYL COMPOUNDS (Cr^{+6} Systems)

<u>COMPOUND</u>	<u>NAME</u>	<u>COMMENTS</u>
1. CrO_2F_2	Chromyl fluoride	m.p. 31.6° (885mm), stable (500°)
2. CrO_2Cl_2	Chromyl chloride	b.p. 116.7° , stable (180°C)
3. CrO_2ClF	Chromyl chlorofluoride	Present in equil. with $\text{CrO}_2\text{Cl}_2 + \text{CrO}_2\text{F}_2$
4. CrO_2Br_2	Chromyl bromide	Stable below -70° , Dec. to Br_2 & $\text{Cr}(\text{IV})$
5. CrO_2I_2	Chromyl iodide	Existence unlikely
6. $\text{CrO}_2(\text{NO}_3)_2$	Chromyl nitrate	b.p. -45°C at 2mm
7. a. $\text{CrO}_2(\text{N}_3)_2$	Chromyl azide	Explodes above -60°
b. $\text{CrO}_2(\text{N}_3)\text{Cl}$	Chromyl azide chloride	Unstable
8. $\text{CrO}_2(\text{ClO}_4)_2$	Chromyl perchlorate	Unstable; has less than 1mm at r.t.
9. a. $\text{CrO}_2(\text{S}_2\text{O}_7)/\text{Cr}(\text{SO}_4)_2$	Chromyl disulfate	Exact structure unknown
b. $\text{CrO}_2(\text{HSO}_4)_2$	Chromyl hydrogen sulfate	Existence is questionable
10. $\text{CrO}_2(\text{CH}_3\text{COO})_2$	Chromyl acetate	m.p. 30.5° ; Explosive
11. $\text{CrO}_2(\text{BO}_2)_2$	Chromyl dimetaborate	50° dec.; existence?
12. $\text{CrO}_2(\text{CNO})_2$	Chromyl isocyanate	Stable only in CCl_4

TABLE I (cont.)

KNOWN CHROMYL COMPOUNDS

<u>COMPOUND</u>	<u>NAME</u>	<u>COMMENTS</u>
13. $\text{CrO}_2(\text{SCN})_2$	Chromyl thiocyanate	Stable short time in CCl_4
14. $\text{CrO}_2(\text{RCOO})_2$	R = Ph and CCl_3	Not isolated
15. $\text{CrO}_2[(\text{CH}_3)_3\text{SiO}]_2$	Bis(trimethylsilyl) chromate	b.p. 60° at 0.2mm; explosive
16. $\text{CrO}_2[(\text{C}_6\text{H}_5)_3\text{SiO}]_2$	Bis(triphenylsilyl) chromate	m.p. $138-140^\circ\text{C}$
17. $\text{CrO}_2(\text{SO}_3\text{F})_2^*$	Chromyl fluorosulfonate	113° dec.
18. $\text{CrO}_2(\text{CF}_3\text{COO})_2^*$	Chromyl trifluoroacetate	m.p. 49°
19. $\text{CrO}_2(\text{CClF}_2\text{COO})_2^*$	Chromyl chlorofluoroacetate	m.p. 66°
20. $\text{CrO}_2(\text{C}_3\text{F}_7\text{COO})_2^*$	Chromyl heptafluorobutyrate	Unstable at r.t.
21. $\text{CrO}_2(\text{SbF}_6)_2$ or $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})^*$	Fluorochromyl-u-fluorobis (pentafluoroantimonate)	m.p. $82-84^\circ$
22. $\text{CrO}_2\text{F}(\text{SbF}_6)^*$	Fluorochromyl hexafluoroantimonate	m.p. $90-93^\circ$ with dec.
23. $\text{CrO}_2\text{F}(\text{TaF}_6)^*$	Fluorochromyl hexafluorotantalate	104° dec.
24. $\text{CrO}_2(\text{PO}_3\text{F}_2)_2^*$	Chromyl difluorophosphate	Stable only in CCl_4

TABLE I (cont.)

KNOWN CHROMYL COMPOUNDS

<u>COMPOUNDS</u>	<u>NAME</u>	<u>COMMENTS</u>
25. $\text{CrO}_2(\text{CF}_3\text{SO}_3)_2^*$	Chromyl trifluoromethanesulfonate	Stable; m.p. $91 \pm 1^\circ$
26. $\text{CrO}_2\text{NO}_3(\text{CF}_3\text{COO})^*$	Chromyl nitrate trifluoroacetate	Red brown solid, m.p. $45-48^\circ$, dec. at 110°
27. $\text{CrO}_2[(\text{RO})_3\text{TiO}]_2$ R = $\text{CH}_3(\text{CH}_2)_3^-$	Chromyl bis(tributyltitanate)	Stable only in CCl_4
28. $\text{CrO}_2[(\text{R}_3\text{Si})_2\text{N}]_2$ R = C_{1-10}	di[bis(trialkylsilyl)amine]	Same as above, polymerize olefins
29. $\text{CrO}_2(\text{OSeF}_5)_2$	Chromyl pentafluoroselenate	m.p. -42.5° ; b.p. 105° with slow dec.
30. $[\text{CrO}_2((\text{CF}_2)_3(\text{COO})_2)]^*$	Chromyl perfluoroglutarate	Tan-brown solid, dec. above 80°
31. $[\text{CrO}_2((\text{CF}_2)_2(\text{COO})_2)]^*$	Chromyl perfluorosuccinate	Dark brown solid
32. $\text{CrO}_2(\text{CO})_2$	Chromyl carbonyl	Very low temp; matrix isolation
33. $\text{CrO}_2[(\text{CF}_3)_3\text{CO}]_2^\#$	Chromyl F-tert butoxide	Stable; light sensitive

* Chromyl compounds prepared and characterized at Portland State University.

Prepared and characterized at University of Idaho and Portland State University.

TABLE II
SOME Cr^{+5} SYSTEMS

<u>REACTANTS</u>		<u>Cr(V)</u> <u>PRODUCTS</u>
$\text{Ag}_2\text{Cr}_2\text{O}_7 + \text{BrF}_3$	--->	2 AgCrOF_4 (8)
$\text{CrF}_3 + \text{F}_2$	--->	CrF_5 (7)
$\text{CrO}_2\text{Cl}_2 + 2/3 \text{BCl}_3$	--->	CrOCl_3 (9)
$\text{XeF}_2 + 2 \text{CrO}_2\text{Cl}_2$	--->	CrOF_3 (5)
$\text{CrOF}_3 + \text{KF} + \text{HF}$	--->	KCrOF_4 (2)

(i) the halides, CrX_4 ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) (10)

(ii) the dialkylamides, $\text{Cr}(\text{NR}_2)_4$ ($\text{R}=\text{Et}, \text{Pr}, \text{MePr}$)

(11)

(iii) the mixed oxides, $\text{M}''_4\text{CrO}_6$ and $\text{M}''_3\text{CrO}_5$ ($\text{M}''=\text{Sr}, \text{Ba}$)

(12)

(iv) the alkoxides, $\text{Cr}(\text{OR})_4$ ($\text{R}=\text{t-Bu}, -\text{SiEt}_3, -\text{C}(\text{CH}_3)_2\text{Et},$
 $-\text{CEt}_3$) (12,13)

Table III summarizes the list of some of the known Cr(IV) compounds and their suggested synthetic pathways.

In CrO_2 , the presence of Cr(IV) has recently been questioned and it has been suggested that it is a Cr(III)-Cr(VI) compound, $(\text{CrO})_2\text{CrO}_4$ (10). The tetrabromide and tetrachloride are very unstable and appear to exist only in the vapor state.

Chromium tetrafluoride. CrF_4 is a very dark greenish-black solid, steel blue in the gas phase, which on exposure to moisture rapidly acquires a brown coating due to hydrolysis. The hydrolysis reaction:

is similar for many Cr(IV) systems. It is surprisingly chemically inert and does not react with ammonia, sulfur dioxide, sulfur trioxide or pyridine(10).

TABLE III

<u>Reactants</u>	<u>Cr(IV) Product</u>
$\text{Cr} + 2\text{F}_2$	CrF_4 (10)
CrO_2F_2 (500-525 atm.)	CrOF_2 (14)
$\text{MCl} + \text{CrF}_4 + \text{BrF}_3$ (M= K, Rb, Cs)	MCrF_5 (10)
$2 \text{CrCl}_3 + \text{Cl}_2$	2CrCl_4 (15)
$\text{MCrO}_4 + \text{Cr}_2\text{O}_3 + 5 \text{M(OH)}_2$ (M=Ba, Sr)	$3 \text{M}_2\text{CrO}_4$ (15)
$\text{CrO}_2\text{Cl}_2 + \text{O}_2$ (12-25 atm.)	$\text{CrO}_2 + \text{Cl}_2$ (15)
$\text{CrCl}_3 \cdot 3\text{THF} + 4 \text{ neo-C}_5\text{H}_{11}\text{Li}$	$\text{Cr}(\text{neo-C}_5\text{H}_{11})_4$ (15)
$\text{Cr}(\text{N(Et)}_2)_4 + 4 \text{ t-BuOH}$	$\text{Cr}(\text{OC(CH}_3)_3)_4$ (11)

CrF_4 is a stable compound prepared by passing fluorine directly over chromium(10).

On heating in vacuo at 100° , CrF_4 sublimes with deposits of a bluish material on the cooler parts of the tube. The rate increases with higher temperature, for example, at 180° and after 15-20 hours the entire sample had sublimed(10). On exposure to air, it is immediately coated with a brown oxide layer, and is responsible for the cinnamon color reported for the tetrafluoride by Von Wartenberg(10).

Chromium oxide difluoride. CrOF_2 is a brown-black solid (brown when in a finely divided state) and is insoluble in water, in acids (HCl , HF , HNO_3), in bases (NH_4OH , NaOH , KOH), and in common organic solvents(14). It is quantitatively obtained as a decomposition product of chromyl fluoride: (14)

CrOF_2 is stable at 1600° in vacuo, but in a nickel crucible at atmospheric pressure and at 1600° it is converted to Cr_2O_3 and presumably NiF_2 (14). The magnetic susceptibility of CrOF_2 (1.1BM) is noticeably lower than that calculated for a Cr(IV) state (theoretical: 2.8BM)(14). This is presumably caused by CrOF_2 not being magnetically dilute. A similar magnetic effect has been

observed in other transition metal oxides and fluorides with a probable d^2 configuration for the metal constituent(14).

Chromium tetradiethylamide. $\text{Cr}(\text{NEt}_2)_4$ was discovered as a product of a remarkable valence disproportionation of Chromium (III) diethylamide(11):

The disproportionation step (Equation I-5) is facilitated by the volatility of the tetrakis(diakylamide) which can easily be removed under vacuum leaving behind the polymeric chromium(II) dialkylamide. The dialkylamides are air and moisture sensitive, soluble in common organic solvents, and react with primary and secondary alcohols to give the chromium(III) alkoxides and the corresponding aldehydes and ketones in unknown yields(11).

With tertiary alcohols or trialkylsilanols, the tetra(alkoxide) is formed(11).

The compounds are all paramagnetic but exhibit no ESR to at least 98°K and they appear to be distorted from tetrahedral to D_{3d} stereochemistry(15).

Chromium(IV) alkoxides. The alkoxides, especially, the volatile blue solid $\text{Cr}(\text{OBu}^t)_4$, are the best authenticated and characterized quadrivalent chromium(IV) compounds. A wide variety of methods is available for the preparations. These include;

- (i) the action of di-t-butyl peroxide on dibenzene chromium(13)
- (ii) alcoholysis of tetrakis(dialkylamides)(11,12)
- (iii) oxidation of $\text{Cr}(\text{OBu}^t)_3$ in the presence of t-butyl alcohol by various reagents, e.g. Bu^t_2O_2 , $\text{CrO}_2(\text{OBu}^t)$, $\text{Pb}(\text{OAc})_4$, Br_2 , or O_2 (12)
- (iv) from the reaction of $\text{CrCl}_3 \cdot 3\text{THF}$ with NaOBu^t and CuCl (12)
- (v) addition of cuprous chloride to a suspension of $\text{LiCr}(\text{OBu}^t)_4$ in refluxing tetrahydrofuran (12)

The first method was used originally to prepare $\text{Cr}(\text{OBu}^t)_4$ and a number of pure tetra-t-alkoxides were prepared through method two.

Benzene is preferred as the solvent since it aids in the removal of tertiary-butyl alcohol through the formation of an azeotrope.

Cr(IV) alkoxides are d^2 systems with a characteristic blue color ascribed to absorption in the $15,000\text{ cm}^{-1}$ region interpreted in terms of the three d-d transitions expected for a tetrahedral d^2 complex:

${}^3T_2(F) \leftarrow {}^3A_2(F) (9100\text{ cm}^{-1})$;
 ${}^3T_1(F) \leftarrow {}^3A_2(15,200\text{ cm}^{-1})$; ${}^3T_1(P) \leftarrow {}^3A_2(25,000\text{ cm}^{-1})$
 with $10Dq = 9430\text{ cm}^{-1}$ and $B = 795\text{ cm}^{-1}$ (16). However, the lowest energy bands were doublets (8700, 9500, and 13,700, $15,750\text{ cm}^{-1}$) suggesting a lowering in symmetry to D_{2d} , which would split the T terms (16).

Bradley et al. (12) has prepared several t-amyl alkoxides and the mixed alkoxides. Table IV lists these compounds along with their physical properties (12).

TABLE IV

Physical properties of Cr(IV)-t-alkoxides (12)

Compound*	MP	Volatility ^b	IR ^c	μ
Cr(OBu ^t) ₄	36-37	66/2.7	623	2.82
Cr(OCMe ₂ Et) ₄	liquid ^a	110/2.5	633	2.79
Cr(OCMeEt ₂) ₄	liquid ^a	135/2.5	625	2.79
Cr(OCe ₃) ₄	liquid ^a	decomp.	-	-
Cr(OSiEt ₃) ₄	viscous	decomp.	-	-
	liquid			

a liquid at 20°; b bath temp, °C/mm₁.
 c Cr-O stretching mode $\nu_3(t_2)$, cm^{-1} .
 * All were royal blue in color.

They are all low-melting solids, paramagnetic, and can be easily distilled in vacuo; molecular-weight determinations (cryoscopic in cyclohexane) showed that they are monomeric(12). Thermochemical measurements(17) have shown that for $\text{Cr}(\text{OBu}^t)_4$ $\Delta H^\circ_f = -305$ kcal/mole, implying considerable thermodynamic stability. Also it was noticed, in the spectroscopic work (UV region) with dilute solutions in cyclohexane, that $\text{Cr}(\text{OBu}^t)_4$ was less readily hydrolyzed than $\text{Ti}(\text{OBu}^t)_4$. This hydrolytic effect can be related to a kinetic effect with the ligand-field stabilized d^2 system for Cr(IV) having a higher activation energy to nucleophilic attack by water than the d^0 , Ti(IV) system(12).

$\text{Cr}(\text{OBu}^t)_4$ shows a noticeably slow alcoholysis and a mixed alkoxide $\text{Cr}(\text{OBu}^t)_2(\text{OCMe}_2\text{Et})_2$ was obtained from a reaction involving $\text{Cr}(\text{OBu}^t)_4$ and t-pentyl alcohol(12). The Cr(IV) system retains a high oxidizing potential ($E^\circ = +2.1$ Volts) and attempts to prepare primary or secondary alkoxides led to oxidation of the ligand with formation of the Cr(III) alkoxide, aldehydes or ketones, e.g. (12).

