Rhenium Carbonyl Fluorides: Preparation of $[Re(CO)_6][ReF_6]$† and Some Reactions of $[Re(CO)_5F{\cdot}ReF_5]$‡

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The compound $[Re(CO)_6][ReF_6]$ has been prepared by the reaction of $[Re(CO)_5F{\cdot}ReF_5]$ with carbon monoxide in anhydrous hydrogen fluoride. It is also formed in the fluorination of $[Re_2(CO)_{10}]$ by xenon difluoride in Genetron 113 (1,1,2-trichloro-1,2,2-trifluoroethane) as solvent if carbon monoxide released in the reaction is allowed to accumulate in the system. The compound $[Re(CO)_5F{\cdot}ReF_5]$ undergoes ligand-substitution reactions in anhydrous hydrogen fluoride to give products containing $[Re(CO)_5L]^+$ ions (L = PF_3 or CH_3CN). No permanent reaction was observed with L = SO_2. When β-$[Re(CO)_6][Re_2F_{11}]$ is treated with carbon monoxide in anhydrous hydrogen fluoride it is slowly converted into a new crystal modification, γ-$[Re(CO)_6][Re_2F_{11}]$, and a small amount of $[Re(CO)_6][ReF_6]$ is also formed.

Transition-metal carbonyl fluorides are highly reactive compounds of which few well characterized examples are known. The rhenium system is the most closely studied,[1–6] the existence of $[Re(CO)_5F]$,[2,4] $[Re(CO)_5F{\cdot}ReF_5]$,[3,4] and $[Re(CO)_6][Re_2F_{11}]$[3,6] being well established. Single-crystal structures have been determined for $[Re(CO)_5F{\cdot}ReF_5]$[3,5] and the α modification of $[Re(CO)_6][Re_2F_{11}]$.[3,6] These compounds were obtained in this laboratory by reaction of controlled amounts of ReF_6 with $[Re_2(CO)_{10}]$ in anhydrous hydrogen fluoride,[3,6] and $[Re(CO)_5F{\cdot}ReF_5]$ was found to be the sole product of the oxidation of $[Re_2(CO)_{10}]$ by a stoicheiometric amount of XeF_2 in anhydrous HF or Genetron 113 (1,1,2-trichloro-1,2,2-trifluoroethane) as solvents.[4] Other workers, however, reported $[Re(CO)_3F_3]$, which they formulated as a molecular monomer, to be a product of both the $[Re_2(CO)_{10}]$–ReF_6[1] and $[Re_2(CO)_{10}]$–XeF_2[2] reactions in anhydrous HF.

According to a 'building-block' scheme,[7] which has been successfully used to rationalize the structures of most of the known carbonyl fluorides, molecular $[Re(CO)_3F_3]$, with a 16-electron configuration, is unlikely to be a stable species. The ionic compound, $[Re(CO)_6][ReF_6]$, having the same empirical formula, is much more likely to be stable. The $[Re(CO)_6]^+$ cation is a well known, stable, 18-electron species, while the anion $[ReF_6]^-$ is known in a number of its salts.[8–10] This formulation also concentrates CO ligands on a low-oxidation-state Re atom and F ligands on a high-oxidation-state Re atom, in accordance with their known bonding preferences. It has already been suggested however,[3,4] on the basis of its reported i.r. spectrum and *X*-ray powder diffraction pattern,[1] that '$[Re(CO)_3F_3]$' is almost certainly a form of $[Re(CO)_6][Re_2F_{11}]$, so that when the work reported here was started there was little firm evidence for the existence of ionic $[Re(CO)_6][ReF_6]$. We were led to attempt its preparation, in the hope that the study might also help to throw some light on the discrepancies in the earlier reports on the reactions of $[Re_2(CO)_{10}]$ with XeF_2 and ReF_6.[1–4,6]

Two potential synthetic routes were investigated: the reaction of carbon monoxide with $[Re(CO)_5F{\cdot}ReF_5]$, which we find provides a facile route to the desired compound; and the reaction of carbon monoxide with $[Re(CO)_6][Re_2F_{11}]$, which, although it gave small amounts of $[Re(CO)_6][ReF_6]$, is slow and incomplete and unsuitable as a preparative route. The reaction between $[Re_2(CO)_{10}]$ and XeF_2 in Genetron 113 has been re-examined and it has been found that, under certain conditions, $[Re(CO)_6][ReF_6]$ is the major product, rather than $[Re(CO)_5F{\cdot}ReF_5]$ as previously reported. We have also studied reactions of $[Re(CO)_5F{\cdot}ReF_5]$ with the potential ligands PF_3, CH_3CN, and SO_2, in anhydrous HF.

