Rhenium Carbonyl Fluorides: Preparation of Pentacarbonylfluororhenium and Preparation and Chemistry of Pentacarbonylfluororhenium–Rhenium Pentafluoride †

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The rhenium carbonyl fluoride, $[\mathrm{Re(CO)_5F}]$, has been prepared by the reaction of $[\mathrm{Re(CO)_5Cl}]$ with anhydrous hydrogen fluoride, and the carbonyl fluoride adduct, $[\mathrm{Re(CO)_5F{\cdot}ReF_5}]$, by the room-temperature fluorination of $[\mathrm{Re_2(CO)_{10}}]$ with xenon difluoride in Genetron 113 (1,1,2-trichlorotrifluoroethane) or anhydrous HF solvents. Partial hydrolysis of $[\mathrm{Re(CO)_5F{\cdot}ReF_5}]$ yields $[\mathrm{Re(CO)_6}][\mathrm{ReF_5O}]$. Preliminary investigations of the reactions of $[\mathrm{Re(CO)_5F{\cdot}ReF_5}]$ with liquid $\mathrm{SbF_5}$ and with $\mathrm{TaF_5}$ dissolved in HF suggest that the compounds $[\mathrm{Re(CO)_6}]$-$[\mathrm{Sb_2F_{11}}]$ and $[\mathrm{Re(CO)_5F{\cdot}TaF_5}]$ respectively are formed.

TRANSITION-METAL carbonyl fluorides are a little known class of compounds.[1–9] In the case of rhenium, although carbonyl chlorides, bromides, and iodides are well known,[10,11] early attempts to prepare rhenium carbonyl fluorides either resulted in failure or produced metal fluorides.[12–14] Low stabilities for carbonyl fluorides were not unexpected. Fluorine is a powerful oxidizing agent and does not normally stabilize low oxidation states in transition metals, especially in the presence of reducing ligands like CO. Furthermore, unlike the other halides, fluorine has no empty d orbitals for π back donation from the metal to stabilize low-oxidation-state complexes. More recently the preparations of $[\mathrm{Re(CO)_5F}]$ [6] and $[\mathrm{Re(CO)_3F_3}]$ [4,6] have been reported and the first carbonyl fluoride adduct, $[\mathrm{Re(CO)_5F{\cdot}ReF_5}]$, and the related salt $[\mathrm{Re(CO)_6}][\mathrm{Re_2F_{11}}]$, prepared by the reaction of $[\mathrm{Re_2(CO)_{10}}]$ with $\mathrm{ReF_6}$ in anhydrous HF, have been characterized by single-crystal X-ray crystallography.[5]

We now report the results of a systematic study of reactions of $[\mathrm{Re_2(CO)_{10}}]$ with $\mathrm{XeF_2}$ in Genetron 113 (1,1,2-trichlorotrifluoroethane) and hydrogen fluoride solvents. This investigation has led to the first preparation of pure $[\mathrm{Re(CO)_5F{\cdot}ReF_5}]$. Some of its physical and chemical properties are described and our earlier work on the reactions of $[\mathrm{Re_2(CO)_{10}}]$ with other fluorinating agents [13,15,16] is discussed. We have also repeated the reaction of $[\mathrm{Re(CO)_5Cl}]$ with HF reported by O'Donnell *et al.*[6] and find that $[\mathrm{Re(CO)_5F}]$ is indeed formed, although it is difficult to obtain free from unchanged $[\mathrm{Re(CO)_5Cl}]$.

RESULTS

Preparation of $[\mathrm{Re(CO)_5F}]$.—Non-oxidative halogen exchange occurred when chloropentacarbonylrhenium(I) was allowed to stand in a large excess of anhydrous HF in Kel-F [poly(chlorotrifluoroethylene)] or FEP (tetrafluoroethylene–perfluoropropylene co-polymer) apparatus over 5—14 d. Hydrogen chloride was liberated, and a light brown involatile solid, $[\mathrm{Re(CO)_5F}]$, was slowly formed. The reaction only went substantially to completion when the liberated HCl and the residual HF were frequently removed and replaced by fresh solvent. The overall stoicheiometry of the reaction is represented by equation (1) (r.t. = room temperature).

$$[\mathrm{Re(CO)_5Cl}] + \mathrm{HF\ (excess)} \overset{\text{r.t.}}{\rightleftharpoons} [\mathrm{Re(CO)_5F}] + \mathrm{HCl}\uparrow \qquad (1)$$

The compound $[\mathrm{Re(CO)_5F}]$ has an infrared spectrum which is closely analogous to that of other $[\mathrm{Re(CO)_5X}]$ (X = halogen) species, as noted by O'Donnell *et al.*,[6] and can be interpreted in terms of a molecule of C_{4v} symmetry (Table 1).

