When CO_2 was introduced into the suspension of $Co(OCH_3)_2$ or $Ni(OCH_3)_2$ in pyridine, neither the dissolution nor the color change was observed.

The facile insertion of CO_2 to cupric methoxide, **1** and **3**, and the liberation of CO_2 from copper methyl carbonate, **2** and **4**, may be regarded as a reversible CO_2 fixation by cupric methoxide, and these observations may be utilized for synthetic organic reactions using CO_2.

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A Carbonyl Fluoride of Rhenium

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There are many molecular carbonyl halides of transition metals in which the halogen is chlorine, bromine, or iodine,[1] but only two carbonyl fluorides of transition metals have been reported: tetrafluorodicarbonylmolybdenum(IV) which probably has a dimeric structure[2] and difluorotricarbonylruthenium(II) which has been shown to have a tetrameric structure.[3]

The only known carbonyl chlorides, bromides, and iodides of rhenium are the monomeric pentacarbonyls and the dimeric tetracarbonyls of rhenium(I).[1]

We have isolated trifluorotricarbonylrhenium(III), $Re(CO)_3F_3$, from the reaction of a limited amount of rhenium hexafluoride with decacarbonyldirhenium(0) in Kel-F apparatus. Anhydrous hydrogen fluoride is used as a solvent for the rhenium hexafluoride during the preparation, and tungsten hexafluoride is used as a solvent to purify the product by removing rhenium pentafluoride which is also formed. This solvent would also remove any oxide fluorides of rhenium which are possible impurities in the rhenium hexafluoride. A porous disk of sintered PTFE is used for separation of solids from liquids. The general procedure is similar to that which we have previously described.[2]

Anhydrous hydrogen fluoride and some rhenium hexafluoride are condensed onto the decacarbonyldirhenium(0) at −196° and the frozen solid mixture is allowed to melt. The mixture becomes dark brown and carbon monoxide gas is evolved. The gas can be removed after the reaction mixture is again solidified. Additions of rhenium hexafluoride are repeated until the mixture separates to a dark brown solid and a pale green solution. The solid is trifluorotricarbonylrhenium(III) and the green color in the liquid hydrogen fluoride is due to rhenium pentafluoride.[4] If more rhenium hexafluoride is added, there is rapid evolution of carbon monoxide, the brown solid is rapidly decomposed, and only the green solution remains.

When the mixture separates, no more rhenium hexafluoride is added, instead, the solution is poured off through the porous disk and the hydrogen fluoride is distilled from the apparatus. Tungsten hexafluoride is condensed onto the brown solid, allowed to melt, and then the resulting solution, green due to rhenium pentafluoride, is separated from the solid by pouring through the filter. This process of washing the solid with tungsten hexafluoride is repeated several times to remove all traces of the rhenium pentafluoride. The final product is a finely divided, free flowing, dark brown solid.

Results

Analyses for both rhenium and fluoride in aqueous solution can be obtained if the rhenium is present as perrhenate. There is no chemical interference between the two anionic species, the perrhenate can be determined from its uv absorbance,[5] and the fluoride can be determined using an ion-selective electrode. However, it was found to be difficult to oxidize the rhenium in this compound to oxidation state VII. After the compound was heated with sodium peroxide, an insoluble yellow-brown gelatinous material formed in water instead of the expected colorless perrhenate. A similar result followed fusion with a mixture of potassium nitrate and potassium hydroxide. The original compound dissolves slowly in water but addition of hydrogen peroxide forms the insoluble gelatinous material. It is known that some yellow-brown compounds of rhenium(IV) containing hydroxo and/or oxo groups are oxidized only very slowly.[6] Apparently the rhenium in the compound is oxidized from oxidation state III to IV but further oxidation is slow because of formation of intractable polymeric materials of indefinite composition. Repeated additions of hydrogen peroxide to the compound in aqueous alkali and prolonged boiling for several hours eventually gives a colorless solution containing perrhenate and fluoride, and this was analyzed.