Similarly, attempts to synthesize Cr(IV) compounds in

higher co-ordination states by exchange reactions with chelating ligands, e.g. acetic anhydride, hexafluoroacetone, always led to redox reactions and formation of Cr(III) tris-chelates(12). For example, the reaction of $\text{Cr}(\text{OBu}^t)_4$ with hexafluoroacetylacetone forms the chromium(III) complex, t-butyl alcohol and hexafluoroacetone; acetic anhydride reacted to yield acetone, and t-butyl alcohol. The stability of Cr(IV) tertiary butoxide is clearly due to the absence of alpha CH bonds and this also explains the ready formation of the triethylsilyloxy derivative, $\text{Cr}(\text{OSiEt}_3)_4$ (12).

General Overview of the Chemistry of Transition Metal Alkoxides as Related to Chromium Alkoxides.

Transition metal alkoxides have been known for a long time but an intensive study of their chemistry has only been recently attempted; most of these studies have centered around the preparation and characterization of the transition metal alkoxides(15).

Physical properties. The tendency to expand their coordination by polymerization through alkoxy bridging is a characteristic feature of the alkoxides(15).

The degree of polymerization of the solids seems to depend on the coordination number of the metal and the steric bulk of the surrounding groups. Thus, the more highly branched the alkoxy group, the lower the degree of polymerization(15). The monomeric nature of t-butoxides, in many cases, is ascribed to large steric effect(15). A similar trend is observed in the alkoxides; the lower, less sterically hindered alkoxides are less volatile due to a higher degree of polymerization. The alkoxides do not seem to form many coordination compounds with donor molecules such as alcohols or amines(15). The few adducts known include:

An explanation by Bradley(15) implies that since these compounds all contain the iso-propyl or iso-butyl group, it may indicate that these molecules are too sterically hindered to polymerize, but still can accept donor molecules(15). Hagikara and Yamazaki found that $\text{Cr}(\text{OBu}^t)_4$ did not polymerize styrene in benzene solution but on addition of methanol polymerization occurred along with the formation of $\text{Cr}(\text{OMe})_3$, Bu^tOH , and formaldehyde(15). Apparently, methanol produced radicals during the reaction. Wiberg and Foster(19) using

^{15}O -labelled water in a medium of 91% acetic acid and 0.23 M perchloric acids showed that in the hydrolysis of $\text{Cr}(\text{OBu}^t)_4$, the Cr-O bonds were cleaved. Subsequently, they also observed that $\text{Cr}(\text{OBu}^t)_4$, dissolved in styrene, was stable for a week showing that butoxo radicals were not produced, thus confirming the earlier work of Hagihara and Yamazaki(18). Magnetic susceptibility showed that for all of the $\text{Cr}(\text{OR})_4$ compounds measured, the magnetic moments are close to the spin-only value of 2.83 for a d^1 system(12).

Chemical properties.

a) Hydrolysis: With the simple exception of alkoxides with extremely bulky ligand groups, all transition metal alkoxides undergo rapid hydrolysis giving hydrated metal oxides(20):

The hydrolysis reaction involves cleavage of the M-O bond. In the hydrolysis of $\text{Ti}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_4$, only neo-pentyl alcohol was formed; if C-O bond cleavage occurred, there would have been a rapid Meerwein rearrangement of the intermediate carbonium ion to give t-amyl alcohol(15).

b) Alcoholysis: Interchange reaction between alcohol and many alkoxides has been used by Bradley as a preparative method(15):

Exchange is fast in cases where steric hindrance is not a major factor. However, for bulky ligands (e.g. t-butyl, t-amyl, etc.) the exchange is slow(15). The mechanism of the reaction is not fully understood; Varma and Mehrota(21) gave the following comparative reactivity of alkoxy groups in alcoholysis as: $\text{MeO} > \text{EtO} > \text{Pr}^i\text{O} > \text{Bu}^t\text{O}$.

c) Reaction with Carbonyl Compounds. The products from the reaction of alkoxides and carbonyl compounds were found to depend on the basicity of the alkoxide(15). In a Cannizzaro-like reaction, the Tischenko reaction converts alkoxides into esters using metal alkoxides such as aluminium ethoxide(15):

As is characteristic of Cannizzaro reactions, the reaction probably goes through a hydride transfer. In the well-known Meerwein-Ponndorf-Verley reaction, aldehydes or ketones are converted to alcohols in the presence of alkoxides(15):

d) Reaction with Anhydrides and Ethers. Metal alkoxides react with anhydrides and esters to give transesterification products(15):

Statement of purpose.

The purpose of the present study was to prepare, characterize and study the chemistry of new chromium(IV) butoxides. Several exchange reactions were performed as well as oxidation of fluorinated alcohols. Chromium(IV) tertiary butoxide was selected as the most convenient compound in the group. A summary of the reactions studied is given in Table V.

TABLE V

REACTIONS DISCUSSED IN CHAPTER III.

<u>REACTANTS</u>		<u>PRODUCTS</u>
$\text{CrF}_3 + \text{F}_2$	--->	CrF_5
$\text{CrF}_5 + \frac{1}{2} \text{Cl}_2$	--->	$\text{CrF}_4 + \text{ClF}$
$\text{CrCl}_3 + 3 \text{LiNEt}_2$	--->	$\text{Cr(NEt}_2)_4 + \text{Cr(NEt}_2)_2$
$\text{Cr(OC}_4\text{H}_9)_4 + 4 \text{AgCF}_3\text{COO}$	--->	$\text{Cr(CF}_3\text{COO)}_4 + 4 \text{C}_4\text{H}_9\text{OAg ?}$
$\text{Cr(OC}_4\text{H}_9)_4 + 4 \text{HF}$	--->	$\text{CrF}_4 + 4 \text{C}_4\text{H}_9\text{OH ?}$
$\text{Cr(OC}_4\text{H}_9)_4 + 4 \text{CF}_3\text{CH}_2\text{OH}$	--->	$\text{Cr(OCH}_2\text{CF}_3)_4 + 4 \text{C}_4\text{H}_9\text{OH ?}$
$\text{Cr(OC}_4\text{H}_9)_4 + 4 (\text{CF}_3)_2\text{CHOH}$	--->	$\text{Cr(OCH(CF}_3)_2)_4$ $+ 4 \text{C}_4\text{H}_9\text{OH ?}$
$\text{Cr(OC}_4\text{H}_9)_4 + \text{C}_6\text{F}_5\text{OH}$	--->	*
$\text{Cr(OC}_4\text{H}_9)_4 + (\text{C}_6\text{H}_5)_3\text{SiOH}$	--->	*
$\text{Cr(OC}_4\text{H}_9)_4 + (\text{CF}_3)_3\text{COH}$	--->	*
$\text{Cr(NEt}_2)_3 + 3 \text{CF}_3\text{CH}_2\text{OH}$	--->	$\text{Cr(OCH}_2\text{CF}_3)_3$ *
$\text{Cr(NEt}_2)_3 + 3 (\text{CF}_3)_2\text{CHOH}$	--->	$\text{Cr(OCH(CF}_3)_2)_3$ *

? the +4 oxidation state of chromium in these products is questionable.

* products not fully characterized.

B. FLUORINATED HYPOCHLORITES.

For many years, research with organic hypochlorites was limited due to the instability of the hydrocarbon systems. In 1969, perfluorinated alkyl hypochlorites were reported(22). These new compounds, unlike their hydrocarbon analogs, are stable. For example, CH_3OCl decomposes explosively at room temperature while CF_3OCl is stable up to 150°C . The fluorinated hypochlorites have generated much interest and excitement in this field. In addition to the hypochlorite, $(\text{CF}_3)_3\text{COCl}$ (23), various fluorinated hypochlorites have been prepared. The list include:

CF_3OCl , $\text{C}_2\text{F}_5\text{OCl}$, $i\text{-C}_3\text{F}_7\text{OCl}$, $\text{CF}_2\text{ClCF}(\text{CF}_3)\text{OCl}$, $\text{ClO}(\text{CF}_2)_5\text{OCl}$, and SF_5OCl (22).

The preparation of fluorinated hypochlorites seem to follow a regular pattern: the first five in the above list are most conveniently prepared through the cesium fluoride catalyzed addition of chlorine monofluoride to the appropriate carbonyl compound at low temperatures. Pentafluorosulfur hypochlorite is prepared through an analogous reaction in which F_4SO is used rather than a carbonyl compound(22).

F-(tert-butyl) hypochlorite, $(\text{CF}_3)_3\text{COCl}$, was first prepared by the reaction between $(\text{CF}_3)_3\text{COH}$ and ClF at room

temperature(23). The reaction of sodium hydride with the parent alcohol in diethyl ether to form the sodium salt of F-(tert-butyl) alcohol provided an alternative preparative method. Further reaction of the purified salt with ClF under ambient temperature gave the product in essentially quantitative yield(23).

Previous to the formation of F-(tert-butyl) hypochlorite, only primary and secondary perfluoroalkyl hypochlorites had been synthesized(23). The new perhaloalkyl hypochlorites are easily prepared in high yields, in most cases, through the metal fluoride catalyzed reaction of perhaloalkyl carbonyl compounds with chlorine monofluoride.

The general preparation of hypochlorites involved the addition of ClF across a carbonyl double bond in the presence of a catalyst:

The catalyst normally employed was either a metal fluoride, generally CsF, but not KF or RbF(22,24); a Lewis

acid HF, BF₃, AsF₅ but not PF₅(42); or the gaseous FNO(26) have been successfully used. The chlorofluorination technique appears to be quite general and was also used to prepare the difunctional compound, decafluoropentane-1,5-dihypochlorite:

as well as the inorganic pentafluorosulfur hypochlorite:

The hydrolytic stability of the fluorinated hypochlorites appear to be related to the degree of fluorination in the compound, with the more highly fluorinated compound having a higher degree of susceptibility towards hydrolysis. Thus (CF₃)₃COC1 was shown to be least hydrolytically stable in the series:

The thermal stability of the hypochlorites is shown by the ease with which they decompose at elevated temperatures. In particular, CF₃OCl decomposes slowly at 150°(22). The other hypochlorites are, in general, less stable (or more reactive) than CF₃OCl with the order of stability given by the series(22):

Hypochlorites have provided a convenient route to the

preparation of various butoxides. Many of these are listed in Table VI(31). Table VII also lists the reactions of F-(tert-butyl) hypochlorite studied in our laboratory by Dr. G. L. Gard, JoAnn Canich et al.(27).

Polyfluoroalkyl hypochlorites add readily and, in most cases, nearly quantitatively to both unsubstituted and halogen-substituted terminal olefins.

The use of mercurial, $(\text{CF}_3)_2\text{COHgCl}$, from the reaction of F-(tert-butyl) hypochlorite with mercury metal in the presence of a solvent(28) has provided yet another useful reagent for the introduction of the F-(tert-butoxy) groups into a number of compounds containing a labile halogen. Table VIII lists several of these reactions(31).

Heptafluoroisopropyl hypochlorite. While a great deal of attention has been given to CF_3OCl and $(\text{CF}_3)_3\text{COCl}$, only a limited number of studies have been carried out with $(\text{CF}_3)_2\text{CFOCl}$. The preparation of heptafluoroisopropyl hypochlorite, $i\text{-C}_3\text{F}_7\text{OCl}$, follows the usual preparative technique(22). Hexafluoroacetone and a slight excess of ClF were condensed into a CsF vessel at -20° . Reactions are normally left overnight, although 2 to 3 hours is sufficient for reaction completion. Heptafluoroisopropyl hypochlorite is a clear yellow liquid; the infrared spectrum shows absorptions at 1320(s), 1250(s), 1215(m),

TABLE VI

SOME OF THE KNOWN REACTIONS OF F-t-BUTYL HYPOCHLORITE(31)

<u>REACTANTS</u>		<u>PRODUCTS</u>
$(\text{CF}_3)_3\text{COC1} + \text{SO}_2$	---->	$(\text{CF}_3)_3\text{COSO}_2\text{C1}$
$(\text{CF}_3)_3\text{COC1} + \text{CO}$	---->	$(\text{CF}_3)_3\text{COC(O)C1}$
$(\text{CF}_3)_3\text{COC1} + \text{CF}_2=\text{CF}_2$	---->	$(\text{CF}_3)_3\text{COCF}_2\text{CF}_2\text{C1}$
$(\text{CF}_3)_3\text{COC1} + \text{CH}_2=\text{CH}_2$	---->	$(\text{CF}_3)_3\text{COCH}_2\text{CH}_2\text{C1}$
$2 (\text{CF}_3)_3\text{COC1} + \text{CF}_3\text{SC1}$	---->	$[(\text{CF}_3)_3\text{CO}]_2\text{SC1CF}_3 + \text{Cl}_2$
$(\text{CF}_3)_3\text{COC1} + \text{CF}_3\text{S(O)C1}$	---->	$\text{CF}_3\text{S(O)OC}(\text{CF}_3)_3 + \text{Cl}_2$
$4 (\text{CF}_3)_3\text{COC1} + \text{SCl}_2$	---->	$\text{S}[\text{OC}(\text{CF}_3)_3]_4 + 3 \text{Cl}_2$
$8 (\text{CF}_3)_3\text{COC1} + \text{S}_2\text{Cl}_2$	---->	$2 \text{S}[\text{OC}(\text{CF}_3)_3]_4 + 5 \text{Cl}_2$
$(\text{CF}_3)_3\text{COC1} + \text{CS}_2$	---->	$\text{S}[\text{OC}(\text{CF}_3)_3]_4$
$(\text{CF}_3)_3\text{COC1} + \text{PClF}_4$	---->	$(\text{CF}_3)_3\text{COPF}_4 + \text{Cl}_2$
$2 (\text{CF}_3)_3\text{COC1} + \text{PCl}_2\text{F}_3$	---->	$[(\text{CF}_3)_3\text{CO}]\text{PF}_3 + 2 \text{Cl}_2$
$5 (\text{CF}_3)_3\text{COC1} + \text{PCl}_5$	---->	$\text{P}[\text{OC}(\text{CF}_3)_3]_5 + 5 \text{Cl}_2$
$3 (\text{CF}_3)_3\text{COC1} + \text{PCl}_3$	---->	$\text{P}[\text{OC}(\text{CF}_3)_3]_3 + 3 \text{Cl}_2$
$2 (\text{CF}_3)_3\text{COC1} + \text{PF}_3$	---->	$[(\text{CF}_3)_3\text{CO}]_2\text{PF}_3 + \text{Cl}_2$
$(\text{CF}_3)_3\text{COC1} + \text{NOCl}$	---->	$(\text{CF}_3)_3\text{CONO} + \text{Cl}_2$
$4 (\text{CF}_3)_3\text{COC1} + \text{S}_4\text{N}_4$	---->	$\text{N}_4\text{S}_4[\text{OC}(\text{CF}_3)_3]_4 + 2 \text{Cl}_2$
$3 (\text{CF}_3)_3\text{COC1} + \text{BCl}_3$	---->	$\text{B}[\text{OC}(\text{CF}_3)_3]_3 + 3 \text{Cl}_2$
$2 (\text{CF}_3)_3\text{COC1} + \text{CrO}_2\text{Cl}_2$	---->	$\text{CrO}_2[\text{OC}(\text{CF}_3)_3]_2 + 2 \text{Cl}_2$
$4 (\text{CF}_3)_3\text{COC1} + \text{TiCl}_4$	---->	$\text{Ti}[\text{OC}(\text{CF}_3)_3]_4 + 4 \text{Cl}_2$
$(\text{CF}_3)_3\text{COC1} + \text{Hg}$	---->	$(\text{CF}_3)_3\text{COHgCl}$

