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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Contribution from the Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Australia

## 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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(1) T. A. O'Donnell, K. A. Phillips, and A. B. Waugh, *Inorg. Chem.*, 12, 1435 (1973).

(2) R. Colton and I. B. Tomkins, *Aust. J. Chem.*, 19, 1143 (1966).

(3) J. A. Bowden and R. Colton, *Aust. J. Chem.*, 21, 2657 (1968).

(4) J. Schroeder and F. J. Grewe, *Angew. Chem., Int. Ed. Engl.*, 7, 132 (1968).

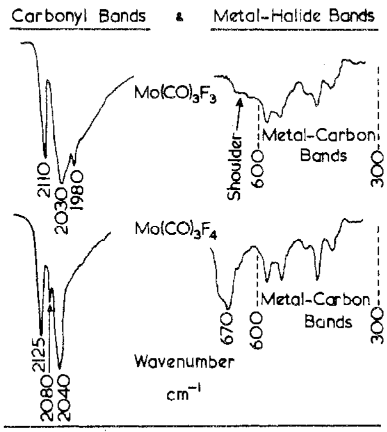

**Figure 1.** Absorptions in the ir spectra of Nujol mulls of (top) trifluorotricarbonylmolybdenum(III) and (bottom) tetrafluorotricarbonylmolybdenum(IV).

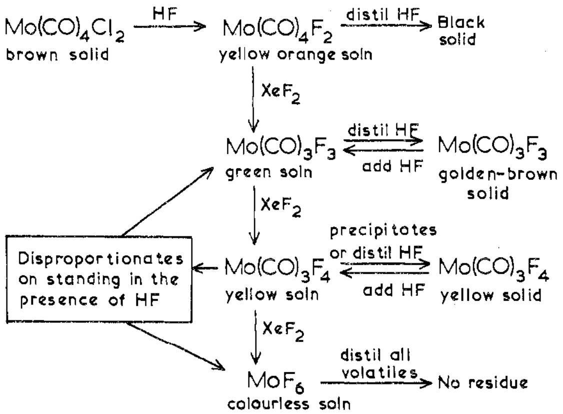

**Figure 2.** Related series of reactions of molybdenum carbonyl fluorides obtained using xenon difluoride as oxidant.

so the spectrum is not consistent with two carbonyl ligands.

Both ir spectra (Figure 1) have similar bands in the metal-carbon region. In the case of the molybdenum(IV) compound, the band at 670 $cm^{-1}$ is in the region for terminal fluorides.[5] In the case of the molybdenum(III) compound, the metal-fluoride absorption would be expected at a slightly lower wave number, where the weak absorption shoulder just above 600 $cm^{-1}$ appears. In our previous work,[1] we found that the metal-halide absorptions may have intensities similar to those of the metal-carbon absorptions.

Hence, from their predetermined compositions, the gases evolved during their preparations, and their ir spectra, the products of the oxidations appear to be trifluorotricarbonylmolybdenum(III) which is green in hydrogen fluoride and golden brown as a solid and tetrafluorotricarbonylmolybdenum(IV) which is unstable in hydrogen fluoride and is yellow both in solution and as a solid. See Figure 2.

Yellow tetrafluorotricarbonylmolybdenum(IV) is unstable in hydrogen fluoride, but it does not decompose by eliminating one carbonyl ligand to form orange tetrafluorodicarbonylmolybdenum(IV).[5] Instead, it decomposes to form the green soluble products as described above. One factor favoring this is the higher entropy change associated with formation of soluble rather than insoluble products. This instability can be applied to isolation of pure samples of carbonyl fluorides in the following way. To prepare the molybdenum(III) compound, use slightly *more* than the stoichiometric amount of oxidant; on standing, the small amount of molybdenum(IV) compound decomposes and evaporation leaves the pure golden brown product. To prepare the molybdenum(IV) compound, first prepare the molybdenum(III) compound, and then add slightly *less* than the stoichiometric amount of oxidant; filter immediately and dry the yellow solid by evaporation of volatile compounds.

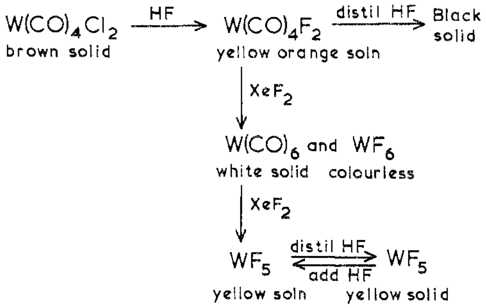

**Figure 3.** Related series of reactions of tungsten carbonyl fluoride obtained using xenon difluoride as oxidant.

**Tungsten System.** Oxidation of the tungsten(II) compound did not form higher oxidation state carbonyl fluorides. This different behavior, as compared with the molybdenum system, is consistent with the greater stability of tungsten hexafluoride as compared with molybdenum hexafluoride.[6] Thus, attempted oxidation to tungsten(III) or -(IV) results in disproportionation so as to form the stable hexafluoride. See Figure 3.[7]

**Registry No.** HF, 7664-39-3; $XeF_2$, 13709-36-9; $Mo(CO)_4Cl_2$, 15712-13-7; $Mo(CO)_4F_2$, 38703-63-8; $Mo(CO)_3F_3$, 38708-79-1; $Mo(CO)_3F_4$, 38703-64-9; $MoF_6$, 7783-77-9; $W(CO)_4Cl_2$, 22172-29-8; $W(CO)_4F_2$, 38703-66-1; $W(CO)_6$, 1440-11-0; $WF_6$, 7783-82-6; $WF_5$, 19357-83-6.

**Acknowledgment.** Financial support from the Australian Atomic Energy Commission is gratefully acknowledged.

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(5) T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 9, 2611 (1970).

(6) T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 5, 1434 (1966).

(7) Our attention has been drawn by a reviewer to a conference report that xenon difluoride has been used in reactions with metal carbonyls: C. J. Marshall and R. D. Peacock, Abstracts of Papers, 6th International Symposium on Fluorine Chemistry, 1971, No. C-33.

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## Nuclear Overhauser Studies on Formato and Formamido Complexes of Pentaamminecobalt(III)

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We wish to report the results of nuclear Overhauser effect (NOE) studies on some complexes of pentaamminecobalt(III). The NOE has been used to determine the conformation of the coordinated formate ion and to help in the assignment of the pmr spectrum of a new dinuclear formamide complex.

In the first application it was of interest to determine if an NOE could be observed and then to use it to study the con-