Results and Discussion

Reaction of $[Re(CO)_5F{\cdot}ReF_5]$ *with* CO *in* HF: *Preparation of* $[Re(CO)_6][ReF_6]$.—When carbon monoxide at *ca.* 1 000 mmHg pressure was admitted to a Teflon–FEP tube containing solid $[Re(CO)_5F{\cdot}ReF_5]$ in contact with its saturated solution in anhydrous HF, a rapid, smooth reaction occurred at room temperature. Within a few minutes all the solid originally present had dissolved and the bright orange solution had become a very pale green. Uptake of CO was observed, corresponding approximately to the stoicheiometry (1). On removal

$$[Re(CO)_5F{\cdot}ReF_5] + CO \longrightarrow [Re(CO)_6][ReF_6] \quad (1)$$

of excess of CO and the solvent, $[Re(CO)_6][ReF_6]$ was recovered as a white, crystalline, extremely moisture-sensitive solid, which darkened rapidly on exposure to moist air.

The i.r. spectrum of the solid product is remarkably simple and strongly supports the formulation $[Re(CO)_6][ReF_6]$, in which both ions have local O_h symmetry. All the bands in the carbonyl stretching region can be unambiguously assigned to the $[Re(CO)_6]^+$ cation by comparison with spectra of other compounds containing this ion (Table).[4,6,11] Some very weak bands can be assigned to formally forbidden modes which are activated by small departures from strict O_h symmetry in the crystal environment. For example, a single strong band at 622 cm^{-1} can be assigned to the ν_3(Re–F)(t_{1u}) stretching mode (*cf.* 627 cm^{-1} in the i.r. spectra of K$[ReF_6]$[12] and $[N_2H_6][ReF_6]_2$[10]) and the very weak shoulder at 690 cm^{-1} may be due to the formally forbidden $\nu_1(a_{1g})$ mode of $[ReF_6]^-$ (*cf.* 695 cm^{-1} in the Raman spectrum of $[NO]^+[ReF_6]^-$[13]). All other bands

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† Hexacarbonylrhenium(I) hexafluororhenate(V).

‡ *abcde*-Pentacarbonyl-*f*-μ-fluoro-*ghijk*-pentafluororhenium(I)-rhenium(V).

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Non-S.I. units employed: atm = 101 325 Pa, mmHg ≈ 133 Pa.

Table. Infrared spectra (2 500—400 cm^{-1}) of species containing the $[Re(CO)_6]^+$ ion[a]

			$[Re(CO)_6][Re_2F_{11}]$		
$[Re(CO)_6][ReF_6]$[b]	$[Re(CO)_6][AsF_6]$[c]	Assignment[d]	α[e]	β[f]	γ[b]
2 192vw	2 191w	$\nu_1(C\equiv O)(a_1)$	2 194vw	2 194vw	2 192vw
				2 154vw	
	2 122[g]	$\nu_3(C\equiv O)(e_g)$	2 126m	2 126w 2 118m	2 120m
				2 105 (sh)	
2 084vs	2 086vs	$\nu_6(C\equiv O)(t_{1u})$	2 070s	2 078s	2 080s
2 064m	2 062 (sh)	$\nu_6(^{13}C\equiv O)(t_{1u})$			
2 043 (sh)			2 041 (sh)	2 052 (sh)	
1 070vw	1 070m		1 072vvw	1 067vw	1 070vw
1 044vw			1 041vvw	1 052w	1 056m
1 015w	1 010m	o/c	1 012vw	1 012vw	1 015w
936w	940m		*ca.* 943vw	941vw	943w
880w	878m		*ca.* 885vw	886vw	888w
			ca. 740 (sh)		766 (sh)
			721w	719vw	
	700br	$\nu(As–F)$			
690vw (sh)		$\nu_1(Re–F)(a_{1g})$[h]			
			688w	680 (sh)	690vw (sh)
		$\nu(Re–F)$	663 (sh)	665vw	662s
			649s	642vs	640s
622s		$\nu_3(Re–F)(t_{1u})$[h]			
582vs	584vs	$\delta(Re–C–O)(t_{1u})$	582s 576 (sh)	582vs	582vs
				542s	540m
524mw	522m	$\delta(Re–C–O)(t_{2u})$	515vw	527 (sh)	515w
480 (sh)	487vw	$\delta(Re–C–O)(t_{2g})$	485vw	491vw	480w
420vw (sh)	420vw	$\nu_4(M–C)(e_g)$			415vw (sh)