TABLE VII

SOME OF THE REACTIONS OF F-t-BUTYL HYPOCHLORITE
STUDIED IN DR. GARD'S LABORATORY AT
PORTLAND STATE UNIVERSITY

<u>REACTANTS</u>		<u>PRODUCTS</u>
$(\text{CF}_3)_3\text{COCl} + \text{VOCl}_3$	---->	$\text{VO}[\text{OC}(\text{CF}_3)_3]_3$
$(\text{CF}_3)_3\text{COCl} + \text{SbCl}_5$	---->	$\text{Sb}[\text{OC}(\text{CF}_3)_3]_x\text{Cl}_y$
$(\text{CF}_3)_3\text{COCl} + \text{Cu}_2\text{Cl}_2$	---->	no reaction occurred
$(\text{CF}_3)_3\text{COCl} + \text{MCl}_4$	---->	no reaction occurred
(M=Sn, Si, Ti)		
$(\text{CF}_3)_3\text{COCl} + \text{Pb}$	---->	$\text{Pb}[\text{OC}(\text{CF}_3)_3]_2$
$(\text{CF}_3)_3\text{COCl} + \text{Te}$	---->	$\text{Te}[\text{OC}(\text{CF}_3)_3]_4$
$(\text{CF}_3)_3\text{COCl} + \text{Bi}$	---->	$\text{Bi}[\text{OC}(\text{CF}_3)_3]_3$
$(\text{CF}_3)_3\text{COCl} + \text{Si}$	---->	no reaction occurred
$(\text{CF}_3)_3\text{COCl} + \text{S}_8$	---->	$\text{S}[\text{OC}(\text{CF}_3)_3]_4$
$(\text{CF}_3)_3\text{COCl} + \text{Br}_2$	---->	$[(\text{CF}_3)_3\text{COBr}]$
	---->	$(\text{CF}_3)_2\text{CO} + \text{CF}_3\text{Br}$
$(\text{CF}_3)_3\text{COCl} + \text{I}_2$	---->	$\text{I}[\text{OC}(\text{CF}_3)_3]_3$
$(\text{CF}_3)_3\text{COCl} + \text{CF}_3\text{I}$	---->	$\text{CF}_3\text{I}[\text{OC}(\text{CF}_3)_3]_2$
$(\text{CF}_3)_3\text{COCl} + \text{ICF}_2\text{CF}_2\text{I}$	---->	$[(\text{CF}_3)_3\text{CO}]_2\text{ICF}_2\text{CF}_2\text{I}[(\text{CF}_3)_3\text{CO}]_2$ *
$(\text{CF}_3)_3\text{COCl} + \text{SF}_5\text{CF}_2\text{CF}_2\text{I}$	---->	$\text{SF}_5\text{CF}_2\text{CF}_2\text{I}[(\text{CF}_3)_3\text{CO}]_2$ *
$(\text{CF}_3)_3\text{COCl} + \text{C}_6\text{F}_5\text{I}$	---->	$\text{C}_6\text{F}_5\text{I}[(\text{CF}_3)_3\text{CO}]_2$ *

* Dr. G. L. Gard et al., accepted for publication, Inorg. Chem. 1986.

TABLE VIII
THE REACTIONS OF $(\text{CF}_3)_3\text{COHgCl}$ (31)

<u>REACTANTS</u>		<u>PRODUCTS</u>
$(\text{CF}_3)_3\text{COHgCl} + \text{CH}_3\text{I}$	--->	$\text{CH}_3\text{OC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + \text{CF}_3\text{SCl}$	--->	$\text{CF}_3\text{SOC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + \text{CF}_3\text{C}(\text{O})\text{Br}$	--->	$\text{CF}_3\text{C}(\text{O})\text{OC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + \text{CF}_3\text{C}(\text{O})\text{SCl}$	--->	$\text{CF}_3\text{C}(\text{O})\text{SOC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + (\text{CH}_3)_3\text{SiCl}$	--->	$(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + (\text{CH}_3)_3\text{SiH}$	--->	$(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_3$ + $(\text{CF}_3)_3\text{COH}$
$(\text{CF}_3)_3\text{COHgCl} + \text{CH}_3\text{C}(\text{O})\text{Cl}$	--->	$\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CF}_3)_3$
$(\text{CF}_3)_3\text{COHgCl} + \text{CNCI}$	--->	$(\text{CF}_3)_3\text{COCN}$

1190(m), 1155(s), 1005(s), 795(w), 755(m), 728(m), and 665(w); these include the characteristic absorptions of C-F and O-Cl bonds(22). The ^{19}F NMR spectrum contains unresolved peaks at +81.3 and +143, relative to a CCl_3F internal standard(22).

Due to the hydrolytic instability of these hypochlorites in general, melting point and boiling point of the heptafluoroisopropyl hypochlorite have not been determined. However, Gould et al.(22) have calculated a boiling point of 22° for the hypochlorite and a latent heat of vaporization of $6378 \text{ cal.mol}^{-1}$.

Heptafluoroisopropyl hypochlorite is fairly stable at room temperature. However, at higher temperatures it decomposes to $\text{CF}_3\text{C}(\text{O})\text{F}$, CF_3Cl , $(\text{CF}_3)_2\text{C}=\text{O}$ and ClF according to the following mechanistic scheme(22):

However, with heptafluoroisopropyl hypochlorite, its reaction with olefins has been reported for only one system; $(\text{CF}_3)_2\text{CFOCl}$ adds to TFE quantitatively to yield the corresponding ether according to the equation:(29)

PERFLUORO-tert-AMYL HYPOCHLORITE:

As the chemistry of fluorine and its organic compounds progresses in Dr. Gard's laboratory, it becomes increasingly evident that a vast new field of study is being opened up. The knowledge that one trifluoromethyl group in the alpha position of an alcohol is all that is necessary to allow preparation of the corresponding hypochlorite by reaction with chlorine monofluoride and the experimental evidence provided by the use of other known hypochlorites, prompted this inquisition into the preparation of the new perfluoro-t-amyl hypochlorite from the parent perfluoro-t-amyl alcohol.

This study thus reports the first preparation of the perfluoro-t-amyl hypochlorite, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OC1}$. Its preparation followed an adaptation of the method used by Gould, Anderson, Young and Fox to prepare other

hypochlorites(22). The parent alcohol, perfluoro-t-amyl alcohol, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$, prepared through the method used by Graham and Weinmayr(30), and chlorine monofluoride were condensed into a reaction vessel and maintained at low temperatures for several hours. Subsequent transfer to a CsF metal reaction vessel and fractionation at -78°C gave the hypochlorite in quantitative yield.

The fluoro-t-amyl hypochlorite represents yet another significant extension of the new class of compounds, known as fluoroalkyl hypochlorites. All previous fluorine-substituted hypochlorites (R_fOCl) are structurally related to known fluoxy compounds (R_fOF), although the two types of materials differ significantly in their chemical behavior(23). Interestingly, treatment of fluoro alcohols containing carbon-hydrogen bonds with such a powerful oxidizing agent as chlorine monofluoride did not produce extensive degradation(40).

While no information is available on the use of $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$ in the hypochlorite synthesis, in the series; CH_3OH , $\text{CF}_3\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$, $(\text{CF}_3)_3\text{COH}$, where hydrogen atoms are progressively replaced by trifluoromethyl groups, the last three members react readily and non-violently with ClF to produce excellent yields of the corresponding hypochlorite(23). The hypochlorite will probably provide routes for synthesizing

other fluorinated systems with the parent fluoro-amyl group. The reactions studied are summarized in Table IX.

Applications of F-(tert-butoxides) have included use as textile-treating agents, monomers, plasticizers, solvents and surfactants(31). Being volatile, the metal F-(tert-butoxides) have potential uses as metal vapor sources and gas transport reagents.

Following the work done on F-(tert-butyl) hypochlorite in preparation of new F-(tert-butoxides) by G. L. Gard and JoAnn Canich et al.(27,31) in our laboratory, the purpose of this study was to

- i) study the chemistry of heptafluoroisopropyl hypochlorite via its reaction with metals, non-metals and olefinic systems.
- ii) prepare and study the chemistry of a new hypochlorite, perfluoro-t-amyl hypochlorite.

PERFLUORO-t-AMYL ALCOHOL:

Several perfluoro alkyl carbinols- C_6F_5OH , $[CF_3(CF_2)_n]_2CHOH$ and $(CF_3)_3COH$ (not including the one described here), have been prepared through the interaction of the perfluoro alkyl Grignard reagents with suitable reagents such as fluoroester, (e.g. CF_3COOEt), perfluoroketones (e.g. CF_3COCF_3), perfluoroaldehydes (e.g. CF_3CHO) (32,33,34).

TABLE IX

REACTIONS DISCUSSED IN CHAPTER IV

<u>Reactants</u>			<u>Product</u>
$(\text{CF}_3)_2\text{CFOCl}$	+ I_2	--->	*
$(\text{CF}_3)_2\text{CFOCl}$	+ Hg	--->	*
$(\text{CF}_3)_2\text{CFOCl}$	+ TiCl_4	--->	*
$(\text{CF}_3)_2\text{CFOCl}$	+ $\text{SF}_5\text{CH}=\text{CH}_2$	--->	$(\text{CF}_3)_2\text{CFOCHSF}_5\text{CH}_2\text{Cl}$
$(\text{CF}_3)_2\text{CFOCl}$	+ $\text{SF}_5\text{CH}=\text{CF}_2$	--->	$(\text{CF}_3)_2\text{CFOCHSF}_5\text{CF}_2\text{Cl}$
$(\text{CF}_3)_2\text{CFOCl}$	+ $\text{CH}_2=\text{CH}_2$	--->	$(\text{CF}_3)_2\text{CFOCH}_2\text{CH}_2\text{Cl}$
$\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$	+ ClF	--->	$\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$

* Products not fully characterized

Perfluoro-t-pentyl alcohol, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$, was first made by Graham and Weinmayr(30) 1965, through the TFE interaction with hexafluoroacetone on a CsF catalyst surface.

The mechanism of the reaction is believed to involve the anion: CF_3CF_2^- formed by the interaction of TFE and CsF(30):

Subsequent attack of the anion on the equilibrium concentration of the ketone gives the perfluoro-t-amyl anion which upon acidification releases the alcohol in high yield. Graham and Weinmayr(30) have established the structure of $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$ by means of F^{19} resonance spectrum with three peaks at +4.08, +42.73 and -3.37ppm and relative areas of 3,2, and 6 respectively(30).

Other catalyst systems have also been used; NaF and LiF with diglyme produced small yields of the product but required higher temperatures and pressures(30). The use of acetonitrile and benzonitrile with KF, characterized by the near absence of side-reaction TFE polymerization, produced small to moderate yields(30).

CHAPTER II

EXPERIMENTAL METHODS

Apparatus

Vacuum systems. A glass vacuum system was used for most operations requiring the use of a high vacuum or inert atmosphere conditions. The vacuum system consisted of a manifold constructed from 20 mm O.D. Pyrex glass tubing and fitted with four Eck and Krebs 2mm high vacuum stopcocks to which Pyrex 10/30 \$ ground glass outer joints were attached. The manifold was evacuated through a liquid nitrogen (-196°C) cooled trap by a Welch Duo-seal rotary pump. The vacuum was monitored by a Televac thermocouple gauge, and was generally maintained between 10^{-3} to 10^{-2} torr. Higher pressures within the manifold could be measured when desired, by a two legged mercury manometer to ± 0.1 torr. All joints in the vacuum system were lubricated with Apiezon-M grease. Figure 1 depicts the basic features of the vacuum system.

For the manipulation of gaseous materials capable of attacking the Pyrex glass, a metal vacuum line was used. An example is the fluorine line. Elemental fluorine was

Figure 1. Glass vacuum manifold

transferred in a manifold constructed from a $\frac{1}{4}$ in. O.D. copper tubing, to which one VWR valve and one Whitey brass valve terminated in an outer 10/30 \$ brass joint and the outer terminated in $\frac{1}{4}$ in. copper tubing and was used as a venting outlet. Between the fluorine tank and the manifold was fitted a $\frac{1}{2}$ in. O.D. copper U-tube cooled to -100°C . which is used to remove HF impurity. The fluorine was connected directly to the line by Swagelok fittings, and an ACCO diaphragm type vacuum pressure gauge was employed to measure pressures up to 30 psi. The fluorine line was set up in the laboratory hood. Figure 2 is a diagram of this line.

Reaction vessels.

Reaction vessels used in this study could be divided broadly into two types: low pressure systems and high pressure ones. For most low pressure reactions performed, a 75ml or 100ml Pyrex glass reaction vessel equipped with a Kontes high vacuum Teflon valve and Teflon stirring bar, and tipped with a Pyrex 10/30 \$ inner joint for attachment to the vacuum line was used. High pressure reactions were performed in a 75ml to 100ml Hoke Monel vessel equipped with a Whitey stainless steel valve, and tipped with a metal 10/30 \$ inner joint. Reactions which were not compatible with either glass or stainless steel, were carried out in a 35ml Kel-F reaction vessel fitted with a

Figure 2. Fluorine Vacuum Line

Whitey brass valve and a brass 10/30 \$ inner joint.

Vacuum traps. These were constructed of two concentric Pyrex glass tubes of 10mm and 20mm I.D. A piece of a 10mm I.D. Pyrex glass tubing connected the outer tube to a Kontes high vacuum Teflon valve. The inner tube, used to trap substances that would otherwise attack glass, was connected to another Kontes high vacuum Teflon valve. Both valves were fitted with 10/30 \$ inner joints for attachment to the vacuum line or other vessels.

Dry Box. All air sensitive compounds were handled under an atmosphere of nitrogen in a Kewaunee Scientific Equipment dry box. Nitrogen was passed into the box through a CaSO_4 tube and inside the box was a constant exposure of a large surface area of phosphorus pentoxide used as a drying agent; air circulation inside the box provided a proper contact between the nitrogen atmosphere and the surface of the P_4O_{10} ; this was achieved by the use of an electric circulating fan placed inside the dry box.

Glove bag. A plastic glove bag made of polyethylene provided a quick alternative to the dry box. This was usually flushed with liquid nitrogen and regularly maintained under an atmosphere of nitrogen whenever in use.

Physical methods.

Infrared spectra. The infrared spectra over the range of 4600cm^{-1} to 400cm^{-1} were recorded on a FT-IR, Nicolet 20DX spectrophotometer equipped with Disk module, Data processor unit and a 7470A Hewlett-Packard plotter. Gaseous samples were run in a glass gas cell fitted with brass 10/30 \$ inner joint for attachment to the vacuum line. The cell windows were NaCl, KBr, or KRS-5 and the path length of the cell is 8.25cm. The spectra of non-volatile liquids were obtained neat between NaCl or KBr windows. Spectra calibration was achieved with internal polystyrene film.

Nuclear Magnetic Resonance Spectra. Nuclear magnetic resonance spectra were recorded with a Varian Model EM-390 spectrometer operating at 90MHz for proton and 84.67MHz for fluorine resonances.

