Osmium Carbonyl Halides and their Derivatives. Part II.[1]

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The reaction of carbon monoxide with osmium halides has been investigated and, on the basis of infrared evidence, structures have been assigned to $Os(CO)_4X_2$ and $Os(CO)_3X_2$. The carbonyl halides react with a variety of ligands to give compounds $Os(CO)_2L_2X_2$. Infrared spectra are reported and discussed.

OSMIUM carbonyl halides were first prepared by Manchot and König [2] who passed carbon monoxide over heated osmium trichloride and obtained a white compound to which they assigned the formula $Os(CO)_3Cl_2$. The only subsequent work on these compounds is by Hieber and Stallmann [3] who carried out an extensive investigation of the effect of carbon monoxide at high temperature and pressure on osmium halides. We now describe some reactions of the osmium carbonyl halides.

The reaction between osmium oxyiodide and carbon monoxide at 100 atmospheres pressure and 140° leads to the formation mainly of osmium tricarbonyl di-iodide but some of the more volatile osmium tetracarbonyl di-iodide is also formed. The tetracarbonyl di-iodide is not particularly stable and when heated in benzene slowly loses carbon monoxide to form the tricarbonyl di-iodide. The conversion into tricarbonyl di-iodide is quantitative on heating at 140° in air. Osmium thus differs from iron and ruthenium, for which tricarbonyl di-iodides are unknown.

The infrared spectrum of osmium tetracarbonyl di-iodide shows four bands in the fundamental CO stretching frequency region, a fairly weak high-frequency band and three strong bands.[1] This is typical of *cis*-$ML_2(CO)_4$ complexes of C_{2v} symmetry, and similar to the band structures observed for $Ru(CO)_4I_2$ (which has [4] C_{2v} symmetry, from *X*-ray diffraction data) and for $Fe(CO)_4I_2$. Osmium tetracarbonyl dibromide shows an exactly analogous infrared spectrum.

Osmium tricarbonyl dihalides prove to be the major products in the reaction of carbon monoxide at 100 atm. on osmium trichloride, osmium enneabromide, or osmium oxyiodide. They are considerably less soluble

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[1] Part I, R. J. Irving and L. A. W. Hales, *J. Chem. Soc.* (*A*), 1967, 1389.

[2] W. Manchot and J. König, *Ber.*, 1925, **58**, 229.

[3] W. Hieber and H. Stallmann, *Ber.*, 1942, **75**, 1472.

[4] L. F. Dahl and D. L. Wampler, *Acta Cryst.*, 1962, **15**, 946.

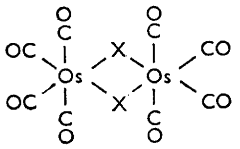
and less volatile than the tetracarbonyl dihalides and are considered to be dimeric although, because of their low solubility, molecular weights have never been measured. Hieber and Stallmann suggested structures involving carbonyl bridging, but the infrared spectra refute this possibility showing only two carbonyl stretching bands both above 2000 cm.$^{-1}$. Reasonable structures will involve bridging *via* two halogen atoms if osmium is to be hexaco-ordinated and the complex diamagnetic. The molecule is assumed to be symmetrical about a plane joining the bridging halogens. For practical purposes the interaction between CO stretching vibrations in the separate halves of the molecule will be negligible, and the expected CO stretching frequencies should correspond to those observed for monomeric *cis*- or *trans*-$ML_3(CO)_3$ complexes, namely two or three peaks, respectively.

The observed spectra for $Os(CO)_3X_2$ (X = Cl, Br, or I) exhibit two absorption bands, a fairly sharp high-frequency band and a broad very intense band corresponding to the A_1 vibration and the doubly degenerate E (B_1) mode (Table 1).