[a] w = Weak, m = medium, s = strong, v = very, sh = shoulder, br = broad, o/c = overtone and combination bands. [b] This work, powdered solids. [c] Ref. 11, Nujol mull. [d] Assignments for $[Re(CO)_6]^+$ in O_h symmetry based on ref. 11. [e] Ref. 4, Nujol mull. [f] Ref. 6, Nujol mull. [g] Observed only in CH_3CN solution. [h] Assignment for $[ReF_6]^-$ in O_h symmetry.

in this region can be assigned to $[Re(CO)_6]^+$ and arise from Re–C–O bending or Re–C stretching modes.

The *X*-ray powder diffraction pattern of the product is virtually identical to that of $[Re(CO)_6][ReF_5O]$, which initially caused us some concern, since $[Re(CO)_5F{\cdot}ReF_5]$ is readily converted into this compound by traces of moisture in HF solutions.[4] It is clear, however, that our product does not contain the $[ReF_5O]^-$ ion, since the prominent Re–O stretching band at 997 cm^{-1} and the two Re–F stretching bands at 658 and 611 cm^{-1}, characteristic of this ion,[4] are absent from the i.r. spectrum, which contains only the single strong Re–F stretching band at 622 cm^{-1} which we assign to $[ReF_6]^-$.

We were unable to obtain single crystals of $[Re(CO)_6][ReF_6]$ of sufficient quality for a full *X*-ray structure determination. We were, however, able to determine approximate values of the unit-cell parameters: orthorhombic, a = 6.63(5), b = 10.92(4), c = 8.80(4) Å, space group *Pnn*2 or *Pnnm*. These are identical, within experimental error, to the unit-cell parameters of $[Re(CO)_6][ReF_5O]$: a = 6.67(1), b = 10.95(2), c = 8.81(1) Å.[4] Since $[ReF_6]^-$ and $[ReF_5O]^-$ are expected to be almost identical in size, and $[ReF_5O]^-$ in $[Re(CO)_6][ReF_5O]$ has been shown to be orientationally disordered,[4] it is not surprising that the two compounds should be isostructural.

It is evident that the compound $[Re(CO)_6][ReF_6]$ which we have obtained is not the same as the previously reported $[Re(CO)_3F_3]$.[1,2] The *X*-ray powder patterns of the two products are completely different. The Re–F stretching frequency of $[Re(CO)_6][ReF_6]$ (622 cm^{-1}) is also quite different from that reported for $[Re(CO)_3F_3]$ (650 cm^{-1}). The band at 582 cm^{-1} which was also ascribed[1] to an Re–F stretch of $[Re(CO)_3F_3]$ is, as we have previously noted, almost certainly due to an Re–C–O bending mode.[4] The Re–F stretching frequency of $[Re(CO)_3F_3]$ agrees much more closely with those of the strongest Re–F stretching bands of $[Re(CO)_6][Re_2F_{11}]$ (α, 649; β, 642 cm^{-1}).[6] The similarity of their *X*-ray powder patterns has also been noted.[3,6] Thus, our earlier suggestion[3,6] that '$[Re(CO)_3F_3]$' is a form of $[Re(CO)_6][Re_2F_{11}]$ still seems valid, although it does not appear to be identical with either the α or β forms, or indeed with the new γ form reported below.

