CARBONYL FLUORIDES OF RHENIUM

AND OTHER TRANSITION METALS

A   thesis

presented   for   the   degree   of

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by

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"The Crystal and Molecular Structure of $Re(CO)_5F.ReF_5$",

"The Preparation and Crystal Structure of $(Re(CO)_6)^+(Re_2F_{11})^-$",
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"Rhenium Carbonyl Fluorides; Preparation of Pentacarbonyl-monofluororhenium and Preparation and Chemistry of Pentacarbonylmonofluororhenium-Rhenium Pentafluoride",
D.M.Bruce, A.J.Hewitt, J.H.Holloway, R.D.Peacock and I.L.Wilson : submitted to J.Chem.Soc.(D), 1976.

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D.M.Bruce, J.H.Holloway, et alia : reference 31.

FOR   THE   GLORY   OF GOD

"When I consider Thy heavens, the work of Thy fingers,

What is man that Thou art mindful of him?"

"Whatsoever God does endures for ever; nothing can be

added to it, nor anything taken from it;

God has made it so that man should fear before Him"

(From Psalm 8 and Ecclesiastes ch.3)

Acknowledgements

"Let us not grow weary in well-doing, for in due season we shall reap, if we do not lose heart."

Paul's letter to the Galatians, ch.6, v.9.

ABSTRACT

Rhenium carbonyl reacts with three moles of XeF_2 in Genetron 113 to produce the novel carbonyl fluoride-pentafluoride complex $Re(CO)_5F \cdot ReF_5$ This is decomposed to ReF_6 by three further moles of XeF_2. The use of proportions intermediate between these gives only mixtures of $Re_2(CO)_{10}$ and $Re(CO)_5F \cdot ReF_5$, or $Re(CO)_5F \cdot ReF_5$ and ReF_6. When HF is used as the solvent, a similar process is indicated, but partial hydrolysis of HF solutions of $Re(CO)_5F \cdot ReF_5$ frequently occurred, to give $(Re(CO)_6)^+ (ReOF_5)^-$. No conclusive evidence for $Re(CO)_5F$ was found.

$Re_2(CO)_{10}$ also forms $Re(CO)_5F \cdot ReF_5$ with two moles of ReF_6, in HF solution, but with four moles, the new, ionic 1:2 complex $(Re(CO)_6)^+ (Re_2F_{11})^-$ is produced. $Re(CO)_5F \cdot TaF_5$ and $(Re(CO)_6)^+ (Sb_2F_{11})^-$ were produced by exchange reactions of $Re(CO)_5F \cdot ReF_5$ with TaF_5 and SbF_5 respectively. The oxidation of $[(\eta^5 - C_5H_5)Fe(CO)_2]_2$ with AgF in acetone produced evidence for a new fluoride, $(\eta^5 - C_5H_5)Fe(CO)_2F$.

It was surmised that the maintenance of stable $(Re(CO)_5F)$ or $(Re(CO)_6)^+$ units governs the course of these fluorinations, and that, in general, carbonyl fluorides will only exist with certain, specific, stable units. Analogous units were proposed for other carbonyl fluoride systems, and a general progression for metal carbonyl fluorinations was established, through simple carbonyl fluoride to carbonyl fluoride-pentafluoride complex(es), and finally binary fluoride. The carbonyl fluoride-pentafluoride complex plays a fundamental role in these systems which has no parallel in other organometallic halides, although related complexes are known in a few cases.

Full X-ray crystal structures of $Re(CO)_5F \cdot ReF_5$ and $\alpha-(Re(CO)_6)^+(Re_2F_{11})^-$ were performed, and a partial investigation made of $(Re(CO)_6)^+(ReOF_5)^-$. $Re(CO)_5F \cdot ReF_5$ is an essentially covalent, fluorine-bridged complex whose bond lengths are of value for comparing other fluorine-bridged interactions. Polymorphism is found in $(Re(CO)_6)^+(Re_2F_{11})^-$. The $\alpha-$ phase has an ionic lattice, with a centrosymmetric anion. Anion-cation interactions in other $(M_2F_{11})^-$ structures were discussed.

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LAYOUT OF THE THESIS

The thesis is in two sections, chapters 1-4 and 5-8. The field of transition metal carbonyl fluorides is first introduced, with a discussion of the problems attending earlier investigations (chapter 1). My results are then described for each of three rhenium carbonyl fluorination systems, and for sundry related reactions, establishing the identity of the compounds isolated and describing their properties (chapter 2). In chapter 3, these results are discussed with reference to carbonyl fluoride and related systems as a whole. Initially an understanding of the $Re_2(CO)_{10}/XeF_2$ system is deduced, in terms of fundamental units (3-1.). This is then broadened to include other fluorinating agents, and in particular (3-2.) the $Re_2(CO)_{10}/ReF_6/$ HF system. After considering other preparative routes (3-3.), an overall picture of the rhenium carbonyl fluoride system is established (3-4.). This is discussed as a model for transition metal carbonyl fluoride systems in general, with predictions of the fundamental units and basic types of species expected (3-4.). This model is contrasted with carbonyl and other organometallic halide systems not containing fluorine (3-5.). After discussing the formation of $cpFe(CO)_2F$ (3-6.), suggestions are made for future work on the rhenium system (3-7.). The detailed experimental work is described in chapter 4.

The X-ray crystal structure investigations of the compounds $Re(CO)_5F \cdot ReF_5$ (chapter 6), $\alpha-(Re(CO)_6)^+(Re_2F_{11})^-$ (chapter 7), and $(Re(CO)_6)^+(ReOF_5)^-$ (chapter 8), form the second part of the thesis, preceded by a brief résumé of crystal structure determination (chapter 5). A brief epilogue, two appendices of structure amplitudes, and a cumulative list of references conclude the thesis.

ABBREVIATIONS

Me	methyl, $-CH_3$	vs	very strong
Et	ethyl, $-C_2H_5$	s	strong
^{i}Pr	isopropyl, $-CH(CH_3)_2$	m	medium
^{n}Bu	normal butyl, $-C_4H_9$	w	weak
^{t}Bu	tertiary butyl, $-C(CH_3)_3$	vw	very weak
Ph	phenyl, $-C_6H_5$	vvw	very, very weak

cp = $\eta^5-C_5H_5$ = pentahaptocyclopentadienyl

triars   tris-1,1,1-(dimethylarsinomethyl)ethane $(Me_2As-CH_2-)_3C-CH_3$

diars   o-phenylene(dimethylarsino) $Me_2As-C_6H_4-AsMe_2$

(1)   liquid phase

m/e   mass number: charge ratio for a charged molecular
       fragment

o.d.   outside diameter;   i.d. internal diameter.

CHAPTER 1

A SURVEY OF TRANSITION METAL

CARBONYL FLUORIDE WORK PRIOR TO THIS STUDY

1-1. THE EARLY NEGLECT OF THE FIELD OF CARBONYL FLUORIDES

Transition metal carbonyls and their derivatives have been the subject of an enormous amount of research over many decades. Since Schutzerberger's original discovery,[1] in 1870, that carbon monoxide could bond directly to a metal in the compound $Pt(CO)_2Cl_2$, and the extensive work by Hieber and his co-workers from the late 1920's onwards,[2] carbonyl-containing compounds have been prepared for nearly every transition metal. Substituted derivatives, $M(CO)_xL_y$, are known for an extraordinarily wide variety of ligands, including derivatives of nearly every non-metal (e.g. L= OEt, N_2, PPh_3, $\eta^5-C_5H_5$, carboranes, H), and many metals (e.g. in the compounds $Me_3Sn-Co(CO)_4$, $U(Mn(CO)_5)_4$).[3] Until recently, however, carbonyl fluorides have been little investigated. The first member was not identified until 1968,[4] and even now only a handful have been thoroughly characterised.

The reasons for this neglect are partly theoretical. Fluorine is far more powerfully oxidising than the other halogens, and might be expected to destroy the oxidation-sensitive metal carbonyl framework, rather than complex with it. Fluorine is also an extreme example of a "hard" ligand, whereas CO, and π-acceptor ligands generally are "soft".[5] It has also been suggested that carbonyl fluorides might be thermodynamically unstable with respect to stable decomposition products such as lower metal fluorides, COF_2, or CO itself.[6]

Another major problem has been that, until recently, the practical techniques used were not sufficiently soph- isticated for handling and characterising the often highly reactive products. The classical organometallic approach

for preparing carbonyl halides was of little use for

carbonyl fluorides. This usually involved the reaction of

a metal carbonyl with the halogen, dissolved in a suitable

organic solvent, or of a metal halide with CO (either at

atmospheric or high pressure, with or without a solvent)

or a carbonylating agent such as formic acid.[3] However,

few organometallic chemists had elemental fluorine readily

available, or had access to the specialist techniques

required to manipulate either fluorine or higher metal

fluorides. In addition there are few such fluorides which

can be readily handled in organic solvents.

The early failure of the organometallic approach

is exemplified by the following two reactions:

1. $M(CO)_6$ + $R_4N^+X^-$ $\xrightarrow{\text{diglyme}}$ $(R_4N)^+(M(CO)_5X)^-$ + CO.
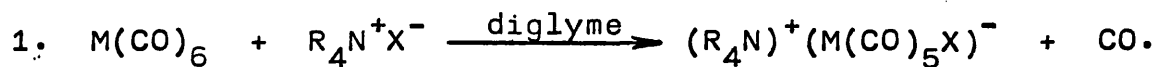
   M = Cr, Mo, W ;   X = Cl, Br, I ;   R = Et, ^nBu.

   X = F gave CO evolution, but no isolable carbonyl

   fluoride.[7] **

2. K_2ReX_6 + CO $\xrightarrow[\text{and temperature}]{\text{high pressure}}$ $Re(CO)_5X$ + KX, etc.
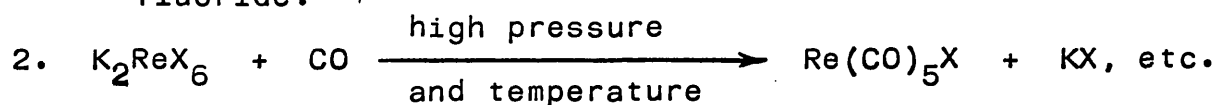
   X = Cl, Br, I.[10,11]

   X = F gave traces of $Re_2(CO)_{10}$ in the presence of

   Al, but failed to react otherwise.[11]

1-2.   THE PROBLEMS OF APPLYING FLUORINE CHEMISTRY TO AN

                                ORGANOMETALLIC SYSTEM

The outcome of the above has been that carbonyl

** More recently this reaction has been found to give chromium

and tungsten $(M(CO)_5F)^-$ anions, using the novel cations

$[(Ph_3P)_2N]^+$ [8] or crown ether-solvated K^+,[9] with ultra-violet

irradiation.

fluoride preparation has moved largely out of the realms of organometallic chemistry into the technically specialised field of inorganic fluorine chemistry. The latter has developed over the past 35 years, in the wake of nuclear energy research, so that general preparative chemistry has become possible. Nevertheless, many problems arise when fluorine chemistry is applied to organometallic systems. Some of these are summarised below, in the context of carbonyl fluorides.

1-2.1 The problems of fluorine as a powerful oxidant

Mention has already been made of the extreme oxidising power of fluorine, with reference to organometallic systems. Particularly delicate control of the reaction conditions may, therefore, be required in order to prepare carbonyl fluorides, especially as the products may not be very stable thermodynamically. High temperatures and pressures, and very vigorous fluorinating agents normally have to be avoided. The action of elemental fluorine on metal carbonyls has often given rise to explosions, even when nitrogen was used as a diluent.[12,13] Even when pre-parative conditions are mild, most possible first-row transition metal carbonyl fluorides may be too unstable to exist under ordinary conditions. In the analogous carbonyl nitrates, $Mn(CO)_5NO_3$ is the only known first-row example.[14]

1-2.2 The moisture sensitivity or solvolysis of covalent
fluorides

Many covalent fluorides are solvolysed in the presence of water, and most other protic species. The

driving force for such reactions is believed to be the
formation of the very stable HF molecule.[15] Scrupulously
anhydrous conditions are usually required, therefore, for
the preparation of even the more air-stable carbonyl fluorides
such as $(Ru(CO)_3F_2)_4$.[16] Most protic solvents, and solvents
miscible with water, such as alcohols, acetone, acetonitrile
and dimethyl sulphoxide, cannot normally be employed.

1-2.3   The difficulty in finding suitable solvents

        Solvents for use in carbonyl fluoride preparations
need to be inert (e.g. free from "available" chlorine
which might displace co-ordinated fluorine*), and yet
polar enough to be effective with the predominantly polar
compounds involved. This, together with problem 1-2.2 above,
means that most of the solvents commonly used in organo-
metallic chemistry are unsuitable. This has limited the
choice to anhydrous HF, tungsten hexafluoride, and chloro-
fluorocarbons such as Genetron 113 (1,1,2-trichlorotri-
fluoroethane). Other alternatives include liquid SO_2,
SO_2ClF and $(SF_5)_2O$.

1-2.4   The tendency to produce mixtures of non-volatile
                                              compounds

        Carbonyl fluoride preparations have often given
rise to mixtures of involatile solids which are very difficult
to separate and identify.

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* Such exchange has been reported for the metal phosphine
fluoride complex $[(Ph_3P)_3PtF]^+[HF_2]^-$ in the presence of
dichloromethane.[17]

1-2.5 The problems of separating, purifying and charact-

erising the products, under scrupulously anhydrous

conditions, possibly without a solvent

The combination of the previous four problems may

result in unsatisfactory reactions for the following reasons:

poor mixing, incomplete reaction, or difficulty in the

separation, sublimation or recrystallisation of the products.

In addition many analytical techniques may be difficult to

apply: e.g. N.M.R., E.S.R., infrared (solution phase),

and U.V.-visible spectroscopy, electrical conductivity,

molecular weight determination, and chromatography.

This leaves the following general techniques: infrared

(mull or dry powder) and laser Raman spectroscopy (though

many carbonyl fluorides either absorb strongly, fluoresce

or decompose in the laser beam), mass spectrometry (if the

compound is volatile enough), X-ray diffraction (powder,

and possibly single crystal), magnetic measurements, mass

balance and/or thermogravimetric analysis, and elemental

microanalysis (though analyses on fluorine-containing

compounds can be notoriously unreliable without very good

additional supporting evidence[18,4]).

The unequivocal identification of the product has

often required a crystal structure determination.

1-3   CARBONYL FLUORIDE INVESTIGATIONS BY THE FLUORINE

CHEMICAL APPROACH

1-3.1   Early Work

The earliest attempt at preparing a carbonyl

fluoride was in 1952, when Peacock found that the action

of carbon monoxide on RuF_5 gave a yellow, reactive solid.[19]

Between 1957 and 1961, Peacock and Hargreaves made the first

concerted effort at synthesising carbonyl fluorides by

a fluorine-chemical approach. They attempted to fluorinate

the hexacarbonyls of chromium,[20] molybdenum[21-23] and tung-

sten[24,23,25], and $Re_2(CO)_{10}$,[23] using a variety of fluorinating

agents. These included fluorine-nitrogen mixtures (in a

flow system), bromine trifluoride,[20] iodine pentafluoride,

and the hexafluorides of molybdenum,[20] tungsten,[20] rhenium,[23]

and osmium.[25] These reactions, however, almost invariably

displaced all of the CO, producing metal fluorides.**

Had they been able to use suitable solvents to moderate some

of these reactions, carbonyl fluorides should certainly

have been produced in some cases[26] (see also section 3-5.2).

The alternative method, involving the reaction of

a metal fluoride with CO under pressure or in a flow system,

was investigated by Sharp and Russell at Glasgow during

the period 1960-63. A wide range of metal fluorides were

found to be reduced to the metal, but the RuF_5/CO product

contained carbonyl bands in its infrared spectrum.[27]

Compounds prepared by Sharp from the tetrafluorides of

platinum and rhodium were formulated as $Pt(CO)_2F_8$ and

$(Rh(CO)_2F_3)_2$ respectively, but their nature was not under-

stood.[18]

Following these discouraging series of results,

the area lay dormant. Indeed, as late as 1970, Abel and

Stone proposed that, on thermodynamic grounds, carbonyl

**As it happened, the method provided some useful preparative

routes to new metal pentafluorides.

fluorides were unlikely to be stable, except perhaps as fluorine-bridged polymers.[6] Moreover, in 1967, Kemmitt, Peacock and Wilson reinvestigated Sharp's two compounds and showed that they were the carbonyl <u>bromides</u> $Pt(CO)_2Br_2$ and $(Rh(CO)_2Br)_2$, arising from BrF_3 impurities in the tetrafluorides.[4,28]

They returned to the RuF_5/CO reaction, however, and deduced that the yellow product was a ruthenium carbonyl fluoride - ruthenium pentafluoride complex, for which the formula $(Ru(CO)_2F^+RuF_6^-)_n$ was postulated.[4] Evidence was obtained for similar compounds of osmium, iridium, and possibly platinum.[28]

1-3.2   The Use of Xenon Difluoride with Metal Carbonyls

Having shown that carbonyl fluoride derivatives could be prepared, they went back to the fluorination of metal carbonyls, but with a new fluorinating agent, xenon difluoride, discovered only 5 years before.[29] This had the advantages that it could be sublimed in dynamic vacuum, was soluble in a wide variety of solvents, and that it produced only xenon gas as a by-product during fluorinations. In solution in the inert chlorofluoroalkane Genetron 113, this provided the necessary control and specificity for the first general synthetic method for carbonyl fluorides. Preliminary experiments indicated that whereas the first-row carbonyls tended to produce only lower fluorides, those of Mo, W, Re, Ru, Os and Rh all gave carbonyl fluoride species.[12,13,30] Tentative formulations were proposed for some of these, but none was fully characterised.

Between 1968 and 1971, Marshall examined the ruthenium and osmium carbonyl reactions, and Misra the molybdenum system, in more detail.[13,31] Though no unequivocal identification of the products of these reactions was possible, Marshall characterised a ruthenium carbonyl fluoride, $(Ru(CO)_3F_2)_4$, by an X-ray structure on a single crystal obtained from Wilson's further carbonylation of "$(Ru(CO)_2F^+RuF_6^-)_n$". This was the first definitive characterisation of a carbonyl fluoride,[32] and as a result, the species $(Ru(CO)_2F^+RuF_6^-)_n$ was reformulated as a mixture which contained a majority of the compound $(Ru(CO)_3F_2 \cdot RuF_5)_2$.[13] *

1-3.3   Other Preparative Attempts

At about the same time, a molybdenum carbonyl fluoride was reported by O'Donnell and Phillips in Australia. This synthesis employed the earlier method of combining a metal carbonyl $(Mo(CO)_6)$ with its own hexafluoride (MoF_6), but used anhydrous HF as a solvent.[33] A fourth preparative method was investigated during the course of the Leicester work, which involved halogen exchange between a carbonyl chloride and an appropriate fluorinating agent. Among the latter were anhydrous HF, and AgF or XeF_2 in organic solvents. [12,13,34] The early results were not very successful - in marked contrast to the very facile preparations of the phosphino carbonyl fluorides, $(Ph_3P)_2M(CO)F$ (M = Rh, Ir), by similar routes.[35-37]

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* In recent work at Leicester, Hewitt and Holloway have obtained this compound pure, and established the identity of the ruthenium and osmium compounds of Marshall and Peacock.[16]

1-4. THE PRESENT STUDY - THE RHENIUM SYSTEM

By 1971, the results obtained suggested that the molybdenum, rhenium, ruthenium and osmium systems looked most promising for yielding stable carbonyl fluorides. Accordingly this present work on the rhenium system was undertaken as the first attempt at a systematic investigation of the carbonyl fluoride chemistry of one element. The aim was to obtain as complete a picture as possible, to use as a backbone for studying other systems. Full char- acterisation of any compounds obtained was deemed essential.

The unsuccessful early attempts to prepare rhenium carbonyl fluorides have already been mentioned. Later, preliminary studies on the reaction of $Re_2(CO)_{10}$ with XeF_2 in Genetron 113 were made by Wilson[12] and by Misra.[34] Wilson isolated an extremely air-sensitive, straw-yellow solid, from reactions of unspecified stoicheiometry. The solid analysed to $Re_2(CO)_5F_6$, and a formulation of $Re(CO)_5F \cdot ReF_5$ was tentatively proposed on the basis of infrared, mass spectrometric and magnetic data. Yields of up to 91% (based on rhenium) were reported, but the use of excesses of XeF_2 lowered the yields, and produced some volatile rhenium species. With large excesses of XeF_2, all the rhenium was lost as volatiles.

In the light of these results, it was decided to study the $Re_2(CO)_{10}/XeF_2/Genetron$ 113 system over a range of accurately known stoicheiometries, and to examine similar reactions using anhydrous HF as solvent, in view of pre- liminary evidence of its potential as a solvent for recrystallising carbonyl fluorides.[13,34]

       During the course of this work, O'Donnell and Phillips reported that a reaction of $Re_2(CO)_{10}$ with an unspecified amount of ReF_6 in anhydrous HF, gave a compound formulated as $Re(CO)_3F_3$.[38] This did not seem to correlate with any of our results, and it was therefore felt necessary to perform a thorough investigation of this system too. O'Donnell subsequently published some results on the $Re_2(CO)_{10}/XeF_2/HF$ system, and again "$Re(CO)_3F_3$" was reported, together with another compound $Re(CO)_5F$.[39] These reports are discussed in the light of my own results in chapter 3.

CHAPTER   2

RESULTS : THE FLUORINATION OF RHENIUM CARBONYL,

AND RELATED CHEMISTRY

General Outline

    This chapter describes, in turn, the investigation

of three rhenium carbonyl fluorination systems: $Re_2(CO)_{10}/$

XeF_2/Genetron 113, $Re_2(CO)_{10}/XeF_2$/HF and $Re_2(CO)_{10}/ReF_6$/HF.

The products are identified, with the appropriate physical

data. Two exchange reactions involving $Re(CO)_5F \cdot ReF_5$

(section 2-4.), and preliminary work on related carbonyl

fluoride systems (section 2-5.), are also described. All

experiments except for the $[(\eta^5-C_5H_5)Fe(CO)_2]_2$/AgF reaction

were performed in vacuum systems, and the solid products

handled in nitrogen-filled dry-boxes.

2-1. THE $Re_2(CO)_{10}/XeF_2$/GENETRON 113 SYSTEM

2-1.1 General Description of the Reactions

    Decacarbonyl dirhenium and xenon difluoride were

combined in molar proportions of 1:1, 1:2, 1:3, 1:4 and

1:5, in a series of experiments using 1,1,2-trichlorotri-

fluoroethane (Genetron 113) as the solvent in a glass

apparatus. Smooth reactions took place at or slightly

below $25^\circ C$, with the evolution of gas, and the apparent

conversion of the white, scarcely soluble, $Re_2(CO)_{10}$ to

extremely moisture-sensitive, yellow solids. Complete

solution was not observed at any time during the reactions.

Darkening of the reactor walls around the maniscus, and

black deposits on the upper walls were noted in the 1:4

and 1:5, and occasionally the 1:3 reactions. The solids

from these three reactions were orange-yellow, and those

from the 1:1 and 1:2 reactions pale yellow.

    The volatile products were characterised by mass

spectrometry and infrared spectroscopy. The mass spectra

all showed the characteristic isotopic abundance pattern
(the relative percentages are quoted in parentheses) assoc-
iated with Xe^+ (m/e = 136(9), 134(10), 132(27), 131(21),
130(4), 129(26), 128(2), and sometimes 126(0.1) and 124(0.1)
if the Xe concentration was sufficiently high), and Xe^{2+}
(68, 67, 66, 65½ and 64½ only; 65, 64, 63, and 62 were
generally too weak to be observed), as well as the solvent
breakdown pattern. There was also evidence for small amounts
of SiF_4^+ (104, vw), SiF_3^+ (85, vs), SiF_2^{+} (also COF_2^{+},
$^{132}Xe^{2+}$, and $CF^{35}Cl^+$) (66, s), and $SiF^{.+}$ (also COF^+, and
$C^{35}Cl^+$) (47, s). A high resolution mass spectrum of the
m/e = 28 region showed two distinct peaks due to $^{14}N^{14}N$
and $^{12}C^{16}O$, in each of the reactions. This was found to
provide a reliable test for the production of CO from
carbonyl fluoride reactions in general. (Conclusive evidence
from infrared spectra depends on having a substantial
pressure of CO in the infrared cell.) Infrared spectra
showed peaks due to the solvent, but no COF_2 or other species
were observed.

No physical data were obtained for the volatile
species which caused the darkening of the reactor walls,
but the behaviour observed strongly resembled that of
metallic deposition from rhenium hexafluoride in glass
apparatus.[40] This deposition may have been caused by
reduction by organic trace impurities from the solvent.
The presence of ReF_4 and ReF_5 was ruled out on the grounds
of their low volatility, and $ReOF_4$ would have been recognised
from its characteristic blue colour.[23,41] $ReOF_5$ or ReF_7
could not be discounted as possible sources of the deposit.

2-1.2   Identification of Re(CO)$_5$F.ReF$_5$

The orange-yellow solids from the 1:3, 1:4 and

1:5 reactions had powder patterns identical with that of

powdered orange crystals, obtained from reactions of

Re$_2$(CO)$_{10}$ with ReF$_6$, which were, in due course, shown to

be Re(CO)$_5$F.ReF$_5$ by means of an X-ray crystal structure

(see chapter 6.). There was no evidence of lines due to

Re$_2$(CO)$_{10}$, ReF$_5$ or the compounds Re(CO)$_5$F and Re(CO)$_3$F$_3$

of O'Donnell.[38,39]

The infrared spectra of the orange-yellow solids

were identical with those of Re(CO)$_5$F.ReF$_5$ from the Re$_2$(CO)$_{10}$/

ReF$_6$/HF system, and also with those obtained by Wilson

from his Re$_2$(CO)$_{10}$/XeF$_2$/Genetron 113 reactions. A typical

spectrum is shown in table 2.1. The basic pattern for the

ν(C≡O) region is consistent with the presence of an

(Re(CO)$_5$F) unit, with peaks at 2172, 2063 and 2013 cm^{-1}

derived from the three infrared-allowed modes in C$_{4v}$

symmetry: A$_1$, E and A$_1$ respectively.[42] The additional

peaks indicate a lowering of the overall symmetry to a

sub-group of C$_{4v}$. The region below 600 cm^{-1} is also typical

of an (Re(CO)$_5$X) species, and the bands at 642 and 620 cm^{-1}

are (Re-F) modes of the (-F-ReF$_5$) half of the molecule.
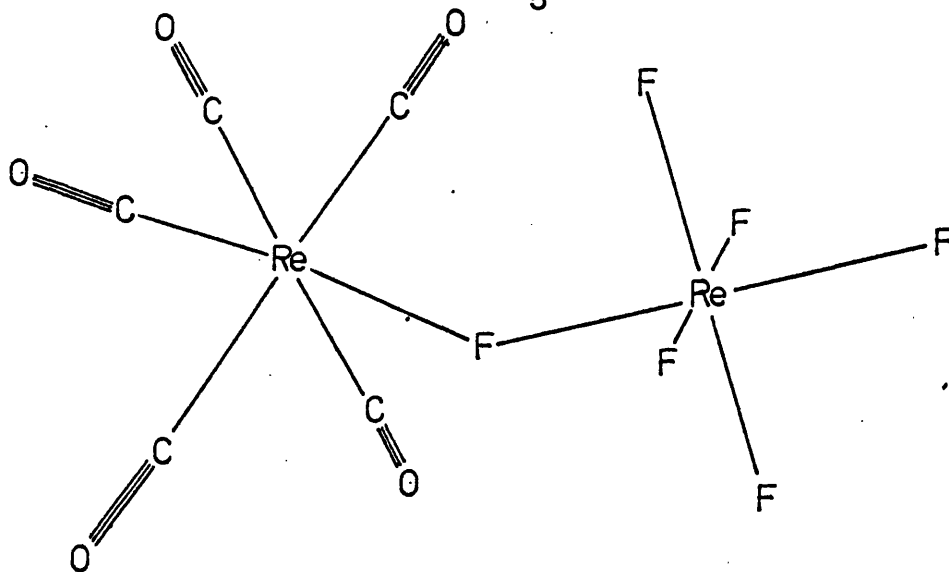
Table 2.1 Infrared and Raman Spectra of Re(CO)$_5$·MF$_5$

(M = Re, Ta, As)

Assign-ment	Re(CO)$_5$F·ReF$_5$ IR(this work)	Re(CO)$_5$F·ReF$_5$ RM(this work)	Re(CO)$_5$F·TaF$_5$ IR(this work)	Re(CO)$_5$F·AsF$_5$ IR(ref.43)
ν(C≡O)	2172 w 2100 vw 2082 m 2063 s 2046 m 2022 sh 2013 ms 1980 w	2172 w 2104 s 2062 w 2029 w	2171 w ~2075 sh 2057 m,sh 2044 s 2008 m 1985 w,m	2173 vw 2059 vs 2019 s
ν(M-F) δ(ReCO) ν(ReFM) ν(Re-F) ν(Re-C)	722 m 705 vw 642 s 620 s 588 vs 552 ms 528 w 485 w 439 vw 420 w	707 m 662 w 595 vw,br 522 ms 497 m 437 w,br 361 vw	722 m 700 vw ~605 m,sh 585 ⎫ s,br -570 ⎭ 550 m,sh 522 w ~485 vw	730 s 712 m 675 m

Table 2.2 The ν(M-F) Region of Re(CO)$_5$F·MF$_5$ and

(Ru(CO)$_3$F$_2$·MF$_5$)$_2$ Infrared Spectra

Complex	ν(M-F) in complex	δ(Re-C-O) in complex	ν$_3$(M-F) in K$^+$MF$_6^-$ [a]	Ref.
Re(CO)$_5$F·ReF$_5$	642, 620	590	627	b
Re(CO)$_5$F·TaF$_5$	~605,~575	~585	580	b
Re(CO)$_5$F·AsF$_5$	730,712,675	?	700	43.
(Ru(CO)$_3$F$_2$·RuF$_5$)$_2$	655	555	640	16.
(Ru(CO)$_3$F$_2$·TaF$_5$)$_2$	581	549	580	28.

a = ref.44,   b = this work

The Raman spectrum is also given in table 2.1. Although not entirely unequivocal, owing to sample decomposition in the laser beam, it may similarly be interpreted in terms of an $(Re(CO)_5F)$ unit and $\nu(Re-F)$ modes. There is no evidence in either infrared or Raman spectra for $(Re(CO)_6)^+$ species, or for $Re(CO)_5F$ or $Re(CO)_3F_3$. A full discussion of the vibrational assignment for $Re(CO)_5F \cdot ReF_5$ is given in Chapter 6.

Commercial analyses on 1:3 reaction products confirmed the formulation $Re(CO)_5F \cdot ReF_5$, and are in good agreement with Wilson's figures.

Found (a typical sample)   :   9.73% C, 18.0% F.

Found (Wilson)   :   9.58% C, 17.8% F.

Calc. for $Re(CO)_5F \cdot ReF_5$:   9.59% C, 18.2% F.

A single determination for rhenium gave Re = 62.9% (calc. 59.5%).

When heated in a sealed, evacuated, glass capillary, a single crystal of $Re(CO)_5F \cdot ReF_5$ decomposed, without melting, over the range 115 to 145°C. $Re(CO)_5F \cdot ReF_5$ is exceptionally moisture-sensitive, and requires scrupulously dry apparatus and conditions for manipulation. In dry-box manipulations, it only remained stable at moisture levels below about 20 p.p.m. of water. Above this level, the yellow solids quickly became buff. The tendency for high oxidation state rhenium compounds to scavenge oxygenated species to form Re=O bonds is well established.[45]

Although $Re(CO)_5F \cdot ReF_5$ dissolves rapidly in previously-dried acetone[46] to give a yellow solution, darkening occurs within minutes to yield a brown solution and precipitate. Molecular weight and conductivity meas-

urements were therefore not attempted. The complex is

fairly soluble in other polar solvents (anhydrous hydrogen

fluoride, acetonitrile, ethanol), with similar decomposition

in the latter two cases, but is scarcely soluble in non-

polar solvents (Genetron 113, 60-80°C petroleum ether,

dichloromethane, trichloromethane, benzene).

The 1:3 reaction gave pure $Re(CO)_5F \cdot ReF_5$. The

1:4 reaction was carried out stepwise by using 1:3 proport-

ions of $Re_2(CO)_{10}$:XeF_2 to produce $Re(CO)_5F \cdot ReF_5$, and then

adding a further molar equivalent of XeF_2. Darkening of

the reactor walls occurred only during this latter stage,

and the final yield of $Re(CO)_5F \cdot ReF_5$ was lower than that

(based on rhenium) from a 1:3 reaction alone. This suggests

that $Re(CO)_5F \cdot ReF_5$ is fluorinated to a volatile species,

presumed to be ReF_6, by additional XeF_2. The 1:5 reaction

was performed in a single step, and similarly produced

$Re(CO)_5F \cdot ReF_5$ and ReF_6.

2-1.3   The Reactions of Lower Stoicheiometries

The infrared spectra of the solid products from

the 1:1 and 1:2 reactions showed them to be mostly $Re_2(CO)_{10}$,

with additional, weak peaks (2170, 2040 and 620 cm^{-1}) due

to $Re(CO)_5F \cdot ReF_5$. The spectrum obtained from a preliminary

1:1 reaction of Misra[34] was re-examined, and was now ident-

ified as showing a similar mixture of $Re_2(CO)_{10}$ and

$Re(CO)_5F \cdot ReF_5$. The product of an $Re_2(CO)_{10}$ + F_2/N_2 reaction

of Wilson[12] was also found to have an infrared spectrum

showing mostly $Re_2(CO)_{10}$, with additional $Re(CO)_5F \cdot ReF_5$

peaks at 2163, 2045, 622, 554 and 525 cm^{-1}. His analytical

data of C = 11.84%, F = 13.9% can now be rationalised in

terms of a very approximate composition of 2 $Re_2(CO)_{10}$:
5 $Re(CO)_5F \cdot ReF_5$.

If these pale yellow solids were handled in any
but the most rigorously dry conditions, they turned buff.
X-ray powder patterns of the buff solids confirmed that they
were largely unchanged $Re_2(CO)_{10}$, but showed small amounts
of a new compound. Separation of the two materials was
achieved by adding anhydrous HF to a sample in a poly-
chlorotrifluoroethylene (Kel-F) apparatus. The $Re_2(CO)_{10}$
remained as a white, insoluble solid, but evaporation to
dryness of the brown, filtered solution gave a brown solid
whose powder pattern showed lines due only to the second
component.** An identical powder pattern was given by the
buff solid, obtained by handling the orange-yellow 1:3
reaction product under slightly moist conditions. Finally,
the compound was obtained as a bulk sample from a 1:3
reaction of $Re_2(CO)_{10}$ and XeF_2, in liquid HF containing
traces of water, and was identified as $(Re(CO)_6)^+(ReOF_5)^-$,
(see section 2-2.2).

It is concluded that the original products of the
1:1 and 1:2 reactions were $Re_2(CO)_{10}$ and a little
$Re(CO)_5F \cdot ReF_5$ (explaining the paler yellow colour), which
began to decompose in the dry-box. The short time required
to run an infrared spectrum was insufficient to allow
significant hydrolysis on what was, in any case, a minor

** The low solubility of rhenium and some other carbonyls
in HF suggests this as a means of separating soluble carbonyl
fluoride species from unreacted starting materials.

component. In the X-ray powder technique there was much
more time for decomposition, and also the possibility of
the hydrolysis being enhanced by the glass walls of the
capillary, in an autohydrolytic cycle:

$$4 \text{ M-F} + 4 \text{ H}_2\text{O} \longrightarrow 4 \text{ M-OH} + 4 \text{ HF},$$

$$\text{SiO}_2 + 4 \text{ HF} \longrightarrow \text{SiF}_4 + 2 \text{ H}_2\text{O}.$$

Subsequently powder samples were obtained in a capillary
attatched directly to the reactor, obviating the need to
go via a dry-box.

2-1.4   Summary

The products of the $\text{Re}_2(\text{CO})_{10}/\text{XeF}_2/\text{Genetron}$ 113
system were thus $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{F}\cdot\text{ReF}_5$, $\text{Re}(\text{CO})_5\text{F}\cdot\text{ReF}_5$
alone, or $\text{Re}(\text{CO})_5\text{F}\cdot\text{ReF}_5$ and ReF_6 depending on the reaction
stoicheiometry. Xenon and carbon monoxide gas were
liberated in every case. In the presence of traces of
moisture, $\text{Re}(\text{CO})_5\text{F}\cdot\text{ReF}_5$ decomposes to $(\text{Re}(\text{CO})_6)^+(\text{ReOF}_5)^-$.

2-2.   THE $\text{Re}_2(\text{CO})_{10}/\text{XeF}_2/\text{HF}$ SYSTEM

2-2.1   General Description of the System, and Discussion
of 1:1 Reactions

Reactions were performed for proportions of Re:F
of. 1:1, 1:3 and 1:5. In the former two, exact amounts of
XeF_2 dissolved in doubly-distilled liquid HF were added to
solid $\text{Re}_2(\text{CO})_{10}$, or $\text{Re}_2(\text{CO})_{10}$ under a few mls. of HF, in
Kel-F apparatus. 1:5 proportions were achieved by adding
2 molar equivalents of XeF_2 in HF to a sample of fresh
$\text{Re}(\text{CO})_5\text{F}\cdot\text{ReF}_5$ dissolved in HF. Instant reactions took
place (despite, in the first two cases, the insolubility

of $Re_2(CO)_{10}$), with the evolution of gas, and a variety

of colour changes. Mass spectra of the volatiles showed

the presence of only xenon and carbon monoxide for the

1:1 and 1:3 reactions, and xenon and some rhenium-containing

species (notably Re^+, m/e 185 and 187), for the 1:5.*

The 1:1 reactions produced a pale yellow solution

over pale yellow, unreacted solid, after a blue-green

colouration had been observed in the solution in the initial

stages. Infrared spectra and X-ray powder patterns conclus-

ively established that the filtered solid was $Re_2(CO)_{10}$.

The general behaviour was suggestive of partial $Re(CO)_5F \cdot ReF_5$

formation, in an analogous manner to the 1:1 XeF_2/Genetron

113 reaction. When the yellow solution was concentrated,

however, a very viscous, brown oil was produced, which

gave a brittle, dark brown solid after many hours pumping.

It is concluded that traces of impurity in the HF, or

leached out of the Kel-F by the HF, caused the decomposition

of the soluble species at higher concentrations.

Definitive characterisation of the brown material

has not been possible because of the difficulty of removing

the last traces of HF. Weak, but reproducible Raman bands

obtained from the concentrated brown HF solution, and from

pale crystals**precipitated from this solution below $-80^\circ C$,

suggest the presence of $(Re(CO)_6)^+$ (2205 w, 2134 m, 494 w,

441 w cm^{-1}, c.f. 2204 s, 2134 vs for $(Re(CO)_6)^+(Re_2F_{11})^-$

in HF, see section 2-3.4, and 486 and 441 for $(Re(CO)_6)^+(AsF_6)^-$

in $MeCN^{47}$), and possibly of the $(Re(CO)_5F)$ moiety (2179 w,

2113 w cm^{-1}, c.f. 2170 m, 2106 s for solid $Re(CO)_5F \cdot ReF_5$).

---

* No special search was made for CO (m/e 28) in this latter
    experiment.
** These crystals also turned to a brown oil on removal of
    the HF at low temperature.

2-2.2   1:3 and 1:5 Reactions : Identification of

$(Re(CO)_6)^+(ReOF_5)^-$
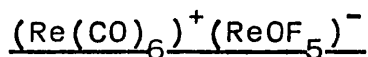
The 1:3 reactions also gave rise to initial,
transient, blue-green colourations, but soon formed orange
solutions of a similar colour to those of $Re(CO)_5F \cdot ReF_5$ in
HF, with no unreacted solid. On standing at room temperature,
the solutions gradually became a pale blue-green colour.
The 1:5 reaction formed a similar pale blue-green solution
almost immediately.

Colour change phenomena were observed in these
final solutions between pale green and pale blue. This
resembled the behaviour of solutions of ReF_6 in liquid HF
containing a few per cent of water, attributed to $(Re^{VI}OF_5)^-$
and similar anions, [48] and suggested that partial hydrolysis
of $Re(CO)_5F \cdot ReF_5$ had occurred. E.S.R. spectra of these
solutions at $-196^\circ C$ were obtained, and these were identical
to the $(ReOF_5)^-$ spectra found in the $ReF_6/HF/H_2O$ system.[48]
These show the 6-line spectrum resulting from the odd
d-electron of the rhenium (VI) species, hyperfine split by
the rhenium nuclei of spin $I = \frac{5}{2}$. Raman spectra of these
1:3 and 1:5 reaction solutions show unequivocal evidence of
$(Re(CO)_6)^+$ (see table 2.3), but only a weak band at 714 cm^{-1}
can be attributable to anionic absorbtions in these solution
spectra. The combined data establish the presence of $(Re(CO)_6)^+$
and $(ReOF_5)^-$ ions in the pale blue-green solutions.

When HF was distilled slowly off at low temperatures,
white or pale-green crystals remained. The volatiles that
were removed from the 1:5 reaction were colourless at room
temperature, and pale-yellow at $-196^\circ C$. This behaviour
demonstrated the presence of ReF_6 in the HF.[40] The absence

Table 2.3. The Raman Spectrum of $(Re(CO)_6)^+(ReOF_5)^-$

in HF Solution

$(Re(CO)_6)^+(ReOF_5)^-$ in HF (this work)	$(Re(CO)_6)^+(AsF_6)^-$ in MeCN ref. 47	Assignment
2201 s	2197 s P	A_{1g} $\nu(C\equiv O)$
2132 vs	2122 vs	E_g $\nu(C\equiv O)$
714 w		$\nu(Re-F)$?
497 w	486 w	T_{2g} $\delta(Re-C-O)$
439 s	441 s P	A_{1g} $\nu(Re-CO)$
	426 sh	E_g $\nu(Re-CO)$

P = polarised band.

Table 2.4. The Infrared Spectrum of $(Re(CO)_6)^+(ReOF_5)^-$

$(Re(CO)_6)^+(ReOF_5)^-$ (this work)	$(Re(CO)_6)^+(AsF_6)^-$ ref. 47	Assignment
2193 sh	2191 w	$A_{1g}\nu(C\equiv O)$
~2125 sh	2122 *	E_g $\nu(C\equiv O)$
2084 vs	2086 vs	T_{1u} $\nu(C\equiv O)$
2063 sh	2062 sh	T_{1u} $\nu(^{13}C\equiv O)$
2044 sh		
1167 w		}
1070 w	1070 m	} o/c
1010 sh	1010 m	}
997 m		$\nu(Re=O)$
969 vvw		
936 w	940 m	o/c
910 vw,br		
880 w	878 m	}
~845 sh	844 w	} o/c
~772 vvw,br	775 w †	}
736 sh		} ?
722 m		}
	700 br	T_{1u} $\nu(AsF_6^-)$
658 m		
611 s		} $\nu(Re-F)$
582 vs	584 vs	} T_{1u} $\delta(Re-C-O)$
574 sh	576 sh	}
~ 540 m		T_{1u} $\nu(ReF_6^{2-})$
522 w	522 m	T_{2u} $\delta(Re-C-O)$
480 w	487 vw	T_{2g} $\delta(Re-C-O)$
421 w	420 vw	E_g $\nu(Re-CO)$

All are nujol mulls except the peak *, which is in MeCN soln.
† Value observed for $(Re(CO)_6)^+(ClO_4)^-$, owing to obscuration
by AsF_6^- peak. o/c = overtone/combination bands.

Fig.2.1 Infrared Spectrum of $(Re(CO)_6)^+(ReOF_5)^-$
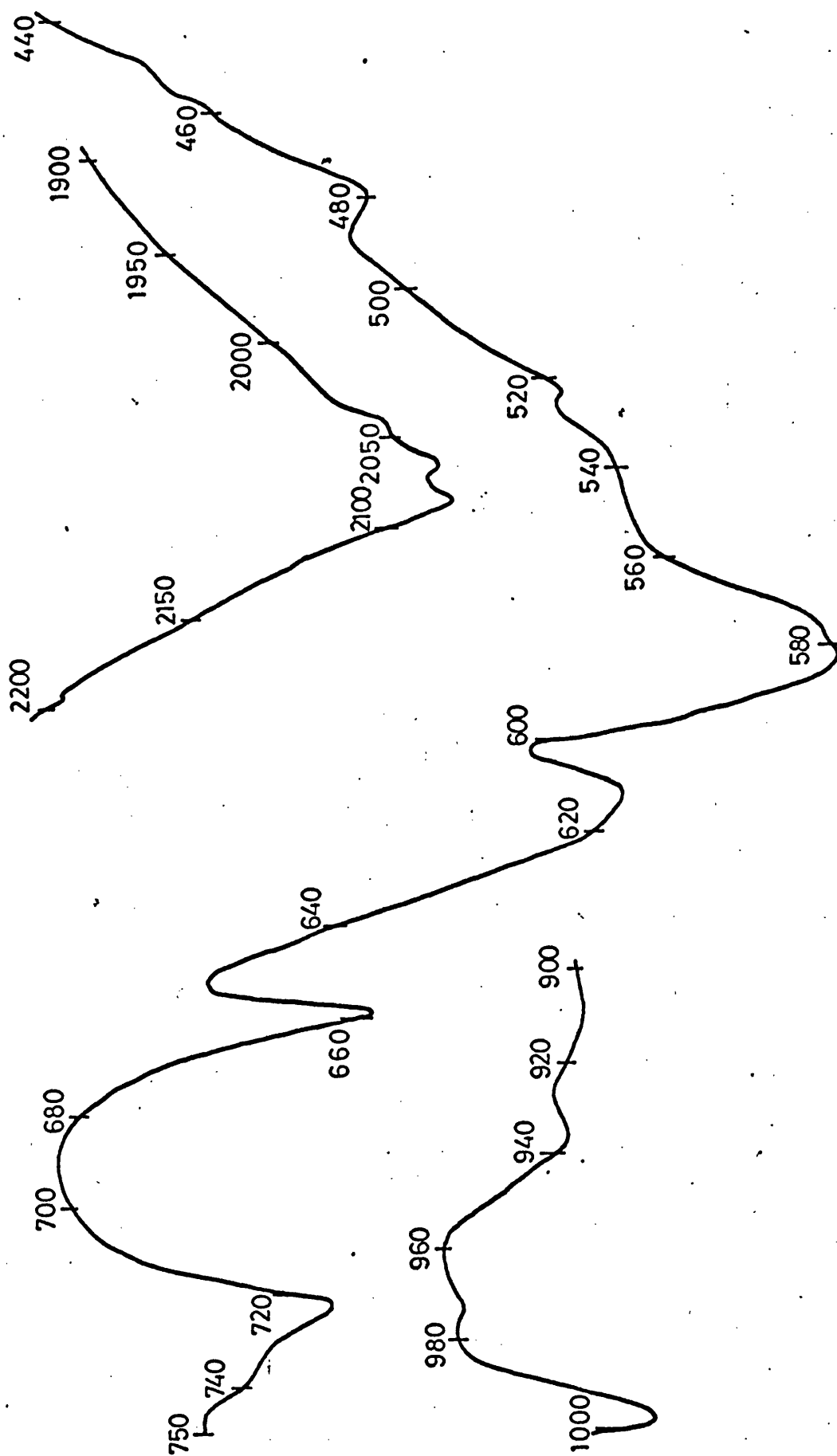
of clear ReF_n^+ series in the mass spectrum of these volatiles

can be attributed to loss of the parent ReF_6 as it fluorinated

the mass spectrometer inlet system.

The infrared spectra of the solids (figure 2.1)

confirm the carbonyl species as $(Re(CO)_6)^+$, and the various

$\nu(C\equiv O)$, $\delta(Re-C-O)$ and $\nu(Re-C)$ bands can be assigned on

the basis of published data on $(Re(CO)_6)^+(AsF_6)^-$,[47] (see

table 2.4). The shoulder at 2044 cm^{-1} may be due to solid

state effects or impurities, and the peak at $\sim$540 cm^{-1} is

attributed to the ν_3 (Re-F) stretching mode of the $(ReF_6)^{2-}$

anion (reported value 541 cm^{-1} [44]), arising from the dis-

proportionation of $Re(CO)_5F \cdot ReF_5$ in the presence of moisture

to give $(Re^{IV}F_6)^{2-}$ and $(Re^{VI}OF_5)^-$ ions.

The remaining bands at 997, 658 and 611 cm^{-1} are

assigned to the $(ReOF_5)^-$ anion. Although no infrared data

have been reported for this anion, its Raman spectrum in

HF solution has been obtained from $ReF_6/H_2O/HF$ solutions.[48]

Vibrational data are known for the molybdenum and tungsten

analogues $(NO)^+(MOF_5)^-$ [49,50] and $(Ph_4P)^+(WOF_5)^-$,[51] and

several full vibrational assignments of other (MOF_5) species

have been made.[52] By comparison with the $\nu(M=O)$ vib-

rational modes of related species, the peak* at 997 cm^{-1} is

assigned to the A_{1g} $\nu(Re=O)$ mode of the C_{4v} $(ReOF_5)^-$ anion:

	Raman(HF)	Raman(s)	IR(s)	(R=alkyl)	IR(s)
$(ReOF_5)^-$	1008 vs[48]	-	997*	[53]$(R_4N)^+(ReOCl_5)^-$	966
$(NO)^+(WOF_5)^-$	1010	1001	1003	[54]$(R_4N)^+(WOCl_5)^-$	960-970

By comparison with the $\nu(M-F)$ region of solid

$(MOF_5)^-$ salts ($[Ph_4P]^+[WOF_5]^-$ 670 vs, 610 vs;[51] $(NO)^+(WOF_5)^-$

625 s, br[49] and 680 sh, 610 vs, br;[50] $(NO)^+(MoOF_5)^-$ 650 vs, br,

550 sh ^{50} cm^{-1}), the bands at 658 and 611 cm^{-1} are consistent

with the major ν(Re-F) modes. The two peaks at 736 and

722 cm^{-1} may be ν(Re-F) modes (c.f. the 736 and 700 cm^{-1}

Raman peaks of (ReOF$_5$)$^-$/HF), or else carbonyl overtone /

combination bands (peaks at around 736 and 722 cm^{-1} are

frequently found in rhenium carbonyl fluoride spectra,

and have been reported, though not assigned, in solid

Re$_2$(CO)$_{10}$^{55}). Lower frequency anion modes ($\sim$450 cm^{-1})

cannot be distinguished because of the presence of carbonyl

bands in this region. Reproducible Raman spectra of the

solid could not be obtained because of decomposition in the

laser beam.

A mass spectrum was obtained from the solid on

heating to 200°C in a glass capillary held in the probe of

the (unseasoned) mass spectrometer. The spectrum shows

fragmentation patterns associated with the species

$\overset{O}{\underset{F}{\diagdown}}$C-Re(CO)$_5$$^+$, ReOF$_5$$^+$, ReO$_3F^+$ and ReO$_2$F$_2$$^+$. No spectrum

could be obtained without heating the probe.

Steps Re(CO)$_n$F$^+$ $\xrightarrow{-C}$ Re(CO)$_{n-1}$OF$^+$

(n = 5-1) are omitted

for clarity .

Two series of doubly-charged

species were also found:

$$ReF_4^{2+}$$

$$\downarrow -F$$

$$ReOF_3^{2+} \xrightarrow{-O} ReF_3^{2+}$$

$$-2F \downarrow\ \text{stepwise} \qquad \downarrow$$

$$ReOF^{2+} \xrightarrow{-O} ReF^{2+}$$

$$ReO_3F^{2+} \xrightarrow{-O} ReO_2F^{2+} \xrightarrow{-O} ReOF^{2+} \qquad\qquad \downarrow -F \qquad\qquad \downarrow -F$$

$$\downarrow -F \qquad\qquad \downarrow -F \qquad\qquad \downarrow -F$$

$$ReO_3^{2+} \xrightarrow{-O} ReO_2^{2+} \xrightarrow{-O} ReO^{2+} \qquad ReO^{2+} \xrightarrow{-O} Re^{2+}$$

The relative intensities of the peaks are given in table 2.5.

The spectrum can be interpreted in terms of the

decomposition of the ionic, involatile $(Re(CO)_6)^+(ReOF_5)^-$ giving

the volatile species $ReOF_5$, $ReOF_4$, ReO_3F, ReO_2F_3, (c.f.ref.56)

$$\overset{O}{\underset{F}{\diagdown}}C\text{-}Re(CO)_5$$ and $Re(CO)_5F$. These species may be produced

by the following processes:

$$ReOF_5^- + e^- \longrightarrow ReOF_5 + 2e^-$$

$$ReOF_5^- \xrightarrow{\text{HEAT}} ReOF_4 + F^- \text{ , perhaps aided}$$

by moisture from the glass, by O_2 or SiO_2, or by electron

impact.

$$ReOF_5^- + O_2 \xrightarrow{\text{HEAT}} ReO_3F + F_2 + F^- \text{, ditto.}$$

$$ReOF_5^- + 2H_2O \longrightarrow ReO_3F^- + 4HF, \text{ followed by:}$$

$$ReO_3F^- + e^- \longrightarrow ReO_3F + 2e^- \ .$$

ReO_2F_3, the probable precursor of $ReO_2F_2^+$, will be produced

in a similar fashion to ReO_3F.

$$(Re(CO)_6)^+ + F^- \xrightarrow{\text{HEAT}} \overset{O}{\underset{F}{\diagdown}}C\text{-}Re(CO)_5 \text{ , which can fragment by:}$$

$$\overset{O}{\underset{F}{\diagdown}}C\text{-}Re(CO)_5 \longrightarrow Re(CO)_5F + CO$$

$$\overset{O}{\underset{F}{\diagdown}}C\text{-}Re(CO)_5 + e^- \longrightarrow Re(CO)_5OF^+ + C$$

$$(Re(CO)_6)^+ + F_2 \longrightarrow Re(CO)_5F + COF^+ \ .$$

Table 2.5. Mass spectrum from $(Re(CO)_6)^+(ReOF_5)^-$ at 200^oC

m/e	Ion	%Abundance*	m/e	Ion	%Abundance*
374/72	$Re(CO)_5 \cdot C(O)F^+$	4.0	131½/30½	ReF_4^{2+}	3.8
362/60	$Re(CO)_5OF^+$	5.6	130/29	$ReOF_3^{2+}$	33
346/44	$Re(CO)_5F^+$	13	127/26	ReO_3F^{2+}	4.0
334/32	$Re(CO)_4OF^+$	6.0	122/21	ReF_3^{2+}	11
327/25	$Re(CO)_5^+$	11	120½/19½	$ReOF_2^{2+}$	46
318/16	$Re(CO)_4F^+$	16	119/18	ReO_2F^{2+}	5.9
306/04	$Re(CO)_3OF^+$	5.2	117½/16½	ReO_3^{2+}	3.6
298/96	$ReOF_5^+$	7.5	112½/11½	ReF_2^{2+}	15
290/88	$Re(CO)_3F^+$	25	111/10	$ReOF^{2+}$	22
279/77	$ReOF_4^+$	100	109½/08½	ReO_2^{2+}	4.8
278/76	$Re(CO)_2OF^+$	8.6	107½/106½	$Re(CO)^{2+}$	4.3
271/69	$Re(CO)_3^+$	6.7	103/02	ReF^{2+}	24
263/61	ReF_4^+	32	101½/00½	ReO^{2+}	15
262/60	$Re(CO)_3F^+$	15	93½/92½	Re^{2+}	46
260/58	$ReOF_3^+$	>230			
257/55	$ReO_2F_2^+$	25			
254/52	ReO_3F^+	58			
250/48	$Re(CO)OF^+$	7.1			
244/42	ReF_3^+	37			
243/41	$Re(CO)_2^+$	5.9			
241/39	$ReOF_2^+$	84			
238/36	ReO_2F^+	24			
235/33	ReO_3^+	14			
234/32	$Re(CO)F^+$	11			
225/23	ReF_2^+	56			
222/20	$ReOF^+$	48			
219/17	ReO_2^+	13			
215/13	$Re(CO)^+$	5.6			
206/04	ReF^+	54			
203/01	ReO^+	30			
199/97	ReC^+	6.0			
187/85	Re^+	91			

* Rhenium has two stable isotopes of mass numbers 185 (37% abundant) and 187 (63%). The abundance of each particular fragment is based on the intensity of the ^{187}Re peak.

Non-rhenium containing peaks are not tabulated.

The major peaks in the spectrum are the series $ReOF_4^+$, $ReOF_3^+$ and $ReOF_2^+$ and the highest mass peak in this fragmentation series is, as expected, $ReOF_5^+$. This indicates that the major species from the anion fragmentation are $ReOF_5$ and $ReOF_4$ ($ReOF_3$ being involatile).[56] This is further supported by the principal peaks in the secondary spectrum $ReOF_3^{2+}$, $ReOF_2^{2+}$, $ReOF^{2+}$ and ReF^{2+}. These results are entirely consistent with the anion of the solid being $(ReOF_5)^-$. The other oxyfluoride species result from the oxygenation of this anion, as shown above, under the conditions in the probe. The low intensity of the carbonyl-containing fragments indicates either that only small decomposition of the $(Re(CO)_6)^+$ ion occurs, or, alternatively, rapid degradation to CO and rhenium metal.

X-ray powder patterns of the ground crystals from the 1:3 and 1:5 reactions were identical to those of the buff solid obtained after handling $Re(CO)_5F \cdot ReF_5$ under moist conditions (c.f. section 2-1.3). There are similarities in the general spacing and intensity distribution of the major lines with the powder pattern of $Re(CO)_5F \cdot ReF_5$, but the pattern is unlike that of any other carbonyl fluoride. The d-spacings are tabulated with the crystallographic data in table 8.1, page **207**.

A single crystal of the bulk solid was mounted for X-ray structural work, which is described more fully in chapter **8**. Though a definitive structural analysis could not be achieved, the essential details confirm the formulation of $(Re(CO)_6)^+(ReOF_5)^-$. The unit cell dimensions are consistent with the theoretical volume required for $(Re(CO)_6)^+(ReOF_5)^-$ calculated on the basis of established

principles. The electron density maps of the unit cell show a regular array of rhenium atoms with highly symmetrical co-ordination spheres, with the light atoms contributing very little to the data. The $(Re(CO)_6)^+$ cation was distinguished, but the identity of the anion could not be established, probably because of disorder.

These crystal data, together with the other information described above, serve to show that the solid product of both the 1:3 and 1:5 $Re_2(CO)_{10}$:XeF_2/HF reactions is predominately the ionic salt $(Re(CO)_6)^+(ReOF_5)^-$. This was produced, along with $(ReF_6)^{2-}$ derivatives, by the partial hydrolysis of $Re(CO)_5F \cdot ReF_5$ by traces of moisture, or other oxygen-containing impurities, in the HF. The remarkable affinity of rhenium (V) fluorides for such species has already been noted. That $Re(CO)_5F \cdot ReF_5$ was the precursor of $(Re(CO)_6)^+(ReOF_5)^-$, and thus the original product of the 1:3 reaction, is supported by the fact that solid $Re(CO)_5F \cdot ReF_5$ is hydrolysed by traces of moisture to give $(Re(CO)_6)^+(ReOF_5)^-$, and that this same final product was obtained from the 1:5 reaction where XeF_2 and HF were added to freshly-prepared $Re(CO)_5F \cdot ReF_5$. The mechanism of the hydrolysis is discussed in section 3-2.5.

2-2.3   Summary of the $Re_2(CO)_{10}$/XeF_2/HF System

The results obtained can be summarised in the following three equations:

$Re_2(CO)_{10}$ + XeF_2 $\longrightarrow$ $\sim\frac{1}{2}$ $Re_2(CO)_{10}$ + brown solid of indef-

inite composition + CO and Xe.

$$Re_2(CO)_{10} + 3\ XeF_2 \longrightarrow Re(CO)_5F \cdot ReF_5 + 5\ CO + 3\ Xe$$

$$\Big\downarrow \text{hydrolysis}$$

$$(Re(CO)_6)^+(ReOF_5)^- + (ReF_6)^{2-}\ \text{species}$$

$$Re(CO)_5F \cdot ReF_5 + 2\ XeF_2 \longrightarrow \tfrac{1}{3}\ Re(CO)_5F \cdot ReF_5 + \tfrac{2}{3}\ ReF_6 + 2Xe\ (+\ CO)$$

$$\Big\downarrow \text{hydrolysis}$$

$$(Re(CO)_6)^+(ReOF_5)^- + (ReF_6)^{2-}\ \text{species.}$$

2-3.   THE $Re_2(CO)_{10}$ / ReF_6 / HF SYSTEM

2-3.1   General Description of the System, and Discussion of

1:2 Reaction

Proportions of $Re_2(CO)_{10}$ to ReF_6 of 1:2, 1:3 and
1:4 were used. The stoicheiometric amounts of ReF_6 were
condensed on to frozen mixtures of $Re_2(CO)_{10}$ and anhydrous
HF, in a metal and Kel-F apparatus, and the mixture warmed
to room temperature. Complicated colour-change phenomena
were observed, particularly during the 1:3 reaction, where
the ReF_6 was added stepwise. In all three reactions, a
transient blue colour was visible on the surface of the
solid rhenium carbonyl, with a pale yellow solution above,
as the first traces of ReF_6 dissolved into the molten HF.
This behaviour was similar to that of the $Re_2(CO)_{10}/XeF_2/HF$
reactions. The colour dispersed immediately the bulk of
the ReF_6 had dissolved. There was no gas evolution in any
of the reactions. The absence of CO was demonstrated
by the lack of a measureable vapour pressure above the
reaction mixture at $-196^\circ C$.

The 1:2 reaction gave a bright orange-red solution
from which orange crystals of $Re(CO)_5F \cdot ReF_5$ were obtained
as the sole product. These were identified by comparison of

the X-ray powder pattern and infrared spectrum with those

of the orange product of the 1:3 reaction (see below), and

with $Re(CO)_5F.ReF_5$ from the XeF_2/Genetron reactions.

2-3.2 The 1:3 Reaction and the Isolation of $(Re(CO)_6)^+(Re_2F_{11})^-$

The 1:3 reaction gave a red-brown solution and

dark solid when approximately 1:2 proportions had been added,

but on addition of the last molar equivalent of ReF_6, the

solution became green, with only small amounts of undissolved

residue. After filtering, orange, brick-shaped crystals

and green needles were gradually precipitated from the

solution at 0^oC, and further crystals of both sorts were

obtained on slowly distilling off the HF. Single crystal

X-ray structures on the two types of crystals established

the orange to be $Re(CO)_5F.ReF_5$ (see chapter 6), and the

green to be a new, ionic species $(Re(CO)_6)^+(Re_2F_{11})^-$ (see

chapter 7). Definitive infrared and Raman spectra, and

X-ray powder patterns, of these two compounds were also

obtained, and were used as the basis for interpreting the

results of the XeF_2 systems.

Rather more $(Re(CO)_6)^+(Re_2F_{11})^-$ seemed to be formed

than $Re(CO)_5F.ReF_5$. The presence of small quantities of

other solid species could not be ruled out, but no definitive

evidence was obtained.

2-3.3 The 1:4 Reaction, and Identification of a Second
Modification of $(Re(CO)_6)^+(Re_2F_{11})^-$

The 1:4 reaction produced a yellow solution,

(which gradually turned green during several days at room

temperature) over a considerable amount of golden yellow,
crystalline solid. Undissolved solid was always present
in the reaction. The yellow crystals were filtered off and
gave an X-ray powder pattern <u>almost</u> identical to that of
the green $(Re(CO)_6)^+(Re_2F_{11})^-$ from the 1:3 reaction, (see
table 2.6 page 36). The infrared spectrum was also almost
identical (see table 2.7 page 37). Elemental analysis
confirmed that the formula was $(Re(CO)_6)^+(ReF_{11})^-$:

> Yellow crystals (found) :   7.69% C , 21.2% F .

> $Re(CO)_6{}^+Re_2F_{11}{}^-$ (calc.) :   7.70% C , 22.3% F .

This suggested that the yellow solid was a different
crystalline modification of $(Re(CO)_6)^+(Re_2F_{11})^-$ from the
green crystals from the 1:3 reaction. It seemed significant
that the former were produced by a heterogeneous reaction,
whereas the latter were precipitated from solution. Recry-
stallisation from HF thus seemed a possible means of con-
verting the yellow form to the green. A sample of the
yellow solid was duly treated with HF, and gave a green
solution, together with an undissolved dark residue. The
latter probably resulted from surface hydrolysis from
handling in the dry-box and subsequent storage in glass.
An E.S.R. spectrum of the green solution after decanting
gave a weak signal due to $(ReOF_5)^-$, at about a twentieth
the concentration of the signal from the 1:3 XeF_2/HF
reaction (see section 2-2.2). This confirmed that trace
hydrolysis of the yellow solid had occurred, giving a small
concentration of $(ReOF_5)^-$ in solution, and some insoluble
residue. Evaporation of the green solution to dryness
produced green, needle crystals whose powder pattern and
infrared spectrum were identical to those of the green

crystals of $(Re(CO)_6)^+(Re_2F_{11})^-$ from the 1:3 reaction.

