

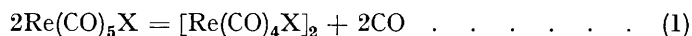
638. Tetracarbonyl Halides of Rhenium.

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The three rhenium tetracarbonyl halides $[\text{Re}(\text{CO})_4\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), prepared by thermal decomposition of the corresponding pentacarbonyl halides, with elimination of carbon monoxide, have been shown to be dimeric by molecular-weight determinations. They are reconverted into the pentacarbonyl halides by carbon monoxide at high temperature and pressure. The tetracarbonyl iodide reacts with pyridine to give the monomeric bis-pyridinerhenium tricarbonyl iodide, which is identical with the product obtained by the action of pyridine on rhenium pentacarbonyl iodide. The structures of these compounds are discussed, and the carbonyl stretching frequencies in the infrared spectra are recorded.

RHENIUM pentacarbonyl halides $[\text{Re}(\text{CO})_5\text{X}]$ were first prepared by Schulten¹ by the action of carbon monoxide on the corresponding hexahalogenorhenates. They were also prepared by Heinz and Leschewski² and by Hieber, Schuh, and Fuchs.³ The latter reported the monomeric nature of these compounds, and stated that rhenium carbonyl halides with lower carbonyl content than the pentacarbonyl halides were not produced.

By thermal decomposition of the rhenium pentacarbonyl chloride, bromide, and iodide, we have now produced the corresponding rhenium tetracarbonyl halides:



Molecular-weight determinations have shown that these compounds are dimeric. The reaction can be carried out by careful heating of the pentacarbonyl halide alone, but, in view of difficulties due to sublimation of the compounds, the reaction was best carried out by refluxing the pentacarbonyl halide in a high-boiling inert solvent. The progress of the dimerization was shown by the rate of evolution of carbon monoxide, and the reaction appeared to be fastest for the iodide and slowest for the chloride, in accordance with the reported order of chemical reactivity.³

These dimeric rhenium tetracarbonyl halides are sparingly soluble in organic solvents but can be recrystallized with difficulty from chloroform or cyclohexane. They decompose on heating without melting. The chloride and bromide form fine white crystals, but the iodide crystallizes in the form of long needles whose yellow colour undoubtedly accounts for the slight yellow colour of rhenium pentacarbonyl iodide reported previously.^{1,2,3} Very pure samples of the latter, prepared both by Brimm *et al.*⁴ and by us, are white. Schuh⁵ has observed that rhenium pentacarbonyl iodide in hexane decomposes in ultra-violet light to give a yellow solution, the spectrum of this decomposition product being similar to that of the dimeric rhenium carbonyl. Thus Schuh probably observed the spectrum of the dimeric carbonyl iodide, and we have shown that the dimeric iodide is indeed produced by irradiation of hydrocarbon solutions of the monomer.

Nitric oxide under normal conditions does not react with rhenium tetracarbonyl halides. Carbon monoxide, however, under conditions of high temperature and pressure, breaks the dimeric bridge structure to re-form the monomeric pentacarbonyl halide; reaction (1) is thus reversible, depending upon the experimental conditions.

The most reasonable structure for the tetracarbonyl halides is (I), in which there is a conventional halogen bridge as, for example, in the well-known carbonyl halides of platinum and ruthenium. The infrared spectra of the compounds in the carbonyl region (Table 1) are consistent with this formulation. Other possibilities would involve a carbonyl

¹ Schulten, *Z. anorg. Chem.*, 1939, **243**, 164.

² Heinz and Leschewski, *ibid.*, 1941, **248**, 164.

³ Hieber, Schuh, and Fuchs, *ibid.*, p. 243.

⁴ Brimm, Lynch, and Sesney, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.

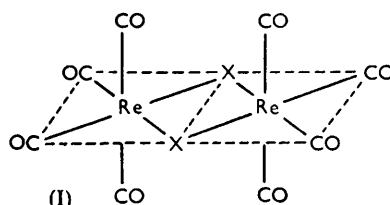
⁵ Schuh, *Z. anorg. Chem.*, 1941, **248**, 276.

bridge (although carbonyl stretching frequencies in the accepted bridging region are not observed) or a structure involving a metal-metal bond.

Infrared spectra of rhenium carbonyl halides.