Chemical shifts were reported relative to TMS for proton spectra, and Freon-11 for fluorine spectra with downfield resonances reported as positive values.

Gas Chromatography. Gas chromatographs were obtained with the use of a Varian 3700 Gas Capillary chromatograph. The instrument contained a strip chart recorder, a Varian CDS III Chromatography Data System capable of automatically integrating the sample peaks and retention

times. The capillary column used was a 30 meter SE-54 with an O.D. of 0.8mm; a split ratio of 90 to 1 was needed for a typical sample injection of 0.6 microliters. Column temperatures were appropriately adjusted to give the best possible separation within a 15 minute run time.

Reagents.

Benzene. Spectral grade benzene was purchased from Mallinckrodt, washed and distilled.

Cesium fluoride. CsF was purchased from Specialty Chemicals and was dried under vacuum before use.

Chlorine. Cl_2 was purchased from Matheson, Coleman and Bell Company, and was used without further purification.

Chlorine monofluoride. ClF was purchased from Ozark Mahoning Company and used without further purification.

Chromium(III) chloride. CrCl_3 was obtained from Alfa Products and used without further purification.

Chromium(III) diethylamine. $\text{Cr}(\text{NEt}_2)_3$ was prepared in Dr. G. L. Gard's laboratory by Dr. R. Sheets.

Chromium pentafluoride. CrF_5 was prepared in the laboratory through the fluorination of chromium trifluoride at 270-303°C for 29 hours.

Chromium tetradiethylamide. $\text{Cr}(\text{NEt}_2)_4$ was synthesized by an adaptation of the method used by Bradley

et al.(17). CrCl_3 in THF was added to a cold LiNEt_2 in diethyl ether and stirred for 8 hours at room temperature. Subsequent filtration and disproportionation gave the tetradiethylamide in quantitative yield.

Chromium tetrafluoride. CrF_4 was prepared in the laboratory through the chlorination of CrF_5 at 183°C for 22 hours.

Chromium tetra-tertiary butoxide. $\text{Cr}(\text{OBu}^t)_4$ was synthesized by the alcoholysis of the chromium tetradiethylamide, a method originally used by Bradley et al.(17).

Chromium trifluoride. CrF_3 , (98% purity), was purchased from Research Organic/Inorganic Chemical Company and was used without further purification.

Dibenzene chromium. $(\text{C}_6\text{H}_6)_2\text{Cr}$ was purchased from Alfa Products and used without further purification.

Di-tertiary-butyl peroxide. (98% purity) was obtained from PFALTZ and Bauer, Inc., and was used without further purification.

Ethylene. $\text{CH}_2=\text{CH}_2$ was purchased from Airco Inc., Rare and Specialty Gas Dept., and was used without further purification.

Fluorine. F_2 (98% purity), was purchased from Air Products. The fluorine was transferred directly from the tank, through a copper U-tube containing nickel helices

and cooled to -100°C to remove HF. All manipulations involving the use of fluorine were carried out on a metal line as described under "Physical Methods" section.

Heptafluoroisopropyl hypochlorite. $i\text{-C}_3\text{F}_7\text{OCl}$ was synthesized by an adaptation of the method used by Gould, Anderson, Young and Fox(22). $(\text{CF}_3)_2\text{C=O}$ was condensed into a reaction vessel containing CsF catalyst and excess ClF was immediately added. The vessel was allowed to warm to -20°C and remain there for 8 hours. Fractionation between -95°C and -196°C gave the product (-95°C) in quantitative yield.

Heptafluorosulfur ethylene. $\text{SF}_5\text{CH=CF}_2$ was prepared in Dr. Gard's laboratory by R. J. Terjeson.

Hexafluoroacetone. $(\text{CF}_3)_2\text{C=O}$ was purchased from DuPont and Co., Freon Products Division, and was used as received.

Hexafluoropropanol. $\text{CF}_3\text{CHOHCF}_3$ was purchased from Eastman Chemicals and was used without further purification.

Hydrogen fluoride. HF was purchased from Matheson Company and was used without further purification. All manipulations involving the use of HF as a solvent were carried out in a Kel-F vessel.

Iodine. I_2 was purchased from Mallinckrodt and was ground into finer particles for a larger surface area

prior to use.

Lithium diethylamine. LiNEt_2 was purchased from Alfa Products and was used without further purification. Great care was used in handling this chemical due to its high flammability.

Mercury. Analytical reagent grade mercury was purchased from American Scientific and Chemical Company, Amachem, and was used without further purification.

Pentafluorophenol. $\text{C}_6\text{F}_5\text{OH}$ was obtained from PCR/SCM and was used without further purification.

Pentafluorosulfur ethylene. $\text{SF}_5\text{CH}=\text{CH}_2$ was prepared in Dr. G. L. Gard's laboratory by R. J. Terjeson.

Perfluoro-t-pentyl alcohol. $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$ was synthesized by an adaptation of the method used by Graham and Weinmayr(30). Cesium fluoride was slurried in diglyme in a pressure vessel. $(\text{CF}_3)_2\text{C}=\text{O}$ was condensed at room temperature into the reaction vessel and TFE was subsequently added at 95-100°C (with terpene inhibitor) over a 50 hour period. Filtration and acidification gave the alcohol in good yields.

Perfluoro-t-pentyl hypochlorite. $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$ was synthesized through the reaction of $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$ and ClF on a CsF catalyst surface, following the method used by Young, Anderson, Gould and Fox(22) to prepare other hypochlorites. The parent alcohol,

perfluoro-tert-pentyl alcohol, prepared by the adaptation of the method used by Graham and Weinmayr(30) and a slight excess of ClF were condensed into a passivated stainless steel reaction vessel and left at -20°C for 17 hours. The contents of the vessel were then condensed into a second metal reaction vessel containing a dried excess of CsF catalyst. The vessel was shaken frequently while slowly warming to 0°C . Fractionation method was employed to separate the $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OC1}(-78^{\circ})$ from excess ClF (-196°) and $\text{HF}\cdot\text{CsF}$ complex.

tert-Butanol. was purchased from EM Science Company and used without further purification.

Tetrafluoro ethylene. TFE was purchased from PCR/SCM and was used without further purification.

Titanium tetrachloride. TiCl_4 (99.5%) was purchased from MCB and used without further purification.

Trifluoroethanol. $\text{CF}_3\text{CH}_2\text{OH}$ was purchased from Specialty Chemicals and was used without further purification.

Triphenyl Silanol. $(\text{C}_6\text{H}_5)_3\text{SiOH}$ was obtained from PCR/SCM and was used without further purification.

Solvents.

The following solvents were used in the course of

this study: Benzene, Tetrahydrofuran (THF), Petroleum ether, Diethyl ether, Pentane, Carbon tetrachloride (CCl_4), Freon-11, Dichloromethane, Diethylene glycol dimethyl ether (diglyme). Each was dried and refluxed from appropriate drying agent prior to use.

CHAPTER III

SYNTHESIS OF Cr(IV) COMPOUNDS

INTRODUCTION.

Chromium tetrafluoride.

The preparation of CrF_4 reported by Von Wartenberg in 1941 was repeated in the study. Von Wartenberg prepared the tetrafluoride by passing F_2 over chromium metal, chromium(III) chloride or fluoride at $300^\circ - 350^\circ\text{C}$. In a collaborative study with Dr. Hedberg at the Oregon State University, CrF_4 was prepared and purified by reacting CrF_5 with Cl_2 and subliming the CrF_4 solid. This method was preferred in part due to its ease in preparing small quantities of CrF_4 .

Chromium tetradiethylamide.

$\text{Cr}(\text{NEt}_2)_4$ prepared through an adaptation of the method used by Basi et al. provided a good route to the synthesis of the chromium(IV) butoxide. $\text{Cr}(\text{NEt}_2)_4$ synthesis was enhanced by the fact that it is highly volatile, thereby easily removed from the chromium(II) dialkylamide during the disproportionation step:

Alcoholysis of the $\text{Cr}(\text{NEt}_2)_4$ gives the tetra(alkoxide) in good yield:

Synthesis of Cr(IV) compounds: Reactions of Chromium(IV)-t-butoxide.

Reactions carried out with $\text{Cr}(\text{OC}_4\text{H}_9)_4$ are twofold: exchange reactions and oxidation reactions. It was the purpose of this study to prepare and characterize new and interesting Cr(IV) alkoxides using $\text{Cr}(\text{OC}_4\text{H}_9)_4$ in exchange reactions with alcohols and metal salts.

In previous studies with primary and secondary alcohols, $\text{Cr}(\text{OC}_4\text{H}_9)_4$ was found to yield essentially Cr(III) alkoxides and oxidation products. Thus the rate of exchange was slow, and in these cases much slower than oxidation. Table X lists the results of alcoholysis with 1° and 2° alcohols(12).

Chromium(IV) has been of interest for some time because of its role as an intermediate in chromic acid oxidation reactions. From the work of Rocek and Radkowsky(35) and a number of investigators(15,36,37,38), the role of chromium(IV) in the chromic acid oxidation of alcohols has been elucidated. The work of these investigators has led to the following mechanism(15):

TABLE X

RESULTS OF THE REACTION OF $\text{Cr}(\text{OC}_4\text{H}_9)_4$ WITH
PRIMARY AND SECONDARY ALCOHOLS

<u>Alcohol</u>	<u>Alkoxide Produced</u>	<u>Drying Temp. °C</u>	<u>Cr(%)</u>		<u>Oxidation Product</u>
			<u>Found</u>	<u>Calc.</u>	
MeOH	$\text{Cr}(\text{OMe})_3$	150-160	35.3	35.7	Formaldehyde
EtOH	$\text{Cr}(\text{OEt})_3$	80	27.5	27.8	Acetaldehyde
$\text{Pr}^{\text{n}}\text{OH}$	$\text{Cr}(\text{OPr}^{\text{n}})_3$	120-130	22.5	22.7	Propionaldehyde
$\text{Bu}^{\text{n}}\text{OH}$	$\text{Cr}(\text{OBu}^{\text{n}})_3$	80	19.1	19.2	n-Butyraldehyde
$\text{Pr}^{\text{i}}\text{OH}$	$\text{Cr}(\text{OPr}^{\text{i}})_3$	60	22.3	22.7	Acetone

Both Rocek and Trahanovsky have defined the role of Cr(IV) on the basis of disproportionation reactions. When cyclobutanol was introduced into this system under conditions in which its reaction with Cr(VI) is slow, the formation of an organic oxidation product, gamma-hydroxybutyraldehyde, was observed(35).

The use of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ in the oxidation of alcohols and selected metal and non-metal ions have also been studied; see Table XI.

A mechanism for the chromium(IV) oxidation reaction has been postulated as follows(15):

primary isotope effect of 1.6 to 2.4 $k_{\text{H}}/k_{\text{D}}$

TABLE XI

<u>Reactants</u>		<u>Product</u>
Cr(IV)-t-butoxide + primary alcohol		---> Cr(III) + Aldehyde
Cr(IV)	+ secondary alcohol	---> Cr(III) + Ketone
Cr(IV)	+ Phenols	---> Cr(III) + Hydroquinones
Cr(IV)	+ I^-	---> Cr(III) + I_2
Cr(IV)	+ Fe(II)	---> Cr(III) + Fe(III)
Cr(IV)	+ Sn(II)	---> Cr(III) + Sn(IV)

In the reaction with fluorinated alcohols, it was our hope to isolate new fluorinated Cr(IV) compounds. Instead, in all cases the results were not satisfactory. The products contained Cr(III) systems and other side reaction products that were not easily separated and consequently, were not well characterized.

In reactions with HF, the presence of CrF_4 was doubtful. Attempts to sublime the brown solid product obtained, resulted in the formation of a viscous liquid which evidently affected the sublimation process. This prevented further purification and characterization of the products. A similar difficulty was encountered in the CF_3COOAg reaction.

The reactions of $\text{Cr}(\text{OC}_4\text{H}_9)_4$, $\text{C}_6\text{F}_5\text{OH}$ and $(\text{C}_6\text{H}_5)_3\text{SiOH}$ resulted in the formation of products not fully characterized. There were associated difficulties in purification and separation of the products obtained. In most cases, the presence of Cr(III) was detected.

The reactions of $\text{Cr}(\text{OC}_4\text{H}_9)_4$, while they did not yield the desired products, revealed a lot of information on the chemistry of the transition metal alkoxides in the +4 oxidation state and in particular, the Cr(IV) alkoxide. The high stability, high rate of hydrolysis, low degree of polymerization and slowness to alcoholysis characteristic of chromium(IV) alkoxides were manifested in these

reactions. Owing to the hydrolytic and light sensitivity of $\text{Cr}(\text{OC}_4\text{H}_9)_4$, reactions were generally carried out in thoroughly dried vessels, well-shielded from light. Solvents were distilled with appropriate drying agents. The major factor affecting these reactions is presumably steric hinderance. With the bulky t-butyl group in $\text{Cr}(\text{OC}_4\text{H}_9)_4$, exchange reactions for example, were highly hindered.

EXPERIMENTAL.

Preparation of CrF_5 . To 32.0 mmole of pre-dried CrF_3 in a passivated 100 ml Monel vessel equipped with two stainless steel ball bearings and a Whitey stainless steel valve, was added 156 mmole of F_2 . The reaction vessel was maintained at $270\text{--}303^\circ\text{C}$ for 29 hours with shaking at 15 minute intervals. The vessel was later cooled to -196°C for 4 minutes and the top heated so as to move any CrF_5 trapped on the top sides of the vessel. The vessel was then brought up to -78°C to remove any excess F_2 . 32.0 mmole of red CrF_5 (100% yield based on CrF_3) was obtained.

Preparation of CrF_4 .

To 32.0 mmole of CrF_5 was added 16 mmole of Cl_2 in a 100 ml Monel vessel equipped with two stainless steel ball bearings and a Whitey stainless steel valve. The reaction vessel was heated at 183°C for 22 hours with intermittent

shaking. Excess Cl_2 , ClF and ClF_3 were removed at -78°C after condensing all trapped CrF_4 at -196°C ; 32.0 mmole of trapped CrF_4 (100% yield based on CrF_5) was obtained. The infrared spectrum of CrF_4 , see appendix, contained the following absorptions: 730-845(s), 470-642(m).

Preparation of $\text{Cr}(\text{OC}_4\text{H}_9)_4$:

$\text{Cr}(\text{OC}_4\text{H}_9)_4$ was prepared through the alcoholysis of $\text{Cr}(\text{NEt}_2)_4$. Different methods were adapted for the preparation of $\text{Cr}(\text{NEt}_2)_4$. However, in the method frequently employed in this study, 42.3 mmole of CrCl_3 was dissolved in 50 ml THF and slowly added to 126.8 mmole of LiNEt_2 in 50 ml diethyl ether at -20°C . The mixture was maintained at -20°C for 10 minutes. It was then slowly brought to room temperature and stirred for 20 hours. After removing the solvent in vacuo, the green solid was extracted with 30/60 petroleum ether. The bulk of the petroleum ether was removed in vacuo, leaving a dark green viscous liquid which was treated with 274.4 mmole of tert-butanol dissolved in 75 ml petroleum ether under the conditions of reflux for 60 minutes. Upon removal of the solvent in vacuo, 4.43g of a dark blue solid was obtained. The infrared spectrum of the blue solid consists of absorptions at 2973(s), 2924(mw), 1560(vw), 1461(mw), 1384(mw), 1356(ms), 1229(m), 1160(s), 1124(m), 1025(w), 927(vs), 899(m), 786(s), 625(s), and $470(\text{m})\text{ cm}^{-1}$.