It was concluded that the green and yellow crystals are indeed differing crystalline modifications of $(Re(CO)_6)^+$ $(Re_2F_{11})^-$, hereafter known as α- and β- respectively. Polymorphism is a common feature amongst compounds with mononuclear cations and binuclear anions.

The green solution from the 1:4 reaction was itself concentrated, precipitating grass-green, needle crystals which may have been α-$(Re(CO)_6)^+(Re_2F_{11})^-$. As the last traces of HF were removed, however, the mixture became an intractible, brown tar, probably due to traces of impurity, and was not examined further. It is possible the tar may have contained ReF_5 which is known to form a solid mass initially, rather than crystallise.[61] The HF and volatiles that were taken off formed a pale yellow solid at $-196^\circ C$, and a colourless solution at room temperature, suggesting the presence of some unreacted ReF_6 in the HF. In the presence of traces of water this colourless solution became pale blue from the formation of $(ReOF_5)^-$.

The probable equation for the 1:4 reaction (see section 3-2.3) is:

$$3 \; Re_2(CO)_{10} + 12 \; ReF_6 \longrightarrow 5 \; (Re(CO)_6)^+(Re_2F_{11})^- + ReF_5 +$$

$$2 \; ReF_6 \; \text{(unreacted)}$$

On this basis, the yield of β-$(Re(CO)_6)^+(Re_2F_{11})^-$ is approximately 86%.

2-3.4 The Properties of α- and β- $(Re(CO)_6)^+(Re_2F_{11})^-$

α-$(Re(CO)_6)^+(Re_2F_{11})^-$ decomposed without melting at $259^\circ C$, when heated in an evacuated Pyrex glass capillary.

Both α- and β- forms dissolve completely in acetone, to give brown, presumably hydrolysed, solutions. Like other rhenium (V) species, both forms are extremely moisture-sensitive, turning black in moist air. The yellow solid darkened even on handling in a recirculating dry-box atmosphere, but X-ray powder photographs showed that this was only a surface effect, the bulk being unchanged. This agrees with the E.S.R. evidence for only traces of $(ReOF_5)^-$ in HF solution. Pure $(Re(CO)_6)^+(Re_2F_{11})^-$ exhibits neither E.S.R. nor N.M.R. signals in HF solution, as expected for a high-spin, d^2 Re^V anion.

Table 2.6 compares the X-ray powder patterns of α- and β- $(Re(CO)_6)^+(Re_2F_{11})^-$, as well as of O'Donnell's product of his $Re_2(CO)_{10}/ReF_6/HF$ reaction, "$Re(CO)_3F_3$".[38] The d-spacings of the α-form are indexed from the single crystal data (see table 7.4, page 193). The most striking differences between the α- and β- forms lie in the region d = 3.50 to d = 3.00 Å; otherwise they are very similar. It is apparent that the pattern of "$Re(CO)_3F_3$" parallels those of $(Re(CO)_6)^+(Re_2F_{11})^-$ quite closely, at least as far as d = 3.00 Å, although more marked divergence is shown at lower d-spacings.

The infrared data on $(Re(CO)_6)^+(Re_2F_{11})^-$ are summarised in table 2.7. The $(Re(CO)_6)^+$ bands may be identified unambiguously in both forms, just as in the case of $(Re(CO)_6)^+(ReOF_5)^-$. Peaks at 688, 663 and 649 cm^{-1} (α-) and 680, 665 and 642 cm^{-1} (β-) are ν(Re-F) modes of the anion. Only β-$(Re(CO)_6)^+(Re_2F_{11})^-$ has given a reproducible Raman spectrum, the α- phase tending to decompose in the

Table 2.6. X-ray Powder Pattern d-spacings for

$(Re(CO)_6)^+(Re_2F_{11})^-$ and Related Compounds

α-$(Re(CO)_6)^+(Re_2F_{11})^-$			β-$(Re(CO)_6)^+$ $(Re_2F_{11})^-$		$(Re(CO)_6)^+$ $(Sb_2F_{11})^-$		"$Re(CO)_3F_3$"	
hkl	d_{hkl}	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o
	7.60	1	7.54	1				
	7.10	4	7.12	1	7.18	1		
			6.90	3	6.89	4	6.81	6
210	6.67	7	6.58	6	6.62	4		
	6.39	4	6.27	2	6.35	2	6.44	6
201	5.56	3	5.53	3	5.62	1	5.68	4
							5.41	4
			5.05	1	5.09	2	5.04	1
121	4.97	10	4.88	10	4.95	9	4.83	10
			4.41	1	4.43	2		
221	4.33	10	4.29	10	4.32	10	4.21	10
311	4.10	1	4.12	1				
230	3.92	6	3.93	8	3.94	6		
400	3.79	6	3.82	9	3.85	4	3.82	6
321	3.65	4	3.63	5	3.65	4	3.66	7
122/240	3.44	5			3.46	5	3.54	4
420	3.33	3	3.36	8	3.36	1	3.41	5
302	3.16	6	3.19	8	3.19	6	3.23	3
312/421	3.09	2	3.10	3	3.12	1	3.06	5
132/241	2.93	1	2.96	1				
322	2.90	1	2.88	3	2.91	1		
511/402	2.79	1	2.81	3	2.82	1		
			2.75	1				
521	2.63	3	2.65	5	2.68	2	2.69	1
142/051	2.59	6	2.61	1	2.59	5		
600/440	2.55	3	2.56	6			2.55	4
			2.53	5				
610	2.49	2	2.49	1	2.50	1		
	2.44	1	2.46	2				
	2.40	5	2.42	1	2.42	3		
			2.37	6				
	2.33	5	2.32	8	2.35	5	2.34	2
	2.28	2	2.30	3			2.29	3
	2.26	1	2.27	1				
			2.23	1				
	2.19	2	2.19	2	2.20	3	2.20	1
	2.14	2	2.12	2	2.13	2	2.15	1
			2.09	4			2.09	1
	2.06	1	2.06	1				
			2.04	3				
	2.03	1	2.03	1				

Table 2.7 Infrared Spectra of $(Re(CO)_6)^+(Re_2F_{11})^-$ and

Related Compounds

$Re(CO)_6^+Re_2F_{11}^-$ $\alpha-$	$Re(CO)_6^+Re_2F_{11}^-$ $\beta-$	$Re(CO)_6^+$ $Sb_2F_{11}^-$	$Re(CO)_6^+$ AsF_6^-	$Re(CO)_3F_3$	Assignment
	2470 vw	2474 vw	2480 sh		o/c
2194 vw	2194 vw	2195 vw	2191 w		
	2154 vw	2153 w ‡	2165 sh		
2126 m	2126 w	2121 sh	2122 *	2120 m	
	2118 m				$\nu(C{\equiv}O)$
	2105 sh				
2071 s	2078 vs	2083 vw	2086 vs	2070 s	
2041 sh	2052 sh		2062 sh	2040 sh	
1072 vvw	1067 vw	~1070 vw	1070 m		
1041 vw	1052 w	~1040 sh			
1012 vw	1012 vw	~1010 vw	1010 m		o/c
		966 w			
~943 vw	941 vw	~944 vw	940 m		
~885 vw	886 vw	886 vw	878 m		
~740 sh					?
721 w	719 vw	720 sh			
688 w	680 sh	701 ms	700 br		
663 sh	665 vw	680 s			$\nu(M-F)$
649 s	642 vs	663 vs		650 m	
582 s	582 vs	582 vs	$\left\{\begin{matrix}584\ vs\\576\ sh\end{matrix}\right\}$	580 m	$\delta(Re-C-O)$
	542 s				?
515 vw	527 sh	522 w	522 m		$\delta(Re-C-O)$
		497 vw			
485 vw	491 vw	485 vw	487 vw		$\nu(Re-CO)$
This work	This work	This work	ref.47	ref.38	

All peaks are nujol mulls except * (MeCN solution)
‡ An additional peak at 2174 w may be due to an impurity.
o/c = overtone/combination bands.

laser beam. Characteristic $(Re(CO)_6)^+$ peaks occur at 2196 vw

cm^{-1} (A_{1g} ν_{CO}), 2122 vs(Eg ν_{CO}), 487 m,sh(T_{2g} δ_{ReCO}) and 435 s

(A_{1g} ν_{ReC}), with an extra 2178 vw peak, and anion bands at 718

m, 707 sh, 462 m,sh and 314 vw. A solution spectrum in HF also

showed $(Re(CO)_6)^+$ ν_{CO} absorbtions (2204 s, 2134 vw cm^{-1}), but

no clear signals at lower frequencies. Definitive vibrational

assignments of $(M_2F_{11})^-$ species have not so far been made.[65]

It has not been possible to obtain a mass spectrum

from $(Re(CO)_6)^+(Re_2F_{11})^-$ on account of its involatility.

2-3.5 The Reaction of $(Re(CO)_6)^+(Re_2F_{11})^-$ with an Excess of XeF_2.

An excess of XeF_2 was added to $(Re(CO)_6)^+(Re_2F_{11})^-$

in HF, to see whether further oxidation might take place,

or whether an XeF_2 complex like $XeF_2 \cdot 2ReF_5$ would be formed.

A pale blue solution was produced, with the evolution

of xenon gas, but not of CO (from a mass spectrum of the

volatiles). The solution became colourless on standing,

and yielded very pale green, needle crystals on removal of

the HF. Once again the condensible volatiles were pale

yellow at $-196^\circ C$ and colourless at room temperature, indic-

ating ReF_6 dissolved in the HF. The pale solid gave a

powder pattern identical to that of $(Re(CO)_6)^+(ReOF_5)^-$,

except for a few extra lines. While confirming the presence

of $(Re(CO)_6)^+$ as the only carbonyl species, the infrared

and Raman spectra (table 2.8) of the solid show significantly

different $\nu(Re=O)$ and $\nu(Re-F)$ regions from those associated

with $(ReOF_5)^-$.

Mass spectra from the solid heated to $100^\circ C$ in

a glass capillary, held in the spectrometer probe, show only

Table 2.8. Vibrational Spectra of the $(Re(CO)_6)^+(Re_2F_{11})^-$ /

XeF$_2$ / HF Product

IR(nujol mull)	Raman(powder)	Raman(HF soln)	Assignment
2198 vvw	2201 m	2203 w	$A_{1g}\nu(C\equiv O)$
2122 sh	2126 vs	2133 s	$E_g\nu(C\equiv O)$
2078 vs			$T_{1u}\nu(C\equiv O)$
2065 sh			$T_{1u}\nu(^{13}C\equiv O)$
988 vw	989 vw		$\nu(Re=O)$
969 w	970 m		
935 w	938 w		o/c
912 vw			
876 vvw			o/c
	720 vw ?	742 vw ?	o/c ?
656 vw	660 vw		$\nu(Re-F)$
638 sh			
635 w	641 vw		
619 sh			
614 w			
582 m			$T_{1u}\delta(Re-C-O)$
		553 w	
542 vw			$T_{1u}\nu(ReF_6^{2-})$
511 vw		502 vw	$T_{2u}\delta(Re-C-O)?$
482 vw	486 vw	486 vw	$T_{2g}\delta(Re-C-O)$
	444 s	442 s	$A_{1g}\nu(Re-CO)$
	410 vw		$E_g\nu(Re-CO)?$
	325 vw		

o/c = overtone or combination band

Table 2.9. Mass Spectra from the $(Re(CO)_6)^+(Re_2F_{11})^-$

/XeF_2 Product at $100^\circ C$ and $200^\circ C$

Probe at $100^\circ C$ ‡

m/e •	Ion	% Abundance •
328	$HRe(CO)_5^+$ 328/26	13
327	$Re(CO)_5^+$ 327/25	47
326	$Re_2(CO)_{10}^{2+}$ 327/26/25	16
325		39
300/298	$HRe(CO)_4^+$	24
299/97	$Re(CO)_4^+$	34
272	$HRe(CO)_3^+$ 272/70	58
271	$Re(CO)_3^+$ 271/69	55
270	$Re_2(CO)_6^{2+}$ 271/70/69	55
269		32
244	$HRe(CO)_2^+$	95
243	$Re(CO)_2^+$	100
242	$Re_2(CO)_4^{2+}$	45
241		22
216/14	$HRe(CO)^+$	21
215/13	$Re(CO)^+$	34
203/01	ReO^+	<8
200/198	$HReC^+$	7.9
199/97	ReC^+	32
188/86	HRe^+	13
187/85	Re^+	71

• For the bracketed groups of m/e values and abundances, there is sufficient deviation from the normal ^{185}Re 37%, ^{187}Re 63% isotopic abundance, to indicate a significant intensity of $Re_2(CO)_n^{2+}$ peaks (n=10,6,4 and 2), or peak overlap from other ions (≠). Otherwise abundances are quoted for the ^{187}Re peak of each fragment.

‡ Weak evidence was also found for the series $Re_2(CO)_n^+$ (n=10 and 7-0), $HRe(CO)_n^{2+}$ (n=5-0), $Re(CO)_n^{2+}$ (n=5-0), and ReC^{2+}. Non-rhenium containing peaks are omitted.

Table 2.9 cont.

Probe at 200°C

m/e	Ion	%Abundance*
346/44	$Re(CO)_5F^+$	10
334/32	$Re(CO)_4OF^+$	10
328/26 327 326 325	$HRe(CO)_5^+$ 328/26 $Re(CO)_5^+$ 327/25 $Re_2(CO)_{10}^{2+}$ 327/26/25	21 12 17 10
318/16	$Re(CO)_4F^+$	8.6
306/04	$Re(CO)_3OF^+$	7.4
300/298	$HRe(CO)_4^+$	12
299/97	$Re(CO)_4^+$	12
298/96	$ReOF_5^+$	very weak
290/88	$Re(CO)_3F^+$	20
282/80	ReF_5^+	very weak ?
281/79	$Re(CO)_2F_2^+$	11
279/77	$ReOF_4^+$	very weak
278/76	$Re(CO)_2OF^+$	10
272 271 270 269	$HRe(CO)_3^+$ 272/70 $Re(CO)_3^+$ 271/69 $Re_2(CO)_6^{2+}$ 271/70/69	22 28 23 19
262 260 258	≠ $Re(CO)_2F^+$ 262/60 ≠ $ReOF_3^+$ 260/58	11 33 19
254/52	ReO_3F^+	100
244 243 242 241 239	$HRe(CO)_2^+$ 244/42 $Re(CO)_2^+$ 243/41 $Re_2(CO)_4^{2+}$ 243/42/41 ≠ $ReOF_2^+$ 241/39	41 23 28 15 6.2
238/36	ReO_2F^+	35
235/33	ReO_3^+	22
234/32	$Re(CO)F^+$	12
225/23	ReF_2^+	11
222/20	$ReOF^+$	17
219/17	ReO_2^+	15
216 215 214 213	$HRe(CO)^+$ 216/14 $Re(CO)^+$ 215/13 $Re_2(CO)_2^{2+}$ 215/14/13	8.6 19 12 6.2
296/04	ReF^+	14
203/01	ReO^+	21
199/97	ReC^+	17
187/85	Re^+	48

the breakdown patterns of $HRe(CO)_5^+$ and (very weakly)

$Re_2(CO)_n^+$ (n = 10 and 7-0), with the doubly charged series

of $HRe(CO)_5^{2+}$ and $Re_2(CO)_n^{2+}$ (n = 10, 6 and 4). At 200°C

however, the spectra show patterns from ReO_3F^+ (the most

intense series), $Re(CO)_5F^+$ and (very weakly) $ReOF_5^+$, in

addition to a weaker $HRe(CO)_5^+$ series. The relative

intensities of the peaks are given in table 2.9.

$HRe(CO)_5^+ \xrightarrow{-H} Re(CO)_5^+$ $\qquad\qquad Re(CO)_5F^+$

$\downarrow$-5CO stepwise $\quad\downarrow$ $\qquad\qquad -C\nearrow\qquad \downarrow -CO$

$HRe^+ \xrightarrow{\quad -H \quad} Re^+$ $\qquad Re(CO)_4OF^+ \xrightarrow{-O} Re(CO)_4F^+ \xrightarrow{-F} Re(CO)_4^+$

$\qquad\qquad\qquad\qquad\qquad\downarrow -4\ CO \qquad \downarrow stepwise \qquad \downarrow$

$\qquad\qquad\qquad ReOF^+ \xrightarrow{\quad -O \quad} ReF^+ \xrightarrow{\quad -F \quad} Re^+$

Steps $Re(CO)_nF^+ \xrightarrow{-C} Re(CO)_{n-1}OF^+$

(n=4-1) are omitted for clarity .

As with $(Re(CO)_6)^+(ReOF_5)^-$ (section 2-2.2) the

spectra result from volatile decomposition products

$ReOF_5$, ReO_3F and $Re(CO)_5F$, and also $HRe(CO)_5$, produced

by heating the sample in a glass capillary, in the probe,

to 200°C. The much greater abundance of the ReO_3F^+

series than the $ReOF_5^+$ indicates a greater degree of

hydrolysis in the sample than in $(Re(CO)_6)^+(ReOF_5)^-$,

producing an anion richer in oxygen, perhaps $(ReO_2F_3)^-$

or $(ReO_3F)^-$ (but not $(ReO_4)^-$, which may be excluded on

account of the vibrational spectra). $HRe(CO)_5$ probably

resulted from a high temperature hydrolysis of $(Re(CO)_6)^+$:

$(Re(CO)_6)^+ + H_2O \xrightarrow{\text{HEAT}}$ $\begin{smallmatrix}O\\ \diagdown\\ HO \diagup\end{smallmatrix}C-Re(CO)_5 + H^+$, which fragments

by:- $\begin{smallmatrix}O\\ \diagdown\\ H-O \diagup\end{smallmatrix}C-Re(CO)_5 \longrightarrow HRe(CO)_5 + CO_2$, c.f. ref.57, and

also the hydrolysis of $(Mn(CO)_6)^+$ [58]). The absence of

this fragmentation in $(Re(CO)_6)^+(ReOF_5)^-$ is consistent

with the smaller proportion of H_2O present.

No definite conclusion can be drawn about the

formula of the anion, in view of the general lack of data

on rhenium oxide fluoride anions.

2-4. REACTIONS OF $Re(CO)_5F \cdot ReF_5$ WITH PENTAFLUORIDES

Reactions of $Re(CO)_5F \cdot ReF_5$ with TaF_5 and SbF_5

were investigated, in preliminary attempts to exchange

the pentafluoride fragment, which would give $Re(CO)_5F \cdot MF_5$,

or to add a second, which would give $Re(CO)_5F \cdot ReF_5 \cdot MF_5$.

2-4.1 $Re(CO)_5F \cdot ReF_5$ and TaF_5

The reaction of $Re(CO)_5F \cdot ReF_5$ with TaF_5 in HF

solution gave a golden yellow solution, with no evolution

of gas. Decomposition of the solution occurred on standing,

with much darkening. The solid that was isolated, however,

gave an infrared spectrum similar to that of $Re(CO)_5F \cdot ReF_5$

(table 2.1), except that the ν(Re-F) peaks at 642 and

620 cm^{-1} are absent, and the δ(Re-C-O) peak at 588 cm^{-1}

is unusually broad, with a new shoulder at ~605 cm^{-1}.

Comparing the bands in this region with those of $(TaF_6)^-$,[44]

$(ReF_6)^-$,[44] $Re(CO)_5F \cdot ReF_5$, and the recently-reported

$Re(CO)_5F \cdot AsF_5$,[43] (table 2.2), the solid may be formulated

as $Re(CO)_5F \cdot TaF_5$. An analogous mixed complex was prepared

by Wilson from the carbonylation of RuF_5/TaF_5,[28] and can

be identified as $(Ru(CO)_3F_2 \cdot TaF_5)_2$ from a similar infrared

comparison with $(Ru(CO)_3F_2 \cdot RuF_5)_2$.

X-ray powder patterns of the solid showed the
presence only of $(Re(CO)_6)^+(ReOF_5)^-$ and an unidentified
second phase. As no evidence for $(Re(CO)_6)^+$ or $(ReOF_5)^-$
could be found in the infrared spectrum, it is likely that
hydrolysis of the ReF_5 by-product occurred in the X-ray
capillary to give rise to $(Re(CO)_6)^+(ReOF_5)^-$:

$$Re(CO)_5F \cdot ReF_5 + TaF_5 \longrightarrow Re(CO)_5F \cdot TaF_5 + ReF_5$$

$$ReF_5 + moisture/glass \longrightarrow ReOF_5^-, ReF_6^{2-}, etc.$$

No further data were obtained from this reaction.

2-4.2 $Re(CO)_5F \cdot ReF_5$ and SbF_5

An excess of SbF_5 was added to freshly prepared
$Re(CO)_5F \cdot ReF_5$, in the absence of a solvent. A lime-green
suspension in molten SbF_5 was fomred, and there was no gas
evolution. The more volatile components were distilled
off as a pale green syrup, the colour showing the presence
of a second species of comparable volatility with SbF_5.
Gas phase infrared and liquid phase Raman spectra of this
syrup showed characteristic bands for SbF_5 and a suggestion
of weak bands* due to a second species. (I.R.: 759 cm^{-1} w,
726 m, 709 w, and 691 w*; reported for $SbF_5(g)$[59]: 760 s,
727 s, 710 s and 684 s. Raman : 720 s, 684 sh*, and 673 s;
reported for $SbF_5(l)$[60] : 718 s and 670 s). On concentrating
the syrup, the 691 (IR) and 684 (Raman) bands increased
in intensity relative to the SbF_5 signals, indicating that
the bands belonged to the green species. It was not
possible, however, to isolate this material free from SbF_5.

The colour, inseparability from SbF_5, and rel-
uctance to crystallise, of the green species are all sugg-

estive of ReF_5,[61] but the volatility is too high for ReF_5.
In addition the vibrational bands show no clear correlation
with unpublished data on ReF_5 supplied by Dr. R.T. Paine
(e.g. Raman of ReF_5 melt at $\sim45^\circ C$: 746 s, 690 w).[62]
Transition metal pentafluorides are known to increase in
volatility in adducts with SbF_5.[63] The compound $NbF_5 \cdot SbF_5$
has been established,[64] and there is preliminary evidence
for the adducts $MF_5 \cdot SbF_5$ (M = Ta, Ru).[63] It is likely that
the green material is a similar adduct $ReF_5 \cdot nSbF_5$. This
would be expected to have significantly different vibrational
spectra from pure ReF_5.

    The involatile products were a pale green,
crystalline solid, and a red-brown or violet powder. The
latter appeared to have undergone some decomposition, but
the green solid was investigated further. It gave an
X-ray powder pattern very similar to those of $(Re(CO)_6)^+$
$(Re_2F_{11})^-$, but with enough minor variations to indicate
that it was a different phase (table 2.6). The infrared
spectrum (table 2.7) confirmed the presence of $(Re(CO)_6)^+$,
but instead of the ν(Re-F) peaks at 649, 663 and 688 cm^{-1}
(α-) and 642, 665 and 680 cm^{-1} (β-) for $(Re_2F_{11})^-$, new
peaks at 663 vs, 680 s and 701 ms cm^{-1} were observed.
These are in the region expected for ν(Sb-F) bands in
$(Sb_nF_{5n+1})^-$ anions.[65]

    In view of the indications of ReF_5 formation in
the volatiles, and the absence of ν(Re-F) absorbtions
in the solid, the green solid is unlikely to be
$(Re(CO)_6)^+(ReSbF_{11})^-$, and is therefore believed to be
$(Re(CO)_6)^+(Sb_2F_{11})^-$. Conclusive evidence could not be
found for $Re(CO)_5F$ derivatives.

2-5. REACTIONS OF OTHER CARBONYL FLUORIDE SYSTEMS

2-5.1 · Re(CO)$_5$Cl + HF

In the light of a report by O'Donnell et alia

of the solvolysis of Re(CO)$_5$Cl by anhydrous HF, to produce

Re(CO)$_5$F and HCl,[39] a preliminary reaction was investigated.

The Re(CO)$_5$Cl was found to be insoluble in HF, and no

detectable reaction occurred.

2-5.2 Mn$_2$(CO)$_{10}$ + HF

Having noted an apparent solvent dependence on

the course of the Re$_2$(CO)$_{10}$/XeF$_2$ reactions (sections 2-1.

and 2-2.), information was required on the solvation of

metal carbonyls by HF. The closely analogous η^5-cyclo-

pentadienyl irondicarbonyl dimer, $[(\eta^5\text{-}C_5H_5Fe(CO)_2]_2$,

had been shown to dissolve in a variety of acid solvents,

including anhydrous HF and HCl, and 98% H$_2$SO$_4$, to produce

solutions containing the protonated, linear Fe-H-Fe

bridged species, $[H\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+$.[66,67] Tentative

evidence had been obtained from U.V.-visible spectra that

Mn$_2$(CO)$_{10}$ dissolved partially in 98% H$_2$SO$_4$ to form a

similar cation, but that Re$_2$(CO)$_{10}$ was insoluble.[66] In

order to provide a model for the mode of the (very low)

solubility of Re$_2$(CO)$_{10}$ in HF, evidence was required for

the formation of (HMn$_2$(CO)$_{10}$)$^+$ in solution.

Mn$_2$(CO)$_{10}$ was partially soluble in anhydrous HF,

producing a pale, golden yellow solution. The ^{1}H N.M.R.

spectrum of this solution (after filtering) gave signals

at +2.4τ (HF) and +36.4τ. It is apparent that the known

carbonyl hydride species fall into various N.M.R. groups.[68]

Terminal M-H protons resonate in the approximate region

+15 to +25 τ , and singly-bridging M-H-M protons in the

regions +20 to +30 τ (neutral and anionic), and +30 to

+40 τ (cationic species).[69,70] By comparison with published

data on related compounds (table 2.10), the 36.4 τ signal

can be assigned to the species $[(OC)_5Mn-H-Mn(CO)_5]^+$. No

^{19}F N.M.R. signal could be observed, and no attempt was

made to isolate the $(HMn_2(CO)_{10})^+$ cation as a salt.

This is the first positive identification of a

hydrogen-bridged cation of an unsubstituted metal carbonyl.

It therefore seems very likely that the species in solution

in the rhenium system is $(HRe_2(CO)_{10})^+$. Linear M-H-M

bridged cations, $[H\{M(CO)_3(\eta^5-C_5H_5)\}_2]^+$ (M = Mo, W), also

exist in HF and 98% H_2SO_4 solutions.[66] The decreasing

solubility in HF and H_2SO_4 in the series $[(\eta^5-C_5H_5)Fe(CO)_2]_2$,

$[(\eta^5-C_5H_5)M(CO)_3]_2 > Mn_2(CO)_{10} > Re_2(CO)_{10}$, correlates

with the increasing difficulty in breaking the metal-metal

bond, suggesting that to dissolve such carbonyls in acid

solvents HX, requires the cleaving of that bond, and the

formation óf hydrogen-bridged cations.

2-5.3 $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ +   AgF/Acetone

The fluorination of the $Mn_2(CO)_{10}$ analogue,

$[(\eta^5-C_5H_5)Fe(CO)_2]_2$, was studied briefly. $[(\eta^5-C_5H_5)Fe(CO)_2]_2$

was refluxed under nitrogen with a suspension of silver (I)

fluoride in acetone. Metallic silver was precipitated and

filtered off. Evaporation of the solution to dryness, and

recrystallisation of the resulting solid from benzene /

(60-80°) petroleum ether, gave blood-red, needle crystals and

a large quantity of brown powder.

Table 2.10. ^{1}H N.M.R. Chemical Shifts (τ) of Protonated

Metal Carbonyls

[H{Fe(CO)$_2$cp}$_2$]$^+$	36.3-36.6[a,b]	[H{Mn(CO)$_5$}$_2$]$^+$	36.4[d]
HFe(CO)$_2$cp	21.91[c]	HMn(CO)$_5$	17.5[e]
[cp(OC)$_2$Fe-H-Mn(CO)$_5$]$^+$ 38.07[a]			
[H{Mo(CO)$_3$cp}$_2$]$^+$	30.99[a]	[H{W(CO)$_3$cp}$_2$]$^+$	34.77[a]
HMo(CO)$_3$cp	15.65[c]	HW(CO)$_3$cp	17.55[c]
[cp(OC)$_3$Mo-H-W(CO)$_3$cp]$^+$ 32.88[a]			

cp = (η^5-C$_5$H$_5$)   c. ref 71 (cyclohexane)
a.   ref. 66 ⎤ various   d. this work (HF)
b.   ref. 67 ⎦ solvents   e. ref. 72 (liquid HMn(CO)$_5$)

Table 2.11. ^{1}H N.M.R. Chemical Shifts (τ) of the cp-ring

Protons in cpFe(CO)$_2$X and Related Species

X	cpFe(CO)$_2$X	[X{Fe(CO)$_2$cp}$_2$]$^+$
F	4.75[a]	
Cl	4.94-4.99[b,c,d]	4.71[f]
I	4.96-4.99[b,c]	4.71[f]
H	5.26[e]	4.76-4.77[g]
NCS	4.94[b]	
SCN	4.86[b]	
OC(O)Ph	4.73[h]	
OS(O)$_2$·C$_6$H$_4$Me	4.70[h]	
[cpFe(CO)$_2$(OCMe$_2$)]$^+$	4.39[j]	
[cpFe(CO)$_3$]$^+$	3.85-3.87[k,l]	

cp = (η^5-C$_5$H$_5$)   f. ref. 76 (acetone)
a. this work (acetone solvent)   g. refs. 66 & 67 (various)
b. ref. 73 (CDCl$_3$)   h. ref. 77 (D^6 acetone)
c. ref. 74 (CDCl$_3$)   j. ref. 77 (acetone)
d. ref. 75 (CH$_3$CN)   k. ref. 78 (acetone)
e. ref. 71 (C$_6$H$_{12}$)   l. ref. 75 (acetone)

The X-ray powder patterns of these two products showed the absence of either starting material. The red crystals gave an infrared spectrum very similar to the other halides $(\eta^5-C_5H_5)Fe(CO)_2X$ (table 2.12),but with a new peak at 587 cm^{-1}, assigned to $\nu(Fe-F)$. A proton N.M.R. spectrum of the red, acetone solution of these crystals gave a singlet resonance at 4.75τ, consistent with the five equivalent protons of the $(\eta^5-C_5H_5)$ ring in a $(\eta^5-C_5H_5)Fe(CO)_2X$ system. No ^{19}F N.M.R. peaks could be observed because the solution was too weak. After an hour the red solution had become pale brown, with the deposition of a brown solid. The proton N.M.R. was then re-run. The 4.75τ signal had shifted to 4.85τ, and was of a weaker intensity. The red crystals decomposed very slowly in air (a matter of weeks), and quickly (1 hour) in acetone or chloroform solution.

By comparison with proton N.M.R. data on related systems (table 2.11), and in view of the infrared data, the red crystals are most probably $(\eta^5-C_5H_5)Fe(CO)_2F$. The yield was too small for further data to be obtained. The brown solid gave proton N.M.R. resonances at 5.05τ and 7.88τ in methanol solution, but reliable infrared spectra could not be obtained owing to the tendency of the solid to coagulate on mulling. The solid appears to be air-stable. By comparison with some reported resonances for the $(\eta^5-C_5H_5)$ ring in $(\eta^5-C_5H_5)Fe(CO)_2R$ species,[74] the proton N.M.R. signal at 5.05τ may indicate the co-ordination of an organic ligand:

R=-CH$_3$ 5.70τ; -CF$_3$ 5.01 ; -CO.CH$_3$ 5.13 ; -CO.OCH$_3$ 5.14 ; -CH$_2$.CO.CH$_3$ 5.10.

Table 2.12.   Infrared Spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$

X = F[a]	X = Cl[b]	X = Br[b]	X = I[b]	Assignment
3126 w 3104 sh 3091 w	3113 sh 3086 m	3105 sh 3089 m	3115 m 3086 sh	} ν(C-H)
2065 s 2008 s 1985 m,sh 1980 m,sh	2053 s* 2006 s*	2048 s* 2002 s*	2039 s* 1996 s*	} ν(C≡O)
1427 m 1423 sh	1429 m	1426 m	1429 m	ν(C-C)
1364 m	1361 vw	1357 vw	1357 vw	ν(C-C)
1270 s	(1259 vw)	(1256 w)	1261 vw	δ(C-H)
1170 vw 1148 vvw,br	1166 w,br 1130 vw	1170 sh,br 1130 vw	1166 vw,br (1125 sh?)	} δ(C-H)
1115 vvw,br	1112 vw,br	1112 vw,br	1114 w,sh	Ring"breathing"
1068 vvw 1057 vw 1012 sh 1002 sh 993 s	(1060 w) 1036 w 1012 sh 1004 m	(1060) w 1038 w (1010 sh) 1005 m	(1059 w) 1040 w (1008 sh) 1007 m	} δ(C-H)
962 w ~895 vvw,br	962 vw 915 vw	940 vw 915 vw	935 vw 926 vw	} δ(C-C)
867 vvw 855 wm 837 vvm 833 vw	875 s 842 vs 832 sh	876 s 844 vs (833 vs)	843 vs (835 vs)	} δ(C-H)
599 m	603 vs	603 vs	605 vs	δ(Fe-C-O)
587 m	302 ≠	229 vs +	137 ≠	ν(Fe-X)
559 m 530 m	567 vs 532 vs	564 vs 535 vs	566 vs 54 vs	} δ(Fe-C-O)
466 m 429 m	479 w 436 w	479 m 434 m	488 w 434 w	} ν(Fe-CO)

All nujol mulls, except *(KBr discs), + (CHCl$_3$ solution) and bracketed figures (CS$_2$ solution).

References: a. this work, b. 3200-3000 cm^{-1} ref. 79; 2200-1800 cm^{-1} ref. 76*; 1600-800 cm^{-1} ref. 79, 700-420 cm^{-1} ref.80, + ref.80, ≠ ref.81.
$(\eta^5\text{-}C_5H_5)Fe(CO)_2F$ has additional bands at 796 w, 761 vvw,br and 707 cm^{-1}, for which region there are no published data.

CHAPTER   3

DISCUSSION OF THE RHENIUM CARBONYL

FLUORIDE SYSTEM

3-1. THE Re$_2$(CO)$_{10}$/XeF$_2$ SYSTEM, AND ITS ANALOGUES

3-1.1 Previous Reactions of Rhenium Carbonyl with the Halogens

Dirhenium decacarbonyl has been shown to react

with chlorine, bromine, or (with the aid of u.v. irradiation)

iodine, dissolved in dichloro- or tetrachloro-methane, to

produce the monomeric pentacarbonyl halides, Re(CO)$_5$X.[82,83]

The ease of reaction is in the order Cl>Br>I. Dimeric,

doubly halogen-bridged, tetracarbonyl halides, (Re(CO)$_4$X)$_2$,[11]

and tricarbonyl halides, of uncertain structure (Re(CO)$_3$X)$_n$,[84,85]

are also known. They are best prepared by the elimination

of CO on refluxing Re(CO)$_5$X in an inert solvent. These

series of compounds are among the most stable, and best

established of the carbonyl halides.

Early results[23,12] indicated that direct fluorination

with fluorine/nitrogen mixtures in a flow system did not

provide the necessary control over the conditions for

preparing carbonyl fluorides in a pure state. The use of

xenon difluoride, in a suitable solvent, has successfully

overcome this problem, especially as it allows exact control

over the number of gram atoms of fluorine added to the

carbonyl.

3-1.2 The Re$_2$(CO)$_{10}$/XeF$_2$/Genetron 113 System

The results obtained in this system over the range

of molar proportions of Re$_2$(CO)$_{10}$:XeF$_2$ from 1:1 to 1:5 are

summarised in table 3.1, together with the preliminary

results of Wilson.[12]

Though the system is formally analogous to above

halogenations of rhenium carbonyl, it is clear that it is not

the pentacarbonyl fluoride, Re(CO)$_5$F, that is being formed,

Table 3.1 Results of the $Re_2(CO)_{10}$/XeF_2/Genetron 113 Reactions

Reaction	$Re_2(CO)_{10}$:XeF_2	Rhenium-containing Products
1.	1:1	$Re_2(CO)_{10}$ + a little $Re(CO)_5F \cdot ReF_5$
2.	1:2	$Re_2(CO)_{10}$ + $Re(CO)_5F \cdot ReF_5$
3.	1:3	$Re(CO)_5F \cdot ReF_5$
4.	1:4*	$Re(CO)_5F \cdot ReF_5$ + ReF_6
5.	1:5	$Re(CO)_5F \cdot ReF_5$ + ReF_6
6.	large excess XeF_2 †	ReF_6, with no involatile products

All reactions produced both xenon and CO.

* 1:4 proportions were achieved by addition of one molar

    equivalent of XeF_2 to $Re(CO)_5F \cdot ReF_5$ freshly-prepared

    by a 1:3 reaction.

† I.L. Wilson, ref.12.

Table 3.2 Results of the $Re_2(CO)_{10}$/XeF_2/HF Reactions

Reaction	$Re_2(CO)_{10}$:XeF_2	Rhenium-containing Products
1.	1:1	$Re_2(CO)_{10}$ + probably $Re(CO)_5F \cdot ReF_5$
2.	1:3	$Re(CO)_5F \cdot ReF_5$ ‡
3.	1:5*	$Re(CO)_5F \cdot ReF_5$ ‡ + ReF_6

All reactions produced both xenon and CO

* 1:5 proportions were achieved by adding two molar

    equivalents of XeF_2 to freshly-prepared $Re(CO)_5F \cdot ReF_5$

‡ $Re(CO)_5F \cdot ReF_5$ eventually hydrolysed to $(Re(CO)_6)^+(ReOF_5)^-$

    in both reactions.

but the complex carbonyl fluoride, $Re(CO)_5F \cdot ReF_5$. In

accordance with the stoicheiometry, this complex is the

single rhenium-containing product in the 1:3 reaction, but

it is also formed, in smaller yields, when lower proportions

of rhenium to fluorine are used (the 1:1 and 1:2 reactions)

together with a majority of unreacted $Re_2(CO)_{10}$. In these

latter cases, $Re(CO)_5F \cdot ReF_5$ is formed until all the XeF_2

is used up, rather than lower carbonyl fluorides such as

$Re(CO)_5F$ or $Re(CO)_4F_2$.

When proportions greater than 1:3 are used,

$Re(CO)_5F \cdot ReF_5$ is formed until all the $Re_2(CO)_{10}$ is consumed,

then the complex is itself fluorinated. If enough XeF_2 is

used, all of the $Re(CO)_5F \cdot ReF_5$ is converted to ReF_6 (reaction 6,

table 3.1). With less than that required amount, ReF_6 is

formed until all the "extra" XeF_2 has been used up, and a

smaller amount of $Re(CO)_5F \cdot ReF_5$ remains. Again, this occurs

in preference to the formation of higher carbonyl fluoride

complexes such as $Re(CO)_3F_3 \cdot ReF_5$ (reaction 4.), or of ReF_5

(reaction 5.).

The fluorination evidently proceeds stepwise.

First one $-Re(CO)_5$ unit of $(OC)_5Re^O \text{---} Re^O(CO)_5$ is fluorinated

to an "ReF_6" unit - producing $(OC)_5Re^I \text{---} F \text{---} Re^V F_5$, and then

the other - producing two moles of free ReF_6. Reactions

1.,2. and 3. are thus respectively analogous to reactions

4.,5. and 6. In this way, controlled oxidation has been

achieved through $Re(CO)_5F \cdot ReF_5$ to ReF_6, given by the

equations:

$$Re_2(CO)_{10} + 3 \ XeF_2 \longrightarrow Re(CO)_5F \cdot ReF_5 + 5 \ CO + 3 \ Xe \quad (3.1),$$
$$Re(CO)_5F \cdot ReF_5 + 3 \ XeF_2 \longrightarrow 2 \ ReF_6 + 5 \ CO + 3 \ Xe \quad (3.2).$$

The earlier, preliminary results of Wilson and Misra can now be seen to be in full agreement with this scheme.

3-1.3   The $Re_2(CO)_{10}$/XeF_2/HF System

The results from this system (table 3.2) follow a similar course to those obtained using Genetron 113 as the solvent. $Re(CO)_5F \cdot ReF_5$ is predominant in the reactions, although problems encountered over hydrolysis in this medium prevented isolation of the complex itself.

Thus $Re(CO)_5F \cdot ReF_5$ is the initial product of the 1:3 reaction, and addition of two further moles of XeF_2 to a fresh sample of $Re(CO)_5F \cdot ReF_5$ gives rise to a mixture of $Re(CO)_5F \cdot ReF_5$ and ReF_6. In both reactions, the $Re(CO)_5F \cdot ReF_5$ was ultimately converted to its hydrolysis product $(Re(CO)_6)^+(ReOF_5)^-$ by traces of oxygen-containing impurities. This is discussed in section 3-2.5.

The 1:1 reaction also appears to follow the same course as the analogous reaction in Genetron, with evolution of CO, and at least half of the $Re_2(CO)_{10}$ remaining unreacted, intimating a fluorination product richer in fluorine than $Re(CO)_5F$. Although decomposition occurred on concentrating, the original formation of $Re(CO)_5F \cdot ReF_5$ in the solution seems likely. Thus the three HF reactions 1:1, 1:3 and "1:5", seem to parallel their analogues in Genetron.

3-1.4   Comparison with the Results of O'Donnell; Reformulation
of $Re(CO)_3F_3$

During the course of this work a study of the $Re_2(CO)_{10}$/XeF_2/HF system was reported by O'Donnell et alia.[39]

In their 1:1 reaction, they record that all the $Re_2(CO)_{10}$ is consumed, with the evolution only of xenon gas, to give a brown solution, which yielded as a single product a brown solid identified as the simple carbonyl fluoride $Re(CO)_5F$. The analytical, infrared and powder diffraction data for this material are consistent with the formulation, but no supporting evidence was given for the nature of the volatiles.

The consumption of all the $Re_2(CO)_{10}$, the "absence" of CO evolution, and the production of $Re(CO)_5F$ from this reaction all conflict with the present study. It may be that there are conditions under which $Re(CO)_5F$ can be formed, and others under which more complete fluorination of <u>some</u> $Re_2(CO)_{10}$ molecules occurs, producing $Re(CO)_5F \cdot ReF_5$. With the evidence currently available, it is not possible to define what the appropriate conditions might be. The most significant procedural differences were that the author used considerably more solvent than O'Donnell, and that the reaction was complete in a shorter time. Assuming neither study is in error, it appears that an intermediate stage in the $Re_2(CO)_{10}$ fluorination, producing $Re(CO)_5F$, is possible.

O'Donnell also reported the reaction of $Re(CO)_5F$ with a further molar equivalent of XeF_2 (equivalent to the author's $Re_2(CO)_{10}:3XeF_2$ reaction). Another brown solid was produced. It was formulated from its infrared spectrum and X-ray powder pattern as "$Re(CO)_3F_3$", the same material that had been reported earlier as the major product of the reaction of $Re_2(CO)_{10}$ with a defficiency of ReF_6 in HF.[38] The original formulation was based largely on the elemental analysis and an infrared spectrum, but the present study shows that this formulation is incorrect.

The X-ray powder pattern of "$Re(CO)_3F_3$" is similar to those of α- and β-$(Re(CO)_6)^+(Re_2F_{11})^-$, produced in the author's $Re_2(CO)_{10}/ReF_6/HF$ reactions, and also to that of $(Re(CO)_6)^+(Sb_2F_{11})^-$, see table 2.6. In addition, the infrared data are similar to those for α-$(Re(CO)_6)^+(Re_2F_{11})^-$, see table 2.7. The positions and shape of the $\nu(C\equiv O)$ bands had been interpreted in terms of a fac-$Re(CO)_3F_3$ pattern, but $(Re(CO)_6)^+$ is equally satisfactory. Furthermore, the band at 580 cm^{-1} correlates with the characteristic, strong $\delta(Re-C-O)$ fundamental of $(Re(CO)_6)^+$.[47] O'Donnell's interpretation of the 580 and 650 cm^{-1} peaks as rhenium (III) fluoride modes is most unlikely, compared with the well-established series of $\nu(Re-F)$ fundamentals of $(ReF_6)^{2-}$ 541, $(ReF_6)^-$ 627-639, and ReF_6 715 cm^{-1}.[44,86,87] O'Donnell proposed electron withdrawal by the trans- carbonyl groups to account for the high values, but no unusually high frequency $\nu(Ru-F)$ modes are found in $(Ru(CO)_3F_2)_4$ or $Ru(CO)_3F_3$, both of which possess fac-$Ru(CO)_3F_3$ co-ordination.[16] A more likely explanation is that the 650 cm^{-1} band is a $\nu(Re^V-F)$ fundamental of $(ReF_6)^-$ or $(Re_2F_{11})^-$, (c.f. the $\nu(Re^V-F)$ modes in $(ReF_6)^-$, $(Re_2F_{11})^-$ and $Re(CO)_5F\cdot ReF_5$ in the 625-665 cm^{-1} region).

In addition, it is most unlikely that $Re^{III}(CO)_3F_3$ would be a d^4 octahedral monomer, having only 16 valence electrons, two short of the nearest noble gas configuration, when 18-electron, 7-co-ordinate, d^4 carbonyl halides are well-established,[88] e.g. $(\eta^5-C_5H_5)Re(CO)_3Cl^+$ [140] and $(Mo(CO)_4Cl)_2$.[88] Any polymeric formulation, $(Re(CO)_3F_3)_n$ would have at least local $Re(CO)_3F_4$ 7-co-ordination, which could not give such a simple infrared spectrum. The molecular weight evidence

for monomeric $Re(CO)_3F_3$, and the conductivity data, came

from measurements made in acetone solutions. In view of

the extreme difficulty in drying acetone sufficiently to

prevent fast hydrolysis of rhenium(V) fluorides (see section

3-2.5), these measurements are almost certainly invalid.

It seems most likely that "$Re(CO)_3F_3$" is another

crystalline modification of $(Re(CO)_6)^+(Re_2F_{11})^-$, or the

hitherto unknown $(ReF_6)^-$ salt. O'Donnell's original

analytical data[38] point to the latter formulation, but from

his second paper,[39] it appears that his $Re_2(CO)_{10}/ReF_6/HF$

reaction produces $Re(CO)_5F$ as well as "$Re(CO)_3F_3$". This

must throw doubt on the validity of the analytical data

of "pure" $Re(CO)_3F_3$.

The stoicheiometry of the $Re(CO)_5F/XeF_2/HF$ reaction,

however, suggests that the formula $(Re(CO)_6)^+(ReF_6)^-$ may

be correct. This would correlate with the production of its

"covalent analogue" $Re(CO)_5F \cdot ReF_5$, from the same proportions

of rhenium to fluorine of 1:3, in the author's $Re_2(CO)_{10}/$

$3XeF_2$ reactions. (An equivalent pair of compounds

$Re(CO)_5F \cdot AsF_5$[43] and $(Re(CO)_6)^+(AsF_6)^-$ [47] is now known.) In

O'Donnell's reaction the $Re(CO)_5F \cdot ReF_5$ evidently incorporates

liberated CO in situ (c.f. section 3-2.3):

$2\ Re(CO)_5F\ +\ 2\ XeF_2 \longrightarrow Re(CO)_5F \cdot ReF_5\ +\ 5\ CO\ +\ 2\ Xe$ (3.3),

$Re(CO)_5F \cdot ReF_5\ +\ CO \longrightarrow (Re(CO)_6)^+(ReF_6)^-$ (3.4).

The results of the Genetron 113 system suggest that the

$Re(CO)_5F/XeF_2$ reaction should produce $Re(CO)_5F \cdot ReF_5$, if

Genetron were used as the solvent.

Further fluorination of "$Re(CO)_3F_3$" with an excess

of XeF_2 was reported[39] to give a green solution similar to

that produced from $Re_2(CO)_{10}$ and a defficiency ReF_6 in HF.[38]

The colour was attributed to ReF_5, though no evidence was

cited to support this. In view of the results of the

author's study of the $Re_2(CO)_{10}/ReF_6/HF$ system, this green

colour seems almost certainly to be due to $(Re(CO)_6)^+(Re_2F_{11})^-$,

or the $(ReF_6)^-$ derivative. No examination was made of the

volatiles, and so it is not possible to say whether ReF_6

was also produced, but this would be expected by analogy

with the author's $Re(CO)_5F \cdot ReF_5/XeF_2$ reactions.

3-1.5   Interpretation of the $Re_2(CO)_{10}/XeF_2$ Fluorinations

The fluorination of rhenium carbonyl with xenon

difluoride is summarised in fig.3.1. The reason for the

different courses of the two sets of reactions is not yet

clear, but a definite progression has been established for

the fluorination of rhenium carbonyl, which may be represented:

$$Re_2(CO)_{10} \rightleftarrows Re(CO)_5F \rightarrow Re(CO)_5F \cdot ReF_5 \longrightarrow ReF_6 \cdot$$

Re:F   0   1:1   1:3   1:6

The most significant feature of these reactions

is the predominance of $Re(CO)_5F \cdot ReF_5$, even where the molar

proportions of the starting materials were not favourable.

It is the exclusive carbonyl fluoride species in the Genetron

113 system, though $Re(CO)_5F$ (and $(Re(CO)_6)^+$ species derived

from $Re(CO)_5F \cdot ReF_5$) may also be present under certain

conditions in the HF system. The formation of $Re(CO)_5F \cdot ReF_5$

is remarkable in that one half of the $Re_2(CO)_{10}$ molecule

has been fully fluorinated, and the other half has not.

By the application of some basic principles, a framework

can be built up in which the course of these reactions, and

the particular formation of $Re(CO)_5F \cdot ReF_5$, can be understood.

Re:F	This Work[*]	O'Donnell[‡], reinterpreted
0	$Re_2(CO)_{10}$	$Re_2(CO)_{10}$
	$\downarrow$ 1.XeF_2	$\downarrow$ 1.XeF_2
1:1	$\frac{2}{3} Re_2(CO)_{10} + \frac{1}{3} Re(CO)_5F \cdot ReF_5$	2.$Re(CO)_5F$
	$\downarrow$ 3.XeF_2	$\downarrow$ 2.XeF_2
1:3	$Re(CO)_5F \cdot ReF_5$	$(Re(CO)_6)^+(ReF_6)^-$
	$\downarrow$ 5.XeF_2	$\downarrow$ xs.XeF_2
1:5	$\frac{1}{3} Re(CO)_5F \cdot ReF_5 + \frac{2}{3} ReF_6$	$(Re(CO)_6)^+(Re_2F_{11})^-$ and/or ReF_6 ?
	$\downarrow$ xs.XeF_2[≠]	
1:6	2 ReF_6	

* Genetron 113 or HF as solvent

‡ HF as solvent, ref.39.

≠ Wilson, ref.12.

Fig.3.1 Stepwise Fluorination of $Re_2(CO)_{10}$ by XeF_2

To prepare stable carbonyl fluorides, a balance
has to be achieved between the preference of the fluoride
ligand for high oxidation states, and of the carbonyl ligand
for low oxidation states. Thus the fluorination of metal
carbonyls must involve opening the $M(CO)_x$ shell, without
then completely oxidising the metal to some higher fluoride,
MF_y.$^{\neq}$ Too weak a fluorinating agent gives no reaction, but
conditions that are too vigorous result in complete degrad-
ation of the carbonyl. This is illustrated by two of
Hargreaves and Peacock's earlier reactions[20]:

$$Re_2(CO)_{10} + WF_6 \rightleftharpoons \text{charge-transfer solution} \qquad (3.5).$$

$$Re_2(CO)_{10} + 4\ BrF_3 \longrightarrow 2\ ReF_6 + 10\ CO + 2\ Br_2 \qquad (3.6).$$

This phenomenon sets such a restraint on carbonyl
fluoride formation that the necessary balance will be
achieved only for particularly stable metal carbonyl con-
figurations. By applying some well-established principles,
the number of expected carbonyl fluorides becomes limited
to a small group. The main principles are as follows:

i). The "Noble Gas Rule" requirement of an effective valence
shell of 18 electrons (that of the nearest noble gas) should
generally be obeyed.

ii). Carbonyl bridging will not generally be found.[3,89] To
date only one confirmed carbonyl-bridged halide is known,
$(Pd^I(CO)Cl)_n$.[90]

iii). Only single fluorine bridges will be found. Multiple,
covalent fluorine bridging is rare. Proven cases are almost
entirely limited to very large metal ions such as the actin-
ides, and the d^o transition metal species $(Ti(NMe_2)_2F_2)_4$,[91]

$\neq$ The converse applies to the carbonylation of metal fluorides.

VOF_3,[92] CrO_2F_2,[93] and various fluorozirconates (IV).[94]

iv). There will be a preference for particularly stable metal

co-ordination spheres and d-electron configurations,

especially octahedral d^6, but also 7-co-ordinate d^4, square

planar d^8 (a 16-electron system), etc.

For rhenium, this results in the possibilities

shown in table 3.3.

In the rhenium carbonyl system, the $Re(CO)_5F$

unit is found to be particularly important, and the

$Re_2(CO)_{10}/XeF_2$ reactions can be interpreted in terms of the

maintenance and stability of this group. All the compounds

formed contain only this unit, or fully fluorinated species.

Intermediate units like $Re(CO)_3F_2$ do not occur; once an

$Re(CO)_5F$ group has been broken into, complete degradation

takes place, with the displacement of all the CO ligands by

fluoride.

$Re(CO)_5F$ itself is only formed under certain

circumstances. It should be the product of the 1:1

$Re_2(CO)_{10}:XeF_2$ reactions, by a simple one-electron oxidation,

but in both the Genetron 113 system and the author's HF

reactions, it is not stable. Formally it may be considered

that further oxidation occurs to produce ReF_6, which then

reacts with unchanged $Re_2(CO)_{10}$ to form the new, fluorine-

bridged, mixed oxidation state, $Re(CO)_5F$ complex,

$Re(CO)_5F \cdot ReF_5$. This process may take place either by

a). the in situ degradation of an $Re(CO)_5$ group within

each $Re_2(CO)_{10}$ molecule, or b). the separation of individual

$Re(CO)_5F$ moieties which then react further.

Table 3.3   Noble Gas Rule Rhenium Carbonyl Halide Structures

$Re^I(d^6)$

	$Re(CO)_5X$	$(Re(CO)_4X)_2$	$(Re(CO)_4X)_4$	$(Re(CO)_3X)_4$
Bridging mode	M—X	M⟨X,X⟩M	M—X—M / X / X / M—X—M	cubane (X,M)
(Co-ord. No.)	(6)	(6)	(6)	(6)

$(Re(CO)_4X)_m$ M—M—M triangle (M at apex)   (7) m=3,4,etc

$(Re(CO)_4X)_n$ –M–X–M–X–   (6)

$Re^{II}(d^5)$

$(Re(CO)_4X_2)_2$	$(Re(CO)_3X_2)_2$	$(Re(CO)_3X_2)_4$	$(Re(CO)_2X_2)_n$
M–M	M≡M	tetrahedral M₄ cluster	–M⟨X,X⟩M⟨X,X⟩M–
(7)	(6)	(8)	(7)

$(Re(CO)_3X_2)_2$ M⟨X,X⟩M   (7)

tetrahedron with X bridges   (7)

$Re^{III}(d^4)$

$Re(CO)_4X_3$	$(Re(CO)_3X_3)_2$	$(Re(CO)_3X_3)_4$	$(Re(CO)_2X_3)_n$
M—X	M⟨X,X⟩M	M—X—M / X / X / M—X—M	M⟨X,X⟩M⟨X,X⟩M
(7)	(7)	(7)	(7)

$(Re(CO)_3X_3)_m$ M—M—M triangle   (7) m=3,4,etc

$(Re(CO)_3X_3)_n$ –M–X–M–X–   (7)

$(Re(CO)_2X_3)_4$ cubane structure is unlikely in 7 co-ordn.

a). $(OC)_5Re-Re(CO)_5 \xrightarrow{\ 3XeF_2\ } (OC)_5Re \cdot ReF_6$ i.e. $Re(CO)_5-F-ReF_5$ (3.7)

b). $(Re(CO)_5)_2 + XeF_2 \longrightarrow 2\ Re(CO)_5F + Xe$ (3.8)

$\quad 2\ Re(CO)_5F + 5\ XeF_2 \longrightarrow 2\ ReF_6 + 10\ CO + 5\ Xe$ (3.9)

$\quad (Re(CO)_5)_2 + 2\ ReF_6 \longrightarrow 2\ Re(CO)_5F \cdot ReF_5$ (3.10)

In $Re(CO)_5F \cdot ReF_5$, the $Re(CO)_5F$ moiety has been stabilised by acting as a donor to a co-ordinatively unsaturated ReF_5 molecule. In this form the $Re(CO)_5F$ group is resistant to further oxidation for proportions of $Re_2(CO)_{10}:XeF_2$ up to 1:3 (the exact proportions required for complete conversion of the $Re_2(CO)_{10}$ to $Re(CO)_5F \cdot ReF_5$), but it is decomposed by additional XeF_2 to <u>free</u> ReF_6, as there is no remaining $Re_2(CO)_{10}$. The use of intermediate proportions gives rise to mixtures of $Re(CO)_5F \cdot ReF_5$ and unchanged $Re_2(CO)_{10}$ (the 1:1 and 1:2 reactions), or of ReF_6 and unchanged $Re(CO)_5F \cdot ReF_5$ (the 1:4 and 1:5 reactions). These entities are more stable, evidently, than species of intermediate formula such as $Re(CO)_4F_2$ or $Re(CO)_3F_3 \cdot ReF_5$. The production of mixtures of unchanged metal carbonyl and a higher carbonyl fluoride has also been observed in other systems. For example, 1:1 reactions of $Mo(CO)_6$ and $W(CO)_6$ with XeF_2, in either HF or halocarbon solvents, give complexes like $Mo(CO)_3F_2 \cdot MoF_5$ together with unreacted carbonyl.[95]

The stability of the $Re(CO)_5F$ unit is especially remarkable in that it can co-exist with a rhenium(V) species in the same molecule. Such stability is reflected in the electronic configuration, viz. d^6 octahedral with 18 valence electrons, which is particularly favourable for partially filled d-electron shells. It will be seen later that d^6 species play a dominant role in other carbonyl

fluoride systems, and form similar complex carbonyl fluorides.

The stable existence of $Re(CO)_5F \cdot ReF_5$ is also favoured by the fact that ReF_5 is a _reducing_ Lewis acid, despite its high oxidation state. In other words, it is very readily oxidised to ReF_6, but does not so readily act as an oxidising agent itself. Indeed, ReF_5 has only been prepared to date by the reduction of ReF_6.[23,96] The pentafluorides MoF_5, WF_5, and OsF_5 are somewhat similar in these respects, and might well form analogous $Re(CO)_5F \cdot MF_5$ complexes. In the case of tungsten, the fact that WF_6 does not fluorinate $Re_2(CO)_{10}$ may indicate that $Re(CO)_5F$ is capable of oxidising WF_5! This provides an illustration of the point that a higher oxidation state in a given element does not necessarily mean a greater effective oxidising power. Another example is found in manganese chemistry, where the Mn^{3+}/Mn^{2+} oxidation potential is greater than that of MnO_2/Mn^{2+}. The main group pentafluorides AsF_5 and SbF_5 are also only weakly oxidising, and a complex $Re(CO)_5F \cdot AsF_5$ has recently been reported.[43]

Because of the ready oxidation of ReF_5, the final fluorination product is ReF_6. This is domonstrated most clearly by the 1:5 reactions, where the products are a mixture of $Re(CO)_5F \cdot ReF_5$ and ReF_6, rather than ReF_5, despite the stoicheiometry. The presence of rhenium(V) in $Re(CO)_5F \cdot ReF_5$ is a consequence of the ready reduction of ReF_6 by any unreacted $Re_2(CO)_{10}$; as soon as all the $Re_2(CO)_{10}$ has been consumed, any further ReF_6 that is formed remains unreacted as free ReF_6.

$$3Re_2(CO)_{10} + 15XeF_2 \longrightarrow Re(CO)_5F \cdot ReF_5 + 4ReF_6 + 25\,CO + 15Xe, \quad 3.11$$

It is also noteworthy that reaction 4 of table 3.1

gave ReF_6 instead of proceeding according to:

$$Re(CO)_5F \cdot ReF_5 + XeF_2 \longrightarrow Re(CO)_5F + XeF_2 \cdot ReF_5 \qquad (3.12).$$

Evidently, ReF_5 is unstable towards oxidation by XeF_2. This

agrees with the generally established fact that xenon can

be oxidised by only the most thermodynamically unstable

transition metal hexafluorides, PtF_6, RhF_6 and RuF_6, and

not by those of intermediate (IrF_6, OsF_6, TcF_6) or lowest

reactivity (ReF_6, MoF_6, WF_6).[29] Further, it is known that

XeF_2 forms stable complexes with PtF_5, RuF_5 and IrF_5, but

that $XeF_2 \cdot OsF_5$ is rather less stable.[97,98] The present

observations on the XeF_2/Re^V system** thus suggest that

complexes $XeF_2 \cdot MF_5$, for metals whose hexafluorides belong

to the "lowest reactivity group" (M= Re,Mo,W), may not be

stable with respect to the hexafluorides (or possibly ReF_7)

and xenon, at ordinary temperatures.

$$XeF_2 + 2 MF_5 \longrightarrow Xe + 2 MF_6 \qquad (3.13)$$

3-1.6   Concerning the Reaction Mechanism

Rhenium carbonyl is scarcely soluble in either

Genetron 113 or HF. In Genetron, it probably reacts in

simple, molecular form. Insoluble $Re(CO)_5F \cdot ReF_5$ is formed

and CO escapes freely. In HF, the carbonyl probably reacts

as the $[(OC)_5Re-H-Re(CO)_5]^+$ cation (see section 2-5.2),

producing an initial, transient, blue species in solution

which may possibly be $(FRe_2(CO)_{10})^+$. ($Fe(CO)_5$ and

$[(\eta^5-C_5H_5)Fe(CO)_2]_2$ both dissolve in liquid HF[99,66] and

---

** $(Re(CO)_6)^+(Re_2F_{11})^-$/xs XeF_2/HF also gave ReF_6, though
   the cation remained unchanged.

HCl[100,67] as protonated species, and react with Cl_2 in

liquid HCl to produce $(Fe(CO)_5Cl)^{+}$ [100] and

$(Cl[Fe(CO)_2(\eta^5-C_5H_5)]_2)^{+}$ [67] ions, both isolable as BCl_4^{-}

salts.) $Re(CO)_5F$ and $Re(CO)_5F \cdot ReF_5$ are soluble in HF, and

it is evident both from O'Donnell's further reactions of

$Re(CO)_5F$ with XeF_2, and from the author's $Re_2(CO)_{10}/ReF_6/HF$

reactions, that the CO liberated is capable of reacting with

$Re(CO)_5F \cdot ReF_5$ to produce $(Re(CO)_6)^{+}$ salts, see section 3-2.3.

The formation of $Re(CO)_5F \cdot ReF_5$ in both Genetron and

HF systems underlines its fundamental importance in the

fluorination of $Re_2(CO)_{10}$.

3-1.7   The Use of Other Fluorinating Agents with $Re_2(CO)_{10}$

The reactions of rhenium carbonyl with fluorine/

nitrogen mixtures follow a similar course to the XeF_2

reactions above. Under very mild conditions ($-75^{\circ}C$), there

is no reaction.[20] Above room temperature, probably with

Genetron 113 as a solvent, some $Re(CO)_5F \cdot ReF_5$ seems to be

formed, together with unreacted carbonyl (see section 2-1.3),

and at higher temperatures, ReF_6 is produced.[23] The

author has observed that $Re_2(CO)_{10}$ reacts violently with

300 torr. of undiluted fluorine gas, producing considerable

black deposits and some yellow solid which may be

$Re(CO)_5F \cdot ReF_5$.

The rationale employed for the XeF_2 system can be

applied successfully to interpret the reactions of $Re_2(CO)_{10}$

with many other fluorinating agents in the early work of

Peacock and Hargreaves.[20] WF_6 failed to fluorinate.

$Re_2(CO)_{10}$, but BrF_3 was too reactive and gave only the hexa-

fluoride (equations 3.5 and 3.6). Similar results were

obtained with Mo(CO)$_6$ and W(CO)$_6$. An excess of liquid IF$_5$,

however, gave an intermediate reaction with Re$_2$(CO)$_{10}$,

producing yellow crystals and iodine, but with no CO evolution.