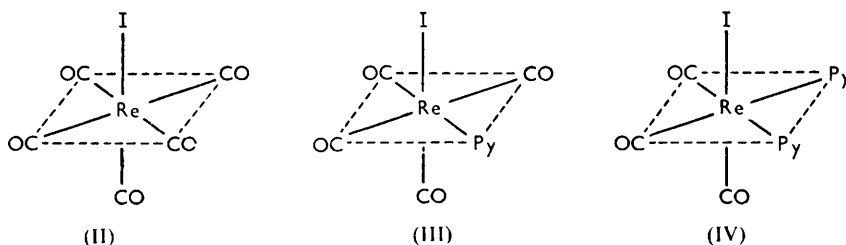
Compound	Solvent	Carbonyl stretching modes (cm. ⁻¹)	Compound	Solvent	Carbonyl stretching modes (cm. ⁻¹)
Re(CO) ₅ Cl	CCl ₄	2056, 1987	[Re(CO) ₄ Cl] ₂	CHCl ₃	2043, 2010, 1964
Re(CO) ₅ Br	CCl ₄	2057, 1993	[Re(CO) ₄ Br] ₂	CHCl ₃	2044, 2012, 1970
Re(CO) ₅ I	CCl ₄	2055, 1995	[Re(CO) ₄ I] ₂	CHCl ₃	2042, 2012, 1971
			(C ₅ H ₅ N) ₂ Re(CO) ₃ I ...	CCl ₄	2041, 1934, 1891

Hieber and Fuchs ⁶ reported the reaction of the rhenium pentacarbonyl halides with certain tertiary amines at high temperature to produce amine substitution products. We have found it possible to prepare the bis-pyridine compound (C₅H₅N)₂Re(CO)₃I under mild conditions by the direct action of pyridine on both rhenium penta- and tetra-carbonyl iodides. The latter however reacted faster, presumably owing to the ease of attack on the halogen bridge by the amine.



The configuration of the amine substitution product can be reasonably deduced by considering the nature of the ligands present and their relative ability to form multiple bonds and produce the *trans*-effect.^{7,8}

In the carbonyl halide (II), the carbonyl groups predicted to be most labile are those *cis* to the iodine atom, as iodine has the lower *trans*-effect. The first substitution product (III) may be presumed to be an intermediate in the reaction, but attempts to isolate it failed. In (III) the active carbonyl groups are those *cis* to both pyridine and iodine, as both of these have considerably lower *trans*-effects than the carbonyl group,⁷ which leads to the structure (IV) for the final bis-pyridine compound. A similar argument can be



used to show that the product obtained from pyridine and the dimeric tetracarbonyl iodide should also have structure (IV). The products were identical in both cases. In the thermal or photochemical decomposition of the pentacarbonyl iodide to give the dimer, a carbon monoxide group *cis* to the iodine will be the one most readily removed.

Attempts to substitute further carbon monoxide groups in compounds such as (C₅H₅N)₂Re(CO)₃I have failed; with three essentially non-accepting ligands present, the metal-carbon multiple-bond character will be at a maximum since the carbon

⁶ Hieber and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 269.

⁷ Chatt, Duncanson, and Venanzi, *J.*, 1955, **4456**.

⁸ Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.

monoxide ligands will have essentially exclusive use of the d_{π} orbitals for multiple-bond formation and the stability of such complexes both thermally and towards further substitution is in accord with this.

Several attempts by different methods to prepare a rhenium carbonyl fluoride from potassium hexafluororhenate were made, but none was successful. Small quantities of rhenium carbonyl, however, were isolated from the reaction between the fluororhenate and carbon monoxide in the presence of aluminium; thus the carbonyl fluoride may have been formed as an intermediate in this reaction. Similarly all attempts to prepare a rhenium carbonyl cyanide from potassium cyanorhenate $[\text{K}_3\text{Re}(\text{CN})_8]$ failed.

EXPERIMENTAL

Microanalyses and molecular weights are by the Microanalytical Laboratories, Imperial College, London.

Preparations and Techniques.—The light petroleum (b. p. 100–120°) was carefully distilled. The rhenium pentacarbonyl halides were prepared by the previous methods.^{1,2,3} Molecular weights were determined ebullioscopically in benzene.

Infrared spectra were taken (in CCl_4 or CHCl_3) on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics.