Analysis for coordinated carbon monoxide in most transition metal carbonyl complexes can be accomplished by displacing the ligands with a bromine carrier,[7] but this method does not displace any carbon monoxide from trifluorotricarbonylrhenium(III). However, it was found that the carbonyl ligands are displaced when a mixture of the compound with solid iodine is heated strongly. This mixture was placed in an evacuated glass apparatus and heated with a flame to liberate gaseous carbon monoxide, which was then determined by pressure–volume measurements. The solid residue in the apparatus had no ir absorptions near 2000 cm^{-1} which indicates that all of the carbonyl ligands had been displaced. *Anal.* Calcd for $Re(CO)_3F_3$: Re, 56.9; CO, 25.7; F, 17.4. Found: Re, 55; CO, 25; F, 16.7.

Nujol mulls of trifluorotricarbonylrhenium(III) and decacarbonyldirhenium(0) were prepared in an atmosphere of dry argon to avoid contamination by hydrolysis or oxidation.[8] The ir absorptions in the carbonyl stretching region[9] for the spectrum of the carbonyl fluoride are at higher wave numbers than those

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[1] F. Calderazzo in "Halogen Chemistry," Vol. 3, V. Gutmann, Ed., Academic Press, London, 1967, p 383 ff.

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

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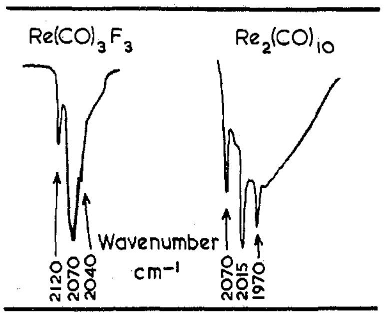

Figure 1.—Carbonyl absorptions in the ir spectra of Nujol mulls of (left) trifluorotricarbonylrhenium(III) and (right) decacarbonyldirhenium(0).

in the spectrum of the original carbonyl (Figure 1). There are no absorptions in the bridging carbonyl ligand region, *i.e.*, between 1900 and 1700 cm^{-1}. There are two, narrow, moderately intense bands in the fluoride ligand region[10] at 650 and 580 cm^{-1}. Also, there is a sharp, weak peak at 350 cm^{-1} which is within the region for metal–carbon stretching or metal–carbon–oxygen bending modes.[9]

The X-ray diffraction pattern of powdered trifluorotricarbonylrhenium(III) was obtained using Cu Kα radiation. The *d* values and relative intensities based on the most intense lines equal to 10 are listed (Table I).

TABLE I

d_{hkl} VALUES AND RELATIVE INTENSITIES (ARBITRARY SCALE) FOR THE X-RAY DIFFRACTION PATTERN OF POWDERED TRIFLUOROTRICARBONYLRHENIUM(III)

d_{hkl}, Å	I/I_0	d_{hkl}, Å	I/I_0
6.81	6	2.55	4
6.44	6	2.34	2
5.68	4	2.29	3
5.41	4	2.20	1
5.04	1	2.15	1
4.83	10	2.09	1
4.21	10	1.93	1
3.82	6	1.86	1
3.66	7	1.74	1
3.54	4	1.72	1
3.41	5	1.68	1
3.23	3	1.63	2
3.06	5	1.61	2
2.69	1	1.41	1

This pattern contains no lines corresponding to decacarbonyldirhenium(0).[11] The absence of these lines together with the comparison of the ir spectra given above indicates that no decacarbonyldirhenium(0) is present and therefore the solid is indeed a carbonyl fluoride and not merely a mixture of unreacted carbonyl contaminated with a fluoride.

The compound is insoluble in nonpolar and slightly polar solvents but is soluble in more polar solvents. Thus, it is insoluble in benzene, *n*-hexane, tetrachloromethane, trichloromethane, and dichloromethane. It is slightly soluble in diethyl ether and dioxane. It is readily soluble in methanol, ethanol, and acetone and is also fairly soluble in water. Dilute solutions in these solvents are yellow and more concentrated solutions are brown. An ir absorption band at about 2090 cm^{-1} is observed for those solutions where this region is free from absorptions due to the solvent. The solutions appear to be unchanged for several hours unless exposed to atmospheric oxidation when insoluble brown or black residues are formed. The solution in acetone was the least affected in this way and was therefore used for further investigation.