TABLE 1

Infrared spectrum ($\mathrm{cm^{-1}}$) of solid chloropentacarbonylrhenium(I) in a Nujol mull in the 400—2 500 $\mathrm{cm^{-1}}$ region

Wavenumber	Assignment	Description
2 161w (sh)	ν_1 (a_1)	CO stretch
2 033s	ν_4 (e)	CO stretch
1 971ms	ν_2 (a_1)	CO stretch
1 960ms		CO stretch
631vw (sh)		carbonyl deformations
590s		
555m		
480w	ν_3 (a_1)	Re–F stretch
455vw		Re–C stretch

The mass spectra of all the preparations showed fragmentation patterns of $[\mathrm{Re(CO)_5F}]$ together with $[\mathrm{Re(CO)_5Cl}]$. The observation of $[\mathrm{Re(CO)_5Cl}]$ in the product underlines the difficulty in obtaining $[\mathrm{Re(CO)_5F}]$ in 100% yield. The mass spectrum of $[\mathrm{Re(CO)_5F}]$ (Scheme) correlates well with those of other pentacarbonylhalogenorhenium compounds.[17] No m/e values due to rhenium fluoride species other than $[\mathrm{ReF}]^+$ were observed.

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† Some preliminary information has already been published—D. M. Bruce, J. H. Holloway, R. D. Peacock, and I. L. Wilson, Abs. *5th European Symp. Fluorine Chem.* Aviemore, 1974, 122.

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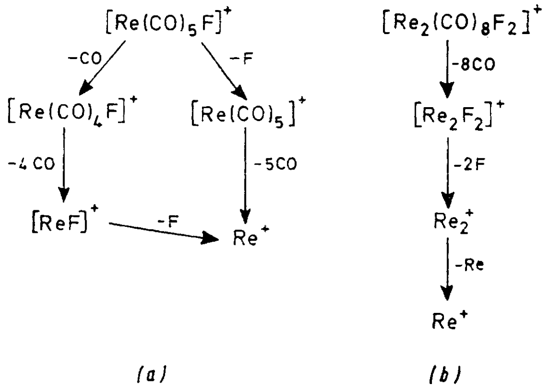
Preparation, Characterization, and Chemistry of [Re(CO)$_5$F·ReF$_5$].—Rhenium carbonyl, [Re$_2$(CO)$_{10}$], was smoothly fluorinated by 3 mol of xenon difluoride at room temperature, in a Pyrex-glass apparatus, using Genetron 113 as solvent. Carbon mono-oxide and xenon were liberated, and [Re(CO)$_5$F·ReF$_5$] was produced in high yield as an extremely moisture-sensitive, involatile, orange-yellow solid. The overall stoicheiometry of the reaction is represented by equation (2). The volatile products were characterized by

$$[Re_2(CO)_{10}] + 3XeF_2 \xrightarrow{\text{Genetron 113}} [Re(CO)_5F{\cdot}ReF_5] + 5CO\uparrow + 3Xe\uparrow \quad (2)$$

mass spectrometry and i.r. spectroscopy. The mass spectrum showed the characteristic isotopic abundance patterns associated with Xe$^+$ and Xe^{2+} as well as the solvent breakdown pattern. A high-resolution spectrum of the *m/e* 28 region showed two distinct peaks, indicative of the presence of N$_2^+$ (background) and [CO]$^+$ from gaseous CO. Evidence for the presence of trace amounts of SiF$_4$ from the fluorination of the glass was also obtained. The absence of COF$_2$ was confirmed by i.r. analysis.



SCHEME Mass-spectrometric fragmentation of (*a*) [Re(CO)$_5$F] and (*b*) [Re(CO)$_5$F·ReF$_5$]. In addition to the fragmentation pattern associated with the Re(CO)$_5$F unit, the ions [ReF$_2$]$^+$, [ReF]$^+$, and a fragmentation pattern which can be associated with [Re$_2$(CO)$_8$F$_2$] were also observed.

The *X*-ray powder diffraction pattern and i.r. spectrum of the orange-yellow solid product of the reaction are identical with those of ground crystals of [Re(CO)$_5$F·ReF$_5$] obtained from the reaction of [Re$_2$(CO)$_{10}$] with ReF$_6$,[5] and the powder pattern indexes on the basis of the single-crystal data. This clearly establishes the material as a single phase with the same composition. This is further supported by the analytical results. The i.r. and Raman spectra of [Re(CO)$_5$F·ReF$_5$] in the 1 800—2 200 and the 400—760 cm^{-1} regions are in Table 2. It should be noted, however, that the compound decomposes readily in a laser beam and the Raman spectrum, therefore, cannot be regarded as unequivocal.