Decomposition of Rhenium Pentacarbonyl Iodide.—The pentacarbonyl iodide (57.8 mg.) was dissolved in light petroleum (50 c.c.) to give a colourless solution which when refluxed for 10 min. became pale yellow. Further refluxing (2 hr.) caused the deposition of fine yellow crystals and the evolution of carbon monoxide. When no further gas was evolved, solvent was removed (25°/0.2 mm.); the yellow crystalline residue was recrystallized from boiling chloroform to give *rhenium tetracarbonyl iodide* (45.2 mg., 83%) (Found: C, 11.1; O, 15.3; I, 30.1%; M , 801. $\text{C}_8\text{O}_8\text{I}_2\text{Re}_2$ requires C, 11.3; O, 15.1; I, 29.8%; M , 850).

This reaction was repeated in the absence of solvent, by heating rhenium pentacarbonyl iodide (43.5 mg.) in an open flask in an oven (130°). After 5 hr. the white crystals had completely changed to rhenium tetracarbonyl iodide (22.7 mg., 55%) (Found: C, 11.4; O, 15.4%). The low yield was due to sublimation of the volatile pentacarbonyl iodide before decomposition.

Decomposition of Rhenium Pentacarbonyl Bromide.—The pentacarbonyl bromide (123.6 mg.) was refluxed for 5 hr. in light petroleum (as above). After removal of solvent and recrystallization from boiling chloroform, *rhenium tetracarbonyl bromide* was obtained (95.3 mg., 80%) (Found: C, 12.9; O, 17.1; Br, 21.0%; M , 722. $\text{C}_8\text{O}_8\text{Br}_2\text{Re}_2$ requires C, 12.7; O, 16.9; Br, 21.1%, M , 756).

Decomposition of Rhenium Pentacarbonyl Chloride.—The pentacarbonyl chloride (285 mg.) was refluxed for 10 hr. in light petroleum (as above). After removal of solvent (20°/0.1 mm.) and recrystallization from boiling cyclohexane *rhenium tetracarbonyl chloride* was obtained (235 mg., 86%) (Found: C, 14.9; O, 19.6; Cl, 10.0%; M , 687. $\text{C}_8\text{O}_8\text{Cl}_2\text{Re}_2$ requires C, 14.4; O, 19.2; Cl, 10.6%; M , 667).

Interaction of Rhenium Tetracarbonyl Iodide and Carbon Monoxide.—The very finely powdered tetracarbonyl iodide (93.7 mg.) was heated in carbon monoxide (150°/200 atm.). After cooling, a fall in pressure was observed. The contents of the autoclave were extracted with benzene and the solution filtered; removal of solvent from the colourless filtrate left white crystals. Sublimation (60°/0.1 mm.) yielded rhenium pentacarbonyl iodide (82.1 mg., 82%) [Found: C, 13.5; I, 27.8%; M (cryoscopic in benzene), 477. Calc. for $\text{C}_5\text{O}_5\text{ReI}$: C, 13.3; I, 28.0%; M , 453].

Interaction of Rhenium Tetracarbonyl Iodide and Pyridine.—The tetracarbonyl iodide (76.3 mg.) was suspended in pyridine (2 c.c.) and the mixture gently warmed under reflux. As the liquid boiled there was a rapid evolution of carbon monoxide. Heating was continued (30 min.) until gas was no longer evolved. After removal of solvent (20°/0.1 mm.) the pale yellow crystalline residue was recrystallized from chloroform to give pure bispyridinerhenium tetracarbonyl iodide (78.4 mg., 79%) (Found: C, 28.4; H, 1.7; O, 8.9; N, 5.2; I, 22.5%; M , 598. Calc. for $\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_2\text{ReI}$: C, 28.1; H, 1.8; O, 8.6; N, 5.1; I, 22.8%; M , 555).

Interaction of Rhenium Pentacarbonyl Iodide and Pyridine.—The pentacarbonyl iodide (103.5 mg.) in pyridine (5 c.c.) was refluxed gently for 5 hr., after which no more carbon monoxide was evolved. Removal of solvent (20°/0.1 mm.) left pale yellow crystals which were

recrystallized from chloroform to give bispyridinerhenium tricarbonyl iodide (91.5 mg., 72%) (Found: C, 28.3; H, 1.8; N, 4.9%; *M*, 586).

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