The apparent molecular weight in a freshly prepared acetone solution was determined by vapor pressure osmometry and was found to be 300 ± 30. Subsequent measurements gave lower results as the solution slowly changed to form the black residue. The molar conductivity in a freshly prepared acetone solution was found to be only 6 cm^2 ohm^{-1} mol^{-1} and subsequent measurements gave higher results as the solution decomposed.

The mass spectrum of ions generated by electron bombardment of the solid includes pairs of species at *m/e* 270 and 272 (*i.e.*, Re(CO)F$_3^+$; these are the heaviest ions detected) and at *m/e* 254 and 256 (*i.e.*, ReCF$_3^+$), and also, ions at *m/e* 28 (*i.e.*, CO$^+$). These are possible fragments of trifluorotricarbonylrhenium(III). Several other ions containing rhenium with only oxygen and/or fluorine were detected. Since these could have been formed either from the compound or from possible impurities due to oxidation, they do not provide such definite evidence as the carbon containing species given above.

Attempts to prepare a triphenylphosphine derivative were unsuccessful because there was no replacement of carbonyl ligands from any of the solutions of the compound at room temperature. When the solutions were allowed to stand for long times, or when they were heated, decomposition to form black residues occurred.

The room temperature, effective paramagnetic moment of the compound is approximately 1.0 BM/atom of rhenium.

Discussion

The pair of ir absorptions for trifluorotricarbonylrhenium(III) at 650 and 580 cm^{-1} can be compared with the absorptions at 715 cm^{-1} for rhenium hexafluoride, 627 cm^{-1} for the hexafluororhenate(V) anion, and 541 cm^{-1} for the hexafluororhenate(IV) anion,[12] and hence they are in the rhenium–fluoride bond stretching region but are at comparatively high wave numbers for fluoride bonded to rhenium(III), and this will be discussed below. The appearance of the two ir peaks indicates that the compound has the fac[13] structure (C_{3v} point symmetry, a$_1$ and e modes are ir active for the Re–F bonds)[14] rather than the mer[13] structure (C_{2v} point symmetry, 2a$_1$ and b$_2$ modes are ir active for Re–F bonds).[14]

In the isomers of M(CO)$_3$X$_3$ molecules, the symmetry, and hence the ir active modes for the C–O bonds, and the M–X bonds are the same. Thus, two ir bands in the carbonyl region would also identify the fac isomer, whereas no definite conclusion can be drawn from the appearance of three absorptions.[9]

The ir spectrum for trifluorotricarbonylrhenium(III) in the carbonyl region does not provide easily interpreted evidence but this could be due to distortion of the molecules in the solid state. Distortion of bond angles could affect linearity of the Re–C–O bonds but,

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[13] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1407 (1966).

[14] M. J. Cleare and W. P. Griffith, *ibid.*, 372 (1969).

even in a distorted molecule, the Re–F bonds could retain C_{3v} symmetry. Hence, the two clearly defined absorptions in the metal–fluoride region are consistent with the fac structure and the more complex spectrum in the carbonyl region is probably the result of distortions due to crystal effects.

In the fac structure, each fluoride is opposite a carbonyl ligand and the electron withdrawing nature of these π-acceptor ligands could account for the comparatively high wave numbers observed for the rhenium(III)–fluoride stretching frequencies, as was pointed out above.

The solubility in polar solvents, the molecular weight of about 300, and the molar conductivity of only 6 cm^2 ohm^{-1} mol^{-1} in acetone, compared to values of 110–175 cm^2 ohm^{-1} mol^{-1} for 1:1 electrolytes,[15] indicate that trifluorotricarbonylrhenium(III) is a molecular monomer.

The room temperature paramagnetic moment of 1.0 BM is not easily interpreted, but this is also the case in the simple octahedral rhenium hexafluoride molecule which has a moment of only 0.25 BM, although the moment of the hexachloride is 2.07 BM.[16] The comparatively low result with fluoride ligands may be due to strong spin–orbit coupling.