CF₃CH₂OH with Cr(OC₄H₉)₄:

To a three neck 100 ml round bottom flask containing 45 ml benzene was dissolved 4.848 mmole Cr(OC₄H₉)₄. 23.84 mmole of CF₃CH₂OH was added dropwise and a refluxing unit was connected. After refluxing at 75-80°C temperature for 24 hours there was no appreciable change from the initial green color formed upon mixing, the refluxing was continued for 20 days. The color changed slowly from green to dark green during the refluxing. At the end of the refluxing, the solvent was removed in vacuo and a deep green solid (1.0 g) was left behind. The solid decomposed without melting at 190°C. The infrared spectrum of the product (see appendix) was similar to that found when Cr(NEt₂)₃ reacted with CF₃CH₂OH (see appendix). Analysis of the trap materials showed the presence of the starting alcohol and the solvent.

(CF₃)₂CHOH with Cr(OC₄H₉)₄. Two preparative techniques, a and b, were employed:

a. To a 75ml Pyrex glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar was added 1.631 mmole of Cr(OC₄H₉)₄. The reaction vessel was briefly pumped on the vacuum line before 13.27 mmole of (CF₃)₂CHOH was condensed at -196°C. The reaction vessel was allowed to attain room temperature and then stirred for 11 hours.

After checking for volatile materials, the solvent was removed in vacuo leaving 0.720g of a brown solid which was dried in vacuo for several hours. The infrared spectrum of the volatile materials showed the presence of unreacted alcohol. The brown solid was stable to 360°C and did not sublime when subjected to vacuum sublimation at 200°C. Interestingly, the infrared spectrum (see appendix) of this solid was found to be similar to the green solid obtained in part b after it has been extracted (by R. Sheets) with CCl_4 . However, the result obtained when the same alcohol reacted with $\text{Cr}(\text{NEt}_2)_3$ was different in its infrared patterns.

b. To a 200 ml round bottomed flask equipped with a Teflon stirring bar was added 4.651 mmole of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ and 50 ml of benzene. The reaction vessel was flushed with N_2 and 22.14 mmole of $(\text{CF}_3)_2\text{CHOH}$ was added. The resulting dark mixture was refluxed at 50-60°C for 25 days. During the refluxing period, the mixture turned from blue to blue-green and finally 1.0g of a moist-looking dark-green solid was formed. After removing solvent and volatile materials in vacuo, the green solid was dried for several hours. The infrared spectrum of the volatile materials showed the presence of the starting alcohol and the solvent. The solid was soluble in

benzene, THF and hydrolyzed in H_2O . It was stable in air and decomposed without melting at $182^\circ C$.

$(CF_3)_3COH$ with $Cr(OC_4H_9)_4$.

To a 75 ml Pyrex glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, was added 0.431 mmole of $Cr(OC_4H_9)_4$ and 2.966 mmole of $(CF_3)_3COH$. The reaction vessel was warmed up slowly from $-196^\circ C$ to $0^\circ C$. Formation of a green colored solid was noticed within 10 minutes at $0^\circ C$. After removing the volatile materials in vacuo, the recovered green solid was pumped for several hours to dryness. 0.0376 g was obtained. The infrared spectrum of the volatile materials showed the presence of the unreacted alcohol. Other than taking the IR spectrum of this solid, the reaction was not further studied.

C_6F_5OH with $Cr(OC_4H_9)_4$.

To a 100 ml 3-necked round bottomed flask equipped with a Telfon stirring bar was added 1.860 mmole of $Cr(OC_4H_9)_4$ dissolved in 15 ml benzene and stirred under nitrogen. 9.890 mmole of C_6F_5OH dissolved in 10 ml benzene was added dropwise to the stirring $Cr(OC_4H_9)_4$ solution in the hood. The reaction was slowly warmed to $63^\circ C$ in a water bath. A green compound formed after two hours at this temperature. The infrared spectrum of the trap materials showed the presence of the starting

alcohol. After removing solvent and volatile materials in vacuo, 0.32g of a green solid was obtained. The IR spectrum of this solid, (see appendix) was not conclusive and the reaction was not studied further.

(C₆H₅)₃SiOH with Cr(OC₄H₉)₄.

To a 100 ml 3-neck round bottomed flask equipped with a Teflon stirring bar was added 0.291 mmole of Cr(OC₄H₉)₄ and 15 ml of benzene. Under nitrogen, 1.154 mmole of (C₆H₅)₃SiOH dissolved in 10 ml of benzene was added dropwise and allowed to stir for 15 minutes. A refluxing apparatus was connected and the mixture was refluxed at 75-80°C for one hour. Analysis of the volatile materials showed the presence of a mixture of unreacted alcohol and benzene. The green solid obtained after removing solvent in vacuo was dried for several hours. The solid was insoluble in common solvents and decomposed at 230°C without melting. An IR spectrum (see appendix) of the solid was not conclusive and further studies were not undertaken.

HF with Cr(OC₄H₉)₄.

To a 35 ml Kel-F reaction vessel fitted with a Whitey brass valve and a brass 10/30 \$ inner joint was added 7.171 mmole of Cr(OC₄H₉)₄. 79.0 mmole of HF was condensed into the reaction vessel at -196°C. The reaction vessel

was allowed to warm up to room temperature. On warming slowly, different colors were noted- dark blue, blue-green and green. Upon stirring, presumably HF fumes were noted in the reaction vessel. After 6 hours at room temperature, volatile materials were removed in vacuo leaving 1.67g brown solid. An attempt was made to sublime the solid in vacuo at different temperatures: 55°C (4 min.), 60°C (11 min.), 67°C (25 min.) and slowly to 171°C (20 min.). Although the solid did not sublime, some viscous liquid material was seen on the sides of the reaction vessel. Attempt to obtain an IR sample of these viscous material was not successful. The solid was stable in air but hydrolyzed in water, forming a yellow-green mixture. It was stable to 360°C and was slightly soluble in benzene, THF and carbon tetrachloride. The infrared spectrum is shown in the appendix. Analysis of the product indicated that possibly a mixed alkoxide fluoride, $\text{Cr}[(\text{CH}_3)_3\text{CO}]_2\text{F}_2$ (not CrF_4) was produced. The peak at 498cm^{-1} indicated strongly the presence of a Cr-F bond. Thus, based on the product yield, a partial exchange reaction presumably occurred during the reaction.

CF_3COOAg with $\text{Cr}(\text{OC}_4\text{H}_9)_4$.

To a 75 ml Pyrex glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 0.6387 mmole of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ was added and stirred in 15 ml of benzene. The

reaction mixture was stirred at room temperature while 1.973 mmole of CF_3COOAg dissolved in 10 ml benzene was slowly added. A constant nitrogen (gas) supply was maintained for 20 minutes. A greenish compound resulted within 30 minutes. The mixture was slowly heated to 70° in a water bath and then left overnight. Upon removal of the solvent in vacuo, 0.450g green-brown solid was obtained, with a melting point of $238-244^\circ\text{C}$. The infrared spectrum of the solid (see appendix) was not conclusive and further studies were not undertaken.

$\text{CF}_3\text{CH}_2\text{OH}$ with $\text{Cr}(\text{NEt}_2)_3$.

To a 100 ml round bottomed flask equipped with a Teflon stirring bar was added 3.358 mmole of $\text{Cr}(\text{NEt}_2)_3$ dissolved in pentane. 14.80 mmole of $\text{CF}_3\text{CH}_2\text{OH}$ was added dropwise, each drop resulting in an immediate formation of a purple-brown solid. The reaction vessel was flushed with N_2 gas and refluxed at 36°C for one hour and then stirred at room temperature for 18 hours. After removing solvent and volatile materials in vacuo, the brown solid was washed with dried CH_2Cl_2 to remove the amine by-product. The infrared spectrum of the volatile materials indicated the presence of the solvent. The brown solid left behind weighed 0.710g. The solid was soluble in CH_2Cl_2 , slightly soluble in Freon-11 and

decomposed with slight melting at 166°C. IR spectrum of the solid was obtained and analyzed (see appendix).

(CF₃)₂CHOH with Cr(NEt₂)₃.

To a 250 ml round bottomed flask equipped with a Teflon stirring bar was added 4.104 mmole of Cr(NEt₂)₃ dissolved in pentane. 16.66 mmole of (CF₃)₂CHOH was added dropwise, each drop resulting in the formation of brown fumes and a purple brown solid. The reaction vessel was flushed with N₂ gas, refluxed for one hour and then stirred at room temperature for 18 hours. After removing solvent and volatile materials in vacuo, the brown solid obtained was washed with CH₂Cl₂ to remove the amine by-product. The infrared spectrum of the volatile materials showed the presence of the solvent and the alcohol. The 1.720g brown solid left behind was soluble in CH₂Cl₂ and Freon-11 and has a melting point of 99-100°C. IR spectrum of the solid was obtained and analyzed (see appendix).

INFRARED SPECTRA.

The infrared absorptions are tabulated in Table XII and the actual spectra are shown in the Appendix. For the fluorinated compounds, strong absorptions observed in the region 1145-1305 cm⁻¹ were attributable to the C-F stretching frequency(49,50). Therefore in these solids

TABLE XII

INFRARED ABSORPTION BANDS FOR Cr(IV)/Cr(III)

(cm⁻¹) **CrF₄

470(m), 530(s,b), 580(m),
648(m), 750(ms), 810(m),
845(m).

CF₃CH₂OH with Cr(OC₄H₉)₄

2938(m), 2882(w,sh),
1454(w), 1278(m), 1204(m,sh),
1165(vs), 1104(s,sh),
961(s), 899(w), 831(m),
796(w), 739(w), 686(m),
676(m), 595(w,b), 475(m).

(CF₃)₂CHOH with Cr(OC₄H₉)₄

1616(b), 1468(w), 1363(s),
1278(s), 1257(mw), 1215(m),
1180(vs), 1131(s,sh),
1089(s), 969(w), 892(m),
857(s), 744(s), 688(s),
667(w), 533(m).

(CF₃)₃COH with Cr(OC₄H₉)₄

2973(m), 1700(w), 1616(mw),
1462(w), 1370(m), 1250(vs),
1201(s), 1166(s), 1124(w,sh),
962(vs), 899(w), 744(w),
723(s), 533(w).

** m=medium, s=strong, vs=very strong, sh=shoulder,
w=weak, ms=medium strong, mw=medium weak, b=broad.

TABLE XII (cont.)

 C_6F_5OH with $Cr(OC_4H_9)_4$

1698(m), 1653(vw), 1501(vs),
 1468(s,sh), 1377(vw), 1196(w),
 1162(ms), 1123(m), 1044(m,sh),
 790(vs), 893(w,b), 763(vw),
 739(m), 645(w), 581(w,b),
 505(w,b).

 $(C_6H_5)_3SiOH$ with $Cr(OC_4H_9)_4$

2973(w), 2924(w), 1960(m),
 1890(m), 1778(w), 1665(w),
 1588(s), 1567(w), 1482(s),
 1426(s), 1377(mw), 1335(mw),
 1257(w), 1187(m,sh), 1117(m),
 997(w), 969(m,b), 892(m,b),
 737(m), 695(m), 632(vw),
 596(m), 547(w), 499(m),
 463(w), 435(ms), 414(vw).

 HF with $Cr(OC_4H_9)_4$

2959(s), 2868(m,sh), 1637(m,b),
 1468(s), 1364(s), 1201(s),
 1124(w), 969(m), 899(mw),
 498(m,b).

 CF_3COOAg with $Cr(OC_4H_9)_4$

2980(w), 1785(vw,sh), 1679(vs),
 1475(w), 1433(s), 1370(s),
 1194(vs), 1124(s), 962(ms),
 899(m), 850(m), 793(ms),
 723(s), 653(w), 617(m), 596(w),
 519(m), 463(m).

TABLE XIII (cont.)

 $\text{CF}_3\text{CH}_2\text{OH}$ with $\text{Cr}(\text{NEt}_2)_3$

2973(w), 2924(mw), 2846(mw),
1616(m,b), 1454(m), 1384(w),
1271(s), 1201(w), 1124(vs),
955(vs), 894(mw), 828(ms),
674(ms), 512(m,b).

 $(\text{CF}_3)_2\text{CHOH}$ with $\text{Cr}(\text{NEt}_2)_3$

2980(m), 2938(m), 2875(m),
1609(mw), 1461(w,sh), 1510(s),
1457(w), 1440(ms), 1321(ms),
1278(s), 1250(m), 1208(ms),
1166(vs), 1089(s), 976(m),
941(w), 786(m), 744(s),
681(vs), 639(w), 533(m).

containing fluoroligands, the absorptions at 1124 to 1321 cm^{-1} are attributable to C-F stretching frequencies. Also the absorptions at 723 to 744 cm^{-1} are ascribed to CF_3 deformation modes usually observed at 715 to 750 cm^{-1} (50). The metal oxygen (M-O) stretching vibrations are generally below 650 cm^{-1} (48) and thus the characteristic absorptions observed below 650 cm^{-1} are attributable to these bands. In the compounds formed from the reactions of $\text{Cr}(\text{OC}_4\text{H}_9)_4$ with HF, $(\text{C}_6\text{H}_5)_3\text{SiOH}$, CF_3COOAg and $\text{C}_6\text{F}_5\text{OH}$ other absorptions not fully characterized are noted.

Due to incomplete exchange/oxidation reactions in some alcohol compounds, absorptions at 3300 to 3600 cm^{-1} are attributable to O-H bands with their associated deformation modes at 1000 to 1300 cm^{-1} (39). The latter absorptions are masked by the stronger C-F absorptions in the case of fluorinated alcohols.

Summary/Conclusion.

The study of Cr(IV) tetrafluoride was conducted in part with Dr. Kenneth Hedberg at the Oregon State University in order to determine its structure in the gas phase. Previously, Dr. Gard's group at Portland State University has worked with Dr. Hedberg's group in studying the structures of CrO_2F_2 and CrF_5 . A summary of their

results show that for CrO_2F_2 , the Cr-F has a single bond length of 1.71Å. The length of the Cr=O double bond was found to be 1.56Å(1). Observed values were close to calculated values, for single Cr-F and double Cr=O bonds. Similar conclusion was reached in the case of the bond types in CrO_2Cl_2 (40). It was also found that chromyl halides, unlike the sulfonyl halides, in general, did not obey the valence shell electron-pair repulsion (VSEPR) theory. In the chromyl halides, the angle between the bonds to the oxygen atom is found to be slightly smaller than that between halogen bonds(1). Both Garner et al. and Beattie et al., in comparing F-M-F (M=S or Cr) angles in SO_2F_2 and CrO_2F_2 , observed that coulombic repulsion between the fluorine atoms should be greater in CrO_2F_2 than in SO_2F_2 due to the larger atomic charges in CrO_2F_2 (41,42).

For CrF_5 , Dr. Hedberg's group found that the average symmetry of CrF_5 molecule was appreciably different from D_{3h} symmetry. The average bond angles in CrF_5 are significantly distorted (3° - 10°) from the trigonal bipyramidal values(6).

