Controlled Thermal Decomposition of III (and III-*d*). In a typical experiment III (0.073 mmol) was slowly volatilized by warming the solid to 80°. The vapor was pumped through a hot zone (9-in. heavy-wall Pyrex tube, 25-mm o.d.) maintained at 250–300°. Condensable materials were trapped at −80 and −196° while noncondensable products were continuously removed by pumping. Unreacted III, which was retained in the −80° trap along with I, was extracted by fractionation and recycled through the hot zone. Only B_2H_6 (0.008 mmol) was obtained in the −196° trap and only I (0.037 mmol; n^{20}D 1.4112; lit.[20] n^{20}D(cis) 1.4266, n^{20}D(trans) 1.4116) was isolated at −80°. Very slightly volatile and nonvolatile white solids coated the walls of the hot zone and the regions immediately outside the hot zone.

The decomposition of III-*d* (0.403 mmol) gave I (0.203 mmol; n^{25}D 1.4119) and B_2D_6 (0.084 mmol; 94% D_2 on hydrolysis with D_2O).

Registry No. I, 692-48-8; II, 38781-17-8; III, 38832-81-4; III-*d*, 38781-19-0; B_2Cl_4, 13701-67-2; $LiBH_4$, 16949-15-8; $LiBD_4$, 15246-28-3.

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Fluoropentacarbonylrhenium(I). Preparation and Oxidation to Trifluorotricarbonylrhenium(III)

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In this work, we report preparation of fluoropentacarbonylrhenium(I) by a nonoxidative halogen-exchange reaction starting with the corresponding carbonyl chloride and also by oxidation reactions starting with the metal carbonyl. We have previously reported an oxidation of decacarbonyldirhenium(0) with rhenium hexafluoride to form trifluorotricarbonylrhenium(III),[1] and we now find that the fluoropentacarbonyl was formed during that reaction. We also report a new oxidation of the carbonyl using xenon difluoride, which gives both of the rhenium carbonyl fluorides, successively.

Experimental Section

Reactions were carried out using vacuum-line techniques and Kel-F apparatus.[2] Rhenium and tungsten hexafluorides, xenon difluoride, and chloropentacarbonylrhenium(I) were prepared by standard methods.[3-6] Hydrogen fluoride was purified by fractional distillation.[7] Decacarbonyldirhenium(0) (Alfa Inorganics) was stored in the dark and under dry argon. Six reactions were studied.

(a) Hydrogen Fluoride with Chloropentacarbonylrhenium(I). Prior to reaction, 0.15 mmol of the solid carbonyl chloride was wrapped in PTFE filter paper secured with PTFE tape, as though in a "tea bag," in order to keep the solid separate from soluble products. Reaction with about 5 ml of liquid anhydrous hydrogen fluoride at room temperature slowly formed a brown solution. After every 12 hr for 3 days the vapors above the solution were removed, and then all volatile compounds were evaporated leaving a brittle noncrystalline brown solid.

The collected vapors were condensed onto excess sodium fluoride to absorb hydrogen fluoride, and 0.14 ± 0.02 mmol of gas remained (measured tensiometrically).

(b) Rhenium Hexafluoride with Decacarbonyldirhenium(0). About 0.15 mmol of decacarbonyldirhenium(0) with about 5 ml of liquid anhydrous hydrogen fluoride was allowed to react with about 0.05 mmol of rhenium hexafluoride at room temperature. A brown solution formed rapidly, and after 10 min, the solution was poured through a PTFE filter into another Kel-F tube. The hydrogen fluoride was condensed back onto the unreacted carbonyl, and the cycle of operations was repeated as long as solid remained in the first tube. The brown product in the second tube was washed with tungsten hexafluoride to remove rhenium pentafluoride which is also formed.

