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ICA Review

Advances in Platinum Metal Carbonyls and Their Substituted Derivatives. I. Ruthenium and Osmium Carbonyls

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Contents

1. Introduction

Although platinum metal carbonyls have come into existence in the last decade of the nineteenth century, serious attention has been paid on these compounds only in recent years. Since then more than a thousand research papers have appeared which describe the syntheses, structures, and catalytic uses of platinum metal carbonyls and their derivatives. It is not surprising, therefore, that these compounds, which attracted little notice for more than seventy years after their discovery, have in recent times become the subject of lively interest throughout the world. Except a few review articles[1–5] which contain only a very brief account of this class of metal carbonyls, attempt has not been made for a really comprehensive coverage of the subject. This situation has prompted us to write the survey of platinum metal carbonyls and their substituted derivatives.

2. Binary Carbonyls

Although triruthenium dodecacarbonyl is known since long when Mond *et al.*[6–7] prepared an orange crystalline solid by the action of carbon monoxide on metallic ruthenium at 350–450 atm/300° C, the product could not be identified at that time. A number of ruthenium and osmium carbonyls have been identified since then. The binary carbonyls known so far may be classified according to the following types: (A) $M(CO)_5$, (B) $M_2(CO)_9$, (C) $M_3(CO)_{12}$.

The synthesis of a novel compound of ruthenium containing six metal atoms, formulated as $Ru_6(CO)_{18}$, has also been claimed.

A. $M(CO)_5$ Class

The monomeric pentacarbonyls of ruthenium,[8] $Ru(CO)_5$, and osmium,[9] $Os(CO)_5$, had been reported in the literature some thirty five years ago as volatile colourless liquids. These compounds, however, were not fully characterised at that time, although their formulae were well established. $Ru(CO)_5$ was prepared by the action of carbon monoxide on ruthenium trihalides[8] 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[10] obtained it by the action of a mixture of CO and H_2 on ruthenium triacetylacetonate using heptane[11] as solvent.

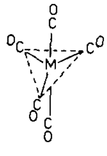
In a recent communication[12] a convenient method of preparation of $Ru(CO)_5$ by the action of CO and H_2 has been described. A hydridocarbonyl, $H_4Ru_4(CO)_{12}$, is also formed in this reaction.

The only method[9] for the preparation of $Os(CO)_5$ so far known is by the action of CO on OsO_4 at 160° C/100–200 atm. Its formation has also been observed[13] when CO reacts with *cis*-$(CH_3)_2Os(CO)_4$ at elevated temperature and pressure.

TABLE I. Infrared CO Stretching Vibrations of Metal Pentacarbonyls.

Compound	νCO (cm^{-1})	Phase	Ref.
$Fe(CO)_5$	2022s, 2000vs	Heptane	14
	2034, 2014	Gas	15
$Ru(CO)_5$	2035s, 1999vs	Heptane	11
$Os(CO)_5$	2034s, 1991vs	Heptane	11
	2047s, 2006vs	Gas	11

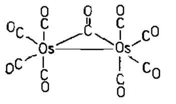
The trigonal bipyramidal structures (I) of these carbonyls have been confirmed by measurement of their infrared spectra. Both the carbonyls have two ir active C–O stretching vibrations (Table I) analogous to $Fe(CO)_5$ confirming the D_{3h} symmetry[14, 15] of the molecules.



(I)

B. $M_2(CO)_9$ Class

Very little is known about this class of compounds but in recent years, the doubtless existence of diosmium enneacarbonyl has been proved. Osmium tetraoxide[16] reacts with CO at 155 atm pressure and 230° C to yield $Os_2(CO)_9$. It has also been prepared by irradiating[17] with UV light a heptane solution of $Os(CO)_5$ at –40° C. It has been proposed[17] that it contains a bridging carbonyl group and a Os–Os bond (structure II).



(II)

No evidence for the existence of analogous ruthenium derivative is available.

