# STUDY-MATERIAL

## M.Sc. IV SEMESTER

## Paper IIIB: Organotransition Metal Chemistry

## UNIT-4

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# (I) Ruthenium and Osmium Carbonyls

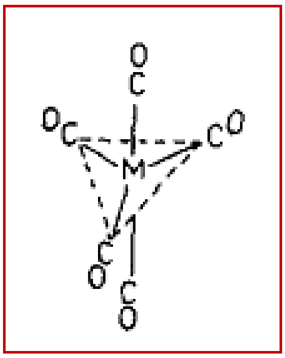
The binary carbonyls known so far may be classified according to the following types:
(A) $M(CO)_5$, (B) $M_2(CO)_9$, (C) $M_3(CO)_{12}$.

## (A) $M(CO)_5$

$Ru(CO)_5$ was prepared by the action of carbon monoxide on ruthenium trihalides in the presence of reducing agents like hydrazine or silver in an autoclave at high temperature (170-300°C) and pressure (400-455 atm). The triiodide was more reactive than the trichloride. Pino and coworkers obtained it by the action of a mixture of CO and $H_2$, on ruthenium triacetylacetonate using heptane as solvent.

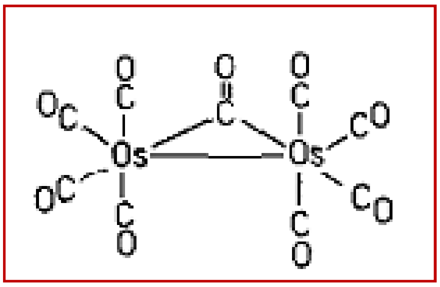
$Os(CO)_5$ was prepared by the action of CO on $OsO_4$, at 160 °C/100-200 atm. Its formation has also been observed when CO reacts with cis-$(CH_3)_2Os(CO)_4$ at elevated temperature and pressure.

The trigonal bipyramidal structures of these carbonyls have been confirmed by measurement of their infrared spectra. Both the carbonyls have two IR active C-O stretching vibrations analogous to $Fe(CO)_5$ confirming the $D_{3h}$,, symmetry of the molecules.



## B. $M_2(CO)_9$ Class

Osmium tetraoxide reacts with CO at 155 atm pressure and 230°C to yield $Os_2(CO)_9$. It has also been prepared by irradiating with UV light a heptane solution of $Os(CO)_5$ at -40°C. It has been proposed that it contains a bridging carbonyl group and a Os-Os bond.



## C. $M_3(CO)_{12}$ Class

Triruthenium dodecacarbonyl, $Ru_3(C0)_{12}$, was first prepared by Hieber et al. by treating $RuS_2$ with CO at 200 °C and at 200-300 atm pressure. The reaction is promoted by S-binding elements like Cu, Zn, Pb etc. It has also been obtained as a side reaction product in the polymethylene synthesis from CO and $H_2$ using Ru catalyst and by ultraviolet irradiation of ruthenium pentacarbonyl.

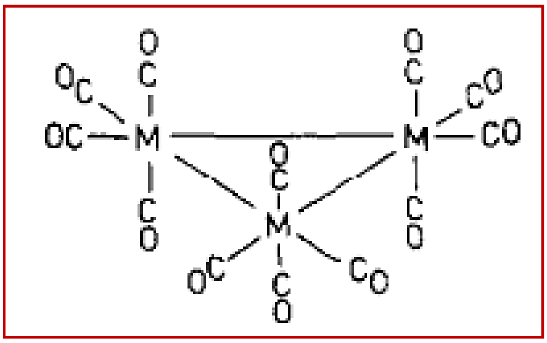
The osmium analogue, $Os_3(CO)_{12}$, has been obtained by the following methods: (i) By the treatment of CO with $0s0_4$, at high temperature and pressure using methanol or xylene as solvent;

(ii) It may also be obtained when the halides or carbonyl halides of osmium react with CO at high pressure using methanol, substituted glycols or ethers as solvents and zinc as catalyst;

(iii) CO displaces triphenylphosphine from $[Os(CO)_3(Ph_3P)]_3$ to yield $Os_3(CO)_{12}$;

(iv) Its formation has also been observed in the decomposition of $CH_3Os(CO)_4H$.