The crystals decomposed above 50°C liberating IF$_5$, and pre-

sumably CO, to produce (Re(CO)$_4$I)$_2$. The yellow crystals

were tentatively formulated Re(CO)$_5$I·IF$_5$ on the basis of

weight increase, and ν(C≡O) infrared absorbtions in CCl$_4$

solution. In the light of the present study, a formula of

Re(CO)$_5$F·IF$_5$ seems rather more plausible.. This would account

for the first stage much better, IF$_5$ oxidising Re$_2$(CO)$_{10}$

to Re(CO)$_5$F, which then complexed with the excess IF$_5$:

$$Re_2(CO)_{10} + 2\ IF_5 \longrightarrow 2\ Re(CO)_5F + 2(IF_3)$$

$$IF_5 \downarrow \qquad\qquad \longrightarrow \tfrac{2}{5}\cdot I_2 + \tfrac{6}{5}\cdot IF_5$$

$$Re(CO)_5F·IF_5 \qquad\qquad (3.14).$$

The decomposition to (Re(CO)$_4$I)$_2$ is less obvious, though.

The infrared spectrum of "Re(CO)$_5$I·IF$_5$" was said to be

identical to that of Re(CO)$_5$I, and so may well be of

Re(CO)$_5$I itself, produced by decomposition in CCl$_4$. It

is not clear how quantitative the weight loss data were.

By contrast, IF$_5$ oxidised both Mo(CO)$_6$[22] and W(CO)$_6$[24,20]

to their hexafluorides (with MoF$_4$ and MoF$_5$ for Mo(CO)$_6$).

Evidently there is no equivalent unit stable enough under

these conditions for molybdenum and tungsten to form

complexes.

3-1.8   Summary of Section 3-1.

A stepwise fluorination of Re$_2$(CO)$_{10}$ by XeF$_2$ has

been established, through Re(CO)$_5$F and Re(CO)$_5$F·ReF$_5$ to ReF$_6$.

Results with other fluorinating agents are consistent with

this progression. The maintenance of the $Re(CO)_5F$ unit

is of fundamental importance for the formation of carbonyl

fluorides by oxidative methods, but it is degraded to ReF_6

by excesses of the more vigorous fluorinating agents.

3-2. THE $Re_2(CO)_{10}/ReF_6/HF$ SYSTEM

3-2.1 Introduction: the Significance of ReF_6; Previous

Reactions

The most significant of the alternative fluorinating

systems for rhenium carbonyl is that using a higher fluoride

of the same element, in this case ReF_6. This allows the

possibility of three different types of reaction:-

i)   Producing carbonyl fluorides by "scrambling",

$$\tfrac{1}{2} Re_2(CO)_{10} + ReF_6 \longrightarrow Re(CO)_3F_3 + Re(CO)_3F_2 \quad (3.15)$$

ii) ReF_6 acting as a simple fluorinating agent to produce

a carbonyl fluoride and a lower rhenium fluoride,

$$\tfrac{1}{2} Re_2(CO)_{10} + ReF_6 \longrightarrow Re(CO)_5F + ReF_5 \quad (3.16)$$

iii) As ii), but the lower fluoride might also complex with

the product,

$$\tfrac{1}{2} Re_2(CO)_{10} + ReF_6 \longrightarrow Re(CO)_5F \cdot ReF_5 \quad (3.17).$$

The reaction of $Re_2(CO)_{10}$ with ReF_6 was first

attempted by Hargreaves and Peacock in 1959-60,[23] along

with other metal carbonyl/metal hexafluoride systems, see

section 3-2.6. An excess of liquid ReF_6 was used, and

mixtures of $ReOF_4$, ReF_4[20] and CO were produced. The present

work systematically examined $Re_2(CO)_{10}/ReF_6$ reactions

using HF as a solvent. A more limited study of the, same

system was performed concurrently by O'Donnell and Phillips,[38]

their somewhat equivocal results are discussed in section 3-2.4.

3-2.2   The $Re_2(CO)_{10}$/ReF_6/HF Reactions

The results of the reactions in this system, with molar proportions of $Re_2(CO)_{10}$:ReF_6 of 1:2, 1:3 and 1:4, are summarised in table 3.4. It was found that reaction type iii). predominated. Only two major products were obtained, $Re(CO)_5F.ReF_5$ and the new compound $(Re(CO)_6)^+(Re_2F_{11})^-$. No CO was liberated.

The 1:2 reaction is very straightforward. Two moles of $Re(CO)_5F.ReF_5$ are formed by splitting the $Re_2(CO)_{10}$ molecule in two, and attatching one ReF_6 molecule to each half by means of an Re-F-Re bridge:

$$Re_2(CO)_{10} + 2\ ReF_6 \longrightarrow 2\ Re(CO)_5F.ReF_5 \qquad (3.18)$$

This reaction of a rhenium(0) species with a rhenium(VI) to produce a Re^I-Re^V complex may be described as "oxidative halogenation / complex-formation". Another example of this unusual type of reaction is that between xenon(0) gas and platinum(VI) hexafluoride to give Xe^{II}-Pt^{IV}/Pt^V complexes, the first noble gas compounds.[101]

e.g. $Xe + 2\ PtF_6 \longrightarrow (XeF)^+(Pt_2F_{11})^- \qquad (3.19)$.

A similar reaction, but where it is the oxidant itself that acts as the acceptor, is that between $Re_2(CO)_{10}$ and IF_5 giving $Re(CO)_5F.IF_5$ (equation 3.14, section 3-1.7).

The 1:4 reaction gives a greater than 80% yield of a 1:2 complex which is not $Re(CO)_5F.2ReF_5$, but an ionic compound related to this, $(Re(CO)_6)^+(Re_2F_{11})^-$. The 1:3 reaction, as would be expected, gives a mixture of $Re(CO)_5F.ReF_5$ and $(Re(CO)_6)^+(Re_2F_{11})^-$.

Table 3.4 The Results of the $Re_2(CO)_{10}/ReF_6/HF$ Reactions

$Re_2(CO)_{10}:ReF_6$	Products
1:2	$Re(CO)_5F \cdot ReF_5$
1:3	$Re(CO)_5F \cdot ReF_5 + (Re(CO)_6)^+(Re_2F_{11})^-$ *
1:4	$(Re(CO)_6)^+(Re_2F_{11})^- + $ unreacted ReF_6 *

No CO was produced in these reactions.

* ReF_5 may have been a minor product.

Table 3.5 Reactions of Metal Carbonyls with Metal Hexafluorides

Carbonyl	Products with	MoF_6 [a]	ReF_6 [b]	OsF_6 [c]
$Mo(CO)_6$	$MoF_5 + CO +$	MoF_4	ReF_5 + residue	
$W(CO)_6$	$WF_6 + CO +$	MoF_4, MoF_5	ReF_4, ReF_5 + residue*	$OsF_4 OsF_5$ + Os
$Re(CO)_{10}$	$ReF_4 + CO +$		residue	

* With WF_6 as solvent. All other reactions without a solvent.

a. refs. 20 and 111; b. refs. 20,23 and 109; c. ref. 25.

$ReOF_4$ was a frequent by-product of ReF_6 reactions, by
   hydrolysis

All 3 carbonyls, and $Cr(CO)_6$, gave red, charge-transfer
   solutions with WF_6.

3-2.3   The Mechanism of $(Re(CO)_6)^+(Re_2F_{11})^-$ Formation

The most remarkable feature of these reactions is the formation of the new compound $(Re(CO)_6)^+(Re_2F_{11})^-$, from $Re(CO)_5$-species, without any CO evolution. This can be explained by a closely analogous mechanism to that proposed for the reaction of $Re(CO)_5F \cdot ReF_5$ with XeF_2.

With 1:2 proportions of $Re_2(CO)_{10}:ReF_6$, $Re(CO)_5F \cdot ReF_5$ is formed, and there is no CO evolution. An excess of ReF_6 causes the fluorination of some of the $Re(CO)_5F \cdot ReF_5$ molecules, just as an excess of XeF_2 did in the $Re_2(CO)_{10}/XeF_2$ system. It is probable that the ReF_6 attacks the $(Re(CO)_5F)$ units of $Re(CO)_5F \cdot ReF_5$, causing initial oxidation to an $(Re(CO)_4F_2)$ unit with the release of CO:

$$(Re^I(CO)_5F) + ReF_6 \longrightarrow (Re^{II}(CO)_4F_2) + CO + ReF_5 \quad (3.20).$$

Precedence for such a step is found in the reactions of the analogous rhenium(I) dinitrogen complex $(Me_2PhP)_4Re(N_2)Cl$ with Lewis acids.[102] Poorly-oxidising halides like TaF_5 form dinitrogen-bridged adducts, but TiF_4 performs a one-electron oxidation producing $[(Me_2PhP)_4Re^{II}(N_2)Cl]^+$, a stable cation isolable as a salt. $(Re^{II}(CO)_4F_2)$ is not stable, as has already been demonstrated in the $Re_2(CO)_{10}/XeF_2$ system, and complete degradation occurs, but with two significant differences. Firstly, ReF_5 is produced not ReF_6, because ReF_6 itself is the oxidant:

$$Re(CO)_5F \cdot ReF_5 + 4\ ReF_6 \longrightarrow 6\ ReF_5 + 5\ CO \quad (3.21).$$

Secondly, instead of the CO being evolved as gas, it becomes incorporated with the unreacted $Re(CO)_5F \cdot ReF_5$ molecules, together with the ReF_5, to produce

$(Re(CO)_6)^+(Re_2F_{11})^-$:

$5 \; Re(CO)_5F \cdot ReF_5 + 5 \; CO + 6 \; ReF_5 \longrightarrow 5(Re(CO)_6)^+(Re_2F_{11})^-$

$$+ \; ReF_5 \quad (3.22),$$

This may take place in a concerted fashion, or by a stepwise process involving either the prior reaction of the CO (to produce $(Re(CO)_6)^+(ReF_6)^-$, which then picks up ReF_5), or of the ReF_5 (to give $Re(CO)_5F \cdot 2ReF_5$, which then takes up CO):

$Re(CO)_5F \cdot ReF_5 + CO \longrightarrow (Re(CO)_6)^+(ReF_6)^-$

$\searrow^{ReF_5}$

$(Re(CO)_6)^+(Re_2F_{11})^-$

$\nearrow^{CO}$

$Re(CO)_5F \cdot ReF_5 + ReF_5 \longrightarrow Re(CO)_5F \cdot 2ReF_5 \qquad (3.23).$

Whichever process occurs, the uptake of CO must be rapid, or it would be lost as gas, and it takes place at room temperature, in solution and at atmospheric pressure. This is remarkable because the usual method for preparing $(M(CO)_6)^+$ salts (M=Mn,Tc,Re) requires the use of a considerable pressure of CO on the appropriate pentacarbonyl halide, in the presence of a good halide ion acceptor.[103]

e.g. $Re(CO)_5Cl + CO + AlCl_3 \longrightarrow (Re(CO)_6)^+(AlCl_4)^- \quad (3.24)$.

There are examples where amounts of $(Re(CO)_6)^+$ have been isolated from an atmospheric pressure process, but these are of poor yield, e.g.:

$EtO.C(O).Re(CO)_5 + 2 \; HCl \xrightarrow{\text{benzene}}$

$(Re(CO)_6)^+(HCl_2)^- + EtOH$ [58] $\quad (3.25)$.

$Re(CO)_5Cl + \text{sym-}C_6H_3Me_3 + AlCl_3 \xrightarrow[95^\circ C]{\text{ligroin}}$

$(Re(CO)_6)^+(AlCl_4)^-$ by-product [104] $\quad (3.27)$.

By contrast, the analogous $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ ion is readily prepared from the much more labile $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ derivatives.[103]

The substitution of CO in these generally rather stable pentacarbonyl derivatives L-M(CO)$_5$, (L= -M(CO)$_5$, halogen, etc), requires there to be:

i)   A sufficient concentration of CO, either free, or co-ordinated but in some suitably "available" form,

ii) Sufficient labilisation of the ligand L to make it a good potential leaving group, and

iii) A good enough Lewis acid present to act as a driving force for ionising off the ligand (and so provide the necessary anion), e.g. M-Cl + AlCl$_3$ $\longrightarrow$ M$^+$ + AlCl$_4$$^-$,
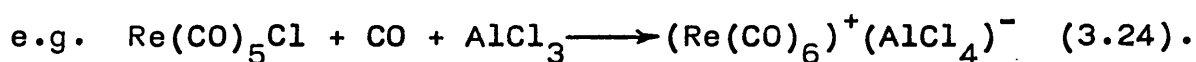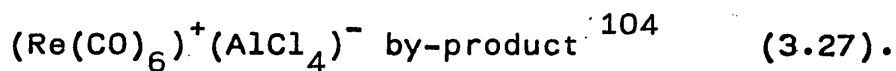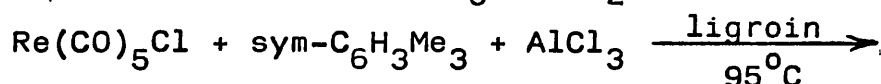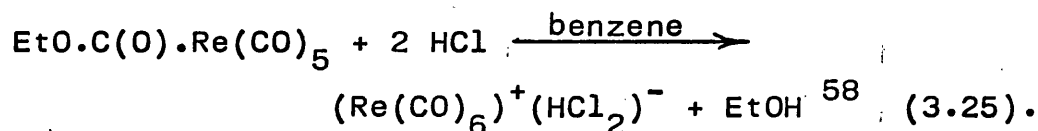
In the previous preparations of (Re(CO)$_6$)$^+$ species, the combined effects of leaving group and Lewis acid have not been enough for efficient reaction under one atmosphere of CO, the chloride ion in Re(CO)$_5$Cl, for example, being too tightly bound to the rhenium. In Re(CO)$_5$F.ReF$_5$ there is a much better leaving group, the (ReF$_6$)$^-$ ion, and presumably the complex must be sufficiently labile for attack to be possible even by the CO generated in situ by (Re(CO)$_5$F) unit decomposition. This being so, it should be possible, simply by bubbling CO through an HF solution of Re(CO)$_5$F.ReF$_5$, to produce the (Re(CO)$_6$)$^+$ derivative (Re(CO)$_6$)$^+$(ReF$_6$)$^-$. Indeed, it is very likely (see section 3-1.4) that this latter is the compound "Re(CO)$_3$F$_3$" obtained by O'Donnell in his 3 Re$_2$(CO)$_{10}$/ReF$_6$/HF [38] and Re(CO)$_5$F/XeF$_2$/HF reactions.[39]

Incorporation of CO was not observed, however, in the author's Re$_2$(CO)$_{10}$/3XeF$_2$/HF reactions, where Re(CO)$_5$F.ReF$_5$ was being produced accompanied by the liberation of CO.**

**In the Re$_2$(CO)$_{10}$/3XeF$_2$/Genetron 113 reactions, the insolubility of Re(CO)$_5$F.ReF$_5$ in Genetron 113 should preclude any reaction with the CO.

In this latter case it may be that the rate of CO production was too fast to allow the $Re(CO)_5F \cdot ReF_5$ to react. In contrast the conversion of $Re(CO)_5F \cdot ReF_5$ into $(Re(CO)_6)^+(Re_2F_{11})^-$ is a slow process, which is governed by the gradual oxidation of the $(Re(CO)_5F)$ groups by ReF_6 producing a rate of CO generation slow enough for it all to be incorporated, rather than lost as gas.

The process may be aided by the presence of ReF_5, increasing the ease of dissociation of $Re(CO)_5F \cdot ReF_5$ through forming $(Re_2F_{11})^-$. It is well-established that M_2F_{10} groups have a greater fluoride ion affinity than single MF_5 species.[105] Hence $(Re_2F_{11})^-$ should be a better leaving group than $(ReF_6)^-$. It should be possible to combine $Re(CO)_5F \cdot ReF_5$ with ReF_5 in HF, in the strict absence of CO, to produce the 1:2 covalent complex $Re(CO)_5F \cdot 2ReF_5$, which should react very readily with CO to give $(Re(CO)_6)^+(Re_2F_{11})^-$.

Thus, the production of $(Re(CO)_6)^+(Re_2F_{11})^-$, rather than its covalent relative, is a consequence of the slow production of CO in the reaction, and of the extreme susceptibility of $Re(CO)_5F \cdot ReF_5$ itself to incorporate CO and eliminate its $(ReF_6)^-$ group (either associatively or dissociatively**). This is supported by a recent report by Mews[43] that the complex $Re(CO)_5F \cdot AsF_5$ (see section 3-3.2) dissolves readily in liquid SO_2, a much weaker donor ligand than CO, to give the ionic complex $[Re(CO)_5(SO_2)]^+[AsF_6]^-$,

---

** Cotton has proposed that the reaction of $(\eta^5-C_5H_5)Fe(CO)_2I$ with $AgBF_4$ in liquid SO_2 to produce $[I\{Fe(CO)_2(\eta^5-C_5H_5)\}_2]^+$ $[BF_4]^-$, proceeds dissociatively via the $(\eta^5-C_5H_5)Fe(CO)_2^+$ ion.[106]

whose SO_2 group may, in turn, be easily displaced even by such poor ligands as acetone and water.

The $Re(CO)_5F \cdot ReF_5/ReF_6/HF$ system is evidently capable of CO "fixation". It is just possible that by bubbling nitrogen gas through an $Re(CO)_5F \cdot MF_5$ solution (M = As, Re or, better still, Sb) at low temperature ($-80^\circ C$?), N_2 might be co-ordinated. A very unstable neutral species $Mo(CO)_5(N_2)$ has been isolated in argon matrices at $-253^\circ C$,[107] but the cation $[Re(CO)_5(N_2)]^+$ should offer the best chance of isolating a more stable metal carbonyl dinitrogen species.

The equation for the conversion of $Re(CO)_5F \cdot ReF_5$ to $(Re(CO)_6)^+(Re_2F_{11})^-$ can be written:

$$6\ Re(CO)_5F \cdot ReF_5 + 4\ ReF_6 \longrightarrow 5(Re(CO)_6)^+(Re_2F_{11})^- + ReF_5 \quad (3.27).$$

The $Re_2(CO)_{10}/3ReF_6/HF$ reaction therefore proceeds by a fast initial step of $Re(CO)_5F \cdot ReF_5$ formation (c.f. the red colour of the initial solution, see section 2-3.2).

$$4\ Re_2(CO)_{10} + 8\ ReF_6 \longrightarrow 8\ Re(CO)_5F \cdot ReF_5 \qquad (3.28).$$
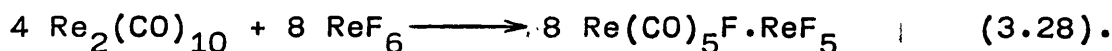
This is followed by a slow, partial conversion to $(Re(CO)_6)^+ (Re_2F_{11})^-$ after equation 3.27, giving an overall reaction of:

$$4\ Re_2(CO)_{10} + 12\ ReF_6 \longrightarrow$$

$$2\ Re(CO)_5F \cdot ReF_5 + 5(Re(CO)_6)^+(Re_2F_{11})^- + ReF_5 \qquad (3.29).$$
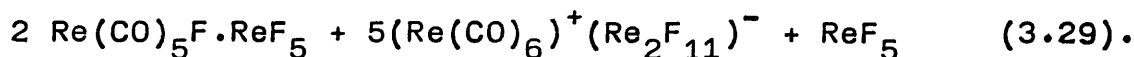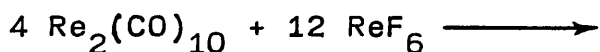
It was impossible to separate the two main products except by crystal picking by hand, but their expected relative proportions of 2:5 agree well with visual estimates. The stoicheiometry requires there to be residual ReF_5, both in this reaction and in the 1:4. This may well have been present in the residues of both reactions.

The $Re_2(CO)_{10}/4ReF_6/HF$ reaction itself has a

theoretical excess of ReF_6 over the proportions required

(3.33 moles) for the production of $(Re(CO)_6)^+(Re_2F_{11})^-$

free from $Re(CO)_5F \cdot ReF_5$ by the above process.

$$3\ Re_2(CO)_{10}\ +\ 12\ ReF_6 \longrightarrow$$

$$5(Re(CO)_6)^+(Re_2F_{11})^-\ +\ 2\ ReF_6\ +\ ReF_5 \qquad\qquad (3.30).$$
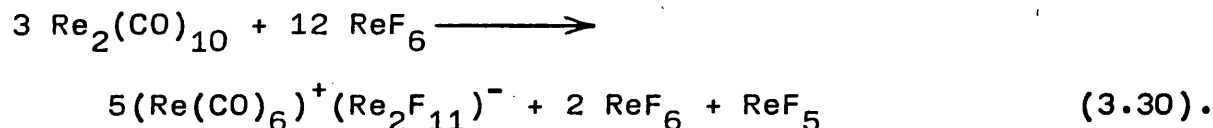
This agrees with the experimental observation that there

was indeed unreacted ReF_6 in the volatiles removed from the

reaction. The final yield of $(Re(CO)_6)^+(Re_2F_{11})^-$, based

on rhenium, by equation 3.30 was 86%.

These fluorinations of rhenium carbonyl by ReF_6

in liquid HF can thus be said to follow a similar pattern to

that established for XeF_2, except that, under the more

forcing conditions where $Re(CO)_5F \cdot ReF_5$ is being decomposed,

the more stable $(Re(CO)_6)^+$ ion is formed — by the reaction

of CO liberated from $(Re(CO)_5F)$ unit decomposition. This

ion remains stable with respect to further oxidation, in

contrast to the final formation of ReF_6 in the XeF_2 system.

In a separate experiment an excess of XeF_2 in HF oxidised

the anion of $(Re(CO)_6)^+(Re_2F_{11})^-$ to ReF_6 yet failed to

affect the cation. This indicates a remarkable stability

for $(Re(CO)_6)^+$ amongst the normally oxidation-sensitive

metal carbonyl derivatives.

3-2.4   An Assessment of the Results of O'Donnell et alia.

O'Donnell and Phillips have reported an $Re_2(CO)_{10}/$

ReF_6/HF reaction with a three-fold excess of the <u>carbonyl</u>,

but there is confusion in their results. The original

paper[38] gave $Re(CO)_3F_3$, ReF_5 and CO as the products, though without citing evidence for the latter two species. A subsequent report[39] maintained on the basis of rather limited infrared data, that $Re(CO)_5F$ was the major product, with only small amounts of $Re(CO)_3F_3$ and ReF_5.

It was shown in section 3-1.4 that the formulation of $Re(CO)_3F_3$ is in error, and that this material is almost certainly either $(Re(CO)_6)^+(ReF_6)^-$ or $(Re(CO)_6)^+(Re_2F_{11})^-$, and that the green "$ReF_5$" solution contains similar species. Furthermore the report of CO evolution must be viewed with some scepticism when none could be detected in the author's reactions. Clearly, O'Donnell's work needs careful re-examination before definite conclusions can be drawn.

3-2.5   The Hydrolysis of $Re(CO)_5F \cdot ReF_5$

Having considered the oxidation of $Re(CO)_5F \cdot ReF_5$ by XeF_2 and ReF_6, the hydrolysis reaction to give $(Re(CO)_6)^+$ $(ReOF_5)^-$ can now be discussed. This also involves oxidation of the rhenium(V) moiety and conversion of the $Re(CO)_5F$ group to $(Re(CO)_6)^+$, and an analogous mechanism can be proposed.

The hydrolysis is probably caused by traces of water in HF solutions or in nitrogen atmospheres above solid $Re(CO)_5F \cdot ReF_5$. By comparison with Mews' reaction of $Re(CO)_5F \cdot AsF_5$ dissolved in liquid SO_2 with water,[43] an initial step is proposed:

$$Re(CO)_5F \cdot ReF_5 + H_2O \longrightarrow [Re(CO)_5(OH_2)]^+ + (ReF_6)^- \qquad (3.31).$$
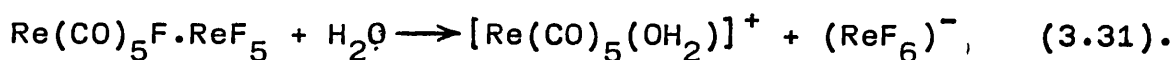
$(ReF_6)^-$ is the anion derived from ReF_5. ReF_5 is known to disproportionate rapidly in water to give $(Re^{VII}O_4)^-$,

$(Re^{IV}F_6)^{2-}$ and ReO_2,[23] a reaction typical of many penta-fluorides. With only traces of water, the $(ReF_6)^-$ ion probably undergoes less complete hydrolysis, forming $(ReOF_6)^-$ as the rhenium(VII) species:

$$3(ReF_6)^- + H_2O \longrightarrow (ReOF_6)^- + 2(ReF_6)^{2-} + 2 H^+ \qquad (3.32).$$
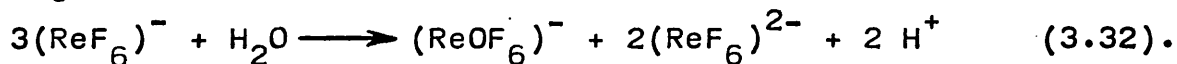
The $(ReOF_6)^-$ ions so formed now oxidise $[Re^I(CO)_5(OH_2)]^+$ cations in much the same way as ReF_6 does the $(Re(CO)_5F)$ units, degrading the carbonyl cation by an initial step:

$$Re(CO)_5(OH_2)^+ + (ReOF_6)^- \longrightarrow [Re^{II}(CO)_4F(OH_2)]^+.$$
$$(\text{or } Re^{II}(CO)_4F(OH) + H^+) + (Re^{VI}OF_5)^- + CO \qquad (3.33).$$
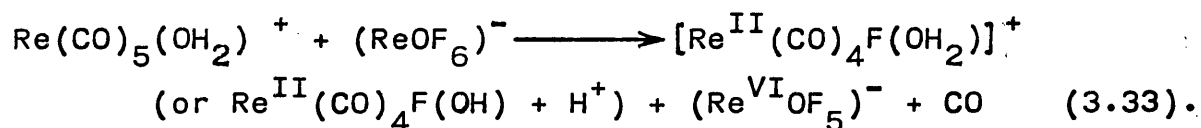
The rhenium(II) species is ultimately degraded to $(ReOF_5)^-$, giving an overall equation:

$$[Re(CO)_5(OH_2)]^+ + 5(ReOF_6)^- \longrightarrow 6(ReOF_5)^- + 5CO + 2H^+ \qquad (3.34).$$
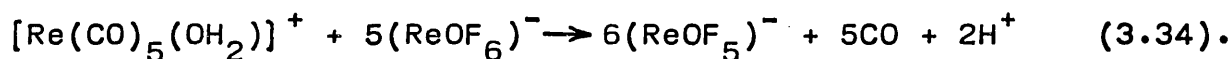
Again, the CO is not liberated, but displaces H_2O from unreacted $[Re(CO)_5(OH_2)]^+$ cations, so giving $(Re(CO)_6)^+(ReOF_5)^-$ as the primary hydrolysis product:

$$5[Re(CO)_5(OH_2)]^+ + 5\ CO + 5(ReOF_5)^- \longrightarrow$$
$$5(Re(CO)_6)^+(ReOF_5)^- + 5\ H_2O \qquad (3.35).$$
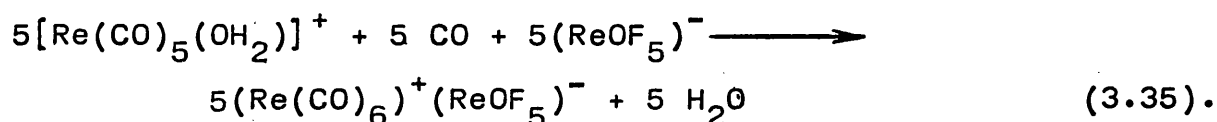
A possible complete equation for the hydrolysis can be written:-

$$15\ Re(CO)_5F \cdot ReF_5 + 15\ H_2O \longrightarrow 5(Re(CO)_6)^+(ReOF_5)^- + 6\ H_2ReF_6 +$$
$$[Re(CO)_5(OH_2)]^+(ReOF_5)^- + 4\{[Re(CO)_5(OH_2)]^+\}_2(ReF_6)^{2-} \quad (3.36).$$
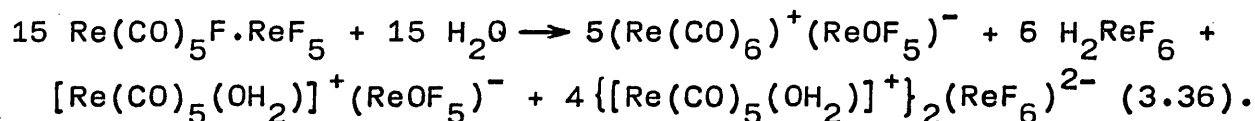
This suggests that H_2ReF_6 and $[Re(CO)_5(OH_2)]^+$ are by-products. The latter may undergo further degradation to produce more $(Re(CO)_6)^+$ species. Further hydrolysis could be envisaged with excesses of water to give $(ReO_2F_3)^-$, $(ReO_3F)^-$ and eventually $(ReO_4)^-$. Such species may have been produced in the $(Re(CO)_6)^+(Re_2F_{11})^-$ hydrolysis mentioned in section 2-3.5.

This hydrolysis produces the first carbonyl oxide fluoride species, and the first Re^I-Re^{VI} compound. The mechanism is a consequence of the instability to oxidation of rhenium carbonyl species of oxidation states greater than 1, and of the ready incorporation of CO by labile $Re(CO)_5X$ species. $Re(CO)_5F \cdot ReF_5$ probably hydrolyses in acetone solution in a similar fashion, initially producing $[Re(CO)_5(OCMe_2)]^+(ReF_6)^-$ followed by disproportionation of the $(ReF_6)^-$ by dissolved water.

3-2.6   A Review of the $Re_2(CO)_{10}/ReF_6$ System and its Analogues

Early work by Hargreaves and Peacock shows that, in the absence of a solvent, ReF_6 is capable of liberating all the CO from the carbonyls $Mo(CO)_6$ $W(CO)_6$ <u>and</u> $Re_2(CO)_{10}$, producing MoF_5, WF_6 and ReF_4 respectively (as well as $ReOF_4$ hydrolysis products), see table 3.5.[23,20] Thus it may be possible to oxidise $(Re(CO)_6)^+$ with <u>liquid</u> ReF_6. By comparison, a calculated excess of ReF_6 slowly converts the isoelectronic $W(CO)_6$ to WF_6 and CO even when using a solvent, WF_6.[23,108]

$$W(CO)_6 + 6\ ReF_6 \xrightarrow[\text{4 weeks, room T.}]{WF_6} WF_6 + 6\ ReF_5 + 6\ CO \quad (3.37).$$
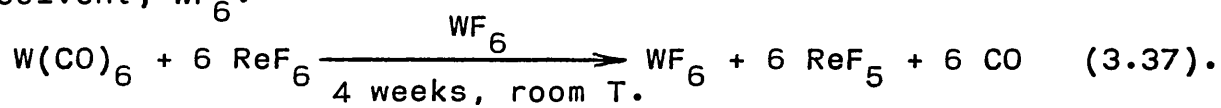
$ReOF_4$ and ReF_4 are by-products. Jones has reported that a yellow solid floated to the surface of the WF_6 in the earlier stages of this reaction.[108] This may well have been a tungsten carbonyl fluoride complex $W(CO)_xF_y \cdot ReF_5$, which later decomposed. (On the present evidence,[12,109] tungsten carbonyl fluorides are much less stable than those of rhenium or even molybdenum). All these $M(CO)_x/ReF_6$ reactions gave unidentified solid residues, some of which may have resulted from carbonyl fluoride species that were intermediates in

the fluorinations.

It seems that the $Re_2(CO)_{10}/ReF_6$ system may be represented by a stepwise oxidation, as shown in figure 3.2. In this case two stable and isolable intermediates are known, $Re(CO)_5F \cdot ReF_5$ and $(Re(CO)_6)^+(Re_2F_{11})^-$. If it were possible to remove the CO rapidly from the $Re(CO)_5F \cdot ReF_5$ oxidation stage, and so prevent $(Re(CO)_6)^+$ formation, the complete fluorination would proceed much more readily.
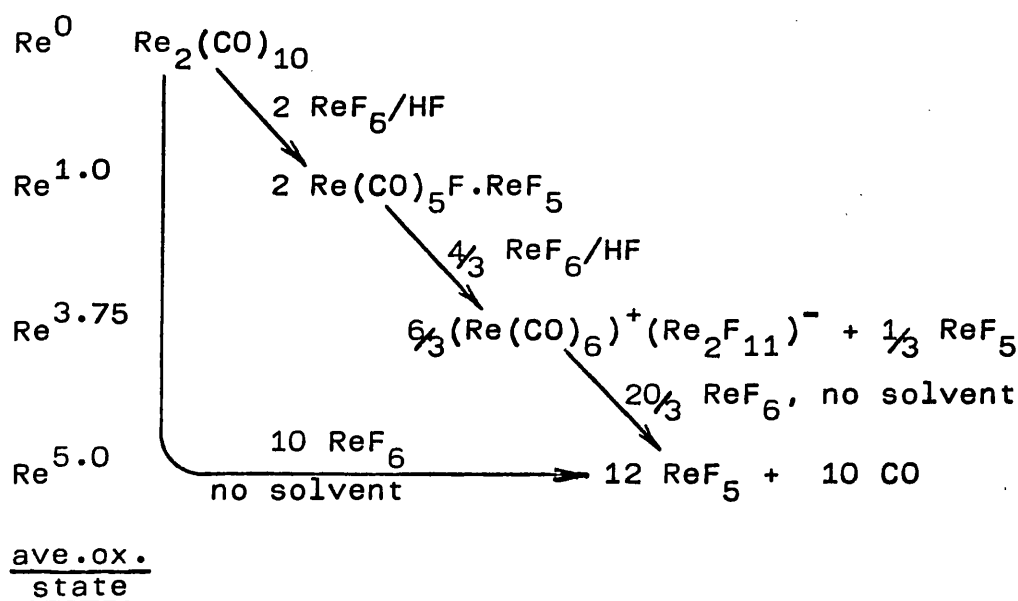
Fig.3.2 Scheme for Stepwise Fluorination of $Re_2(CO)_{10}$ by ReF_6

$Re(CO)_5F \cdot 2ReF_5$ would be the second intermediate, but would be as vulnerable to oxidation as its 1:1 analogue, unlike the stable $(Re(CO)_6)^+(Re_2F_{11})^-$. Further oxidation would continue, giving a smaller and smaller concentration of $(Re(CO)_5F)$ groups amongst ReF_5 molecules, until they had all been decomposed.

This same effect of a "brake" provided by the $(Re(CO)_6)^+$ ion probably does not occur with the $Mo(CO)_6/$ and

$W(CO)_6/ReF_6$ systems, nor are they likely to have such stable $M(CO)_xF_y \cdot ReF_5$ complexes. It should be possible, nonetheless, to moderate these $M(CO)_6/ReF_6$ reactions, especially by the use of a solvent, and so isolate any analogous intermediate complexes.

The metal carbonyl/MoF_6 systems provide similar possibilities, MoF_6 having a similar fluorinating ability to ReF_6. Thus, excesses of liquid MoF_6 have been shown by Edwards, Peacock and Small to oxidise $Mo(CO)_6$ and $W(CO)_6$ to give, respectively, MoF_5, MoF_4 and CO, and WF_6, MoF_5 and CO.[110] With more controlled conditions, Wilson was able to isolate a red, intermediate carbonyl fluoride complex from the room temperature $Mo(CO)_6/MoF_6(l)$ reaction.[12] The analyses of this solid were variable, but the high proportion of fluorine, together with the infrared spectrum suggest an $Mo(CO)_xF_y \cdot MoF_5$ type of complex, (though apparently a different one from that, "$Mo(CO)_3F_2 \cdot MoF_5$", isolated from his $Mo(CO)_6/XeF_2/Genetron$ 113 reactions). O'Donnell and Phillips obtained what appears from their infrared spectrum to be the same material, from a reaction of $Mo(CO)_6$ with MoF_6 using anhydrous HF as a solvent.[33] Their formulation of $(Mo^{IV}(CO)_2F_4)_n$ (based on elemental analysis) is unlikely to be correct, but gives an idea of the overall stoicheiometry. A simple carbonyl fluoride of such a high oxidation state is improbable in view of the stable existence of the simple molybdenum(IV) fluoride MoF_4 (which is in fact the major product of the $Mo(CO)_6/MoF_6(l)$ reaction at $100^\circ C$[12]), and with respect to the proven prevalence of carbonyl fluoride-pentafluoride complexes in other systems. The intermediacy of such complexes in metal carbonyl fluorination systems is

further illustrated by the fact that with an excess of

MoF$_6$, O'Donnell's "Mo(CO)$_2$F$_4$" is oxidised to MoF$_5$.[33] Hence

one may write an analogous scheme for the Mo(CO)$_6$/MoF$_6$

reactions (fig.3.3).

Mo(CO)$_6$

MoF$_6$/HF, or MoF$_6$(l) not xs

Mo(CO)$_x$F$_y$·MoF$_5$ + CO

xs MoF$_6$

xs MoF$_6$
no solvent → (MoF$_4$) + MoF$_5$ + CO
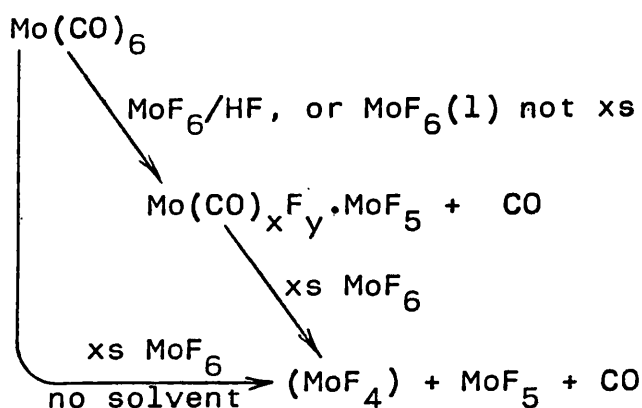
Fig.3.3 Scheme for Stepwise Fluorination of Mo(CO)$_6$ by MoF$_6$

The W(CO)$_6$/MoF$_6$ system would be expected to give

similar, though less stable, intermediate complexes, rather

easily oxidised to WF$_6$ and CO. The Re$_2$(CO)$_{10}$/MoF$_6$ system

has never been examined, however, and is rather interesting

because it should produce stable analogues Re(CO)$_5$F·MoF$_5$

and (Re(CO)$_6$)$^+$(Mo$_2$F$_{11}$)$^-$, of the products of the Re$_2$(CO)$_{10}$/

ReF$_6$/HF system.

In other early studies,[25] an excess of the slightly

more reactive OsF$_6$ was shown to react with W(CO)$_6$ very much

as an excess of ReF$_6$ does. In liquid HF, therefore, OsF$_6$

should give the analogous rhenium/osmium complexes with

Re$_2$(CO)$_{10}$, and, under carefully controlled conditions,

molybdenum/osmium and tungsten/osmium complexes with Mo(CO)$_6$

and W(CO)$_6$. The other metal hexafluorides except tungsten

are all probably too highly oxidising to form similar

complexes. WF_6 is only a very weak oxidant, and merely
forms red, charge-transfer solutions with the carbonyls of
chromium, molybdenum, tungsten and rhenium.[20] The unusual
stability of WF_6 probably accounts for the observed instability
of tungsten carbonyl fluorides.

Carbonyl fluoride complexes might also be expected
to result from metal carbonyl/metal hexafluoride reactions
in other groups, e.g. $Os_3(CO)_{12}/OsF_6$, but these have not
yet been investigated. The more stable metal carbonyls such
as $Ir_4(CO)_{12}$ may allow the use of very reactive hexafluorides
like IrF_6. The carbonyls of the first-row are generally
less stable, and may be decomposed even by ReF_6 and MoF_6.
It would be particularly interesting in view of the isolation
of $Mn(CO)_5F.AsF_5$ by Mews,[43] to see whether $Mn_2(CO)_{10}$ and
$Tc_2(CO)_{10}$ would form $M(CO)_5F.ReF_5$ complexes with ReF_6, or
simply be oxidised to binary fluorides and CO.

3-3.   OTHER RHENIUM CARBONYL FLUORIDE PREPARATIONS

The stepwise fluorination of $Re_2(CO)_{10}$ by XeF_2, the
action of other fluorinating agents, and the special example
of ReF_6 were examined in the preceding sections. To complete
the contemporary picture of the rhenium carbonyl fluoride
system, preparative attempts by the remaining two methods,
carbonylation and halogen exchange, are now discussed briefly.

3-3.1   Carbonylation Reactions

The failure to prepare a carbonyl fluoride from
high pressure carbonylations of K_2ReF_6[11] has already been
discussed in section 1-1. More recently Wilson passed a

mixture of CO and ReF_6/ReF_7 vapour through a Pyrex tube at about $120^{\circ}C$. A volatile, dark blue solid ($ReOF_4$?), and a white residue were produced, but these were not analysed.[12] As a similar method successfully produced carbonyl fluorides from RuF_5,[4,16] IrF_5, OsF_6 and possibly PtF_5,[28] the rhenium reaction is worth repeating, either with ReF_6 or ReF_5. $Mo(CO)_6$ and $W(CO)_6$ merely reduce liquid ReF_6 to ReF_5[23] (see section 3-2.6).

3-3.2 Halogen Exchange and Related Methods

Halogen exchange methods have had mixed success when applied to rhenium carbonyl fluoride preparations. $Re(CO)_5I$ failed to react with liquid AsF_3 in an early reaction of Wilson.[12] More recently, O'Donnell et alia reported that $Re(CO)_5Cl$ reacts with anhydrous HF to produce $Re(CO)_5F$,[39] but it is evident from the author's investigations and subsequent studies[111] that this reaction does not go to completion.

$Re(CO)_5Br$ reacts with $AgSCF_3$ in dichloromethane to produce the trifluoromethylthio derivatives $Re(CO)_5SCF_3$ and $(Re(CO)_4SCF_3)_2$.[112] The former fragments in a mass spectrometer, with the elimination of SCF_2, to produce a series of $Re(CO)_nF^+$ ions (n=3-0). Similar series have been observed in the mass spectra of $F_3Si-Re(CO)_5$ (the product of $Re_2(CO)_{10}$ + $SiHF_3$)[113] and sundry fluoroalkyl analogues.

In contrast, $(\eta^5-C_5H_5)_2TiCl_2$ spontaneously eliminates SCF_2 in its reaction with $AgSCF_3$, to produce $(\eta^5-C_5H_5)_2TiF_2$ as a stable compound.[112] This process is favourable because the $Ti^{IV}-F$ bond is much stronger than the

Re^I-F, but with a less tightly-bound leaving group than

SCF_2, SiF_2, etc., a facile fluorine-atom shift to rhenium

does become feasible. This is found in Mews' reaction of

$Re(CO)_5Br$ with $Ag^+AsF_6^-$ in liquid SO_2.[43] AgBr is precipitated,

and the vacant octahedral co-ordination site of the hypo-

thetical $(Re(CO)_5)^+$ cation is filled with a solvent molecule,

giving the ionic complex $[Re(CO)_5(SO_2)]^+(AsF_6)^-$. SO_2, is,

however, a very weakly co-ordinating ligand, and is slowly

displaced by pumping on the solid, allowing the co-ordination

of the extremely poor nucleophile AsF_6^- at the vacant site

of the highly reactive intermediate $Re(CO)_5^+$, to produce

the new carbonyl fluoride derivative $Re(CO)_5F \cdot AsF_5$.

$$Re(CO)_5Br + AgAsF_6 + SO_2(l) \longrightarrow [Re(CO)_5(SO_2)]^+(AsF_6)^-$$
$$40\text{-}50^\circ C \Big\downarrow pump \qquad\qquad (3.38).$$
$$Re(CO)_5F \cdot AsF_5 + SO_2(g)$$
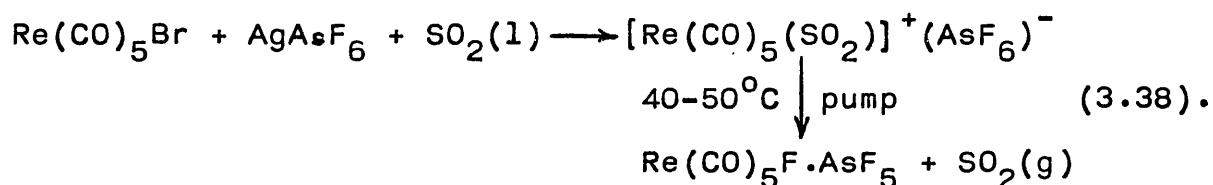
This has effected a combined halogen exchange

and complex-formation reaction, equivalent to adding AgF,

to produce $Re(CO)_5F$, followed by AsF_5. An analogous scheme

has been used to prepare $Me_3SnF \cdot AsF_5$ and similar species,[114,115]

though with no intermediate SO_2 complex. Simple exchange

reactions with AgF have not been attempted, but should be

successful in a solvent capable of dissolving either or both

reactants, and precipitating AgBr, e.g. liquid SO_2, acetone

(in view of the ready formation of $[Re(CO)_5(OCMe_2)]^+(AsF_6)^-$

from the SO_2 complex[43]), thf and HF.

3-3.3   Pentafluoride Group Exchange in $Re(CO)_5F \cdot ReF_5$

The complex $Re(CO)_5F \cdot TaF_5$ was prepared in the

present work by the reaction of TaF_5 with $Re(CO)_5F \cdot ReF_5$ in

HF solution. In contrast, excess liquid SbF_5 reacted with

$Re(CO)_5F \cdot ReF_5$ to produce mainly $(Re(CO)_6)^+(Sb_2F_{11})^-$. The formation of this $(Re(CO)_6)^+$ salt, and not $Re(CO)_5F \cdot 2SbF_5$, may result from the oxidation of $(Re(CO)_5F)$ groups by $(ReOF_6)^-$, produced by partial hydrolysis of ReF_5 in the system. Traces of $(Re(CO)_6)^+(ReOF_5)^-$ were detected in the products.

These two reactions, and the preparation of $Re(CO)_5F \cdot AsF_5$ above, show that the pentafluoride moiety of $Re(CO)_5F \cdot ReF_5$ may be exchanged by a range of suitable acceptor pentafluorides. A similar heterometallic complex $(Ru(CO)_3F_2 \cdot TaF_5)_2$ has been prepared in the ruthenium system.[28] Pentafluoride displacement seems to be preferable to addition, mixed complexes of the type $Re(CO)_5F \cdot MF_5$ being as yet unknown. Brownstein and others have also reported difficulties in isolating solid $E^+(MM'F_{11})^-$ salts, even where these exist in solution.[116,117]

3-4. FUNDAMENTAL UNITS IN RHENIUM AND OTHER CARBONYL
FLUORIDE SYSTEMS

3-4.1 The Fundamental Rhenium Units

The various rhenium carbonyl fluoride preparations discussed in the previous three parts of this chapter are now summarised in table 3.6. The routes to the major species are shown schematically in fig 3.4. The predominance of the $Re(CO)_5F$ and $(Re(CO)_6)^+$ units, established in the XeF_2 and ReF_6 reactions respectively, can be seen to extend over the whole range of reactions so far attempted. The $Re(CO)_5F$ unit is the major species under milder oxidising conditions, the $(Re(CO)_6)^+$ cation, or else fully fluorinated species, under more forcing ones.

The importance of these units lies in their being rhenium(I) species, with the particularly stable, octahedral d^6 configuration, and 18 valence electrons. It is quite possible that other species fulfilling these requirements might be found in the rhenium carbonyl fluoride system. One such, the $[(OC)_5Re-F-Re(CO)_5]^+$ cation, has already been referred to in section 3-1.6. Two other plausible species are based on the $-F-Re^I(CO)_4F-$ unit. These are the anion $(Re(CO)_4F_2)^-$, completing the well-established series $(Re(CO)_4X_2)^-$ (X=halogen), and $(Re(CO)_4F)_4$, the fluoride equivalent of the tetracarbonyl halide <u>dimers</u> $(Re(CO)_4X)_2$, but which, by analogy with the related ruthenium carbonyl fluoride $(Ru(CO)_3F_2)_4$, should be a single-fluorine-bridged tetramer. This latter species might be easily prepared by a simple exchange reaction (see section 3-3.2) on $(Re(CO)_4Br)_2$ (or the chloride). Addition of fluoride ion should produce $(Re(CO)_4F_2)^-$. Addition of ReF_5 could produce a cyclic complex,

Table 3.6 Summary of Rhenium Carbonyl Fluoride Preparations

Reactions giving Carbonyl Derivatives but not Carbonyl Fluorides

K_2ReF_6 + 300 atm.CO/300°C/Al, (refs.11,20) ⟶ trace $Re_2(CO)_{10}$

$Re_2(CO)_{10}$ + F_2/N_2/(s)/-75°C, (ref.20) ⟶ no reaction

$Re_2(CO)_{10}$ + WF_6(l), (ref.20) ⇌ charge-transfer soln.

$Re(CO)_5Br$ + $AgSCF_3$/CH_2Cl_2, (ref.112) ⟶ $Re(CO)_5SCF_3$

$Re(CO)_5I$ + AsF_3(l), (ref.12) ⟶ no reaction

Reactions giving $Re(CO)_5F$

$Re_2(CO)_{10}$ + 1 XeF_2/HF, (ref.39) ⟶ $Re(CO)_5F$

$Re(CO)_5Cl$ + HF(l), (ref.39) ⇌ $Re(CO)_5F$ + HCl

Reactions giving $Re(CO)_5F \cdot MF_5$

$Re_2(CO)_{10}$ + F_2/N_2/Gnt./25°C, 1 XeF_2/Gnt. or/HF ⟶

$Re_2(CO)_{10}$ + $Re(CO)_5F \cdot ReF_5$

$Re_2(CO)_{10}$ + 3 XeF_2/Gnt. or/HF, 2 ReF_6/HF ⟶ $Re(CO)_5F \cdot ReF_5$

$Re_2(CO)_{10}$ + IF_5(l), (ref.20) ⟶ $Re(CO)_5F \cdot IF_5$

$Re(CO)_5Br$ + $AgAsF_6$/SO_2(l) and heat, (ref.43) ⟶ $Re(CO)_5F \cdot AsF_5$

$Re(CO)_5F \cdot ReF_5$ + TaF_5/HF ⟶ $Re(CO)_5F \cdot TaF_5$

Reactions giving $(Re(CO)_6)^+ (M_nF_{5n+1})^-$

2 $Re(CO)_5F$ + 2 XeF_2/HF, (see 3-1.4) ⟶ $(Re(CO)_6)^+ (ReF_6)^-$

$Re_2(CO)_{10}$ + $^{10}\!/\!_3$ ReF_6/HF ⟶ $(Re(CO)_6)^+ (Re_2F_{11})^-$

$Re(CO)_5F \cdot ReF_5$ + $^2\!/\!_3$ ReF_6/HF ⟶ $(Re(CO)_6)^+ (Re_2F_{11})^-$

$Re(CO)_5F \cdot ReF_5$ + SbF_5(l) ⟶ $(Re(CO)_6)^+ (Sb_2F_{11})^-$
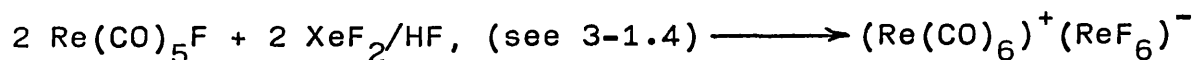
Reactions giving Binary Rhenium Fluorides

$Re_2(CO)_{10}$ + ReF_6(l), (refs.20,23) ⟶ ReF_4

ReF_6(l) + $Mo(CO)_6$ or $W(CO)_6$, (ref.23) ⟶ ReF_5

$Re_2(CO)_{10}$ + F_2/N_2/(s)/25°C, 6 XeF_2/Gnt., BrF_3(l)* ⟶ ReF_6

$Re(CO)_5F \cdot ReF_5$ + 3 XeF_3/Gnt. or/HF ⟶ ReF_6
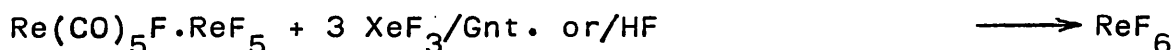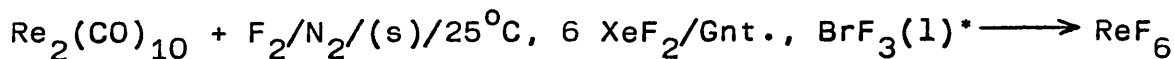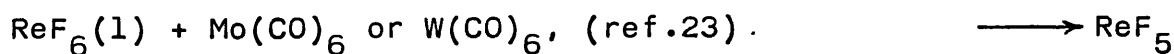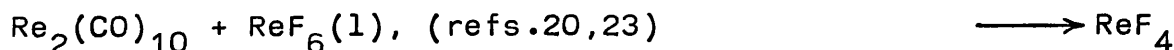
Gnt. = Genetron 113.   * Refs. 23, 12, 20 respectively.

Fig.3.4 Major Species of the Rhenium Carbonyl Fluoride System

$\underline{O}$ =ave.ox.state

$(Re(CO)_5)_2$

1.XeF$_2$/HF

3.XeF$_2$/*

2.ReF$_6$/HF

F$_2$/N$_2$/Gnt. /25°C

$\underline{1.0}$ 2.Re(CO)$_5$F

2.XeF$_2$/HF   2.XeF$_2$/ Gnt.

6.XeF$_2$/Gnt.

BrF$_3$(l)

F$_2$/N$_2$/(s)/ 25°C

$\underline{3.0}$ Re(CO)$_6{}^+$ReF$_6{}^-$ $\xleftarrow{\ -CO\ }$ Re(CO)$_5$F$\cdot$ReF$_6$

$\frac{2}{3}$ReF$_6$/HF

3.XeF$_2$/*

$\underline{3.75}$ $\frac{5}{3}$.Re(CO)$_6{}^+$Re$_2$F$_{11}{}^-$ $+\frac{1}{6}$.ReF$_5$

(xs ReF$_6$(l)?)

(XeF$_2$)

$\underline{5\ or\ 6}$ ReF$_5$ $----------\to$ 2.ReF$_6$

$--\underline{(\ \ )}\to$ are postulated reactions.   Gnt.= Genetron 113.

* either in Genetron 113 or HF

$(Re(CO)_5)_2$

IF$_5$(l)

Re(CO)$_5$F $\longleftarrow$ $\underline{\quad HF(l)\quad}$ Re(CO)$_5$Cl

Re(CO)$_5$Br

AgAsF$_6$/ SO$_2$(l)

Re(CO)$_5$F$\cdot$IF$_5$
Re(CO)$_5$F$\cdot$AsF$_5$ $\longleftarrow$
Re(CO)$_5$F$\cdot$TaF$_5$ $\longleftarrow$ TaF$_5$/HF

Re(CO)$_5$F$\cdot$ReF$_5$

Re(CO)$_6{}^+$Sb$_2$F$_{11}{}^-$ $\longleftarrow$ $\underline{\quad SbF_5(l)\quad}$
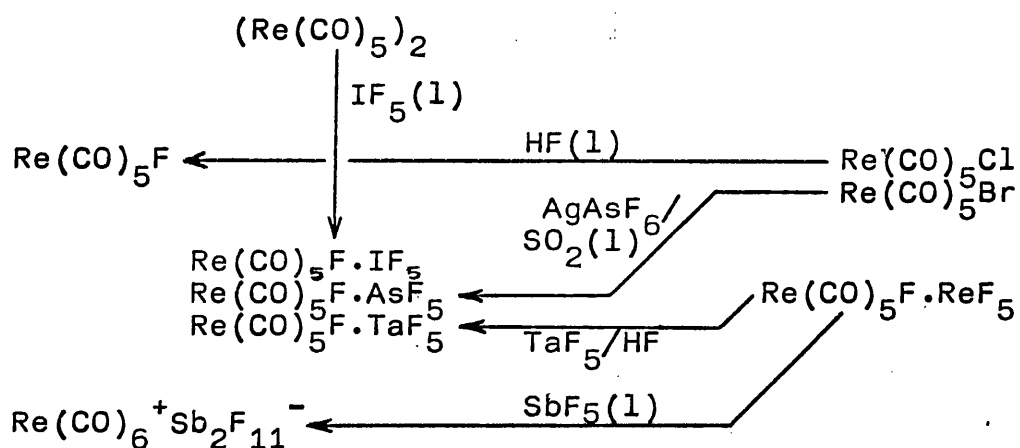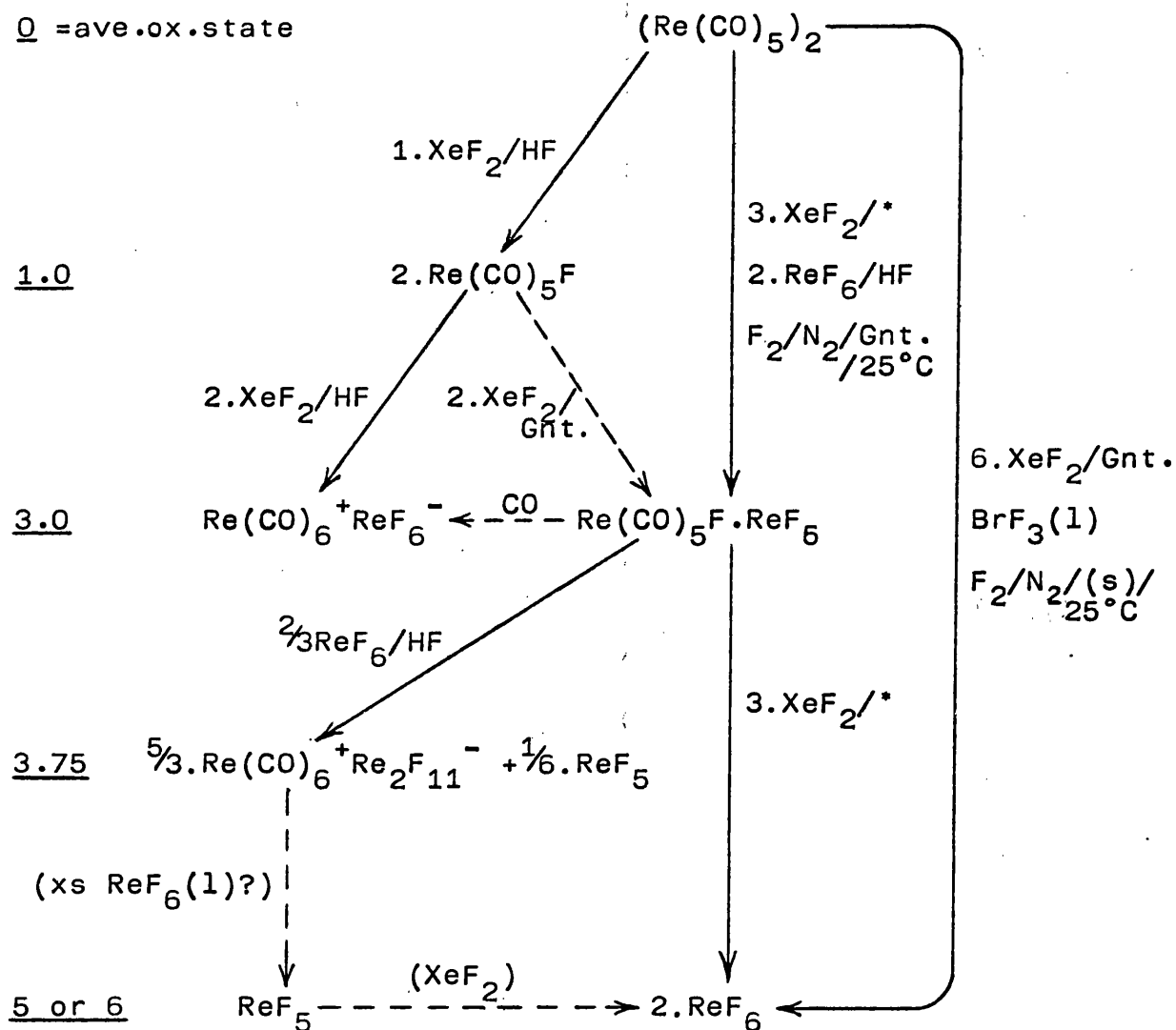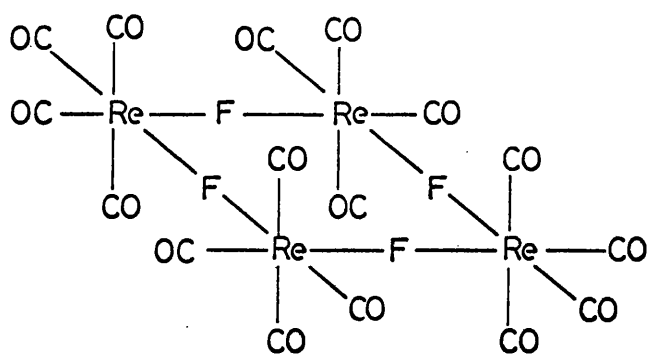
A Possible Tetrameric Carbonyl Fluoride (Re(CO)$_4$F)$_4$

$(Re(CO)_4F \cdot ReF_5)_2$, based on the same $-F-Re(CO)_4F-$ unit.
Alternatively the unit may prefer to give infinite chain
structures, as in ReF$_5$.

3-4.2 The Building Blocks Principle for Carbonyl Fluoride

Formulae

On the basis of the compounds discovered so far,
it is to be expected that all rhenium carbonyl fluorides
will be built up from a very small number of basic units
which are either rhenium(I) species satisfying the above
conditions, or fully-fluorinated rhenium(V) species, e.g.
$Re(CO)_5F \cdot ReF_5$, $(Re(CO)_4F)_4$. It is possible that there could
be other units, but the existing knowledge of the rhenium
system gives no precedent for this.

This 'building blocks' principle is not exclusive
to carbonyl fluorides, and is found in such mixed-ligand
systems as the antimony(V) chlorofluorides. In both these
systems, the known compounds can be built up as a progression

Fig.3.5 The "Building Blocks" Principle in the $Re(CO)_{x-y}F_y$ and $SbCl_{x-y}F_y$ Systems

CO:F ratio	Empirical Formula	Structure	Empirical Formula	Structure	Cl:F ratio
∞	$Re(CO)_5$	$(Re(CO)_5)_2$ [a]	$SbCl_5$	unknown	∞
5.00	$Re(CO)_5F$	$Re(CO)_5F$	$SbCl_4F$	$(SbCl_4F)_4$ [c]	4.00
1.00	$Re(CO)_3F_3$	$Re(CO)_6^+ReF_6^-$	$SbCl_3F_2$	unknown [d]	1.50
0.83	$Re(CO)_{2.5}F_3$	$Re(CO)_5F \cdot ReF_5$	$SbCl_2F_3$	$SbCl_4^+Sb_2Cl_2F_9^-$ [e]	0.67
0.55	$Re(CO)_2F_{3.67}$	$Re(CO)_6^+Re_2F_{11}^-$	$SbCl_{1.67}F_{3.33}$	$SbCl_4^+Sb_2ClF_{10}^-$ [f]	0.50
0.46	$Re(CO)_{1.67}F_{3.67}$	$Re(CO)_5F \cdot 2ReF_5$	$SbCl_{1.33}F_{3.67}$	$SbCl_4^+Sb_2F_{11}^-$ [g]	0.36
0.00	ReF_5	$(ReF_5)_n$ [b]	SbF_5	$(SbF_5)_4$ [h]	0.00

References: a. 118, b. 119, c. 120, d. 121, e. 122, f. 123, g. 124, h. 125.

of stoicheiometries, starting from $Re(CO)_5$ and $SbCl_5$ at

one extreme, to ReF_6 and SbF_5 at the other, by using

combinations of the basic units of each system. This is set

out in fig 3.5. Thus simple stoicheiometries like $Re(CO)_3F_3$

may only occur where these happen to coincide with those

of stable complexes, as in the case of $(Re(CO)_6)^+(ReF_6)^-$.

The concentration of similar types of ligand on

one atom in some of these species $(Re(CO)_5F$, $SbCl_4^+$, ReF_6^-,

etc.) gives the most favourable electron distribution.

Ligands, such as carbonyl, which require a high electron

density at the metal to form strong bonds, concentrate on

a low oxidation state atom, ligands which prefer a low

electron density at the metal, e.g. fluoride, on a higher

oxidation state atom. The phenomenon may also be seen in

the related platinum metal phosphine fluorides, where Dixon

has postulated[126] that to stabilise the fluoride ligand on

an electron-rich metal centre like platinum(II) (d^8) may

require a minimum of three strongly electron-withdrawing

ligands. The cation $[(Et_3P)_3PtF]^+$ is stable, but no

confirmed species have been found where there is a less acidic

ligand in the co-ordination sphere, such as $[(Et_3P)_2Pt(CO)F]^+$

or $(Et_3P)_2PtFCl$.[127,17,126]

3-4.3 Fundamental Units in Other Carbonyl Fluoride Systems

The same principle of fundamental units as building

blocks may be applied to the other carbonyl fluoride systems.

