291. *Carbonyl Halides of Manganese and Some Related Compounds.*

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Thermal decomposition of the corresponding pentacarbonyl halide has produced the three bridged manganese tetracarbonyl halides $[Mn(CO)_4X]_2$ (X = Cl, Br, and I). A number of disubstitution products $L_2M(CO)_3X$ ($L = C_5H_5N$, Ph_3P, and Ph_3As; L_2 = dipy) have been prepared. The carbonyl stretching frequencies in the infrared spectra of the compounds are recorded.

Since the discovery of manganese carbonyl, and its treatment with iodine at 140° to produce [1] the pentacarbonyl iodide, other manganese carbonyl halides have been prepared. Except for the infrared spectra of the bromide [2] and iodide,[1] no properties of these compounds have been given, although the chloride [2,3] and bromide [4] have been mentioned.

Manganese pentacarbonyl chloride and bromide have been made by the action of the halogen on a solution of manganese carbonyl at a lower temperature than that required [1] for the iodide. Bromine reacted rapidly with the carbonyl at 40°, and chlorine at 0°. Higher temperatures led to almost complete decomposition to manganese halides. The pentacarbonyl halides were purified either by vacuum sublimation or by recrystallisation from light petroleum.

Thermal decomposition ot the manganese pentacarbonyl chloride, bromide, and iodide produced the corresponding tetracarbonyl halides:

$$2Mn(CO)_5X \longrightarrow [Mn(CO)_4X]_2 + 2CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The reaction is best carried out in an inert solvent at 120°, but in contrast to the very good yields of the tetracarbonyl halides of rhenium formed [5] in this way, the yields are low (*ca.* 40%) owing to the concurrent decomposition and formation of manganese halides.

Molecular-weight measurements of these tetracarbonyl halides of manganese have

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[1] Brimm, Lynch, and Sesny, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.
[2] Wilson, *Z. Naturforsch.*, 1958, **13**b, 349.
[3] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13**b, 339.
[4] Coffield, Kozikowski, and Closson, *J. Org. Chem.*, 1957, **22**, 598.
[5] Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.

shown them to be dimeric, and analogous to the corresponding[5] rhenium compounds. In both the pentacarbonyl and the tetracarbonyl halides of manganese there is a gradual darkening in colour from chloride to iodide (Table 1). The dimeric carbonyl halides are considerably less soluble in organic solvents than the monomeric pentacarbonyl halides, but are more soluble than the corresponding rhenium compounds, and can be recrystallised readily from benzene. Also, unlike their rhenium analogues, the manganese tetracarbonyl halides can be sublimed *in vacuo*, in each case at a temperature about 70° higher than for the corresponding monomeric pentacarbonyl halide.

TABLE 1. *Carbonyl halides of manganese.*

Compound	Colour	CO stretching modes (cm.$^{-1}$) *	Compound	Colour	CO stretching modes (cm.$^{-1}$) *
$Mn(CO)_5Cl$	Pale yellow	2070, 2016	$[Mn(CO)_4Cl]_2$	Orange	2061, 2023, 1982, 1952
$Mn(CO)_5Br$	Yellow	2064, 2017	$[Mn(CO)_4Br]_2$	Brown	2056, 2023, 1982, 1954 (sh.)
$Mn(CO)_5I$	Orange	2056, 2017	$[Mn(CO)_4I]_2$	Dark brown	2048, 2022, 1983

* All strong unless otherwise noted.

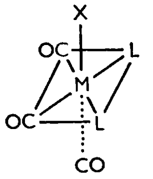
The infrared spectra of the manganese tetracarbonyl halides in the 1700—2200 cm.$^{-1}$ region are similar to those of the rhenium analogues,[5] and the structure is undoubtedly the same as that of the rhenium compounds, with a halogen bridge, as in a number of other carbonyl halide structures. The manganese tetracarbonyl halides reacted with carbon monoxide under high temperature and pressure to form the pentacarbonyl halides, thus showing reaction (1) to be reversible depending upon conditions.