Re-examination of the Reaction of $[Re_2(CO)_{10}]$ *with* XeF_2 *in Genetron* 113.—Carbon monoxide readily displaces the $[ReF_6]^-$ ion from the co-ordination sphere of Re^I in $[Re(CO)_5F{\cdot}ReF_5]$ in hydrogen fluoride solution and, as shown above, this reaction provides a convenient and facile route to $[Re(CO)_6][ReF_6]$. It is thus somewhat surprising that in previous work in this laboratory[4] the reactions of $[Re_2(CO)_{10}]$ with XeF_2, both in hydrogen fluoride and in Genetron 113, gave exclusively $[Re(CO)_5F{\cdot}ReF_5]$, according to equation (2),

$$[Re_2(CO)_{10}] + 3\,XeF_2 \longrightarrow [Re(CO)_5F{\cdot}ReF_5] + 5\,CO + 3\,Xe \qquad (2)$$

despite the presence of evolved CO throughout the reaction. Competition by CO for a site in the co-ordination sphere of Re^I is presumably favoured by a high concentration of CO in the reaction system. In our earlier work, the gaseous reaction products were allowed to expand into a vacuum manifold, large in volume relative to the reaction vessel, and were frequently pumped away so that high partial pressures of CO did not develop in the system. Under these conditions the reaction product was exclusively the yellow $[Re(CO)_5F{\cdot}ReF_5]$. We have now repeated this reaction, allowing the combined pressures of Xe and CO to reach approximately 1 atm before quenching the reaction mixture at −78 °C and pumping away the gaseous products. Under these conditions we obtained a buff coloured product, whose i.r. spectrum showed it to be mainly $[Re(CO)_6][ReF_6]$ with only weak shoulders in the C–O stretching region corresponding to the bands of $[Re(CO)_5F{\cdot}ReF_5]$ below 2 050 cm^{-1}. The strong Re^V–F stretching band of $[Re(CO)_5F{\cdot}ReF_5]$ at 642 cm^{-1} was not observed, the only strong band in the 600—700 cm^{-1} region being the 622 cm^{-1} band of $[ReF_6]^-$. The *X*-ray powder pattern likewise showed no lines arising from $[Re(CO)_5F{\cdot}ReF_5]$, but only those of $[Re(CO)_6][ReF_6]$. Repetition of the reaction, allowing the combined pressure of the gaseous products to reach only *ca.* 450 mmHg before pumping them away, gave a product whose i.r. spectrum and *X*-ray powder pattern showed it to be a mixture of $[Re(CO)_6][ReF_6]$ and $[Re(CO)_5F{\cdot}ReF_5]$, though still with a preponderance of the former. These, together with our earlier results,[4] show that it is possible, by careful control of the pressure of CO in the system, to obtain either of the two compounds in an essentially pure form.

While these findings do not entirely clear up the discrepancies between our earlier results and those of O'Donnell *et al.*[1,2] it does seem likely that differences in the partial pressures of CO prevailing in the reaction systems were responsible, at least in part, for the different products reported in reactions of $[Re_2(CO)_{10}]$ with XeF_2.

Reactions of $[Re(CO)_5F{\cdot}ReF_5]$ *with Other Neutral Ligands in Anhydrous* HF.—The reaction of $[Re(CO)_5F{\cdot}ReF_5]$ with CO is a ligand-substitution reaction, in which the neutral ligand, CO, displaces the $[ReF_6]^-$ anion from the co-ordination sphere at Re^I. Similar reactions [equation (3)] are expected to occur

$$[Re(CO)_5F{\cdot}ReF_5] + L \longrightarrow [Re(CO)_5L][ReF_6] \quad (3)$$

with other suitable neutral ligands (*e.g.*, L = PF_3, SO_2, or CH_3CN). The related compound $[Re(CO)_5F{\cdot}AsF_5]$ has been reported to undergo displacement of co-ordinated $[AsF_6]^-$ even by the weak ligand SO_2, when present in excess as the solvent. A variety of compounds of the type $[Re(CO)_5L][AsF_6]$ can be formed by replacement of SO_2 by other ligands.[14] It was thus of interest to see whether $[Re(CO)_5F{\cdot}ReF_5]$ could undergo $[ReF_6]^-$ displacement reactions with ligands other than CO. We chose to study PF_3, because of its close similarity to CO as a π-acid ligand, CH_3CN, and SO_2.