Since the completion of the author's work, a detailed study

of the ruthenium system has been made,[12] and the

$-F-Ru^{II}(CO)_3F_2-$ group has emerged as the fundamental unit

of the system. This is another d^6 species, but is analogous

not to $Re(CO)_5F$ but to $-F-Re(CO)_4F-$. It is present in

the two major species of the system, $(Ru(CO)_3F_2)_4$ and

$(Ru(CO)_3F_2 \cdot RuF_5)_2$, cyclic compounds based on the (Ru_4F_4)

ring of $(RuF_5)_4$. These are the relatives of $Re(CO)_5F$ and

$Re(CO)_5F \cdot ReF_5$, formed in preference to their direct analogues

$Ru(CO)_4F_2$ and $Ru(CO)_4F_2 \cdot RuF_5$.

Only fragmentary data are available on the other

systems, but similar fundamental units can be proposed.

There is a series of octahedral d^6 units which should be of

particular importance in the chromium, manganese, iron and

cobalt triads: $W(CO)_6$, $Re(CO)_5F$, $Os(CO)_4F_2$ and $Ir(CO)_3F_3$

(giving the third-row examples), together with their first-

and second-row homologues, and derived units such as

$(W(CO)_5F)^-$ and $-F-Os(CO)_3F_2-$.

Square planar d^8 species will be important for

rhodium and iridium ($M^I(CO)_3F$, etc.), and especially for

palladium and platinum ($M(CO)_2F_2$, etc.), where the +4

oxidation state required for the corresponding d^6 species

$M(CO)_2F_4$ is effectively unattainable in carbonyl derivatives.

Indeed the reactivity of palladium and platinum fluorides

may preclude carbonyl fluoride formation altogether. For

silver and gold, the likely species is d^{10} $M(CO)F$.

For the chromium triad, the d^6 species are the parent

hexacarbonyls $M(CO)_6$. Therefore the formation of higher

oxidation state carbonyl fluorides should not be very

favourable because of the consequent requirement to adopt

less stable electronic configurations. Accordingly, such

molybdenum and tungsten carbonyl fluorides have been found

to be less thermodynamically stable than those of rhenium

and ruthenium.

Nevertheless, by analogy with other group VIB

carbonyl halides, basic units can be proposed for carbonyl

fluorides of higher oxidation states, namely 7-co-ordinate

d^4 ($M^{II}(CO)_5F_2$ or $-F-Mo(CO)_4F_2-$) and perhaps octahedral

d^3 ($M^{III}(CO)_3F_3$). d^6 carbonyl fluorides can, of course,

be found in the anions $(M^0(CO)_5F)^-$.

Table 3.7 Predicted Basic Units in Carbonyl Fluoride Systems

Triad	Cr	Mn	Fe	Co	Ni/Cu
d^{10} d^8 d^6 d^4 d^3	$(M^0(CO)_5F)^-$ $-F-M^{II}(CO)_4F_2^-$ $M^{III}(CO)_3F_3$	$M^I(CO)_5F$	$-F-M^{II}(CO)_3F_2^-$	$-F-M^I(CO)_2F-$ $M^{III}(CO)_3F_3$	$Cu^I(CO)F$ $Ni^{II}(CO)_2F_2$

Other species are possible, but because of the requirement

for particularly stable units in order to balance the carbonyl

and fluoride ligands on the same metal atom, such cases should

be rare.

The few species that have been characterised in these

other systems comfirm this picture. Osmium studies to date

show that $(Os(CO)_3F_2)_4$ predominates in $Os_3(CO)_{12}/XeF_2$

reactions.[111] $Mn(CO)_5F \cdot AsF_5$,[43] and the group VIB anions

$(M(CO)_5F)^-$ (M=Cr,W)[8,9] have been reported recently. In the

cobalt triad, the d^8 phosphine carbonyl fluorides

$(Ph_3P)_2M(CO)F$ (M=Rh, Ir) are well known.[35-37]

It might be expected that once these systems have

been studied in depth, the above pattern of units will be

confirmed.

3-5. DISCUSSION OF THE METAL CARBONYL FLUORIDE SYSTEM

AND ITS ANALOGUES

3-5.1 An Analysis of the Metal Carbonyl Fluoride System

Having established the principle of fundamental units as building blocks in carbonyl fluoride systems, and on the basis of the total work on the rhenium and ruthenium systems, a general sequence of reactions for carbonyl fluoride preparations has been established. This is shown schematically in fig.3.6.

$M(CO)_n$ ← CO/pressure ?

$\searrow XeF_2$

$M(CO)_x F_y$

XeF$_2$ or MF$_5$ ↖ CO/pressure

XeF$_2$ or MF$_6$ → $M(CO)_x F_y \cdot MF_5$ ← CO/flow

MF_5 ↖ CO/flow

XeF$_2$

$M(CO)_x F_y \cdot 2MF_5$*

XeF$_2$ or MF$_6$ ↖ CO/flow

xs XeF$_2$ → MF$_z$
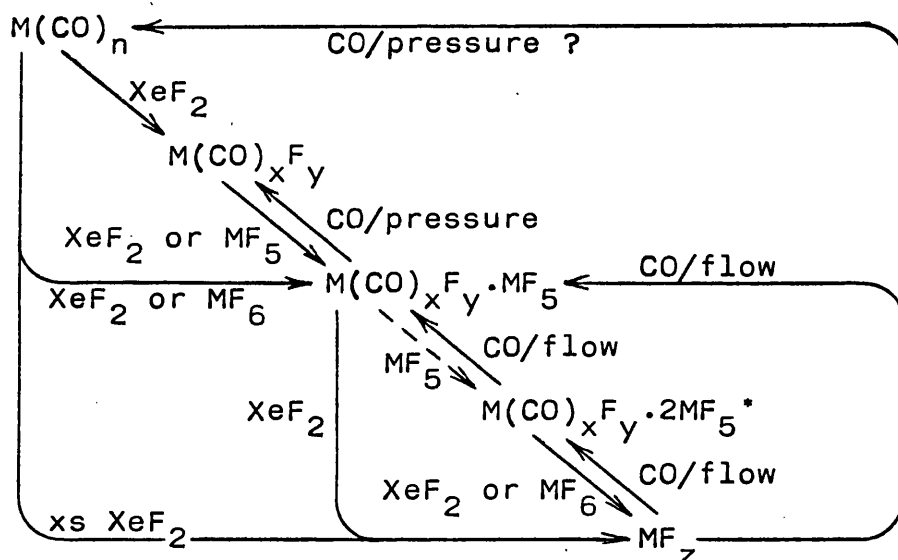
* or some other 1: 1 adduct, e.g. $(Ru(CO)_3F_2 \cdot 3RuF_5)$;

    1: 1 adducts are also possible

The above requirements for atmospheric (flow system), or

  higher, pressures of CO are suggestions only.

Fig. 3.6   A Generalised Carbonyl Fluoride System

In the light of the rhenium results, metal carbonyl fluorinations can be expected to follow a progression from metal carbonyl, to simple carbonyl fluoride, through carbonyl fluoride-pentafluoride complex(es), to a final, fully-fluorinated species, which will not in general be the

highest fluoride unless very vigorous conditions are used.

The particular species obtained depends very much on the

conditions, but also on which are the most stable species

for that system. For example, the complex $Re(CO)_5F \cdot ReF_5$

is the predominant species for the $Re_2(CO)_{10}/XeF_2$ system,

whereas for another (e.g.Mn ?) it may be that only the simple

carbonyl fluoride is stable.

From the ruthenium studies,[16,13] the carbonylation

of metal fluorides should follow the reverse proceedure,

although it may be difficult to avoid mixtures of carbonyl

fluoride complexes in the initial stages, and complete

reduction to the metal in the final stage.

3-5.2   The Suggested Means of Investigating a Carbonyl

Fluoride System

A. Study the $M(CO)_x/XeF_2$/Genetron 113 and /HF systems in

stepwise fashion, to establish the progression of compounds

in the system. Consider the use of other solvents for

precipitation, separation, and especially recrystallisation

(e.g. WF_6, SO_2, SO_2ClF, $CFCl_3$, etc.). The more stable

systems may require more vigorous oxidants to achieve the

more highly fluorinated species (e.g. osmium[111]), or even,

in the case of iridium[16], to prepare a carbonyl fluoride

at all. Possible alternative fluorinating agents include

XeF_6, BrF_3, SF_4 and N_2F_2, all preferably diluted in a

suitable solvent. Conversely, the more delicate systems

may require milder fluorinating agents (e.g. $Mn_2(CO)_{10}$ +

$AgF/SO_2(1)$?), or else other methods of obtaining carbonyl

fluorides altogether, particularly halogen exchange techniques.

<u>B</u>. Explore MF_n/CO reactions to see if they follow the
the reverse of i).

These two methods set out the basic sequence of metal
carbonyl fluoride species, but individual compounds may be
better prepared by other methods.

<u>C</u>. Perform $M(CO)_x$/$M'F_6$/HF reactions (where M=M' if possible),
in controlled proportions, to obtain pure $M(CO)_xF_y$, MF_5
complexes and ultimately higher fluorides (see 3-2.5). Also
investigate the preparation of heterometallic complexes
(M≠M'), and the use of oxidising pentafluorides which can
themselves complex with a carbonyl fluoride (e.g. IF_5, [20]
AsF_5 and SbF_5).

<u>D</u>. Attempt halogen exchange reactions on the known carbonyl
chlorides (or bromides). This method is more specific for
a particular formulation than the others, and involves no
oxidation. Simple carbonyl fluorides are therefore probably
best prepared this way, provided the right conditions can
be found. Important requirements are a good solvent, a
driving force/means of removing the unwanted halide (e.g.
precipitating out AgCl), and the absence of undue moisture.

As a general principle, organometallic fluoride
formation seems only likely in halide systems where the
metal-halogen bond is particularly polar, e.g. $Re(CO)_5$-X,
$(Ph_3P)_2Ir(CO)$-X,[37] $(Ph_3P)_3Cu$-X,[128,129] $(\eta^5-C_5H_5)Cr(NO)_2$-X,[130]
$(\eta^5-C_5H_5)Ti$<^X_X,[131] Me_3Sn-X,[132,114] where X= F, Cl, Br and I.
Often such series have a fairly easily-formed, co-ordinat-
ively-unsaturated intermediate which is very susceptible
to nucleophilic attack, a situation very amenable to the
simple exchange of one halide ion by another, e.g.

$(Ph_3P)_2Ir(CO)Cl + AgF \xrightarrow{\text{acetone}} (Ph_3P)_2Ir(CO)F,[36,127]$ (3.39),

and the subsequent exchange of the fluoride ion for numerous

halides, pseudohalides, etc.[37] A further characteristic

is the ready dissociation into ionic species in co-ordinating

solvents, by the ligation of a solvent molecule which can

be readily displaced by even such a weak nucleophile as

F^-, e.g.[133]

$(Ph_3P)_2Ir(CO)Cl + AgClO_4 + MeCN \longrightarrow (Ph_3P)_2Ir(CO)(NCMe)^+ClO_4^-$

$+ AgCl$

$(Ph_3P)_2Ir(CO)F \xleftarrow{\text{Et}_2\text{NH/aq.HF}}$

(3.40)

This provides two versatile methods of halogen

exchange, neither of which have been properly examined in

carbonyl fluoride syntheses. Early attempts at the first

method were not very encouraging $[(Mo(CO)_4Cl_2)_2$ [34] and

$(Os(CO)_3Cl_2)_2$ [13] with AgF/acetone, $(Rh(CO)_2Cl)_2$ with

AgF/MeCN[12]] possibly due to moist conditions and/or an

unsuitable solvent, but Mews' preparation of $Re(CO)_5F \cdot AsF_5$ [43]

is a successful variant on the second method.

AgF is probably the best exchanging agent, with

acetone,[127] MeCN, thf,[8] or aq.HF,[134] as the solvent for

the less moisture-sensitive compounds, liquid SO_2 or HF for

the others. TlF/HF solutions (prepared simply by dissolving

thallium metal in HF)[15] may be suitable for some compounds,

but HF on its own does not give completed reactions with

$Re(CO)_5Cl$ (see section 3-3.2), $(Rh(CO)_2Cl)_2$ [12] or

$(Ph_3P)_2Ir(CO)Cl,$[36] and is therefore unlikely to be useful.

F_2/N_2 mixtures[36] and XeF_2 [13] in Genetron 113 or MeCN have

also been unsuccessful.

<u>E</u>. Investigate the possible complexes of simple carbonyl

fluorides prepared by <u>D</u>. with pentafluorides, by simple

addition reactions in a suitable solvent. On the evidence

of $Re(CO)_5F$ and apparently $Ru(CO)_3F_2$, carbonyl fluorides

are likely to be quite stable fluoride ion donors, capable

of complexing with Lewis acids in the same way as more

recognised fluoride bases such as SeF_4, BrF_3 and XeF_2.

Certain of the more reactive pentafluorides, e.g. CrF_5 and

BiF_5, may, however, oxidise the carbonyl fluoride instead.

These above investigations should be performed

for the Mo, W, Tc, Ru, Os, Rh and Ir systems. For the first

row series Cr, Mn, Fe, etc., only methods <u>A</u>. and <u>D</u>. are

applicable, for Pd, Pt, Cu, Ag and Au, only <u>B</u>. and <u>D</u>.

Single crystal X-ray structures may be necessary to char-

acterise many of the products, until enough data has been

assembled to predict structures on the basis of vibrational

spectroscopy, magnetic resonance, etc.

3-5.3 Metal Carbonyl Halide-Acceptor Halide Complexes of

Chlorine, Bromine and Iodine

The general outline of the transition metal

carbonyl fluoride system has been established. It differs

significantly from that of the other carbonyl halides both

in the general instability of the compounds, with their

ready conversion into binary fluorides (the first-row and

the molybdenum and tungsten carbonyl halides[38] are perhaps

their closest relatives in this respect), and in fundamental

role of the $M(CO)_xF_y \cdot MF_5$ complex. Analogous complexes of

formula $M(CO)_xX_y \cdot MX_n$ are almost unknown, and play little

part in the particular carbonyl halide system. Both the

halogenation of metal carbonyls and carbonylation of metal

halides give, in general, only simple carbonyl halides. This

is because the suitable acceptor halides are either inaccess-

ible or unstable under the halogenation or carbonylation

conditions employed, whereas high oxidation state acceptor

fluorides, especially the unique series of pentafluorides, can

be stable even in the presence of CO.

The odd carbonyl chloride-metal chloride complexes

that have been reported have all resulted from simple

addition (method $\underline{E}$. of the previous section) or an oxidative

chlorination involving an acceptor chloride (method $\underline{C}$.),

rather than orthodox chlorination or carbonylation.

$$(Me_3P)_2Fe(CO)_2Cl_2 + FeCl_3 \xrightarrow{CH_2Cl_2} (Me_3P)_2Fe(CO)_2Cl_2 \cdot FeCl_3,$$

also $(\eta^5-C_5H_5)Fe(CO)_2Cl \cdot FeCl_3$, both in solution only[135] (3.41).

$$(R_3P)_2Fe(CO)_3 + 3 FeCl_3 \xrightarrow{CH_2Cl_2} [(R_3P)_2Fe(CO)_3Cl]^+ [FeCl_4]^-$$

(R=Me, OMe) $+ 2 FeCl_2$ [136]   (3.42).
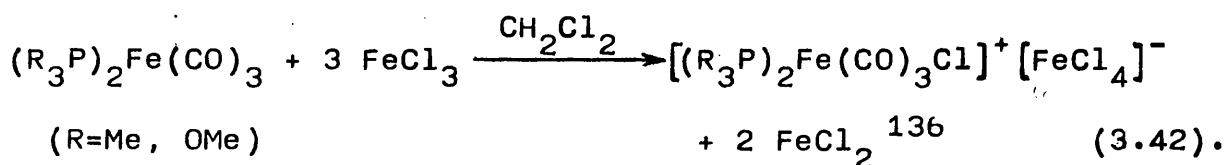
An intermediate $W^{II}-W^V$ species, $Cl(OC)_4W\underset{Cl}{\overset{Cl}{\diamond}}WCl_4$

(c.f. $Mo(CO)_3F_2 \cdot MoF_5$), has been proposed in the method $\underline{C}$.

reaction of $(W(CO)_5Cl)^-$ with WCl_6,[137] but the final products

of both this and $M(CO)_6/MCl_6$ reactions (M=Mo,W) are mostly

the metal(IV) and (V) chlorides and CO.[137-139]

There is, however, quite a range of heterometallic

complexes, $M(CO)_xX_y \cdot M'X_n$, prepared by the oxidation of the

parent carbonyl by, or in the presence of, an acceptor

halide of a different element, particularly $SbCl_5$. The

dimeric carbonyls $Re_2(CO)_{10}$ [140] and $(cpFe(CO)_2)_2$ [141]

$(cp=\eta^5-C_5H_5)$ are oxidised by $SbCl_5$ in dichloromethane to

d^6 2:1 ($L_3M(CO)_2Cl$) complexes ($L_3 = (CO)_3$ or cp), where a second mole of the oxidant acts as an acceptor molecule, with $SbCl_3$ as a by-product.

e.g. $Re_2(CO)_{10}$ + 2 $SbCl_5 \longrightarrow (Re(CO)_5Cl)_2SbCl_5$ + $SbCl_3$ (3.43).
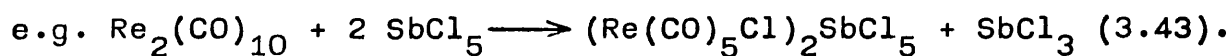
This is similar to the $Re_2(CO)_{10}/IF_5$(l) reaction discussed in section 3-1.7, but contrasts with the $Re_2(CO)_{10}/2ReF_6/HF$ reaction of section 3-2.3 where it is the reduced form of the oxidant which is the acceptor. Antimony trihalides can themselves act as acceptors, and oxidise $(cpFe(CO)_2)_2$ in dichloromethane to give traces of the analogous $(cpFe(CO)_2X)_2SbX_3$ complexes (X=Cl,Br), along with numerous Fe-Sb bonded complexes.[141] $AsBr_3$ gives a 3:1 complex.[141] A 1:1 complex $cpFe(CO)_2Cl.SbCl_3$ is a by-product of an $Na^+(Fe(CO)_2cp)^-/SbCl_3$ reaction.[142]

These complexes are generally covalent, with 2 (or 3) single M-X-Sb(As) bridges (c.f. $(OC)_5Re-F-ReF_5$), but the oxidation of $(cpFe(CO)_2)_2$ by X_2 in the presence of a non-co-ordinating anion (in benzene), or performed in the ionising solvent liquid HCl, gives ionic 2:1 complexes of formula $(cp(OC)_2M-X-M(CO)_2cp)^+Y^-$ (M=Fe,[143a] Ru,[143b] X=Cl Br,I, Y=BPh_4, or M=Fe,[67] X=Cl, Y=HCl_2 (in solution only), respectively).

With $SbCl_5/CH_2Cl_2$ or $CHCl_3$, the monomeric carbonyls $W(CO)_6^*$, $(C_6Me_6)W(CO)_3$, $(triars)W(CO)_3$, $cpMn(CO)_3^*$ and $cpRe(CO)_3$ all give 7-co-ordinate d^4 ionic derivatives $(L_3M(CO)_3Cl)^+(SbCl_6)^-$, ($L_3$= $(CO)_3$, C_6Me_6, triars, cp), some of them* very unstable.[140,144]

$L_3M(CO)_3$ + 2 $SbCl_5 \longrightarrow (L_3M(CO)_3Cl)^+(SbCl_6)^-$ + $SbCl_3$ (3.44).
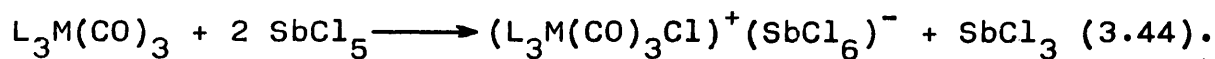
Similarly, $Fe(CO)_5$ dissolved in liquid HCl reacts with the halogens to produce d^6 $(Fe(CO)_5X)^+$ species (X=Cl,Br,I),

precipitateable as BCl_4^- salts by adding BCl_3.[100] To

form covalent complexes in these monomeric cases would

require the loss of a molecule of CO to maintain a noble

gas electron configuration, and this is evidently unfavourable

under these conditions. In contrast, $Fe(CO)_5$ reacts with

$SbCl_5$ in CCl_4 at $-5^\circ C$, with CO evolution, to produce the

covalent $Fe(CO)_4Cl_2 \cdot SbCl_3$.[145] A yellow precipitate formed

without CO evolution at $-20^\circ C$ may, in hindsight, be unstable

$(Fe(CO)_5Cl)^+(SbCl_6)^-$.

Heterometallic complexes have also been formed by

the addition of the acceptor to the appropriate carbonyl

halide. The complexes $(Re(CO)_5Cl)_2SbCl_5$ and (in much

improved yield) $(cpFe(CO)_2Cl)_2SbCl_3$ have been prepared from

the carbonyl chlorides and $SbCl_5$.[140,141] There is also

evidence for a whole range of adducts in dihalomethane

solutions,[135,136] e.g. $Mn(CO)_5Cl \cdot FeCl_3$, $cpFe(CO)_2Cl \cdot SbCl_5$

and $(Me_3P)_2Fe(CO)_2Br_2 \cdot 2AlBr_3$, none of which have, however,

been isolated. Ionic $(X(Fe(CO)_2cp)_2)^+Y^-$ complexes have also

been prepared from the halides $cpFe(CO)_2X$ by addition of

98% H_2SO_4[146] or BF_3 etherate,[147] or of a Lewis acid in an

ionising solvent $(AlX_3/SO_2$,[148] BCl_3/HCl[67]), all followed

by a non-co-ordinating anion Y^- (y=BF_4 or PF_6), or of AgY

in benzene[106] or toluene.[146]

The choice of an ionic or covalent form depends

partly on the stability of the possible cation, partly on

the nucleophilicity of the anion, and partly on the solvent.

For 1:1 complexes such as $Mn(CO)_5Cl \cdot FeCl_3$,[135] the free

cation $(Mn(CO)_5)^+$ is unstable, and the covalent form exists

in a non-co-ordinating solvent (c.f. $Mn(CO)_5F \cdot AsF_5/SO_2$[43]).

Stable dimeric $(X(Fe(CO)_2cp)_2)^+$ and monomeric $(L_3M(CO)_3Cl)^+$ cations allow the formation of 2:1 d^6 and 1:1 d^4 ionic complexes, confirmed by the crystal structures of the cations $(I(Fe(CO)_2)_2)^+$ [106] and $(diars)_2Mo(CO)_2I^+$, [149] but the weak complex $[(cpFe(CO)_2Cl)_2SbCl_3]_2$** adopts a covalent structure, [150] see fig.3.7a.

Presumably an equilibrium must exist in solution:

$$2\ cpFe(CO)_2X \rightleftharpoons (X(Fe(CO)_2cp)_2)^+ + X^- \qquad (3.45).$$
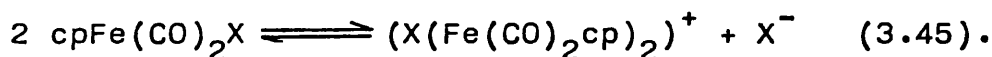
Addition of a non-co-ordinating anion forces the equilibrium over to the right, a process aided by an ionising solvent. With a more nucleophilic anion such as $SbCl_4^-$, the solvent may govern the position of the equilibrium, the complex** being produced in ether. The 2:1 $SbCl_5$ complexes are also probably covalent in CH_2Cl_2 solution, but might be ionic in liquid HCl.

The prevalence of 2:1 stoicheiometry, despite frequent large excesses of acceptor halide is partly due to the stability of dimeric cations, but is also a consequence of the electronic requirements of $SbCl_3$ and $SbCl_5$. These attain a stable $5s^2, 5p^6, 5d^6$ valence shell configuration with $(Sb^{III}Cl_6)$ and (Sb^VCl_7) co-ordination spheres, respectively. $SbCl_5$ thus requires two molecules of a chloride ion donor to complete an $(SbCl_7)$ unit. $SbCl_3$, however, achieves $(SbCl_6)$ co-ordination be dimerising a 2:1 adduct**, see fig.3.7a., or by tetramerising a 1:1 adduct, in a similar, weak complex $(cpFe(CO)_2Cl.SbCl_3)_4$, [142] which adopts a cubane-like structure, with $SbCl_3$ antimony atoms and $cpFe(CO)_2Cl$ chlorine atoms occupying alternate corners of a distorted cube, fig.3.7b. (simplified).

a. $[(cpFe(CO)_2Cl)_2SbCl_3]_2$ [150]   b. $(cpFe(CO)_2Cl \cdot SbCl_3)_4$ [142]
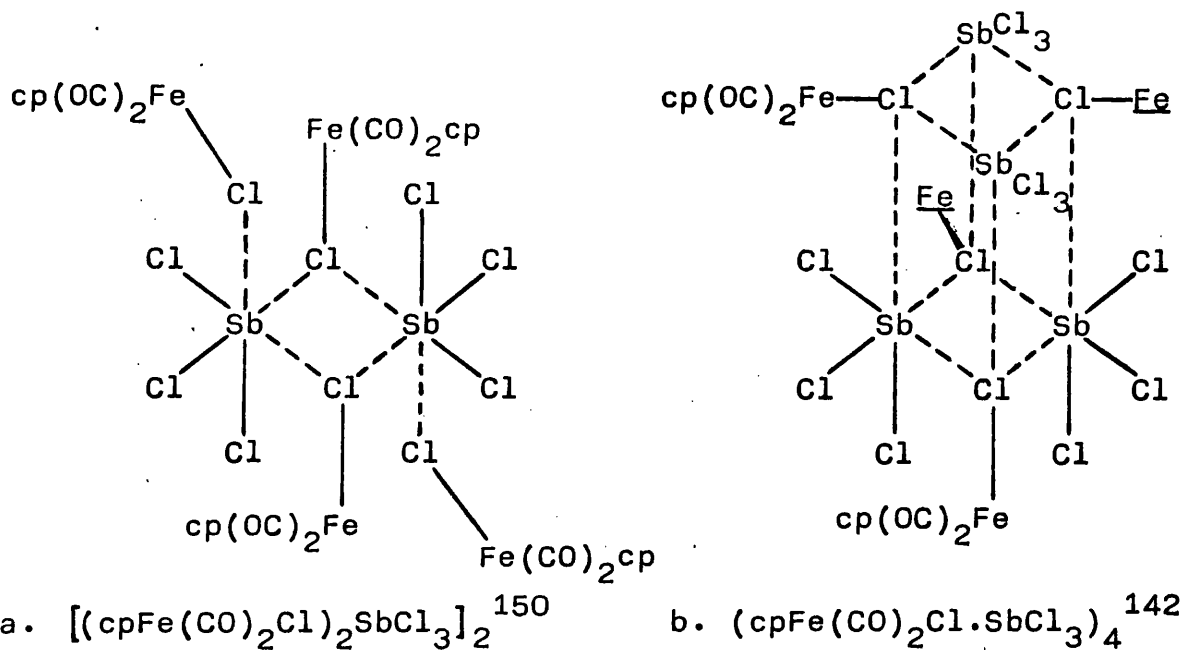
Fig.3.7   Crystal Structures of cpFe(CO)_2Cl-SbCl_3 Complexes

The monomer-favouring $AsBr_3$ system achieves $(AsBr_6)$ co-ordination by a monomeric 3:1 adduct.[141] The above behaviour contrasts with that of the pentafluorides, which prefer to form 1:1 and 1:2 complexes because of the stability of the $(MF_6)^-$ and $(M_2F_{11})^-$ anions and their covalent analogues, unless there happens to be stable dimeric cation such as $(Xe_2F_3)^+$.[65] An $Re_2(CO)_{10}/xsSbF_5$ reaction should produce $Re(CO)_5F \cdot nSbF_5$ complexes (n=1,2), though with only two moles of SbF_5, in an ionising solvent, $[(OC)_5Re-F-Re(CO)_5]^+$ $[SbF_6]^-$ might be formed.

Metal carbonyl halides can therefore act as reasonable donor halides, but only for the fluorides is complex formation of fundamental importance. As little is known about most of these halide complexes, there is considerable scope for exploration in this area. The complexes mostly seem to exhibit single halogen bridges, which is rare in metal carbonyl halides, except in the fluorides where

the formation of single fluorine bridges (e.g. $(Ru(CO)_3F_2)_4$)
is an important factor in carbonyl fluoride stability.[6]

Reactions like (3.43) are very interesting,
because they show that analogues of $Re(CO)_5F \cdot MF_5$ can be
produced under orthodox halogenation conditions, though a
crystal structure of $(Re(CO)_5Cl)_2 \cdot SbCl_5$ is required to
establish its true formulation. It is just possible that
a 1:1 complex $Re(CO)_5Cl \cdot ReCl_5$ might be formed by the analog-
ous reaction of $Re_2(CO)_{10}$ with $ReCl_5$ in CH_2Cl_2, and even
more likely by $Re(CO)_5Cl/ReCl_5/CH_2Cl_2$.

3-5.4 Carbonyl and Dinitrogen Bridged Donor-Acceptor Complexes

Donor-acceptor complexes where the bridging made
is via the carbonyl group are rare, and are restricted to
those with $M-C\equiv O \rightarrow M'$ bridges to very electropositive sites
such as: aluminium trialkyls AlR_3 (e.g.$[cpFe(CO)(COAlMe_3)]_2$,[151]
$(Ph_3P)_2Re(CO)_2(COAlMe_3)Cl$[152]), metal pyridyls[153] and lanthan-
ide η^5-cyclopentadienyls.[154] Interesting analogues are the
Friedel-Crafts acylation intermediates $R.C(O)X \cdot MX_n$. (R=organic,
MX_n = $AlCl_4$,SbF_6, etc.), formed by the addition of the
appropriate acyl halide to a Lewis acid. Both covalent
and ionic forms are possible. Both occur in the p-toluyl
chloride-$SbCl_5$ complex (fig.3.8a.).[155]
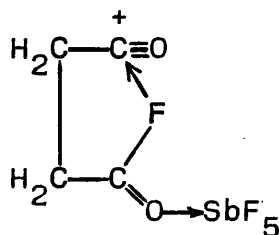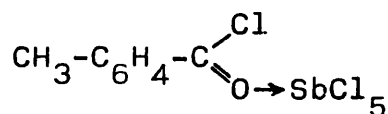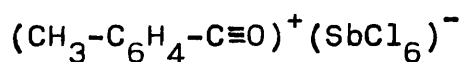
Fig.3.8a.[155]   Fig.3.8b.[158]
Covalent and Ionic Forms of Acyl Halide-SbX_5 Complexes

The fluorides all adopt the ionic form[156] (e.g. $CH_3CO^+SbF_6^-$ [157]), with the exception of the succinyl fluoride.$2SbF_5$ complex, where one SbF_5 group is bound by a $-C=O-SbF_5$ linkage because of cyclisation (fig.3.8b).[158]

C=O....M bridging interactions have also been proposed to account for the N.M.R. spectra of mixtures of COF_2 and $COClF$ with SbF_5 or AsF_5 in SO_2ClF solution, e.g. $F_2C=O$ SbF_5.[159]

Metal dinitrogenyl halides can also form complexes with acceptor molcules, but in marked contrast to carbonyl halides, bridging is exclusively via the dinitrogen group, rather than the halide, in all complexes so far characterised. Thus the $Re(CO)_5Cl$ analogue $(Me_2PhP)_4Re(N_2)Cl$ forms a large range of complex with acceptor halides via linear Re-N≡N-M bridges, but $(Me_2PhP)_4Re(CO)Cl$ forms almost none.[102] Crystal structures have been performed of the 1:1 and 1:2 complexes $ClP_4Re-N≡N-MoCl_4(OMe)$[160] and $ClP_4Re-NN-MoCl_4-NN-ReP_4Cl$,[161] ($P=PMe_2Ph$). The latter has both molecules of $P_4Re(N_2)Cl$ acting as donors, in the same sense as $(Re(CO)_5Cl)_2SbCl_5$,[140] but in contrast to complexes which have a "dimeric" cation e.g. $(I(Fe(CO)_2cp)_2)^+(BF_4)^-$,[102] $(N_2(Fe(dmpe)cp)_2)^{2+}(BF_4^-)_2$,[162] (dmpe = 1,2-bis(dimethyl-phosphino)ethane). $TiCl_4$ forms a similar 2:1 complex, for which there is also a carbonyl analogue $(ClP_4Re-C≡O-)_2TiCl_4$.[163] Excesses of the tetrachlorides $TiCl_4$ or $MoCl_4L_2$ ($L=Et_2O$, thf, $PMePh_2$) give incompletely characterised 1:2 dinitrogen complexes of probably formula $ClP_4Re-N_2-M_2OCl_5L'$ (M-Ti, $L'=Cl$[163]; M=Mo, $L'=L$[102]) in which the two acceptor molecules may either be bound in a chain $Re-NN-MX_n-MX_m$, or both to the same nitrogen

atom Re-N≡N$\underset{MX_m}{\overset{MX_n}{<}}$. The carbonyl analogue is, however, oxidised

to $P_3Re(CO)Cl_3$.[102,163]

Thus a considerable variety of dinitrogen-bridged

[rhenium(I)-transition metal](III),(IV) or (V) complexes

can be formed. Amongst these there is evidence for a

homometallic complex $Cl(Me_2PhP)_4Re^I$-NN-$Re^V(PPh_3)OCl_3$,[102,164]

an interesting relative of $(OC)_5Re^I$-F-$Re^V F_5$. Only two fluoro

complexes have been reported, of probable formula

ClP_4Re-NN-MF_5 (M=P,Ta).[102] It would be interesting to see

if $P_4Re(N_2)F$ could be prepared, and if this would prefer to

bridge to TaF_5 via the fluorine atom: $P_4(N_2)Re$-F-TaF_5.

There is also a large range of metal-metal bonded

carbonyl halide complexes but these are beyond the scope of

this review. It is interesting to note that BF_3[165] and SbF_3[166]

complexes of $(Ph_3P)_2Ir(CO)Cl$ are probably Ir-M bound, not

Ir-Cl-MF_3 bonded.

3-6. η^5-CYCLOPENTADIENYL IRON DICARBONYL FLUORIDE

It has been demonstrated in the preceding sections
that carbonyl fluoride formation is only expected within a
fairly limited range of compounds. It should be possible
to extend this range to other metals (e.g. first-row trans-
ition metals) and to other formulations, by allowing the
substitution of some of the carbonyl groups by suitable
electron-withdrawing ligands, (e.g. tertiary phosphines,
η^5-cyclopentadienyl), capable of stabilising a metal-fluorine
bond by giving the metal a greater effective positive charge.
For example, the compound $(Ph_3P)_2Ir(CO)F$ is well-established,[127]
but the "parent" $Ir(CO)_3F$ is as yet unknown.

A η^5-cyclopentadienylchromium dinitrosyl fluoride,
$cpCr^o(NO)_2F$, had been known since 1954,[130] but despite the
similarity between the halides $cpCr(NO)_2X$ (X=Cl,Br,I) and
the isoelectronic iron dicarbonyl series $cpFe(CO)_2X$,[167] the
corresponding iron fluoride, $cpFe(CO)_2F$, had not been isolated.
The well-established analogy between these two d^6 series
and the manganese-triad pentacarbonyl halides made it part-
icularly interesting to attempt to prepare this compound, not
only as a first-row carbonyl fluoride, but also as an analogue
of $Re(CO)_5F$.

$cpCr(NO)_2F$ was prepared by displacement of the
solvent molecule from $[cpCr(NO)_2(OH_2)]^+(NO_3)^-$ by fluoride
ion, and extracting the covalent complex into chloroform,
(c.f. section 3-5.2). However an attempt by Meyer et alia[168]
to displace acetone from $[cpFe(CO)_2(OCMe_2)]^+$ (prepared in
solution by the oxidation $(cpFe(CO)_2)_2/Fe(ClO_4)_3/acetone$)
with sodium fluoride in methanol merely regenerated the parent

carbonyl, though the other halides and even the nitrate were
synthesised by this route. The reasons for the failure were
the lack of a suitable driving force, and possibly the use of
a hydroxylic solvent.

In a later study,[77] Williams and Lalor prepared
various derivatives in a single step, by using the approp-
riate silver salt as both oxidant and nucleophile, where
these were soluble in acetone, e.g.

$$(cpFe(CO)_2)_2 + 2AgNO_3 \xrightarrow{\text{Me}_2\text{CO}} 2\ cpFe(CO)_2(ONO_2) + 2\ Ag \quad (3.46).$$
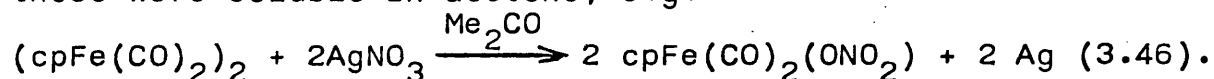
Here the driving force is the precipitation of silver.

Despite the fairly low solubility of AgF in
acetone, this method proved successful in preparing $cpFe(CO)_2F$
in the present study (see section 2-5.2). Difficulties
experienced in extracting the compound, because of its tendency
to decompose in solution, meant that the yield obtained
was low, but it should be possible to improve this with a
more rapid work-up. The decomposition probably occurs by
the substitution of an organic ligand, R:

$$cpFe(CO)_2F + R\text{-}H \longrightarrow cpFe(CO)_2R + HF \qquad (3.47).$$
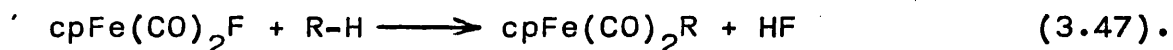
The metal-fluorine bond in $(Ph_3P)_2Ir(CO)F$ is also very labile.[37]
An AgF suspension in thf has recently effected a low-yield
oxidation of $(Cr_2(CO)_{10})^{2-}$ to $(Cr(CO)_5F)^-$.[8]

Because of the ready solubility of both AgF and
$(cpFe(CO)_2)_2$,[66] anhydrous HF may be a better medium for
preparing $cpFe(CO)_2F$. Other possible methods include
$cpFe(CO)_2Cl/AgF/L$, where L= acetone, thf, SO_2 or HF, or a
solvent elimination method with a suitable driving force,
e.g. $(cpFe(CO)_2L)^+(ClO_4^-)^-/AgF/L$. XeF_2 is probably too
vigorous an oxidant to be used here.

By analogy with the behaviour of $cpFe(CO)_2Cl$ in

liquid HCl,[67] HF solutions of $cpFe(CO)_2F$ should contain the cation $(cp(OC)_2Fe-F-Fe(CO)_2cp)^+$, which might be precipitated by adding a non-co-ordinating anion, e.g. $AgBF_4$. This, however, may give rise to a complication not found in the analogous pentacarbonyl manganese and rhenium(I) systems (where $XM_2(CO)_{10}^+$ ions have not been observed), in attempts to prepare $cpFe(CO)_2F \cdot M'F_5$ complexes. Addition of half a mole of AsF_5 to $cpFe(CO)_2F$ may produce $(F(Fe(CO)_2cp)_2)^+(AsF_6)^-$ instead of $cpFe(CO)_2F \cdot AsF_5$. To prepare the covalent type of complex, other methods may be required, such as $cpFe(CO)_2Br/$ $AgAsF_6/SO_2$ (after Mews[43]) or $(cpFe(CO)_2)_2/2AgAsF_6/acetone$ (after Lalor[77]), both followed by pumping out the solvent molecule L from the $(cpFe(CO)_2L)^+(AsF_6)^-$ complex.

$cpFe(CO)_2F$ is the first η^5-cyclopentadienyl carbonyl fluoride, but many others should be preparable, including the ruthenium and osmium analogues, and group VIB derivatives $cpM(CO)_3F$.

3-7. SUGGESTIONS FOR FURTHER WORK ON THE RHENIUM SYSTEM

One of the aims of this work was to achieve an understanding in some depth of one carbonyl fluoride system, (rhenium), on which to base future studies of the other transition metals' systems. Having achieved this, it is clear that there is enormous scope for further exploring the carbonyl fluoride chemistry of rhenium itself, let alone the other metals. This section summarises some suggested future work on the rhenium system.

$Re_2(CO)_{10}/XeF_2/HF$ System

In order to clarify uncertain features about this system (see section 3-1.4), three reactions in particular should be checked:- $Re_2(CO)_{10}/1.XeF_2$, $Re_2(CO)_{10}/3.XeF_2$ and $Re(CO)_5F/1.XeF_2$, to establish the conditions under which $Re(CO)_5F$, $Re(CO)_5F.ReF_5$ or $(Re(CO)_6)^+(ReF_6)^-$ are formed, and confirm the true identity of "$Re(CO)_3F_3$".

$Re(CO)_5F$ Preparations

New preparative routes for $Re(CO)_5F$ are required, to check O'Donnell's data, and obtain more detailed information (Raman, ^{19}F N.M.R., Re-F bond length, etc). The following are suggested: $Re(CO)_5Cl/AgF/SO_2./acetone$ or/thf, $Re(CO)_5Cl/TlF/HF$, $Re_2(CO)_{10}/2AgF/acetone$ or /thf (under ultra-violet irradiation), and also the precipitation of insoluble KMF_6 salts by adding KF to $Re(CO)_5F.ReF_5/HF$ or $Re(CO)_5(SO_2)^+$ $(AsF_6)^-/SO_2$ solutions, to leave $Re(CO)_5F$ in solution.

$Re(CO)_5F.MF_5$ Complexes

Covalent complexes $Re(CO)_5F.nReF_5$ (n=1,2) should be prepared by $Re(CO)_5F/ReF_5/HF$, and also CO bubbled through

their HF solutions to prepare the ionic salts $(Re(CO)_6)^+$

$(Re_nF_{5n+1})^-$. A crystal structure of $Re(CO)_5F \cdot 2ReF_5$ (and of

$Re(CO)_5F$) would provide an interesting comparison of the

bonding in these complexes.

The exchange/addition properties of other penta-

fluorides with $Re(CO)_5F \cdot ReF_5$ should be further explored, and

new $Re(CO)_5F \cdot MF_5$ and perhaps mixed $Re(CO)_5F \cdot MF_5 \cdot M'F_5$

complexes should be prepared by $Re(CO)_5F/MF_5/HF$ methods.

Also reactions of $Re_2(CO)_{10}/HF$ with MoF_6, TcF_6 and OsF_6 and

of $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ with ReF_6 and TcF_6, should be

examined for new $M(CO)_5F \cdot M'F_5$ complexes, especially

$Re_2(CO)_{10}/MoF_6/HF$ and $Mn_2(CO)_{10}/ReF_6/HF$.

By analogy with $Re_2(CO)_{10}/SbCl_5$, the $Re_2(CO)_{10}/SbF_5$

reaction should be studied, in a suitable solvent (Genetron

113, CH_2Cl_2 ?, HF, SO_2ClF, etc.).

Miscellaneous Reactions

Preparations of possible $(Re(CO)_4F)_n$, $(Re(CO)_4F \cdot ReF_5)_n$,

and $(Re(CO)_4F_2)^-$ species should be attempted by halogen exchange

with $(Re(CO)_4Cl)_2$, followed by addition of the ReF_5, F^-, etc.

Crystal structures may be required to show the extent of poly-

merisation. The carbonylation of ReF_5 or ReF_6 needs a proper

investigation. Finally some chemistry of $Re(CO)_5F \cdot ReF_5$ should

be examined, to explore a). its potential as a co-ordinator of

small molecules to give $(Re(CO)_5L)^+(ReF_6)^-$ species (e.g. $L=N_2$,

NO, CO_2, "CS", $(C\equiv CH)^-$), and b). any unusual phenomena assoc-

iated with the close proximity of two co-ordination sites $(Re^I$

and Re^V) of widely different character and oxidation states,

e.g. reactions with olefins and fluoro-olefins, with a view to

assessing the possible catalytic activity of these sort of

complexes.

CHAPTER   4

EXPERIMENTAL SECTION

4-1.   GENERAL TECHNIQUES

4-1.1   Vacuum Systems

Because of the air sensitivity of most of the fluorine-containing reactants and products used in this work, reactions were carried out in high vacuum systems, (1×10^{-4} torr, or better), with the exception of the $cpFe(CO)_2F$ and SbF_5 preparations, which were performed under dry nitrogen. Glass systems were baked out under vacuum, and the metal systems, and metal, glass and fluoroplastic equipment attached to them, were pre-treated with 300 torr of ClF_3 or elemental fluorine for about 15 minutes, to remove the last traces of moisture and other impurities.

An all-Pyrex glass system was used for the reactions in Genetron 113, see section 4-4.1 and fig.4.2. The number of valves and joints was minimised, to reduce possible sources of leaks. "Quickfit" joints and valves, lubricated with Voltalef-90 Kel-F grease or Apiezon M, were generally employed. In regions where attack on the grease was likely, greaseless "Rotaflo" valves with PTFE stems, and Young's O-ring joints (with "Viton" O-rings) were used. Checks for leaks were made with a high frequency coil.

Manipulations involving HF or ReF_6 were carried out in metal and fluoroplastic systems. The basic metal manifold was made up of "316" stainless steel needle valves, crosses, tees and elbows (supplied by Autoclave Engineers, Erie, Pennsylvania, U.S.A.), and argon-arc welded nickel U-traps, connected by ⅜"o.d., ⅛"i.d. nickel 200 tubing, see fig.4.3. A separate single-stage rotary pump, fitted with a soda-lime trap to absorb volatile fluorides, F_2 and

HF, was used to evacuate large quantities of volatiles from the manifold. The manifold also included facilities for the direct introduction of F_2, H_2 or Ar. Fluorine for seasoning and ReF_6 were handled in detachable, welded, nickel cans, fitted with stainless steel valves.

Translucent Kel-F (polytrichlorotrifluoroethylene), and occasionally Teflon F.E.P. (fluorinated ethylene-propylene, a $C_2F_4-C_3F_6$ co-polymer) equipment was attached to the manifold by adaptors consisting of brass or copper connections, hard silver-soldered to standard nickel tubing. Kel-F apparatus was connected by ¼" o.d. Kel-F tubing (Pampus Fluoroplast Ltd., Stoke-on-Trent). Kel-F valves, based on a design developed at Argonne National Laboratory, Chicago, U.S.A., were fabricated from Kel-F blocks (Pampus). Kel-F reaction vessels were of three types: ¾" o.d. moulded tubes of approximately 28ml. volume, purchased from Argonne Laboratory, and 3/16" N.M.R. and ¼" tubes, made by sealing a length of the appropriate tubing, and flaring the opposite end to fit the 45° taper of the nipples of the Kel-F valves and N.M.R. adaptors. Kel-F adaptors were constructed to attach the ¾" tubes to the valves. Seals were made by accurate compression-fittings, secured by backing nuts. Checks for leaks were made using a helium leak-detector.

4-1.2 Handling the Products

Solid products with the exception of $cpFe(CO)_2F$ were handled in nitrogen-filled dry boxes. Initially a non-regenerable, non-recirculating box, with P_2O_5 as a dessicant, was used, but this was found unsatisfactory for handling $Re(CO)_5F.ReF_5$. Subsequent work was in a closed-

system, auto-recirculating box with regenerable, on line,

molecular sieves and MnO columns, for water and oxygen

removal, respectively (Lintott Engineering Ltd., Horsham,

Sussex; mark 11). The box was used at moisture levels

between 30 and 1 p.p.m. Static problems were minimised by

exposing samples and tubes to a 2 millicurie ^{204}Tl β-emitter

(Radiochemical Centre, Amersham). Weighings in the box

were made on an Oertling two-pan balance, reliable to ±1mg.

under optimum box conditions, with the pumps temporarily

turned off. Accurate weighings (±0.1mg.) of all reactants

and products were made by difference, on a Stanton Unimatic

CL41 single-pan balance, outside the box.

4-2. ANALYSES AND PHYSICAL MEASUREMENTS

4-2.1 Elemental Analysis

Elemental microanalyses for carbon and fluorine

were performed by Beller Mikroanalytisches Laboratorium,

34 Göttingen, Theatrestrasse 23, and Pascher Mikroanalytisches

Laboratorium, 53 Bonn, Buschstrasse 54, West Germany.

Samples were loaded in the dry box into seasoned 13mm. o.d.

glass ampoules fitted with valves, and sealed under vacuum.

A single determination for rhenium was carried out

by a modification of the published Re_2S_7 procedure.[169]

About 50 mg. of sample was converted to the perrhenate by

heating with a mixture of aqueous NaOH and 30 volume H_2O_2

in a platinum crucible. After prolonged boiling and further

additions of H_2O_2,[38] an insoluble, flocculent white precipitate

dissolved on adding a little 1:1 HCl. Rhenium was then pre-

cipitated as nitron perrhenate as described,[169] after having

made the colourless final solution up to 50mls., and
adjusted to pH 6 with NaOH solution. 97.0mg. of nitron
perrhenate were obtained, equivalent to a rhenium content
of 62.9(5)%, c.f. $Re(CO)_5F.ReF_5$ calc. 59.5%.

4-2.2 X-Ray Powder Diffraction

        Powder samples for X-ray work were ground in the
dry-box, and loaded into pre-seasoned glass capillaries,
which were then re-evacuated. Samples were sealed using a
micro-torch. Photographs were taken using a Philips 11.64cm.
diameter camera with Ni-filtered Cu-Kα radiation, using
exposures between 4 and 12 hours. Photographs were measured
on a cold light box fitted with a rule and vernier scale.

4-2.3 Vibrational Spectra

        Infrared spectra were obtained using a Perkin-Elmer
225 Grating Spectrophotometer, and a Hilger-Watts Infragraph
H1200, and KBr and AgCl windows (4000-400 cm^{-1}) or polythene
discs (400-200 cm^{-1}). Solid samples were prepared in the
dry box by sprinkling finely-ground solid on to the windows,
or in the form of mulls with sodium-dried Nujol (stored in
the box). Gas phase spectra were performed in evacuable all-
glass or copper cells of 10 cm path length, fitted with valves,
and side arms.

        Raman spectra were obtained on Coderg PH1 and T800
instruments, using 50mW 5370Å He/Ne (red) and 250mW 4880Å
Ar^+ (blue) lasers (Coherent Radiation Laboratories) as the
excitation sources. Solid samples were contained in glass
X-ray capillaries or ampoules, prepared as above. Solution
spectra were obtained on concentrated solutions in Kel-F or

F.E.P. tubes. Low temperature solution spectra were
obtained by passing a current of cold, dry nitrogen, boiled
out of a liquid nitrogen Dewar vessel, up past the $\frac{3}{16}$"
Kel-F N.M.R. tube containing the sample. Temperatures down
to -80°C and below were easily obtained, measured using a
thermocouple and Comark thermometer, and adjusted by controlling
the rate of gas flow.

4-2.4   Magnetic Resonance

        N.M.R. and E.S.R. spectra were carried out in $\frac{3}{16}$"o.d.
Kel-F tubes attached to Kel-F values, or standard glass tubes.
Varian T60 (^{1}H,60MHz.), Varian DA60 (^{1}H,60MHz.; ^{19}F,56.4MHz.)
and JEOL 100 (^{1}H,100MHz.; ^{19}F,94.1MHz.) N.M.R. instruments
were used. E.S.R. spectra were obtained by Dr.J.B.Raynor on
a Varian E.3 machine.

4-2.5   Mass Spectra

        Mass spectra were obtained on an A.E.I. MS9 spectro-
meter operating at 70eV ionisation potential. Volatiles

Fig 4.1 Insertion of Air-Sensitive Solids into the Mass
                                        Spectrometer
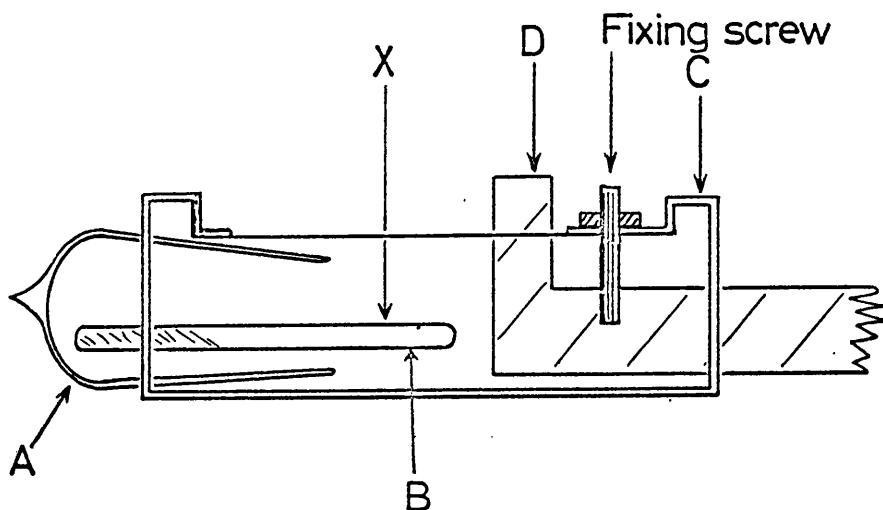
were introduced from glass bulbs through the standard inlet

system, air-sensitive solids via the solids probe of the

instrument. An X-ray capillary B, containing the solid

sample (fig.4.1),   rested in a glass jacket A, which was

wedged inside a copper adaptor C on the end of the probe D.

The outer tip of the capillary was broken at X, while sprayed

with a jet of helium, and the probe inserted immediately

into the spectrometer. This minimised the amount of moisture

admitted to the sample and prevented solid falling out of

the sample tube.

4-2.6 Melting Point

        Melting points were obtained on X-ray capillary

samples on a Reichert microheating stage.

4-3. STARTING MATERIALS AND SOLVENTS

4-3.1 Available Materials

        Standard chemicals were obtained as follows, and

used without further purification, except where specified.

        Re metal: Johnson Matthey Metals Ltd.; $Re_2(CO)_{10}$

and $Mn_2(CO)_{10}$*: Strem Chemicals Inc. (*stored at $-20^{o}C$, in

the dark); $(cpFe(CO)_2)_2$: Alfa Inorganics.

        Genetron 113 (1,1,2-trichlorotrifluoroethane):

Fluka AG (stored over P_2O_5; degassed over fresh P_2O_5 prior

to use); acetone$^+$ and methanol for the $cpFe(CO)_2F$ preparation:

B.D.H. "AnalaR" grade, ($^+$ acetone for attempted solution

studies on $Re(CO)_5F.ReF_5$ was dried via the NaI adduct.[46]).

        Diethyl ether,$^{\neq}$ benzene,$^{\neq}$ $(60-80^{o})$ petroleum ether,

nitromethane, dichloromethane, chloroform and carbon tetra-

chloride: May and Baker Ltd. ($\neq$ stored over sodium wire);
acetonitrile: Fisons Ltd.; trichlorofluoromethane: B.D.H. Ltd.

Aqueous HF (40%): Hopkin and Williams Ltd. Anhydrous
HF: supplied in steel cylinders by I.C.I. Ltd. and by
Imperial Smelting Ltd. The quality varied considerably from
cylinder to cylinder, the former giving generally lower
moisture and impurity levels. The HF was purified by trap-
to-trap distillation, discarding the first and last fractions
each time, followed by two fluorinations at about $100^{\circ}C$ and
950 torr, in a 1 litre nickel can. The purified HF was
stored in pre-seasoned Kel-F tubes.

Argon and nitrogen (high purity "white spot" grade):
British Oxygen Ltd. Fluorine for seasoning and for preparing
ReF_6 was supplied by the Matheson Co. Ltd., in steel cylinders,
which were connected to the metal vacuum manifold.

Xenon difluoride was prepared by Miss G.M. Warren
by the method of Holloway,[170] and stored at $-20^{\circ}C$ in weighed
breakseal ampoules. Tantalum pentafluoride was prepared by
Mr. J. Fawcett from the elements, in a flow system.

4-3.2 Preparation of Starting Materials

Rhenium hexafluoride was prepared from the elements
in 1.5 and 5g. quantities by the method of Malm and Selig,[171]
and stored in a seasoned 75ml. nickel can. Its purity was
checked by its gas phase infrared spectrum.

Antimony pentafluoride was prepared in a flow system,
attached to the fluorine generator. After flushing with
nitrogen, a 1:1 fluorine:nitrogen mixture (cell at 4 amps)
was passed over 24g. Sb metal in nickel boats in a 30cms.
long, 1.6cm. o.d. silica tube with a 20° downward slope.

Heat was required to initiate the reaction. Thereafter the heat
of reaction maintained a constant flow of SbF_5 into a Pyrex
U-trap, fitted with a breakseal, cooled to $-183^{\circ}C$. The lower
end of the reactor required periodic heating to clear solid
deposits of Sb^{III}/Sb^{V} fluorocomplexes (such as $Sb_{11}F_{43}$[172,173]).
Moisture was excluded from the system by a $-183^{\circ}C$ trap before
the reactor, and a $-80^{\circ}C$ trap and conc. H_2SO_4 bubbler after
the U-trap. The excess of fluorine was vented to the fume
cupboard. Reaction was complete after 7 hours. The U-trap was
sealed off, and the SbF_5 purified from white and yellow
involatile solid by-products by trap-to-trap distillation
under dynamic vacuum, in a flamed-out Pyrex system. The
purified material was stored in breakseal ampoules.

        Silver(I) fluoride was prepared be the procedure
described by Kemmitt,[174] from a slight excess of aqueous
HF (40%) and freshly prepared silver carbonate, but in a
polythene beaker. Adherence to the recommended quality of
reagents, and the proportions of 5g. Ag_2CO_3 : 10ml. "AnalaR"
methanol : 300ml. sodium-dried ether, was important to
prevent moisture contamination affecting the AgF precipitation.

        $Re(CO)_5Cl$ was prepared by passing chlorine gas through
a benzene solution of $Re(CO)_5I$ (supplied by Drs. S. Fieldhouse
and N. Forbes), followed by recrystallisation from hot
benzene.[175]

4-4.   CARBONYL FLUORIDE PREPARATIONS AND REACTIONS

4-4.1   The $Re_2(CO)_{10}$/XeF$_2$/Genetron 113 Reactions

        The apparatus (fig.4.2 and plates 4.1 and 4.2) was
evacuated overnight, with the XeF_2 breakseal ampoules G

W   Ball joints
X   Sinter
Y   Penning vacuum gauge
Z   Buderberg pressure gauge
✫   O-ring joints ; other joints
     are mostly 'Quickfit' B14.

Plate 4.1

General View of the Apparatus for

$Re_2(CO)_{10}$/XeF_2/Genetron 113 Reactions
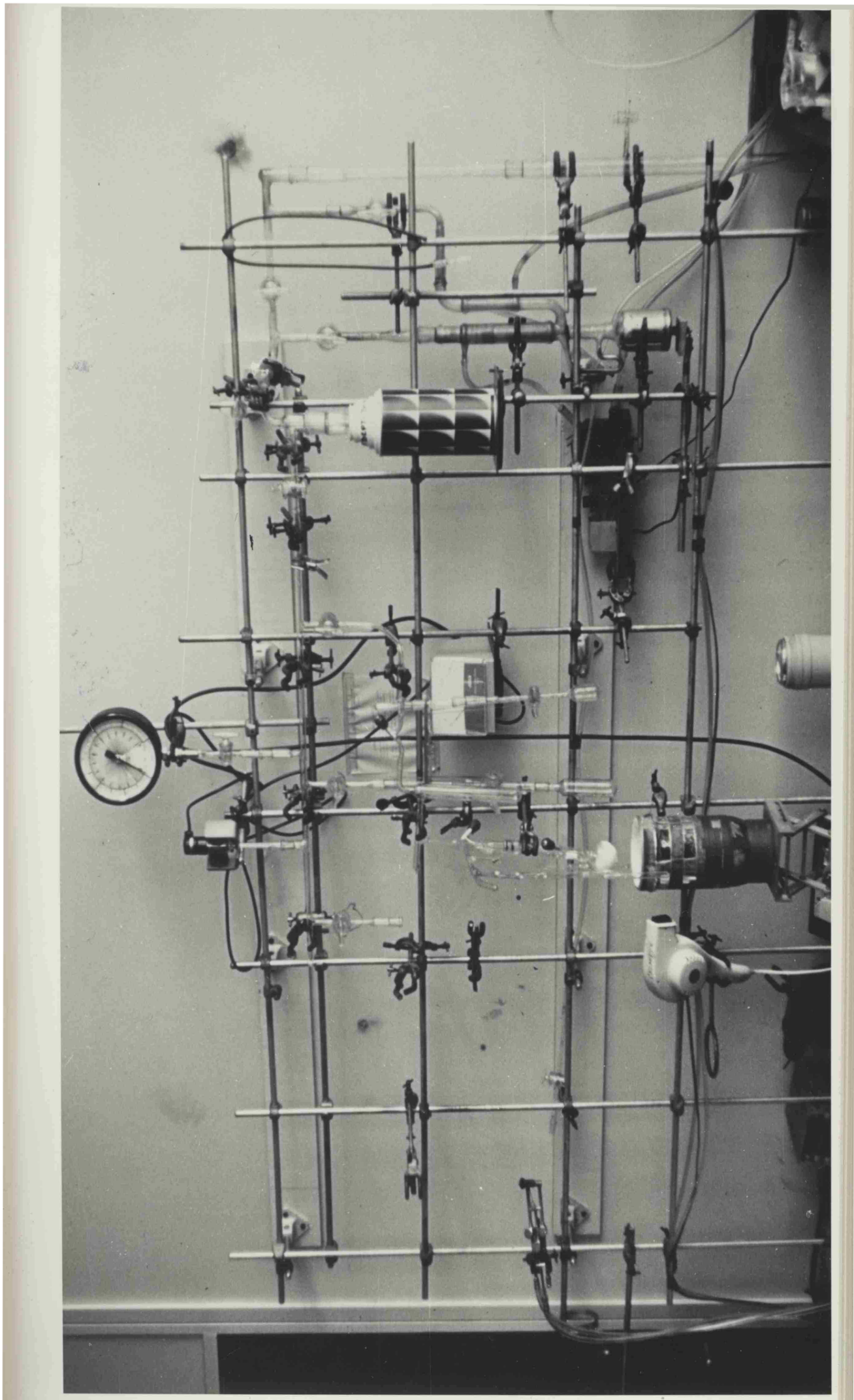
Plate 4.2

An $Re_2(CO)_{10}$/3XeF$_2$/Genetron 113 Reaction

Nearing Completion
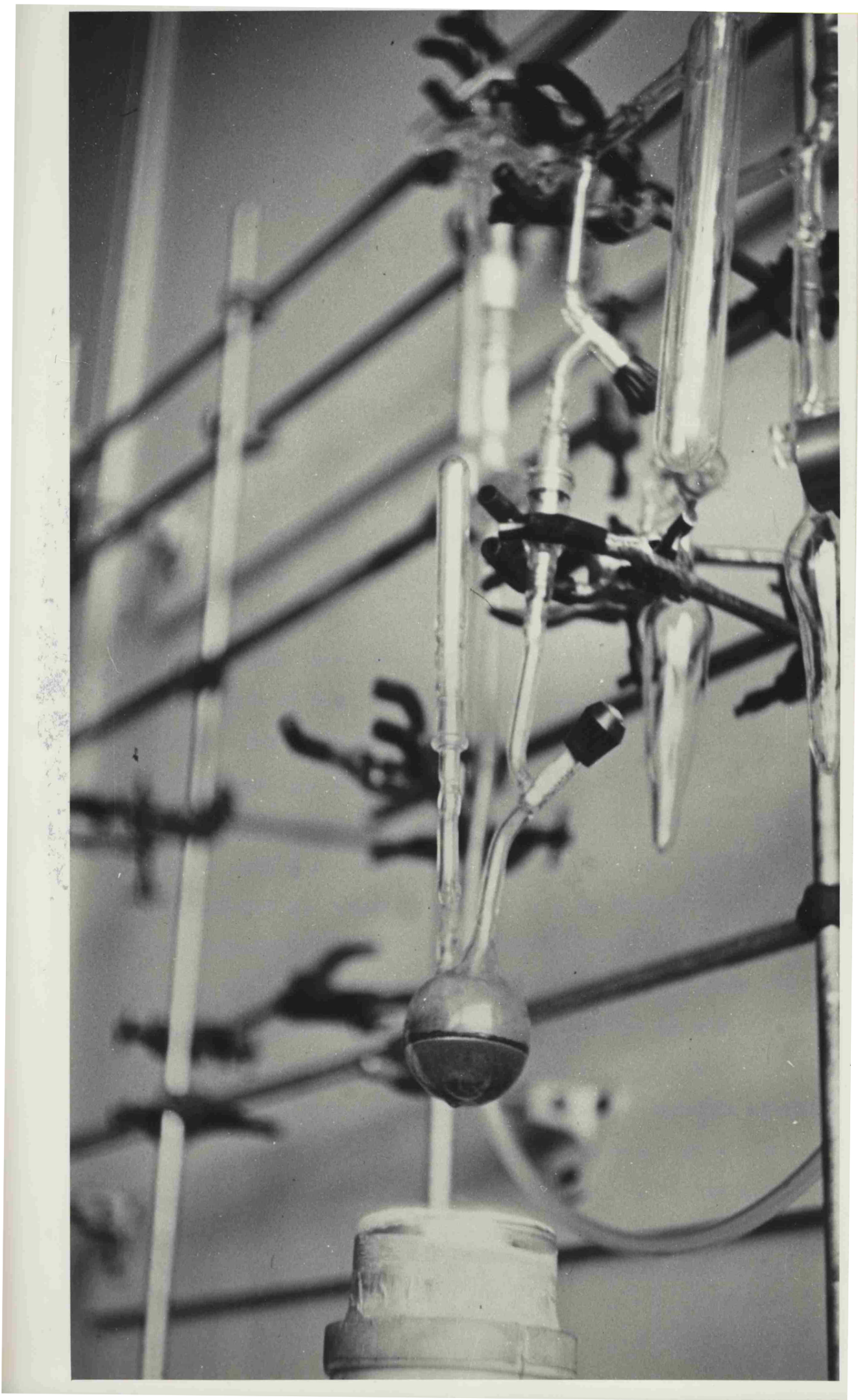
cooled in acetone/CO_2, and then flamed out at least three

times. Valve 1 was closed, and P_2O_5-dried nitrogen admitted

at K. The XeF_2 ampoules were removed at F, with nitrogen

blowing through the apparatus, and both outlets plugged with

B14 stoppers. Valve 5 was closed, and the 100ml. volume

reactor E was removed at C. The required amount (0.2 to

0.5g.) of $Re_2(CO)_{10}$, was weighed in accurately via the delivery

tube. The weight was calculated according to the known weight

of XeF_2 in the ampoule(s), to give a 15% excess of XeF_2 over

the required proportions, to allow for XeF_2 decomposition

on standing or on transference. The reactor was replaced

on the line, valve 5 re-opened, the stoppers removed from

the reactor and the XeF_2 "bank", and the latter replaced at

F. The stream of nitrogen was now stopped by closing valve

7, and the apparatus pumped to a high vacuum for an hour.