A few substituted rhenium carbonyl halides have previously been prepared[6,7] by the interaction of the rhenium pentacarbonyl halides with certain ligands, and we have already mentioned[5] the formation of bispyridinerhenium tricarbonyl iodide from the dimeric tetracarbonyl halide. We have now prepared (Table 2) a number of substitution products of the rhenium and manganese carbonyl halides in which nitrogen, phosphorus, and arsenic act as donor atoms. These compounds have been prepared by the direct action of the ligand, with either the metal pentacarbonyl halide (method A) or the tetracarbonyl halide (method B), or in some cases both, to show the identity of the product:

$$M(CO)_5X + 2L \longrightarrow L_2M(CO)_3X + 2CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$[M(CO)_4X]_2 + 4L \longrightarrow 2L_2M(CO)_3X + 2CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

In every case the reaction was notably faster for the tetracarbonyl halide, owing to the bridging structure's providing a reactive centre in the molecule. We believe all these compounds have the general structure (inset), in which the two ligands are introduced into the carbonyl compound in the *cis*-position to each other, from arguments already cited.[5] This view is now further supported by the preparation of the 2 : 2′-dipyridyl compounds, in which the infrared spectra of the carbonyl stretching region are very similar to those of the corresponding bispyridine compounds.



The compound $[(Ph_3P)_2Re(CO)_4]^+Cl^-$ has been reported[7] to be formed by reaction between triphenylphosphine and rhenium pentacarbonyl chloride. The substitution product which we have prepared from these reagents we regard to be $(Ph_3P)_2Re(CO)_3Cl$ on the basis of infrared spectrum and molecular-weight analogies with the other complexes. The difference in analytical figures for the two possible structures is not sufficiently large to differentiate, and it is unfortunate that a direct analysis for oxygen in presence of phosphorus is not possible. It may be noted, however, that the value of the conductivity [$\mu = 0{\cdot}66$ ohm^{-1} cm.^{2}, V(l./mole) = 541] quoted by Hieber and Schuster as evidence for the ionic structure $[(Ph_3P)_2Re(CO)_4]^+Cl^-$, appears to be rather low for an ionic compound;

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

[7] Hieber and Schuster, *ibid.*, 1956, **287**, 214.

for acetone solutions, Reynolds and Kraus [8] give values of $\mu = 100$ ohm^{-1} cm.^{2} for ionic compounds, and for a very bulky ionic species, hexaformylpiperidineiron tridecacarbonyl tetraferrate, a value $\mu = 249$ ohm^{-1} cm.^{2} has recently been reported.[9] We have in fact found conductivities of the same order as for the triphenylphosphine complex for the rhenium pentacarbonyl halides themselves, *viz.*, $Re(CO)_5Cl$ [$\mu = 0{\cdot}48$ ohm^{-1} cm.^{2}, V(l./mole) = 200], $Re(CO)_5Br$ [$\mu = 0{\cdot}22$ ohm^{-1} cm.^{2}, V(l./mole) = 156], $Re(CO)_5I$ [$\mu = 0{\cdot}16$ ohm^{-1} cm.^{2}, V(l./mole) = 132]. These small values can reasonably be regarded as due to the slight ionic character of the Re–X bond in these compounds. Finally, the sample of $(Ph_3P)_2Re(CO)_3Cl$ obtained quantitatively from the reaction of the phosphine with rhenium *tetracarbonyl* chloride with evolution of carbon monoxide is identical with product from the pentacarbonyl chloride. The formulation of the phosphine complex as a tetracarbonyl complex thus appears to be eliminated.

TABLE 2. *Substituted carbonyl halides of manganese and rhenium.*

Compound	Colour	Method of preptn.	CO stretching modes (cm.$^{-1}$)
$Mn(CO)_3I(Py)_2$	Dark yellow	A + B	2037, 1954, 1906
$Mn(CO)_3IDipy$	Dark orange	A	2036, 1943, 1929
$Mn(CO)_3Cl(Ph_3P)_2$	Cream	B	2049, 1954, 1917
$Mn(CO)_3Br(Ph_3P)_2$	Light brown	A	2046, 1955, 1916
$Mn(CO)_3I(Ph_3P)_2$	Light brown	A	2042, 1955, 1915
$Mn(CO)_3Cl(Ph_3As)_2$	Yellow	B	2050, 1960, 1915
$Mn(CO)_3Br(Ph_3As)_2$	Orange	A	2025, 2055, 1958 (w), 1918 (w)
$Mn(CO)_3I(Ph_3As)_2$	Dark orange	A + B	2012, 2041, 1955 (w), 1918 (w)
$Re(CO)_3Cl(Py)_2$	White	A	2041, 1934, 1891
$Re(CO)_3I(Py)_2$	Cream	B	2041, 1934, 1891
$Re(CO)_3IDipy$	Yellow	A	2037, 1932, 1903
$Re(CO)_3Cl(Ph_3P)_2$	White	A	2050, 1961, 1901
$Re(CO)_3I(Ph_3P)_2$	Cream	A	2049, 1966, 1904
$Re(CO)_3Cl(Ph_3As)_2$	White	B	2049, 1960, 1904
$Re(CO)_3I(Ph_3As)_2$	Pale yellow	A + B	2047, 1961, 1908