TABLE 1

Infrared stretching frequencies

					Solvent
$Os(CO)_4Br_2$	2178	2090	2113	2051	Cyclohexane
$Os(CO)_4I_2$...........	2165	2086	2101	2050	,,
$Os(CO)_3Cl_2$	2136		2061		CCl_4
$Os(CO)_3Br_2$	2129		2057		,,
$Os(CO)_3I_2$...........	2119		2051		,,
$Os(CO)_2I_2$...........	2119		2045	1988	Nujol (mull)



(I)

The symmetrical structure (I) is suggested for these compounds.

When osmium tricarbonyl di-iodide is heated at 300° in nitrogen a molecule of carbon monoxide is lost and the insoluble yellow dicarbonyl di-iodide is obtained. This is much more stable than iron dicarbonyl di-iodide and of comparable stability with its ruthenium analogue. Like ruthenium dicarbonyl di-iodide it is diamagnetic and presumably polymeric, but there are differences between ruthenium and osmium dicarbonyl di-iodides. The ruthenium compound is a red ochre-coloured amorphous powder, completely insoluble in inert solvents. Its osmium analogue is yellow and crystalline, but only very sparingly soluble in inert solvents. The ruthenium compound has two sharp bands at 2050 and 1995 cm.$^{-1}$ with a weak shoulder at 1975 cm.$^{-1}$ while the osmium compound has three strong sharp bands, at 2119, 2045, and 1988 cm.$^{-1}$.

It is unlikely therefore that the degree of polymerisation and the stereochemistry of the two compounds is the same although the infrared stretching frequencies show that the possibility of bridging carbonyl groups is precluded in both.

The tetra- and tri-carbonyl dihalides react quite readily with amines, phosphines, arsines, and other ligands giving in all cases compounds of the type $Os(CO)_2L_2X_2$. In general, reaction is effected by refluxing the appropriate carbonyl halide in benzene with a slight excess of ligand, and the white or yellow product can be isolated by removal of the bulk of the solvent. Diphenylchloro- and phenyldichloro-phosphine are air-sensitive so their reactions with osmium tricarbonyl di-iodide were carried out in tetrachloroethylene under nitrogen. The compounds were not isolated and the reaction mixtures were used directly for infrared studies. In the case of phosphorus trichloride the ligand itself acted as solvent.

In every case the infrared spectra had two strong CO stretching frequency bands, showing that the carbon monoxide groups occupied *cis* co-ordination sites.

Two bidentate chelating ligands, ethylenebisdiphenylphosphine and o-phenylenebisdimethylarsine, also gave products of the type $Os(CO)_2LI_2$ with osmium tricarbonyl di-iodide. Their infrared absorption spectra again showed two strong bands in the CO stretching frequency region at positions and separations comparable with those of the other derivatives. As these ligands are constrained to occupy *cis* co-ordination sites it appears that the general structure of the $Os(CO)_2L_2X_2$ complexes is with each pair of ligands in the *cis* arrangement.

Carbonyl Stretching Frequencies.—In a series of isostructural metal carbonyl halides in which the metal remains the same but the halogen is changed, the CO stretching frequencies drop from chloride to bromide to iodide.[5] The π-bonding capabilities are generally considered to increase along this series, and the inductive effect to decrease. If the former were important in metal carbonyl halides the CO frequencies would be expected to rise, but if the latter were the over-riding factor the CO frequencies would decrease. It is thus

TABLE 2

CO stretching frequencies (cm.$^{-1}$) for $Os(CO)_2L_2X_2$

		Assignment	
L	X	A_1	B_1
$(PhO)_3P$	I	2065	2004
	Br	2067	2003
	Cl	2068	2001
Ph_3P..........................	I	2041	1975
	Br	2043	1974
	Cl	2043	1971
Ph_3As	I	2037	1971
	Br	2040	1971
	Cl	2038	1967
Ph_3Sb	I	2031	1966
	Br	2032	1966
	Cl	2032	1964
Ph_2PCl [a]	I	2051	1991
$PhPCl_2$ [a]	I	2063	2008
PCl_3 [b]	I	2074	2023
$Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$	I	2051	1984
Diars [c]	I	2043	1972
C_5H_5N	I	2041	1974

All spectra were measured in dichloromethane except (*a*) where the solvent was tetrachloroethylene and (*b*) phosphorus trichloride. (*c*) *o*-Phenylenebis(dimethylarsine).