The crystal structure shows that[5] the two [Re(CO)$_5$F·ReF$_5$] molecules in the asymmetric unit have an average Re–F–Re bond angle of 141° which confers C_s microsymmetry on the molecular units. The symmetry of half the molecular units in the solid state can therefore be regarded as $C_s(\sigma_v)$ and the remainder as $C_s(\sigma_d)$. If the symmetry differences between the crystallographically distinct molecules are neglected and the spectrum is examined in terms of C_s symmetry for the molecular unit, the i.r.- and Raman-active modes ($4A' + A''$) are expected. In the carbonyl region the peaks at 2 172 cm^{-1} (i.r. and Raman), 2 100 (i.r.), and 2 104 cm^{-1} (Raman), the factor-group split bands at 2 082, 2 063, 2 046 (i.r.), and 2 062 cm^{-1} (Raman), and that at 1 980 cm^{-1} (i.r.) can be attributed to A' modes whilst the bands at 2 029 cm^{-1} (Raman) and the factor-group split peaks at 2 022 and 2 013 cm^{-1} (i.r.) can be associated with the A'' mode.

TABLE 2

Infrared and Raman spectra (cm^{-1}) of solid [Re(CO)$_5$F·ReF$_5$] and [Re(CO)$_5$(ONO$_2$)][a] with tentative assignments based on C_{4v} symmetry

[Re(CO)$_5$F·ReF$_5$]			[Re(CO)$_5$(ONO$_2$)][a]	
I.r.	Raman	Assignment	I.r.	Raman
2 172w	2 172m	ν(C≡O) (a_1)	2 161w	2 166m
2 100vw	2 104s	ν(C≡O) (b_1)	2 099w	2 092s
2 082m 2 063s 2 046m	2 062w	ν(C≡O) (e)	2 047s	2 033w
2 022 (sh) 2 013ms	2 029w	ν(C≡O) (e)		2 022w
1 980w		ν(C≡O) (a_1')	1 986m	1 977vs
			1 945w (sh)	1 948vw
722m				
705vw	707m	ν(Re^V–F) (a_1)		
	662w	ν(Re^V–F) (b_1)		
642s		ν(Re^V–F) (e)		
620s		ν(Re^V–F–Re^I) (a_1)		
588vs	595vw, br	δ(Re^I–C–O) (e)	592s 597 (sh)	596w
552ms		δ(Re^I–C–O) (e)	550m	555vw
528w	522ms	δ(Re^I–C–O) (a_1)		
485w[b]	497m[b]	ν(Re^I–F) (a_1)		
439vw	437w, br	ν(Re–C) (a_1)	490w	485s
420w		ν(Re–C) (e)	437vw 407w	440m 414vw
	361vw	ν(Re–C) (a_1)	347m	344m

[a] Ref. 20. [b] These bands are assigned as ν(Re^I–F) (a_1) {*cf.* Re^I–F in [Re(CO)$_5$F]} rather than as δ(Re–C–O) (e) as suggested by the [Re(CO)$_5$(ONO$_2$)] data.[20]

An alternative is to seek parallels with pentacarbonyl halides (Cl, Br, or I),[18,19] an approach which has already been used in the assignment of the vibrational spectra of [Re(CO)$_5$(NO$_3$)][20] which also has C_s microsymmetry about the ReONO$_2$ unit. On this basis it is possible to discuss the metal-carbonyl vibrations in terms of C_{4v} microsymmetry of the Re(CO)$_5$F unit. Three i.r.-allowed bands in the C–O stretching region are predicted ($2A_1 + E$). However, lowering of the overall molecular symmetry 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 mode. These results suggest that the previously unassigned peaks at 2 032 and 2 035 cm^{-1} in the i.r. spectra of solid [ReBr(CO)$_5$] and [Re(CO)$_5$Cl][18] respectively should also be assigned to factor-group split E modes.

In the 300—800 cm^{-1} regions of the i.r. and Raman spectra five sets of modes are expected: δ(Re–C–O), 500—650; ν(Re–C), 350—500; ν[Re^V–F(terminal)], 600—750 cm^{-1}; ν[Re^V–F(bridge)]; and ν[Re^I–F(bridge)]. The crystallographic study shows that a fluorine bridge occurs between the two rhenium atoms and, therefore, the microsymmetry about Re^V will be close to C_{4v}. Our assignments (Table 2) were made on this basis. Few unambiguous assignments

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of vibrations due to Re–C stretching and Re–C–O deformation modes have been attempted. Our assignments in this region follow those of previous workers.[18,19]

The mass spectrum of $[Re(CO)_5F{\cdot}ReF_5]$ may be explained in terms of simultaneous fragmentation of the species $[Re(CO)_5F]$, $[Re_2(CO)_8F_2]$, and ReF_x ($x \geqslant 2$). Thus the spectrum is more complex than that of pentacarbonylmonofluororhenium itself (see Scheme). The two carbonyl fluoride species presumably arise from reactions (3)—(6). The spectrum contained no $[ReF_x]^+$ peaks greater than

$$[Re(CO)_5F{\cdot}ReF_5] \xrightarrow{-e^-} [Re(CO)_5F{\cdot}ReF_5]^+ \longrightarrow [Re(CO)_5F]^+ + ReF_5 \quad (3)$$

$$[Re(CO)_5F{\cdot}ReF_5] \xrightarrow{-e^-} [Re(CO)_5F] + [ReF_5]^+ \quad (4)$$

$$2[Re(CO)_5F] \longrightarrow [Re_2(CO)_8F_2] + 2CO \quad (5)$$

$$[Re_2(CO)_8F_2] \xrightarrow{-e^-} [Re_2(CO)_8F_2]^+ \quad (6)$$

$[ReF_2]^+$, and this is almost certainly due to loss of the parent, ReF_5, as it fluorinates the inlet system of the mass spectrometer.