Efforts to produce monosubstitution derivatives of the rhenium and manganese pentacarbonyl halides have not been successful, and all attempts to substitute more than two carbonyl groups have resulted in complete decomposition of the molecule. Substituted carbonyl halides in which the bridging structure is intact have not been obtained.

EXPERIMENTAL

Microanalyses and molecular-weight measurements are by the Microanalytical Laboratory of Imperial College.

Preparations and Techniques.—Infrared spectra were recorded in chloroform on a model 21 Perkin-Elmer double-beam spectrometer, with sodium chloride optics. Conductivity was measured in anhydrous acetone with a Type E.7566 Mullard bridge. Rhenium carbonyl halides and manganese pentacarbonyl iodide were prepared as previously described.[1,5]

Preparation of Manganese Pentacarbonyl Chloride.—A slow stream of chlorine was passed into manganese carbonyl (4·00 g.) in carbon tetrachloride (75 c.c.) at 0°. Pale yellow crystals were rapidly precipitated in the exothermic reaction, but were soon obscured by the precipitation of manganese chloride as a fine white powder. After 20 min. the flow of gas was stopped and volatile matter removed (20°/10 mm.). From the residual solid was sublimed (40°/0·1 mm.) pure *manganese pentacarbonyl chloride* (3·03 g., 64%) [Found: C, 26·2; Cl, 15·5; O, 34·8. $Mn(CO)_5Cl$ requires C, 26·0; Cl, 15·4; O, 34·7%].

Preparation of Manganese Pentacarbonyl Bromide.—Bromine (2·46 g., 1·3 mol.) was added to manganese carbonyl (4·6 g., 1 mol.) in carbon tetrachloride (50 c.c.), and the mixture gently shaken at 40°. Carbon monoxide was evolved and considerable manganese bromide was precipitated. After 1 hr. volatile matter was removed (20°/10 mm.). The residual solid mass was washed with water (3 × 25 c.c.) and after drying was sublimed (55°/0·1 mm.), to give

[8] Reynolds and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709.

[9] Hieber and Kahlen, *Chem. Ber.*, 1958, **91**, 2223.

manganese pentacarbonyl bromide (4·75 g., 73%) [Found: C, 21·6; Br, 29·1; O, 30·0. $Mn(CO)_5Br$ requires C, 21·8; Br, 29·1; O, 29·1%].

Thermal Decomposition of the Manganese Pentacarbonyl Halides. Reaction (1).—The pentacarbonyl halides (*ca.* 1·0 g.) in light petroleum (b. p. 100—120°) were heated under reflux in a stream of nitrogen. After 1 hr. heating was stopped and a mixture of dark crystals and fine powder separated. After removal of solvent (20°/0·1 mm.) and washing with water (3 × 25 c.c.), then drying, the residue was extracted with hot benzene (3 × 10 c.c.) and the filtered extract cooled (0°). Fine crystals of the tetracarbonyl halides separated, and after decantation of the liquid these were washed rapidly with light petroleum (5 c.c.) and then excess of solvent was removed (20°/0·1 mm.) to leave the pure product (Table 3).

TABLE 3.

Compound	Yield (%)	Mol. wt. Found	Mol. wt. Calc.	Found (%) C	Found (%) O	Found (%) Hal.	Required (%) C	Required (%) O	Required (%) Hal.
$[Mn(CO)_4Cl]_2$	45	425	403	24·1	30·8	17·1	23·8	31·6	17·6
$[Mn(CO)_4Br]_2$	53	476	494	19·6	25·5	32·2	19·5	26·1	32·4
$[Mn(CO)_4I]_2$	47	629	588	16·4	22·5	42·1	16·3	21·8	43·2

Interaction of Carbon Monoxide and the Manganese Tetracarbonyl Halides.—The finely powdered tetracarbonyl halide (*ca.* 0·5 g.) was placed under carbon monoxide in a metal autoclave at 180°/150 atm. After cooling, a fall in the initial pressure was observed. The contents of the cooled autoclave were extracted with benzene, and after filtration of the solution and removal of solvent (20°/10 mm.) the crude product was subimed to give the pure pentacarbonyl halide (Table 4).