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[5] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1958, 2283.

obvious that the change in inductive effect along the series Cl, Br, I is the major operative factor.

The derivatives $Os(CO)_2L_2X_2$, *e.g.*, $Os(CO)_2(PPh_3)_2X_2$, show very little variation of CO stretching frequency as X is varied (Table 2). This is understandable since the large organic ligands possess readily polarisable metal–donor atom σ-bonding orbitals which can absorb the majority of the change in electron density at the metal caused by the change in inductive power of the substituent halogen.

For changes of ligand L, however, there are relatively large changes in the carbonyl stretching frequencies, and in the series PCl_3, Ph_3PCl_2, $(Ph)_2PCl$, Ph_3P, where there is decreasing π-bonding ability, the CO stretching frequencies show the expected steady decrease.[6]

EXPERIMENTAL

The determination of osmium is difficult and, as there are many methods of unproven reliability, ours will be described in detail.

The precipitation of sulphide and subsequent ignition is a satisfactory macro-method,[7] but with milligram quantities we find it gives low results. Strychnine has been suggested as a precipitant for osmium on a semimicro scale[8] but in agreement with Ayres and Wells[9] we find that it yields very erratic results.

Consistent results were obtained by oxidising the compounds, and converting the osmium tetroxide so formed into the red thiourea complex which was then determined colorimetrically. Compounds were converted into potassium osmate by fusion with a 5 : 1 potassium hydroxide–potassium nitrate in a silver crucible. The cooled melt was dissolved in water and transferred to a distilling flask. Attached to the flask *via* a condenser was a series of three receivers each containing 0·2 g. of thiourea in 10 ml. of 0·5M-perchloric acid. All joints were moistened with water and leakage was eliminated by drawing a continuous stream of air through the apparatus. The solution in the distilling flask was made strongly acid with nitric acid, and boiled for 15 min. to distil off all the osmium as tetroxide. The stream of air was continued for 20 min. after distillation had ceased to remove oxides of nitrogen. The solutions from the receiving flasks were combined, made up to 100 ml. with 0·5M-perchloric acid, and after 30 minutes the optical densities at 480 and 550 mμ were measured on a Unicam SP500 spectrophotometer. The red species obtained by this treatment is $[Os(NH_2CSNH_2)_6]^{3+}$ and its absorption curve in perchloric acid shows a sharp maximum at 480 mμ and a plateau centred at 550 mμ. Beer's law holds over the concentration range 1—5 × 10^{-4}M for both wavelengths.

Ammonium hexachloro-osmate rather than osmium tetroxide was chosen as a primary standard. It can be prepared in high yield from osmium tetroxide, is readily purified, and is much more convenient to handle than the tetroxide. A series of determinations on known quantities of ammonium hexachloro-osmate carried through our fusion and distillation procedure gave results within 2% of the calculated value.

The fusion stage is critical. After the fusion mixture had melted and during reaction the surface of the melt was turbid, but as soon as all the osmium had been converted into sodium osmate a clear red liquid was obtained. Some osmium volatilised if heating continued for much more than 5 min. after this stage. Maximum sensitivity is attained if the final solution is 10^{-3}—10^{-4}M with respect to Os.

Halogens were determined gravimetrically by treatment of the solution remaining in the distillation flask with silver nitrate.

Phosphorus was determined gravimetrically by precipitation of ammonium phosphomolybdate after all organic matter and osmium had been removed by the ' catalytic wet oxidation ' procedure.[10]

Infrared spectra were recorded on a Grubb–Parsons GS.2A double-beam recording spectrometer, and all frequencies quoted are believed accurate to ±2 cm.$^{-1}$.