With PF_3. Phosphorus trifluoride, in a small excess over the amount required for a 1 : 1 molar ratio, reacted rapidly at room temperature with $[Re(CO)_5F{\cdot}ReF_5]$ in HF. The colour of the solution changed from orange to pale yellow, with dissolution of the solid originally present. Measurement of the pressure of PF_3 remaining indicated 1 : 1 reaction stoicheiometry [equation (3), L = PF_3]. A buff coloured solid was obtained on removal of the volatiles. The reaction stoicheiometry and the i.r. spectrum of the product support its formulation as $[Re(CO)_5(PF_3)][ReF_6]$.

The i.r. spectrum of the solid shows the single strong band at 622 cm^{-1} in the Re–F stretching region, due to $[ReF_6]^-$. Five bands are observed in the C–O stretching region, as expected for the $[Re(CO)_5(PF_3)]^+$ ion, in which the local C_{4v} symmetry of the $Re(CO)_5$ moiety is lowered by the non-axially symmetric PF_3 ligand, so that the B_1 mode, i.r. inactive under C_{4v} symmetry, becomes weakly allowed, and the degeneracy of the E mode is lifted.[15] The observed bands in this region, with tentative assignments, are as follows: 2 180m (A_1), 2 115w (B_1), 2 082s, 2 070s (E), and 2 050m (A_1) cm^{-1}. Phosphorus trifluoride has very similar π-bonding properties to CO, and this is reflected in the very similar frequencies of the most intense CO stretching bands of $[Re(CO)_5(PF_3)]^+$ and $[Re(CO)_6]^+$. Three strong bands at 935, 902, and 860 cm^{-1} may be assigned to P–F stretching vibrations of the PF_3 ligand.[16] Other bands in the 700—400 cm^{-1} range may reasonably be ascribed to Re–C–O bending and Re–C stretching modes of the $Re(CO)_5$ moiety.

The *X*-ray powder pattern of the product was well defined and showed a general similarity to that of $[Re(CO)_6][ReF_6]$, although the two compounds are clearly not isostructural.

With CH_3CN. Acetonitrile reacted rapidly with an equimolar amount of $[Re(CO)_5F{\cdot}ReF_5]$ at room temperature, to give a pale yellow solution which became lime-green during removal of the solvent and yielded a pale green solid. The i.r. spectrum of the solid is consistent with the presence of the known cation $[Re(CO)_5(CH_3CN)]^+$. Bands occur in the C–O stretching region at 2 172w, 2 135vw, 2 050s, and 2 014m cm^{-1} {published[17] values for $[Re(CO)_5(CH_3CN)][PF_6]$ in acetone solution: 2 159w, 2 050vs, and 2 021 (sh) cm^{-1}}. Bands due to co-ordinated CH_3CN occur at 2 985vw, 2 930w [ν(C–H)], 2 330w, 2 290w [ν(C≡N)], and 1 030w cm^{-1} [$\rho_{asym}(CH_3)$]. However, the anion present is $[ReF_5O]^-$ and not $[ReF_6]^-$, as shown by the occurrence of bands at 998, 660, and 611 cm^{-1}, rather than at 622 cm^{-1}. This result was obtained in repeated attempts of this reaction, despite stringent precautions to exclude traces of moisture.

With SO_2. In view of the reaction of $[Re(CO)_5F{\cdot}AsF_5]$ with SO_2,[14] it was of interest to see whether a similar reaction would occur with $[Re(CO)_5F{\cdot}ReF_5]$. Addition of an eight-fold molar excess of SO_2 to $[Re(CO)_5F{\cdot}ReF_5]$ in HF led to the dissolution of the excess of solid present, and a change in the colour of the solution from orange to bright yellow. Removal of volatiles under static vacuum, followed by pumping under high vacuum at room temperature, gave an orange solid whose i.r. spectrum and *X*-ray powder pattern showed it to be mainly unreacted $[Re(CO)_5F{\cdot}ReF_5]$. Two very weak bands in the i.r. spectrum at 1 318 and 1 122 cm^{-1} are probably due to stretching modes of co-ordinated SO_2 {*cf.* 1 313, 1 307, and 1 114 cm^{-1} for $[Re(CO)_5(SO_2)][AsF_6]$}.[14] Dissolution of undissolved $[Re(CO)_5F{\cdot}ReF_5]$, and the change in the colour of the solution on addition of SO_2, suggests that reaction to give $[Re(CO)_5(SO_2)][ReF_6]$ in solution may indeed occur, but that this loses SO_2 more readily than the $[AsF_6]^-$ compound, which is reported to be stable under high vacuum up to 50 °C.[14] The $[ReF_6]^-$ anion thus behaves as a stronger ligand towards the $[Re(CO)_5]^+$ moiety than does $[AsF_6]^-$.