TABLE 4.

Compound	Yield (%)	Found C	Found O	Calc. C	Calc. O	CO stretching modes (cm.$^{-1}$)
$Mn(CO)_5Cl$	74	25·8	34·8	26·0	34·7	2072, 2015
$Mn(CO)_5I$	82	18·0	24·0	18·3	24·8	2055, 2018

Interaction of Manganese and Rhenium Pentacarbonyl Halides with Certain Ligands. Method (*A*). *Reaction* (2).—The carbonyl halide (*ca.* 0·1 g.) was heated (120°) in nitrogen with an excess (*ca.* 5 mols.) of the ligand. Heating was continued (*ca.* 30 min.) until the steady stream of carbon monoxide ceased. After cooling, excess of ligand was removed by washing with ether (3 × 5 c.c.). The residual solid was extracted with chloroform in the cold (2 × 2 c.c.), and to the filtered chloroform solution was added light petroleum (15 c.c.). The solution was allowed to crystallise overnight, and after removal of mother liquor the crystals were washed with light petroleum (2 × 2 c.c.) and excess of solvent was removed (20°/0·1 mm.) to leave the pure product (Table 5).

TABLE 5 (*Method A*).

Compound	Yield (%)	Found (%) C	H	O	N	P	As	Hal.	Required (%) C	H	O	N	P	As	Hal.
$Me(CO)_3IPy_2$	74	36·8	2·8	11·4	6·9				36·8	2·4	11·3	6·6			
$Mn(CO)_3IDipy$	81	37·0	2·2	11·5	6·6			29·8	37·0	1·9	11·4	6·6			30·0
$Mn(CO)_3Br(Ph_3P)_2$	67	63·5	4·4					10·2	63·1	4·0					10·8
$Mn(CO)_3I(Ph_3P)_2$	81	58·3	4·0			7·3		15·9	59·2	3·8			7·8		16·1
$Mn(CO)_3Br(Ph_3As)_2$	72	57·0	4·2				18·4		56·3	3·6				18·1	
$Mn(CO)_3I(Ph_3As)_2$	67	52·8	3·6	5·2			17·2		53·4	3·4	5·5			17·1	
$Re(CO)_3ClPy_2$	77	33·1	1·9		6·4				33·6	2·2		6·0			
$Re(CO)_3IDipy$	74	28·9	1·8	8·7	5·3			23·6	28·2	1·5	8·7	5·1			22·9
$Re(CO)_3Cl(Ph_3P)_2$	65	56·4	4·2			7·4		4·5	56·5	3·6			7·5		4·3
$Re(CO)_3I(Ph_3P)_2$	79	50·9	3·7			6·6			50·9	3·3			6·7		
$Re(CO)_3I(Ph_3As)_2$	68	46·3	3·1	4·5			15·1		46·4	3·0	4·4			14·9	

Interaction of Manganese and Rhenium Tetracarbonyl Halides with Certain Ligands. Method (*B*). *Reaction* (3).—The procedure adopted was the same as that adopted for the pentacarbonyl halide reactions described above. It was noted, however, that the reaction in general started at a temperature about 20° lower in each case and on this scale was completed at 120° in 15 min. (Table 6).

TABLE 6 (*Method B*).

Compound	Yield (%)	Found (%) C	H	O	As	Hal.	Required (%) C	H	O	As	Hal.
$Mn(CO)_3I(Py)_2$	67	36·6	2·9	11·7			36·8	2·4	11·3		
$Mn(CO)_3Cl(Ph_3P)_2$	74	62·8	4·7				62·0	4·3			
$Mn(CO)_3Cl(Ph_3As)_2$ ...	61	59·9	4·5			4·1	59·5	3·8			4·5
$Mn(CO)_3I(Ph_3As)_2$	56	53·2	3·8			14·9	53·2	3·4			14·5
$Re(CO)_3Cl(Ph_3As)_2$ ...	77	50·8	3·6		16·9		51·0	3·3		16·4	
$Re(CO)_3I(Ph_3As)_2$	61	46·2	3·5	4·9			46·4	3·0	4·4		

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