Corey and Dahl have shown that $Os_3(CO)_{12}$ has approximately $D_{3h}$ molecular symmetry in the crystalline state and $Ru_3(CO)_{12}$ is isomorphous with $Os_3(CO)_{12}$. The triangular clusters are held together by metal-metal bonds alone (Structure III), all the carbonyls being terminal.



Two of the four carbonyl groups attached to each metal atom are approximately perpendicular to the plane of the Os atoms while the other two are essentially in the plane; the average Os-Os distance is 2.88 Å. In $Ru_3(CO)_{12}$ the mean Ru-Ru bond length is 2.848 Å.

### D. $Ru_6(CO)_{18}$

The preparation of a new, deep red, diamagnetic compound $Ru_6(CO)_{18}$ which serves as a carbonylation catalyst, has been claimed by heating $Ru_3(CO)_{12}$ in a closed container at 150-170 °C under 0.2-1 atm partial pressure of CO, or by heating in benzene or cyclohexane. Aromatic hydrocarbon solvents are preferred in the synthesis. Its IR spectrum in cyclohexane shows two strong bands at 2066 and 2047 $cm^{-1}$ and two very weak bands at 2002 and 1850 $cm^{-1}$.

Mixed metal carbonyls containing Fe and Ru or Os, $FeRu_2(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $FeOs_2(CO)_{12}$ and $Fe_2OsCO_{12}$ have been obtained by the following methods:

$$\text{(i) } Fe(CO)_5 + [Ru(CO)_3Cl_2]_2 \xrightarrow{90-100°\,C/30\,h} H_2FeRu_3(CO)_{13} + FeRu_2(CO)_{12} + Fe_2Ru(CO)_{12}$$

$$\text{(ii) } Fe_3(CO)_{12} + Ru_3(CO)_{12} \xrightarrow{\text{dry petr. ether}} H_2FeRu_3(CO)_{13} + FeRu_2(CO)_{12}$$

$$\text{(iii) } Fe(CO)_5 + Ru_3(CO)_{12} \xrightarrow{60-80°\,C/20\,h} Fe_2Ru(CO)_{12} + FeRu_2(CO)_{12} + H_2FeRu_3(CO)_{13}$$

$$\text{(iv) } Ru_3(CO)_{12} + Fe(CO)_5 \xrightarrow{UV} Fe_2\,Ru(CO)_{12}$$

## (II) Rhodium, Iridium, Palladium and Platinum Carbonyls

Due to the distinctly different chemical nature of rhodium, iridium, palladium and platinum it seemed essential to classify their derivatives according to the following two pairs of metals which resemble considerably: (i) Rhodium and Iridium, (ii) Palladium and Platinum.

### Rhodium and Iridium

#### (A) Binary Carbonyls

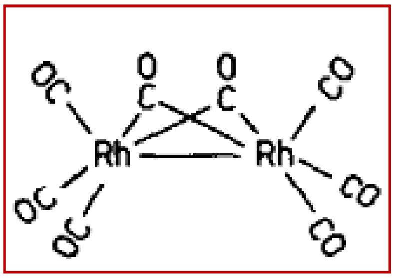
Rhodium and iridium form three types of binary carbonyls, namely, $M_2(CO)_8$, $M_4(CO)_{12}$ and $M_6(C0)_{16}$.

**$M_2(CO)_8$ Class**

In 1943, Hieber and Lagally reported the preparation of dirhodium octacarbonyl (orange, m.p. 76 °C) by the reaction of carbon monoxide on freshly prepared rhodium metal at 460 atm pressure and 200°C. There has been no subsequent confirmatory evidence to support the existence of this compound. However, IR spectral evidence for the reversible formation of bridged form of $Rh_2(CO)_8$ from $Rh_4(CO)_{12}$ under high pressure of carbon monoxide (490 atm) and low temperature (-19 °C) has been presented:

$$\boxed{Rh_4(CO)_{12} + 4CO \rightleftharpoons 2Rh_2(CO)_8}$$

The band maxima at 2086s 2061s 1860mw and 1845s cm$^{-1}$ suggest that probably the bridged form of $Rh_2(CO)_8$ is stabilised under these conditions. No evidence has been obtained for the formation of a non-bridged isomer of $Rh_2(CO)_8$ in contrast to the $Co_2(CO)_8$ system.