Reaction of $[Re(CO)_6][Re_2F_{11}]$ *with* CO *in* HF.—Carbon monoxide at *ca.* 1 400 mmHg pressure reacted only slowly and incompletely with β-$[Re(CO)_6][Re_2F_{11}]$ in anhydrous hydrogen fluoride at room temperature. The observed pressure drop in the system, over a period of several days, was only 15—20% of that expected for complete reaction according to equation (4). Most of this pressure drop occurred within the first few hours. The solution, and the solid in contact with it, gradually changed from the pale yellow colour of β-$[Re(CO)_6][Re_2F_{11}]$ to a pale green. Close examination of the solid recovered on evaporation of the solvent showed it to consist mainly of green crystals, with a much smaller number of white crystals. Analysis of a sample consisting mainly of the green material gave a chemical composition corresponding to that of $[Re(CO)_6][Re_2F_{11}]$. The *X*-ray powder pattern of the green solid showed strong similarities to those of the α and β forms of $[Re(CO)_6][Re_2F_{11}]$, but differed from these in significant details. It is clear from the powder pattern that this product is neither of the previously known forms of $[Re(CO)_6][Re_2F_{11}]$, nor a mixture of either of them with another substance. It is

$$2\,[Re(CO)_6][Re_2F_{11}] + 8\,CO \longrightarrow 3\,[Re(CO)_6][ReF_6] + 2\,COF_2 \quad (4)$$

suggested that the green crystals are a new crystal modification, which will be designated as γ-$[Re(CO)_6][Re_2F_{11}]$. The i.r. spectrum of the green crystals is consistent with this suggestion (Table). There is no band at 622 cm^{-1}, showing that $[ReF_6]^-$ is absent. The i.r. spectrum of the white solid showed it to be $[Re(CO)_6][ReF_6]$, and this was confirmed by determination of the unit-cell parameters of a small single crystal. Thus, the main process occurring in the system is simply the conversion of one crystal modification of $[Re(CO)_6][Re_2F_{11}]$ into another. While a small amount of $[Re(CO)_6][ReF_6]$ is also formed, the reaction certainly does not provide a convenient synthesis of this compound.

The reaction of $[Re(CO)_6][Re_2F_{11}]$ with CO [equations (4a) and (4b)] may be formally regarded as involving the release of ReF_5 from the $[Re_2F_{11}]^-$ ion, and subsequent reaction of this with CO.

$$[Re(CO)_6][Re_2F_{11}] \longrightarrow [Re(CO)_6][ReF_6] + ReF_5 \quad (4a)$$

$$2\ ReF_5 + 8\ CO \longrightarrow [Re(CO)_6][ReF_6] + 2\ COF_2 \quad (4b)$$

The β-$[Re(CO)_6][Re_2F_{11}]$ used in this study was prepared *in situ* by the reaction of $[Re_2(CO)_{10}]$ with ReF_6 in a 1:4 molar ratio.[6] Free ReF_5 is expected to be a minor product of this reaction and some excess of ReF_6 is also present [equation (5)].

$$3[Re_2(CO)_{10}] + 12\ ReF_6 \longrightarrow 5[Re(CO)_6][Re_2F_{11}] + ReF_5 + 2\ ReF_6 \quad (5)$$

It was shown in separate experiments that, whereas ReF_6 does not react with CO in HF at room temperature, ReF_5 reacts, giving in the course of a few hours a solid product whose *X*-ray powder pattern matches that of γ-$[Re(CO)_6][Re_2F_{11}]$. Thus reaction of CO with free ReF_5 present could account for most of the initial pressure drop observed when the β-$[Re(CO)_6][Re_2F_{11}]$ solution is exposed to CO. Further reaction with 'ReF_5' bound in the $[Re_2F_{11}]^-$ ion, necessary for the formation of $[Re(CO)_6][ReF_6]$, is expected to be much slower, consistent with the very slow and incomplete formation of the latter compound.