(c) Xenon Difluoride and Decacarbonyldirhenium(0). An accurately weighed, 0.15-mmol sample of decacarbonyldirhenium(0) was placed in an evacuated reaction tube connected to Kel-F tubing (~1-mm bore, 12.5-cm length ≡ 1.00 ml of solution). Then 0.15 mmol of xenon difluoride dissolved in anhydrous hydrogen fluoride (0.60 ml of 0.25 *M* solution) was added. After 2–3 hr, all the solid had dissolved in the hydrogen fluoride to form a brown solution, which was evaporated to leave a brown solid.

(d) Xenon Difluoride with the Soluble Brown Product. It was assumed that the soluble brown products from the "tea bag" reaction of (a) and the oxidation reaction of (c) were fluoropentacarbonylrhenium(I), and accurately weighed 0.3-mmol samples were oxidized with 0.3-mmol amounts of xenon difluoride, as above. The solid dissolved immediately forming a brown solution, gas was evolved, rapidly at first and then slowly for 20–30 min, and a brown solid slowly precipitated leaving a pale brown solution.

(e) Same Reaction as in (d) except That More Xenon Difluoride Was Added. The brown solid was rapidly consumed and a green solution remained.

(f) Boron Trichloride with the Soluble Brown Product. A sample of the brown product of the reaction in (a) was allowed to react with liquid boron trichloride at room temperature for about 30 min. The mixture was evaporated and then heated to 50° to drive off all the boron trichloride. The residue was a white solid.

Results and Discussion

The results of the above six reactions, which are discussed below, are shown in Table I.

The brown product of the "tea bag" reaction in (a), between hydrogen fluoride and chloropentacarbonylrhenium(I), was analyzed. It was readily oxidized by aqueous alkaline peroxide to form perrhenate and fluoride which can be both determined.[1] *Anal.* Calcd for $Re(CO)_5F$: Re, 53.9; F, 5.5. Found: Re, 56; F, 5.8. Confirmation of this formulation was obtained as follows.

The ir spectra in Figure 1 and the X-ray powder patterns in Tables II and III are shown for both the white reactant, chloropentacarbonylrhenium(I), and the brown product, fluoropentacarbonylrhenium(I).

The similar patterns in the carbonyl regions of the ir spectra are consistent with similar symmetries for the five carbonyls in both compounds. The bands at 350 cm^{-1} are due to Re–C modes, and the band at 294 cm^{-1} is due to Re–Cl modes.[8] The new band at 475 cm^{-1} is therefore due to Re–F modes. The reaction in (f), between boron trichloride and fluoropentacarbonylrhenium(I), was used because boron trichloride has been shown to be an effective chlorinating reagent with fluorides.[4] The result of this reaction confirms the assignment of the 475-cm^{-1} band because the white product so formed had an ir spectrum identical with the original carbonyl chloride starting material. The poorly defined X-ray powder pattern (Table II) is consistent with the noncrystalline appearance of the solid. These ir spectra and X-ray powder patterns were found to be particularly useful in checking the complete-

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Table I. Summary of Reactions Involving Rhenium Carbonyl Fluorides

Reaction	Reactants	Products
a	HF, $Re(CO)_5Cl$	$Re(CO)_5F$, HCl
b	ReF_6, $Re_2(CO)_{10}$	$Re(CO)_5F$, $Re(CO)_3F_3$, ReF_5, CO
c	XeF_2, $Re_2(CO)_{10}$	$Re(CO)_5F$, Xe
d	XeF_2, $Re(CO)_5F$	$Re(CO)_3F_3$, Xe, CO
e	XeF_2, $Re(CO)_3F_3$	ReF_5, Xe, CO
f	BCl_3, $Re(CO)_5F$	$Re(CO)_5Cl$, BF_3

Table II. d_{hkl} Values and Relative Intensities (Arbitrary Scale) for the X-Ray Diffraction Pattern of Powdered Fluoropentacarbonylrhenium(I)

d_{hkl}, Å	I/I_0	d_{hkl}, Å	I/I_0
6.3	3	3.7	7
5.83	8	3.2	1
5.70	10	3.0	1
5.2	2	2.8	2
4.2	2	1.8	2