The formulation of the molecule as a covalent fluorine-bridged compound $(OC)_5Re{-}F{-}ReF_5$ [5,21] with mixed $Re^I(d^6)$ and $Re^V(d^2)$ oxidation states is not out of line with the bulk susceptibility at 298 K, which is $\chi = 1.90 \times 10^{-6}$ m^3 kg^{-1}. This yields a value of $\mu_{eff.} = 1.67$ B.M.* per mol of Re^V at 25 °C which is consistent with a $^3T_1$ ground state distorted by an axially symmetric crystal field. Presumably the paramagnetism is derived only from the $Re^V(d^2)$ atom in each molecule and the value, like those for ReF_5 [14] and the fluororhenates(V),[22] does not follow any simple theoretical treatment.

When heated in a sealed capillary $[Re(CO)_5F{\cdot}ReF_5]$ decomposed without melting between 115 and 145 °C. It is scarcely soluble in non-polar solvents [Genetron 113, light petroleum (b.p. 60—80 °C), dichloromethane, chloroform, or benzene] but fairly soluble in polar solvents (anhydrous hydrogen fluoride, ethanol, or methyl cyanide). The compound is extremely air sensitive, darkening rapidly on exposure to the atmosphere. It requires scrupulously dry apparatus and conditions for manipulation. Thus, although $[Re(CO)_5F{\cdot}ReF_5]$ dissolves rapidly in previously dried acetone [23] to give a yellow solution, darkening occurs within minutes to yield a brown solution and precipitate. Similar behaviour occurs in methyl cyanide and ethanol. Reliable molecular-weight and conductivity measurements were not, therefore, possible.

If traces of moisture are present in orange solutions of $[Re(CO)_5F{\cdot}ReF_5]$ in anhydrous HF the colour changes to pale blue-green. E.s.r. spectra of this frozen solution at −196 °C were identical to that of $[ReF_5O]^-$,[24] and a Raman spectrum of the solution gave peaks characteristic of $[Re(CO)_6]^+$ [25] (Table 3). Infrared spectra of the pale green solid remaining after removal of the solvent (Table 4) confirmed the carbonyl species as $[Re(CO)_6]^+$ [25] and the remaining bands at 997, 658, and 611 cm^{-1} are assigned to $[ReF_5O]^-$ by comparison with related species.[26] The unit-cell parameters of crystals selected from the solid are orthorhombic, $a = 6.67(1)$, $b = 10.95(2)$, $c = 8.81(1)$ Å, $U = 644$ Å^3, $Z = 2$, $D_c = 3.37$ g cm^{-3}, space group P_{nnm} or P_{nn_2}. Electron-density maps showed a regular array of rhenium atoms with highly symmetrical co-ordination spheres. The $[Re(CO)_6]^+$ cation was distinguished but the identity of the anion could not be clearly defined, probably because of disorder. We have found that, for many carbonyls and carbonyl fluorides, unit-cell volumes calculated assuming close-packed arrays and atomic volumes for carbon, oxygen, and fluorine atoms of 21, 19, and 17 Å^3 respectively, correlate closely with experimentally obtained values (Table 5). For $[Re(CO)_6][ReF_5O]$ (M 651.5) the calculated and observed volumes are 688 and 644 Å^3. These data seem to confirm the correctness of the formulation.

TABLE 3

Raman spectra (cm^{-1}) of $[Re(CO)_6][ReF_5O]$ in solution

$[Re(CO)_6][ReF_5O]$ in HF (this work)	Assignment (O_h cation and C_{4v} anion)	$[Re(CO)_6][AsF_6]$ in MeCN (ref. 25)
2 201s	$\nu(C{\equiv}O\ )a_{1g})$	2 197s
2 132vs	$\nu(C{\equiv}O)$ (e_g)	2 122vs
714w	$\nu(Re{-}F)$?	
497w	$\delta(Re{-}C{-}O)$ (t_{2g})	486w
439s	$\nu(Re{-}C)$ (a_{1g})	441sp
	$\nu(Re{-}C)$ (e_g)	426 (sh)

TABLE 4

Infrared spectra (cm^{-1}) of $[Re(CO)_6][ReF_5O]$ and related species in Nujol mulls in the 400—2 500 cm^{-1} region