In a similar fashion (though with valve 4 closed),

the 20cm. long solvent tube was removed at J, half-filled

with Genetron 113 (20-30ml.) with 2cm. of P_2O_5 at the

bottom, and replaced. Valve 7 was closed, the solvent tube

cooled to $-196^{\circ}C$ and the whole apparatus pumped. The Genetron

was "degassed" to remove dissolved air, by warming to room

temperature with valves 1 and 4 closed, recooling to $-196^{\circ}C$

and pumping. This process was repeated twice, and then the

reactor was cooled to $-196^{\circ}C$, and the Genetron warmed towards

$0^{\circ}C$ to distill it carefully across with valve 1 closed.

The sinter at X prevented solid P_2O_5 entering the main system.

The solvent tube section was sealed off at H. The

XeF_2 breakseal(s) were broken, and the XeF_2 distilled into

the reactor (at $-196^{\circ}C$) under dynamic vacuum. The XeF_2 bank

was then sealed below F, and the fragment from the reactor

weighed.

Valve 1 was closed off and the reactor allowed to warm towards room temperature. The XeF_2 dissolved as soon as the Genetron melted (~-70°C), but the $Re_2(CO)_{10}$ remained as a white solid at the bottom. Reactions began at or just below room temperature, with vigorous gas evolution and the formation of flocculent, yellow solid at the liquid surface. With larger proportions of XeF_2, judicious cooling with a liquid nitrogen bath was used to moderate the reaction, whose progress was monitored by the pressure increase on the gauge. The reactions were generally complete in 20 minutes, forming an insoluble yellow solid below a pale yellow solution. The volatiles were sampled via ports K and L for infrared and mass spectra (the cell and bulb were previously well pumped out), and the remainder carefully pumped away, cooling the auxilliary trap B to -196°C to trap the solvent and other condensibles. The reactor was pumped to dryness for an hour, closed off by valve 5, removed and weighed evacuated. A sample of the powdery, yellow solid was tipped into the capillary D and sealed for an X-ray powder photograph. The reactor was then transferred to the dry-box, to work up the solid products.

This basic procedure was used for all the reactions of this system. The 1:4 reaction was performed in two stages. Three molar equivalents of XeF_2 were added from one ampoule, and allowed to react to completion, before adding the calc- ulated fourth equivalent from a second ampoule. Volatiles were sampled after the second stage. The $Re(CO)_5F \cdot ReF_5$/ SbF_5(1) reaction was performed by first preparing $Re(CO)_5F \cdot ReF_5$ from $Re_2(CO)_{10}$ using 3 molar equivalents of XeF_2 from one

ampoule, removing the Genetron to the <u>waste</u> trap, and adding

the large excess of SbF_5 from the second ampoule. The final

excess of SbF_5 and $ReF_5 \cdot nSbF_5$ was distilled into B, which

was subsequently built into a separate apparatus for analysing

these volatiles.

4-4.2   The $Re_2(CO)_{10}$/XeF_2/HF Reactions

The apparatus for this system, and reactions in

HF generally, is shown in fig.4.3 and plate 5.3, with detail

differences for certain reactions as shown. The apparatus

was initially pumped and seasoned with ClF_3 or F_2. Thereafter

removal or addition of vessels was performed with dry argon

blowing through <u>that part</u> of the system, and open connections

capped while the manipulation was carried out.

Known weights (0.2 to 0.5g.) of $Re_2(CO)_{10}$ (the 1:1

and 1:3 reactions) and $Re(CO)_5F \cdot ReF_5$ (freshly-prepared for

the "1:5" reaction by a 1:3/Genetron reaction) were loaded

into the ¾" Kel-F tube A in the dry-box. For the 1:1

reactions the calculated weight of XeF_2 was distilled under

dynamic vacuum from the weighed glass U-tube C into the ¾"

Kel-F tube B, fitted with a 2-arm head, held at $-196^\circ C$. For

this process, valves 1,4,5 and 7-9 were open, the remainder

closed. C was removed for check weighing(s) until the

required amount had been added. Then, with valves 8-10

closed, tube B was detached from the system above valve 8,

to allow it to be tipped freely as part of the Y-piece

system. For the 1:3 and 1:5 reactions, the XeF_2 was distilled

under static vacuum into a single-arm ¾" tube B', attached

only at P. B' was then removed and mounted on the Y-piece

as shown.

Fig. 4.3 Apparatus for Reactions in HF
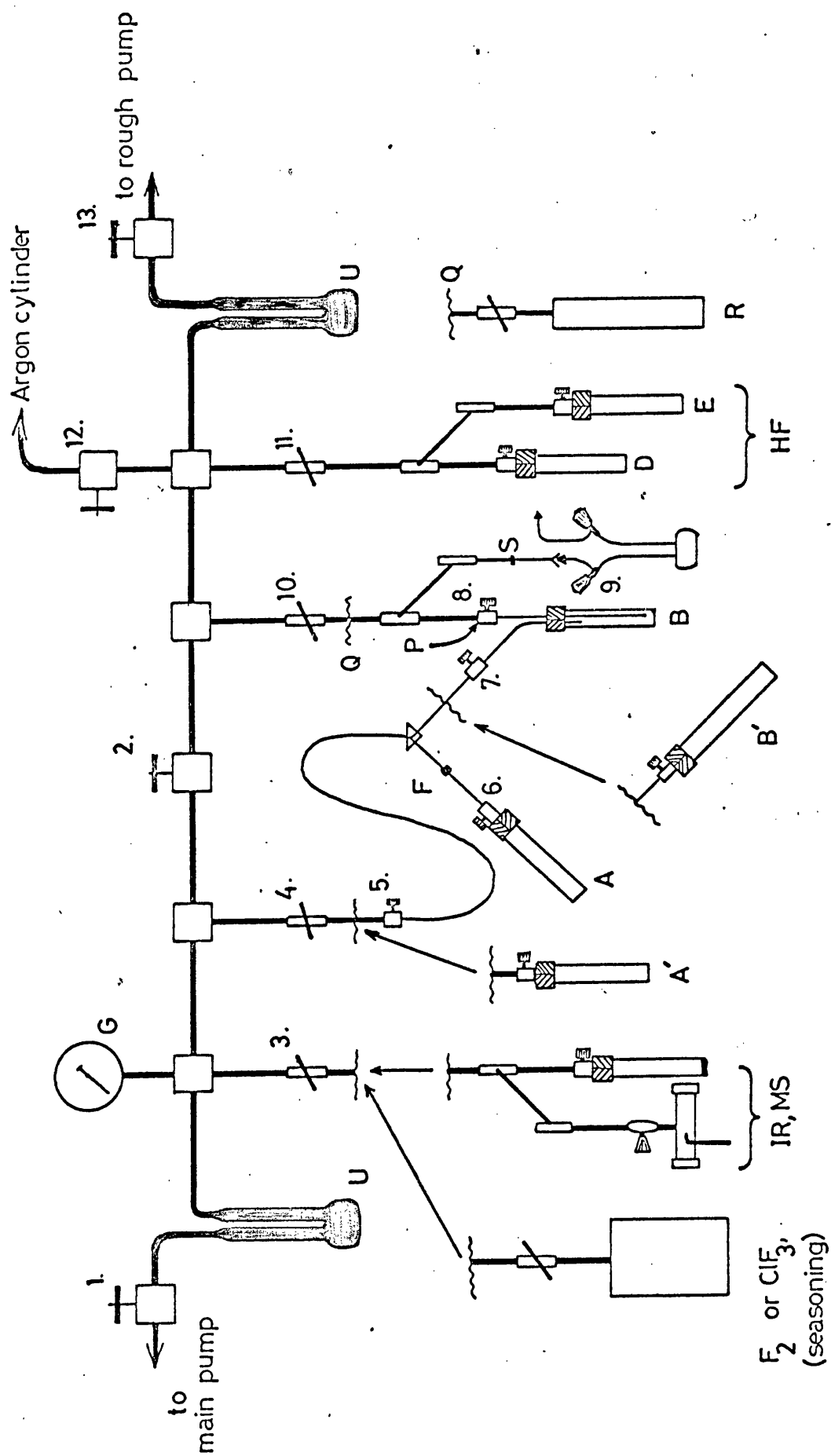
KEY
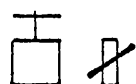
☐ ✗ Stainless steel valves

☐ ☐ Crosses, Tees and Elbows

——— Ni (or Cu) tubing

——— $\frac{1}{4}$″ Kel-F or FEP
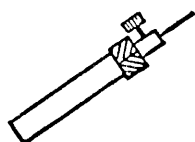
⬙ $\frac{3}{4}$″ Kel-F or FEP tube
+ Kel-F valve
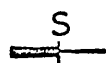
—S— Copper-glass seal

G Monel Pressure Gauge (2 atm.)

U Argon-arc welded Ni U-trap

F PTFE sintered frit

C Glass XeF_2 U-trap

Plate 4.3

General View of the Apparatus for

$Re_2(CO)_{10}$/XeF_2/HF Reactions

XeF₂ STORE

TUBE FOR XeF₂

HF STORE

REACTOR

TO COMMON Pt₃(CO)₆
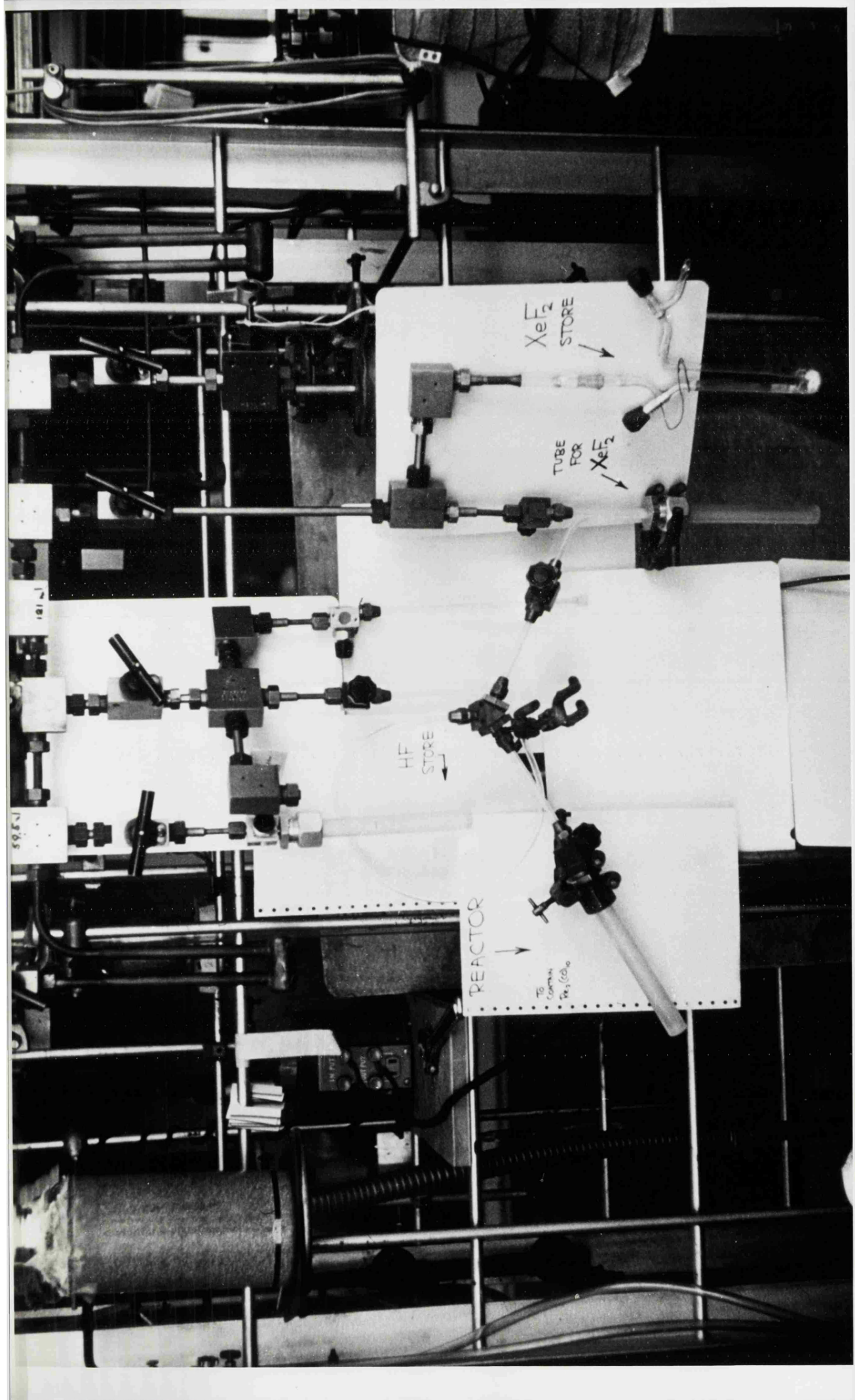
1cm. depth of liquid HF was distilled from the storage vessel D into each tube at -196°C. The tubes were warmed to room temperature with valves 6 and 7 closed, and the colourless XeF_2/HF solution in B tipped on to the $Re_2(CO)_{10}$/HF mixture in A, using the flexibility of the ¼" Kel-F tubing of the Y-piece. Reactions commenced immediately, as described in section 2-2. Once gas evolution had ceased, the volatiles were sampled for infrared and mass spectra, and pumped away (with valves 6 and 7 closed). Tube A was cooled to -196°C (with valves 6 and 7 re-opened) to ensure all the XeF_2 had been transferred out of B, and then warmed to room temperature, refluxed briefly, then allowed to stand for one hour, to ensure completion of reaction.

The 1:1 reaction mixture required filtering through the sinter F into tube B, to remove unreacted $Re_2(CO)_{10}$, and the latter was pumped dry. Tube A was exchanged for a $\frac{3}{16}$" Kel-F N.M.R. tube (and valve), which was then seasoned, and half the solution in B was tipped into this, and concentrated, for N.M.R. and low-temperature Raman studies The remaining solution in tube B was cooled between -60 and -20°C, as required, and evaporated slowly to dryness to attempt to crystallise the soluble product. The HF and condensible volatiles were distilled into the collection tube E. The 1:3 and 1:5 reactions gave only soluble products, and so half the solution in A was tipped into B, and evaporated to dryness as above, and the other half tipped into a seasoned N.M.R. tube put on in place of tube B. The tubes of the final solids were removed, weighed and transferred to the dry-box.

4-4.3   The $Re_2(CO)_{10}$/ReF_6/HF Reactions

A single reactor A' was used for the 1:2 and (initially) 1:3 reactions. The 1:4 reaction was performed with tube A already in position on the Y-piece, with evacuated tube B' on the other limb.

HF was condensed on to a weighed amount of $Re_2(CO)_{10}$ at $-196^{o}C$ to give 2cm. depth when molten. Aliquots of ReF_6, expanded from a 75ml. nickel storage can R attached at Q, were measured by the pressure developed in the 120.0ml. basic vacuum manifold with valves 1,3,4 and 10-13 closed, and condensed into A(A') at $-196^{o}C$, up to the required amount. The reactor was warmed to room temperature, at which point reaction commenced.

The 1:2 reaction was complete in minutes, giving an orange-red solution, which soon precipitated orange, $Re(CO)_5F.ReF_5$ crystals when cooled to $0^{o}C$. These were slowly evaporated to dryness, and the tube removed to the dry-box.

The 1:3 reaction required periodic warming, and standing overnight, to dissolve most of the solid and give a green solution. The formation of $Re(CO)_5F.ReF_5$ is a much faster process than its subsequent conversion to $(Re(CO)_6)^+$ $(Re_2F_{11})^-$. The green solution was filtered from traces of residue into a second tube B', using the Y-piece. Orange and green crystals began to be precipitated on cooling the filtrate to $0^{o}C$. The original tube was pumped dry, and replaced on the Y-piece by a third $\frac{3}{4}$" tube, into which (after pumping and seasoning) the green solution was decanted from tube B'. This final solution was evaporated to dryness, yielding a further crop of predominantly green crystals, with

some orange, and a brown gum. Both tubes were pumped, and

removed to the dry-box.

The 1:4 reaction took 4-5 days to complete, giving

a green solution and copious, golden-yellow crystals. The

solution was filtered into a ¼" Kel-F tube, concentrated

for Raman studies, and finally pumped dry (see section

2-3.3). The yellow crystals were pumped dry and the tube

removed to the dry box.

4-4.4   Other HF System Reactions

β-$(Re(CO)_6)^+(Re_2F_{11})^-$ Recrystallisation from HF

β-$(Re(CO)_6)^+(Re_2F_{11})^-$ was dissolved in 1cm. of HF

in a seasoned ¾" tube, attached to the Y-piece. The green

solution was filtered from undissolved residues into a second

¾" tube, and green crystals of the α-phase were precipitated

on concentrating the filtrate. The original tube was

replaced by a ³⁄₁₆" Kel-F N.M.R. tube, and a sample of the

green solution tipped in for Raman, N.M.R. and E.S.R. studies.

The remaining solution was evaporated to dryness, and the

tube removed to the dry-box.

$(Re(CO)_6)^+(Re_2F_{11})^-$/xsXeF$_2$/HF and $Re(CO)_5F \cdot ReF_5/TaF_5$/HF

The β-$(Re(CO)_6)^+(Re_2F_{11})^-$(0.079g.)/XeF$_2$(0.145g.)/HF

and $Re(CO)_5F \cdot ReF_5$(0.315g.)/TaF$_5$(0.123g.)/HF reactions were

each performed in a single tube into which weighed amounts

of both solid reactants had been loaded in the dry-box

(the XeF$_2$ and TaF$_5$ from glass ampoules, the rhenium complexes

from their reactors). After sampling the volatiles of both

reactions, the tubes were transferred to the Y-piece. The

former reaction gave a pale blue, and finally colourless

solution over two days. The HF was distilled at between

-40 and $0^\circ C$ into the second tube at $-196^\circ C$, to test the

condensible volatiles for ReF_6. The colourless crystals

left behind in the reactor were pumped dry (0.047g.) and

the tube removed to the dry-box. If the solid were a

single $(Re(CO)_6)^+(ReX_n)^-$ species, the weight loss corresponds

to a loss of at least ReF_6 from each $(Re(CO)_6)^+(Re_2F_{11})^-$

molecule to give a species of molecular weight 568

$(\sim Re(CO)_6^+ReF_{1.5}^-)$. The product is more likely therefore

to contain a <u>mixture</u> of $(HF_2)^-$ and $(ReO_xF_y)^-$ anions.

Found: C=14.02%, Calc: $Re(CO)_6^+ReF_x^-$ (M.W.=568) C = 12.6%.

In the TaF_5 reaction, the brown solution was

filtered from dark, undissolved residues (weight=0.078g.) and

then evaporated to dryness to give a brown solid (0.351g.),

and both tubes removed to the dry-box. The mass balance

indicated a total weight loss of 9mg., probably from ReF_5

decomposition.

Re(CO)$_5$Cl/HF

1cm. depth of HF was condensed on to 0.066g.

$Re(CO)_5Cl$ in a ¾" Kel-F tube, but no solution was observed.

Periodically the mixture was refluxed and shaken, and the

volatiles above the HF expanded into a tube of sodium

fluoride, to absorb HF and leave HCl. Pressure changes

and mass spectra, however, gave little evidence for HCl.

After three days the HF was removed. The infrared spectrum

and powder pattern of the solid showed it to be largely

unchanged. The above procedure follows that of O'Donnell,[39]

except that no "tea bag" was used.

Mn$_2$(CO)$_{10}$/HF

HF was condensed on to $\sim$0.1g. $Mn_2(CO)_{10}$ in a ³⁄₁₆"

Kel-F N.M.R. tube to give a depth of ~45mm. when molten.

Some of the carbonyl dissolved to give a golden yellow

solution. This was cooled to -196°C, and the tube sealed

near the valve using an electrical, annular heater. ^{1}H and

^{19}F N.M.R. spectra were then run on the saturated solution.

4-4.5   cpFe(CO)$_2$F Preparation

1.071g. (cpFe(CO)$_2$)$_2$ were dissolved in 50ml.

acetone, freshly redistilled over molecular sieves 4A, in

a 250ml., 3-necked, round-bottomed flask fitted with a reflux

condenser and nitrogen bleed. The deep red solution was

purged with nitrogen for 30 minutes. A similarly-flushed

suspension of 0.784g. fresh AgF in 30ml. acetone was added

via a separating funnel. The mixture was refluxed under

nitrogen, with vigorous stirring for an hour, silver precip-

itating as a grey suspension in the deep red solution.

The acetone was removed on a rotary evaporator, and

the brown solid extracted with 50ml. of dry benzene, forming

a red solution. This was decanted, and various solvents

were added to portions, to attempt to precipitate the product.

A very small amount of red, needle crystals of cpFe(CO)$_2$F

was precipitated overnight from 1:>1 benzene:(60-80°)

petroleum ether, with a little CFCl$_3$, and filtered off.

They were air-stable, and gave an infrared spectrum and

X-ray powder pattern different from the starting materials.

Attempts to extract further quantities from the solution or

the original residue only gave brown solids after this,

owing to the decomposition of cpFe(CO)$_2$F in solution.

CHAPTER 5

CRYSTAL STRUCTURE DETERMINATION

BY X-RAY DIFFRACTION

The theory and standard methods of crystallography
have been well documented by several comprehensive
accounts.[176-178] This chapter summarises some of the major
principles, especially with regard to features referred to
in the structure determinations in chapters 6 to 8.

5-1. X-ray Diffraction

X-rays are scattered by the lattice arrays of atoms
in crystals, to give a pattern of emergent rays characteristic
of the unit cell of the crystal. Each emergent ray comes
from a stack of parallel planes in the lattice which satisfy
the Bragg condition. This is that the stack has an angle,
θ_{hkl}, to the incident ray, and a spacing, d_{hkl}, between
its individual planes, such that the path difference of the
reflected rays from individual planes is an integral number
(n) of wavelengths (λ), so that all the planes of the stack
reflect the incident ray in phase, producing a single, combined,
reflected ray. This is expressed by the Bragg equation:

$$n = 2d_{hkl} \cdot \sin\theta_{hkl} \qquad (5.1),$$

where (hkl) is the index defining the stack of planes (or
the combined reflection from those planes), and expresses
the fraction of the unit cell edge of the crystal at which
this stack intersects the cell axes a, b and c respectively.

Each reflection (hkl) has a specific geometry, and
intensity. Crystal structure determination is concerned
with the analysis of all the reflections from the stacks
(hkl) in the crystal, in terms of their geometry and intensity.

5-2. Geometric Aspects

The geometry of a reflection depends only on the

unit cell geometry of the crystal. The geometries of the

reflections are monitored as the array of points on Weissenberg

and Precession photographs of the crystal. This array

represents the "reciprocal lattice" of the crystal, where

each point represents a stack of planes (hkl) of the real

lattice, and is located on a normal to that stack, at a

distance of $^1/d_{hkl}$ from the unit cell origin of the real

lattice. The spacings of the reciprocal lattice are related

to the reciprocals of the unit cell spacings a,b and c

and to the cell angles α, β and γ, and enable these to be

determined. Systematic absences in the array of spots on

the photographs are factors of the space group and crystal

habit, which can thus be determined.[179]

5-3. Reflection Intensities - the Structure Factor and

the Phase Problem

The quantity of each combined reflection depends

on the nature of the atoms doing the scattering, and their

location in the unit cell. It is represented by the Structure

Factor, F_{hkl} , of the reflection, which is a vector, with

an amplitude - the Structure Amplitude $|F_{hkl}|$ - and a phase,

ϕ_{hkl}. It is the vector combination of the amplitudes,

$f_{1,2....n}$, and phases, $\phi_{1,2....n}$, of the individual waves

scattered by the atoms 1,2....n in the stack of planes, and

is given by the Fourier series:

$$F_{hkl} = \sum_{j=1}^{n} f_j \cdot \exp(i\phi_j) = |F_{hkl}| \cdot \exp(i\phi_{hkl}) \qquad (5.2).$$

Each component amplitude, f_j , is the atomic

scattering factor of the jth atom, dependent only on the

nature of the atom and on θ_{hkl} , and calculable from published

tables.[180] Each individual phase angle, ϕ_j , depends on

the individual atom position (x_j, y_j, z_j), and the particular

stack (hkl) reflecting the wave. It is given by:

$$\phi_j = 2\pi(hx_j + ky_j + lz_j) \qquad (5.3).$$

As it is the electrons of the atoms which do the

scattering, the sum of the scattering factors, i.e. the

structure amplitude term $|F_{hkl}|$, can be re-expressed as an

integral over the whole unit cell, of the electron density

at any point, $\varrho(x,y,z)$. This version of equation 5.2 may be

re-expressed, by a Fourier transformation, as a Fourier series

for the electron density at a given point, in terms of the

structure factor of every possible reflection from the crystal:

$$\varrho(x,y,z) = \frac{1}{U} \sum_{hkl}\sum\sum F_{hkl} \cdot \exp[-2\pi i(hx + ky + lz)] \qquad (5.4).$$

The structure factors, F_{hkl} , are not experimentally

observable, however. Although the structure amplitudes,

$|F_{hkl}|$, are determinable, because their squares are directly

proportional to the intensities of the observed reflections,

see equation 5.5, the phase angle, ϕ_{hkl} , of each reflection

is dependent on the knowledge of the atom positions, and so

is not experimentally observable. This constitutes the

phase problem in crystallography. The phase angles must be

deduced on the basis of some trial structure, and the principle

of a successful crystal structure determination is to deduce

and refine this trial structure until its set of theoretical

structure amplitudes, $|F_{calc}|$, matches those, $|F_{obs}|$,

derived from the observed reflection intensities, to the best

possible closeness.

5-4. Data Reduction

The manipulation of the raw reflection intensity
data collected by the diffractometer, and its conversion into
the corrected structure amplitudes, $|F_{obs}|$, is known as data
reduction. It was carried out in this study by the programmes
STOWK, ABSCR and PRFTP.

For the best solution of equation (5.4), the
intensities of as many reflections as can be accurately
measured must be obtained, and corrected for secondary effects,
according to:

$$|F_{hkl}| = \sqrt{\frac{K \cdot I_{hkl}}{Lp}} \qquad (5.5),$$

where p is a correction for the polarisation of X-rays on
reflection, known as the polarisation factor, and is a simple
function of 2θ;

L is a correction for the decrease in diffracting power
of the atoms with increasing θ, known as the Lorenz factor.
This depends on 2θ and the precise measurement techniques
used;

K is an overall scale factor, dependent on the crystal
size, X-ray beam intensity and some fundamental constants.
This brings $|F_{obs}|$ to the absolute scale, with the dimensions
of electrons. This scale factor is set to an arbitary
value, and refined by the structure factor least-squares
programme, SFLS.

In addition, the intensities usually need correction
for the effects due to the absorbtion of X-rays by the crystal.

5-5. Deducing a Trial Structure by the Heavy Atom Method

The method used in this study for deducing a suitable

trial structure was the "heavy atom" method. It is assumed

that, to a first approximation, all the scattering from any

given stack of planes is due to a small number of atoms (in

this case, of rhenium) significantly heavier than the others.

Thus the phase angle, ϕ_{hkl} , of the reflection from that stack

is approximately that due to the heavy atoms alone, and can

be determined if the positions of the heavy atoms (X_j, Y_j, Z_j)

can be located (see section 5-9.) by substituting these in

the equation:

$$\phi_{hkl} = \sum_j \exp 2\pi i (hX_j + kY_j + lZ_j) \qquad (5.6).$$

The structure amplitudes of the trial structure,

$|F_{calc}|$, are calculated by substituting the heavy atom positions

into a combination of equations 5.3 and 5.2. Allowance must

be made in this theoretical structure, for the real thermal

vibration of the atoms reducing the scattering power by

spreading out the electron density cloud. This appears as

a reduction of each coefficient f_j from its stationary atom

value $f_{0(j)}$, by a factor of $\exp -B(\sin^2\theta)/\lambda^2$:

$$f_j = f_{0(j)} \cdot \exp[-B_j(\sin^2\theta)/\lambda^2] \qquad (5.7).$$

B_j is the temperature factor of the atom, related to the

mean square amplitude of atomic vibration. The value of B_j

for each f_j is estimated initially, and then refined in the

least squares refinement (see section 5-8.). Towards the

end of the refinement, anisotropy of the electron cloud can

be allowed for by an expression:

$$f_j = f_{0(j)} \cdot \exp[-\tfrac{1}{4}(h^2 a^* B_{11} + k^2 b^* B_{22} + l^2 c^* B_{33} + 2hka^* b^* B_{12} +$$
$$2hla^* c^* B_{13} + 2klb^* c^* B_{23})] \qquad (5.8),$$

where B_{ij} are anisotropic temperature factors, and a^*, b^*, c^*

are the reciprocal lattice parameters.

5-6.   Structure Solution using a Difference Fourier Synthesis

The accuracy of the heavy atom positions is briefly
checked by least squares methods, and the light atoms are
then located by a difference Fourier synthesis. The differ-
ence between the real and trial structure amplitudes, written
$(|F_{obs}| - |F_{calc}|)$, are substituted in equation 5.4, with the
calculated phase angles, ϕ_{calc}, to give a Fourier series for
the residual electron density in the cell after the effect of
the heavy atoms has been removed: $\Delta\rho(x,y,z) =$

$$\frac{1}{U} \sum_{hkl}\sum\sum (|F_{obs}| - |F_{calc}|)\cdot\exp(i\phi_{calc})\cdot\exp[-2\pi i(hx+ky+lz)] \quad (5.8).$$

This electron density is plotted in the form of a 3-dimensional
map of numbers (the Fourier map) which is contoured to reveal
the position of the light atoms. More accurate phase angles
and $|F_{calc}|$'s are derived using these extra atoms, and sub-
stituted into a new difference Fourier, which will remove
all the located atoms as the "minus $|F_{calc}|$" portion of the
synthesis, and reveal the electron density due to any remaining
atoms. Successive difference Fouriers are used until all
the non-hydrogen atoms have been located, and could be used
thereafter to refine the structure using better and better
phase angles and atom positions. Because of series termination
and other errors resulting from the requirements of an infinite
Fourier series, and the difficulty of refining temperature
factors by Fourier methods, structure refinement is normally
carried out by least squares methods.

5.7   Least Squares Refinement

The technique involves minimising a weighted function
of $(|F_{obs}| - |F_{calc}|)$, with respect to the parameters of which

these amplitudes are functions, to achieve "best" atomic

parameters, assuming a normal distribution of errors. This

is achieved by taking the derivative of the function

$\sum_{hkl} w_{hkl}(|F_{obs}|-k'|F_{calc}|)^2$, written $w\Delta^2$, with respect to

each of the positional, thermal or scale parameters,

$p_1, p_2 \cdots p_n$, of which $|F_{calc}|$ is a function, and setting the

derivative equal to zero. w_{hkl} is the weight for each term

in the series, a measure of the reliability of each observed

reflection, and k' is the overall scale factor to scale the

$|F_{obs}|$ values to the same units as $|F_{calc}|$, (related to K of

equation 5.5). In the programme SFLS, the best values of p_j,

in the resulting n equations in n unknowns, are found by

the block-diagonal matrix approximation, refining positional

parameters by a 3x3 matrix, thermal by a 1x1 (isotropic) or

6x6 (anisotropic), and k' and its interaction with the overall

isotropic temperature factor by a 2x2. Weighting schemes

suggested by Cruickshank et alia[181] were employed.

In the later stages of refinement, the least

squares output is checked for trends in $w\Delta^2$ for groups of

reflections - arranged by their value of $|F_{hkl}|$, by $(\sin\theta)/\lambda$,

and by lattice layer - to look for any significant discrepancies.

Finally the individual reflections are checked for anomalous

values of $w\Delta^2$, and these edited out.

The discrepancy between the (correctly scaled)

observed and calculated data at the end of each refinement

cycle is expressed by the residual factor R, summed over all

reflections:

$$R = \frac{\sum_{hkl} ||F_{obs}|-k'|F_{calc}||}{\sum_{hkl}|F_{obs}|} \qquad (5.9).$$

The value of R reflects the accuracy of the proposed structure

model with respect to the observed data. A value of 0.035

or below, when the last atom has been introduced, generally

indicates a reasonably accurate structure which will refine

to a good solution with R below 0.010. R is also affected by .

i). the precision with which the $|F_{obs}|$'s were measured, and

how well they were corrected for experimental effects, ii).

how well the theory on which the $|F_{calc}|$'s were calculated

represents the true state of affairs in the crystal (e.g.

correct temperature factor estimation), iii). the dominance

of the data by the heavy atoms (so that R scarcely monitors

light atom inaccuracies, a problem in this present study),

and iv). the proportion of weak reflections in the data.

Other accuracy guides are the achievement of low

temperature factors and of chemically reasonable bond distances

and angles, with low standard deviations.

5-8. Heavy Atom Location by the Patterson Method

The heavy atoms were located in this work by the

Patterson method. This involves summing a Fourier series for

a function P_{uvw}, which represents the vectors at points in

the unit cell (u,v,w), between the atoms in the cell.

$$P_{uvw} = \frac{1}{U^2}\sum_{h,k,l=-\infty}^{\infty} |F_{hkl}|^2 \cdot \cos 2\pi(hu+ kv+ lw) \qquad (5.10).$$

The coefficients are $|F_{hkl}|^2$, directly obtainable from the

intensity data (equation 5.5). A vector at (u,v,w) indicates

that there exist in the crystal atoms at (x_1,y_1,z_1) and

(x_2,y_2,z_2) such that $u= x_1-x_2$, $v= y_1-y_2$, and $w= z_1-z_2$.

Printing out a map of Patterson vector density in the same

way as the Fourier electron density (using a variant of the

Fourier programme) enables the vector peaks to be picked out.

Assuming the heavy atoms dominate these vectors, the positions of the atoms can be deduced by analysing all the vectors.

5-9. Computer Programmes

The computer programmes used in this study were written by Dr.D.R.Russell of the University of Leicester, except for ORTEP.[181] The STOE CONTROL TAPE GENERATOR programme and the $(\sin\theta)/\lambda$ listing (for comparison with powder diffraction data) were used on an Elliott 803 computer, the remaining programmes on an Elliott 4130.

STOE CONTROL TAPE GENERATOR calculates μ and ω for each
reflection, layer by layer, on the basis of a set $(\sin\theta)/\lambda$
range and the unit cell parameters. It also sets the
scan range and rate. See section 6-1.3.

STOWK calculates the structure amplitudes according to
$|F_{hkl}|^2 = I_{hkl}/K_{hkl}$, where K embodies L and p corrections
and instrumental constants.

ABSCR corrects all $|F_{obs}|$'s for absorbtion by $I = I_0 \cdot e^{-\mu s}$.

PRFTP writes the absorbtion-corrected $|F_{obs}|$'s on to magnetic
tape in order of hkl, in a form to act as the input to
FOUR and SFLS. It calculates all f_j's for each reflection,
and has facilities for setting layer scale factors, weights
and temperature factors, and calculation of the $|F_{hkl}|^2$
coefficients for a sharpened Patterson synthesis.

FOUR calculates the Patterson, Fourier and Difference Fourier
syntheses.

SFLS performs the least-squares refinement of positional and
thermal parameters, and scale factors. It calculates R,
weights the $|F_{obs}|$'s, analyses $w\Delta^2$ by $|F|$, $(\sin\theta)/\lambda$ and
layer, and calculates bond distances and angles, and

standard deviations.

EDIT removes unwanted reflections from the SFLS input.

ORTEP draws perspective views of the molecules on the basis
   of the atomic thermal ellipsoids.

$(\mathrm{Sin}\theta)/\lambda$ calculates $(\sin\theta)/\lambda$ for each reflection and sorts
   them in order of hkl.

CHAPTER   6

THE CRYSTAL STRUCTURE

OF Re(CO)$_5$F$\cdot$ReF$_5$

6-1. OBTAINING THE GEOMETRIC AND INTENSITY DATA

6-1.1 Mounting the Orange and Green Crystals

        Mixtures of orange and green crystals from an $Re_2(CO)_{10}$/

$3ReF_6$/HF reaction were transferred in a recirculating dry-box

to a Pyrex, multiple-capillary apparatus (fig.6.1), which had

been previously evacuated, and seasoned with ClF_3 to remove

moisture.
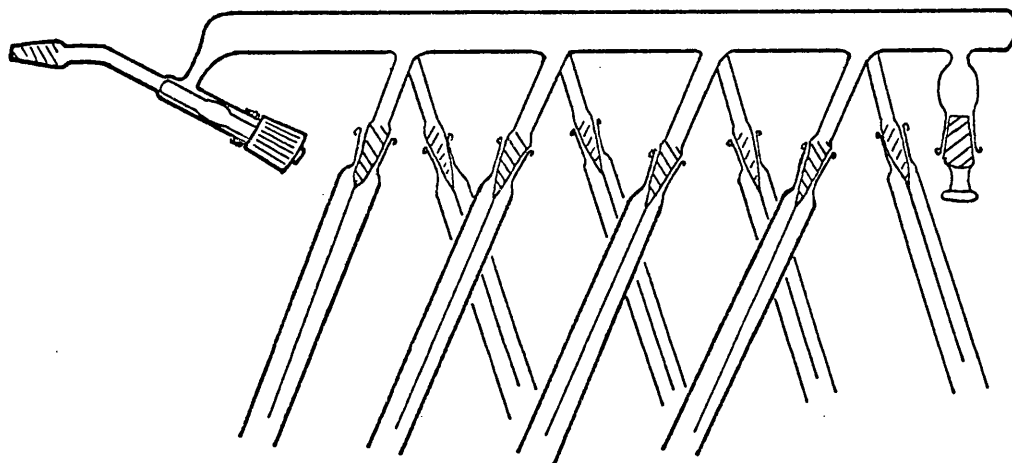
Fig.6.1 Capillary Apparatus for Single Crystal X-ray Studies

        The apparatus was re-evacuated and individual crystals

were introduced into the capillaries by very careful tapping

with a glass tube. By this means, separation of the orange

and green crystals was achieved. Capillaries containing

either green or orange crystals were sealed in 2-3" lengths,

and examined under a microscope. Suitable; single crystals

of each sort which were wedged in the capillaries were sealed

in shorter lengths of capillary. These were mounted on

goniometer heads for crystallographic examination.

6-1.2 The Geometric Data

        The orange crystal used was in the form of an irregular

platelet (see section 6-1.4), and was aligned by cone axis

and precession photographs. Zero layer precession photographs

were taken about two orthogonal, reciprocal axes, using

Zr-filtered, Mo-K_{α} radiation (λ=0.7107Å). The true spacing of

the first layer was determined by a cone axis photograph,

and a first layer precession photograph was taken about one

of the axes. Initially, axis symbols were assigned arbitrarily.

The symmetry of the photographs suggested that the

crystal adopted the orthorhombic habit. There were no general

systemmatic absences of reflections (hkl). This indicated a

primitive space group. The specific absences were:

hOO h= 2n+1 only; OkO k= 2n+1 only; 1Ol missing.
OOl l= 2n+1 only; Okl l= 2n+1 only; 1kO k= 2n+1 only.
hOl h= 2n+1 only.

These three sets of absences implied, respectively, an a-glide

perpendicular to b, a c-glide perpendicular to a, and a b-glide

perpendicular to c, suggesting a space group of Pcab. Compar-

ison with the listed space groups[179] showed that only the

space group Pbca had these absences. The a- and b-axes were

thus interchanged, and the crystal assigned to the orthorhombic

space group Pbca.

Accurate unit cell dimensions were obtained by measuring

the zero layer precession photographs. The values, a=22.34(3),

b=15.51(1), c=13.67(1) Å, $\alpha=\beta=\gamma=90°$, gave a unit cell volume

of 4737Å^3. For numerous fluoride crystal structures, it

appears that the lattice may be considered as a close-packed

array of fluorine atoms of 17 or 18Å^3 volume, the other elements

occupying the interstices between the close-packed spheres.

This principle has been used to elucidate formula units,[163]

and to obtain other information.[184] In the present study, a

Table 6.1 Observed and Calculated Unit Cell Volumes of

Relevant Carbonyl Compounds

Molecule	Crystal Habit	Z	Unit Cell Volume	
			Obs.	Calc.
$(Ru(CO)_3F_2)_4$	Tetragonal	2	1146	1232
$(Re(CO)_5)_2$	Monoclinic	4	1480	1600
$(Re(CO)_4H)_2$	Monoclinic	4	1263	1280
Orange crystal	Orthorhombic	8?	4737	4824

Table 6.2 Formula Unit Volumes of Rhenium Carbonyl Fluorides

Empirical Formula	Vol.of 8 units	Probable Structure
$Re(CO)_5F$	1736	$8 \times Re(CO)_5F$
$Re(CO)_4F_2$	1552	$8 \times Re(CO)_4F_2$
$Re(CO)_4F$	1416	$2 \times (Re(CO)_4F)_4$
$Re(CO)_3F_2$	1232	$2 \times (Re(CO)_3F_2)_4$
$Re(CO)_{2.5}F_3$	1208	$4 \times Re(CO)_5F \cdot ReF_5$
$Re(CO)_{2.5}F_{2.5}$	1140	$4 \times Re(CO)_5 \cdot ReF_5$
$Re(CO)_2F_3$	1048	$2 \times (Re(CO)_2F_3)_4$
$Re(CO)_2F_4$	1184	$8 \times Re(CO)_2F_4$
Orange crystal	4x1184	$16 \times Re(CO)_5F \cdot ReF_5$

correlation was sought between observed and calculated unit

cell volumes, assuming close-packed arrays of carbon, oxygen

and fluorine atoms. Atomic volumes of 21(C), 19(O), and

17$\overset{\circ}{A}^3$(F) were calculated on the basis of the covalent radii,[165]

and gave satisfactory agreement for the related structures

$(Ru(CO)_3F_2)_4$, $Re_2(CO)_{10}$[118a] and $(Re(CO)_4H)_2$,[186] (table 6.1).

As there are eight general symmetry positions in the Pbca

unit cell of the orange crystal, the volumes required by eight

formula units of various plausible carbonyl fluoride species

were calculated, and these compared with the observed unit

cell volume (table 6.2). It was apparent that the asymmetric

unit contained four rhenium atoms, possibly indicating a

tetrameric compound like $(Ru(CO)_3F_2)_4$. The absence of CO

evolution in the reactions suggested that, of the possible

structures, those maintaining the $Re(CO)_5$ unit were the most

likely, especially favouring $Re(CO)_5F \cdot ReF_5$.

6-1.3   Intensity Data Collection

        The goniometer head was mounted on a Stöe-Guttinger

Weissenberg diffractometer, for collection of the intensity

data about the c-axis. The diffractometer records reflected

intensities under equi-inclination Weissenberg conditions,

with a scintillation counter replacing the photographic film.

These conditions are fulfilled when the angle (μ') between

the crystal rotation axis and the incident beam is equal in

magnitude to the angle (ν') between the counter and the

rotation axis (figure 6.2). This is achieved in practice by

setting the angles $\mu(=90-\mu')$ and $\nu(=90-\nu')$ for each reciprocal

layer in turn.

        The diffraction maxima for each individual reflection

are located by rotating the crystal (ω arc) at specified

settings of the counter (2θ arc). In fact, the angle measured
by the counter arc is strictly Υ, the vertical component of 2θ
for non-zero layers. The settings of Υ and ω for each reflec-
tion were generated in the form of a control paper tape for
each layer, using the STOE CONTROL TAPE GENERATOR programme.
For this purpose, a- and b-axis cell parameters were determined
on the diffractometer, by adding the θ values for the maximum
pen-recorder deflection, for a series of h00 and 0k0 reflections.
The rotation axis (c-) parameter used was that obtained from
the precession photographs, and this figure was also employed
to calculate the values of μ for each layer. With these values,
the alignment of the crystal could be optimised using the pen
recorder trace, for a series of reflections 00l.

The intensity data were collected by scanning through
a range in ω, whilst the reflection was measured, and taking a
stationary background count of 10 seconds before and after
each reflection. For reciprocal layers hk0 to hk5, ω was
scanned at 1.00 deg.min^{-1} over a range of 1.2°, up to a maximum
ω value of 30° and Υ of 60°. Because of peak broadening in
higher layers, a 1.25° range was used for layers hk6 to hk12,
up to a maximum ω of 25°. The intensities of the background and
the reflections were recorded by a paper tape output, and were
also monitored on a pen recorder chart. The net intensity,
I_{hkl}, for each reflection was given by:

$$I_{hkl} = C_r - \frac{1}{2}\left[C_1 \cdot \frac{t_r}{t_1} + C_2 \cdot \frac{t_r}{t_2}\right] \qquad (6.1),$$

where C_r is the number of counts for the reflection, recorded
in time t_r, and C_1 and C_2 are the number of counts for the
background, recorded in times t_1 and t_2 respectively. A check
reflection for each layer was measured every 30 reflections,
to indicate any changes in the crystal alignment. The intensity

Fig.6.2 Schematic Representation of the Stoe Diffractometer

Geometry (after ref.13, p.37).

* actually measures Υ, the vertical component of Θ for an

   upper layer (ν being the horizontal component).

μ sets the incident beam for the layer in question.

ν for each reflection is set by the instrument angles ω and

   2Θ. ω rotates the crystal (about the rotation axis),

   and 2Θ rotates the counter up and down to receive each

   reflection.

   ω = Weissenberg drum setting + ~135° + Θ.

   Θ = Bragg angle for the reflection = $\sin^{-1} \dfrac{m\lambda}{2d}$,

where m is h, k or l for the reflection along the appropriate

   axis, and d is the cell dimension of that axis.

data were processed as described in section 5-4.

6-1.4   The Crystal Data

$C_5F_6O_5Re_2$, M=626.4, orange orthorhombic crystals, a= 22.34(3),
b= 15.51(003), c= 13.67(1)Å, U= 4737Å^3, Z= 16, D_{calc}= 3.51g.cm^{-3},
space group Pbca. 2047 reflections (before editing) to
(sin θ)/λ = 0.70, collected at 22-25°C with graphite-monochromated
Mo-K_α radiation (λ = 0.7107Å), and corrected for absorbtion.

Density measurements were impracticable owing to the
extreme air-sensitivity of the compound.

6-1.5   The Absorbtion Correction

The correction for the absorbtion of X-rays by the
crystal was made on the observed structure amplitudes on the
basis of the relationship $I_{hkl} = I_0 \cdot exp(-\mu s)$, employing the
programme ABSCR. Here, I_0 is the intensity of the incident
beam, I_{hkl} are the corrected intensities of the reflections
(hkl), μ is the linear absorbtion coefficient of the crystal
(see below), and s is the path length of the reflection in
question.

The crystal could be approximated to an irregular
brick with 5 edges parallel with, and the top and bottom faces
perpendicular to, the a*-axis, as shown.
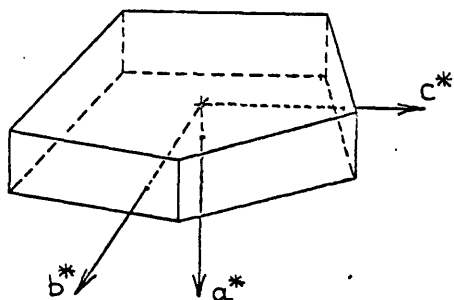
longest diagonal 0.0812 cms
longest face   0.0597 cms
thickness   0.0145 cms

To calculate the parameter s, ABSCR requires the determination of the coefficients A,B,C and D of an equation for each face:

$$D = Ax + By + Cz \qquad\qquad (6.2),$$

where D is the perpendicular distance from some fixed reference point inside the crystal (in this case the centroid), and (xyz) is a cartesian system whose origin is the reference point, and whose axes are parallel to the reciprocal axes of the crystal. The crystal size was measured using a monocular microscope fitted with a cursor eyepiece, with the goniometer head remounted on a crystal orienter (Charles Supper Co.). A plan view of the crystal was plotted on graph paper, and the drawing measured to obtain the appropriate equations for each face.

The linear absorbtion coefficient, μ, which depends solely on the composition of the compound and not on atomic arrangement, was calculated assuming a molecular formula of $Re(CO)_5F \cdot ReF_5$.

$$\mu = \frac{n}{V} \cdot \sum_i (\mu_a)_i \qquad\qquad (6.3),$$

where n is the number of molecules in the unit cell, V is the volume of the unit cell, and $\sum_i (\mu_a)_i$ is a summation of the absorbtion coefficients $(\mu_a)^{180}$ for all the atoms of one molecule. This gave a figure of μ of 216.8 cm^{-1}.

The figures for A,B,C,D and μ were substituted into the ABSCR programme, and the structure amplitude for each reflection was thereby corrected for the effects of the absorbtion of X-rays by the crystal.

6-2.   THE STRUCTURE SOLUTION

6-2.1   Location of the Rhenium Atoms by Patterson Syntheses

The absorbtion-corrected structure amplitude data were

written by the programme PRFTP on to magnetic tape to become

the input for the Fourier and least squares programmes.

Layer scale factors and weights were set at unity, and an

arbitrary temperature factor of 1.50Å^2 was assigned to all

atoms for possible Patterson sharpening.

A three-dimensional Patterson synthesis was performed,

using the programme FOUR, for the asymmetric unit of the unit

cell, the boundaries of this volume being x=0-120, y=0-120,

z=0-120, 240ths. of the cell edges. The map was sectioned

along the z-axis, at intervals of $^6/240$ths. Peak resolution

was insufficient for the precise location of the vectors,

and a "Sharpened" Patterson synthesis was used, assuming point

atoms.

On the basis of the space group and the unit cell

volume, it was assumed that there were 32 rhenium atoms

comprising an asymmetric unit with 4 at each of the eight

Pbca general symmetry positions. The expected Patterson

map co-ordinates (u,v,w) were derived for vectors (e.g. Re_2-Re_2)

between rhenium atoms at general positions (x,y,z) and the

equivalent atoms at the other seven symmetry-related positions.

The map was then searched for the peaks corresponding to

these vectors. The rhenium atom x-, y-, and z-co-ordinates

were deduced in turn, by locating vectors specified by two

fixed co-ordinates (Harker lines).

Thus, peaks on the Harker line (u=0, v=120-2y, w=120),

derived from the symmetry position (x,½-y,½+z), were found

at v=0 (intensity 2804), 10(958), 85(1406) and 102(1128).

From these v-co-ordinates, the values of 2y were calculated

to be 120, 110, 35 and 18, respectively. The values of 2x

and 2z were deduced in a similar way. The set of 2x, 2y and

2z values were then confirmed by locating the Harker plane

vectors such as ($\frac{1}{2}$-2x,-2y,$\frac{1}{2}$), with only one co-ordinate fixed.

   2x = ~116 (2 vectors), 4 (2 vectors),

   2y =   120, 110, 35, 8 (1 vector each),

   2z =   98 (2 vectors), 26 (2 vectors).

   The particular combination of these values giving the

four correct atoms positions was deduced by assigning a pair

of co-ordinates for two atoms, and searching for the appro-

priate cross-vectors (e.g. Re_2-Re_3) between them. The correct

choice of co-ordinates was indicated by identifying all the

cross-vectors (heavy atom-heavy atom only), and locating the

four vector peaks (2x,2y,2z) — the only same-atom vectors

with no co-ordinate fixed. The peaks located for the latter

were (u,v,w) = (2x,2y,2z) = 0,120,24(816): Re_1-Re_1; 9,19,96(334):

Re_2-Re_2; 115,33,99(228): Re_3-Re_3; and 115,110,24(302): Re_4-Re_4.

The rhenium atoms were thus assigned the Fourier co-ordinates:

Re_1(0,60,12), Re_2(5,9,48), Re_3(62,17,70) and Re_4(62,65,108).
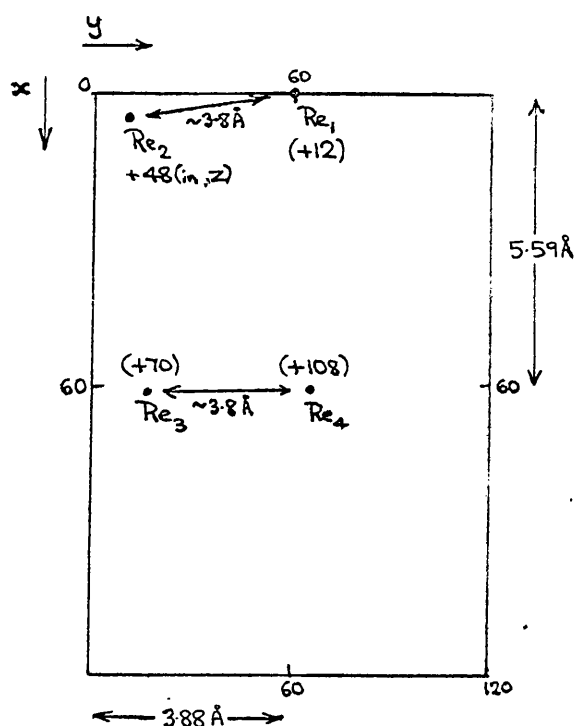
Fig.6.3. Rough Projection of the 4 Rhenium Positions of the Asymmetric Unit down 001.

A rough plot of these positions on a projection looking down z (fig.6.3), showed that the pairs of atoms Re_1 and Re_2, and Re_3 and Re_4, were at reasonable distances (~3.8Å) to be linked by single fluorine bridges, Re_1-F-Re_2 and Re_3-F-Re_4, but that Re_1 and Re_4, and Re_2 and Re_3, were too far apart (>5.4Å) to be linked. This suggested that the asymmetric unit was probably not a single tetrameric molecule, but a pair of asymmetric, fluorine-bridged molecules.

6-2.2 Location of the Light Atoms, and Least Squares Refinement

The four rhenium positions were entered, and subjected to three cycles of structure factor least squares refinement by the programme SFLS. 1981 unique reflections with 0.70 (sin θ)/λ > 0.10 and I $\geqslant$ 3σI were used, thus removing 66 of those collected which were of low angle (with consequent shielding by the back-stop) or were very imprecise, weak reflections. An arbitrary value of 10.0 was set for the overall scale factor (to scale the $|F_{obs}|$ values to the same standard as $|F_{calc}|$), and one of 5.0Å^2 for the rhenium atom temperature factors. Accurate figures for these were obtained by refinement in the least squares programme. Unit layer scale factors and weights were used initially. Over the three cycles the R-factor fell from 0.384 to 0.329.

A difference Fourier synthesis was then performed using the programme FOUR, the effect of the heavy atoms being subtracted from the electron density map, to reveal the light atom positions. The light atom peaks obtained were traced on to layers of perspex sheet, to simulate the atom distribution in three dimensions. Several light atoms associated with each rhenium were located. Re_2 and Re_4 both had six single-atom

near neighbours, arranged roughly octahedrally, suggesting

two (ReF_6) units. The positions of atoms F_{21}, F_{22}, F_{24}, F_{25}

and F_{41} to F_{44} were estimated, and entered in a subsequent

least squares cycle. The environment of the atoms Re_1 and

Re_3 appeared to contain peaks consistent with carbonyl groups,

but at this stage only atoms O_{11} and O_{31} were entered. The

light atoms were given initial temperature factors of $5.0Å^2$.

   After one cycle of refinement the R-factor fell to

0.307, and temperature factors were 3.1 to $3.8Å^2$ for the rhenium

atoms and 4.7 to 8.4 for the light atoms. Another difference

Fourier was calculated, and the remaining light atoms were

located. Re_1 and Re_3 could then each be seen to be associated

with a roughly square pyramidal arrangement of 5 terminal

carbonyl groups. The sixth position of an octahedral co-

ordination sphere was occupied by the fluorine atoms F_{21} and

F_{41}, bridging Re_1 to Re_2, and Re_3 to Re_4 respectively. The

asymmetric unit thus contained two discrete molecules of the

expected formula $(OC)_5Re-F-ReF_5$.

   A least squares cycle with all the atoms included

reduced R to 0.299. The temperature factors and interatomic

distances suggested the co-ordinates of F_{23}, F_{26}, C_{31}, C_{35}

and the carbonyl groups $(CO)_{12}$, $(CO)_{13}$ and $(CO)_{15}$ needed to

be modified slightly. This was done over two further refine-

ment cycles, but the R-factor was still as high as 0.290. A

refinement of the scale factors for each layer was now

commenced, to take into account the affect on the observed

structure factors of having realigned the collimator after

collecting layer hk5. As a result, R was reduced to 0.169

after two cycles, and to 0.085 after a further four. This

confirmed that the structure was predominantly correct,

though minor adjustments of the light atoms positions continued,
to correct for anomalies in the temperature factors and bond
distances. Temperature factors were by this time 1.8 to 2.6
for the rhenium atoms, and 1.4 to 7.4 for most of the light
atoms.

After four more cycles, R had fallen to 0.075 and most
atom positions were fairly constant. Layer scale factor
refinement was ceased, and the rhenium atom temperature factors
were allowed to become anisotropic. A weighting scheme for
the observed structure factors was introduced at the same time.
This had the form:

$$ w = (\ 10\ +\ |F_{obs}|\ +\ 0.02|F_{obs}|^2\ )^{-1} \qquad (6.4), $$

and replaced the unit weights used hitherto. After four
cycles of refinement, R was reduced to 0.065, and the weighting
scheme was altered to the form:

$$ w = (\ 10\ +\ |F_{obs}|\ )^{-1} \qquad (6.5), $$

to obtain a better agreement between the individual layer R-
factors. This brought R to a steady value of 0.064, but an
error was then discovered in the original absorbtion correction.
ABSCR was therefore re-run, followed by PRFTP, and a series of
least squares refinements which brought R to a steady value of
0.066, with anisotropic temperature factors for the rhenium
atoms only.

Twelve reflections of the 1981 used in the least squares
cycles had large discrepancies between $|F_{obs}|$ and $|F_{calc}|$,
indicated by values of $w\Delta^2 > 3$, and were edited out using the
programme EDIT. This reduced the R-factor to its final value
of 0.061. A difference Fourier map (scale factor 1.0) showed
no peaks above 11 or below -17, confirming that no significant
electron density had been left unaccounted for.

The final atomic and thermal parameters are listed
in table 6.3, and the bond lengths and angles in tables 6.4
to 6.6. ORTEP drawings of the structure are shown in figs.
6.4 to 6.7, and a complete listing of the observed and cal-
culated structure amplitudes is given in Appendix 1. The
standard deviations of the bond lengths and angles are fairly
high, but not so as to prevent their detailed analysis with
respect to the nature and properties of the compound. The
high values are chiefly caused by the proportion of heavy atoms
in the structure, which lowers the precision of the location
of the light atoms, and of the non-ideal size and shape of
the crystal, which was unavoidable.

Table 6.3 Final Re(CO)$_5$F.ReF$_5$ Positional and Thermal Parameters

Atom	x/a	y/b	z/c	B(Å^2)
Re(1)	0.00508(5)	0.25151(7)	0.04928(13)	⎫
Re(2)	0.02047(7)	0.04076(8)	0.20123(14)	⎬ see
Re(3)	0.25882(6)	0.06940(8)	0.28522(14)	⎰ below
Re(4)	0.26004(7)	0.27430(8)	0.44986(14)	⎭
C(11)	0.075(2)	0.318(3)	0.097(4)	4.8(9)
C(12)	0.050(1)	0.226(2)	-0.075(3)	2.8(6)
C(13)	-0.065(2)	0.186(2)	-0.003(3)	3.0(6)
C(14)	-0.033(2)	0.272(3)	0.179(4)	4.7(9)
C(15)	-0.025(2)	0.357(2)	-0.004(3)	3.4(7)
O(11)	0.112(1)	0.364(2)	0.124(2)	7.0(7)
O(12)	0.069(1)	0.209(2)	-0.150(3)	4.7(6)
O(13)	-0.106(1)	0.148(2)	-0.032(3)	5.8(7)
O(14)	-0.063(1)	0.286(2)	0.241(3)	6.2(8)
O(15)	-0.044(1)	0.423(1)	-0.029(2)	3.2(5)
F(21)	0.042(1)	0.131(1)	0.109(2)	4.4(5)
F(22)	0.099(1)	0.006(1)	0.205(2)	6.3(6)
F(23)	-0.009(1)	-0.039(2)	0.293(2)	6.0(6)
F(24)	-0.056(1)	0.083(1)	0.193(2)	5.0(5)
F(25)	0.036(1)	0.120(2)	0.299(2)	6.1(6)
F(26)	0.004(1)	-0.034(1)	0.104(2)	5.6(6)
C(31)	0.200(1)	0.149(2)	0.225(3)	2.2(5)
C(32)	0.321(2)	0.123(4)	0.211(4)	6.1(11)
C(33)	0.320(2)	-0.007(3)	0.354(4)	5.4(10)
C(34)	0.194(2)	0.023(3)	0.375(4)	5.7(11)
C(35)	0.244(2)	-0.008(3)	0.185(4)	4.9(9)
O(31)	0.164(1)	0.191(2)	0.195(3)	6.3(8)
O(32)	0.358(2)	0.145(2)	0.156(3)	7.3(9)
O(33)	0.354(1)	-0.052(2)	0.373(3)	5.6(7)
O(34)	0.155(2)	0.005(3)	0.427(4)	10.0(13)
O(35)	0.231(2)	-0.059(3)	0.119(4)	9.1(11)
F(41)	0.282(1)	0.160(1)	0.397(2)	5.7(6)
F(42)	0.339(1)	0.306(2)	0.444(2)	6.1(6)
F(43)	0.239(1)	0.385(2)	0.507(2)	5.8(6)
F(44)	0.182(1)	0.238(2)	0.456(2)	5.8(6)
F(45)	0.246(1)	0.311(2)	0.328(2)	6.8(7)
F(46)	0.272(1)	0.235(2)	0.574(2)	5.5(6)

Figures in parentheses here, and in subsequent tables are the estimated standard deviations for the least significant figures.