Table III. d_{hkl} Values and Relative Intensities (Arbitrary Scale) for the X-Ray Diffraction Pattern of Powdered Chloropentacarbonylrhenium(I)

d_{hkl}, Å	I/I_0	d_{hkl}, Å	I/I_0
5.83	9	2.37	2
5.25	10	2.32	1
4.87	8	2.20	2
4.17	4	2.17	3
3.90	6	2.13	2
3.39	3	2.09	2
3.22	5	2.05	1
3.12	6	2.03	1
2.90	4	1.97	1
2.83	7	1.96	1
2.66	4	1.90	3
2.59	5	1.82	1
2.55	2	1.78	1
2.49	4	1.76	2

ness of the reaction in (a). Unless the volatile product is removed several times as described, the halogen exchange is found to be incomplete.

Other properties of fluoropentacarbonylrhenium(I) were observed. Solubility in organic solvents followed the same pattern as for trifluorotricarbonylrhenium(III),[1] and osmometry and conductivity measurements in acetone gave the following results: molecular weight for $Re(CO)_5F$: calcd, 345; found, 370 ± 30; *molar conductance* for 1:1 ionic solutes in acetone: calcd, 110-175 $cm^2\ ohm^{-1}\ mol^{-1}$;[9] found, 6 $cm^2\ ohm^{-1}\ mol^{-1}$. The solid is diamagnetic at room temperature, as would be expected for a d^6 Re(I) atom in an octahedral complex. These properties are consistent with a molecular monomer. Attempts to obtain mass spectral data gave inconclusive results.

The brown product of the reaction in (b), between rhenium hexafluoride and decacarbonyldirhenium(0), was identified by comparison with ir spectra and X-ray powder patterns of decacarbonyldirhenium(0),[1,10] trifluorotricarbonylrhenium(III),[1] and fluoropentacarbonylrhenium(I) (Figure 1, Table II). The presence in the product of both carbonyl fluorides of rhenium was detected, but there was no unreacted carbonyl. The fluoropentacarbonyl was detected by the ir absorptions at 1950-1975 cm^{-1}, and the trifluorotricarbonyl by the sharp peak at 2120 cm^{-1}. Absorptions at 2040-2070 cm^{-1} were observed, but they are not diagnostic because both carbonyl fluorides absorb in this region. The presence of the trifluorotricarbonyl was also detected by its strong X-ray powder pattern. Products obtained from different preparations varied in composition, but the fluoropentacarbonyl was always the major component of the product. Because mixtures were formed, this reaction does not provide a satisfactory preparative method for fluoropentacarbonylrhenium(I). Nevertheless, the result is of interest because it shows that the reaction forms this compound as an intermediate, before formation of the ultimate products, which have previously been shown to be the trifluorotricarbonyl and then the pentafluoride of rhenium.[1]

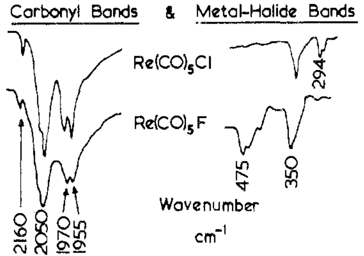

Figure 1. Absorptions in the ir spectra of Nujol mulls of (top) chloropentacarbonylrhenium(I) and (bottom) fluoropentacarbonylrhenium(I). The two spectra are very similar in the carbonyl region and also at 350 cm^{-1} (this is due to a metal-carbon mode). The absorption band with a maximum at 294 cm^{-1} is due to metal-chloride vibrations and the band at 475 cm^{-1} is due to metal-fluoride vibrations.