Osmium Tricarbonyl Di-iodide.—This was prepared by a modification of the technique of Hieber and Stallman. Osmium oxyiodide (1 g.) was mixed with copper turnings (2 g.) and heated in a rocking autoclave for 24 hr. at 130°/100 atm. of carbon monoxide. The cooled product was extracted with benzene and the yellow crystals (0·2 g.) obtained by evaporation of the solvent were recrystallised from benzene [Found: I, 47·5; Os, 35·7. Calc. for $Os(CO)_3I_2$: I, 48·1: Os, 36·0%].

Osmium Tetracarbonyl Di-iodide.—This was obtained in small yield as a sublimate on the lid of the autoclave during the preparation of osmium tricarbonyl di-iodide. It also sublimed in small amounts when a stream of carbon monoxide at atmospheric pressure was passed over osmium oxyiodide and copper turnings at 200°. It is a yellow compound purified by repeated extraction in tetrachloroethylene and removal of the solvent at room temperature at reduced pressure. The main impurity is osmium tricarbonyl iodide which has a strong absorption at 2119 cm.$^{-1}$; the most convenient way of following the purification is by inspection of this band [Found: I, 45·1; Os, 34·5. Calc. for $Os(CO)_4I_2$: I, 45·7; Os, 34·2%].

Action of Heat.—Hieber and Stallmann showed that $Os(CO)_4I_2$ lost carbon monoxide stepwise as the temperature increased. We have studied this reaction on a Stanton thermobalance type HTD. The sample was heated in a platinum crucible from 25 to 300° in dry nitrogen at a slow heating rate (2°/min.). There were two plateaux in the weight–temperature graph, one at 140 and one at 300°. Isolation and analysis of the products obtained at each plateau showed the first to be $Os(CO)_3I_2$ and the second $Os(CO)_2I_2$.

Further information such as the number of molecular weight units lost at each stage could not be obtained owing to the simultaneous weight loss due to the volatility of the carbonyl halides.

Osmium Dicarbonyl Di-iodide.—This was obtained as yellow crystals by heating osmium tricarbonyl di-iodide at 290° (Found: I, 50·2; Os, 37·6. Calc. for $Os(CO)_2I_2$: I, 50·8; Os, 38·0%).

Osmium Tricarbonyl Dibromide.—Osmium enneabromide carefully dehydrated (1·0 g.) was sealed in a thin-walled

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[6] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723.

[7] W. R. Schoeller and A. R. Powell, 'Analysis of Minerals and Ores of the Rarer Elements,' Griffin, 3rd edn., 1955, p. 352.

[8] F. E. Beamish, *Talanta*, 1958, **1**, 3; I. Hoffman, J. E. Schweitzer, D. E. Ryan, and F. E. Beamish, *Analyt. Chem.*, 1953, **25**, 1091.

[9] G. H. Ayres and W. N. Wells, *Analyt. Chem.*, 1950, **22**, 317.

[10] N. H. Furman, ' Standard Methods of Chemical Analysis,' D. Van Nostrand, 6th edn., 1962, p. 812.

glass ampoule. The autoclave was then charged with the ampoule, pressurised with carbon monoxide to 100 atm. (thus breaking the ampoule and allowing the reaction to proceed), and heated to 150° for 24 hr. Rigorous exclusion of moisture is essential. The cooled product was extracted with benzene and on recrystallisation from benzene 0·2 g. of white compound was obtained [Found: Br, 36·3; Os, 44·2. Calc. for $Os(CO)_3Br_2$: Br, 36·8; Os, 43·8%].

Osmium Tetracarbonyl Dibromide.—This was obtained in traces as a by-product in the preparation of osmium tricarbonyl dibromide if the reaction was carried out at 160° in the presence of a large excess of copper turnings. It was purified by extraction with tetrachloroethylene and subsequent removal of the solvent under vacuum at room temperature (Found: Br, 34·9; Os, 42·3. Calc. for $Os(CO)_4Br_2$: Br, 34·6; Os, 41·2%).