Anisotropic Rhenium Atom Temperature Factors (Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Re(1)	2.69(5)	2.05(4)	2.06(7)	0.03(5)	0.31(7)	0.08(4)
Re(2)	4.26(7)	2.03(5)	2.68(9)	-0.04(5)	0.39(8)	-0.36(4)
Re(3)	3.12(5)	2.23(5)	3.67(10)	0.02(6)	0.01(8)	0.14(4)
Re(4)	3.83(6)	2.74(5)	2.90(10)	0.12(6)	-0.22(8)	0.50(5)

Table 6.4 Bond Distances (Å) in Re(CO)$_5$F.ReF$_5$

Re(1)-C(11)	1.98(4)	Re(3)-C(31)	1.98(3)
Re(1)-C(12)	2.01(4)	Re(3)-C(32)	1.91(5)
Re(1)-C(13)	2.00(4)	Re(3)-C(33)	2.03(5)
Re(1)-C(14)	1.99(5)	Re(3)-C(34)	2.04(5)
Re(1)-C(15)	1.91(4)	Re(3)-C(35)	1.86(5)
C(11)-O(11)	1.16(5)	C(31)-O(31)	1.10(5)
C(12)-O(12)	1.14(5)	C(32)-O(32)	1.18(7)
C(13)-O(13)	1.16(5)	C(33)-O(33)	1.07(6)
C(14)-O(14)	1.11(6)	C(34)-O(34)	1.15(7)
C(15)-O(15)	1.16(4)	C(35)-O(35)	1.23(7)
Re(1)-F(21)	2.20(2)	Re(3)-F(41)	2.13(3)
Re(2)-F(21)	1.95(2)	Re(4)-F(41)	1.98(2)
Re(2)-F(22)	1.84(3)	Re(4)-F(42)	1.83(3)
Re(2)-F(23)	1.88(3)	Re(4)-F(43)	1.94(3)
Re(2)-F(24)	1.84(2)	Re(4)-F(44)	1.83(3)
Re(2)-F(25)	1.85(3)	Re(4)-F(45)	1.78(3)
Re(2)-F(26)	1.80(3)	Re(4)-F(46)	1.83(3)

Table 6.5 Bond Angles(°) in Re(CO)$_5$F.ReF$_5$

F(21)-Re(1)-C(11)	91.4(1.4)	F(41)-Re(3)-C(31)	92.8(1.2)
F(21)-Re(1)-C(12)	87.3(1.1)	F(41)-Re(3)-C(32)	84.9(1.8)
F(21)-Re(1)-C(13)	89.7(1.2)	F(41)-Re(3)-C(33)	83.5(1.6)
F(21)-Re(1)-C(14)	88.3(1.4)	F(41)-Re(3)-C(34)	88.7(1.7)
F(21)-Re(1)-C(15)	178.5(1.3)	F(41)-Re(3)-C(35)	176.2(1.6)
C(11)-Re(1)-C(12)	89.4(1.7)	C(31)-Re(3)-C(32)	89.3(1.8)
C(11)-Re(1)-C(13)	178.3(1.9)	C(31)-Re(3)-C(33)	176.2(1.8)
C(11)-Re(1)-C(14)	87.5(1.9)	C(31)-Re(3)-C(34)	90.0(1.7)
C(11)-Re(1)-C(15)	87.7(1.7)	C(31)-Re(3)-C(35)	88.8(1.7)
C(12)-Re(1)-C(13)	89.4(1.5)	C(32)-Re(3)-C(33)	91.0(2.1)
C(12)-Re(1)-C(14)	174.6(1.6)	C(32)-Re(3)-C(34)	173.5(2.2)
C(12)-Re(1)-C(15)	91.4(1.6)	C(32)-Re(3)-C(35)	91.6(2.2)
C(13)-Re(1)-C(14)	93.7(1.7)	C(33)-Re(3)-C(34)	89.3(2.0)
C(13)-Re(1)-C(15)	91.1(1.5)	C(33)-Re(3)-C(35)	95.0(2.0)
C(14)-Re(1)-C(15)	93.0(1.8)	C(34)-Re(3)-C(35)	94.8(2.1)
Re(1)-C(11)-O(11)	173.9(3.7)	Re(3)-C(31)-O(31)	175.2(3.1)
Re(1)-C(12)-O(12)	171.5(3.0)	Re(3)-C(32)-O(32)	169.1(4.5)
Re(1)-C(13)-O(13)	179.2(3.8)	Re(3)-C(33)-O(33)	166.1(4.9)
Re(1)-C(14)-O(14)	167.5(4.1)	Re(3)-C(34)-O(34)	172.8(4.2)
Re(1)-C(15)-O(15)	174.7(3.7)	Re(3)-C(35)-O(35)	177.5(4.0)
Re(1)-F(21)-Re(2)	138.8(1.2)	Re(3)-F(41)-Re(4)	142.0(1.4)
F(21)-Re(2)-F(22)	89.0(1.1)	F(41)-Re(4)-F(42)	88.8(1.1)
F(21)-Re(2)-F(23)	173.5(1.0)	F(41)-Re(4)-F(43)	177.5(1.2)
F(21)-Re(2)-F(24)	86.6(1.0)	F(41)-Re(4)-F(44)	88.9(1.1)
F(21)-Re(2)-F(25)	87.0(1.1)	F(41)-Re(4)-F(45)	88.9(1.3)
F(21)-Re(2)-F(26)	91.8(1.1)	F(41)-Re(4)-F(46)	90.4(1.1)
F(22)-Re(2)-F(23)	97.3(1.2)	F(42)-Re(4)-F(43)	90.7(1.1)
F(22)-Re(2)-F(24)	175.3(1.1)	F(42)-Re(4)-F(44)	177.5(1.1)
F(22)-Re(2)-F(25)	89.4(1.2)	F(42)-Re(4)-F(45)	92.2(1.3)
F(22)-Re(2)-F(26)	91.6(1.2)	F(42)-Re(4)-F(46)	89.1(1.2)

Table 6.5 Bond Angles(^{o}) in Re(CO)$_5$F.ReF$_5$ (cont.)

F(23)-Re(2)-F(24)	87.1(1.1)	F(43)-Re(4)-F(44)	91.6(1.1)
F(23)-Re(2)-F(25)	91.2(1.2)	F(43)-Re(4)-F(45)	93.5(1.3)
F(23)-Re(2)-F(26)	90.0(1.2)	F(43)-Re(4)-F(46)	87.2(1.1)
F(24)-Re(2)-F(25)	89.0(1.2)	F(44)-Re(4)-F(45)	88.9(1.3)
F(24)-Re(2)-F(26)	90.0(1.2)	F(44)-Re(4)-F(46)	89.8(1.2)
F(25)-Re(2)-F(26)	178.4(1.2)	F(45)-Re(4)-F(46)	178.6(1.2)

Table 6.6 Selected Non-Bonded Distances (Å) in Re(CO)$_5$F.ReF$_5$

Re(1)-Re(2)	3.89		Re(2)-Re(3)	5.46
Re(1)-Re(4)	7.91		Re(3)-Re(4)	3.89
Re(1)-F(25)	4.04		Re(3)-F(46)	4.72
Re(1)-F(44)	6.84		Re(3)-F(22)	3.85
Re(1)-F(41)	7.94		Re(3)-F(21)	5.49
Re(2)-F(41)	6.69		Re(4)-F(21)	7.10
Re(2)-C(31)	4.36		Re(4)-C(11)	6.39
Re(2)-O(31)	3.97		Re(4)-O(11)	5.72
F(22)-C(31)	3.17		F(44)-C(11)	5.61
F(22)-O(31)	3.21		F(44)-O(11)	5.18
F(22)-C(34)	3.15			
F(22)-O(34)	3.27			
F(21)-O(31)	3.11,	the closest non-bonding approach		

Table 6.7 Comparison of X-ray Powder Diffraction and Single

Crystal Data for Re(CO)$_5$F.ReF$_5$

hkl	Crystal		Powder		hkl	Crystal		Powder	
	*I$_{obs}$	d$_{hkl}$	d	I'		*I$_{obs}$	d$_{hkl}$	d	I'
020	1424	7.75	7.78	1	133	1145	3.38	3.38	2
021	5538	6.75	6.72	5	042	1935	3.37		
			6.51	1	440	4237	3.19	3.20	2
			6.04	2	441	3216	3.10	3.10	4
400	6248	5.58	5.62	10	124	3774	3.10		
022	21142+	5.13	5.13	8	442	1419	2.89	2.89	2
421	1390	4.30	4.31	4	324	3817	2.88		
023	6452	3.93	3.88		134	5078	2.83	2.81	2
040	6303	3.88			152	1022	2.80		
422	7579	3.78	3.77	9	640	4236	2.68	2.70	2
041	5481	3.73	3.73	2	334	2638	2.66	2.65	br
141	973	3.68	3.66	1	352	1352	2.64		
323	1196	3.48	3.49	1					

+ Inaccurately measured reflection; $w\Delta^2 > 3$

I' = Visually estimated I$_{obs}$.   d in Å.

* Units are arbitrary. Values under 950 are excluded.

Reflections with no clear powder counterpart are:

    341 d=3.34 I=1212   432 d=3.37 I=1124

Fig.6.4 Asymmetric Pair of Re(CO)$_5$F.ReF$_5$ Molecules Drawn with Both the

Re-F-Re Bridges in the Plane of the Paper
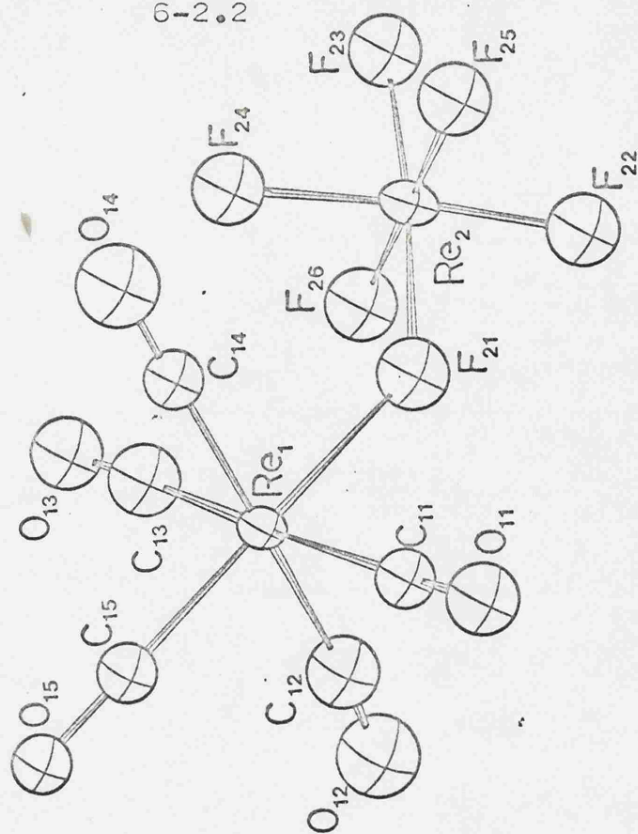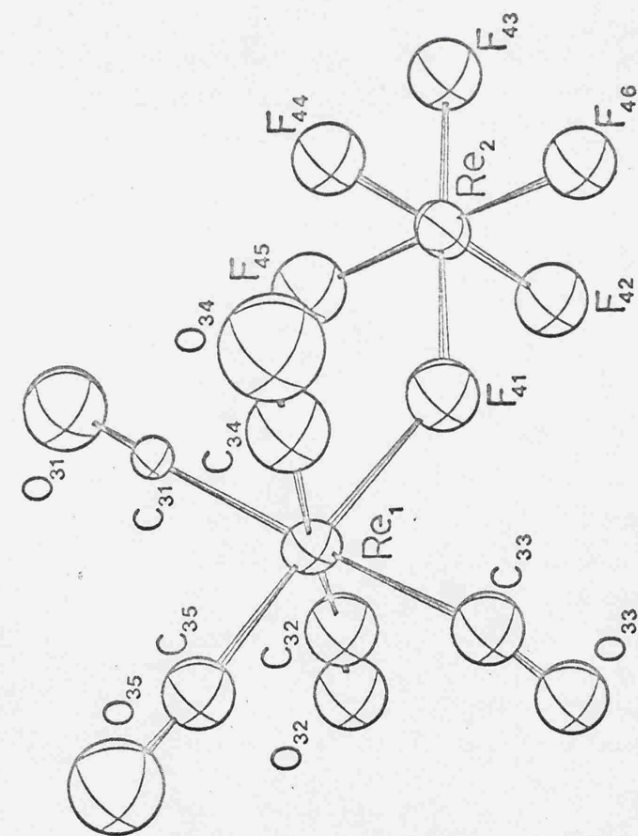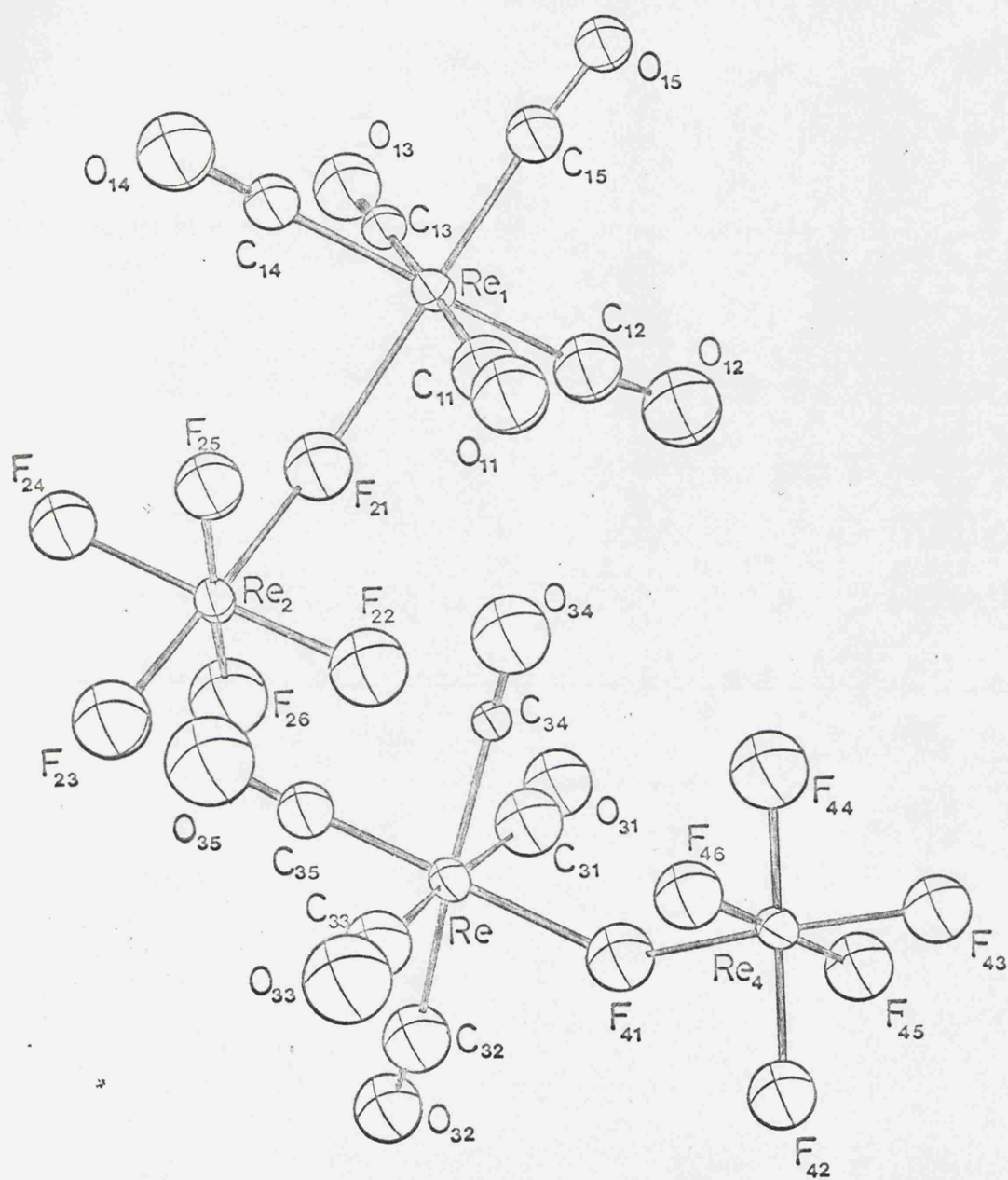
Fig.6.5 Asymmetric Pair of Re(CO)$_5$F.ReF$_5$ Molecules as

Arranged in the Unit Cell

Fig.6.6   Stereoscopic View of Re(CO)$_5$F.ReF$_5$ Unit Cell down c-
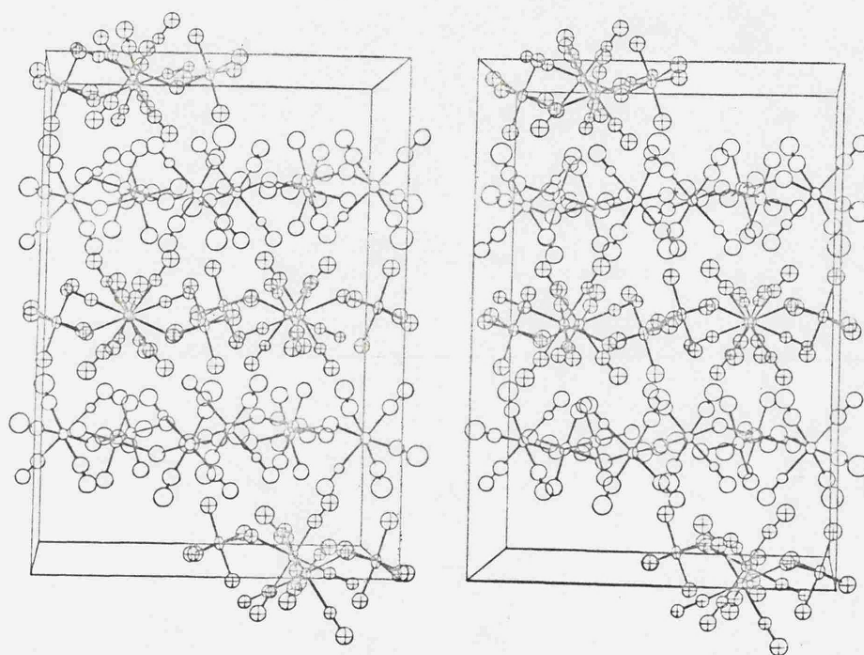
Fig.6.7   "Psuedo-dimeric" Pair of Re(CO)$_5$F.ReF$_5$ Molecules
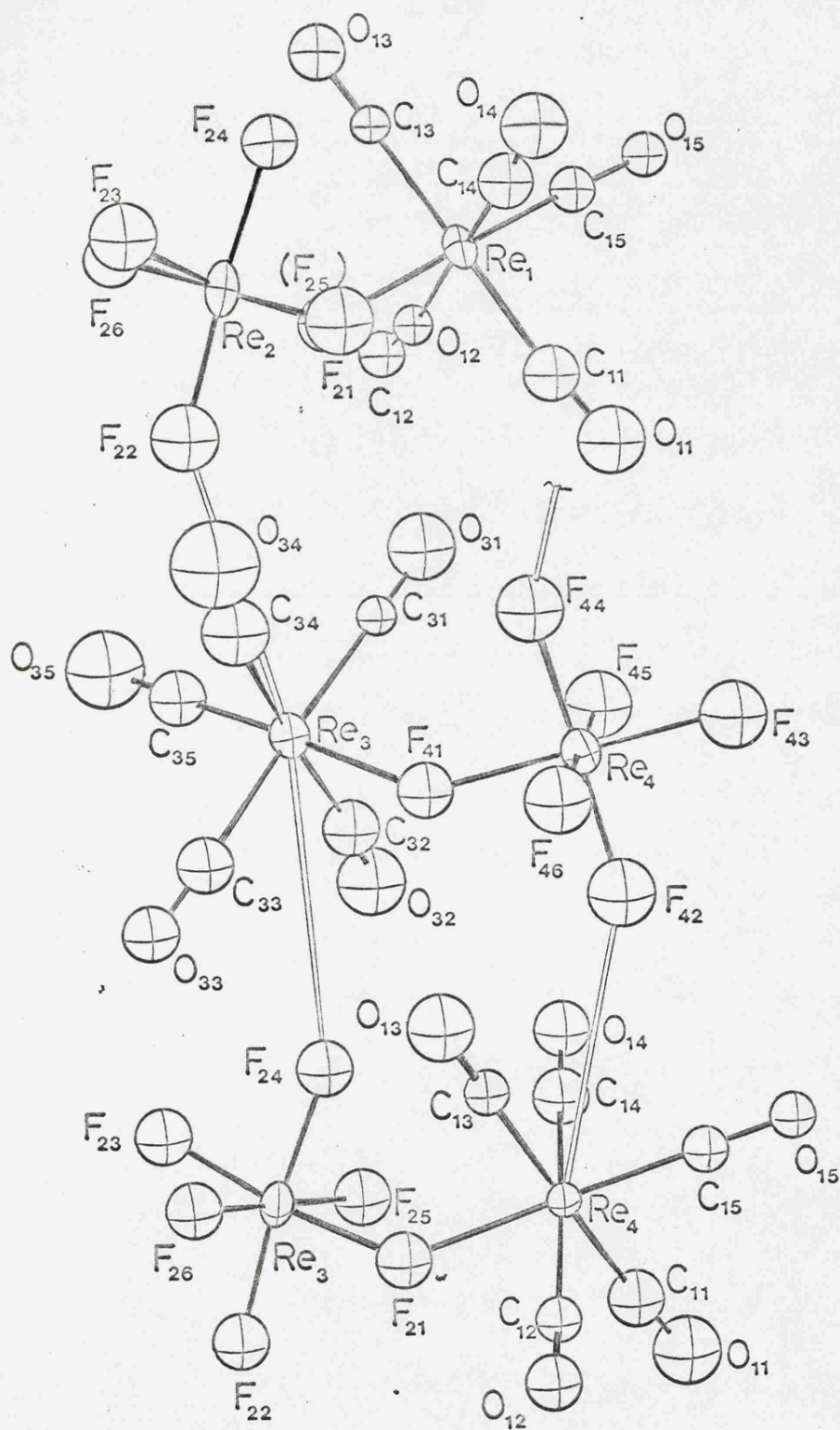
Fig.6.8 Average Molecular Geometry of Re(CO)$_5$F.ReF$_5$
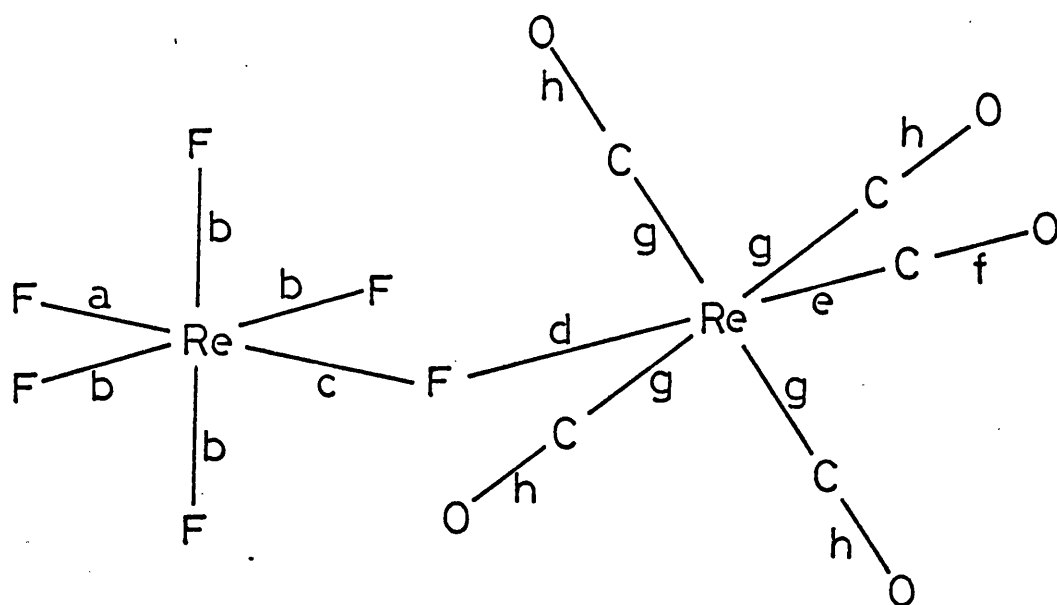
Average bond lengths (Å) with s.d.s., taken from the two

non-equivalent molecules.

a = 1.91(3),   b = 1.83(3),   c = 1.97(2),   d = 2.17(4)

e = 1.89(3),   f = 1.19(4),   g = 1.99(4), h = 1.13(3)

The e.d.s.'s of the individual bonds are:

Re-F 0.03,   Re-C 0.05,   C-O 0.07.

Average Re-F-Re angle is 141(1)$^\circ$.

6-3. DISCUSSION OF THE STRUCTURE

6-3.1 The Establishment of the Formula

The X-ray structural analysis of the orange crystal confirmed the predicted formula of $Re(CO)_5F \cdot ReF_5$. The crystal was shown to be typical of the bulk orange solid by the agreement between the d-spacings obtained from a powder photograph of ground orange crystals, and those calculated from the stronger single crystal reflections (table 6.7). This result also established the formula of the orange-yellow solid from the $Re_2(CO)_{10}/3XeF_2/Genetron\ 113$ reaction.

6-3.2 The Molecular Units and Packing

Each formula unit consists of slightly distorted $Re(CO)_5F$ and ReF_6 octahedra, sharing one vertex, forming a bent, planar Re-F-Re linkage. This plane confers C_s symmetry on the molecule, giving rise to two crystallographically non-equivalent types of molecule, of symmetry $C_s(\sigma_v)$ and $C_s(\sigma_d)$, differing only in the orientation of the $(Re(CO)_4)$ and (ReF_4) equatorial planes, relative to the Re-F-Re plane (see fig.6.4). The Re_1-Re_2 molecule(A) has the ReF_4 unit eclipsed with respect to the Re-F-Re bridge, and the $Re(CO)_4$ unit staggered. The opposite situation holds for the Re_3-Re_4 molecule(B).

Fig.6.5 shows how the two molecules are oriented relative to one another in the crystal. There are eight of these asymmetric pairs in the unit cell, packed so as to form alternate layers of Re_1-Re_2 and Re_3-Re_4 molecules, perpendicular to the c-direction, see fig.6.6. The Re_3-Re_4 layers comprise alternate parallel chains stretching diagonally across the bc plane, whereas the Re_1-Re_2 layers consist of alternate zig-zag chains. Each Re_1-Re_2 molecule has four Re_1-Re_2 and

"one and two halves" Re_3-Re_4 nearest neighbours, and vice

versa. There are thus two distinct types of interaction between

Re_1-Re_2 and Re_3-Re_4 molecules, see fig.6.7. In one, the

$(Re(CO)_5)$ half of an Re_3-Re_4 molecule is close to the (ReF_5)

half of its Re_1-Re_2 asymmetric relative, lying slightly below

it in c- (the $Re_3\cdots F_{22}-Re_2$ approach = 3.85Å), but the (ReF_5)

half is close to the $(Re(CO)_5)$ half of an Re_1-Re_2 molecule

of a different asymmetric pair, lying slightly _above_ it in c-

$(Re_4{-}F_{44}\cdots Re_1$ = 4.16Å). The other interaction is "broad-

side-on" to a _complete_ molecule, $Re_1{'}-Re_2{'}$, lying above it in

a-, but almost on the level in c-. This forms a pseudo-dimeric,

8-membered ring arrangement, which bears some resemblance to

the 8-membered ring in $(Ru(CO)_3F_2)_4$.[32] The order of magnitude

of the two long Re$\cdots$F contacts ($Re_3\cdots F_{24}{'}$ = 4.14,

$Re_1{'}\cdots F_{42}$ = 3.80Å), however, shows that there is no significant

bonding between the $Re(CO)_5F \cdot ReF_5$ molecules.** These Re$\cdots$F

distances, and the remaining intermolecular approaches confirm

that the structure comprises molecular monomers of $Re(CO)_5F \cdot ReF_5$

packed in infinite chains.

6-3.3   The Detailed Geometry, and the Nature of the $Re(CO)_5F \cdot ReF_5$
Molecule

Having established the molecular character of the

compound, it is important to consider its chemical interpret-

ation. It may be most satisfactorily regarded as an adduct

between $Re^I(CO)_5F$ and Re^VF_5, but the nature of the interaction

needs deducing from a detailed analysis of the bond lengths.

This is of particular interest with respect to the continuing

---

** Similar loose oligomeric units are found in $(XeF_5)^+(AsF_6)^-$
(dimers),[187] and $(SeF_3)^+(NbF_6)^-$ (tetramers, in a cuboid
arrangement).[188]

discussion on the nature of fluorine-bridged interactions (see

for example, refs. 189,97 and 98).

The average bond lengths of the two asymmetric mole-

cules are given in fig.6.8, where they are divided into stat-

istically equivalent sets. For example, the eight equatorial

Re^V-F bonds of the asymmetric pair are equivalent, with a mean

value of 1.83Å, the standard deviation between these eight

values being identical to the estimated standard deviations

of the individual Re^V-F bonds (0.03Å). For comparison purposes,

typical values for mean Re^V-F bond distances of 1.84(2) (terminal)

and 2.01(1)Å (bridging) are taken from the $(Re_2F_{11})^-$ anion of

$(Re(CO)_6)^+(Re_2F_{11})^+$, a discrete, centrosymmetric anion with

no close interatomic contacts (see chapter 7). The equatorial

Re^V-F bonds of $Re(CO)_5F \cdot ReF_5$ may thus be regarded as of typical

length.

The axial Re^V-F distances of 1.91(4) (terminal) and

1.97(2)Å (bridging), however, show that the ReF_6 unit has been

distorted tetragonally, so that the $(-F-ReF_4-)$ moiety is

nearly identical to its counterpart in $(Re_2F_{11})^-$. The bridging

Re^V-F distance in $Re(CO)_5F \cdot ReF_5$ is very slightly shorter than

the value for the completely symmetrical Re^V-F-Re^V bridge of

$(Re_2F_{11})^-$. This implies that the Re^V-F bond has a marginally

greater share of the electron density, in a <u>covalent</u> Re^I-F-Re^V

bridge, i.e. that there is only a small polarisation:

$(OC)_5\overset{\delta+}{Re}-F-\overset{\delta-}{Re}F_5$. This also accounts for the lengthening

of the terminal Re^V-F bond trans- to the bridge, relative to

its counterpart in $(Re_2F_{11})^-$ which is indistinguishable from

the other terminal bonds.

There are no directly comparable data for the Re^I-F

bond, but an estimate of 2.16Å for a terminal Re^I-F bond can

be obtained from the covalent radii of fluorine (0.64Å after

Pauling[185]) and of rhenium (taken as 1.52Å, half the Re-Re

distance in $Re_2(CO)_{10}$[118b,**]). This suggests at first sight

that the value of 2.17Å is too short for an Re^I-F bridging

bond, by comparison with the normal substantial lengthening

of bridging bonds relative to terminal. However, consideration

of the bond lengths of many carbonyl halides and their deriv-

atives, including the only comparable low oxidation state metal

fluoride $(Ru(CO)_3F_2)_4$, shows that there is often little or

no difference between terminal and bridging distances for

metals in <u>low</u> oxidation states (table 6.8). In interpreting

the similarity between the Mn-Br distances quoted, Ibers has

suggested that these distances are largely controlled by non-

bonding interactions.[198]

The $Re(CO)_5F$ unit is closely similar to $Re(CO)_5L$ units

in $Re_2(CO)_{10}$,[118] $Re(CO)_5ONO_2$,[199] $Cl.C_6H_4-C(O)-Re(CO)_5$,[200]

$Re(CO)_5H.Cr(CO)_5$[201] and $Re(CO)_5H.Mn(CO)_4.Re(CO)_5$,[202] with

four equivalent Re-C and C-O bonds in the axial plane, and

the Re-C bond length being close to 2.00Å (table 6.9). As

expected, the Re-C bond of the axial carbonyl (trans- to the

ligand L) is lengthened relative to the equatorial carbonyls,

with a corresponding shortening of the C-O bond. This dist-

ortion results from the back-donation of electron density from

the metal dπ orbital to the CO π* orbital, the amount of which

increases the weaker the π-acceptor ability of the ligand L.

Consequently $-F-ReF_5$ is a stronger π-acceptor than $-H-Mn(CO)_4^-$,

but weaker than the benzoyl group in $p-Cl.C_6H_4C(O).Re(CO)_5$,

which has a conjugated π-system.[200] Though the electron

** A value of 1.51Å has been calculated for rhenium $η^5-C_5H_5$

complexes.[190]

Table 6.8   Terminal and Bridging Metal-Halogen Bond Lengths

in Carbonyl Halides

Terminal	Bridging	Structure	Ref.
1.99(3)*	2.01(6)*	$(Ru(CO)_3F_2)_4$	13
2.40(2)	2.40(2)	$(Ru(CO)_3Cl)_2$	191
2.534(4)	2.571(4)	$(Ru(CO)_3Br)_2$	192
2.50(1)	-	$Mn(CO)_5Br$	193
2.527(8)	-	$Mn(CO)_3(CNPh_2)Br$	194
-	2.526(5)	$(OC)_4Mn\underset{Br}{\overset{Br}{<}>}Mn(CO)_4$	195
2.790(2)	-	$(Cr(CO)_5I)^-$	196
-	2.79(1)	$[(OC)_5Cr-I-Cr(CO)_5]^-$	197
-	2.581(2) 2.595(2)	$(cp(OC)_2Fe-I-Fe(CO)_2cp)^+$	106

* Statistically equivalent. Figures taken from final refinement

data (R=0.066) as quoted in ref.13.

$cp = \eta^5-C_5H_5.$

Table 6.9   Bond Lengths in $L-Re(CO)_5$ Structures

Structure	Re-L	Re-C(eq)	Re-C(ax)	C≡O(eq)	C≡O(ax)
$(Re(CO)_6)^+(Re_2F_{11})^-$	-	2.01(4)		1.13(3)	
$(OC)_5Re-Re(CO)_5$ (g)	3.040(5)	2.01(1)	2.01(2)	1.16(2)	1.16(2)
$Re(CO)_5-C(O).C_6H_4Cl$	2.22(1)	2.00(1)	1.96(1)	1.15(3)	1.21(3)
$Re(CO)_5-F-ReF_5$	2.17(4)	1.99(4)	1.89(3)	1.13(3)	1.19(4)
$Re(CO)_5-H-MnRe(CO)_9$	3.392(2)*	2.01(5)	1.86(3)	1.13(5)	1.26(4)
$Re(CO)_5-H-Cr(CO)_5$	3.453(1)*				

The accuracy of the $Re(CO)_5ONO_2$ structure was insufficient to

quote bond lengths.[197]

* Re-Mn and Re-Cr distances.

diffraction study of gaseous $Re_2(CO)_{10}$[118b] failed to detect

a significant difference between the axial Re-C bond length,

X-ray diffraction studies show that this bond is also shorter.[203]

The bond angles show that both rhenium atoms have a

slightly distorted, octahedral arrangement of ligands, but in

view of the high estimated standard deviations, little can be

said about the significance of such distortions.

It is concluded that the Re-F bond distances in

$Re(CO)_5F \cdot ReF_5$ are indicative of an essentially covalent,

fluorine-bridged structure, with a slight polarisation of the

electron distribution in the bridge towards the ReF_5 group.

The fluoride ion donation by $Re(CO)_5F$ is therefore only partial,

and the data give no support for more complete donation to give

an ionic structure $(Re(CO)_5)^+(ReF_6)^-$. The latter structure

would be unlikely in any event, as the $(Re(CO)_5)^+$ cation would

be two electrons short of a noble gas valence-electron config-

uration, and would be formed in the same reaction as that

which produces the extremely stable, 18-electron cation

$(Re(CO)_6)^+$ (equation 3.29). In this respect, the complex is

different from most other fluorine-bridged complexes, such

as $XeF_2 \cdot 2SbF_5$,[189] where chemically reasonable structures may

be written representing the completely ionic form, viz

$(XeF)^+(Sb_2F_{11})^-$. In such cases neither structure accurately

represents the true state of affairs, the latter form neglecting

the substantial covalent interaction between its ions, and the

former the significant polarisation of its fluorine bridge.

$Re(CO)_5F \cdot ReF_5$ may therefore be said to be approaching the

limit of the purely covalent fluorine bridge,** and the bond

** $(Re(CO)_6)^+(Re_2F_{11})^-$ (q.v.), on the other hand, approaches the
opposite limit of a purely ionic lattice, and it is interesting
that the same reaction should have produced two such extremes of
complex interaction.

distances may possibly be used as a yardstick to assess
fluorine-bridging interactions in other complexes (see section
6-4.).

The overall geometry shows $Re(CO)_5F \cdot ReF_5$ to be a carbonyl
halide derivative of the familiar $Re(CO)_5L$ type, but with a
novel "ligand", where the halogen is acting as a donor to an
acceptor halide of the same metal. This is the first structure
of a molecule of this type. The nearest related <u>structure</u>
is of $Re(CO)_5ONO_2$,[204,199] which also possesses C_s symmetry,
with a planar Re-O-N linkage, and has two crystallographically
distinct molecules in the asymmetric unit. Although inaccurately
determined, the Re-O bond distance $(2.15(10)Å)$ appears to be
of the same order as the Re^I-F bond in $Re(CO)_5 \cdot ReF_5$, and again
there seems no doubt of the covalent formulation.

A closer relative is probably the heterometallic
complex $(Re(CO)_5Cl)_2SbCl_5$,[140] but its structure is at present
unknown. Structures have been determined of two
$(\eta^5-C_5H_5)Fe(CO)_2Cl/SbCl_3$ complexes,[142,150] see section 3-5.3,
but these involve only very weak interactions more akin to
those of molecular adducts such as $XeF_2 \cdot IF_5$.[205]

A combination of good carbonyl halide donor ability and
binary halide acceptor strength is required for strong
bridge bonding, and is best achieved where the halogen is
fluorine. The $(OC)_xM$-F bonds are relatively weak, with high
polar contributions, and are thus favourable for bridge
formation to suitable fluoride ion acceptors. This is also
true of other organometallic fluorides as shown by the recent
X-ray structure of the complex $(Ph_3P)_3CuF \cdot BF_3$.[129] This is
particularly interesting, because $(BF_4)^-$ is not normally
regarded as a co-ordinating anion, and the existence of a

discrete $[(Ph_3P)_3Cu]^+$ ion is chemically reasonable. The

Cu---F-BF$_3$ interaction is weak (ave. Cu---F = 2.31Å, c.f.

1.84Å in CuF[206]), but this is in part due to the steric

crowding of the phenyl rings preventing a closer approach of

the tetrafluoroborate group, as the copper co-ordination tends

to tetrahedral. By comparison with $Re(CO)_5F \cdot ReF_5$,

$(Ph_3P)_3CuF \cdot BF_3$ may be regarded as a complex of the known

phosphine fluoride $(Ph_3P)_3CuF$[128] with BF_3, but where the

fluoride ion donation is so nearly complete that the bridging

interaction is very largely ionic, with only a small contri-

bution from the covalent fluorine-bridged form. In contrast,

there is no reason to expect any covalent interaction in the

complex $[(Ph_3P)_3PtF]^+[BF_4]^-$, which contains, presumably, a

square-planar d^8 cation.[127]

The structure determination of $Re(CO)_5F \cdot ReF_5$ confirms

the existence of the carbonyl fluoride-pentafluoride complex,

and now gives credance to earlier postulated structures of

similar species.[30,31] $Re(CO)_5F \cdot ReF_5$ is the first confirmed

compound where the potential octahedral vacancy of a transition

metal pentafluoride has been filled by an organometallic

fluoride donor, and opens up the possibility of a range of

such complexes. In particular, its existence should cultivate

interest in other reported fluorine-bridged organometallic

fluoride complexes $Me_3SnF \cdot BF_3$ and $Me_3SnF \cdot MF_5$(M=As,Sb),[114]

Me_3SbY_2 (Y=BF_4,SbF_6) and $Me_3Sb(SiF_6)$,[115] and $Me_nSiF_{4-n} \cdot SbF_5$

(n=3,2,1).[207] These may show considerable variation in the

nature of their bridging interactions. $Me_3SnF \cdot MF_5$ possibly

possess an infinite chain structure, related to that of the

parent Me_3SnF.[132,208]

Fluorine bridging, also found in the organometallic

structures $(Ru(CO)_3F_2)_4$,[16] $(Me_2N)_2TiF_2$ $_4$,[91] Me_2SnF_2,[209] and

$(Me_2AlF)_4$,[210] is, as predicted,[6] an important stabilising

factor in these complexes. This contrasts with the complexes

of the phosphine dinitrogenyl chloride $(Me_2PhP)_4Re(N_2)Cl$[211]

with numerous acceptors, which are all dinitrogen-bridged.[102]

To bridge via the (trans-) chlorine atom might have significantly

weakened the important $Re \rightarrow N \equiv N$ π-back-donation, whereas

$Re-N \equiv N-M$ bridging[160,161] enhances the co-ordination of the N_2

ligand by back-donation to it from both sides.

6-4. AN ASSESSMENT OF FLUORINE-BRIDGING IN PENTAFLUORIDE ADDUCTS

Having established the predominant covalency of the

fluorine bridge in $Re(CO)_5F.ReF_5$ it was suggested that its bond

distances might be used as model for comparing the nature of

other fluorine-bridged complexes. In the past, such complexes

have frequently been assigned "covalent" or "ionic" structures,

but it has now emerged that the situation is seldom as clear-

cut as such delineations imply, and some monitor of the

strength of the covalent interaction is desireable. One

possibility is the ratio of the bridging metal-fluorine distance

to the terminal, for either the donor species ("cation") or the

acceptor ("anion"). The former criterion has been used by

Edwards[212] to assess the bridging in a related series of MF_3^+

complexes of increasing covalency: $(SF_3)^+(BF_4)^-$ 1.75,

$(SeF_3)^+(Nb_2F_{11})^-$ 1.46, $(TeF_3)^+(Sb_2F_{11})^-$ 1.41 and $(SeF_3^+NbF_6^-)_4$

1.36, (and SbF_3 1.36), approaching the presumed limit of

maximum covalency in the parent base TeF_4 (1.17).[213] Gillespie

et alia have, in effect, followed a similar proceedure in com-

paring the Xe....F bond lengths of XeF^+, XeF_3^+ and XeF_5^+ com-

plexes, and also correlated these with vibrational spectro-

scopic data.[214] These, and subsequent, similar comparisons

(e.g. ClF_2^+ and BrF_2^+ [215] have given satisfactory results within

each restricted series of compounds, but no attempt has been

made to correlate pentafluoride complexes more generally

using the "anion" ratio.

   If the "anion" ratio for $Re(CO)_5F \cdot ReF_5$ of 1.07 is

taken as indicative of a predominantly covalent M-F-M

interaction, the values for other complexes can be compared.

A detailed analysis is beyond the scope of this work, but the

indications are that there is significant correlation in many

cases. Complexes regarded as having a high degree of ionic

character tend to have the bridging bond lengths scarcely

distinguishable (if at all) from the terminal, e.g. $(Xe_2F_3)^+$

$(AsF_6)^-$ 1.00,[187] and $(XeF_5)^+(RuF_6)^-$ 1.01.[216] Complexes

where the interionic interaction is more important have higher

ratios, e.g. $(BrF_2)^+(SbF_6)^-$ [217] and $(SeF_3)^+(Nb_2F_{11})^-$,[218] both

1.04, and in the 1.07-1.08 region are $Re(CO)_5F \cdot ReF_5$,

$NbF_5 \cdot SbF_5$[64] and $AsF_3 \cdot SbF_5$,[219] all of which show evidence of

a largely covalent bridge. Finally, the polymeric and oligomeric

acceptor fluorides themselves[61] have ratios between 1.08 and

1.11 for $(SbF_5)_4$,[125] $(BiF_5)_n$[220] and pentafluorides with the

$(RuF_5)_4$ structure, and 1.15 to 1.17 for $(VF_5)_n$, those with

the $(MoF_5)_4$ structure, and MOF_4 (M=Mo,W,Tc,Re). Thus the

anion ratio monitors a gradation of covalent interaction in

these complexes from essentially ionic lattices (e.g. $(Xe_2F_3)^+$

$(AsF_6)^-$ through to the presumed limit of maximum covalency in

the parent acceptor fluorides.**

   There are, however, less straightforward examples.

Bartlett regarded an ionic formulation for $(XeF)^+(RuF_5)^-$ as

sufficient, without need to invoke covalent contributions.[216]

The anion ratio of 1.07, however, points to a substantially

** This ratio is approached form below in the anion bridge

ratio, and from below in the cation bridge ratio.

covalent formulation, which is also supported by Gillespie's

Xe....F bond correlations. By comparison, $(XeF)^+(Sb_2F_{11})^-$

$(1.05)^{189}$ has a weaker covalent contribution. This again

agrees with Gillespie's correlations, and with the expectations

of the relative fluoride ion donor abilities of RuF_5 and

$2\times SbF_5$.[105] In the remaining XeF_2 complex, $XeF_2 \cdot WOF_4$,[221] the

anion ratio (1.21) is unrepresentative, because the Xe-F-W

bridge is distorted by lying trans- to the short W=O bond.

The bridging W-F distance (2.18Å) is, however, close to its

equivalent (2.19Å) in the revised structure of the parent

$(WOF_4)_4$.[222,223] This suggests predominant covalency in the

Xe-F-W bridge, approaching that in $(WOF_4)_4$ itself, and agrees

with the short Xe....F distance. This both points out a draw-

back to the simple anion ratio criterion, and suggests an

alternative - a direct comparison of the anion bridging bond

length with that of the parent fluoride. Anomalous ratios

may also be caused by structural distortions, as in the case

of the unusual cubic arrangement of $(SeF_3^+NbF_6^-)_4$ (1.12).[188]

Further problems are caused by the small differences involved,

which are often little greater than the standard deviations

of the bond lengths. On the whole, however, for discrete

molecular units, the anion bond length ratio can give qual-

itatively useful comparisons of the covalency of the fluorine

bridge.

6-5.   THE VIBRATIONAL SPECTRA OF $Re(CO)_5F \cdot ReF_5$

With the $Re(CO)_5F \cdot ReF_5$ geometry established, a more

detailed assignment of its vibrational spectra may be attempted.

Because of the effects peculiar to the solid state (such as

lattice interactions and sample inhomogeneity), the assignment

can only be regarded as tentative, but it was felt worthwhile

in view of the interesting nature of the compound, and the
knowledge of its crystal structure. An attempt to obtain a
Raman spectrum of the single crystal resulted in the shattering
of the crystal by the laser beam, and the powder spectrum is
not unequivocal because of decomposition in the beam.

An assignment based on the C_s symmetry of the whole
$Re(CO)_5F \cdot ReF_5$ molecule, neglecting the symmetry differences
between the crystallographically distinct $C_s(\sigma_v)$ and $C_s(\sigma_d)$
molecules of the asymmetric pair, predicts five infrared and
Raman active bands in the carbonyl stretching region (4A' + A").
The peaks at 2172 (i.r. and Raman), at 2100 (i.r.) and 2104
(Raman), and at 2082, 2063, 2046 (factor-group split i.r.)
and 2062 cm^{-1} (Raman), and that at 1980 cm^{-1} (i.r.) can thus
be attributed to A' modes, while the bands at 2022, 2013
(factor-group split i.r.) and 2029 cm^{-1} (Raman) can be
associated with the A" mode, c.f. table 6.10, figs.6.9 and
6.10.

A more instructive alternative is to seek parallels
with the rhenium pentacarbonyl halides (F,Cl,Br,I),[111,224,55]
on the basis of perturbations from the C_{4v} microsymmetry of the
$Re(CO)_5F$ unit. A similar approach has been used in the
assignment of the vibrational spectra of the related C_s molecule
$Re(CO)_5ONO_2$.[204] Three infrared allowed bands in the carbonyl
stretching region are predicted (2A$_1$ + E). The lowering of
the overall microsymmetry by the -F-ReF$_5$ group and coupling
interactions within the crystallographic unit, give rise to
splittings of the degenerate E mode and weak allowance of the
formally forbidden B$_1$, as the perturbation tends towards the
breakdown of four-fold C_{4v} symmetry to that of the C_s point
group.

Table 6.10 Tentative Vibrational Assignment of Re(CO)$_5$F·ReF$_5$, Based on C$_{4v}$ Symmetry

Re(CO)$_5$F·ReF$_5$		Assignment	Re(CO)$_5$ONO$_2$ [204]	
I.R.	Raman		I.R.	Raman
2172 w	2172 m	A$_1$ ν(C≡O)	2161 w	2166 m
2100 vw	2104 s	B$_1$ ν(C≡O)	2099 w	2092 s
2082 m				
2063 s	2062 w	E ν(C≡O)	2047 s	2033 w
2046 m				
2022 sh	2029 w	E ν(C≡O)		2022 w
2013 ms				
1980 w		A$_1$ ν(C≡O)	1986 m	1977 vs
			1945 w,sh	1948 vw
722 m				
705 vw	707 m	A$_1$ ν(Re^V-F)		
	662 w	B$_1$ ν(Re^V-F)		
642 s		E ν(Re^V-F)		
620 s		* ν(Re^V-F)		
588 vs	595 vw, br	E δ(Re-C-O)	592 s / 597 sh	596 w
552 ms		E δ(Re-C-O)	550 m	555 vw
528 w	522 ms	A$_1$ ν(Re-F-Re)[+]		
485 w	497 m	A$_1$ ν(Re^I-X)[‡]	490 w	485 s
439 vw	437 w,br	A$_1$ ν(Re-CO)	437 vw	440 m
420 w		E ν(Re-CO)	407 w	414 vw
	361 vw	A$_1$ ν(Re-CO)	347 m	344 m

i.r. spectra were of nujol mulls, Raman spectra of powdered solids.

* Possibly A$_1$ or E.

+ This band may, alternatively be A$_1$ δ(Re-C-O).

‡ This band is assigned to the ν(Re^I-F) or ν(Re^I-O) mode, c.f. ν(Re^I-F) in Re(CO)$_5$F of 475,[39] or 480 w cm^{-1},[111] but it may, alternatively, be a δ(Re-C-O) mode.[204]
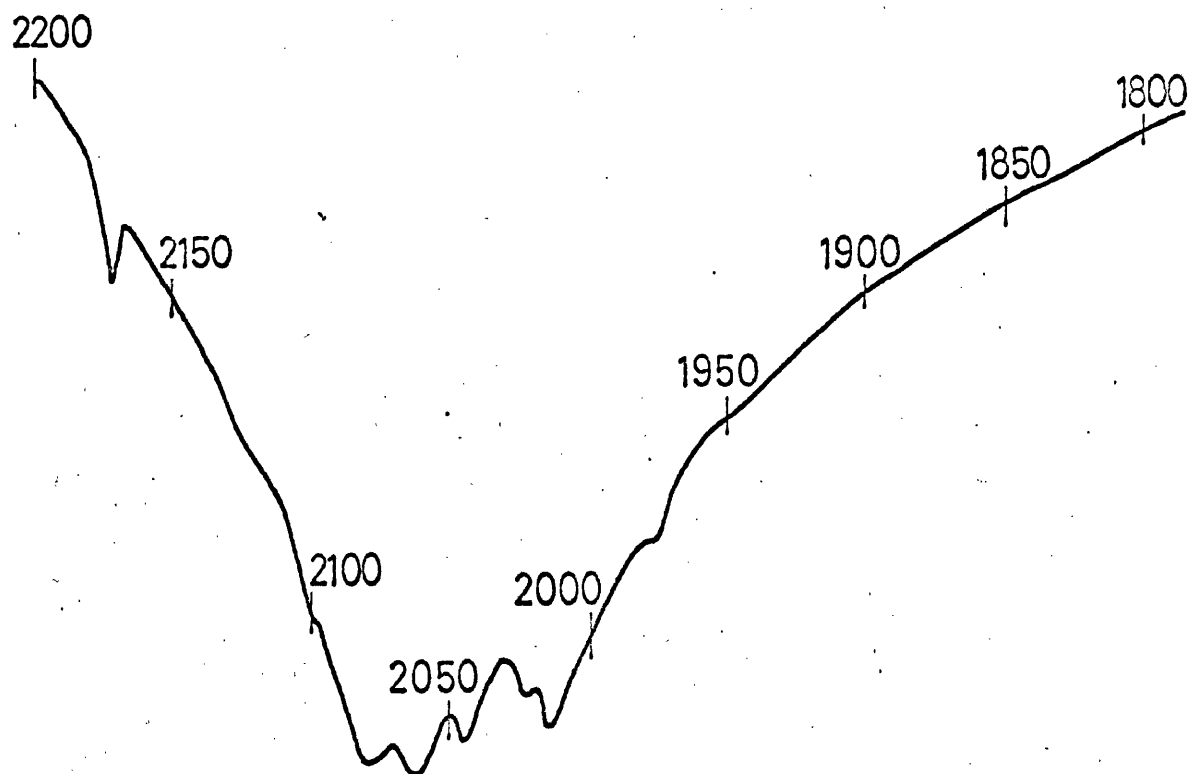
Fig.6.9   Infrared Spectrum of Re(CO)$_5$F.ReF$_5$ (Carbonyl Region)
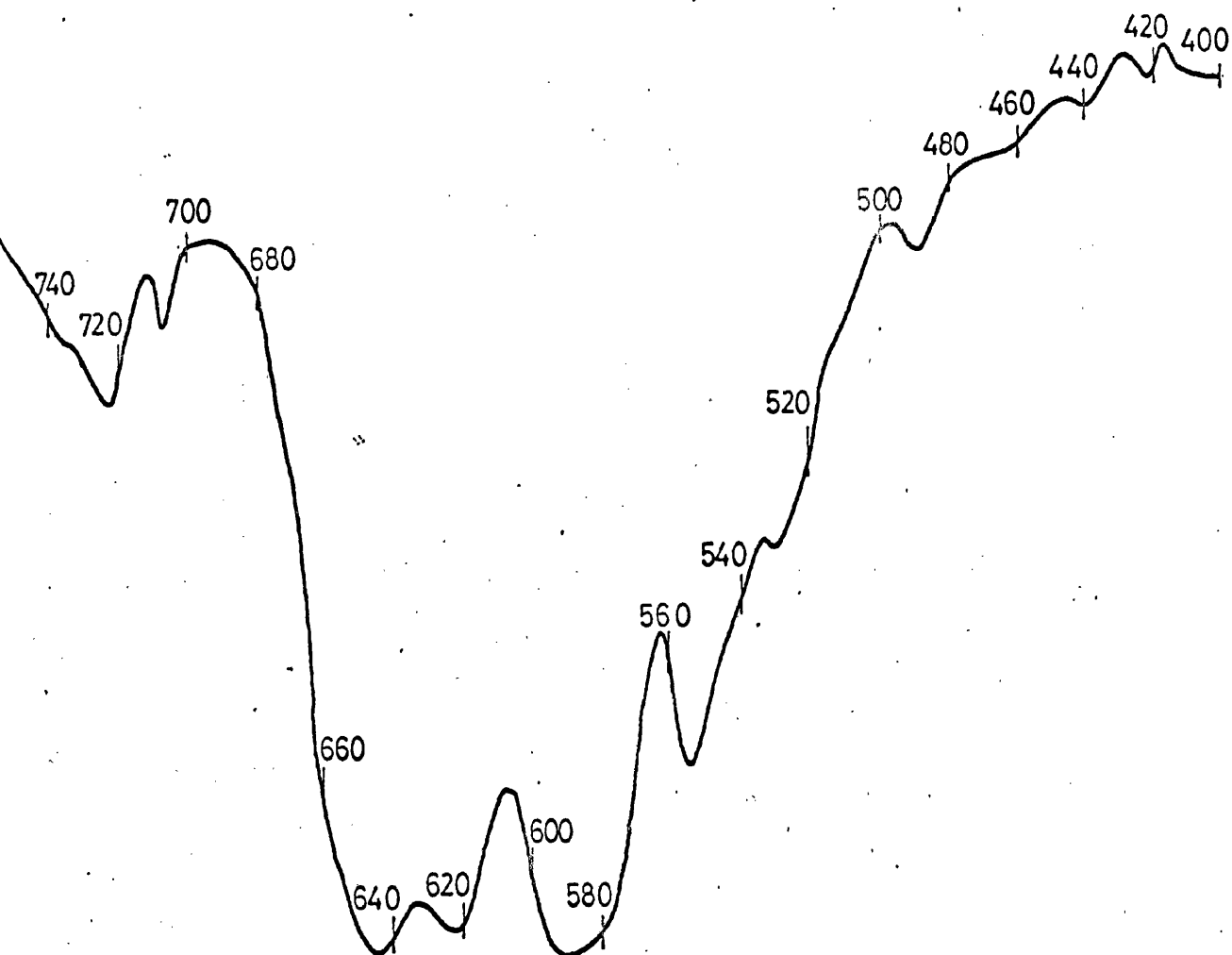
Fig.6.10   Infrared Spectrum of Re(CO)$_5$F.ReF$_5$ (750-400cm^{-1} Region)

	C_{4v}			C_s	
i.r. and Raman	$2A_1$	$\longleftrightarrow$	$2A'$	i.r. and Raman
inactive	A_2	$\longleftrightarrow$	A'	inactive
Raman	B_1	$\longleftrightarrow$	A'	i.r. and Raman
inactive	B_2	$\longleftrightarrow$	A'	inactive
i.r. and Raman	E	$\longleftrightarrow$	$A'+A''$	i.r. and Raman

This gives the assignments listed in table 6.10, and suggests that the previously unassigned peaks at 2032 and 2035 cm^{-1} in the infrared spectra of solid $Re(CO)_5Br$ and $Re(CO)_5Cl$, respectively,[223] should be assigned to factor-group split E modes, as should the 2013 cm^{-1} band in the preliminary spectrum of $Re(CO)_5F \cdot AsF_5$ which Mews' had assigned to the lower A_1 mode.[43] A more detailed spectrum of this latter compound should show bands comparable with $Re(CO)_5F \cdot ReF_5$, including a weak A_1 mode at ~1980 cm^{-1}. Extensive factor group splitting in the carbonyl region has also been found in the infrared spectra of solid $(Ru(CO)_3F_2)_4$, $Ru(CO)_3F_3$ and $(Os(CO)_3F_2)_4$.[16,111]

In the 800-300 cm^{-1} regions, five sets of modes are expected: δ(Re-C-O), (650-500 cm^{-1}); ν(Re-C), (500-350 cm^{-1}); $\nu(Re^V-F_{term})$, (750-600 cm^{-1}); $\nu(Re^V-F_{br})$, and $\nu(Re^I-F_{br})$. Since the crystal structure indicates little ionic character in $Re(CO)_5F \cdot ReF_5$, the microsymmetry about the Re^V atom will be close to C_{4v}, and the assignments have been made on this basis. Few unambiguous assignments of vibrations due to Re-C stretching and Re-C-O deformation modes have been made; those made for this region of $Re(CO)_5F \cdot ReF_5$ follow previous attempts.[223,224]

CHAPTER   7

THE CRYSTAL STRUCTURE

OF $\alpha-(Re(CO)_6)^+(Re_2F_{11})^-$

The proceedure for determining the crystal structure of α-$(Re(CO)_6)^+(Re_2F_{11})^-$ follows that of the previous chapter, and only the unique features of this determination are described.

7-1. OBTAINING THE GEOMETRIC AND INTENSITY DATA

7-1.1 The Geometric Data

Several green crystals from the $Re_2(CO)_{10}$/3ReF$_6$/HF reaction were photographed before finding one which both remained stable and gave satisfactory photographs. This had an irregular wedge shape. Again the symmetry and lack of general systematic absences of the photographs indicated an orthorhombic habit, and a primitive cell. The specific absences were:-

h00 h= 2n+1 only	0k0 k= 2n+1 only	hk0 = 2n+1 only[+]
001 l= 2n+1 only	0kl k+l= 2n+1 only[*]	101 no absences[⊠]
h01 no conditions		

These implied: [*] an n-glide perpendicular to a, [+] an a-glide perpendicular to c, [⊠] no glide perpendicular to b, i.e. a 2-fold rotation axis about b or a mirror plane through b. The two possible space groups are thus Pnma or Pn2_1a, and the former was chosen.

7-1.2 Intensity Data Collection

The crystal was mounted on the diffractometer about the b-axis. For reciprocal layers h0l to h2l, ω was scanned at 1.00 deg.min^{-1} over a range of $1.2°$, up to a maximum ω value of $30°$ and τ of $60°$. A $1.25°$ range was used for layers h3l to h6l. The crystal moved slightly in the capillary during the collection of both of the layers h2l and h3l. This necessitated realigning the crystal (using the diffracto-meter), and repeating the layer both times.

7-1.3   The Crystal Data

$C_6F_{11}O_6Re_3$, M=935.6, green orthorhombic crystals, a= 15.30(9), b= 13.64(7), c= 8.16(3)Å, U= 1703Å^3, Z= 4, D_{calc} = 3.65 g.cm^{-3}, space group chosen Pnma. 763 reflections (before editing) to (sinθ)/λ= 0.70, collected at 22-25°C, with graphite-monochromated Mo-K$_\alpha$ radiation (λ= 0.7107Å), and corrected for absorbtion. Again, the air-sensitivity of the compound rendered density measurements impractical.

The unit cell volume was consistent with one molecule of Re(CO)$_5$F at each of the eight general symmetry positions of the cell (U$_{calc}$= 1736Å^3). The Patterson synthesis, however, showed that there were 12 rhenium atoms in the cell, thus implying a different formula.

7-1.4 Absorbtion Correction

For the highly-irregularly shaped crystal, the method of deMeulenaer and Tompa was used,[225] which involves indexing the faces by means of the orientation with respect to a fixed point in the crystal. The crystal was re-aligned on the diffractometer to have the c*-axis pointing down the goniometer, and the head was transferred to a Nonius Crystal Orienter. The crystal was centred on the microscope crosswires so that, as the crystal was rotated, as many faces as possible appeared edge-on in the field of view intersecting the vertical cross-wire. The intersection point for each edge-on face, and its complementary position 180° away, were noted, to obtain the perpendicular distance D of the face to a central point in the crystal. The x,y and z components of the equation of each face (the coefficients A,B and C) were derived from the corresponding dial readings, and from the angle the face made with the crosswires. These coefficients A-D were substituted·

in the programme ABSCR, together with the calculated linear

absorbtion coefficient, μ, of 226.2 cm^{-1}.

As the formula of the compound was uncertain, the

absorbtion correction was not applied until all the atoms in

the cell had been located by difference Fourier syntheses.

Until then, the uncorrected intensity data, written on to

magnetic tape by the programme PRFTP, were sufficient.

7-2. THE STRUCTURE SOLUTION

7-2.1 Location of the Rhenium Atoms by a Patterson Synthesis

A three-dimensional Patterson synthesis was performed,

exactly as for $Re(CO)_5F \cdot ReF_5$, except that the z-axis was

sectioned at intervals of $^{10}/240$ths. Peak resolution was

sufficient to locate all the rhenium-rhenium vectors, without

the need for a "sharpened" synthesis.

By means of Harker lines and planes, the Fourier co-

ordinates of a rhenium atom at (28,0,30) were deduced. This

accounted for the eight expected Re_1-Re_1 vectors associated

with the eight general symmetry positions of the Pnma space

group, but several other peaks still remained unassigned.

This implied the presence of at least one rhenium atom at one

of the special, symmetry-defined positions of the space group.

The expected co-ordinates were calculated for the four vectors

derived from an atom at the special position $(x', \frac{1}{4}, y')$.

These were found to co-incide with Re_1-Re_1 vectors assigned

to the atom (28,0,30) on the general position. This suggested

co-ordinates for the special atom of (28,60,30).

An atom at this position instead of the general position

still would not have accounted for all the Patterson peaks,

and it was concluded that there was one rhenium atom (Re_1) at

a general position (28,0,30), and one (Re_2) at a special

position. Having fixed Re_1, the correct position of Re_2,

amongst all the possible relatives of (28,60,30), was deduced

to be (92,60,30). This was done by considering all the possible

atom positions which gave rise to the only Re_2-Re_2 Harker

plane (2x',¼,2z'), found at (±56,60,±59) , and searching for

their corresponding Re_1-Re_2 cross-vectors. These two atom

positions successfully accounted for all the Patterson peaks.

As the general position generates a total of eight

symmetry positions, and the special position four, there are

twelve rhenium atoms in the unit cell, ⅔ of type Re_1, ⅓ of

type Re_2. This suggested a 1:2 complex of some description.

