

Carbonyl Halide Complexes of the Platinum Metals

By M. J. Cleare, B.Sc., A.R.C.S.

Research Laboratories, Johnson Matthey & Co Limited

The many advances in the chemistry of the platinum metals made in recent years have been particularly evident in the field of carbonyl group-containing complexes. Improved methods of preparation have been developed and the uses of such complexes in homogeneous catalysis have been and are being actively studied.

The preparation of these carbonyl halide complexes by a variety of techniques has been reported. The production of ruthenium complexes by the decarbonylation of formic

acid by ruthenium (II) species has been studied (1) and there are reports of the reaction of $[\text{IrCl}_6]^{3-}$ or $[\text{IrCl}_6]^{2-}$ with formic acid to yield carbonyl halide species of uncertain formulae (2, 3). Ruthenium complexes have been prepared by the long passage of carbon monoxide through solutions of ruthenium (III) halogen compounds (4) and iridium complexes by the reaction of halogen compounds with carbon monoxide under pressure (5). Similar osmium compounds have not, so far, been reported.

Carbonyl Halide Complexes of Osmium, Ruthenium and Iridium				
Complex	Colour	Reactants	Time	Infra-red C - O Stretching Frequencies cm^{-1}
$\text{Cs}_2(\text{Os}(\text{CO})\text{Cl}_5)$	Orange	$(\text{OsCl}_6)^{2-} + \text{H.COOH}$	Can be found from $\frac{1}{2}$ -5 hr	1968vs
$\text{Cs}_2(\text{Os}(\text{CO})_2\text{Cl}_4)$	White	$(\text{OsCl}_6)^{2-} + \text{H.COOH}$ or $\text{OsCl}_3 + \text{H.COOH}$	~8-9 hr	2014vs 1899vs (2037) (1947)
$\text{Cs}_2(\text{Os}(\text{CO})_2\text{Br}_4)$	Yellow	$(\text{OsBr}_6)^{2-} + \text{H.COOH}$	~12 hr	2005vs 1899vs
$\text{Cs}(\text{Os}(\text{CO})_3\text{Cl}_3)$	White	$(\text{OsCl}_6)^{2-} + \text{H.COOH}$ or $\text{OsCl}_3 + \text{H.COOH}$	~48 hr	2125vs 2046vs 2014vs 2031sh 2023sh 1992m (2128) (2039)
$\text{Cs}(\text{Os}(\text{CO})_3\text{Br}_3)$	White	$(\text{OsBr}_6)^{2-} + \text{H.COOH}$	~60 hr	2120vs 2048vs 2017vs 1996sh
$\text{Cs}_2(\text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4)$	Green	$(\text{RuCl}_5(\text{H}_2\text{O}))^{2-} + \text{H.COOH}$ or $\text{RuCl}_3 + \text{H.COOH}$	1 hr	1951vs
$\text{Cs}_2(\text{Ru}(\text{CO})_2\text{Cl}_4)$	Yellow	„	~7-8 hr	2037vs 1935vs
$\text{Cs}_2(\text{Ru}(\text{CO})_2\text{Br}_4)$	Yellow-Green	$(\text{RuBr}_5(\text{H}_2\text{O}))^{2-} + \text{H.COOH}$ or $\text{RuBr}_3 + \text{H.COOH}$	~6 hr	2032vs 1932vs
$(\text{Ru}(\text{CO})_2\text{Cl}_2)_n$	Yellow	$\text{RuCl}_3 + \text{H.COOH}$	7 hr	2076vs 2018vs
$\text{Cs}_2(\text{Ir}(\text{CO})\text{Cl}_5)$	Pink-Yellow	$(\text{IrCl}_6)^{2-} + \text{H.COOH}$ or $(\text{IrCl}_6)^{3-} + \text{H.COOH}$	2-3 min	2070vs
$\text{Cs}_2(\text{Ir}(\text{CO})\text{Br}_5)$	Orange	$(\text{IrBr}_6)^{3-} + \text{H.COOH}$	2-3 min	2038vs

Infra-red spectra run on Nujol mulls; frequencies in parenthesis in aqueous solution

Recent investigations into the reactions of platinum metal compounds with formic acid have led to the discovery of a new and convenient method of preparing carbonyl halide complexes of osmium, ruthenium and iridium by refluxing the metal halide or halo-complex with 90 per cent formic acid (6). The compounds formed were initially recognised as carbonyl rather than formate complexes by infra-red spectroscopy in the 2000 cm^{-1} region.

The complexes that have so far been prepared and the reaction conditions are set out in the table opposite; all the compounds have been characterised by elemental analysis and their full infra-red spectra have been determined and recorded.

To isolate salts of the anionic species it was found necessary to use caesium as the cation since lighter atomic weight alkali metals yielded salts of very high solubility.

The reaction between sodium hexachlorosmate (IV) (used because of the low solubility of other $[\text{OsCl}_6]^{2-}$ salts) and formic acid is of particular interest since it takes place much more slowly than those between ruthenium and iridium compounds and formic acid. This has made it possible to identify by infra-red spectroscopy intermediate formato-halo species containing one and two monodentate formate groups. These species probably contain formally divalent osmium, that is $[\text{Os}^{\text{II}}(\text{COOH})\text{Cl}_5]^{4-}$ and $[\text{Os}^{\text{II}}(\text{COOH})_2\text{Cl}_4]^{4-}$,

and they further react to give the mono- and dicarbonyl species respectively. The reaction proceeds quickly to the diformate stage and the monocarbonyl complex is formed in small quantities only.

Triphenylphosphine derivatives are easily prepared by warming the complexes with triphenylphosphine in formic acid solution or, more conveniently, by treating the solutions prior to isolation of a carbonyl halide salt with triphenylphosphine. The complexes $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2]$ and $[\text{Os}(\text{CO})_3(\text{PPh}_3)\text{X}_2]$ have been prepared from $\text{Cs}_2[\text{Os}(\text{CO})_2\text{X}_4]$ and $\text{Cs}[\text{Os}(\text{CO})_3\text{X}_3]$ respectively, while $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{X}_2]$ and $[\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2]$ have been prepared from $\text{Cs}_2[\text{Ru}(\text{CO})_2\text{X}_4]$ and $\text{Cs}_2[\text{Ru}(\text{CO})(\text{H}_2\text{O})\text{Cl}_4]$ respectively ($\text{X} = \text{Cl}, \text{Br}$).

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Performance of Platinised Titanium Anodes

The use of platinised titanium as a counter electrode in cathodic protection is well established, even though a detailed mechanism for the excellent performance of these anodes is not fully documented. A recent investigation of this subject by P. Van Laer and J. Van Muylder of CEBELCOR, presented as a paper to the CITCE colloquium on Corrosion and Electrochemical Thermodynamics held in Istanbul in September, is of some considerable help in this direction.

Anodic polarisation studies in synthetic sea-water, using current densities in the range 0 to 600 mA/cm^2 , showed that if corrosion of

the titanium is to be avoided the anodic potential must not exceed +7.0 V_{SCE} . Further, the authors state that at potentials above +2.1 V_{SCE} modification of the platinum surface occurs, and studies in the range +1.3 to 1.4 V_{SCE} suggest that oxidation of platinic oxide PtO_2 to perplatinic oxide PtO_3 may take place.

It was concluded that the long life of platinised titanium anodes in sea-water is due to the titanium surface being protected from high current densities by the platinised areas, thus ensuring that the potential does not exceed the threshold of danger. J. H.