Osmium Tricarbonyl Dichloride.—Osmium tetroxide (1 g.) was converted into ammonium hexachloro-osmate(IV) in almost quantitative yield by the method of Dwyer and Hogarth [11] and thence into osmium trichloride by reaction in a stream of chlorine at 350°. The resulting osmium trichloride (0·6 g.) was then heated in a stream of carbon monoxide at 270° for several hours.

The yellow sublimate was washed with carbon tetrachloride and on recrystallisation from chloroform was white. Reaction of osmium trichloride with carbon monoxide in an autoclave at 120—160°/100 atm. for 24 hr. gave a higher yield of the tricarbonyl chloride (Found: Cl, 20·1; Os, 54·7. Calc. for $Os(CO)_3Cl_2$: Cl, 20·6; Os, 55·1%).

Dicarbonyldipyridinedi-iodo-osmium.— Osmium tricarbonyl di-iodide and excess of pyridine were refluxed in benzene for 1 hr., and the solution evaporated almost to dryness. The yellow residue was washed with ether and light petroleum and finally recrystallised from benzene as a bright yellow *product* (Found: I, 38·1; Os, 28·9. $C_{12}H_{10}I_2N_2O_2Os$ requires I, 38·6; Os, 28·9%).

Reactions with Triphenylphosphine.—An excess of triphenylphosphine was refluxed with the osmium tricarbonyl dihalide in benzene for 2 hr., during which the solution became almost colourless. The solution was evaporated to dryness and excess of ligand was removed by washing with ether followed by light petroleum. Thus were obtained *dicarbonylbis(triphenylphosphine)di-iodo-osmium*, colourless crystals from benzene (Found: I, 24·4; Os, 18·9; P, 6·4. $C_{38}H_{30}I_2O_2OsP_2$ requires I, 24·8; Os, 18·6; P, 6·1%) (this was also obtained from osmium tetracarbonyl di-iodide by the same procedure. Reaction was much slower. Osmium dicarbonyl di-iodide is not soluble in benzene or toluene and under our conditions did not react with triphenylphosphine); *dicarbonylbis(triphenylphosphine)dibromo-osmium*, colourless crystals from benzene (this was also prepared from osmium tetracarbonyl dibromide) (Found: Br, 17·5; Os, 20·8; P, 6·7. $C_{38}H_{30}Br_2O_2OsP_2$ requires Br, 17·2; Os, 20·4; P, 6·7%); and *dicarbonylbis(triphenylphosphine)-dichloro-osmium*, colourless crystals from benzene (Found: Cl, 7·9; Os, 22·3; P, 7·5. $C_{38}H_{30}Cl_2O_2OsP_2$ requires Cl, 8·4; Os, 22·6; P, 7·4%).

Reactions with Triphenyl Phosphite.—An excess of triphenyl phosphite was refluxed with osmium tricarbonyl dihalide in benzene for 1 hr. Excess of ligand was removed by repeated washing with light petroleum. Recrystallisation from benzene yielded colourless crystals of pure *dicarbonylbis(triphenyl phosphite)di-iodo-osmium* (Found: I, 22·8; Os, 17·3; P, 5·6. $C_{38}H_{30}I_2O_8OsP_2$ requires I, 22·7; Os, 17·0; P, 5·5%), *dicarbonylbis(triphenyl phosphite)-dibromo-osmium* (Found: Br, 15·7; Os, 19·0; P, 6·1. $C_{38}H_{30}Br_2O_8OsP_2$ requires Br, 15·6; Os, 18·5; P, 6·0%), and *dicarbonylbis(triphenyl phosphite)dichloro-osmium* Found: Cl, 7·6; Os, 20·8; P, 6·6. $C_{38}H_{30}Cl_2O_8OsP_2$ requires Cl, 7·6; Os, 20·3; P, 6·6%).