$[Re(CO)_6]$-$[ReF_5O]$	Assignment	$[Re(CO)_6]$-$[AsF_6]$ [a]	α-$[Re(CO)_6]$-$[Re_2F_{11}]$ [b]
2 193 (sh)	$\nu_1(C{\equiv}O)$ (a_1)	2 191w	2 194vw
ca. 2 125 (sh)	$\nu_3(C{\equiv}O)$ (e_g)	2 122 [c]	2 126m
2 084vs	$\nu_6(C{\equiv}O)$ (t_{1u})	2 086vs	2 071s
2 063 (sh)	$\nu_6(^{13}C{\equiv}O)$ (t_{1u})	2 062 (sh)	
2 044 (sh)			2 041 (sh)
1 167w	O/C		
1 070 (w)	O/C	1 070m	1 072vvw
1 010 (sh)	O/C	1 010m	1 041vw
			1 012vw
997m	$\nu(Re{\equiv}O)$ (a_1)		
936w	O/C	940m	ca. 943vw, br
880w	O/C	878m	ca. 885vw
ca. 845 (sh)	O/C	844w	
736 (sh)			ca. 740 (sh)
722m			721w
	$\nu(As{-}F)$	700br	688w
658m	$\nu(Re{-}F)$ (a_1)		663 (sh)
611s	$\nu(Re{-}F)$ (e)		649s
582vs 574 (sh)	$\nu_7\delta(Re{-}C{-}O)$ (t_{1u})	584vs 576 (sh)	582s
540m [d]	$\nu(Re{-}F)$ (a_1)		
522w	$\nu_{12}\delta(Re{-}C{-}O)$ (t_{2u})	522m	515vw
480w	$\nu_{10}\delta(Re{-}C{-}O)$ (t_{2g})	487vw	485vw
421w	$\nu_4(Re{-}C)$ (e_g)	420vw	

[a] Ref. 25. [b] Ref. 21. [c] This peak was observed only in MeCN solution. [d] This peak might be assigned to $\nu([ReF_6]^{2-})$ impurity (ref. 30).

When heated in the ionization chamber of a mass spectrometer at 200 °C, $[Re(CO)_6][ReF_5O]$ decomposed and peaks associated with $[ReF_4O]^+$, $[ReF_3O]^+$, and $[ReF_2O]^+$ appeared. The majority of the peaks can be attributed to

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* 1.B.M. ≈ 9.27×10^{-24} A m^2

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fragmentation of the ReF_5O entity.[27] Fragmentation patterns associated with the decomposition of the oxide fluoride species $[ReFO_3]^+$ and $[ReF_2O_2]^+$, formed presumably by oxygenation of the $[ReF_5O]^-$ anion in the probe to give $ReFO_3$ and ReF_3O_2, account for the majority of the remaining peaks.[27] The percentage abundance of carbonyl fragments was low, which indicates either that little decomposition of the $[Re(CO)_6]^+$ ion occurs or that rapid degradation to CO and Re takes place.

TABLE 5

Theoretical and observed volumes of carbonyl and carbonyl fluoride unit cells

Compound	Class	No. of molecules in unit cell	Volume of unit cell/Å³	
			Calc.	Obs.
$[Re(CO)_5F{\cdot}ReF_5]$	Orthogonal	16	4 824	4 737
$[Re(CO)_6][Re_2F_{11}]$	Orthogonal	4	1 708	1 703
$[\{Ru(CO)_3F_2\}_4]$ [a]	Tetragonal	2	1 232	1 146
$[Re_2(CO)_{10}]$ [b]	Monoclinic	4	1 600	1 480
$[Re_2(CO)_8H_2]$ [c]	Monoclinic	4	1 280	1 271

[a] Ref. 2. [b] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750. [c] M. J. Bennett, W. A. G. Graham, J. K. Hoyaro, and W. L. Hutcheon, *J. Amer. Chem. Soc.*, 1972, **94**, 6232.

X-Ray powder photographs show that $[Re(CO)_6][ReF_5O]$ is also produced when yellow powdered $[Re(CO)_5F{\cdot}ReF_5]$ is exposed to atmospheres containing traces of moisture. It is surmised that the hydrolysis proceeds by a disproportionation of the $F{-}ReF_5$ unit in a similar way to that of ReF_5 itself, which produces rhenium-(VII) and -(IV) species.[14] The rhenium(VII) species presumably degrades some of the $[Re(CO)_5F]$ units of $[Re(CO)_5F{\cdot}ReF_5]$ to give CO, $[ReF_6]^{2-}$, and $[ReF_5O]^-$ and the CO reacts with unchanged $[Re(CO)_5F]$ to produce $[Re(CO)_6]^+$.