The brown products of the oxidation reactions in (c) and (d), respectively, using xenon difluoride with decacarbonyldirhenium(0) and fluoropentacarbonylrhenium(I), respectively, were identified by ir spectra and X-ray powder patterns as above. The products were found to be uncontaminated samples of the rhenium fluoropentacarbonyl and the trifluorotricarbonyl, respectively. The green product of the reaction in (e), with excess xenon difluoride, was the pentafluoride. Thus, this reaction sequence is a series of stepwise oxidations to form products in successively higher oxidation states, and so by contrast to the hexafluoride oxidations described above, use of xenon difluoride as an oxidant does provide a satisfactory preparative method for the carbonyl fluorides of rhenium.

Thus, two preparative methods for fluoropentacarbonylrhenium(I) have been proven. Preparation using hydrogen fluoride was investigated because it is well known as a nonoxidative halogen-exchange reagent,[11,12] which reacts with chlorides forming the corresponding fluoride and gaseous hydrogen chloride.[13] Preparation using xenon difluoride was investigated because this reagent is very soluble in anhydrous hydrogen fluoride (which enables the convenient "titration" technique to be used), it is a powerful oxidant, and the only residue after its reduction is xenon gas[14] (which avoids the need for special purification, as was the case in our previous method[1,15]).

With the successful preparation of fluoropentacarbonylrhenium(I), there is for the first time a complete set of corresponding carbonyl halides of a transition metal, $Re(CO)_5X$ (X = F, Cl, Br, I). The preparative route, starting with a halogen-exchange reaction using anhydrous hydrogen fluoride with a carbonyl chloride and followed by spe-

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cific and stepwise oxidation with xenon difluoride, is potentially important. There are known carbonyl chlorides of many transition metals, and it is probable that at least some of these could be used to begin similar reaction sequences. We have investigated this proposition using the carbonyl chlorides of molybdenum and tungsten as starting materials.

Registry No. HF, 7664-39-3; Re(CO)$_5$Cl, 14099-01-5; ReF$_6$, 10049-17-9; Re$_2$(CO)$_{10}$, 14285-68-8; XeF$_2$, 13709-36-9; Re(CO)$_5$F, 38708-78-0; Re(CO)$_3$F$_3$, 38708-80-4; BCl$_3$, 10294-34-5.

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Systematic Preparation of Carbonyl Fluorides of Molybdenum and Tungsten using Xenon Difluoride as Oxidant

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We have shown[1] that a halogen-exchange reaction can be used to change chloropentacarbonylrhenium(I) into the corresponding fluoropentacarbonyl and that this compound can be oxidized with xenon difluoride to the trifluorotricarbonyl. We have now applied a similar method to reactions beginning with the carbonyl chlorides of molybdenum and tungsten.

Experimental Section

Reagents. The dichlorotetracarbonyls of molybdenum and tungsten were prepared[2,3] by direct chlorination of the carbonyls (BDH Ltd.). The investigations were carried out using vacuum-line techniques and Kel-F apparatus as described previously.[1]

Molybdenum Carbonyl Fluoride Investigation. Dichlorotetracarbonylmolybdenum(II) was weighed accurately. Typically, 3.5 mmol of the carbonyl chloride was allowed to react with about 20 ml of liquid anhydrous hydrogen fluoride at room temperature. Hydrogen chloride gas and a pale yellow solution formed slowly. After 1 hr, the gas was removed and the solution was poured into another evacuated Kel-F tube. About 10 ml of the hydrogen fluoride was condensed back onto the solid, and the process was repeated four or five times or until no more colored solution formed. The mass of any residue was determined accurately in order that it can be deducted from the initial mass of solid for calculation of the amount of reactant. The yellow-orange solution of the molybdenum(II) compound was divided into a number of equal volumes by pouring into evacuated Kel-F tubes, and these were used as follows.

(a) Evaporation to dryness yielded some yellow solid, but as the last trace of solvent was removed, the color changed to dark green and then black. The black residue was insoluble in hydrogen fluoride and had no ir absorptions in the carbonyl region.