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

Triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, was first prepared by Hieber *et al.*[18] 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.;* other methods of its preparation are: (i) By treatment of ruthenium benzoate,[19] acetate,[19, 20] succinate,[19] acetylacetonate[10, 19, 21–24] or stearate[25] on a mixture of CO and H_2 or CO alone at high temperature and pressure using hydrocarbons, ketones or low molecular weight aliphatic alcohols as solvents; (ii) By carbonylating ruthenium trihalides[8, 26–30] at high temperature and pressure in presence of solvents like methanol or substituted glycols and zinc as reducing agent. The conversion[31] of $RuCl_3 \cdot 3H_2O$ to $Ru_3(CO)_{12}$ without using super-atmosphere CO pressure can best be achieved by a three-step sequence:

$$RuCl_3 \cdot 3H_2O + 1,3\text{-}C_6H_8 \rightarrow [C_6H_6RuCl_2]_n \quad (C_6H_8 = 1,3\text{-Cyclohexadiene})$$

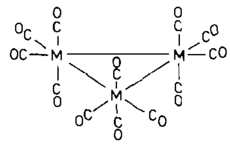
$$2/n[C_6H_6RuCl_2]_n + 6\,CO \rightarrow [Ru(CO)_3Cl_2]_2 + 2C_6H_6$$

$$3[Ru(CO)_3Cl_2]_2 + 6CO + 6Zn \rightarrow 2Ru_3(CO)_{12} + 6ZnCl_2;$$

iii) By the action of K_2CO_3[32] or $Fe(CO)_5$[33] on $[Ru(CO)_3Cl_2]_2$: $3[Ru(CO)_3Cl_2]_2 + 6Fe(CO)_5 \rightarrow 2Ru_3(CO)_{12} + 6FeCl_2 + 24CO$. This has been suggested to be a convenient method; (iv) It has also been obtained as a side reaction product[34] in the polymethylene synthesis from CO and H_2 using Ru catalyst; (v) By ultraviolet irradiation[8] of ruthenium pentacarbonyl.

The osmium analogue, $Os_3(CO)_{12}$, has been obtained by the following methods: (i) By the treatment[30, 35–39] of CO with OsO_4 at high temperature and pressure using methanol or xylene as solvent; (ii) It may also be obtained when the halides[29] or carbonyl halides[29] of osmium react with CO at high pressure using methanol, substituted glycols or ethers as solvents and zinc as catalyst; (iii) CO displaces[40] triphenylphosphine from $[Os(CO)_3(Ph_3P)]_3$ to yield $Os_3(CO)_{12}$; (iv) Its formation has also been observed in the decomposition[41] of $CH_3Os(CO)_4H$.

Corey and Dahl[42–44] 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.



(III)

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[45] is 2.848 Å.

Mass spectral data[46–49] for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ also establish the non C–O bridged structures of these molecules. The mass spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ consist primarily of $M_3(CO)_n^+$ (n = 0–12) series. In the mass spectrum of $Ru_3(CO)_{12}$

singly charged trinuclear species account for 92% of the metal containing fragments, doubly charged ones about 1% and binuclear and mononuclear 5 and 2% respectively. The mass spectrum of $Os_3(CO)_{12}$ consists of 100% $Os_3(CO)_n^+$ and $Os_3(CO)_n^{++}$. These data also reflect the greater stability of Os_3 nucleus compared to Ru_3 nucleus. This is in agreement with the conclusion already drawn that the stability of M–M bond increases in a triad of transition series.[50]

Much attention has been paid on the vibrational studies of $Ru_3(CO)_{12}$[26,31,51–56] and $Os_3(CO)_{12}$.[39,51–55,57,58] There are 34 Raman active and 21 infrared active fundamentals expected for $M_3(CO)_{12}$ molecules with D_{3h} symmetry. Table II gives the predicted symmetries of these vibrations as well as the representations spanned by a complete set of internal coordinates.

In agreement with vibrational analysis, four principal carbonyl stretching ir bands have been observed in the solution spectra of both the carbonyls (Table III) due to the modes ($3E' + A_2''$). In the solid state seven Raman and six or seven infrared active CO bands are observed[52] while only six Raman active and four ir active bands should be present. The extra Raman band may be explained as the inactive A_2' band rendered active by crystal effects. A slight lowering of symmetry to C_{3h} would give Raman activity to this fundamental. In the infrared spectra four bands are prominent and are assigned as the predicted fundamentals. The remaining minor features no doubt arise from crystal effects, since they are absent in solution spectra.[51,57] In an argon matrix more bands are observed[54] probably owing to distortion. These bands appear to be derived from the original solution bands as they divide easily into four groups. By comparison, the spectra of these species isolated in nitrogen[54,55] appear less complicated than in argon (Table III) and in the case of $Os_3(CO)_{12}$ the spectrum is very similar to that of solution. In both, the bands have smaller band-widths than in argon matrix, although all the frequencies suffer a smaller matrix shift. It is observed that these matrix spectra[54] are completely different from the published solid state spectra[52] of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.

TABLE II. Symmetries of Vibrational Modes for $M_3(CO)_{12}$ (D_{3h}).