Preliminary investigations indicated that reaction of excess of SbF_5 with $[Re(CO)_5F{\cdot}ReF_5]$ at room temperature produces a solid with an *X*-ray powder-diffraction pattern which is similar to that of the α and β forms of $[Re(CO)_6]$-$[Re_2F_{11}]$.[21] The i.r. spectrum confirmed the presence of $[Re(CO)_6]^+$, but instead of peaks associated with ν[Re–F] at 688w, 663 (sh), and 649s cm⁻¹ (α) (Table 4) or 680 (sh), 665vw, and 642vs cm⁻¹ (β)[21] for $[Re_2F_{11}]^-$ new peaks at 663vs, 680s, and 703ms cm⁻¹ were observed. These bands are in the region expected for ν(Sb–F) in the $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ anions.[28,29] It is likely, therefore, that the product is $[Re(CO)_6][Sb_2F_{11}]$. Reaction of $[Re(CO)_5F{\cdot}ReF_5]$ with TaF_5 in a 1 : 1 mol ratio in anhydrous HF gave a yellow solution, without gas evolution, from which a dark solid was obtained. Infrared spectra of the solid showed that the strong bands at 642 and 620 cm⁻¹ (Table 2) which are characteristic of $F{-}ReF_5$ had disappeared. In addition to bands characteristic of the $Re(CO)_5F$ entity a new broad band at 580 cm⁻¹ was observed which is close to that reported for ν_3 of the hexafluorotantalate anion.[30] This suggests the formation of $[Re(CO)_5F{\cdot}TaF_5]$.

The $[Re_2(CO)_{10}] + XeF_2$ *System*.—Reactions of rhenium carbonyl with xenon difluoride in Genetron 113 in ratios other than 1 : 3 at room temperature gave rise to the products shown in Table 6. Reactions of $[Re_2(CO)_{10}]$ with XeF_2 in the ratios 1 : 1, 1 : 3, and 1 : 5 were also investigated in anhydrous HF. The results show that similar reaction paths are followed. Because of the extraordinary sensitivity of $[Re(CO)_5F{\cdot}ReF_5]$ to hydrolysis or to trace impurities leached out of Kel-F by the HF solvent, we find that conversion into $[Re(CO)_6][ReF_5O]$ tends to occur if $[Re(CO)_5F{\cdot}ReF_5]$ is allowed to stand in HF solution.

TABLE 6

The $[Re_2(CO)_{10}]$–XeF_2 reaction in Genetron 113 solvent

Reactants	Products
Mole ratios of $[Re_2(CO)_{10}]$: XeF_2	
(1) 1 : 1	$[Re_2(CO)_{10}]$ + trace amounts of $[Re(CO)_5F{\cdot}ReF_5]$
(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) 1 : large excess	ReF_6

All the reactions produced Xe and CO. * 1 : 4 Stoicheiometry was achieved by treating $[Re(CO)_5F{\cdot}ReF_5]$ with 1 mol of XeF_2.

DISCUSSION

Rhenium carbonyl reacts with halogens dissolved in dichloro- or tetrachloro-methane to produce the stable monomeric carbonyl halides $[Re(CO)_5X]$ (X = Cl, Br, or I).[10,11] Early attempts to cause $[Re_2(CO)_{10}]$ to react directly with fluorine diluted with nitrogen, in a flow system, gave no perceptible evidence of reaction at 25 °C but produced ReF_6 and materials of indefinite composition at higher temperatures.[14] Our more recent efforts to repeat this reaction have yielded i.r. evidence that $[Re(CO)_5F{\cdot}ReF_5]$ and $[Re_2(CO)_{10}]$ are the main solid products of the reaction. The use of elemental fluorine, however, carries with it a danger of explosion. Xenon difluoride in an inert solvent, on the other hand, is a relatively safe, clean, and versatile fluorinating agent and has been used for the fluorination of carbonyls of molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, and iridium.[15,16]

Our results show that in Genetron 113 or HF solvents fluorination of $[Re_2(CO)_{10}]$ with XeF_2 takes place in two distinct steps, (2) followed by (7), which involve the selective reaction of first one $-Re(CO)_5$ group and then the other.

$$[Re(CO)_5F{\cdot}ReF_5] + 3XeF_2 \longrightarrow 2ReF_6 + 3Xe\uparrow + 5CO\uparrow \qquad (7)$$

No carbonyl species of composition intermediate between $[Re_2(CO)_{10}]$ and $[Re(CO)_5F{\cdot}ReF_5]$ or $[Re(CO)_5F{\cdot}ReF_5]$ and ReF_6 are observed. The remarkable stability of the $Re^I(CO)_5F$ group is clearly of major importance in influencing the course of these reactions. It is capable of coexisting with a rhenium(V) fluoride moiety in $[Re^I(CO)_5F{\cdot}Re^VF_5]$.[5] Its stability is further exemplified by the fact that the reaction of ReF_6 with $[Re_2(CO)_{10}]$[5,21] also gives rise to this species and fluorination reactions of $[Re_2(CO)_{10}]$ with XeF_2 do not yield ReF_6 until all the carbonyl has been converted into $[Re(CO)_5F{\cdot}ReF_5]$. It

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is interesting to note, however, that although the $Re(CO)_5F$ unit appears to be preserved in reactions with TaF_5, it gives way to $[Re(CO)_6]^+$ with SbF_5. Evidence of the coexistence of similar carbonyl fluoride moieties with a pentafluoride group in the compound $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ [9] and possibly $[Mo(CO)_3F_2{\cdot}MoF_5]$ [31] suggests that adduct formation of this type is of fundamental importance in transition-metal carbonyl fluoride chemistry.