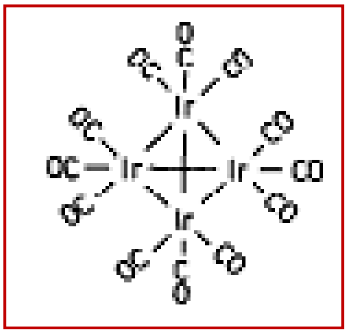
**$M_4(CO)_{12}$ Class**

Originally $Rh_4(C0)_{12}$ was prepared by Hieber and Lagally by the action of CO on anhydrous binary halides of rhodium at high temperature and pressure in presence of Cu or Ag.

The improved method of preparation of this compound is by the carbonylation of $[Rh(CO)_2Cl]_2$ in presence of different catalysts like Ullmann Cu-bronze powder, alkali or water under varying conditions of temperature and pressure.

Firstly, $Ir_4(CO)_{12}$ was prepared by Hieber and Lagally by heating iridium trihalides with CO at 200 atm in a Cu vessel. Later on it was obtained by the carbonylation of iridium halides or alkali metal hexachloroiridates under 40-100 atm pressure and 60 to 100°C in alcohols.

The structure of $Ir_4(CO)_{12}$ has been investigated by vibrational spectra and X-ray crystallography. The vibrational spectrum of this compound suggests a Td symmetry with no bridging CO group (νco: 2072, 2032 cm$^{-1}$). The twelve CO groups are disposed around the four iridium atoms to form a cubooctahedral structure. The Ir-Ir distances are 2.68 Å.

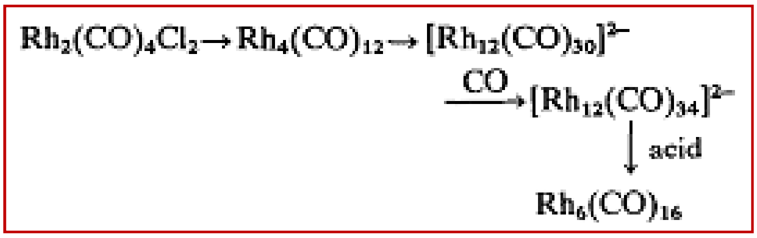


**$M_6(CO)_{16}$ Class**

$Rh_6(CO)_{16}$ is synthesised by the following methods:

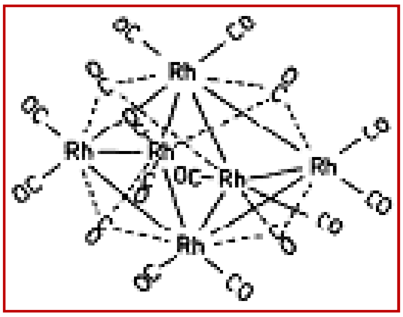
**(i)** By the action of $Fe(CO)_5$, on $RhCl_3$, or $[Rh(CO)_2Cl]_2$ at atmospheric pressure in methanol.

**(ii)** By the CO reduction of $[Rh(CO)_2Cl]_2$ in presence of alkali or water.



$$\begin{tikzcd} Rh_2(CO)_4Cl_2 \arrow[r] & Rh_4(CO)_{12} \arrow[r] & {[Rh_{12}(CO)_{30}]^{2-}} \arrow[r, "CO"] & {[Rh_{12}(CO)_{34}]^{2-}} \arrow[d, "acid"] \\ & & & Rh_6(CO)_{16} \end{tikzcd}$$

It is a black air stable solid which decomposes above 220°C. Its structure has been examined by IR and three dimensional X-ray crystal studies. Vibrational spectra of $Rh_6(CO)_{16}$ suggest an overall Td symmetry based on an octahedron of six Rh atoms with two terminal CO groups per metal atom and four bridging CO groups.