This was further supported by a rough plot of the relevant

$$Re_1 - Re_1' \simeq 4\cdot3\,\text{Å}.$$
$$Re_1 - Re_1'' \simeq 5\cdot1\,\text{Å}.$$
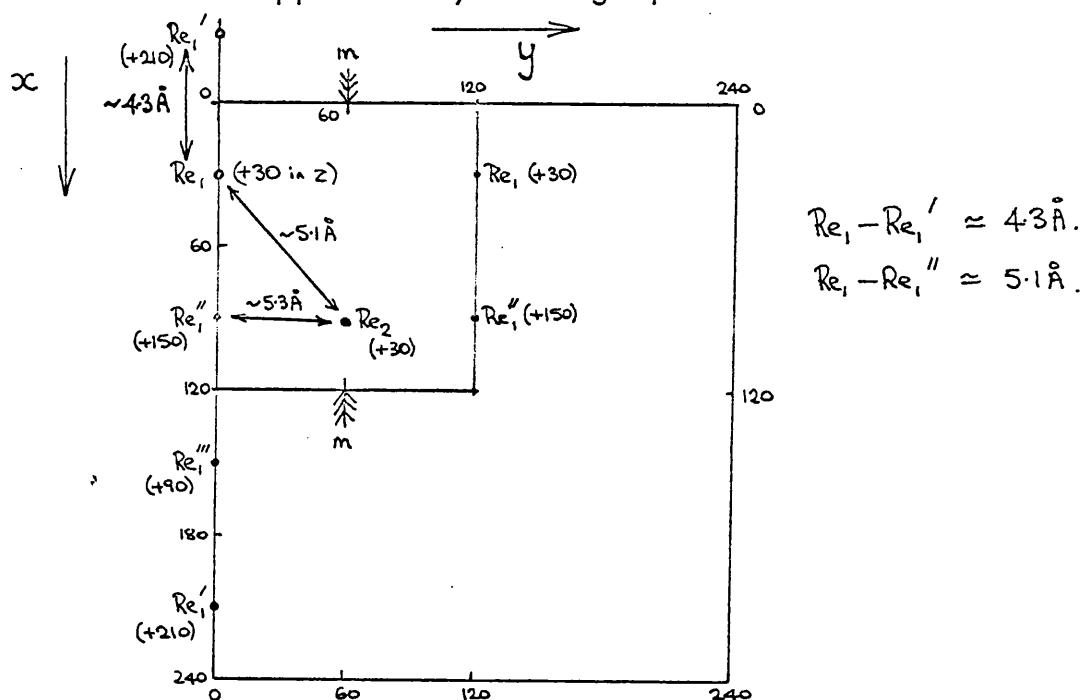
Fig.7.1   Rough Projection of the Rhenium Atom Positions down 001

symmetry-related positions of the unit cell on a projection

down z (fig.7.1). This showed that the Re_1 atoms are grouped

in pairs at a separation of about 4.3Å, consistent with them

being linked by a single fluorine bridge Re_1-F-Re_1. The

distance from the atoms of each pair to the Re_2 or other Re_1

atoms was at least 5.1Å, implying a lattice based on discrete

(Re_1-Re_1) dimers and single Re_2 atoms, with an empirical

formula $Re_3(CO)_xF_y$.

7-2.2 Location of the Light Atoms and Elucidation of the

Formula

After three initial cycles of least squares refinement[**]

with only the position of Re_1 entered, a difference Fourier

synthesis confirmed the position of Re_2 from the electron

density map. With both rhenium atoms entered, three least

squares cycles brought R down to 0.24, and a second difference

Fourier revealed many light atom positions. Because of a

mirror plane at y= 60, the y-range of the map required

changing from 0→120 to -60→+60 in order for both halves of

the asymmetric unit to lie on the Fourier map. Contouring

the map on to perspex sheets revealed an octahedral environ-

ment of six fluorine atoms about Re_1, with F_1 very near the

origin, and three carbonyl groups about Re_2, two lying on the

mirror plane, and one perpendicular to it.
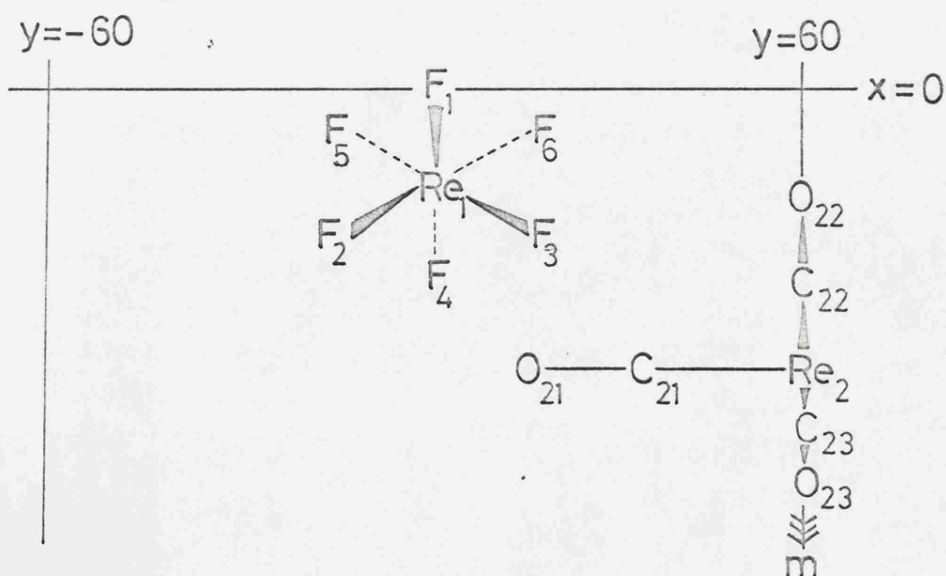
These positions were entered, with initial temperature factors of 3Å^2. Three cycles of refinement brought R down to 0.141, and another difference Fourier was calculated. This established a square plane of 4 carbonyl groups about Re_2, lying on the mirror plane, with $(CO)_{21}$ perpendicular to it, indicating an $(Re(CO)_6)^+$ cation lying astride the mirror plane.

The Pnma space group has a centre of symmetry at (0,0,0), and as a consequence, the ReF_6 octahedron must be related to a second octahedron in the neighbouring asymmetric unit through a shared fluorine atom (F_1) lying at (0,0,0), thus forming an $(Re_2F_{11})^-$ ion, with an exactly linear, single fluorine bridge and with the two halves the Re_2F_{11} unit exactly eclipsed.

The unit cell thus consisted of four molecules of a new ionic salt $(Re(CO)_6)^+(Re_2F_{11})^-$. The calculated volume of 1708 Å^3 (see section 6-1.2) was in excellent agreement with the observed figure of 1703 Å^3. At this stage it was still possible that the space group could be $Pn2_1a$, which would remove the mirror plane through the $(Re(CO)_6)^+$ ion, and the centrosymmetry of the $(Re_2F_{11})^-$ ion. The R-factor was already quite low, however, the subsequent refinement on the basis of Pnma proceeded satisfactorily, and the low anisotropy of the rhenium atom temperature factors indicated that their positions were not being unduly artificially constrained.

7-2.3   Least Squares Refinement

Introduction of all the light atoms lowered R to 0.119 after two cycles of refinement. Temperature factors were between 2.7 and 3.6Å^2 for the rhenium atoms, and 1.6 and 7.6Å^2 for the light atoms. After two more cycles (R= 0.117), the rhenium atom temperature factors were allowed to become

anisotropic, reducing R to 0.102 after four cycles. Some
unrealistic interatomic distances at this stage meant that
the co-ordinates of atoms C_{24}, C_{25}, O_{25} and F_4 had to be changed
slightly. This had little effect, however, as the atoms began
to refine to their previous positions over six cycles, with
R no lower than 0.101, and so their original positions were
restored. The refinement of the rhenium anisotropic temper-
ature factors was ceased to calculate a difference Fourier,
which revealed a low, substantially uniform, residual electron
density in the cell.

Having thus confirmed the formula, the absorbtion
correction was applied (see section 7-1.4), and the corrected
intensity data written on to magnetic tape by PRFTP. After
three refinement cycles, a difference Fourier showed improved
uniformity in the residual electron density. After three
cycles with anisotropic rhenium atom temperature factors,
R was still only 0.116, and thereafter began rising. An
error in the absorbtion correction was amended, and improved
unit cell parameters employed. R fell to 0.101 after three
cycles of isotropic refinement, and to a steady value of
0.077 after three cycles with anisotropic rhenium atom
temperature factors.

Fifteen reflections with $w\Delta^2 > 3$ were edited out by
EDIT, reducing R to a final value of 0.064 after five SFLS
cycles. A difference Fourier map showed no peaks above 15
or below -13, confirming that no significant electron density
remained unaccounted for. A refinement cycle was performed
with the weighting scheme:

$$w = (10 + |F_{obs}|)^{-1},$$

replacing the unit weights used hitherto. No significant
improvement was shown in the temperature factors or bond

distances, and the refinement was ceased.

The final positional and thermal parameters are listed in table 7.1, and the bond lengths and angles in tables 7.2 and 7.3. Again, the standard deviations are fairly high, for reasons similar to the previous structure. ORTEP drawings of the structure are shown in figs.7.2 and 7.3, and a complete listing of the observed and calculated structure amplitudes is given in Appendix 2. The crystal was shown to be typical of the bulk by comparison of the d-spacings of the of the powder photograph with those of the stronger single crystal reflections (table 7.4).

7-3.   DESCRIPTION OF THE STRUCTURE

7-3.1   The Unit Cell Arrangement

Green, $\alpha\text{-}(Re(CO)_6)^+(Re_2F_{11})^-$ consists of a lattice of discrete $(Re(CO)_6)^+$ and $(Re_2F_{11})^-$ ions. The unit cell contents are shown in fig.7.2, and indicate that the cell is made up of zig-zag chains of $(Re_2F_{11})^-$ anions, sandwiched by $(Re(CO)_6)^+$ cations. There is no doubt of the ionic formulation, the closest contacts between the fluorine atoms of the anion and cation atoms being: to Re=4.13Å, to O=2.85Å, and to C=3.19Å, (see figs.7.3 and 7.4). The non-bonded Re....F approaches are slightly longer than those between $Re(CO)_5F \cdot ReF_5$ molecules.

The detailed geometry of the individual ions is shown in fig.7.4. The Re-C, C≡O, and terminal Re-F bond lengths form statistically equivalent sets, with mean values of 2.01(4), 1.13(3) and 1.84(2)Å respectively. The bridging Re-F distance of 2.01(1) is significantly longer than the mean Re-F terminal bond.

Table 7.1 Final Positional and Thermal Parmeters of

$$(Re(CO)_6)^+(Re_2F_{11})^-$$
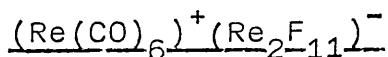
Atom	x/a	y/b	z/c	$B(Å^2)$
Re(1)	0.11220(9)	-0.00105(11)	0.12782(24)	see
Re(2)	0.37747(14)	0.25	0.10831(34)	below
F(1)	0.0	0.0	0.0	7.6(1.0)
F(2)	0.153(2)	-0.092(2)	-0.022(3)	5.9(0.6)
F(3)	0.148(2)	0.105(2)	-0.005(4)	6.3(0.6)
F(4)	0.212(2)	-0.002(3)	0.242(4)	7.7(0.7)
F(5)	0.066(2)	-0.105(2)	0.242(4)	6.2(0.6)
F(6)	0.060(2)	0.088(2)	0.266(3)	5.3(0.5)
C(21)	0.380(2)	0.105(2)	0.097(4)	2.5(0.5)
C(22)	0.267(3)	0.25	0.244(7)	3.4(1.0)
C(23)	0.440(3)	0.25	0.326(7)	3.2(1.0)
C(24)	0.484(4)	0.25	-0.007(10)	4.7(1.4)
C(25)	0.301(4)	0.25	-0.100(9)	5.0(1.3)
O(21)	0.380(2)	0.021(2)	0.099(4)	5.0(0.6)
O(22)	0.206(3)	0.25	0.320(6)	6.5(1.1)
O(23)	0.479(3)	0.25	0.448(6)	6.5(1.2)
O(24)	0.552(3)	0.25	-0.080(6)	5.0(0.9)
O(25)	0.270(4)	0.25	-0.224(7)	7.5(1.3)

Anisotropic Rhenium Atom Temperature Factors $(Å^2)$

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Re(1)	3.26(6)	4.05(7)	4.63(10)	-0.21(7)	0.08(8)	-0.45(7)
Re(2)	2.98(8)	2.81(7)	4.08(14)	0.0	0.15(11)	0.0

Figures in parentheses here, and in the subsequent tables are the estimated standard deviations for the least significant figures.

Table 7.2 Bond Distances (Å) in $(Re(CO)_6)^+(Re_2F_{11})^-$

Re(1)-F(1)	2.009(2)	Re(2)-C(21)	1.98(3)
Re(1)-F(2)	1.85(3)	Re(2)-C(22)	2.03(6)
Re(1)-F(3)	1.89(3)	Re(2)-C(23)	2.02(6)
Re(1)-F(4)	1.79(3)	Re(2)-C(24)	1.89(7)
Re(1)-F(5)	1.84(3)	Re(2)-C(25)	2.07(7)
Re(1)-F(6)	1.84(3)		

C(21)-O(21)	1.14(4)	C(24)-O(24)	1.19(8)
C(22)-O(22)	1.12(7)	C(25)-O(25)	1.12(9)
C(23)-O(23)	1.16(8)		

Table 7.3   Bond Angles (^{o}) in $(Re(CO)_6)^+(Re_2F_{11})^-$

F(1)-Re(1)-F(2)	87.0(0.8)	C(21)-Re(2)-C(22)	92.5(1.0)
F(1)-Re(1)-F(3)	86.9(0.8)	C(21)-Re(2)-C(23)	91.7(1.0)
F(1)-Re(1)-F(4)	179.7(1.1)	C(21)-Re(2)-C(24)	87.6(1.0)
F(1)-Re(1)-F(5)	86.6(0.9)	C(21)-Re(2)-C(25)	88.6(1.0)
F(1)-Re(1)-F(6)	86.8(0.8)	C(22)-Re(2)-C(23)	85.1(2.2)
F(2)-Re(1)-F(3)	92.4(1.2)	C(22)-Re(2)-C(24)	176.8(2.8)
F(2)-Re(1)-F(4)	93.3(1.3)	C(22)-Re(2)-C(25)	88.5(2.4)
F(2)-Re(1)-F(5)	86.8(1.2)	C(23)-Re(2)-C(24)	91.7(2.7)
F(2)-Re(1)-F(6)	173.7(1.1)	C(23)-Re(2)-C(25)	173.6(2.3)
F(3)-Re(1)-F(4)	93.1(1.3)	C(24)-Re(2)-C(25)	94.7(2.9)
F(3)-Re(1)-F(5)	173.4(1.2)	Re(2)-C(21)-O(21)	176.5(3.2)
F(3)-Re(1)-F(6)	88.4(1.1)	Re(2)-C(22)-O(22)	179.7(5.3)
F(4)-Re(1)-F(5)	93.5(1.4)	Re(2)-C(23)-O(23)	177.1(4.7)
F(4)-Re(1)-F(6)	92.9(1.3)	Re(2)-C(24)-O(24)	180.0(5.8)
F(5)-Re(1)-F(6)	91.7(1.2)	Re(2)-C(25)-O(25)	170.3(5.7)
Re(1)-F(1)-Re(1)' 180.0			

Table 7.4   Comparison of X-ray Powder Diffraction and Single

Crystal Data for $(Re(CO)_6)^+(Re_2F_{11})^-$

hkl	Crystal *I_{obs}	d_{hkl}	Powder d	I'	hkl	Crystal *I_{obs}	d_{hkl}	Powder d	I'
			7.60	1	302	4509	3.19	3.16	6
			7.10	4	312	366	3.10	3.09	2
210	509	6.67	6.67	7	421	230	3.09		
			6.39	3	132	?104	2.98	2.93	1
201	993	5.58	5.56	3	241	183	2.91		
121	3793	4.95	4.97	10	322	330	2.89	2.90	1
221	3115	4.32	4.33	10	511	153	2.80	2.79	1
311	175	4.12	4.10	1	402	143	2.79		
230	436	3.91	3.92	6	521	611	2.64	2.63	3
400	4233	3.83	3.79	6	051	423	2.59	2.59	6
321	713	3.65	3.65	4	142	1899	2.58		
122	829	3.41	3.44	5	600	290	2.55	2.55	3
040	7593	3.41			440	1111	2.55		
420	419	3.34	3.33	3	610	259	2.51	2.49	2

I' = Visually estimated I_{obs}.   d in Å.   * Units are

arbitrary. Values under 100 are excluded. Single crystal

reflections with no clear powder counterpart are:

020	d=6.82	I=316	410	d=3.68	I=299
031	3.97	522	411	3.36	200
131	3.84	223	250	2.57	613

Fig.7.2 Unit Cell Contents of $(Re(CO)_6)^+(Re_2F_{11})^-$
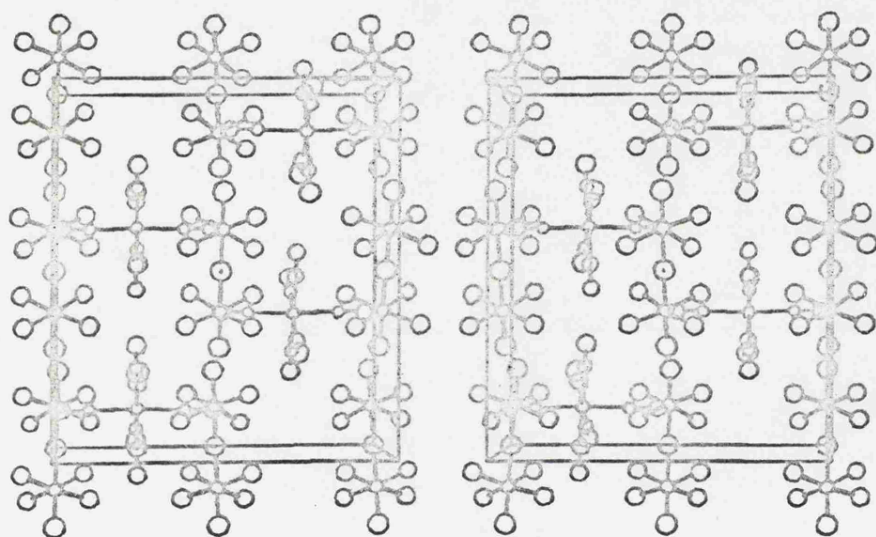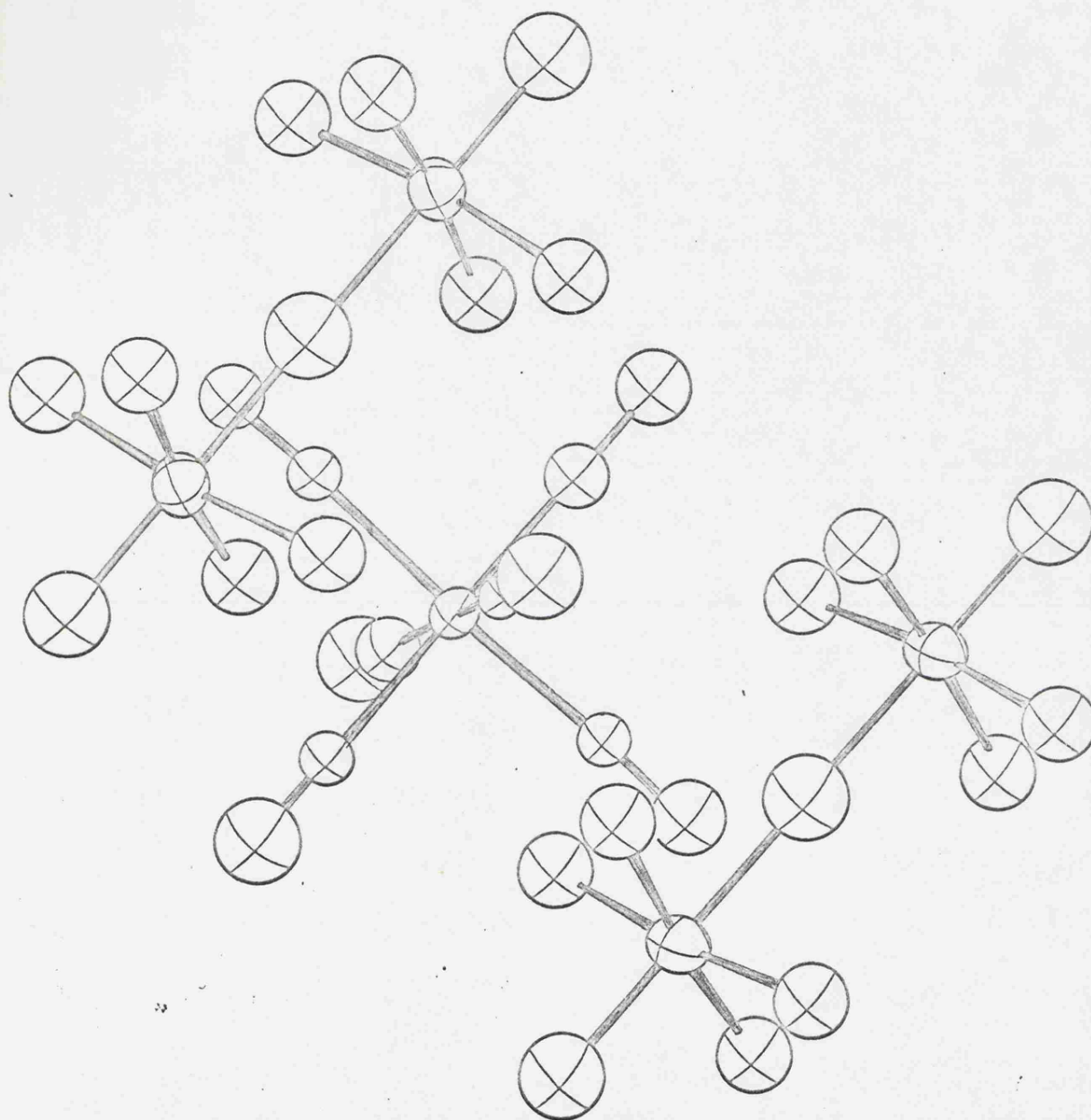
Fig.7.3 Relative Arrangements of One Cation and Two

Anions in $\alpha - (Re(CO)_6)^+ (Re_2F_{11})^-$

Fig.7.4   Detailed Geometry of $\alpha-(Re(CO)_6)^+(Re_2F_{11})^-$
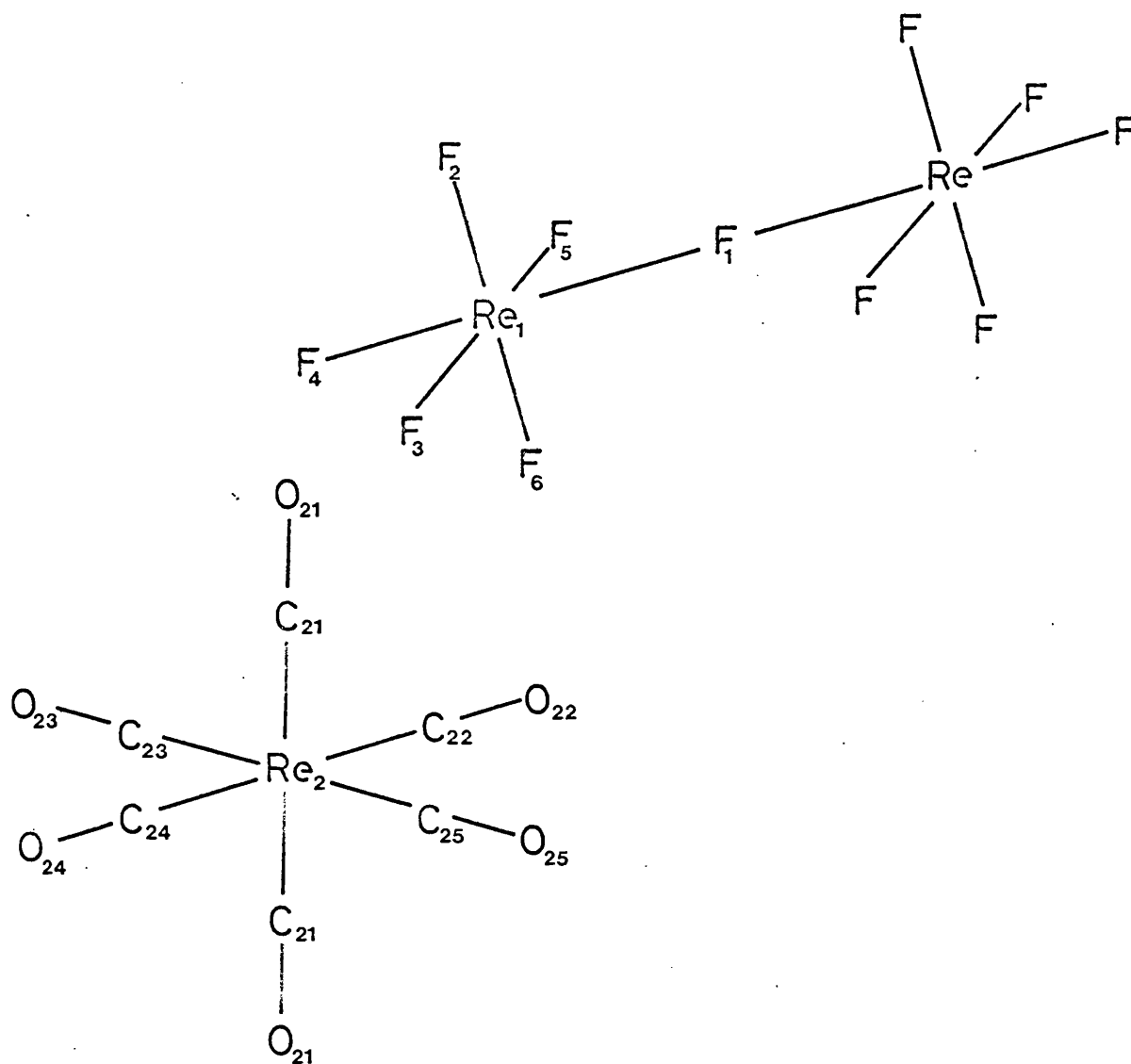
Selected non-bonded Distances:

Re(2)-F(3)	4.13Å	O(21)-F(4)	2.85
Re(2)-F(4)	4.41	C(21)-F(4)	3.19
Re(2)-F(6)	5.30	O(21)-F(3)	3.83
Re(2)-Re(1)	5.31	C(21)-F(3)	3.65

7-3.2   The Cation Geometry

Four carbonyl groups of the cation lie on the Pnma

crystallographic mirror plane, which is also parallel to

the linear F-Re-F-Re-F units of the anions. Two more carbonyl

groups complete an almost exactly regular octahedral $Re(CO)_6$

unit, as expected for an 18-electron, d^6 hexa-co-ordinate

species, and in agreement with the reported vibrational spectra.

Asymmetries in the bond angles are not significant. X-ray

[226] and electron diffraction[227,228] studies have shown the

neutral hexacarbonyls of chromium,[226,227] molybdenum[227,228]

and tungsten[227,228] to exhibit similar geometry, but hitherto

no structure had been performed on any of the isoelectronic

ionic species $(M(CO)_6)^-$ (M=V,Nb,Ta) or $(M'(CO)_6)^+$ (M'=Mn,Tc,Re).

The mean Re-C and C-O bond lengths are comparable

with those of the rhenium carbonyl derivatives previously

listed in table 6.9. It is more interesting, however to

compare these bond distances with those of the isoelectronic

$W(CO)_6$, in the light of the present understanding of bonding

in metal carbonyls.

The $\nu(C\equiv O)$ stretching frequencies in the vibrational

spectra of $(Re(CO)_6)^+$ are known to be increased by some

70 cm^{-1} relative to $W(CO)_6$, as a result of the increased nuclear

charge on the metal.[47] The rhenium $d\pi$ electrons are more

tightly bound, the $d\pi \rightarrow p\pi$ back-bonding to the CO π^* orbitals

is therefore decreased, and the $C\equiv O$ bond strengthened.

Unfortunately the $C\equiv O$ bond length is a poor monitor of such

changes, being largely invariant over a wide range of metal

carbonyl complexes.[229] No particular significance can there-

fore be attached to the probable shortening of this bond

length in $(Re(CO)_6)^+$ (1.13(3)Å) relative to $W(CO)_6$

(1.148(2)Å).[228]

The metal-carbon bond length is, however, more sensitive. Because CO is such a weak σ-donor, the magnitude of the corresponding weakening of the M-C π-system in the above process normally swamps any increase in M$\longleftarrow$:CO σ-donation, and the Re-C bond should be weaker than the W-C. The mean Re-C bond (2.01(4)Å) is unexpectedly shorter than the mean W-C (2.058(3)Å) distance in $W(CO)_6$,[228] or an Re-C bond distance of 2.07Å estimated by Beach and Gray[230] on the basis of early electron diffraction data on $W(CO)_6$.[231]

This lends support, however, to a suggestion made by Abel et alia,[47] on the basis of vibrational data, that considerable strengthening of the M-C σ-bond occurs along the series $(V(CO)_6)^-$, $Cr(CO)_6$, $W(CO)_6$, $(Re(CO)_6)^+$, balancing out the weakening of the M-C π-bond. Accurate bond length data on $(Mn(CO)_6)^+$ and $(V(CO)_6)^-$, where the central atoms are much weaker scatterers, are required to confirm this postulate.

α-$(Re(CO)_6)^+(Re_2F_{11})^-$ is the first crystal structure of an unsubstituted, cationic metal carbonyl. Confirmed species are at present restricted to the manganese triad, the existence of $(Fe(CO)_6)^{2+}$ and $(Os(CO)_6)^{2+}$ [103] now having been questioned, and there being no confirmation of the presence of $(Co(CO)_5)^+$ in the highly unstable $Co_2(CO)_9$.[232] It is interesting that while their carbonyl analogues evade isolation, X-ray structures are known of several unsubstituted cationic isocyanides, e.g. $(Fe(CNMe)_6)^{2+}(Cl^-)_2 \cdot 3H_2O$,[233] and $(Co(CNMe)_5)^+(ClO_4)^-$.[234]

7-3.3   The Anion Geometry and Comparison with Rhenium Fluorides

The anion may be thought of in terms of two ReF_6 octahedra sharing one vertex, which is a centre of symmetry. Consequently the Re-F-Re bridge is exactly linear, and the

two linked octahedra exactly eclipsed. The symmetry and

"isolation" of the anion enabled the use of its bond lengths

as "typical" Re^V-F bridging and terminal distances to inter-

pret the bridge bonding in $Re(CO)_5F \cdot ReF_5$, in the absence of

a full structure on ReF_5. The Re-F distances of both compounds

are compared with those of other rhenium fluorides in table

7.5.

The terminal distances of ReF_7, ReF_6, $^-ReF_5$ (in

$Re(CO)_5F \cdot ReF_5$), and $(Re_2F_{11})^-$ form a group at 1.83-1.84Å,

and those of ReO_3F and $ReOF_4$ a pair at 1.86Å, but in neither

"group" is there a significant variance of the distance with

oxidation state. The long average bond distance of $(ReF_8)^{2-}$

is probably a consequence of the need to avoid ligand

crowding with the larger co-ordination sphere. Long Re-F

bonds also occur when trans- to Re=O bonds in the octahedral

environments of $ReOF_4$[239] and the novel, linear oxygen-bridged,

cubic-cluster anion $(Re_2O_3F_6)_4^{8-}$.[240] Bridging distances

are best considered as individual cases. The Re^I-F bond

in $Re(CO)_5F \cdot ReF_5$ is the first transition metal(I)-fluorine

bond length to be determined apart from CuF and AgF, and is

significantly longer than the higher oxidation state bonds.

The Re....Re separation in $(Re_2F_{11})^-$ (4.02Å) is, however,

longer than that in $Re(CO)_5F \cdot ReF_5$ (3.89Å), but similar to

that in $ReOF_4$ (4.01Å), the respective Re-F-Re bridging angles

being $180°$, $141°$ and $139°$.

7-3.4 A Comparison of the Bridging in $(M_2F_{11})^-$ Structures

and Related Species

A number of crystal structures have been performed

where the M_2F_{11} unit may be identified, with a variety of

Table 7.5   Rhenium-Fluorine Bond Lengths

Compound	O.S.	Re-F(term)	Re-F(br)	Ref
ReF_7 (vapour)[a]	7	1.835	-	233
ReF_6 (vapour)[a]	6	1.832(4)	-	234
K_2ReF_8	6	1.90(4)	-	235
$Re(CO)_5F \cdot ReF_5$	5	$\begin{cases} 1.83(3) \\ 1.91(4)c \end{cases}$	1.97(2)	e
$(Re(CO)_6)^+(Re_2F_{11})^-$	5	1.84(2)	2.01(1)	e
ReO_3F (vapour)[b]	7	1.859(8)	-	236
$ReOF_4$	6	1.86(4)	$\begin{cases} 1.99(4) \\ 2.30(4)d \end{cases}$	237
$(NH_4)_8(Re_2O_3F_6)_4 \cdot 12H_2O$	5	2.02(9)	-	238
$Re(CO)_5F \cdot ReF_5$	1	-	2.17(4)	e

O.S. = Rhenium oxidation state for the Re-F bond in question.

a. Gas phase electron diffraction study.

b. Gas phase microwave study.

c. Bond trans- to bridging fluorine.

d. Bond trans- to Re=O bond.

e. This work.

Table 7.6 Fluorine Bridge Geometry in $(M_2F_{11})^-$ Structures

$$(X)^{+}\text{--}^{e}\text{--}F\underset{a}{\text{---}}M\underset{c}{\text{---}}F\underset{d}{\text{---}}M\underset{b}{\text{---}}F$$
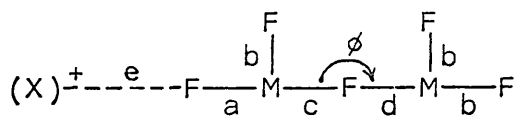
Compound	Extl. Br.	Ave. Term	Extl. Ratio	Intl. Ratio	Cation Ratio*	Intl. Angle	Ref
$(Re(CO)_6)^+(Re_2F_{11})^-$	-	1.84	-	1.0	(4.13)	180°	⊕
$(I_2)^+(Sb_2F_{11})^-$	-	1.85	-	1.0	(2.89)	166	241
$(SbCl_4)^+(Sb_2F_{11})^-$	-	1.87	-	1.0	(~3.0)	155	124
$(ClO_2)^+(Sb_2F_{11})^-$	-	1.82	-	1.03	-	146	242
$(IF_4)^+(Sb_2F_{11})^-$	-	1.87	-	1.0	1.40		243
$(TeF_3)^+(Sb_2F_{11})^-$	1.88	1.84	1.02	1.04	1.41	161	212
$(BrF_4)^+(Sb_2F_{11})^-$	1.86	1.81	1.03	1.11	1.24	173	244
$(XeF_3)^+(Sb_2F_{11})^-$	1.90	1.84	1.03	1.01	1.34	155	245
$(SeF_3)^+(Nb_2F_{11})^-$	1.90	1.82	1.04	1.02	1.46	166	218
$(XeF)^+(Sb_2F_{11})^-$	1.93	1.83	1.05	1.04	1.30	149°	189
	a	b	a/b	c/d	*	∅	

a. Average external bridging M-F bond distance (where one
      can be distinguished), Å.

b. Average terminal M-F distance (Å).

c. and d. Internal bridging M-F distances (Å).

e. Nearest X....F approach (X=Re,I,Sb,etc.)

* Bridging/Terminal X-F ratio in the "cation", where one exists
      For the ionic structures, the value of e is given,
      in parentheses.

⊕ This work.

cations, See table 7.6. $(Re(CO)_6)^+(Re_2F_{11})^-$ is the ideal

limiting case of an undistorted $(M_2F_{11})^-$ anion in an ionic

lattice. $(I_2)^+(Sb_2F_{11})^-$ [241] and $(SbCl_4)^+(Sb_2F_{11})^-$ [124] also

consist of discrete ions, and have a symmetrical Sb-F-Sb

bridge in the anion, but in both cases this bridge is sub-

stantially "bent". The size of the bridging angle in (M_2F_{11})

groups does not therefore appear to bear any relation to the

degree of ionic character of the compounds. The remaining

structures show a significant distortion of the (M_2F_{11}) unit

bond lengths from discrete ion cases, but in contrast to the

complexes discussed in the previous chapter, it is difficult

to establish an order of covalency in the series.

Davies' criterion of the asymmetry of the internal

M-F-M bridge assumes oversimply that this is not affected

significantly by other factors. Thus it fails in the cases

of $(ClO_2)^+(Sb_2F_{11})^-$ [242] and $(Br_2)^+(Sb_3F_{16})^-$,[246] where despite

considerable asymmetry of the anion bridges, the Cation....F

distances clearly indicate predominantly ionic structures.

The external bridging ratio, analogous to the "anion ratio"

used in section 6-4., confirms the substantially ionic nature

of the first five structures in table 7.6, with perhaps a

little covalent interaction in $(ClO_2)^+(Sb_2F_{11})^-$ and

$(IF_4)^+(Sb_2F_{11})^-$, but gives a rather different order for the

remaining structures, compared with that predicted roughly

on the basis of the cation bridge ratios. In particular, the

$(TeF_3)^+$ and $(BrF_4)^+$ structures appear much less covelent than

their positions in their respective cation ratio series would

suggest.

Clearly, though the anion distortions are related to

the degree of covalency in the complexes, they are governed

by a complicated combination of factors, different from those

determining the cation ratios, and currently unravellable.

The number, and angle, of the interactions will be important,

as well as the effect of trans- ligands (most Cation....F-M

bridges lie cis- to the internal M-F-M birdge), and the relative

orientation of the two MF_6 octahedra (usually more or less

eclipsed). These factors are difficult to assess with the

present data on $(M_2F_{11})^-$ complexes.

Discrete, fluorine-bridged, binuclear anions are

still comparatively uncommon, and crystallographic studies

(mostly of antimony species) show that bent bridges are almost

exclusive. Linear arrangements are known only in $(Re_2F_{11})^-$,

$(Zr_2F_{13})^-$ [247] and $(Et_3AlFAlEt_3)^-$,[248] in each case fixed by

a centre of symmetry at the bridging fluorine. Linear

oxygen bridging in the related metal (V) species

$(Re_2O_3(CN)_8)^{4-}$ [249] and $Re_2O_3(S_2CNEt_2)_4$,[250] and the M^{IV} anions

$(Cl_5M-O-MCl_5)^{4-}$ (M=W,Re,Ru,Os[251-254]) are said to be associated

with π-bonding. There is no definite evidence, however, for

π-bonding in pentafluoride derivatives.[255,125] Linear bridging

in the tetrameric MoF_5[110] and WOF_4[222] sturctures, and many

infinite chain structures such as BiF_5[220] and Me_2SnF_2,[209] are

more likely to be determined by symmetry, packing or ionic

bonding considerations, and the same probably applies to

$(Re_2F_{11})^-$.

A compound of formula $Re^{VI}_2OF_{10}$ was proposed for a

by-product of the preparation of ReF_5 and $ReOF_4$ from $W(CO)_6$

and ReF_6, using WF_6 as the solvent,[108] but this has yet to

be confirmed. Non-linear oxygen-bridged $(M_2OF_{10})^{2-}$ anions

(M=As,Sb) have recently been established by X-ray crystal

structures.[256]

7-3.5   The Chemical Significance of $(Re(CO)_6)^+(Re_2F_{11})^-$

$(Re(CO)_6)^+$ is well-known in being amongst the most stable of simple metal carbonyl species, forming salts with a wide variety of anions, including $(PF_6)^-$ [258] and $(AsF_6)^-$.[47] $(Re(CO)_6)^+(Re_2F_{11})^-$ is, however, the first occurrence of an organometallic cation with a transition metal (V) fluoroanion. These latter species had previously been associated only with highly fluorinated systems considered incompatible with oxidation-sensitive organometallic species. The stable co-existence of Re^I and Re^V in the same molecule in $Re(CO)_5F \cdot ReF_5$, and the same lattice in $(Re(CO)_6)^+(Re_2F_{11})^-$, as well as the now growing number of other organometallic compounds exhibiting widely separated oxidation states, imply a greater stability to oxidation of organometallic systems than had been appreciated hitherto. A measure of the stability of $(Re(CO)_6)^+$ has already been noted in its failure to react with an excess of XeF_2 in HF solution. (Section 3-2.3). These compounds also represent a significant extension of the range of penta-fluoride complexes, which would benefit further investigation. $(Re(CO)_6)^+(Re_2F_{11})^-$ in particular provides the first report of the $(Re_2F_{11})^-$ anion, even though analogous ions of most other pentafluorides are well established. This reflects the present neglect of the chemistry of ReF_5, whose only derivatives prior to this study were simply the ReF_6^- salts of NO^+, NO_2^+, K^+, Cs^+ and $(N_2H_6)^{2+}$.[258]

CHAPTER 8

CRYSTALLOGRAPHICAL STUDIES

ON $(Re(CO)_6)^+(ReOF_5)^-$
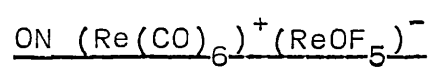
8-1. The Geometric Data

An irregular, brick-shaped, white crystal from the pale green crystalline product of an $Re_2(CO)_{10}/3XeF_2/HF$ reaction was mounted for X-ray studies. Weissenberg and precession photographs revealed spurious spots amidst a pattern of reflections from an orthorhombic unit cell, but the imperfections were not sufficient to prevent analysis of the data. The unit cell parameters (see below) were taken from zero-layer precession photographs, indexed in conjunction with cone-axis and Weissenberg photographs.

There were no general systematic absences, implying a primitive cell. The specific absences were: 0kl, k+l=2n+1; h0l, h+l=2n+1, implying n-glides perpendicular to the a- and b-axes respectively; hk0, no absences. Pnn2 or Pnnm were the only possible space groups consistent with these absences, but a distinction between them was impossible at this stage.

The d-spacings obtained from an X-ray powder pattern of ground white crystals are listed in table 8.1.

8-2. Summarised Crystal Data, and the Formula Unit Volume Fit

$C_6F_5O_7Re_2$, M=651.5, white or pale green orthorhombic crystals, a=6.67(1), b=10.95(2), c=8.81(1)Å, U=644Å^3, Z=2, D_{calc}=3.37g.cm^{-3}, Space group Pnn2 or Pnnm. The data consisted of 415 unique reflections, collected in two parts as described below, using graphite-monochromated Mo-K$_\alpha$ irradiation (λ=0.7107Å).

The probable formula had been deduced to be $(Re(CO)_6)^+$ $(ReOF_5)^-$ on the basis of other physical data (see section 2-2.2). The expected volume for two such molecules, calculated

Table 8.1 X-ray Powder Data for $(Re(CO)_6)^+(ReOF_5)^-$

$\underline{d}$	Intensity	$\underline{d}$	Intensity
5.15	vw	3.48	s
4.98	s	3.12	m
4.84	s	2.45	vw
3.99	w	2.22	w

Table 8.2 Comparative Formula Unit Volumes of Rhenium Carbonyl
Fluorides and Related Species

Molecule	Crystal Habit	V_{obs}	V_{calc}	ΔV_8	Ref.
$(Re(CO)_6)^+(Re_2F_{11})^-$	Orthorhombic	$\frac{3}{2} \times 1135$	$\frac{3}{2} \times 1139$	4	*
$(Re(CO)_4H)_2$	Monoclinic	1×1271	1×1280	9	186
$Re(CO)_5F \cdot ReF_5$	Orthorhombic	4×1184	4×1206	22	
$(Ru(CO)_3F_2)_4$	Tetragonal	1×1146	1×1232	86	32
$(Re(CO)_6)^+(ReOF_5)^-$	Orthorhombic	$\frac{1}{2} \times 1288$	$\frac{1}{2} \times 1376$	88	*
$(Re(CO)_5)_2$	Monoclinic	1×1480	1×1600	120	118a

* This work.

V = Unit cell volume, expressed as a multiple of V_8, the
    volume occupied by the number of molecular units
    required to give a unit containing eight metal
    atoms.

$\Delta V_8 = V_8(calc) - V_8(obs)$, i.e. the scaled difference for
    comparing the fits.

on the basis of the principles established in section 6-1.2,

is 688$Å^3$. This is in reasonable agreement with the observed

unit cell volume, 644$Å^3$, when compared with the correlations

for related compounds (table 8.2). Although the formula

$(Re(CO)_6)^+(ReOF_4)^-$ provides a better fit (U_{calc}=650$Å^3$), it

is not consistent with the other physical data on the compound.

$(Re(CO)_6)^+(ReOF_5)^-$ is thus regarded as the most likely formula.

8-3. A Consideration of the Photographic Intensity Data

The general pattern of the X-ray photographs was of

a regular array of strong reflections, with a few, additional,

and very much weaker reflections lying between major rows.

This suggested that the major reflections monitored primarily

a simple sub-lattice of rhenium atoms, in very similar

environments. The weak reflections, however, only monitored

the light atom positions, or any slight asymmetry of the rhenium

atom positions they might impose.

If the crystal is a simple lattice of $(Re(CO)_6)^+$

and $(ReOF_5)^-$ ions, the co-ordination spheres of the rhenium

atoms are indeed very similar. As the scattering is so

dominated by the rhenium atoms, the intensity data may not

distinguish between the co-ordination spheres of anion and

cation, and may thus monitor only an averaged rhenium atom

environment. This problem is accentuated if the space group

is Pnnm, because in this case both anion and cation are

required to be centrosymmetric. Concomitantly, this would

render a distinction between anion oxygen and fluorine atoms

impossible. With Pnn2, the centrosymmetric requirement is

removed, and the situation is more favourable for distinguishing

between anion and cation. It still might not be possible,

however, to define the anion geometry more than as "an

octahedral array of six light atoms."

8-4. Diffractometer Intensity Data Collection

To minimise the above problems, these vitally import-

ant weak reflection intensity data were collected separately

from the strong, using a longer counting time to improve the

precision of their measurement.

The crystal was mounted on the diffractometer about

the b^*-axis. Systemmatic weaknesses noted in the pattern of

the strong reflections suggested that the rhenium atoms lay

on a body-centred sub-lattice:

Okl: k=2n+1, l=2n+1;   c.f. true absences k+l=2n+1.

1kl: k=2n+1, l=2n   ;   c.f. no true absences,

hk0: h=2n+1, k=2n+1;   c.f. no true absences,

hk1: h=2n   , k=2n+1;   c.f. no true absences.

The strong reflections were therefore collected by selecting

only the reflections of this body-centred lattice, with no

absences. The even layers h0l to h12l (there being no strong

reflections for odd layers in b-) were collected by scanning

a range in ω of 1.20^o, at a rate of 1.00 deg.min^{-1}, up to a

maximum ω value of 30°, and maximum Υ of 60°, using a ten

second background count before and after each reflection. Two

check reflections were measured after every 20 reflections.

The weak reflections were collected in two sets.

The even layer reflections were collected for the full lattice,

using the true absences, but those reflections of body-centred

origin (for which h+k+l=2n) were rejected. For the odd layers,

all reflections were collected. An ω scan range of 1.35^o was

used in both cases, at 0.5deg.min^{-1}, with a 30 second back-

ground, up to a maximum ω of 20° and Υ of 40°, using one

check reflection after every 20.

The data were corrected for absorbtion of X-rays by estimating the crystal to be a rectangular block of dimensions 0.530x0.317x0.270mm., with the a-axis perpendicular to the largest face, and thus obtaining the equation for each face. A value of 199.33 cm^{-1} was calculated for the linear absorbtion coefficient, assuming a formula of $(Re(CO)_6)^+(ReOF_5)^-$. The coefficients A,B,C,D and μ were substituted in the programme ABSCR, as before.

8-5. Attempted Structure Solution.

The subsequent parts of the analysis were performed by Dr. D.R. Russell. A body-centred array of rhenium atoms was found by Patterson and Fourier methods. A pattern of light atom peaks round one atom in the difference Fourier map was consistent with an $(Re(CO)_6)^+$ ion, but it has not yet been possible to identify uniquely the light atom arrangement of the anion, whichever of the two space groups was used.

Thus, a full solution of the crystal structure of the white compound was not found, but the available X-ray diffraction data are consistent with the formula, $(Re(CO)_6)^+$ $(ReOF_5)^-$, already proposed on the basis of other physical and chemical data.

EPILOGUE

This study has set out to establish an understanding of the carbonyl fluoride system of rhenium, and to use that as a basis for understanding the whole field of transition metal carbonyl fluorides, considered in the context of organometallic halides in general. It is the author's opinion, however, that such a work is not just a study in chemistry, but, in a wider sphere, is seeking to unravel some small part of the glory of God, as revealed in creation. I believe that the order of the universe is not a "chance" occurrence, but the handiwork of a wise and compassionate creator, who made man as part of that creation that he might seek after God and enjoy a relationship with Him, and understand and subdue the world around him. No mechanistic understanding of any aspect of the universe, great or small, removes its dependence on the sustaining word of God. The scientist is called to look at his test tube or into his microscope at the wonders of creation, and give praise to Him who created it. And so I do.

"The heavens are telling the glory of the Lord,
and the firmament proclaims His handiwork"

(Psalm 19,v.1)

APPENDIX 1

A listing of the observed and calculated structure amplitudes for $Re(CO)_5F \cdot ReF_5$. Values of $|F_{obs}|$ are multiplied by an overall scale factor, K, of 3.614, while both $K|F_{obs}|$ and $|F_{calc}|$ are multiplied by a factor of 20.

The output is of the form:

*   h   k

l KF_o F_c

```
* H= 0 K= 2        * H= 1 K= 5        10 1934 2138      3 4222 4180      3  715  390    * H= 4 K= 12
  0 3838 3262        1  557  456      * H= 2 K= 3        4 8027 8286      4 1538 1540      0  894  904
  1 7000 7145        2 5000 4492        1 1280 1224      5 1862 1955    * H= 3 K= 17      1 1645 1535
  3 7655 7537        3 1434 1397        5 1403 1274      7 2418 2524      4 3077 3345      2 2750 2628
  4  508  512        4 1698 1450      * H= 2 K= 4        8 4390 4923    * H= 3 K= 18      3 3850 3850
  5  536  424        5 1754 1663        1 4197 3822      9 2566 2886      4  022  872      5 1621 1570
  6 3314 3157        6 9280 8047        1  862  705     10 1296 1391    * H= 3 K= 19      6 1354 1366
  8 3051 3300      * H= 1 K= 6          2 2054 2827    * H= 3 K= 3        2 1387 1701      7 1547 1771
  9 2904 3105        1 3040 2870        4 2301 2184      1  870  748      4 1090 2536     10 2565 2634
 11 2744 3237        2 3170 2811        5 4116 3845      3 2111 2070    * H= 3 K= 21    * H= 4 K= 13
* H= 0 K= 4          3 2183 2117        8 1715 1630      4 7075 6802      4 1611 1881      0  775  745
  0 11207 11150      4 1611 1529        9 1521 1464      5 2803 2753    * H= 4 K= 0        1 1100 1025
  1 9677 10520       5 1240 1255      * H= 2 K= 5        6 1685 1880      4 6391 7529      5  717  630
  2 6084 5600        6 5767 5577        0 1580 1394      7 1969 2126      6 1890 2277    * H= 4 K= 14
  4 3949 3649        8 1381 1389        1 2172 2092      8 2955 3040    * H= 4 K= 1        0 1152 1158
  4 2338 2252        9 3333 3364        5 1406 1390      9 1167 1172      0 3166 3300      1 1863 1990
  5 5662 5458       10 1760 1648        7  884  866     12 1566 1826      1 3254 3486      2 1579 1435
  6 2678 2391      * H= 1 K= 7        * H= 2 K= 6      * H= 3 K= 4        2 1137  870      3  786  878
  7 4413 4566        3 1876 1846        0 1540 1342      1 4786 4738      3 2760 2953      5 1851 1940
  8 7105 7208        4 8268 7630        1 2122 2055      2 1268 1234      4 1593 1702      7 1367 1600
  9 2608 2750        5 1086  953        2 4430 3875      3 2150 2018      6 1390 1530    * H= 4 K= 15
 10 4157 4495        8 3954 3947        3 1825 1770      4 2274 2225      8 1586 1660      0  777  638
 11 2626 2757       12 2192 2035        4 2013 1841      5 5203 4949      9 1700 1614    * H= 4 K= 16
 12 3416 3935      * H= 1 K= 8          5 2124 2081      6 4431 4309    * H= 4 K= 2        0 1030 1068
* H= 0 K= 6          1 3629 3452        7 4107 4041      7 4832 4922      0 2600 2553      3  970 1066
  0 10023 9715       2 1339 1360        8 1055  950      8 1747 1567      1 5164 5585      5 1550 1658
  1 2396 2350        3 3356 3268        9 1108 1137      9 1403 1364      2 12724 14137  * H= 4 K= 18
  2 3213 3085        4 4040 3750       10 2357 2528     11 2032 2405      3 4057 4205      3  830  868
  3 7965 7856        5 1692 1634      * H= 2 K= 7      * H= 3 K= 5        5  794  824    * H= 5 K= 0
  4 5435 4977        6 1903 1984        0 1281 1120      1 1802 1848      6 2729 2734      2 2290 2374
  5 2304 2060        8 2797 2700        2 1868 1865      2 5907 5419      8 3093 3110      4 1261 1123
  6 2637 2613        9 2763 2803      * H= 2 K= 8        5  984  846      9 1948 1900      6 4494 4691
  8 4679 4814       10 1251 1471        0 4896 4387      6 7010 6514     10 7266 8463    * H= 5 K= 1
  9 3145 3512       11 1434 1224        1 3164 2093      7 1354 1201     11 2475 2801      1 1350 1404
 10 3069 3437      * H= 1 K= 9          3 6037 5821    * H= 3 K= 6      * H= 4 K= 3        2 4481 4543
 11 3266 3485        1 1374 1279        4 1818 1753      1 1260 1209      0  991  849      3 3790 4134
 12 3913 4020        2 3740 3440        5 2649 2358      2 1564 1456      1 2303 2242      4 3853 3890
* H= 0 K= 8          3 1744 1658        6 1807 1748      3 4916 4681      2 4985 4872      5 2355 2411
  0  780  550        4  931  942        8 1342 1103      5 3662 3398      3  807  797      6 6175 6332
  1 3673 3630        5 2458 2388        9 2681 2701      6 5580 5142      4  977 1047      7 2502 2491
  2 9729 9244        6 4717 4818       10 1706 1566      9 3544 3485      5  680  668      8 1982 2073
  3 2061 2040        7 1741 1916       11 2439 2327     10 1867 1514      7 1507 1405      9 1752 1745
  4 1036  993      * H= 1 K= 10        12 1968 1854    * H= 3 K= 7       10 2094 2245    * H= 5 K= 2
  5 3092 2924        3 3911 3766      * H= 2 K= 9        2  630  503    * H= 4 K= 4        1 1150 1150
  6 1160 1193        5 2651 2720        0 2313 1944      4 7722 7231      0 10287 10361    2 4301 4433
  7 3413 3322        7 3491 3732        4  758  560      6  723  775      1 8321 8826      3 3424 3610
  8 1681 1628       11 2383 2329      * H= 2 K= 10       8 3285 3275      2 5894 5505      4 1965 1790
 10 4884 5232      * H= 1 K= 11        0 5454 4962     12 1797 1851      3 4041 3986      5 1440 1650
* H= 0 K= 10         1  741  590        1 5389 5284    * H= 3 K= 8        4 1999 1673      6 2082 2050
  0 8230 7883        2 1510 1401        2 1413 1559      1 3377 3143      5 3615 3654      7 1756 1929
  1 2874 2754        3 2196 2193        3 1180 1182      2  694  706      6 1600 1626      8 2320 2334
  3 1666 1532        4 3191 3213        4 1397 1315      3 1521 1398      7 3780 3681      9 2071 2118
  4 2291 2243        5 1648 1703        5 3802 3604      4 4028 4413      8 6040 5975    * H= 5 K= 3
  5 4212 4312        6 1733 1653        7 1072 2111      6 2525 2488      9 2546 2429      1 1670 1754
  6  971  934        7 1497 1720        8 3297 3330      7 1245 1320     10 4132 4166      2 2055 2020
  7 1664 1432        8 1540 1656        9 1386 1459      8 3294 3132     11 2420 2510      4 7740 7826
  8 3264 3460      * H= 1 K= 12        12 2513 2159      9 2043 2153     12 3435 3713      5 2694 2761
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* H= 0 K= 12         3 2820 2753        0  883  793    * H= 3 K= 9        0 3232 2930      7 1861 1652
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  3 3817 3963        9 2608 2732      * H= 2 K= 12       4 1605  901      3 2044 1860    * H= 5 K= 4
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  5 1461 1559        1 1309 1345        1 2087 2080      6 5616 5604      5 1034 1003      2  748  715
  6 1358 1431        2 1081 1192        2 6755 6599      7 1195  874      8 1943 2033      3 1424 1353
  7 1670 1862        3 1318 1390        3 3859 3921    * H= 3 K= 10     * H= 4 K= 6        4 4670 4697
 10 2602 2826        4 2635 2621        5  900  929      1 3347 3195      0 11798 11797    5 1321 1342
* H= 0 K= 14         6 1926 2126        9 1332 1156      2 1670 1562      1 3012 3045      7 2190 2390
  0  880  836        7 1371 1446       10 4121 4414      3  914  963      2 2903 2814      8 2361 2340
  1 1925 1955      * H= 1 K= 14      * H= 2 K= 13        4 1306 1175      3 6756 6775     11 2400 2545
  2 1402 1425        1 1333 1364        1  853  830      5 2050 1754      4 4638 4325    * H= 5 K= 5
  5 1969 2077        2 1738 1733      * H= 2 K= 14        6 2009 2018      5 2367 2145      1 1246 1267
  7 1560 1748        3  896  880        0 7808 7793      7 2811 2909      6 2514 2392      2 4785 4526
  8 1695 1787        4  818  750        2 1251 1146     11 2690 2636      8 4650 4517      3 1180 1100
* H= 0 K= 16         6 2670 2884        3 1075 1204    * H= 3 K= 11      10 3125 3073      6 7870 7509
  0 1235 1110      * H= 1 K= 15        4 2875 2931      1 1152 1110     11 2774 2670    * H= 5 K= 6
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* H= 0 K= 18         5 1170 1318        0 1056  862      5 1945 2111      2 2164 1981      5 1370 1194
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* H= 1 K= 2        * H= 1 K= 16      * H= 2 K= 16        7 1776 1820     10 1467 1468      7 1621 1763
  1 1249 1085        1 1086 1243        1 2537 2832     10 1467 1468    * H= 4 K= 8        8 1865 1926
  2 2008 1773        2 2200 2321        3 1218 1300    * H= 3 K= 12      1 2747 2536      9 2718 2694
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  8 3644 3962        2  835  765        3 1046 2175      1  904  986      7 3387 3275      5 2161 1900
  9 2633 2923        3 1102 1308      * H= 2 K= 20       2 1318 1413      8 1849 1605      8 3456 3348
 10 1131 1286        4 1029 1054        0 3248 3438      3 1907 1890     10 4920 4854      9 1272 1540
* H= 1 K= 3          5 1433 1380        1 1511 1767      4 2698 2794    * H= 4 K= 9       12 2051 1870
  1 1890 1666      * H= 1 K= 19        3 1093 1309      5 2172 2278      0 1871 1784    * H= 5 K= 8
  2 1180  996        2 1416 1569        4 1225 1317      6 1986 2244      1 1548 1468      1 2753 2638
  3 3914 3680        6 1834 2282      * H= 3 K= 0        7 1457 1694      2  773  649      2  842  734
  4 8756 8295      * H= 1 K= 20        2 6141 7323      9 1302  904      5 1222 1042      3 3947 3786
  5 3454 3153        2  955  982        6 7796 9008    * H= 3 K= 14    * H= 4 K= 10       4 2633 2283
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  8 4279 4287      * H= 1 K= 21        1 1590 1552      6 1656 1763      3 1517 1427      7 1058 1071
 12 1774 1990        4 1461 1769        2 3303 3284      7 1228 1303      4 2544 2445      8 1927 1011
* H= 1 K= 4        * H= 2 K= 2          3 2885 2963    * H= 3 K= 15      5 4470 4226     10 1342 1093
  1 4116 3801        1 1554 1362        4 2835 2835      2 2174 2208      6 1211  988    * H= 5 K= 9
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  3 2770 2417        2  759  720        6 3793 3900      4  904 1021      8 3594 3618      2 2754 2498
  4 4925 4732        3 2884 2932        7 2014 2440      5 1596 1636     12 3160 2837      3 1698 1503
  5 4435 3964        6 1152 1050        8 1798 1919      6 2828 3143    * H= 4 K= 11       4 1665 1686
  6 2058 1939        7 2332 2527      * H= 3 K= 2      * H= 3 K= 16      1 1411 1333      5 2020 2054
  7 4339 4523        8 2394 2415        2  958  840      1 1100 1140      3 1393 1390      6 4250 4222
  8 2732 2769                                                            5  853  675
 11 2183 2553
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  7  2425 2503        3  1445 1500        3  2993 2917        0  1753 1690      * H=  8  K= 16        4  2056 2192
  8  1224 1100        4   984  802        4  2281 2271        1  2186 2170        0  1547 1538      * H=  9  K= 14
* H=  5  K= 10        8  1361 1430        5  5265 5268        2  9822 10415       5  1185 1303        0   907  936
  1  4470 4211       10  1443 1426        6  3878 3788        3  3732 3901      * H=  8  K= 17        2  2424 2285
  2   997  881      * H=  6  K=  8        7  4832 4940        6  1781 1401        0   916  893        3   888 1038
  3  1111  988        0  4864 4601        8  1471 1410        8  3283 3082      * H=  8  K= 18        4  1542 1471
  5  3129 2963        1  1956 1066       11  2249 1907       10  6295 6504        3   938 1039        6  3880 3805
  7  3790 3960        3  4486 4371      * H=  7  K=  5      * H=  8  K=  3      * H=  8  K= 19        8  1440 1454
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* H=  5  K= 11        5  2057 1929        2  3522 3360        1  1750 1662      * H=  8  K= 21        3   827  408
  2  1893 1742        6  1403 1295        3   651  781        2  6198 6692        0  1090  711        7  1257  801
  3  2429 2390        9  2153 2093        4  1270 1487        3  1418 1356      * H=  9  K=  0      * H=  9  K= 16
  4  2482 2408       10  1588 1458        5  1258 1260        5  1549 1735        4  1035 1888        1  1159 1207
  5  1735 1696       11  2225 1954        6  3611 3534        6  1128  997        6  2082 2170        3  1038 1130
  6  2394 2246       12  1732 1693        7  1661 1507        7  1961 1786      * H=  9  K=  1        4  2700 2743
  0  1289 1325      * H=  6  K=  9      * H=  7  K=  6        9  1521 1089        1  1565 1524        5  1692 1731
* H=  5  K= 12        0  4227 3901        1  1515 1508       10  3410 3556        3  4253 4288        7  2064 1822
  1  1845 1857        2  1915 1819        2  3289 2899      * H=  8  K=  4        7  1684 1819      * H=  9  K= 18
  2   871  826        3  1361 1300        3  4820 4761        0  7465 7338        4  4408 4480        3  1670 1740
  3  2785 2877        4  1716 1578        4   775  762        1  4724 4999        5  2442 2587        5  1861 1946
  4  3182 3162        5  1505 1390        5  4353 4338        2  4502 4330        6  6158 5566        6  1306 1104
  5  1656 1590        8  1308 1392        6  4857 4516        3  2288 2492        7  2548 2312        7  1440 1484
  6  1092 1282       12  1700 1377        7  2016 2282        4  1991 2004        8  2075 2167      * H=  9  K= 20
  8  2192 2197      * H=  6  K= 10        9  2962 3028        5  3074 3273      * H=  9  K=  2        2  1004 1036
  9  2626 2596        0  4875 4491      * H=  7  K=  7        6  1693 1737        1  2426 2426        3   942 1021
* H=  5  K= 13        1  4777 4654        1  1336 1198        7  2430 2324        2  2064 2330        5  1203 1278
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  2   846  638        3   839  781        3  1029  975        9  1732 1501        6  2389 2314        0  3434 3583
  4  2546 2506        4  1201 1096        4  5563 5296       10  3225 3191        9  1023 1520        2  2413 2611
  5  1391 1299        5  3467 3376        8  2254 2086       11  1647 1652      * H=  9  K=  3        4  1186 1355
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* H=  5  K= 14       12  2268 1710        1  3524 3475        0  7286 7420        3  1095 1042        1  1954 1047
  1  1281 1486      * H=  6  K= 11        2  1546 1587        2  1896 1881        4  7251 7632        2  1125 1356
  2  2519 2453        0  1686 1408        4  5583 5222        4  2393 2296        5  1111 1045        7  1618 1670
  3  1073 1182        1  3128 2933        5  1693 1542        5  1425 1297        6  1842 1890      * H= 10  K=  2
  4  1241 1377        2  1945 1811        6  2555 2400        8  3169 3067        8  4159 4176        0  1201 1185
  6  3487 3697        5   816  799        7  1816 1846       12  2330 2396      * H=  9  K=  4        1  2201 2265
  8  1459 1444        7  1201 1236        8  2791 2895      * H=  8  K=  6        1  1865 2058        3  2008 2007
* H=  5  K= 15      * H=  6  K= 12        9  1660 1485        0  8477 8206        3  1015  962        4  1545 1532
  2  1520 1443        1  1691 1558       10  1885 1355        1  2769 2788        4  3563 3614      * H= 10  K=  3
  3   871  927        2  5844 5415      * H=  7  K=  9        2  2261 2196        6  1161 1138        0  2178 2360
  5   761  670        3  3405 3338        2  3003 2665        3  4713 4698        7  1473 1454        1  1981 1855
  6  2162 2089        5  1007 1103        3  1255 1192        4  3311 3167        8  2084 1935        3  1535 1672
* H=  5  K= 16        7  1212 1167        6  4568 4535        5  1503 1479       11  1940 1780        5  1103 1044
  1  1096 1278       10  3733 3801      * H=  7  K= 10        6  2424 2723      * H=  9  K=  5        8  2077 1788
  4  2931 2935      * H=  6  K= 13        1  2772 2713        7  1125 1109        1  1255 1387      * H= 10  K=  4
  5  1702 1687        0  1001  932        2  2298 2086        8  3202 3143        2  4135 4031        0  2920 2841
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* H=  5  K= 17        3  1756 1759        4  1951 1833       10  2544 2488        4  2251 2367        3   903  762
  4  1832 2018       11  1846 1389        5  1275 1071       11  2235 1749        5  1145 1107        4   924  878
* H=  5  K= 18      * H=  6  K= 14        6  2959 3052       12  3515 3721        6  6912 6837        5  2874 3112
  3  1620 1725        0  7282 6811        7  2398 2161      * H=  8  K=  7      * H=  9  K=  6        8  1410 1023
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  5  1795 1951        4  2412 2491       11  2909 3032        1  1640 1603        2  1764 1680        1  1003 2110
  6  1264 1200        5  1391 1424      * H=  7  K= 11        2  4082 3937        4  1890 1853        2  1740 1694
* H=  5  K= 19        6  1232  879        1  1312 1236        3  3593 3643        5  1660 1719        5  1060 1193
  2   883 1068        8  2850 3034        3   980  853        4   796  671        6  2726 2226        7  1262 1123
  6  1358 1558      * H=  6  K= 15        4  4311 4109        5   833  790        7  2169 2192      * H= 10  K=  6
* H=  5  K= 20        0  2143 2032        5  1681 1603        6  1402 1468        9  1317 1440        1  1896 1691
  2   900 1113        1  1730 1736        6  1317 1338       10  2515 2782        9  1466 1447        1   840  763
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  5  1241 1107        8  1418 1115        8  2083 2304        0   858  858        1  1293 1268        3  2720 2720
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* H=  5  K= 21        0   923  818        1  1004 1158        2  7472 7172        3  2086 1864        7  1691 1752
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* H=  6  K=  0        2  3888 4001        3  2327 2292        5  2176 2090        5  1144 1048      * H= 10  K=  7
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  4  1508 1649      * H=  6  K= 17        5  1579 1500        8  1592 1582        8  2363 2553        2  2210 2158
  6  1244 1008        0   796  807        9  2777 2557       10  4072 3920        9  1852 2005        3  2366 2515
  8  1550 1909        2  1900 1827      * H=  7  K= 13      * H=  8  K=  9       12  1887 1501        4  1190 1143
* H=  6  K=  1      * H=  6  K= 18        2  1703 1535        0  2716 2521      * H=  9  K=  8        8  1538 1545
  1  2271 2288        0  2545 2604        3  2169 2104        1  3069 2896        1  1094 1159       10  1730 1696
  5   881 1045        1  2051 2197        4  2427 2467        5  1886 1910        2   884  820      * H= 10  K=  8
* H=  6  K=  2        2  1765 1931        5  1617 1631        7  1603 1471        3  4028 3944        0  5040 4792
  3  2275 2402        3  1550 1826        6  2396 2427        8  1952 1777        5  2657 2603        1   922  774
  4  2122 2275      * H=  6  K= 19        7  1368 1394        9  1347 1195        7  1167 1041        3  2854 2881
  7  1713 1619        0  1814 1919      * H=  7  K= 14      * H=  8  K= 10        9  2678 2561        4  2202 2130
* H=  6  K=  3      * H=  6  K= 20        1  1693 1722        0  6608 5934      * H=  9  K=  9        5  1522 1480
  0   977  955        0  2975 3200        7  1361 1448        1  2532 2578        1  2204 2260        8  1501 1270
  1   699  659        1  1368 1336      * H=  7  K= 15        3  1018  907        2  2126 2117      * H= 10  K=  9
  3   784  778        3   871 1002        2  1993 2013        4  1676 1577        4  2336 2285        0  3037 3689
  5   675  732        4  1104 1178        3   903 1015        5  3390 3263        6  2674 2710        2  2422 2421
* H=  6  K=  4      * H=  7  K=  0        4  1149 1193        8  2646 2547        7  1813 1881        3  1527 1440
  0  4730 4383        2  4599 4098        5  1227 1268       12  2423 2182        8  1817 1617        4  1304 1263
  1  4359 4297        4  1865 2017        6  2930 3066      * H=  8  K= 11      * H=  9  K= 10        5  1300 1398
  2   672  513        6  8424 9392      * H=  7  K= 16        0   982  930        1  2945 2885        8  1513 1697
  4  1176 1035        8  2231 2450        3   917  924        1  1662 1488        2  1222 1313       12  2065 1667
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  8  1192 1330        2  1899 1766      * H=  7  K= 17        5  1360 1280        6  1606 1602        0  3220 3062
 12  1778 1687        4  2638 2647        2  1512 1560        9  1575 1435        7  3318 3343        1  3057 2901
* H=  6  K=  5        6  2979 2736        6  2243 2338       11  1763 1454       11  1952 1544        2  2342 2222
  1  1532 1587        8  1877 1946      * H=  7  K= 19      * H=  8  K= 12      * H=  9  K= 11        4   893  823
  2   984  993      * H=  7  K=  2        3  1019  742        0  1663 1637        1  1330 1283        5  2518 2516
  3   902  806        1  1602 1445      * H=  8  K=  0        1  1160 1283        2  1789 1777        7  1411 1469
  5  1771 1712        3  3608 3703        2  1506 1543        2  1593 1508        3  1448 1472        8  1717 1857
  7  1091 1288        4  6547 7083        4  4349 4694        3  3254 3317        5  1092 1065      * H= 10  K= 11
  8  1348 1066        5  2853 3011        6  1661 1700        5  1356 1376        6  2752 2609        0  1554 1468
 10  1597 1323        7  2732 2765        8  5406 6195        7  1541 1374        9  1556 1057        1   997 1083
* H=  6  K=  6        8  4564 4710       12  4317 5178      * H=  8  K= 13      * H=  9  K= 12        2  3560 3412
  0  2008 1846        9  2954 3029      * H=  8  K=  1        0   945  782        1  1201 1241        3  2211 2208
  1  1697 1605      * H=  7  K=  3        0  5540 5471        1  1660 1602        2   958  998       10  2640 2407
  2  4649 4426        1  1343 1354        1  4402 4610        2  1088  797        3  2208 2137      * H= 10  K= 12
  3  1827 1806        2  2473 2552        2  1131 1133        5   946  811        4  3555 3538        0  1193 1104
  4  1139 1149        3  1606 1722        3  2841 3123        7  1678 1500        5  1552 1516        1   997 1083
  5  1582 1466        4  3380 3194        4  1317 1125      * H=  8  K= 14        6  1660 1528        2  3560 3412
  7  2991 2990        5   780  740        6  1570 1668        0   878  597        9  2251 2235        3  2211 2208
 10  2351 2193        6  1966 1995        8  2646 2627        1  1465 1368        0  2217 2165       10  2640 2407
* H=  6  K=  7        8  1367 1356        9  2872 2843        2  1727 1753      * H=  9  K= 13      * H= 10  K= 13
  0  2159 2107      * H=  7  K=  4       11  2552 2197        5  1734 1694        1  1077 1022        0  1484 1370
  1   632  786        1  3252 3371      * H=  8  K=  2      * H=  8  K= 15
  2  2735 2552        2  2142 1954                           5   881  801
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 1  2532  2453
 3  2495  2400
 9  1854  1488
* H= 10  K= 14
 0  4906  4657
 4  1715  1660
 5   990   996
 8  2148  2024
* H= 10  K= 15
 0  3001  2773
 1  2170  2172
 3   905  1023
 5   858   846
* H= 10  K= 16
 0   923   937
 1  1285  1370
 2  2966  2868
* H= 10  K= 17
 0   877   797
 2  2486  2486
* H= 10  K= 18
 0  2043  1971
 1  1294  1336
 2  1578  1624
 3  1078  1156
* H= 10  K= 19
 0  2495  2483
* H= 10  K= 20
 0  2527  2553
* H= 11  K= 0
 2  6310  6794
 4  1274  1467
 6  7878  8727
 8  1504  1761
* H= 11  K= 1
 3  1111  1257
 4  1520  1633
* H= 11  K= 2
 3  2634  2636
 4  7295  7673
 5  3167  3355
 7  2693  2520
 8  4412  4568
 9  2488  2307
* H= 11  K= 3
 2  1522  1618
 4   865   650
 6  2374  2334
* H= 11  K= 4
 1  3184  3323
 2  2889  2908
 3  3503  3559
 4  1968  1946
 5  4685  4790
 6  3778  3769
 7  4503  4716
* H= 11  K= 5
 1  1467  1495
 2  1027  1113
 4  2671  2812
 5   895  1029
 7  1298  1362
* H= 11  K= 6
 1   728   713
 2  2635  2522
 3  3648  3920
 4   867   733
 5  3659  3727
 6  3618  3546
 7  1960  1977
 9  2727  2705
* H= 11  K= 7
 1   938   855
 2   913   983
 3  1836  2000
 4  2691  2672
 5  1373  1331
 6  1543  1406
 9  1839  1670
* H= 11  K= 8
 1  2487  2486
 2   794   684
 4  4621  4602
 5  1824  1771
 6  1313  1414
 7  1873  1943
 8  2516  2555
* H= 11  K= 9
 1  1271  1230
 2  1805  1805
 4  1082   742
 6  3373  3269
 7  1305  1167
* H= 11  K= 10
 1  1984  2083
 2  2090  2073
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 6  3023  3145
 7  1488  1321
 8  1424  1095
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 8  2321  2143
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* H= 11  K= 17
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 6  1918  1854
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12  3317  3290
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10  3006  3114
12  2351  2146
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12  3310  2735
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12  2977  2640
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 5  2004  2081
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 8  1538  1704
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* H= 18  K= 4
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  3  1190  1279        7  1644  1449        5  1304  1326       2  2294  2532       4  1387  1301        3  1140   991
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* H= 18  K=  8        2  1197  1214      * H= 20  K=  8        4   858   678       2  1321  1356        1   920   807
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* H= 18  K=  9        6  1834  1839      * H= 20  K=  9        1  1436  1554     * H= 24  K=  2      * H= 26  K=  8
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  2   965   873        4  2295  2371        2  1472  1361     * H= 22  K=  5     * H= 24  K=  3      * H= 26  K=  9
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* H= 18  K= 10        2   981   698        1  1293  1258       5  1002   962     * H= 24  K=  4        3  1107  1086
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  2  2233  2231        7  1921  1837        0  1647  1860     * H= 22  K=  7     * H= 24  K=  5        4  1102  1021
* H= 18  K= 12      * H= 19  K= 10        3  1011  1191       1   992  1022       0  2088  2975        6  1460  1036
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* H= 18  K= 13        6  1462  1715      * H= 20  K= 12      * H= 22  K=  8        4   875  1012        4   805   803
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* H= 18  K= 14      * H= 19  K= 12      * H= 20  K= 14        1  1020   818     * H= 24  K=  7        3   923   958
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* H= 18  K= 15        1  1040   786        0  1398  1380       2  1425  1498       2  1091  1176        2   894   858
  0  2158  1997        6  1630  1835      * H= 21  K=  1      * H= 22  K= 11        3  1512  1627     * H= 28  K=  1
  1  1448  1508      * H= 19  K= 15        2  1593  1631       2  1703  1603     * H= 24  K=  8        0  2041  1866
* H= 18  K= 16        4  1432  1492        4  2153  2308     * H= 22  K= 12        0  1120  1124        2   955   944
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* H= 18  K= 17        2  1984  1983        4   853   960       0  1360  1343       5  1143  1036     * H= 28  K=  3
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* H= 19  K=  1        0  3691  3651        8  2007  2032       2  1007  1094     * H= 25  K=  0        1   770   748
  3  1857  1979        1  2090  2081      * H= 21  K=  5        4   730   580        2  1103   720     * H= 28  K=  7
  4   766   874        2  1110  1234        1  1232  1278       6  1383  1592        4  1066   993        0  1261  1140
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  8  1504  1744        2  1332  1359        2  1823  1795        2  1022  1036     * H= 25  K=  4     * H= 29  K=  3
* H= 19  K=  3        4  1024   867        3  1494  1410        3   767   546        4  1051   800        4  1257  1210
  1  1325  1274        8  1765  1790        6  2057  2267        4  1632  1541     * H= 25  K=  5     * H= 29  K=  4
  2  1355  1310      * H= 20  K=  3      * H= 21  K=  9        5   866   829        1  1053   903        4   882   855
  4  1493  1420        1  1051  1199        1   979  1020        6  1943  1926        4  1369  1429     * H= 30  K=  1
  5  1295  1296        2  3855  3960        4  2408  2561     * H= 23  K=  4        6  1596  1331        1   966   870
  6  2379  2508       10  2574  2470      * H= 21  K= 11        2   932   775     * H= 25  K=  7        3   824   687
  7  1317  1378      * H= 20  K=  4        1  1182  1108        4   934  1028        2  1226  1106     * H= 30  K=  2
* H= 19  K=  4        0  1180  1272        2  1245  1124     * H= 23  K=  5      * H= 25  K=  9        0   920   917
  1   965   855        2  2276  2356        6  1868  1923        1   902   840        4  1693  1700     * H= 30  K=  3
  2  1607  1544       10  1933  1697      * H= 21  K= 13        4  1628  1736     * H= 26  K=  0        0  1208  1110
  3   980  1067      * H= 20  K=  5        3  1439  1510        6  1446  1289        2  1721  1540     * H= 30  K=  5
  4  1383  1488        0  4719  4536        5  1098  1365     * H= 23  K=  7                            2   920   875
```