The behaviour of $[Re_2(CO)_{10}]$ towards XeF_2 is in accord with its behaviour towards other fluorinating agents. Thus, with a stream of elemental fluorine (diluted with nitrogen) at room temperature $[Re(CO)_5F{\cdot}ReF_5]$ is slowly produced. At elevated temperatures or with liquid BrF_3 at room temperature $[Re_2(CO)_{10}]$ is oxidized directly to ReF_6.[13] The much milder fluorinating agent, IF_5, although capable of fully fluorinating the hexacarbonyls of chromium, molybdenum, and tungsten, has been reported [13] to give yellow crystals of $[Re(CO)_5I{\cdot}IF_5]$ and iodine with $[Re_2(CO)_{10}]$. The iodine pentafluoride adduct was identified on the basis of the similarity of its i.r. spectrum with that of $[Re(CO)_5I]$. In the light of our work, however, the formulation $[Re(CO)_5F{\cdot}IF_5]$ seems more likely. With $[Re_2(CO)_{10}]$ the weak fluorinating agent WF_6 produces a deep red solution which has been ascribed to charge-transfer interactions.[13]

The failure to obtain $[Re(CO)_5F]$ from the fluorination of $[Re_2(CO)_{10}]$ with XeF_2 led us to re-examine the work of O'Donnell *et al.*[6] in which they reported that this compound could be prepared by the reaction of $[Re(CO)_5Cl]$ with anhydrous HF. Our observations are in accord with theirs and, in particular, we have confirmed that constant removal of volatile materials during the reaction is vital, and the preparation of $[Re(CO)_5F]$ uncontaminated with the carbonyl chloride is difficult.

Xenon difluoride is an oxidative fluorinating agent. Neither $[Re(CO)_5F]$ nor $[Re(CO)_5F{\cdot}ReF_5]$ are stable in the presence of XeF_2 and it appears, therefore, that the first step in the reaction with $[Re_2(CO)_{10}]$ might be the formation of ReF_6. This then associates with an $Re(CO)_5$ unit to give $[Re(CO)_5F{\cdot}ReF_5]$ in which the Re^I is stabilized by the presence of the fluorine-bridged ReF_5 moiety, which presumably balances the differing influences of the two ligands, CO and F, in $[Re(CO)_5F]$ by redistribution of π-electron density. In the absence of XeF_2, anhydrous HF is unable to oxidize $[Re_2(CO)_{10}]$ but is able to convert $[Re(CO)_5Cl]$ into $[Re(CO)_5F]$ by non-oxidative halogen exchange provided the equilibrium is pushed to the right [equation (1)] by removal of all the HCl.

The results of our investigation of the reaction of XeF_2 with $[Re_2(CO)_{10}]$ disagree with those of O'Donnell *et al.*[6] In hydrogen fluoride, as in Genetron 113 as solvent, we find evidence for only $[Re(CO)_5F{\cdot}ReF_5]$ and ReF_6, but in the same solvent they report the formation of $[Re(CO)_5F]$, $[Re(CO)_3F_3]$, and ReF_5. It is difficult to explain such results. In part, minor differences in preparative procedure may be responsible. Two features, however, are worthy of comment. We have already noted the similarity between the i.r. spectra and *X*-ray powder-diffraction patterns of $[Re(CO)_3F_3]$ and $[Re(CO)_6][Re_2F_{11}]$.[5] The i.r. spectrum reported for $[Re(CO)_3F_3]$ in the carbonyl region [4] is entirely consistent with spectra of $[Re(CO)_6]^+$ [25] and the band at 580 cm^{-1} can more readily be ascribed to $\delta(ReCO)$ in $[Re(CO)_6]^+$ than to an Re^{III}–F stretching frequency. The band at 650 cm^{-1} in $[Re(CO)_3F_3]$, which has also been assigned to $\nu(Re^{III}{-}F)$,[4] is more realistically assigned to $\nu(Re^{V}{-}F)$, *cf.* $[ReF_6]^-$,[30] $[Re_2F_{11}]^-$, and $[Re(CO)_5F{\cdot}ReF_5]$. Thus it seems that $[Re(CO)_3F_3]$ might well be either a third crystalline modification of $[Re(CO)_6][Re_2F_{11}]$ [5,21] or $[Re(CO)_6][ReF_6]$ {which has the empirical formula $[Re(CO)_3F_3]$}. Secondly, the green solution, attributed by O'Donnell *et al.* to ReF_5, is consistent with the presence of $[Re(CO)_6][Re_2F_{11}]$ in solution.[5]

EXPERIMENTAL

Starting Materials.—Rhenium carbonyl was obtained from Strem Chemicals Inc. of Danvers, Mass., U.S.A. Its purity was monitored by i.r. and Raman spectroscopy. Anhydrous HF was provided by Imperial Chemical Industries (99.5% purity) and was further purified by distillation, fluorination, and redistillation. Xenon difluoride was prepared both photolytically and thermally as described previously.[32,33] Genetron 113 was obtained from Fluka A.G. and was purified by distillation from P_4O_{10}. The compound $[Re(CO)_5Cl]$ was prepared by the method of Hieber *et al.*[34] and its purity was monitored by i.r. spectroscopy and *X*-ray powder-diffraction measurements.