Following the above studies, it became of interest to determine the gas phase structure of CrF_4 . Dr. Hedberg's group have completed the experimental studies and preliminary analysis favors a tetrahedral structure for

CrF_4 . Earlier matrix isolation IR studies(43) also favored a tetrahedral structure. The magnitude of the $\text{Cr}^{50}-\text{Cr}^{54}$ separation (10.0 cm^{-1}) indicates a tetrahedral rather than a square planar. Tetrahedral CrF_4 would be expected to have a ${}^3\text{A}_2$ group state, and should not show any static Jahn-Teller distortions. The absorptions found at 784.3 and 303cm^{-1} in the matrix study, were assigned as the T_2 stretch and T_2 bend respectively, and the assignment was supported by an analysis of the isotope pattern for the stretch(43).

Chromium(IV) Butoxides.

The study on Cr(IV) butoxides was primarily undertaken in order to prepare and characterize other Cr(IV) derivatives through simple exchange reactions. Our results show that Cr(IV) butoxide was not a useful reagent for preparing other Cr(IV) systems. Our results with CF_3COOAg , $\text{CF}_3\text{CH}_2\text{OH}$, and HF indicate strong evidence of oxidation/decomposition reactions. The knowledge obtained from Cr(IV) oxidation of alcohols, coupled with the instability of Cr(IV) compounds and steric effects, have enabled us to associate these oxidation reactions with possible decomposition reactions.

Since the Cr(IV) systems were resulting in

oxidation/decomposition products, it was decided to look into some interesting fluorinated Cr(III) alkoxides. It has been shown that $\text{Cr}(\text{NEt}_2)_3$ disproportionates easily into Cr(II) and Cr(IV) according to the reaction:

It is thus possible that similarly, $\text{Cr}(\text{OR})_3$ could undergo such disproportionation reaction and yield the Cr(IV) alkoxide. This possibility has not been investigated.

Recommendation:

Despite the unsatisfactory results obtained in Cr(IV) reactions, much information was obtained and it is hoped that future studies will unveil a clearer understanding of the general chemistry of Cr(IV) derivatives, alkoxides in particular.

CHAPTER IV

FLUORINATED HYPOCHLORITES

INTRODUCTION.

Heptafluoro-iso-propyl and perfluoro-t-amyl hypochlorites.

The chemistry of the fluorinated hypochlorites was extended to include the heptafluoroisopropyl hypochlorite, $i\text{-C}_3\text{F}_7\text{OCl}$, and the newly made perfluoro-t-amyl hypochlorite, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$. Also, since other fluoroalkyl hypochlorites add to olefins, it was of interest to see whether heptafluoroisopropyl hypochlorite would behave in a similar fashion. The reaction of $i\text{-C}_3\text{F}_7\text{OCl}$ with $\text{CF}_2=\text{CF}_2$ suggests that it too may have a rich chemistry in preparing new fluorine containing ethers. Thus the reaction of the hypochlorite with selected olefins other than TFE was studied.

In general, reactions were run at low temperatures in order to limit the thermal decomposition of the hypochlorite. Other precautionary measures include shielding from light since light enhances the rate of decomposition of the hypochlorite. The hypochlorite was handled with extreme care as it was found by accident to

be shock sensitive.

The byproducts, $(\text{CF}_3)_2\text{C}=\text{O}$ and CF_3Cl offer an advantage in the reactions performed with the hypochlorite as they were easily removed from the reaction mixture simply by vacuum transfer, thus leaving in many cases, the desired product in good yield. In some cases, the reaction mechanism favors ClF elimination and when this was observed, the desired product was not found.

In reaction with metal and non-metal oxidants, satisfactory results were not obtained. This was attributed to the labile nature of the lone fluorine atom on the alpha-carbon of the hypochlorite. It is presumed that in these reactions, the fluorine migrated easily, leading to the formation of mixed products.

In this study a more extensive series of reactions between polyfluoroalkyl hypochlorites and selected olefins have been carried out. The reaction was found to be quite general for terminal olefins and in most cases, the addition is predominantly unidirectional. The generalized equation below represents the reactions described in this work:

The results of the addition of $(\text{CF}_3)_2\text{CFOCl}$ to

olefinic compounds have not been fully investigated. However, for a number of systems, it has been found that CF_3OCl adds in such a way as to produce only one isomer. For example CF_3OCl reacted with $\text{CHCl}=\text{CH}_2$ to form only $\text{CF}_3\text{OCHClCH}_2\text{Cl}$ (44). This discounts the possible addition invoking Markonikov's reaction to yield syn products(44,46). In all our compounds, only one isomer was found, the addition being essentially unidirectional with Cl adding to the least hindered position. It has been found that in some olefinic systems, COF_2 elimination occurred either in place of CF_3OCl addition or with CF_3OCl addition(44,45,46). A radical mechanism was invoked to rationalize the observation(44). For $(\text{CF}_3)_2\text{CFOCl}$ addition, the following radical ion mechanism can be postulated:

The above mechanism would explain that chlorine attaches to carbon(b) containing the less electronegative substituents whereas carbon(a) with more electronegative substituents adds F via fluorine abstraction or $(\text{CF}_3)_2\text{CFO}^\bullet$ via recombination. In our compounds, abstraction was not observed. It is possible that a second oxidation-reduction step occurs prior to 4 or 5 as shown in eqn(7).

The heptafluoroalkoxide ion could recombine to give the desired ether or undergo $\text{CO}(\text{CF}_3)_2$ elimination with the resulting F^- adding to the carbocation. It is presumed that unsymmetrical hydrogen-containing olefins would be more susceptible to F/F^- abstraction with concomitant formation of $\text{CO}(\text{CF}_3)_2$ than more symmetrical systems(44).

When $i\text{-C}_3\text{F}_7\text{OCl}$ was reacted with Hg, the product formed was not successfully analyzed but weight comparisons suggested that HgF_2 or HgClF was formed. It was thought that the mercurial, $i\text{-C}_3\text{F}_7\text{OHgCl}$ would be

formed.

With I_2 , presence of IF_5 was detected and the decomposition products of the hypochlorite; similar reaction with $(CF_3)_3COCl$ gave $I[OC(CF_3)_3]_3$. Similarly, the reaction with $TiCl_4$ was not satisfactory as the weight changes suggested that fluorination again occurred. The products were not successfully analyzed.

EXPERIMENTAL.

$TiCl_4$ with $i-C_3F_7OC1$. To a 100 ml Pyrex glass vessel equipped with a Kontes Telfon valve and Teflon stirring bar, was added 0.913 mmole of $TiCl_4$. 4.898 mmole of $i-C_3F_7OC1$ was condensed into the reaction vessel at $-196^\circ C$. The vessel was allowed to warm to $0^\circ C$ and kept there for 18 hours. After removing volatile materials in vacuo, 0.2125g of an orange solid was obtained. The infrared spectrum of the volatile material showed the presence of $(CF_3)_2CO$ and $CF_3(O)F$. Subsequent addition of excess $i-C_3F_7OC1$ did not improve the product yield. The solid was found to decompose at $232^\circ C$ and was unstable in air. IR spectrum of the orange solid was not conclusive and further studies were not undertaken.

I_2 with $i-C_3F_7OC1$.

To a 100 ml Pyrex glass vessel equipped with a Teflon

Kontes valve and Teflon stirring bar was added 0.4196 mmole of I_2 , and 7.211 mmole of $i-C_3F_7OCl$ was condensed into the reaction vessel at $-196^\circ C$. The reaction vessel was allowed to warm to $0^\circ C$. by itself. After 4 hours at $0^\circ C$, a white semi solid was formed. The reaction was left to stir at $0^\circ C$ for another 18 hours since some unreacted materials were noticed. After removing volatiles at $-78^\circ C$, 0.20g white crystalline solid was obtained. The infrared spectrum of the volatile materials showed the presence of $(CF_3)_2C=O$ and the infrared spectrum of the white solid showed the presence of IF_5 . Attempt to determine the melting point of the solid was not successful.

Hg with $i-C_3F_7OCl$.

To a 75 ml Pyrex glass vessel equipped with a Teflon Kontes valve and Teflon stirring bar was added 1.480 mmole of Hg. The reaction vessel was pumped on the vacuum line and reweighed to determine the exact weight of the Hg. 2.402 mmole of Freon-11 and 3.080 mmole of $i-C_3F_7OCl$ were condensed into the reaction vessel at $-196^\circ C$. The reaction vessel was allowed to attain room temperature slowly and then stirred for 16 hours. Additional 1.820 mmole of CCl_3F and 1.950 mmole of $i-C_3F_7OCl$ were condensed into the reaction vessel and then stirred at room temperature for an additional 24 hours. Volatile

materials were removed at -78°C , -27°C , and room temperature respectively. The infrared spectrum of the volatiles showed the presence of $(\text{CF}_3)_2\text{C}=\text{O}$, $\text{CF}_3\text{C}(\text{O})\text{F}$ and CF_3Cl . The 0.387g white solid obtained did not show the characteristic absorptions of the mercury complex in the C-F region. The weight changes suggest that HgClF or HgF_2 presumably were formed. The solid decomposed at 275°C , forming a yellow solid. It was insoluble in common organic solvents and easily attacked by air forming a yellow to orange solid.

$\text{SF}_5\text{CH}=\text{CH}_2$ with $i\text{-C}_3\text{F}_7\text{OCl}$.

To a 75 ml Pyrex glass vessel equipped with a Teflon Kontes valve and Teflon stirring bar was condensed 16.75 mmole of $\text{SF}_5\text{CH}=\text{CH}_2$ and 21.09 mmole of $i\text{-C}_3\text{F}_7\text{OCl}$ at -196°C . The reaction vessel was slowly brought to 0°C and stirred for 15 hours. The infrared spectrum of the volatile materials showed the presence of CF_3COF , $(\text{CF}_3)_2\text{C}=\text{O}$ and CF_3Cl . After removing volatile materials at -196°C , the clear liquid was distilled. The fraction boiling at $89\text{--}127^{\circ}\text{C}$, and the pot residue were mixed, washed with water, and after drying over MgSO_4 for $2\frac{1}{2}$ hours, were redistilled. The liquid boiling at $124\text{--}128^{\circ}\text{C}$, 1.20g, 19.2% was used for IR, NMR and elemental analysis. Elem. Anal.: Calc. for $\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$: S, 8.60;

F, 60.86; C, 16.00; H, 0.81; Cl, 9.47. Found: S, 8.66; F, 60.80; C, 15.97; H, 0.82; Cl, 9.61.

The ^{19}F NMR spectrum for $\text{F}^{\text{a}}\text{SF}_4^{\text{b}}\text{CH}^{\text{c}}\text{ClCH}^{\text{d}}\text{H}^{\text{e}}\text{OC}(\text{CF}_3^{\text{f}})_2\text{F}^{\text{g}}$ contained a doublet at δ 53.2(F^{b}), a doublet of multiplets at δ 73.0(F^{a}), a seven-line pattern at δ -148.5(F^{g}) and a singlet at δ -83.1(F^{f}), with relative areas of 4.0:1.0:1.0:6.0 respectively (theor: 4.0:1.0:1.0:6.0) and coupling constants of $J_{\text{f-g}}=6.0$ and $J_{\text{a-b}}=158$ Hz. The ^1H NMR spectrum contained multiplets at δ 4.7($\text{H}^{\text{d,e}}$) and δ 5.6(H^{c}) ppm, with relative band areas of 1.8:1.0 respectively (theor: 2.0:1.0). The coupling constants are $J_{\text{c-d}}=6.2\text{Hz}$, $J_{\text{c-e}}=6.0\text{Hz}$, $J_{\text{b-c}}=5.1\text{Hz}$ and $J_{\text{d-e}}=6.8\text{Hz}$. See Tables XV and XVI respectively.

$\text{SF}_5\text{-CH=CF}_2$ with $i\text{-C}_3\text{F}_7\text{OCl}$.

To a 100 ml Pyrex glass vessel equipped with a Teflon Kontes valve and Teflon stirring bar was condensed 9.848 mmole of $\text{SF}_5\text{CH=CF}_2$ and 12.38 mmole of $i\text{-C}_3\text{F}_7\text{OCl}$ at -196°C . The reaction was allowed to warm up to 0°C slowly and then stirred at 0°C for 16 hours. Additional stirring was done for $3\frac{1}{2}$ hours at room temperature. The infrared spectrum of the volatile materials showed the presence of $(\text{CF}_3)_2\text{CO}$, CF_3COF , and CF_3Cl . The clear liquid was distilled and the portion boiling at 83°C , (1.16g, 28.7%), was used for IR and NMR studies.

The ^{19}F NMR spectrum for $\text{F}^{\text{a}}\text{SF}_4^{\text{b}}\text{CH}^{\text{c}}\text{ClCF}^{\text{d}}\text{F}^{\text{e}}\text{OC}(\text{CF}_3^{\text{f}})\text{F}^{\text{g}}$

contained multiplets at δ 71.2(F^a) and δ -147.6(F^g) respectively, a doublet at δ 57.4(F^b), and singlets at δ -82.3(F^f) and δ -71.3($F^{d,e}$) respectively. The relative band areas are 1.0:1.0:3.9:6.5:1.5 (theor: 1.0:1.0:4.0:6.0:2.0) respectively; and the coupling constants are J_{a-b} 141.1 Hz and J_{f-g} 21.2 Hz. The 1H NMR spectrum contained multiplets at δ 5.82(H^c) and δ 5.53 (C=C? impurity) respectively and coupling constants of J_{b-c} = 5.4 Hz. See Tables XV and XVI respectively.

$CH_2=CH_2$ with $i-C_3F_7OCl$.

To a 1000 ml Pyrex glass vessel equipped with a Teflon valve was condensed 9.982 mmole of $CH_2=CH_2$ and 10.84 mmole $i-C_3F_7OCl$ at $-196^\circ C$. The reaction vessel was immediately warmed to $0^\circ C$ for 18 hours. Due to the yellow liquid noted, the reaction was presumed incomplete and was stirred at room temperature for an additional 7 hours. The liquid was washed with water, dried over $MgSO_4$ and distilled. The fraction boiling at $79-85^\circ C$, 0.81g, 32.7% was used for IR and NMR studies.

The ^{19}F NMR spectrum for $ClCH_2^aCH_2^bOC(CF_3^c)_2F^d$ contained a doublet at δ -82.5(F^c) and a multiplet at δ -145.2(F^d); with relative band areas of 6.0:1.0 (theor: 6.0:1.0) respectively, and coupling constant of J_{c-d} 2.4 Hz. The 1H NMR contained a set of multiplets

at δ 4.4(H^b) and δ 3.9(H^a) respectively, with relative band areas of 1.0:1.0 (theor: 1.0:1.0) respectively and coupling constant of $J_{a-b}=6.2$ Hz. Elem. Anal.: Calc. for $ClCH_2CH_2OCF(CF_3)_2$. F, 54.00; C, 24.16; H, 1.62; Cl, 14.27. Found: F, 54.20; C, 24.11; H, 1.64; Cl, 14.25.

Preparation of $CF_3CF_2C(CF_3)_2OH$.