$Ir_6(CO)_{16}$ has been prepared as a red crystalline substance by the carbonylation of a suspension of $(Et_4N)_2[Ir_6(C0)_{15}]$ in acetic acid:

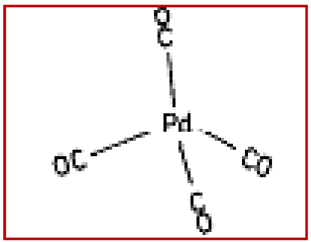
$$[Ir_6(CO)_{15}]^{2-} + 2H^+ \rightarrow H_2Ir_6(CO)_{15} \xrightarrow{CO} Ir_6(CO)_{16}$$

It is a very stable substance and has been identified by analytical data and also by the close similarity of its IR spectrum to those of the well known $Co_6(CO)_{16}$ and $Rh_6(C0)_{16}$.

## Palladium and Platinum

### A. Binary Carbonyls

In 1972 the existence of an unstable palladium carbonyl, $Pd(CO)_4$ has been established by IR spectroscopic studies. It was obtained in argon matrix by vaporising palladium metal at 1800 °K and co-condensing with a mixture of argon and CO at 20°K. Other identified species obtained were $Pd(C0)_3$, $Pd(C0)_2$ and PdCO. A single vCO frequency (2070.3 $cm^{-1}$) and the calculated band intensity provided the confirmation for $Pd(CO)_4$ and the quintet patterns were characteristic for a tetracarbonyl with Td symmetry.

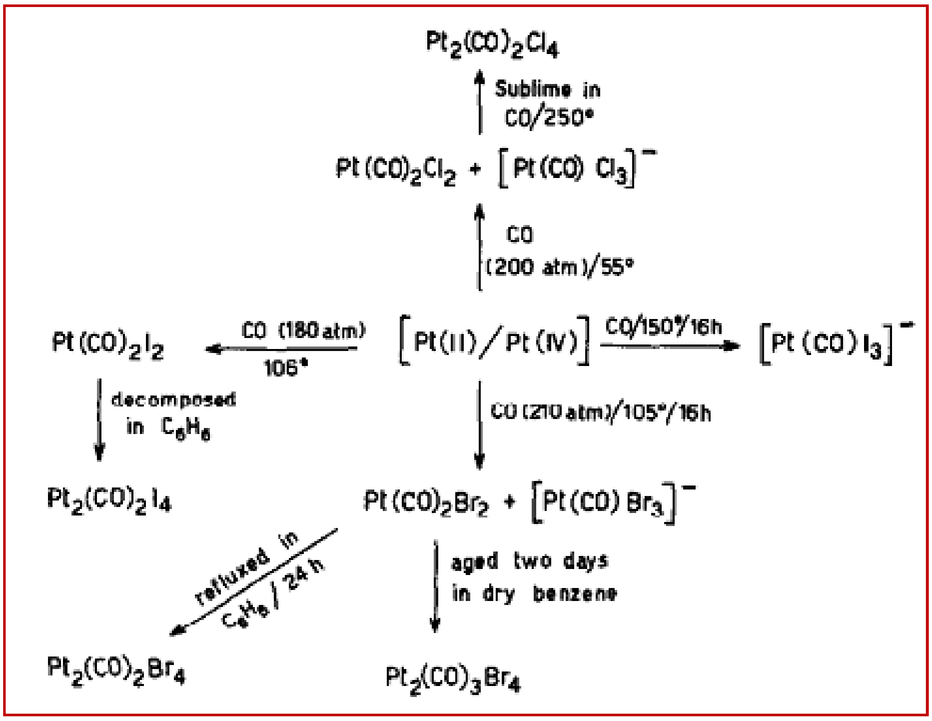


Diffusion studies indicate that the lower carbonyls readily react with excess of CO to yield $Pd(C0)_4$.

A CO adsorbed platinum compound, $Pt_3(CO)_4$ was obtained by vacuum deposition of Pt in CO atmosphere. The nature of the deposit depended to a large extent on the rate of vaporization of platinum.

A binary platinum carbonyl, Pt(CO)n has been described as a red black product which was obtained in the colloidal state by the action of CO on a dilute aqueous solution of chloroplatinic acid.

The preparative methods of different neutral and anionic species are described in the scheme



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2. S. C. Tripathi, S. C. Srivastava, R. P. Mani and A. K. Shrimal, *Inorg. Chim. Acta*, 17 (1976) 257-290. https://www.sciencedirect.com/science/article/abs/pii/S0020169300819921
3. Inorganic Chemistry by G. L. Miessler and D.A. Tarr