Reactions —The reactions were carried out using vacuum techniques in Pyrex, Kel-F [poly(chlorotrifluoroethylene)], or FEP (tetrafluoroethylene–perfluoropropylene co-polymer) apparatus. The compound $[Re_2(CO)_{10}]$ was loaded into the pre-dried vessels under nitrogen, and XeF_2 was added from glass containers by sublimation in a dynamic vacuum or by direct loading from Kel-F containers in a nitrogen-circulating dry-box (Lintott Engineering Limited, Horsham).

$[Re(CO)_5Cl]$ *with* HF. In a typical reaction a large excess of anhydrous HF was distilled on to $[Re(CO)_5Cl]$ (0.075 g) in a previously fluorinated Kel-F or FEP container. Some of the carbonyl chloride dissolved and over 5—14 d the white $[Re(CO)_5Cl]$ turned into a light brown solid. During the reaction period the gaseous products were frequently removed by pumping at −80 °C. The best results were obtained by removing all the solvent and liberated HCl and replenishing with fresh anhydrous HF. On completion of the reaction HF was removed under a static vacuum.

XeF_2 *with* $[Re_2(CO)_{10}]$ *in Genetron* 113. In each case the calculated amount of XeF_2 required was condensed on to $[Re_2(CO)_{10}]$ (*ca.* 0.15 g) partially dissolved in Genetron 113 (*ca.* 30 cm^3 Pyrex) or anhydrous HF (*ca.* 30 cm^3 in Kel-F) apparatus, at liquid-nitrogen temperature. The mixture was allowed to warm to room temperature and smooth reactions took place at, or slightly below, 25 °C with gas evolution and the conversion of the white, scarcely soluble, $[Re_2(CO)_{10}]$ into extremely moisture-sensitive yellow solids. The volatile products were expanded into the vacuum manifold from which samples were taken for mass-spectrometric

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and i.r.-spectroscopic studies. Complete solution was not observed at any time during the reactions. Darkening of the upper walls of the reactor and around the meniscus was noted in the 1 : 4, 1 : 5, and sometimes 1 : 3 reactions (presumably due to metallic deposition from ReF_6). The solids obtained from these reactions after removal of solvent were orange-yellow. Those from the 1 : 1 and 1 : 2 reactions were pale yellow due to the presence of unchanged $[Re_2(CO)_{10}]$.

XeF_2 *with* $[Re_2(CO)_{10}]$ *in anhydrous* HF. Reactions were carried out on a similar scale to those in Genetron 113 and were performed for proportions of $[Re_2(CO)_{10}]$ to XeF_2 of 1 : 1, 1 : 3, and 1 : 5. In the former two, the required amounts of XeF_2 dissolved in doubly distilled liquid HF were added to solid $[Re_2(CO)_{10}]$ or $[Re_2(CO)_{10}]$ under a few millilitres of HF in Kel-F apparatus. The preparations involving 1 : 5 proportions were achieved by adding 2 mol equivalents of XeF_2 dissolved in HF to a sample of freshly prepared $[Re(CO)_5F{\cdot}ReF_5]$ dissolved in HF. Instant reactions took place {despite, in the first two cases, the insolubility of $[Re_2(CO)_{10}]$} with gas evolution.

X-*Ray Diffraction Measurements*.—*X*-Ray diffraction studies were made by the powder technique. Specimens were mounted in evacuated Pyrex capillaries and photographed on a Philips 11.64-cm diameter camera with Cu-K_α filtered radiation.

Spectroscopic Methods.—I.r. spectra of pulverized solid Nujol mulls sandwiched between KBr plates were recorded on a Perkin-Elmer 225 grating spectrometer. Raman spectra were obtained using Coderg modified PHI and T800 instruments; the exciting radiation was either the blue line at 4 880 Å of a Coherent Radiation Laboratories model 52 ion laser or the red line at 6 328 Å of a Spectra Physics 125 helium–neon laser. Mass spectra were obtained on an A.E.I. MS9 spectrometer.

Magnetic-susceptibility measurements were made using a standard Gouy balance. Analyses were by a commercial analyst {Found: C, 16.4; F, 4.35. Calc. for $[Re(CO)_5F]$: C, 17.4; F, 5.50. Found: C, 9.6; F, 17.8. Calc. for $[Re(CO)_5F{\cdot}ReF_5]$: C, 9.6; F, 18.2%).

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