(b) In order to form a molybdenum(III) compound, 0.70 mmol of the yellow-orange molybdenum(II) compound was oxidized with 0.35 mmol of xenon difluoride dissolved in hydrogen fluoride (*i.e.*, 1.40 ml of 0.25 *M* solution). When the oxidant was added, the solution immediately became green, and xenon and carbon monoxide were evolved. On subsequent evaporation of the solvent, the solution became dark green and viscous; then as the last trace of solvent was removed, a golden brown solid formed. The ir spectrum of the solid is shown (Figure 1).

(c) A 0.70-mmol sample of the molybdenum(II) compound was oxidized with 0.70 mmol of xenon difluoride in order to form a molybdenum(IV) compound. In this case, xenon and carbon monoxide were rapidly evolved and the solution immediately became yellow; there may also be a yellow precipitate depending on the volume and temperature of the solution. Subsequent distillation left a yellow solid, and its ir spectrum is also shown (Figure 1).

If the yellow solution of the molybdenum(IV) compound in hydrogen fluoride was left at room temperature for a few hours, it turned green. This green solution contained the molybdenum(III) product (as in part (b)) and it also contained molybdenum hexafluoride (as in part (e)).

(d) A 0.70-mmol sample of the molybdenum(II) compound was oxidized with 1.05 mmol of xenon difluoride in an attempt to form a molybdenum(V) compound. However, once again the solution became yellow and then changed to green. This change to the molybdenum(III) product was faster than the similar process in part (c).

(e) A 0.70-mmol sample of the molybdenum(II) compound was oxidized with 1.40 mmol of xenon difluoride in order to form a molybdenum(VI) compound. Initially, the solution became yellow but then quickly turned colorless. Evaporation of the solution left no residue. The product of this oxidation was identified as molybdenum hexafluoride: the product is colorless and volatile; from the stoichiometry of the preparation the product must be a fluoride of molybdenum(VI); hydrolysis of the product yielded only a colorless solution whereas lower oxidation state aqueous molybdenum species are brown.

Tungsten Carbonyl Fluoride Investigation. A series of reactions similar to those described above were used, beginning with dichlorotetracarbonyltungsten(II). However, only about 0.7 mmol of starting material was used because of the limited solubility of the product in the hydrogen fluoride; thus, a yellow solution is obtained if the solution is warm (above 30°) but if cold (below 10°), the solution is almost colorless and yellow-orange crystals form on the walls of the Kel-F tube. Portions of the yellow solution of the tungsten(II) compound were used as follows.

(a) Evaporation to dryness yielded a black residue which had no ir absorptions in the carbonyl region.

(b) Attempted oxidations of the yellow tungsten(II) compound to tungsten(III) or -(IV) compounds produced only a colorless mixture of tungsten hexafluoride (identified as for the molybdenum analog) and hexacarbonyltungsten(0) (identified by its ir spectrum).

(c) Oxidation of the yellow tungsten(II) compound to the tungsten(V) compound formed a very pale yellow solution which gave yellow crystals on evaporation of the solvent. These yellow crystals turned blue in the presence of the slightest trace of water. No ir absorptions in the carbonyl region were observed. The tungsten(V) product was probably tungsten pentafluoride.[4]

Results and Discussion

In the first stages of both investigations, nonoxidative halogen-exchange reactions with hydrogen fluoride were used. As in our previous report,[1] the reactions were taken to completion by repeated removal of products. Since the only gaseous product was hydrogen chloride, the yellow solutions contained the difluorotetracarbonyls corresponding to the dichlorotetracarbonyl starting materials.

It is important to determine accurately the amounts of the starting materials, so that the amounts of xenon difluoride can be predetermined in order to give the desired F:Mo or F:W molar ratios.

Molybdenum System. Oxidation to molybdenum(III) or -(IV) is accompanied by evolution of carbon monoxide, so these compounds have fewer than four carbonyl ligands. The three distinct ir carbonyl peaks in both spectra (Figure 1) are consistent with three carbonyl ligands. In the case of the molybdenum(IV) compound, the absorptions are at lower wave numbers than for the dicarbonyl of molybdenum(IV),[5]

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