

# Carbonyl Complexes of Osmium

## TRIOSMIUM DODECACARBONYL AND ITS DERIVATIVES

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*The study of the carbonyls of most of the platinum metals has led to the preparation of a whole series of new complexes, some of which have potential usefulness in the field of homogeneous catalysis. In the case of osmium carbonyls, however, research has so far been hampered by difficulties in their preparation. The new method of preparation described here now makes it possible to investigate the chemistry of osmium complexes along the same lines.*

In recent years there has been a tremendous advance in the chemistry of the transition metals including those of the platinum group metals. The preparation and study of carbonyl complexes has proved most fruitful, and it is hoped that further investigation of reactions involving the carbonyls may result in the discovery of compounds having useful properties, particularly in the field of homogeneous catalysis. An improved method has now been developed for the preparation of triosmium dodecacarbonyl,  $\text{Os}_3(\text{CO})_{12}$ , and some of its reactions have been studied.

### Preparation of Osmium Carbonyls

In 1943 Hieber and Stallman (1) produced carbonyls of osmium by the action of carbon monoxide at high pressure either on osmium tetroxide or on osmium trihalides in the presence of silver or copper powder to take up the halogen. They separated two products, a volatile colourless liquid (m.p.  $-15^\circ\text{C}$ ) and a yellow crystalline solid claimed respectively to be  $\text{Os}(\text{CO})_5$  and  $\text{Os}_2(\text{CO})_9$ . An X-ray examination (2) of the latter has, in fact, shown it to be  $\text{Os}_3(\text{CO})_{12}$ , the molecule having three osmium atoms at the corners of an equilateral triangle, each osmium atom having four terminal CO groups, two approximately perpendicular to and two parallel to the plane of the triangle. Attempts to produce the carbonyls by either of these routes

have resulted in very variable and very low yields, and, in the case where osmium tetroxide was the starting material, the formation of large quantities of black decomposition products. A new procedure (3, 4) has now been developed in these laboratories which results in the production of  $\text{Os}_3(\text{CO})_{12}$  in good yields (70 per cent) and, as a by-product, the oxycarbonyl,  $\text{Os}_4\text{O}_4(\text{CO})_{12}$  (5). A solution of osmium tetroxide in xylene is heated at  $175^\circ\text{C}$  for 16 hr in an autoclave containing carbon monoxide at a pressure of 190 atmospheres. The large yellow crystals of  $\text{Os}_3(\text{CO})_{12}$  are readily separated by hand from the white oxycarbonyl  $\text{Os}_4\text{O}_4(\text{CO})_{12}$  and both compounds are finally purified by recrystallisation from benzene. In the presence of xylene there are no signs of the decomposition products which appear when the reaction is carried out in its absence.

### Reactions of $\text{Os}_3(\text{CO})_{12}$

When  $\text{Os}_3(\text{CO})_{12}$  is reacted in hot xylene solution with triphenylphosphine  $[\text{P}(\text{Ph})_3]$  and with o-phenylenebisdimethylarsine (Diars) the substitution products  $[\text{Os}(\text{CO})_3\text{PPh}_3]_3$  and  $[\text{Os}(\text{CO})_2\text{Diars}]_3$  are formed. In both cases molecular weight determinations by osmometry have confirmed that the trinuclear metal cluster in the original carbonyl has been retained in the derivatives. This is similar to the behaviour of the analogous

Triosmium Dodecacarbonyl and Some of its Derivatives				
Compound	Colour	Molecular Weight Found    Calculated		Infra-red C-O Stretching Frequencies, cm <sup>-1</sup> (in Nujol Mull)
Os <sub>3</sub> (CO) <sub>12</sub>	Yellow		907	2070(S), 2041(Sh), 2028(Sh), 2019(S), 1998(M), 1986(M), *2066(S), 2033(S), 2012(M), 2000(M)
Os <sub>4</sub> O <sub>4</sub> (CO) <sub>12</sub>	White	1153	1161	2092(S), 1987(S), 1959(Sh) *2015(S), 2100(S)
[Os(CO) <sub>3</sub> PPh <sub>3</sub> ] <sub>3</sub>	Orange-red	1654	1610	2053(W), 1988(S) 1969(S), 1957(Sh), 1927(S)
[Os(CO) <sub>2</sub> Diars] <sub>3</sub>	Brownish-yellow	1474	1597	1998(M), 1917(S)
Os(CO) <sub>3</sub> (PPh <sub>3</sub> )Cl <sub>2</sub>	White	712	607	2123(W), 2048(S), 2017(W), 1978(S)
Os(CO) <sub>3</sub> (PPh <sub>3</sub> )Br <sub>2</sub>	Light yellow	798	698	2154(W), 2067(S), 2023(S), 1982(Sh)
Os(CO) <sub>3</sub> (PPh <sub>3</sub> )I <sub>2</sub>	Golden yellow		790	Impure
(CO) <sub>3</sub> (PPh <sub>3</sub> )ClOs-HgCl	White		808	2076(W), 2032(M), 1998(S),
(CO) <sub>4</sub> ClOs-HgCl	Light yellow-green	606	574	2127(S), 2092(M), 2036(S), 2000(S)

\*In chloroform solution

ruthenium carbonyl, Ru<sub>3</sub>(CO)<sub>12</sub>, with triphenylphosphine (6). Cleavage of the metal-metal bonds is, however, achieved if [Os(CO)<sub>3</sub>PPh<sub>3</sub>]<sub>3</sub> is reacted in benzene solution with halogens, and compounds of the type Os(CO)<sub>3</sub>PPh<sub>3</sub>X<sub>2</sub>, where X = Cl, Br, or I, have been isolated.

Both the parent carbonyl and the triphenylphosphine derivative react with mercuric chloride to yield interesting new compounds containing Os-Hg bonds. The former reacts in hot xylene solution to yield (CO)<sub>4</sub>Cl Os-HgCl and the latter in cold benzene solution to yield (CO)<sub>3</sub>(PPh<sub>3</sub>)ClOs-HgCl.

Similar Os(O) and Os(II) complexes, e.g. Os(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and Os(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> have been reported by Collman and Roper (7), who have also prepared cationic complexes containing Os-Hg bonds, e.g. [(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>Os-HgCl]HgCl<sub>3</sub> (8). However, these compounds were produced by an entirely different route and the derivatives listed, together with some of their properties, are the first to

have been prepared directly from Os<sub>3</sub>(CO)<sub>12</sub>.

Further work on the reactions of the osmium carbonyl and its derivatives with halogens, halogen acids and mercuric halides is proceeding and will be reported in due course.

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