Thus we postulate that trifluorotricarbonylrhenium(III) is a molecular monomer and that this preparation results in formation of the fac isomer. Reaction between decacarbonyldirhenium(0) and rhenium hexafluoride involves breaking the metal–metal bond and replacement of carbonyl ligands by fluoride ligands until no two carbonyls are axial to each other. This should proceed fairly rapidly because axial carbonyl ligands are more substitution labile than carbonyls trans to ligands which are relatively poor π acceptors.[17] The fac isomer is isolated because the remaining carbonyl ligands are less labile. Only the addition of excess rhenium hexafluoride or heating the compound with iodine displaces the remaining three carbonyl ligands.

Acknowledgment.—Financial support from the Australian Atomic Energy Commission is gratefully acknowledged. K. A. P. thanks the Council of the Royal Melbourne Institute of Technology for granting study leave.

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Hydroxo-Bridge Cleavage in Dicobalt(III) Complexes

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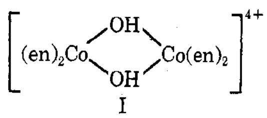
Two kinetic studies have recently been published on the hydroxo-bridge cleavage reactions of the di-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] complex (I) in acidic solutions.[1,2] The corresponding reaction

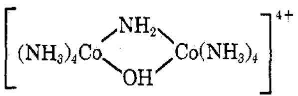


I

of the di-μ-hydroxo-bis[tetraamminecobalt(III)] complex has also been investigated.[3] We wish to comment on the mechanisms which have been proposed in the light of our studies on hydroxo-bridge cleavage of the complexes μ-hydroxo-bis[pentaamminecobalt(III)] (II),[4] and μ-amido-μ-hydroxo-bis[tetraamminecobalt(III)] (III).[5] A mechanism which has not been mentioned previously is suggested, and would seem to merit serious consideration.

$[(NH_3)_5Co\cdot OH\cdot Co(NH_3)_5]^{5+}$

II



III

Pseudo-first-order rate constants, k_{obsd}, for the formation of aquopentaamminecobalt(III) from II, $\mu = 2.0\ M$ ($LiClO_4$) and $[H^+] = 0.0001$–$2.0\ M$, conform to the rate law

$$k_{obsd} = k_a + k_b[H^+] \quad (1)$$

At 25° $k_a = 7.58 \times 10^{-3}$ sec^{-1} and $k_b = 5.37 \times 10^{-3}$ l. mol^{-1} sec^{-1}. Hydroxo-bridge cleavage of III gives stable μ-amido products. In the presence of chloride[5] and bromide,[6] and with $[H^+] = 0.1$–$2.0\ M$, $\mu = 2.0\ M$ (Na–Li–$HClO_4$), (2) applies

$$k_{obsd}/[X^-] = k_a + k_b[H^+] \quad (2)$$

Values obtained at 25° are $k_a = 1.2 \times 10^{-4}$ l. mol^{-1} sec^{-1} (Cl^-) and 1.4×10^{-4} l. mol^{-1} sec^{-1} (Br^-), $k_b = 9.6 \times 10^{-4}$ mol^{-2} sec^{-1} (Cl^-) and 4.33×10^{-4} l.^{2} mol^{-2} sec^{-1} (Br^-). The formation of the bis-aquo complex in aqueous perchloric acid solutions, $\mu = 2.0\ M$, has also been studied,[7] and at 35° $k_b = 1.6 \times 10^{-4}$ l. mol^{-1} sec^{-1}; the path $k_a \ll 4.5 \times 10^{-5}$ sec^{-1} may also contribute but in this case cannot be distinguished from another path.[8]

A variety of mechanisms can be invoked to explain the hydrogen ion dependence observed for bridge cleavage of di-μ-hydroxo complexes. However, since complexes with only a single hydroxo bridge yield a hydrogen ion dependence of the form (1), it seems reasonable to us that any deviation from such a dependence for complexes with two hydroxo bridges is a function of the second hydroxo bridge. We propose therefore that a combination of the two hydroxo-bridge cleavage processes, which independently exhibit rate laws of the

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