It has previously been observed that recrystallization of β-$[Re(CO)_6][Re_2F_{11}]$ from anhydrous HF gives the α modification.[6] The formation of a different modification in the present case may be related to the presence of CO, or possibly to preferential formation of the γ modification in the reaction of ReF_5 with CO, providing nuclei for subsequent recrystallization of the β form.

Experimental

Starting Materials.—Rhenium carbonyl (Strem Chemicals Inc.) was used as received. Rhenium hexafluoride was prepared by the method of Malm and Selig.[18] Its purity was checked by i.r. spectroscopy. Anhydrous HF was provided by Imperial Chemical Industries (99.5% purity) and was further purified by distillation, fluorination, and redistillation. Genetron 113 (Fluka A.G.) and SO_2 (B.D.H. Chemicals Ltd.) were purified by distillation from P_4O_{10}. Acetonitrile (Fluka A.G.) was stored over molecular sieves. Phosphorus trifluoride was prepared by the method of Williams.[19] Its purity was checked by i.r. spectroscopy. Xenon difluoride was prepared photochemically as described previously.[20] Carbon monoxide (British Oxygen Co.) was introduced into the vacuum line *via* a trap cooled in liquid nitrogen.

Procedure.—The reactions were carried out using vacuum techniques in Pyrex, Kel-F [poly(chlorotrifluoroethylene)], or Teflon–FEP (tetrafluoroethylene–perfluoropropylene co-polymer) apparatus. Reaction vessels were pre-dried and seasoned with fluorine before use. Loading of $[Re_2(CO)_{10}]$ into reaction vessels and manipulations of solid products were carried out in a nitrogen-circulating dry-box (Vacuum Atmosphere Co. Dri-Lab.).

Reactions of $[Re(CO)_5F{\cdot}ReF_5]$ *in Anhydrous* HF.—The reactant, $[Re(CO)_5F{\cdot}ReF_5]$, was prepared *in situ* by the reaction of $[Re_2(CO)_{10}]$ (typically 0.12 mmol) with ReF_6 (1:2 molar ratio) in anhydrous HF. The volume of solvent used (*ca.* 0.6 cm^3) was such that the orange solid $[Re(CO)_5F{\cdot}ReF_5]$ was always present, in contact with its saturated solution, prior to the subsequent reaction.

With CO. The prepared solution of $[Re(CO)_5F{\cdot}ReF_5]$ was cooled to −78 °C and CO admitted from the vacuum manifold to give a pressure of *ca.* 1 100 mmHg. On warming to room temperature reaction occurred within a few minutes, all the solid initially present dissolving to give a very pale green, almost colourless solution. This procedure was repeated until no further drop in the pressure of CO was observed. Excess of CO was pumped away and HF was removed under static vacuum to give white needles of $[Re(CO)_6][ReF_6]$, which acquired a brown surface coating as the last traces of HF were removed under high vacuum {Found: C, 11.15; F, 17.0; Re, 57.2. Calc. for $[Re(CO)_6][ReF_6]$: C, 11.0; F, 17.4; Re, 56.9%}.

With PF_3. The prepared solution of $[Re(CO)_5F{\cdot}ReF_5]$ was frozen in liquid nitrogen, and PF_3 in a 20% excess over the amount required for a 1:1 molar ratio was condensed thereon. On warming to room temperature a yellow solution was formed, with no undissolved solid remaining. The residual pressure, with the solution cooled to −78 °C, indicated that reaction had occurred in a 1:1 molar ratio. Removal of volatiles under static vacuum gave a buff coloured solid.

With CH_3CN. The reaction was carried out similarly to that with PF_3, using an equimolar quantity of CH_3CN. A pale yellow solution was formed, with no undissolved solid remaining. On removal of volatiles under static vacuum the solution slowly became lime-green and a pale green solid was obtained.