Γ(vib)	$= 9A_1' + 6A_2' + 15E' + 4A_1'' + 6A_2'' + 10E''$
Γ(M–M)	$= A_1' + E'$
Γ(M–C)def[a]	$= 3A_1' + 2A_2' + 6E' + 2A_1'' + 2A_2'' + 4E''$
Γ(C–O)str	$= 2A_1' + A_2' + 3E' + A_2'' + E''$
Γ(M–C)str	$= 2A_1' + A_2' + 3E' + A_2'' + E''$
Γ(C–O)def	$= 2A_1' + 2A_2' + 4E' + 2A_1'' + 2A_2'' + 4E''$
Γ(Raman)	$= A_1' + E' + E''$
Γ(ir)	$= E' + A_2''$

[a] Contains $1A_1' + 2E'$ redundancies.

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

The preparation of a new, deep red, diamagnetic compound $Ru_6(CO)_{18}$,[59,60] 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[60] in cyclohexane shows two strong bands at 2066 and 2047 cm^{-1} and two very weak bands at 2002 and 1850 cm^{-1}. It is likely that the conclusions drawn for the formation of $Ru_6(CO)_{18}$ might be erroneous and the reported complex may be the carbonyl carbide complex $Ru_6(CO)_{17}C$ (See Carbide Section).

3. Mixed Metal Carbonyls and Their Derivatives

The chemistry of these heteronuclear carbonyls starts only from 1968. Not much structural information is available about these compounds except some crystal studies. In several reactions these products are formed alongwith the hydride derivatives, when the reactions are performed in protic solvents.

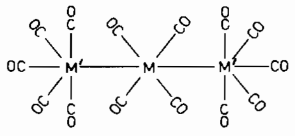
Mixed metal carbonyls containing Ru or Os and Group VI metals are not known at present. Group VII metal carbonyls like dimanganese decacarbonyl[61] or dirhenium decacarbonyl[61] when heated with $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ in 3:1 ratio in sealed tubes at 205° C, yield the products $[M'(CO)_5]_2M(CO)_4$ (M′ = Mn or Re, M = Ru or Os).

The structure (IV) of these derivatives may be represented to contain three linear metal atoms.

TABLE III. CO Stretching Vibrations of $M_3(CO)_{12}$.

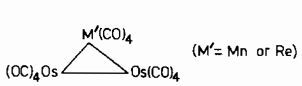
$Ru_3(CO)_{12}$ νCO (cm^{-1})	Reference	$Os_3(CO)_{12}$ νCO (cm^{-1})	Reference
2065s, 2035s, 2012m[a]	31	2068s, 2035s, 2014m, 2002m[b]	57
2070s, 2067s, 2063s, 2038s, 2033m, 2025vw, 2022w, 2016m, 2015m[c]	54	2079s, 2075vs, 2071m, 2042vs, 2036w, 2021m, 2019.5m, 2008m[c]	54
2067vs, 2064s, 2043vw, 2039s, 2034m, 2021w, 2017vw, 2013m[d]	54	2075s, 2070sh, 2045s, 2041sh, 2018.5m, 2004m[d]	55

[a] Carbon tetrachloride. [b] Cyclohexane. [c] Argon matrix. [d] Nitrogen matrix.



(IV)

The anions, $MnOs_2(CO)_{12}^-$ and $ReOs_2(CO)_{12}^-$, formed as a result of the reduction[62,63] of $Os_3(CO)_{12}$ with $Mn(CO)_5^-$ or $Re(CO)_5^-$ show seven and eight absorption bands (νCO: 2080w, 2018s, 1981vs, 1943m, 1914m, 1897sh, 1887m and 2085w, 2021s, 2009s, 1990s, 1954w, 1941sh, 1925sh, 1887w cm^{-1}) respectively in the ir spectra, all in the terminal region. The most likely structure (V) for the anions is therefore one of C_{2v} symmetry, which is analogous to $FeOs_2(CO)_{12}$, and it may be regarded as derivated from that of $Os_3(CO)_{12}$ by replacement of an Os atom by Mn or Re.



(V)

Mixed metal carbonyls containing Fe and Ru or Os, $FeRu_2(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $FeOs_2(CO)_{12}$ and $Fe_2Os(CO)_{12}$, have been obtained by the following methods:[33,64–67]

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

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

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

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

The ir spectrum[64,65] of $FeRu_2(CO)_{12}$ is very similar to the spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The absence of bridging CO absorptions (νCO: 2067s, 2042vs, 2034s, 2002w, 1988w cm^{-1} in cyclohexane) in the spectrum of $FeRu_2(CO)_{12}$ strongly suggests it to be isostructural with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. This is consistent with the often cited tendency of heavier second and third row transition metals to form clusters with strong metal–metal bonds unsupported by bridging groups.