Dicarbonylethylenebis(diphenylphosphine)di-iodo-osmium.—Osmium tetracarbonyl di-iodide was refluxed with an excess of the diphosphine (kindly presented by Dr. R. O'Brien) in benzene for 2 hr. After cooling, addition of a volume of tetrachloroethylene equal to that of the benzene gave a creamy white precipitate. This mixture of carbonyl compounds could not easily be separated. The filtrate when treated with more tetrachloroethylene gave a further white precipitate, which when washed with light petroleum and recrystallised from benzene gave colourless *crystals* (Found: I, 28·0; Os, 21·9; P, 7·0. $C_{28}H_{24}I_2O_2OsP_2$ requires I, 28·3; Os, 21·2; P, 6·9%).

Action of Some Chlorophosphorus Compounds on Tetracarbonyldi-iodo-osmium.—Diphenylphosphorus chloride and phenylphosphorus dichloride were each refluxed with tetracarbonyldi-iodo-osmium in tetrachloroethylene under dry nitrogen for 15 min. For phosphorus trichloride, the ligand was used as solvent.

No compound was isolated but the infrared absorption of the solution in the carbonyl region gave a pattern identical with that of the other *cis*-$Os(CO)_2L_2I_2$ reported here.

Reactions with Triphenylarsine.—An excess of triphenylarsine was refluxed with osmium tricarbonyl halide in benzene for 2 hr. Removal of the benzene left a gum which was induced to crystallise by dissolution in tetrachloroethylene and distilling off the bulk of the solvent. The product which separated on cooling was recrystallised from benzene to yield white crystals of *dicarbonylbis(triphenylarsine)di-iodo-osmium* (Found: I, 21·8; Os, 17·5. $C_{38}H_{30}As_2I_2O_2Os$ requires I, 22·8; Os, 17·1%), *dicarbonylbis(triphenylarsine)dibromo-osmium* (Found: Br, 15·8; Os, 19·2. $C_{38}H_{30}As_2Br_2O_2Os$ requires Br, 15·7; Os, 18·7%), or *dicarbonylbis(triphenylarsine)dichloro-osmium* (Found: Cl, 7·4; Os, 20·6. $C_{38}H_{30}As_2Cl_2O_2Os$ requires Cl, 7·6; Os, 20·5%).

Dicarbonyl-o-phenylenebis(dimethylarsine)di-iodo-osmium.—Osmium tetracarbonyl di-iodide and *o*-phenylenebisdimethylarsine (in slight excess) were refluxed in benzene for 1 hr. Most of the solvent was distilled off and the remaining solution was cooled. The small amount of pale yellow solid which separated was filtered off and tetrachloroethylene was added to the filtrate. The pale yellow precipitate which formed was a complex mixture difficult to purify but the filtrate when treated with light petroleum gave a white precipitate which on recrystallisation from benzene gave white *crystals* (Found: I, 30·9; Os, 23·8. $C_{12}H_{16}As_2I_2O_2Os$ requires I, 32·3; Os, 24·2%).

Reactions with Triphenylstibine.—The following were prepared from osmium tricarbonyl halides and triphenylstibine by the method described for triphenylarsine derivatives and crystallised from benzene: *dicarbonylbis(triphenylstibine)di-iodo-osmium* (Found: I, 20·8; Os, 15·5. $C_{38}H_{30}I_2O_2OsSb_2$ requires I, 21·0; Os, 15·8%), *dicarbonylbis(triphenylstibine)dibromo-osmium* (Found: Br, 14·3; Os, 17·2. $C_{38}H_{30}Br_2O_2OsSb_2$ requires Br, 14·4; Os, 17·1%), and *dicarbonylbis(triphenylstibine)dichloro-osmium* (Found: Cl, 6·5; Os, 17·9. $C_{38}H_{30}Cl_2O_2OsSb_2$ requires Cl, 6·9; Os, 18·6%).

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[11] F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N.S.W.*, 1951, **84**, 194.