With SO_2. An eight-fold excess of SO_2 was condensed onto the prepared solution of $[Re(CO)_5F{\cdot}ReF_5]$ at liquid-nitrogen temperature. On warming to room temperature a yellow solution was formed, with no undissolved solid remaining. Removal of volatiles under static vacuum followed by pumping under high vacuum at room temperature gave an orange solid, identified by its i.r. spectrum and *X*-ray powder pattern as $[Re(CO)_5F{\cdot}ReF_5]$.

Reaction of β-$[Re(CO)_6][Re_2F_{11}]$ *with* CO *in Anhydrous* HF.—Pale yellow crystals of β-$[Re(CO)_6][Re_2F_{11}]$ in contact with its saturated solution in anhydrous HF were prepared by the room-temperature reaction of $[Re_2(CO)_{10}]$ (0.08 mmol) with ReF_6, in a 1:4 molar ratio, over a period of 3 d.[6] Carbon monoxide, at a pressure of *ca.* 1 400 mmHg, was admitted from the vacuum manifold. The reaction was allowed to proceed at room temperature, with frequent agitation, for several days, until no further change was observed in the pressure in the system. This was measured with the reaction tube cooled to −78 °C. During this time the solution and solid in contact with it became pale green. At no time did any significant fraction of the solid dissolve. Removal of excess of CO, and evaporation of solvent under static vacuum, left a pale green crystalline solid which, on closer examination, was found to contain a small amount of white crystalline material {Found (bulk solid): C, 8.00; F, 21.4; Re, 60.1. Calc. for $[Re(CO)_6][Re_2F_{11}]$: C, 7.70; F, 22.3; Re, 59.7%). Small quantities of the green and white crystals were separated as far as possible in the dry-box and their i.r. spectra and *X*-ray powder patterns were recorded. A small single crystal of the white solid was used for a determination of its unit-cell parameters.

Reaction of ReF_5 *with* CO *in Anhydrous* HF.—Rhenium pentafluoride was prepared *in situ* by the reaction of ReF_6 (0.24 mmol) with an excess of PF_3.[21] After pumping away the volatiles, anhydrous HF was condensed into the reaction vessel to give a pale yellow solution. Carbon monoxide was admitted from the vacuum manifold at *ca.* 1 100 mmHg pressure. Over a period of several hours the solution became lime-green, with uptake of CO. Removal of volatiles yielded a brown solid, whose *X*-ray powder pattern was identical to that of γ-$[Re(CO)_6][Re_2F_{11}]$.

Reaction of $[Re_2(CO)_{10}]$ *with* XeF_2 *in Genetron* 113.—The reaction was carried out as described previously[4] in a Pyrex apparatus. In one experiment $[Re_2(CO)_{10}]$ (0.87 mmol) and XeF_2 (3.0 mmol) were used in *ca.* 5 cm^3 of solvent, and the combined pressure of evolved Xe and CO, measured with the reaction vessel cooled to −78 °C to condense solvent vapour, was twice allowed to reach *ca.* 700 mmHg before pumping the gases away. The cream coloured solid obtained on removal of the solvent was shown by the i.r. spectrum and *X*-ray powder pattern to be almost pure $[Re(CO)_6][ReF_6]$. In another experiment, $[Re_2(CO)_{10}]$ (0.49 mmol) and XeF_2 (1.66 mmol) were used in *ca.* 20 cm^3 of solvent. The pressure of Xe and CO in this experiment did not exceed 450 mmHg and the solid product, although still mostly $[Re(CO)_6][ReF_6]$, contained a significant amount of $[Re(CO)_5F{\cdot}ReF_5]$, as shown by the i.r. spectrum and *X*-ray powder pattern.

Characterizations.—I.r. spectra of powdered solids held between KBr plates were recorded on a Perkin-Elmer model 580 spectrometer. Specimens for *X*-ray powder diffraction were sealed into thin-walled glass capillaries and their diffraction patterns recorded photographically on a Philips camera (diameter 11.46 cm) using Cu-K_α filtered radiation. Unit-cell dimensions, for single crystals mounted in Pyrex glass capillaries, were obtained from an oscillation photograph for the rotation axis *b*, and from a Weissenberg photograph, using Cu-K_α filtered radiation.

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