To a 100 ml pretreated Monel vessel equipped with two stainless steel ball bearings and Whitey stainless steel valve containing 105.3 mmole of predried CsF was added 25 ml of diethylene glycol dimethyl ether (diglyme) and 122 mmole of hexafluoroacetone was condensed into the reaction vessel at $-196^\circ C$. 188.4 mmole of tetrafluoro ethylene was added in four portions over a four-day period. The reaction vessel was heated at $90-100^\circ C$ for 90 hours with intermittent shaking. After checking for volatile materials at $-130^\circ C$, the reaction vessel was vented in the hood before a clear liquid was extracted with 178 mmole of 96% H_2SO_4 leaving a fluorocarbon residue. The liquid was distilled and the fractions boiling at $65-100^\circ C$ were redistilled in the spinning band equipment. The 8.18g (27.3% yield) clear liquid fraction boiling at $66-67.2^\circ C$ was used for IR and NMR studies.

The ^{19}F NMR spectrum for $CF_3^aCF_2^bC(CF_3^c)_2OH^d$ contained multiplets at δ -121.8(F^b), δ -82.5(F^a) and δ -75.2(F^c) respectively; with relative band areas of

2.0:3.2:6.2 (theor. 2.0:3.0:6.0) and coupling constants of $J_{a-c}=5.9\text{Hz}$ and $J_{b-c}=11.6\text{Hz}$. The ^1H NMR spectrum contained a singlet at $3.82(\text{H}^d)$. The infrared spectrum contained the characteristic O-H stretching frequency at 3627cm^{-1} . See Table XIV and the appendix for the infrared data and the actual spectrum respectively.

Preparation of $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$.

To a 100 ml pretreated Monel vessel equipped with two stainless ball bearings and a Whitey stainless steel valve was condensed 5.00 mmole of $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$ and 5.67 mmole of ClF at -196°C . The reaction vessel was slowly brought up to 0°C and kept there for approximately 18 hours. After removing some volatile materials (HF and excess ClF) at -95°C , the contents of the vessel were condensed into a second metal reaction vessel containing an excess amount of CsF . This reaction vessel was shaken frequently while slowly warmed to 0°C . The volatile $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$ was removed from the CsF by pumping on the CsF vessel through a trap cooled to -196°C . Prior to this transfer, any volatile material at -196°C in the CsF vessel was removed. Analysis of the volatile materials showed the presence of HF , ClF and the decomposition products of the hypochlorite - $(\text{CF}_3)_2\text{C}=\text{O}$, CF_3Cl , $\text{CF}_3\text{CF}_2\text{Cl}$, and $\text{CF}_3\text{CF}_2\text{COCF}_3$. 3.59 mmole (72% yield) of the product was obtained. The sample was

analyzed through IR and NMR spectra.

The infrared spectrum contained a C=O impurity peak presumably from UV decomposition of the hypochlorite in the gas cell during the infrared operation; see Table XIII and the appendix for infrared data and the actual spectrum respectively.

The ^{19}F NMR spectrum for $\text{CF}_3^a\text{CF}_2^b\text{C}(\text{CF}_3^c)_2\text{OCl}$ contained multiplets at δ -115.7, δ -80.4 and δ -67.9 respectively; with relative band areas of 2.0:3.4:6.3 (theor. 2.0:3.0:6.0) and the coupling constants of $J_{a-c}=5.6\text{Hz}$ and $J_{b-c}=11.6\text{Hz}$.

Elemental Analysis for the F-Hypochlorite Compounds.

The elemental analyses of the new fluorinated ethers were carried out by Beller Microanalytisches Laboratorium, Gottingen, West Germany.

Mass Spectral Analysis for the F-Hypochlorite Compounds.

The mass spectra of the new fluorinated ethers were obtained at the University of Idaho. In both compounds, $\text{SF}_5\text{CHClCH}_2\text{OC}_3\text{F}_7$ and $\text{ClCH}_2\text{CH}_2\text{OC}_3\text{F}_7$, the mass spectra contained prominent peaks (M/e) at 69 (CF_3^+) and 63 ($\text{C}_2\text{H}_4\text{Cl}^+$) respectively. None of the compounds exhibited the parent ions in the mass spectra. The mass spectral peaks for these compounds are listed on Table XIII.

INFRARED SPECTRA.

TABLE XIII

MASS SPECTRA DATA FOR F-HYPOCHLORITE COMPOUNDS

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
42	0.9		$\text{C}_2\text{H}_2\text{O}^+$
43	1.5		CCF^+
44	1.3		$\text{C}_2\text{H}_4\text{O}^+$
45	0.3		?
46	0.5		?
47	10.7		CCl^+ , CFO^+
48	0.3		CHCl^+
49	5.1		CH_2Cl^+
50	1.4		CF_2^+
51	1.6		CH_2Cl^+
52	0.1		C_3O^+
55	0.2		C_3F^+
61	1.8		CH_2CCl^+
63	100.0		$\text{C}_2\text{H}_4\text{Cl}^+$
64	2.6		$\text{C}_2\text{H}_3\text{Cl}^+$
65	31.0		$\text{C}_2\text{H}_4\text{Cl}^+$
66	0.6		$\text{C}_4\text{H}_2\text{O}^+$

$$\text{ClCH}_2\text{CH}_2\text{OCF}(\text{CF}_3)_2 \text{ (cont.)}$$

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
69	32.0		CF_3^+
70	0.2		?
73	0.1		$\text{C}_3\text{H}_2\text{OF}^+$
78	0.2		$\text{C}_2\text{F}_2\text{O}^+$
100	1.7		C_2F_4^+
119	3.6		$\text{C}_4\text{HC10F}^+$
143	0.6		$\text{C}_4\text{H}_3\text{F}_4\text{O}^+$
147	2.4		$\text{C}_3\text{F}_5\text{O}^+$
149	4.3		$\text{C}_5\text{ClF}_2\text{O}^+$
150	0.8		C_3F_6^+
169	4.8		C_3F_7^+
179	0.9		$\text{ClCH}_2\text{CH}_2\text{OC}_2\text{F}_4^+ (\text{M}^+ - \text{CF}_3)$
181	0.2		$\text{ClCH}_2\text{CH}_2\text{OC}_2\text{F}_4^+$
185	0.3		$(\text{CF}_3)_2\text{OCF}^+$
199	34.8		$\text{CH}_2\text{OC}_3\text{F}_7^+$
200	1.5		?
212	0.5		$\text{C}_2\text{H}_3\text{OC}_3\text{F}_7^+$
213	0.5		$\text{C}_2\text{H}_4\text{OC}_3\text{F}_7^+ (\text{M}^+ - \text{Cl})$

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
41	0.9		C_2HO^+
42	5.8		$\text{C}_2\text{H}_2\text{O}^+$
43	16.8		C_2F^+
44	7.3		CS^+
45	17.8		HCS^+
46	3.5		?
47	0.7		CFO^+
48	6.1		CHCl^+
49	12.4		CCl^+
50	7.7		CF_2^+
51	4.7		SF^+
52	1.6		C_3O^+
57	0.4		C_2SH^+
58	0.2		C_2SH_2^+
59	0.3		C_2Cl^+
60	1.2		C_2HCl^+
61	58.0		$\text{C}_2\text{H}_2\text{FO}^+$
62	17.4		$\text{C}_2\text{H}_3\text{Cl}^+$
63	18.0		CSF^+
64	5.8		$\text{C}_2\text{H}_3\text{Cl}^+$
65	8.0		C_4HO^+

$$\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2 \text{ (cont.)}$$

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
66	0.2		$\text{C}_4\text{H}_2\text{O}^+$
67	8.4		$\text{C}_4\text{H}_3\text{O}^+$
69	100.0		CF_3^+
70	5.0		SF_2^+
71	0.1		C_3FO^+
72	0.2		C_3HFO^+
73	1.2		$\text{C}_3\text{H}_2\text{FO}^+$
75	0.3		C_2ClO^+
76	1.1		C_2HClO^+
77	3.1		$\text{C}_2\text{H}_2\text{ClO}^+$
78	1.5		$\text{C}_2\text{F}_2\text{O}^+$
79	1.3		$\text{C}_2\text{H}_2\text{ClO}^+$
80	1.3		$\text{C}_2\text{H}_3\text{ClO}^+$
83	72.0		C_4OF^+
86	0.4		$\text{C}_4\text{H}_3\text{OF}^+$
89	37.5		SF_3^+
90	0.3		$\text{C}_3\text{H}_3\text{ClO}^+$
91	1.6		$\text{C}_3\text{F}_2\text{HO}^+$
97	7.7		C_4HSO^+
98	0.3		$\text{C}_4\text{H}_2\text{SO}^+$
99	3.6		$\text{C}_4\text{H}_3\text{SO}^+$

$\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$ (cont.)

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
100	4.4		C_2F_4^+
101	1.0		SF_3C^+
105	0.4		$\text{C}_3\text{H}_2\text{OSF}^+$
107	1.5		C_2ClSO^+
108	0.6		SF_4^+
109	1.1		C_5HSO^+
111	0.5		$\text{C}_3\text{H}_2\text{F}_3\text{O}^+$
113	0.2		SF_3C_2^+
119	13.7		C_4HClFO^+
120	0.4		SF_4C^+
121	0.4		SF_4CH^+
127	16.8		SF_5^+
128	0.5		$\text{C}_3\text{F}_4\text{O}^+$
129	0.9		$\text{C}_3\text{HF}_4\text{O}^+$
131	4.1		C_3F_5^+
132	0.2		C_4HClOS^+
133	1.4		$\text{C}_4\text{H}_2\text{ClOS}^+$
135	0.3		$\text{SF}_4\text{C}_2\text{H}_3^+$

$$\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2 \text{ (cont.)}$$

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
141	1.1		$\text{C}_4\text{HF}_4\text{O}^+$
143	1.2		$\text{C}_4\text{H}_3\text{F}_4\text{O}^+$
145	0.3		$\text{C}_5\text{H}_2\text{ClSO}^+$
147	5.6		$\text{C}_3\text{F}_5\text{O}^+$
148	0.2		$\text{SF}_3\text{C}_2\text{Cl}^+$
149	10.0		$\text{SF}_3\text{C}_2\text{HCl}^+$
150	1.7		C_3F_6^+
151	0.3		$\text{SF}_4\text{C}_2\text{H}_3\text{O}^+$
156	15.4		SF_4CHCl^+
157	0.7		$\text{C}_4\text{HClF}_3\text{O}^+$
160	0.3		$\text{SF}_4\text{C}_3\text{O}^+$
161	0.9		$\text{SF}_4\text{C}_3\text{HO}^+$
163	0.2		$\text{SF}_4\text{C}_3\text{H}_3\text{O}^+$
170	0.6		$\text{C}_4\text{HSF}_2\text{OC1}^+$
177	1.9		$\text{C}_4\text{H}_2\text{ClF}_4\text{O}^+$
179	0.7		$\text{C}_4\text{H}_2\text{ClF}_4\text{O}^+$
185	1.2		$(\text{CF}_3)_2\text{OCF}^+$
187	0.3		$\text{SF}_5\text{C}_2\text{HCl}^+$
188	0.1		$\text{SF}_5\text{C}_2\text{H}_2\text{Cl}^+$
189	23.0		$\text{SF}_5\text{CHClCH}_2^+$

$\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$ (cont.)

<u>M/e</u>	<u>Rel.</u>	<u>Int.</u>	<u>Type</u>
190	0.7		$\text{SF}_3\text{C}_4\text{H}_2\text{ClO}^+$
191	8.3		$\text{SF}_5\text{CHClCH}_2^+$
199	93.0		$\text{CH}_2\text{OC}_3\text{F}_7^+$
200	4.3		$\text{SF}_3\text{C}_5\text{ClO}^+$
201	0.3		$\text{SF}_3\text{C}_5\text{HClO}^+$
207	0.8		$\text{SF}_5\text{C}_2\text{H}_3\text{ClO}^+$
213	0.2		$\text{SF}_3\text{C}_4\text{H}_3\text{OF}_3^+$
217	0.2		$\text{SF}_5\text{C}_3\text{H}_3\text{ClO}^+$
230	0.4		$\text{C}_5\text{F}_7\text{Cl}^+$
246	2.2		$\text{C}_2\text{H}_2\text{ClOClC}_3\text{F}_7^+$
247	24.0		$\text{C}_2\text{H}_2\text{ClHOC}_3\text{F}_7^+ (\text{M}^+ - \text{SF}_5)$
248	1.9		$\text{SF}_3\text{C}_4\text{H}_3\text{ClF}_3\text{O}^+$
249	7.8		$\text{C}_2\text{H}_2\text{ClHOC}_3\text{F}_7^+$
250	0.5		$\text{SF}_5\text{C}_4\text{H}_2\text{F}_3\text{O}^+$
265	0.1		$\text{SF}_4\text{C}_4\text{HClF}_3\text{O}^+$
281	1.9		$\text{SF}_5\text{C}_2\text{H}_2\text{OC}_3\text{F}_4^+$
282	0.6		$\text{SF}_5\text{C}_2\text{H}_3\text{OC}_3\text{F}_4^+$
283	0.4		$\text{SF}_5\text{C}_3\text{ClOCF}_3^+$
355	0.3		$\text{SF}_5\text{CHClCH}_2\text{OC}_3\text{F}_6^+ (\text{M}^+ - \text{F})$

The infrared absorptions for the new hypochlorite complexes are tabulated in Table XIV and the actual spectra are shown in the appendix.

For the compounds, $\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$ and $\text{SF}_5\text{CHClCF}_2\text{OCF}(\text{CF}_3)_2$, the common feature is the SF_5 - group which absorbs strongly in the $850\text{--}920\text{ cm}^{-1}$ region for the S-F stretching vibrations and in the 600 cm^{-1} region for the S-F deformation modes(47). Thus the bands at $835\text{--}906\text{ cm}^{-1}$ observed for $\text{SF}_5\text{CHClCF}_2\text{OCF}(\text{CF}_3)_2$ and 855 cm^{-1} observed for $\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$ complexes were assigned to the S-F stretching modes. The S-F deformation modes are at 603 and 598 cm^{-1} respectively for the ether complexes. For all the isopropyl hypochlorite complexes, the $(\text{CF}_3)_2\text{CFO-}$ showed strong absorption bands in the $1145\text{--}1305\text{ cm}^{-1}$ region are attributable to C-F stretching frequency(49,50). Similarly absorption bands at $720\text{--}760\text{ cm}^{-1}$ attributable to C-F deformation modes were observed(50). In all of the isopropyl hypochlorite compounds, and the perfluoro-t-amyl group, the absorptions observed at 1110 to 1334 cm^{-1} and 1124 to 1342 cm^{-1} respectively, are attributable to C-F stretching frequencies. Also the bands at 723 to 765 cm^{-1} for the isopropyl hypochlorite complexes and 716 to 765 cm^{-1} for the perfluoro-t-amyl group are assigned to the C-F deformation modes. The absorptions at 970 to 1096 cm^{-1}

TABLE XIV

INFRARED ABSORPTION BANDS FOR F-HYPOCHLORITES

 (cm^{-1}) ** TiCl_4 with $i\text{-C}_3\text{F}_7\text{OC1}$

1725(mw), 1772(mw),
 1334(m), 1300(w),
 1263(w,sh), 1228(m,sh),
 1205(s), 1091(m), 970(s),
 735(vs,b), 521(vs,b)

 I_2 with $i\text{-C}_3\text{F}_7\text{OC1}$

1897(ms), 1454(w,b),
 1342(m), 1216(vs),
 1110(vs), 1025(w),
 969(mw), 831(w), 772(m),
 751(w), 737(ms), 701(w),
 698(mw)

 Hg with $i\text{-C}_3\text{F}_7\text{OC1}$

1834(w), 1447(s,b),
 1229(vs), 1187(vw),
 730(w,b).