APPENDIX 2

A listing of the observed and calculated structure amplitudes of $\alpha-(Re(CO)_6)^+(Re_2F_{11})^-$. Values of $|F_{obs}|$ are multiplied by an overall scale factor, K, of 4.038, while both $K|F_{obs}|$ and $|F_{calc}|$ are multiplied by a factor of 20.

The output is of the form:

$$* \quad h \quad k$$
$$1 \quad KF_o \quad F_c$$

L	Fo	Fc
* H= 0 K= 2		
2	695	676
4	1423	1422
* H= 0 K= 3		
3	1214	1237
5	656	621
* H= 0 K= 4		
0	8033	8295
4	5125	4928
* H= 0 K= 5		
1	1956	1831
3	1672	1454
* H= 0 K= 6		
2	541	563
4	1900	1805
6	858	780
* H= 0 K= 7		
1	1355	1352
3	1520	1438
5	523	455
* H= 0 K= 8		
0	6354	6277
4	3310	3072
6	442	430
* H= 0 K= 9		
1	885	830
3	1180	1148
* H= 0 K= 10		
0	1435	1338
4	598	514
6	517	468
* H= 0 K= 11		
1	995	981
3	703	673
* H= 0 K= 12		
0	3584	3345
4	1927	1773
* H= 0 K= 13		
1	589	614
3	766	725
* H= 0 K= 15		
1	576	506
3	552	545
* H= 0 K= 16		
0	1412	1441
4	1041	963
* H= 1 K= 2		
1	4631	4687
2	2180	2146
3	2507	2493
4	840	787
5	2125	2102
* H= 1 K= 3		
1	1283	1184
2	879	794
3	668	633
4	432	437
5	841	840
* H= 1 K= 4		
1	782	775
2	4254	4206
3	1644	1705
4	534	520
* H= 1 K= 5		
1	1230	1097
2	1387	1343
3	656	545
5	947	991
* H= 1 K= 6		
1	3106	3139
2	1481	1350
3	2600	2436
4	564	580
5	1947	1918
6	404	424
* H= 1 K= 7		
1	1120	1114
2	1064	947
3	524	491
5	899	791
6	476	511
* H= 1 K= 8		
1	722	682
2	3021	2948
3	1064	920
4	431	333
6	1437	1367
* H= 1 K= 9		
1	929	886
2	999	1000
3	497	270
5	568	620
6	592	536
* H= 1 K= 10		
1	2187	2157
2	707	663
3	1401	1251
4	465	394
5	1190	1134
* H= 1 K= 11		
1	606	568
2	468	513
4	403	228
5	550	493
* H= 1 K= 12		
2	1661	1640
6	930	830
* H= 1 K= 13		
1	501	505
2	692	699
5	443	443
* H= 1 K= 14		
1	1105	1113
3	862	761
* H= 1 K= 15		
1	467	443
* H= 1 K= 16		
2	938	819
* H= 2 K= 0		
1	2759	2691
2	514	491
3	950	801
4	723	583
5	1735	1547
* H= 2 K= 1		
2	425	448
4	1710	1770
* H= 2 K= 2		
0	711	793
1	5279	5549
2	570	515
3	3580	3889
4	392	428
5	1989	2299
* H= 2 K= 3		
0	2013	2086
2	404	329
4	1284	1256
* H= 2 K= 4		
1	1460	1492
2	1776	1815
3	795	859
4	801	816
5	1620	1569
6	557	365
* H= 2 K= 5		
0	2866	2701
2	660	676
4	1622	1568
* H= 2 K= 6		
0	373	224
1	3727	3772
2	534	410
3	3993	3864
4	504	491
5	2020	1923
* H= 2 K= 7		
0	1810	1807
4	1077	1114
6	652	636
* H= 2 K= 8		
0	593	501
1	1137	1097
2	434	507
4	423	448
5	992	990
* H= 2 K= 9		
0	1976	1878
4	1223	1137
5	357	56
6	406	398
* H= 2 K= 10		
0	414	388
1	2667	2602
3	2109	2020
5	1233	1173
* H= 2 K= 11		
0	990	941
2	455	354
4	610	628
* H= 2 K= 12		
1	622	559
5	653	551
* H= 2 K= 13		
0	1240	1210
4	840	773
* H= 2 K= 14		
1	1363	1364
3	1419	1320
* H= 2 K= 15		
0	570	629
4	475	404
* H= 2 K= 17		
0	652	575
* H= 2 K= 18		
1	638	614
* H= 3 K= 0		
1	850	747
4	580	630
5	517	508
* H= 3 K= 1		
1	1435	1290
2	2087	1945
3	635	530
4	550	545
5	1175	1122
* H= 3 K= 2		
1	2990	3119
2	2045	2321
3	2254	2334
4	575	573
5	1510	1588
* H= 3 K= 3		
1	821	876
2	1527	1542
3	677	728
4	496	455
5	664	687
* H= 3 K= 4		
1	580	631
3	1102	1193
4	608	419
* H= 3 K= 5		
1	967	1020
2	1599	1673
3	549	490
4	472	418
* H= 3 K= 6		
1	1780	1771
2	1594	1568
3	2343	2265
4	609	597
5	1664	1652
6	675	790
* H= 3 K= 7		
1	991	921
2	1033	1052
3	517	462
5	820	791
6	420	407
* H= 3 K= 8		
2	3746	3636
3	438	404
6	1603	1607
* H= 3 K= 9		
1	846	790
2	1288	1224
5	675	629
6	423	382
* H= 3 K= 10		
1	1725	1618
2	932	919
3	1040	1012
5	935	847
6	503	523
* H= 3 K= 11		
1	505	529
2	536	568
5	416	446
* H= 3 K= 12		
2	2114	1990
6	1071	983
* H= 3 K= 13		
1	605	501
2	811	736
5	487	472
* H= 3 K= 14		
1	895	804
3	731	657
4	417	261
* H= 3 K= 16		
2	971	972
6	566	485
* H= 3 K= 18		
1	530	370
* H= 4 K= 0		
0	7041	7555
1	1150	1070
2	1469	1358
5	472	333
* H= 4 K= 1		
1	1738	1610
3	2110	1992
* H= 4 K= 2		
0	3070	3330
1	1534	1677
3	1098	1142
4	1654	1602
5	536	562
* H= 4 K= 3		
1	1053	1259
3	1288	1324
5	517	484
* H= 4 K= 4		
0	4459	4842
1	475	519
3	956	1007
5	729	900
* H= 4 K= 5		
1	1147	1227
3	1476	1597
* H= 4 K= 6		
0	1488	1402
1	515	466
2	759	820
3	1236	1281
4	1262	1273
5	767	760
6	551	545
* H= 4 K= 7		
1	1144	1178
3	1383	1410
5	431	401
* H= 4 K= 8		
0	4305	4055
4	3105	3178
5	430	414
* H= 4 K= 9		
1	804	785
3	1014	1052
* H= 4 K= 10		
0	1380	1170
1	875	791
3	425	434
4	542	553
6	557	427
* H= 4 K= 11		
1	1122	1157
3	803	820
* H= 4 K= 12		
0	2525	2370
4	1795	1811
* H= 4 K= 13		
1	469	479
3	731	731
* H= 4 K= 15		
1	490	469
3	549	490
* H= 4 K= 16		
0	1240	1151
4	916	916
* H= 5 K= 0		
1	1246	1043
3	2398	2129
5	420	323
* H= 5 K= 1		
1	1688	1619
2	2094	1867
3	707	662
4	760	767
5	937	846
6	478	637
* H= 5 K= 2		
1	3505	3522
3	3119	2985
5	2556	2476
* H= 5 K= 3		
1	1182	1207
2	1077	1232
3	473	491
4	639	651
5	884	903
* H= 5 K= 4		
1	1131	1285
3	1726	1867
* H= 5 K= 5		
1	914	1041
2	1395	1563
3	508	547
4	564	591
5	742	778
* H= 5 K= 6		
1	2856	3023
3	2281	2375
5	1884	2046
* H= 5 K= 7		
1	1090	1157
2	1068	1137
3	556	575
4	566	549
5	641	633
6	396	444
* H= 5 K= 8		
1	751	750
2	1862	1924
3	1188	1200
6	880	861
* H= 5 K= 9		
1	671	756
2	1068	1089
4	389	376
5	495	533
6	521	455
* H= 5 K= 10		
1	1800	1868
3	1510	1504
5	1309	1285
* H= 5 K= 11		
1	615	577
2	808	809
3	478	435
4	429	321
5	441	458
* H= 5 K= 12		
1	438	404
2	1080	1113
3	643	625
6	521	512
* H= 5 K= 13		
1	455	421
2	793	726
* H= 5 K= 14		
1	1061	1107
3	812	823
* H= 5 K= 15		
1	534	423
* H= 5 K= 16		
2	511	563
* H= 6 K= 0		
0	2528	2221
2	1684	1643
3	974	822
4	1896	1608
5	1590	1594
* H= 6 K= 1		
0	2405	2196
2	465	437
4	1816	1621
* H= 6 K= 3		
0	1628	1582
1	3206	3283
3	3707	3502
4	1360	1342
5	2241	2135
* H= 6 K= 3		
0	1410	1415
4	1183	1189
* H= 6 K= 4		
0	1866	2035
1	1122	1157
3	530	451
4	1301	1304
5	978	1024
* H= 6 K= 5		
0	2105	2175
1	1282	1329
* H= 6 K= 6		
0	1226	1270
1	2964	3215
2	478	548
3	2502	2680
4	826	975
5	1334	1461
* H= 6 K= 7		
0	1181	1220
4	949	1026
6	400	513
* H= 6 K= 8		
0	1323	1364
1	599	514
4	870	951
5	714	797
* H= 6 K= 9		
4	1069	1106
6	370	307
* H= 6 K= 10		
0	809	734
1	1657	1714
3	1731	1857
4	547	641
5	1100	1064
* H= 6 K= 11		
0	687	785
* H= 6 K= 12		
0	760	772
4	590	537
5	404	451
* H= 6 K= 13		
0	927	986
4	631	708
* H= 6 K= 14		
1	1150	1081
3	1040	1080
* H= 6 K= 15		
0	522	420
* H= 6 K= 17		
0	561	491
* H= 7 K= 0		
1	461	479
4	457	453
5	740	734
* H= 7 K= 1		
1	1569	1500
3	1242	1262
* H= 7 K= 2		
1	4360	4499
* H= 7 K= 5		
1	1171	1218
2	1049	1202
3	497	488
5	734	760
* H= 7 K= 6		
1	891	894
2	1330	1465
3	758	871
5	728	866
6	691	840
* H= 7 K= 7		
1	874	1026
2	688	696
3	591	582
5	620	654
* H= 7 K= 8		
2	2039	3242
6	1438	1490
* H= 7 K= 9		
1	728	745
2	886	968
5	542	598
* H= 7 K= 10		
1	844	898
2	835	934
5	442	426
6	442	514
* H= 7 K= 11		
1	438	597
* H= 7 K= 12		
2	1829	1872
6	898	876
* H= 7 K= 13		
1	513	500
2	565	615
* H= 7 K= 16		
2	906	919
* H= 8 K= 0		
1	2001	1818
2	1339	1163
3	1049	984
5	850	746
* H= 8 K= 1		
1	1163	1204
3	1712	1585
* H= 8 K= 2		
0	1280	1282
1	1700	1634
3	1183	1104
4	1151	1124
5	853	839
* H= 8 K= 3		
1	1103	1041
3	1373	1286
* H= 8 K= 4		
0	4554	4600
1	1591	1567
3	731	801
4	2616	2557
5	721	772
* H= 8 K= 5		
1	790	787
3	1220	1360
* H= 8 K= 6		
1	1088	1058
1	1267	1297
3	742	845
5	603	724
6	471	502
* H= 8 K= 7		
1	876	1040
3	928	1154
* H= 8 K= 8		
0	2961	3154
1	895	1009
4	1747	2028
5	415	543
* H= 8 K= 9		
1	561	656
3	703	803
* H= 8 K= 10		
1	793	810
3	488	611
4	484	455
5	405	432
6	401	406
* H= 8 K= 11		
3	510	577
3	684	756
* H= 8 K= 12		
0	1713	1789
1	584	524
4	1110	1226
* H= 8 K= 13		
1	465	373
* H= 8 K= 15		
3	494	440
* H= 8 K= 16		
0	952	927
4	646	608
* H= 9 K= 0		
1	961	809
2	1360	1291
3	1604	1489
5	497	417
* H= 9 K= 1		
1	797	778
2	1590	1424
3	500	456
* H= 9 K= 2		
1	3242	3110
2	637	728
3	2554	2638
5	1732	1700
* H= 9 K= 3		
1	820	657
2	1008	1083
3	586	487
* H= 9 K= 4		
1	1332	1301
2	1033	1100
3	991	1050
* H= 9 K= 5		
2	1290	1262
6	604	488
* H= 9 K= 6		
1	2690	2786
2	641	641
3	1597	1859
5	1288	1434
* H= 9 K= 7		
1	721	713
2	853	903
* H= 9 K= 8		
1	589	638
2	686	821
5	414	237
* H= 9 K= 9		
2	760	637
* H= 9 K= 10		
1	1406	1594
2	1053	1319
5	815	977
* H= 9 K= 11		
2	563	505
* H= 9 K= 12		
3	516	476
* H= 9 K= 13		
2	579	628
* H= 9 K= 14		
1	863	988
3	676	707
* H= 10 K= 0		
4	2032	1941
5	865	786
* H= 10 K= 1		
0	1921	1797
4	1103	991
* H= 10 K= 2		
0	2097	1938
1	2327	2244

```
 3  2002 2111     5   767  704      3   833  820    * H= 13 K=  5      4   586  594    * H= 16 K= 10
 4  1297 1345   * H= 11 K=  2    * H= 12 K=  4      2   861  827    * H= 14 K= 12      1   565 -570
 5  1175 1071     2  1611 1606      0  2583 2472    * H= 13 K=  6      0   676  707      3   576  460
* H= 10 K=  3   * H= 11 K=  3      1  1193 1288      1  1731 1755      4   538  532    * H= 16 K= 11
 0  1413 1401     1   856  763      3   640  707      2   744  824    * H= 14 K= 13      1   530  349
 4   650  661     2   625  513      4  1488 1604      3  1137 1230      0   539  544    * H= 16 K= 12
* H= 10 K=  4     5   590  610      5   777  736      6   502  422    * H= 15 K=  0      0   584  524
 0  2770 2684   * H= 11 K=  4    * H= 12 K=  5    * H= 13 K=  9      1   943  834    * H= 17 K=  1
 1   703  715     1   781  874      1   561  568      2   517  641      2  2301 2140      2   790  539
 4  1207 1199     2  3036 3042      3   687  710    * H= 13 K= 10      3   627  566    * H= 17 K=  2
 5   614  567     5   562  487    * H= 12 K=  6      1   938 1035      5   509  575      1  1083 1047
* H= 10 K=  5   * H= 11 K=  5      1  1208 1226      2   531  558    * H= 15 K=  2      2   927  844
 0  1794 1718     1   636  816      3   819  903      3   854  870      1   600  496      3   859  770
 4   922  890     2   774  741      5   657  646      5   647  730    * H= 15 K=  4      5   730  692
* H= 10 K=  6     5   511  581    * H= 12 K=  7    * H= 13 K= 14      1   708  708    * H= 17 K=  6
 1  2089 2047   * H= 11 K=  6      1   747  726      1   734  666      2  1830 1822      1   945  935
 3  1502 1678     2  1121 1076      3   654  763    * H= 14 K=  0      3   566  515      2   654  714
 4   808  783     6   597  573    * H= 12 K=  8      0  1772 1652      5   510  511      3   651  624
 5   814  801   * H= 11 K=  7      0  1762 1805      4  1603 1476    * H= 15 K=  7    * H= 17 K= 10
* H= 10 K=  7     1   686  770      1   765  810    * H= 14 K=  1      1   582  492      1   564  570
 0  1030 1030     3   494  441      3   505  560      0   990  916    * H= 15 K=  8    * H= 18 K=  0
 4   585  615     5   559  542      4  1043 1262      4   769  772      1   576  548      0  1431 1262
 6   434  414   * H= 11 K=  8      5   538  563    * H= 14 K=  2      2  1293 1395      4   865  820
* H= 10 K=  8     1   502  585    * H= 12 K=  9      0  1402 1365      6   622  665    * H= 18 K=  1
 0  1601 1584     2  2051 2283      3   532  517      1  1262 1139    * H= 15 K= 12      0   633  658
 4   886 1056     5   450  431    * H= 12 K= 10      3  1036 1041      2   769  845    * H= 18 K=  2
* H= 10 K=  9     6  1097 1126      1   652  655      4  1133 1121    * H= 16 K=  0      0   987  863
 0  1155 1240   * H= 11 K=  9      3   631  699      5   593  525      0  1410 1259      4   564  606
 4   620  736     2   610  600      5   484  466    * H= 14 K=  3      1   763  757    * H= 18 K=  4
* H= 10 K= 10   * H= 11 K= 10    * H= 12 K= 11      0   740  686      3   559  572      0   940 1055
 0   757  863     2   760  699      3   546  508    * H= 14 K=  4      4   895  820      4   786  743
 1  1014 1170   * H= 11 K= 12    * H= 12 K= 12      0  1719 1709      5   610  606    * H= 18 K=  5
 3  1039 1180     2  1238 1371      0  1058 1076      4  1094 1132    * H= 16 K=  1      0   610  621
 4   669  729     6   672  670      4   758  767    * H= 14 K=  5      1   580  469    * H= 18 K=  6
 5   572  581   * H= 11 K= 16    * H= 12 K= 16      0   880  871      3   530  525      0   636  644
* H= 10 K= 12     2   660  689      0   547  556      4   692  755    * H= 16 K=  2      1   565  369
 0   885  840   * H= 12 K=  0      3   983  997    * H= 14 K=  6      1  1107 1046    * H= 18 K=  8
 4   582  647     0  3242 2920    * H= 13 K=  0      0  1158 1203      3   955  852      0   878  812
* H= 10 K= 13     1  1078 1035      2  1037  897      1   824  872      5   577  570      4   626  561
 0   896  841     3  1129 1071    * H= 13 K=  1      3   987  978    * H= 16 K=  4    * H= 19 K=  0
* H= 10 K= 14     4  2061 1957      1  1900 1915      4   857  797      0   962 1037      1   590  592
 1   733  738     5   932  932      2  1033  984      5   502  483      1   661  695      2   972 1011
 3   669  709   * H= 12 K=  1      3  1589 1616    * H= 14 K=  8      3   584  556    * H= 19 K=  4
* H= 11 K=  0     1   692  781      5  1743 1297      0  1160 1183      4   668  707      2   894  861
 1  1009  834     3   807  878      6   488  477      4   765  895    * H= 16 K=  6    * H= 19 K=  8
 2  3934 3647   * H= 12 K=  2    * H= 13 K=  2    * H= 14 K=  9      1   945  857      2   698  680
 3   639  559     1  1296 1289      2   586  636      0   732  786      3   822  719    * H= 20 K=  2
 5   698  660     3  1232 1286    * H= 13 K=  4      4   518  570    * H= 16 K=  8      1   657  576
* H= 11 K=  1     5   844  862      1   619  647    * H= 14 K= 10      0   810  830
 1  1050  974   * H= 12 K=  3      3   708  745      0   677  695
 2   874  751     1   753  692                       1   610  635
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REFERENCES

1. P.Schutzenberger : Compt.rend., 1870,70,1134, and J.Chem.Soc.,
    (1871),1008.

2. W.Hieber : Adv.Organometallic Chem., 1970,8,1.

3. See for example E.W.Abel and F.G.A.Stone : Quart.Rev.,
    1970,24,498.

4. R.D.W.Kemmitt, R.D.Peacock and I.L.Wilson : Chem.Comm.,
    (1968),772.

5. R.G.Pearson : Chem.in Britain, 1967,3,103.

6. reference 3., Page 534 and 538.

7. E.W.Abel, I.S.Butler and J.G.Reid : J.Chem.Soc., (1963),2068.

8. W.Douglas and J.K.Ruff : J.Organometallic Chem., 1974,65,65.

9. J.L.Cihonski and R.A.Levenson : Inorg.Chem., 1975,14,1717.

10. W.Hieber and H.Schulten : Z.anorg.allgem.Chem., 1939,
    243,164.

11. E.W.Abel, G.B.Hargreaves and G.Wilkinson : J.Chem.Soc.,
    (1958),3149.

12. I.L.Wilson : unpublished results 1968-69.

13. C.J.Marshall : PhD Thesis (Leicester), 1972.

14. C.C.Addison, M.Kilner, and A.Wojcicki : J.Chem.Soc.,
    (1961),4839.

15. M.F.A.Dove and A.F.Clifford : "Inorganic Chemistry in
    Liquid Hydrogen Fluoride", Vieweg and Pergamon, Oxford,
    (1971) - vol.II,part 1 of "Chemistry in Non-aqueous
    Ionising Solvents", G.Jander, H.Spandau and C.C.Addison,
    eds.

16. A.J.Hewitt, J.H.Holloway, R.D.Peacock, J.B.Raynor and
    I.L.Wilson : J.Chem.Soc.(D), (1976), in the press.

17. R.D.W.Kemmitt, R.D.Peacock and J.Stocks : J.Chem.Soc.(A),
    (1971),846.

18. D.W.A.Sharp : Proc.Chem.Soc., (1960),317.

19. E.E.Aynsley, R.D.Peacock and P.L.Robinson : Chem.and
      Ind.(London), (1952),1002, and R.D.Peacock : Progr.
      Inorg.Chem., 1960,2,193.

20. G.B.Hargreaves : PhD Thesis (Imperial College, London),
      1959.

21. R.D.Peacock : Proc.Chem.Soc., (1957),59.

22. G.B.Hargreaves and R.D.Peacock : J.Chem.Soc., (1958),4390.

23. ibid., (1960),1099.

24. ibid., (1958),2170.

25. ibid., (1960),2618.

26. D.M.Bruce, J.H.Holloway and D.R.Russell : Chem.Comm.,
      (1973),321.

27. D.R.Russell : PhD Thesis (Glasgow), 1963.

28. I.L.Wilson : PhD Thesis (Leicester), 1968.

29. J.H.Holloway : "Noble-Gas Chemistry", Methuen, London,
      (1968).

30. C.J.Marshall and R.D.Peacock : 6th Internat.Symposium
      on Fluorine Chemistry (Durham), 1971, Abstract C-33.

31. D.M.Bruce, J.H.Holloway, C.J.Marshall, S.Misra and
      R.D.Peacock : 4th European Symposium on Fluorine
      Chemistry (Ljubljana), 1972, Abstract 1-17.

32. C.J.Marshall, R.D.Peacock, D.R.Russell and I.L.Wilson :
      Chem.Comm., (1970),1643.

33. T.A.O'Donnell and K.A.Phillips : Inorg.Chem., 1970,9,2611.

34. S.Misra : unpublished results 1970-71.

35. A.A.Grinberg, M.M.Singh and Y.S.Varshavskii : Russ.J.
      Inorg.Chem., 1968,13,1399.

36. J.Stocks : PhD Thesis (Leicester), 1969.

37. L.Vaska, J.Peone : Chem.Comm., (1971),418.

38. T.A.O'Donnell and K.A.Phillips : Inorg.Chem., 1972,11,2563.

39. T.A.O'Donnell, K.A.Phillips and A.B.Waugh : Inorg.Chem.,
      1973,12,1435.

40. J.H.Holloway : unpublished observations.

41. R.T.Paine : Inorg.Chem., 1973,12,1457.

42. H.D.Kaesz, R.Bau, D.Hendrickson and J.M.Smith : J.Amer.
      Chem.Soc., 1967,89,2844.

43. R.Mews : Angew.Chem.internat.Edit., 1975,14,640.

44. R.D.Peacock and D.W.A.Sharp : J.Chem.Soc., (1959),2762.

45. R.Colton : "The Chemistry of Rhenium and Technetium", p.54,
      Interscience, London, (1965).

46. A.J.Vogel : "Practical Organic Chemistry", 3rd edit.,
      p.172, Longmans, London, (1957).

47. E.W.Abel, R.A.N.McLean, S.P.Tyfield, P.S.Braterman,
      A.P.Walker and P.J.Hendra : J.Mol.Spectroscopy, 1969,
      30,29.

48. J.H.Holloway and J.B.Raynor : J.Chem.Soc.(D), (1975),737.

49. O.Glemser, J.Wegener and R.Mews : Chem.Ber., 1967,100,
      2474.

50. R.Bougon, T.B.Hui and P.Charpin : Inorg.Chem., 1975,
      14,1822.

51. K.W.Bagnall, J.G.H.du Preez, B.J.Gellatly and J.H.Holloway :
      J.Chem.Soc.(D), (1975),1963.

52. J.H.Holloway, H.Selig and H.H.Claasen : J.Chem.Phys.,
      1971,54,4305; K.O.Christe, C.J.Schack, D.Pilipovitch,
      E.C.Curtis and W.Sawodny : Inorg.Chem., 1973,12,620;
      and E.Mayer and F.Sladky : ibid., 1975,14,589.

53. B.J.Brisdon and D.A.Edwards : ibid., 1968,7,1898.

54. G.W.A.Fowles and J.L.Frost : J.Chem.Soc.(A), (1966),1631.

55. I.J.Hyams, D.Jones and E.R.Lippincott : ibid., (1967),1987.

56. W.A.Sunder and F.A.Stevie : J.Fluor.Chem., 1975,6,449.

57. E.L.Muetterties : Inorg.Chem., 1965,4,1841.

58. T.Kruck, M.Höfler and M.Noack : Chem.Ber., 1966,99,1153,

    and refs. cited therein.

59. J.Gaunt and J.B.Ainscough : Spectrochim.Acta, 1957,10,57.

60. I.R.Beattie, K.M.S.Livingstone, G.A.Ozin and D.J.Reynolds :

    J.Chem.Soc.(A), (1969),958.

61. R.D.Peacock : Adv.Fluorine Chem., 1973,7,113.

62. R.T.Paine : personal communication 1974, see also ref.96.

63. J.Fawcett and J.H.Holloway : unpublished results, see

    also ref.116.

64. A.J.Edwards : J.Chem.Soc.(D), (1972),2325.

65. B.Frlec and J.H.Holloway : ibid, (1975),535.

66. A.Davison, W.McFarlane, L.Pratt and G.Wilkinson : J.Chem.

    Soc., (1962),3653.

67. D.A.Symon and T.C.Waddington : J.Chem.Soc.(A), (1971),

    953.

68. See for example observations made in ref.67 and in

    A.P.Ginsberg and M.J.Hawkes : J.Amer.Chem.Soc.,

    1968,90,5930.

69. A.P.Ginsberg : Transition Metal Chemistry, 1965,1,111;

    tables 11,12 and 14-16, and p.184f.

70. J.C.Green and M.L.H.Green : "Transition Metal Hydrogen

    Compounds", in. "Comprehensive Inorganic Chemistry",

    J.C.Bailar, H.J.Emeleus, R.Nyholm and A.F.Trotman-

    Dickenson, eds., Pergamon, Oxford, vol.4, (1973),

    p.355f, and especially p.402-428.

71. A.Davison, J.A.McCleverty and G.Wilkinson : J.Chem.Soc.,

    (1963),1133.

72. F.A.Cotton, J.L.Down and G.Wilkinson : ibid., (1959),833.

73. T.E.Sloan and A.Wojcicki : Inorg.Chem., 1968,7,1268.

74. R.Ugo, S.Cenini and F.Bonati : Inorg.Chim.Acta, 1967,1,451.

75. W.Jetz and W.A.G.Graham : Inorg.Chem., 1971,10,1159.

76. R.H.Haines and A.L.du Preez : J.Chem.Soc.(A), (1970),2341.

77. W.E.Williams and F.J.Lalor : J.Chem.Soc.(D), (1973),1329.

78. P.M.Treichel, R.L.Shubkin, K.W.Barnett and D.Reichard :
     Inorg.Chem., 1966,5,1177.

79. D.J.Parker and M.H.B.Stiddard : J.Chem.Soc.(A), (1970),
     480.

80. D.J.Parker : ibid., p.1382.

81. D.M.Adams, J.N.Crosby and R.D.W.Kemmitt : ibid., (1968),
     3056.

82. R.B.King : "Transition-Metal Organometallic Chemistry",
     Academic Press, New York, (1969), p.98.

83. K.Moedritzer : Syn.Inorg.Metal-Org.Chem., 1971,1,63.

84. R.Colton and J.E.Garrard : Aust.J.Chem., 1973,26,1781.

85. c.f. a). E.W.Abel, W.Harrison, R.A.N.McLean, W.C.Marsh
     and J.Trotter : Chem.Comm., (1970),1531, and b). M.
     Herberhold and G.Suss : Angew.Chem.internat.Edit.,
     1975,14,700.

86. B.Frlec, H.Selig and H.H.Hyman : Inorg.Chem., 1967,6,1775.

87. H.H.Claasen, J.G.Malm and H.Selig : J.Chem.Phys. 1962,
     36,2890.

88. M.W.Anker, R.Colton and I.B.Tomkins : Rev.Pure Appl.Chem.
     1968,18,23.

89. F.A.Cotton and D.L.Hunter : Inorg.Chem., 1974,13,2044.

90. P.L.Goggin and J.Mink : J.Chem.Soc.(D), (1974),534.

91. W.S.Sheldrick : J.Fluor.Chem., 1974,4,415.

92. A.J.Edwards and P.Taylor : Chem.Comm., (1970),1474.

93. M.F.A.Dove and A.J.Edwards : personal communications, 1974.

94. See for example J.Fischer and R.Weiss : Acta.Cryst.,
     1973,B29,1963.

95. J.H.Holloway and S.Misra : unpublished results, 1971.

96. R.T.Paine and L.B.Asprey : Inorg.Chem., 1975,14,1111,
    and refs. cited therein.

97. J.H.Holloway and J.G.Knowles : J.Chem.Soc.(A), (1969),
    756.

98. F.O.Sladky, P.A.Bulliner and N.Bartlett : ibid., p.2179.

99. M.D.Campbell : Dissert.Abs., 1965,26,2457, also referred
    to in ref.15 p.167.

100. Z.Iqbal and T.C.Waddington : J.Chem.Soc.(A), (1968),2958.

101. N.Bartlett and N.K.Jha in "Noble-Gas Compounds", H.H.
     Hyman, ed., University of Chicago Press, Chicago,
     (1963),p.23.

102. J.Chatt, J.R.Dilworth, G.J.Leigh and R.L.Richards :
     Chem.Comm., (1970),955.

103. E.W.Abel and S.P.Tyfield : Adv.Organometallic Chem.,
     1970,8,117.

104. R.S.Nyholm, M.R.Snow and M.H.B.Stiddard : J.Chem.Soc.,
     (1965),6564.

105. J.Burgess, J.H.Holloway, R.D.Peacock and P.Taylor :
     5th European Symposium on Fluorine Chemistry,
     (Aviemore), 1974, Abstract I3.

106. F.A.Cotton, B.A.Frenz and A.J.White : J.Organometallic
     Chem., 1973,60,147.

107. R.F.Turner and J.J.Turner : personal communication, 1974.

108. G.R.Jones : PhD Thesis, (Birmingham), 1966.

109. T.A.O'Donnell and K.A.Phillips : Inorg.Chem., 1973,12,
     1437.

110. A.J.Edwards, R.D.Peacock and R.W.H.Small : J.Chem.Soc.,
     (1962),4486.

111. A.Hewitt and J.H.Holloway : unpublished results, 1974-76.

112. R.B.King and N.Welcman : Inorg.Chem., 1969,$\underline{8}$,2540.

113. R.R.Schreike and B.O.West : Inorg.Nucl.Chem.Letts.,
     1969,$\underline{5}$,141.

114. H.C.Clark and R.J.O'Brien : Inorg.Chem., 1963,$\underline{2}$,1020.

115. H.C.Clark and R.G.Goel : ibid., 1966,$\underline{5}$,998.

116. P.A.W.Dean and R.J.Gillespie : Can.J.Chem., 1971,$\underline{49}$,1736.

117. Refs. quoted in S.Brownstein : ibid., 1974,$\underline{52}$,4101.

118.a). L.F.Dahl, E.Ishishi and R.E.Rundle : J.Chem.Phys.,
     1957,$\underline{26}$,1750.

118.b). N.I.Gapotchenko, Y.T.Struchov, N.V.Alekseev and
     I.A.Ronova : J.Strukt.Chem., 1973,$\underline{14}$,383.

119. A.J.Edwards and G.R.Jones : J.Chem.Soc.(A), (1969),1651.

120. H.Preiss : Z.Chem., 1966,$\underline{6}$,350.

121. M.F.A.Dove and M.O.Ali : J.Inorg.Nucl.Chem., in the press.

122. H.Preiss : Z.anorg.allgem.Chem., 1972,$\underline{389}$,254.

123. M.O.Ali : PhD Thesis, (Nottingham), 1973.

124. H.B.Miller, H.W.Baird, C.L.Bramlett and W.K.Templeton :
     Chem.Comm., (1972),262.

125. A.J.Edwards and P.Taylor : Chem.Comm., (1971),1377.

126. K.R.Dixon : personal communication, 1974.

127. M.A.Cairns, K.R.Dixon and J.J.McFarland : J.Chem.Soc.(D),
     (1975),1159.

128. F.H.Jardine, L.Rule and A.G.Vohra : J.Chem.Soc.(A),
     (1970),238.

129. A.P.Gaughan, Z.Dori and J.A.Ibers : Inorg.Chem., 1974,
     $\underline{13}$,1657.

130. T.S.Piper and G.Wilkinson : J.Inorg.Nucl.Chem., 1956,
     $\underline{2}$,38.

131. P.M.Druce, B.M.Kingston, M.F.Lappert, T.R.Spalding and
     R.C.Srivastava : J.Chem.Soc.(A), (1969),2106.

132. H.C.Clark, R.J.O'Brien and J.Trotter : J.Chem.Soc.,
     (1964),2332.

133. C.A.Reed and W.R.Roper : J.Chem.Soc.(D); (1973),1370.

134. M.J.Hacker : PhD Thesis, (Leicester), 1972.

135. M.Pánkowski, B.Demerseman, G.Bouquet and M.Bigorgne :
     J.Organometallic Chem., 1972,35,155.

136. B.Demerseman, G.Bouquet and M.Bigorgne : ibid., p.341.

137. W.H.Delphin and R.A.D.Wentworth : Inorg.Chem., 1973,12,
     1914.

138. ibid., 1974,13,2037.

139. ref. cited in M.A.S.King and R.E.McCarley : ibid., 1973,
     12,1972.

140. R.B.King : J.Inorg.Nucl.Chem., 1967,29,2119.

141. W.R.Cullen, D.J.Patmore and J.R.Sams : Inorg.Chem., 1973,
     12,867.

142. Trinh-Toan : Dissert.Abs.Internat., 1972,32B,6938.

143.a). R.J.Haines and A.L.du Preez : J.Amer.Chem.Soc., 1969,
     91,769.

143.b). ibid., 1971,93,2820.

144. M.R.Snow and M.H.B.Stiddard : Chem.Comm., (1965),580.

145. W.Hieber and A.Wirsching : Z.anorg.allgem.Chem., 1940,
     245,35.

146. D.A.Symon and T.C.Waddington : J.Chem.Soc.(D), (1974),
     78.

147. E.O.Fischer and E.Moser : Z.anorg.allgem.Chem., 1966,
     342,156.

148. E.O.Fischer and E.Moser : J.Organometallic Chem.,
     1965,3,16, and Z.Naturforsch, 1965,20B,184.

149. M.G.B.Drew and J.D.Wilkins : J.Chem.Soc.(D), (1973),2664.

150. F.W.B.Einstein and A.C.MacGregor : ibid., (1974),778.

151. N.J.Nelson, N.E.Kime and D.F.Shriver : J.Amer.Chem.Soc.,
    1969,91,5173.

152. J.Chatt, R.H.Crabtree, E.A.Jeffery and R.L.Richards :
    J.Chem.Soc.(D), (1973),1167.

153. T.Blackmore and J.M.Burlitch : Chem.Comm., (1973),405.

154. A.E.Crease and P.Ledzdins : J.Chem.Soc.(D), (1973),1501.

155. B.Chevrier, J.-M.Le Carpentier and R.Weiss : J.Amer.
    Chem.Soc., 1972,94,5718.

156. B.Chevrier and R.Weiss : Angew.Chem.internat.Edit.,
    1974,13,1.

157. F.P.Boer : J.Amer.Chem.Soc., 1966,88,1572.

158. G.A.Olah and M.B.Comisarow : ibid., p.3313.

159. J.Bacon, P.A.W.Dean and R.J.Gillespie : Can.J.Chem.,
    1971,49,1276.

160. M.Mercer, R.H.Crabtree and R.L.Richards : Chem.Comm.,
    (1973),808, and M.Mercer : J.Chem.Soc.(D), (1974),1637.

161. P.D.Cradwick, J.Chatt, R.H.Crabtree and R.L.Richards :
    Chem.Comm., (1975),351.

162. W.E.Silverthorn : Chem.Comm., (1971),1310.

163. R.Robson : Inorg.Chem., 1974,13,475.

164. D.J.Darensbourg : Inorg.Chim.Acta, 1972,6,527.

165. R.N.Scott, D.F.Shriver and D.D.Lehman : ibid., 1970,4,73.

166. R.J.Fitzgerald, N.Y.Sakkab, R.S.Strange and V.P.Narutis :
    Inorg.Chem. 1973,12,1081.

167. T.S.Piper, F.A.Cotton and G.Wilkinson : J.Inorg.Nucl.
    Chem., 1955,1,165, and B.F.Hallam, O.S.Mills and
    P.L.Pauson : ibid., p.313.

168. E.C.Johnson, T.J.Meyer and N.Winterton : Inorg.Chem.,
    1971,10,1673.

169. "Standard Methods of Chemical Analysis", vol.5,p.771,
     W.W.Scott and N.H.Firman, eds., Technical Press,
     London, (1952).

170. J.H.Holloway : J.Chem.Educ., 1966,43,203.

171. J.G.Malm and H.Selig : J.Inorg.Nucl.Chem., 1961,20,189.

172. A.J.Hewitt, J.H.Holloway and B.Frlec : J.Fluor.Chem.,
     1975,5,169.

173. A.J.Edwards and D.R.Slim : Chem.Comm. (1974),178.

174. R.D.W.Kemmitt : PhD Thesis (Imperial College, London),
     1962, and F.A.Anderson, B.Bak and A.Hillebert :
     Acta Chem.Scand., 1953,7,236.

175. R.Colton and J.E.Knapp : Aust.J.Chem., 1972,25,9.

176. G.H.Stout and L.H.Jensen : "X-ray Structure Determination.
     A Practical Guide", MacMillan, London, (1968).

177. M.J.Buerger : "Crystal Structure Analysis", Wiley,
     New York, 1960.

178. M.J.Buerger : "Contemporary Crystallography", McGraw-
     Hill, New York, 1970.

179. "International Tables for Crystallography", vol.1, N.F.M.
     Henry and K.Lonsdale, eds., Kynoch Press, Birmingham,
     (1952).

180. ibid., vol.3, C.H.MacGillavry, G.D.Rieck and K.Lonsdale,
     eds., (1962).

181. D.W.J.Cruickshank, D.E.Pilling, A.Bujosa, F.M.Lovell
     and M.Truter : "Computing Methods and the Phase
     Problem in X-ray Crystal Analysis", Pergamon, Oxford,
     (1961).

182. C.W.Johnson : "ORTEP - A FORTRAN thermal ellipsoid plot
     program for crystal structure illustrations", Oak
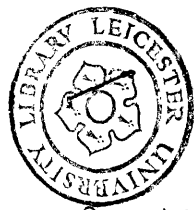   Ridge Natl.Lab., Tennessee, U.S.A., (1965).

183. W.H.Zachariasen : J.Amer.Chem.Soc., 1948,70,2147.

184. S.J.Mitchell and J.H.Holloway : J.Chem.Soc.(A), (1971), 2789.

185. L.Pauling : "The Nature of the Chemical Bond", p.246, Cornell University Press, Ithaca, (1960).

186. M.J.Bennett, W.A.G.Graham, J.K.Hoyano and W.L.Hutcheon : J.Amer.Chem.Soc., 1972,94,6232.

187. N.Bartlett, B.G.de Boer, F.J.Hollander, F.O.Sladky, D.H.Templeton and Z.Zalkin : Inorg.Chem., 1974,13,780.

188. A.J.Edwards and G.R.Jones : J.Chem.Soc.(A), (1970),1891.

189.a). V.M.McRae, R.D.Peacock and D.R.Russell : Chem.Comm., (1969),29.

189.b). J.Burgess, C.J.W.Fraser, V.M.McRae, R.D.Peacock and D.R.Russell : J.Inorg.Nucl.Chem., in the press.

190. V.G.Andrianov, B.P.Biryukov and Y.T.Struchkov : J.Strukt. Chem., 1969,10,1014.

191. S.Merlino and G.Montagnoli : Atti.Soc.Toscana Sci.Nat. Mem., 1969,76,335.

192. ibid. : Acta Cryst., 1968,B24,424.

193. P.T.Greene and R.F.Bryan : J.Chem.Soc(A), (1971),1559.

194. D.Bright and O.S.Mills : J.Chem.Soc.(D), (1974),219.

195. L.F.Dahl and Chin-Hsuan Wei : Acta Cryst., 1963,16,611.

196. H.P.Calhoun and J.Trotter : J.Chem.Soc.(D), (1974),377.

197. L.B.Handy, J.K.Ruff and L.F.Dahl : J.Amer.Chem.Soc., 1970,92,7327.

198. D.Bright and J.A.Ibers : Inorg.Chem., 1969,8,709.

199. J.Hilton : PhD Thesis, Nottingham, (1968).

200. I.S.Astakhova, V.A.Seminon and Y.T.Struchkov : J.Strukt. Chem., 1969,10,419.

201. A.S.Foust, W.A.G.Graham and R.P.Stewart : J.Organometallic Chem., 1973,54,C22.

202. M.R.Churchill and R.Bau : Inorg.Chem., 1967,6,2086,

203. D.R.Russell : personal communication, 1974.

204. C.C.Addison, R.Davis and N.Logan : J.Chem.Soc.(A),
        (1970),3333.

205. F.O.Sladky and N.Bartlett : ibid., (1969),2188.

206. R.W.G.Wyckhoff : "Crystal Structures", vol.I, 2nd edit.,
        Wiley, New York, (1963).

207. G.A.Olah and Y.K.Mo : J.Amer.Chem.Soc., 1971,93,4942.

208. K.Licht, P.Koehler and H.Kreigsmann : Z.anorg.allgem.
        Chem., 1975,415,31.

209. E.O.Schlemper and W.C.Hamilton : Inorg.Chem., 1966,
        5,995.

210. G.Gundersen, T.Haugen and A.Haaland : J.Organometallic
        Chem., 1974,54,77.

211. B.R.Davis and J.A.Ibers : Inorg.Chem, 1971,10,578.

212. A.J.Edwards and P.Taylor : J.Chem.Soc.(D), (1973),2150.

213. A.J.Edwards and F.I.Hewaidy : J.Chem.Soc.(A), (1968),
        2977.

214. R.J.Gillespie, B.Landa and G.J.Schrobilgen : J.Inorg.
        Nucl.Chem., in the press; R.J.Gillespie and B.Landa :
        Inorg.Chem., 1973,12,1383; and B.Landa : PhD Thesis,
        McMaster University, Canada, (1974).

215. H.Lynton and J.Passmore : Can.J.Chem. 1971,49,2539.

216. N.Bartlett, M.Gennis, D.D.Gibler, B.K.Morrell and
        A.Zalkin : Inorg.Chem., 1973,12,1717.

217. A.J.Edwards and G.R.Jones : J.Chem.Soc.(A), (1969),1467.

218. ibid. : (1970),1491.

219. A.J.Edwards and R.J.C.Sills : ibid., (1971),942.

220. C.Hebecker : Z.anorg.allgem.Chem., 1971,384,111.

221. P.A.Tucker, P.A.Taylor, J.H.Holloway and D.R.Russell :
        Acta Cryst., 1975,B31,906.

222. A.J.Edwards and G.R.Jones : J.Chem.Soc.(A), (1968),
     2074.

223. M.J.Bennett, T.E.Haas and J.T.Purdman : Inorg.Chem.,
     1972,11,207.

224. W.A.McAllister and A.L.Marston : Spectrochim.Acta,
     1971,27A,523.

225. J.deMeulenaer and H.Tompa : Acta Cryst., 1965,19,1014.

226. A.Whitaker and J.W.Jeffrey : ibid., 1967,23,977.

227. L.O.Brockway, R.V.G.Evans and M.W.Lister : Trans.Far.
     Soc., 1938,34,1350.

228. S.P.Arnesen and H.M.Seip : Acta Chem.Scand., 1966,20,2711.

229. F.A.Cotton and G.Wilkinson : "Advanced Inorganic Chemistry"
     Wiley Interscience, New York, 3rd edit., (1972),p.685.

230. N.A.Beach and H.B.Gray : J.Amer.Chem.Soc., 1968,90,5713.

231. G.M.Nazarian : PhD Thesis, California Institute of
     Technology, (1957).

232. S.Metlin, I.Wender and H.W.Sternberg : Nature, 1959,
     183,457.

233. H.M.Powell and G.W.R.Bartindale : J.Chem.Soc. (1945),799.

234. F.A.Cotton, T.G.Dunne and J.S.Wood : Inorg.Chem.,
     1965,4,318.

235. J.E.Jacob and L.S.Bartell : J.Chem.Phys., 1970,53,2235.

236. ibid. : p.2231.

237. P.A.Koz'min : J.Strukt.Chem., 1964,5,60.

238. A.Engelbrecht, A.Javan and J.F.Lotspeich : J.Chem.Phys.,
     1959,31,633.

239. A.J.Edwards and G.R.Jones : J.Chem.Soc.(A), (1968),2511.

240. F.Pintchovski, S.Soled, R.G.Lawler and A.Wold :
     Inorg.Chem., 1975,14,1390.

241. C.G.Davies, R.J.Gillespie, P.R.Ireland and J.M.Sowa :
     Can.J.Chem., 1974,52,2048.

242. A.J.Edwards and R.J.C.Sills : J.Chem.Soc.(D), (1974), 1726.

243. A.J.Edwards and P.Taylor : ibid., (1975),2174.

244. M.D.Lind and K.O.Christe : Inorg.Chem., 1972,11,608.

245. D.E.McKee, A.Zalkin and N.Bartlett : ibid., 1973,12,1713.

246. A.J.Edwards and G.R.Jones : J.Chem.Soc., (1971),2318.

247. R.M.Herak, S.S.Malčić and L.M.Manojlovič : Acta Cryst., 1965,18,520.

248. G.Allegra and G.Perego : ibid., 1963,16,185.

249. R.Shandles, E.O.Schlemper and R.K.Murmann : Inorg.Chem., 1971,10,2785.

250. S.R.Fletcher and A.C.Skapski : J.Chem.Soc.(D), (1972),1073.

251. T.Glowiak, M.Sabat and B.Jerowska-Trzebiatowska : Acta Cryst., 1975,B31,1736.

252. J.C.Morrow : ibid., 1962,15,851.

253. J.D.Dunitz and L.E.Orgel : J.Chem.Soc., (1953),2594.

254. K.-F.Tebbe and H.G.von Schnering : Z.anorg.allgem.Chem., 1973,396,66.

255. J.H.Canterford and R.Colton : "Halides of the Second and Third Row Transition Metals", Wiley, New York, (1968),p.19.

256. W.Haase : Acta Cryst., 1974,B30,1722 and 2508, and refs. cited therein.

257. R.W.Brink and R.J.Angelici : Inorg.Chem., 1973,12,1062.

258. R.D.Peacock : "Rhenium", in "Comprehensive Inorganic Chemistry", (c.f. ref.170), vol.3,(1973),p.925.

ABSTRACT

Rhenium carbonyl reacts with three moles of XeF_2 in Genetron 113 to produce the novel carbonyl fluoride-penta-fluoride complex $Re(CO)_5F \cdot ReF_5$ This is decomposed to ReF_6 by three further moles of XeF_2. The use of proportions intermediate between these gives only mixtures of $Re_2(CO)_{10}$ and $Re(CO)_5F \cdot ReF_5$, or $Re(CO)_5F \cdot ReF_5$ and ReF_6. When HF is used as the solvent, a similar process is indicated, but partial hydrolysis of HF solutions of $Re(CO)_5F \cdot ReF_5$ frequently occurred, to give $(Re(CO)_6)^+(ReOF_5)^-$. No conclusive evidence for $Re(CO)_5F$ was found.

$Re_2(CO)_{10}$ also forms $Re(CO)_5F \cdot ReF_5$ with two moles of ReF_6, in HF solution, but with four moles, the new, ionic 1:2 complex $(Re(CO)_6)^+(Re_2F_{11})^-$ is produced. $Re(CO)_5F \cdot TaF_5$ and $(Re(CO)_6)^+(Sb_2F_{11})^-$ were produced by exchange reactions of $Re(CO)_5F \cdot ReF_5$ with TaF_5 and SbF_5 respectively. The oxidation of $[(\eta^5-C_5H_5)Fe(CO)_2]_2$ with AgF in acetone produced evidence for a new fluoride, $(\eta^5-C_5H_5)Fe(CO)_2F$.

It was surmised that the maintenance of stable $(Re(CO)_5F)$ or $(Re(CO)_6)^+$ units governs the course of these fluorinations, and that, in general, carbonyl fluorides will only exist with certain, specific, stable units. Analogous units were proposed for other carbonyl fluoride systems, and a general progression for metal carbonyl fluorinations was established, through simple carbonyl fluoride to carbonyl fluoride-pentafluoride complex(es), and finally binary fluoride. The carbonyl fluoride-pentafluoride complex plays a fundamental role in these systems which has no parallel in other organometallic halides, although related complexes are known in a few cases.

Full X-ray crystal structures of $Re(CO)_5F \cdot ReF_5$ and $\alpha\text{-}(Re(CO)_6)^+(Re_2F_{11})^-$ were performed, and a partial investigation made of $(Re(CO)_6)^+(ReOF_5)^-$. $Re(CO)_5F \cdot ReF_5$ is an essentially covalent, fluorine-bridged complex whose bond lengths are of value for comparing other fluorine-bridged interactions. Polymorphism is found in $(Re(CO)_6)^+(Re_2F_{11})^-$. The α- phase has an ionic lattice, with a centrosymmetric anion. Anion-cation interactions in other $(M_2F_{11})^-$ structures were discussed.