 $\text{SF}_5\text{CH=CH}_2$ with $i\text{-C}_3\text{F}_7\text{OC1}$

2881(vw), 1329(vw),
 1299(m), 1240(s),
 1183(s), 1121(m),
 1002(m), 980(m),
 855(vs), 756(w), 733(mw),
 724(mw), 653(w), 598(mw),
 422(m).

** m=medium, s=strong, vs=very strong, sh=shoulder,
 w=weak, ms=medium strong, mw=medium weak, b=broad.

TABLE XIV (cont.)

$\text{SF}_5\text{CH}=\text{CF}_2$ with $i\text{-C}_3\text{F}_7\text{OC1}$

3107(m,b), 3008(vw),
1314(m), 1250(vw),
1173(s), 1138(s),
1096(m), 990(s),
871(s), 835(m), 758(w),
723(s), 674(m), 639(w),
603(ms), 575(w), 540(w).

$\text{CH}_2=\text{CH}_2$ with $i\text{-C}_3\text{F}_7\text{OC1}$

2973(vw), 1461(vw),
1433(vw), 1328(ms),
1236(s), 1180(s),
1110(ms), 1011(s),
997(w,sh), 765(vw),
730(s), 688(mw), 674(mw),
548(w), 533(w), 477(vw).

$\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$

3627(s), 1342(m), 1300(s),
1138(s), 1075(s), 970(s),
927(w), 878(s), 738(s),
716(s).

$\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OC1}$

1342(s), 1243(vs,b),
1166(w), 1124(vs), 997(w,sh),
976(vs), 885(mw), 786(w),
765(mw), 723(m), 646(w),
533(vw).

are attributed to the C-O stretching frequencies observed around 1000 cm^{-1} (50).

The metal oxygen (M-O) stretching is generally observed below 650 cm^{-1} (48) and are assigned to peaks found in all the compounds below 653 cm^{-1} . For $\text{SF}_5\text{CHClCF}_2\text{OCF}(\text{CF}_3)_2$, $\text{SF}_5\text{CHClCH}_2\text{OCF}(\text{CF}_3)_2$ and $\text{ClCH}_2\text{CH}_2\text{OCF}(\text{CF}_3)_2$ compounds, the absorptions at 2850 to 2973 cm^{-1} are attributable to the C-H stretching frequency and for $\text{ClCH}_2\text{CH}_2\text{OC}(\text{CF}_3)_2$ the absorption at 1433 cm^{-1} is assigned to a CH_2 deformation mode(39). For the $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OH}$, the absorption at 3627 cm^{-1} is assigned to O-H frequency usually observed at $3600\text{--}3650\text{ cm}^{-1}$ (39).

Results and discussion.

The use of the ^{19}F nmr and ^1H nmr spectra have helped us to accurately establish the proposed structures of the new ether complexes. The infrared spectra also gave some structural confirmation for these new compounds. In the discussions of the nmr spectra, comparisons are made with known compounds in terms of their chemical shifts, and the coupling constants.

Nuclear Magnetic Resonance spectra. Both fluorine and proton, nmr spectra were obtained for the new compounds: $\text{FSF}_4\text{CHClCH}_2\text{OC}(\text{CF}_3)_2\text{F}$, $\text{FSF}_4\text{CHClCF}_2\text{OC}(\text{CF}_3)_2\text{F}$, $\text{ClCH}_2\text{CH}_2\text{OC}(\text{CF}_3)_2\text{F}$. Also reported is the fluorine nmr

spectrum for $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$. The ^{19}F nmr shifts are expressed in parts per million relative to Freon-11; for the ^1H nmr spectra, chemical shifts to TMS external standard.

The chemical shifts, and also the nmr coupling constants are listed in Tables XV and XVI respectively. The spectra are generally complex, and this may be attributed to the fluorine splitting of protons and the asymmetric nature of the compounds. There is relatively little nmr data available for similar compounds; as a result, not all of the coupling constants could be determined; however, enough information was presented to confirm the structures of the new compounds as presented in the table.

In SF_5 -containing fluoro ethers, the nmr pattern for the SF_5 group consisted of the expected AB_4 pattern with B_4 equatorial fluorine atoms split into a doublet and the A part split into a multiplet pattern. Analysis of the chemical shifts confirmed the proposed structures. For example, the proton chemical shifts of a CHX group next to an SF_5 group is consistent from one SF_5 -fluoroalkyl derivative to another(44). In our compounds, the proton chemical shift values for $\text{FSF}_4\text{CHClCH}_2\text{OC}(\text{CF}_3)\text{F}$ and $\text{FSF}_4\text{CHClCF}_2\text{OC}(\text{CF}_3)_2\text{F}$ were δ 5.58 and δ 5.82 ppm respectively; the coupling constants were: $J_{f-g}=6.0\text{Hz}$ and

21.2 Hz, J_{a-b} = 158 Hz and 141.1 Hz respectively for the ^{19}F nmr. For other SF_5 systems, such as $\text{SF}_5\text{CHFCFC1Br}$, and $\text{SF}_5\text{-CHC1CF}_2\text{Br}$, the ^1H NMR values were δ 5.41, δ 5.58, δ 5.85, δ 5.68, and δ 5.50 ppm respectively(44); and the J_{a-b} for $\text{F}^a\text{SF}_4^b\text{CHC1CH}_2\text{OCF}_3$, $\text{F}^a\text{SF}_4^b\text{CFC1CF}_2\text{OCF}_3$, $\text{F}^a\text{SF}_4^b\text{OCH}_2\text{CH}_2\text{C1}$ and $\text{F}^a\text{SF}_4^b\text{OCFCF}_2\text{C1}$ were 144, 143, 146, and 153.6 Hz respectively(44). Also for the compounds $\text{SF}_5\text{CHC1CH}_2\text{OCF}_3$, $\text{SF}_5\text{CHC1CF}_3$, and $\text{SF}_5\text{CHC1CF}_2\text{C1}$, the CHX proton chemical shifts were found to be δ 5.62, 5.61, 6.10 ppm, respectively(44). For the ^1H nmr, the coupling constants for the following compounds were found: $\text{F}^a\text{SF}_4^b\text{CH}^c\text{C1CH}^d\text{H}^e\text{OC}(\text{CF}_3^f)_2\text{F}^g$, J_{b-c} = 5.1 Hz, J_{c-e} = 6.0 Hz; for $\text{F}^a\text{SF}_4^b\text{CH}^c\text{C1CF}^d\text{F}^e\text{OC}(\text{CF}_3^f)_2\text{F}^g$, we found J_{b-c} = 5.4 Hz and for $\text{C1CH}_2^a\text{CH}_2^b\text{OC}(\text{CF}_3)_2\text{F}$ we found J_{a-b} = 6.2 Hz. In other compounds, e.g. $\text{F}^a\text{SF}_4^b\text{CH}^c\text{C1CH}^d\text{H}^e\text{OCF}_3$, the ^1H nmr coupling constants were J_{b-c} = 4.5 Hz, and J_{c-e} = 6.9 Hz(44), for $\text{F}^a\text{SF}_4^b\text{OCH}_2^c\text{CH}_2^d\text{C1}$, J_{c-d} = 6.2 Hz and for $\text{C1CH}_2^a\text{CH}_2^b\text{OC}(\text{CF}_3)_2\text{F}$, J_{a-b} = 6.0 Hz.

The ^{19}F nmr chemical shifts of the FSF_4 group of our compounds were comparable to known values; for $\text{FSF}_4\text{CHC1CH}_2\text{OC}(\text{CF}_3)_2\text{F}$, and $\text{FSF}_4\text{CHC1CF}_2\text{OC}(\text{CF}_3)_2\text{F}$, the SF_{ax} chemical shifts were δ 73.0 and δ 71.2 and the $\text{SF}_{4(eq)}$ were δ 53.2 and δ 57.4 ppm respectively. In $\text{FSF}_4\text{CHC1CH}_2\text{OCF}_3$, $\text{FSF}_4\text{CFC1CF}_2\text{OCF}_3$, and $\text{FSF}_4\text{OCH}_2\text{CH}_2\text{C1}$, the chemical shift values were δ 73.3, δ 63.3, δ 74.9 ppm

for the $SF_{(ax)}$ and δ 53.2, δ 46.3 and δ 59.8 ppm for the $SF_{4(eq)}$ respectively(29,44). W. B. Fox et al.(29) found that for impure $(CF_3)_2CFOCF_2CF_2Cl$, the $-C(CF_3)_2-$ chemical shift has a triplet of doublets at δ -80.3 and for $-CF-$, a complex triplet at δ -143.1 ppm(29). In our $(CF_3)_2CFOCH_2CH_2Cl$, the $-C(CF_3)_2-$ group was found to be a doublet at δ -82.5 and for the $-CF-$ group a multiplet at δ -145.2 ppm, respectively. For the perfluoro-t-amyl hypochlorite, $CF_3CF_2C(CF_3)_2OCl$, the chemical shifts, and also the nmr coupling constants are listed on Tables XV and XVI respectively. Analysis of the ^{19}F NMR chemical shifts referenced to the parent alcohol chemical shifts, confirmed the proposed structure of the new hypochlorite. Graham and Weinmayr(30) found, for the perfluoro-t-amyl alcohol, $CF_3CF_2C(CF_3)_2OH$, the following chemical shifts: δ -80.63(F^a), δ -73.18(F^c) and δ -119.28(F^b) respectively; with relative areas of 3, 2, and 6(30). For our alcohol, we found the chemical shifts of these groups at δ -82.5, δ -75.2, and δ -121.8 respectively with relative band areas of 3.2, 2.0, and 6.2 respectively. We also found, in the 1H NMR spectrum, a chemical shift of 3.8 for the OH. From the ^{19}F NMR spectrum, we obtained the following coupling constants: $J_{b-c}=11.5$ Hz and $J_{a-c}=5.8$ Hz. The ^{19}F NMR chemical shift of our new perfluoro-t-amyl hypochlorite was compared to

TABLE XV

NMR CHEMICAL SHIFTS* FOR THE F-HYPOCHLORITES

Compound	SF _(ax) #	SF _(eq) #	CF ₃	CF	CF ₂	CH	CH ₂	C=C?	OH
SF ₅ CHClCH ₂ OCF(CF ₃) ₂	73.0	53.2	-83.1	-148.5	-	5.6	4.7	-	-
SF ₅ CHClCF ₂ OCF(CF ₃) ₂	71.2	57.4	-82.3	-147.6	-71.3	5.8	-	5.5	-
ClCH ₂ CH ₂ OCF(CF ₃) ₂	-	-	-82.1	-145.2	-	-	3.9 4.4	-	-
CF ₃ CF ₂ C(CF ₃) ₂ OH	-	-	-82.5** -75.2	-	-121.8	-	-	-	3.82
CF ₃ CF ₂ C(CF ₃) ₂ OCl	-	-	-80.4** -67.9	-	-115.7	-	-	-	-

* Fluorine and Proton Chemical Shifts are reported in ppm relative to

external CFCl₃ and Si(CH₃)₄ Standards, respectively.** CF₃ terminal

ax=axial, eq=equatorial

TABLE XVI
NMR COUPLING CONSTANTS* FOR THE F-HYPOCHLORITES

COMPOUND	F, F J	F, F J	F, F J	F, F J	F, F J	H, F J	H, H J	H, H J	H, H J
^a _b ^c CH ClCH H OC(CF ₃) ₂ F ^g	-	158	6.0	-	5.1	6.2	6.0	6.8	6.8
^a _b ^c CH ClCF F OC(CF ₃)F ^g	-	141.1	10.6	-	5.4	-	-	-	-
^c _d ^f CH ₂ O(CF ₃) ₂ F ^g	-	-	2.4	-	-	6.2	-	-	-
^a _b ^c CF ₃ CF ₂ (CF ₃) ₂ OH	5.9	-	-	11.6	-	-	-	-	-
^a _b ^c CF ₃ CF ₂ (CF ₃) ₂ OC1	5.6	-	-	11.6	-	-	-	-	-

* Values are measured in cycles per second (Hz)

the parent alcohol. The chemical shifts were found for the compound: $\text{CF}_3^{\text{a}}\text{CF}_2^{\text{b}}\text{C}(\text{CF}_3^{\text{c}})_2\text{OCl}$ at δ -80.4(F^{a}), δ -67.9(F^{c}) and δ -115.7(F^{b}) respectively with relative areas of 3.4:6.3:2.0 (theor: 3.0:6.0:2.0) respectively. The coupling constants were $J_{\text{b-c}}=11.6$ Hz and $J_{\text{a-c}}=5.6$ Hz.

Summary/conclusion.

Prior to this study, little was known concerning the chemistry of the heptafluoroisopropyl hypochlorite, $\text{i-C}_3\text{F}_7\text{OCl}$. We have found that with hydrocarbon olefins new fluorinated ethers are formed. These new ethers were clear and easily distillable liquids and were found to be hydrolytically stable. All of the products were formed unidirectionally as confirmed by the NMR spectra (see discussion section).

In undertaking this study, it was our hope that the heptafluoroisopropyl hypochlorite would react with metal and non-metal systems to provide new and interesting metal complexes. Our results with Hg, I_2 , and TiCl_4 strongly suggest that fluorination and decomposition reactions occurred leading to products that were not fully characterized. In olefin reactions, however, $\text{i-C}_3\text{F}_7\text{OCl}$ was a useful reagent and new fluorinated ethers were synthesized and characterized.

The preparation of the new perfluoro-t-amyl

hypochlorite, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$, was an important aspect of this study. It is hoped that $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$ will provide a great number of perfluoro-t-amyl derivatives and in related reactions with olefins, will provide a route to a wide variety of fluorinated ethers through oxidative addition reactions.

Recommendations.

While the reaction of $i\text{-C}_3\text{F}_7\text{OCl}$ with metal and non-metal systems did not provide the desired complexes (due to possible fluorine migration and decomposition), much information was obtained on the chemistry of this hypochlorite. It is hoped that future studies will explore the possibility of using $i\text{-C}_3\text{F}_7\text{OCl}$ in fluorination reactions.

The chemical properties of the new perfluoro-t-amyl hypochlorite, $\text{CF}_3\text{CF}_2\text{C}(\text{CF}_3)_2\text{OCl}$, have not been fully investigated. Information obtained from its few reactions performed is promising and it is my belief that future workers will find this reagent useful in hypochlorite chemistry.

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APPENDIX

INFRARED SPECTRA

COMPOUND	PAGE
1 CrF_4	101
2 $\text{CF}_3\text{CH}_2\text{OH}$ with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	102
3 $(\text{CF}_3)_2\text{CHOH}$ with $\text{Cr}(\text{OC}_4\text{H}_9)_4$ (a & b)	103
4 $(\text{CF}_3)_3\text{COH}$ with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	104
5 $\text{C}_6\text{F}_5\text{OH}$ with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	105
6 $(\text{C}_6\text{H}_5)\text{SiOH}$ with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	106
7 HF with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	107
8 CF_3COOAg with $\text{Cr}(\text{OC}_4\text{H}_9)_4$	108
9 $\text{CF}_3\text{CH}_2\text{OH}$ with $\text{Cr}(\text{NEt}_2)_3$	109
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CrF₄, SOL/KBr/JU