The spectra[64,66] of $Fe_2Ru(CO)_{12}$ and $Fe_3(CO)_{12}$ are very similar; the bridging CO bands have also been observed in case of $Fe_2Ru(CO)_{12}$ (νCO: 2057s, 2044vs, 2023wsh, 2004mbr, 1859vvw, 1834vvw cm^{-1} in cyclohexane). It may be concluded that $Fe_2Ru(CO)_{12}$ has a molecular structure like that of $Fe_3(CO)_{12}$ where one of the bridging carbonyl groups of $Fe_2(CO)_9$ has been replaced by $Ru(CO)_4$ group. In this respect the structure of $Fe_2Ru(CO)_{12}$ would be similar to that proposed for the anions $MFe_2(CO)_{12}^-$ (M = Mn, Te, Re)[68–70] with a heteronuclear triangle of metal atoms.

Analogous to $FeRu_2(CO)_{12}$ and $Fe_2Ru(CO)_{12}$ the corresponding osmium compounds $FeOs_2(CO)_{12}$ and $Fe_2Os(CO)_{12}$ are also known. $FeOs_2(CO)_{12}$ has been obtained[71] by the action of diiron enneacarbonyl on diosmium octacarbonyl hydride (2:1 ratio in heptane).

When diiron enneacarbonyl reacted with osmium tetracarbonyl hydride in heptane, the formation of $Fe_2Os(CO)_{12}$ was observed in addition to a mixed carbonyl hydride, $H_2FeOs_3(CO)_{13}$, and $Fe_3(CO)_{12}$. The compound $Fe_2Os(CO)_{12}$ has also been obtained by irradiating with UV light[66] a solution of $Fe(CO)_5$ and $Os_3(CO)_{12}$ in acetone. It was characterised by mass spectral studies.[66] The presence of bridging CO groups has been inferred by its ir spectrum (νCO: 2117w, 2055s, 2041s, 2036s, 2013m, 2001m, 1990sh, 1860vw, 1827w cm^{-1} in heptane). It may be concluded that it has the structure similar to $Fe_2Ru(CO)_{12}$, $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$.

Ru and Co containing mixed carbonyls are uninvestigated. The mixed hydrocarbonyl[72] $HRuCo_3(CO)_{12}$ has been obtained by the action between $Ru_3(CO)_{12}$ and $Co_2(CO)_8$. Only one cobalt containing mixed carbonyl, $Co_2Os(CO)_{11}$, is known. It has been prepared[71] alongwith two hydrides, $H_2Co_2Os_2(CO)_{12}$, $HOs(CO)_4Co(CO)_4$ and $Co_4(CO)_{12}$ when $Co_2(CO)_8$ is treated with osmium tetracarbonyl hydride. No structural evidence is available for this compound.

Mixed metal carbonyls, containing ruthenium and osmium atoms, $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$, are also known. These two compounds have been obtained by refluxing[73] $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in xylene under carbon monoxide.

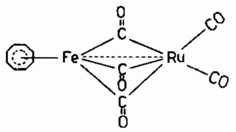
A few derivatives of the mixed carbonyls are also known. The trimethylsilyl derivative containing Ru and Mn carbonyls has been prepared[74] by reducing trimethylsilylruthenium tetracarbonyl dimer with sodium amalgam and further reaction with $Mn(CO)_5Br$:

$$[(Me_3Si)Ru(CO)_4]_2 + Na/Hg \rightarrow [Me_3Si\,Ru(CO)_4]^- \quad \text{in THF}$$

$$\xrightarrow{Mn(CO)_5Br} Me_3SiRu(CO)_4Mn(CO)_5$$

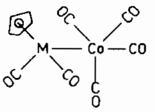
The ir spectrum of $Me_3Si\,Ru(CO)_4Mn(CO)_5$ indicates the presence of only terminal carbonyl groups (νCO: 2041m, 2027s, 1996w, 1977sh, 1973s cm^{-1} in cyclohexane). The analogous trimethylsilyl and trimethylgermyl derivatives of ruthenium and rhenium containing compounds, $Me_3SiRu(CO)_4Re(CO)_5$[75] and $Me_3GeRu(CO)_4Re(CO)_5$,[76] have been obtained by similar reactions. With the measurement of the ir spectra of these derivatives (νCO: 2053m, 2018s, 1997w, 1984m, 1978 cm^{-1} and 2119vw, 2053m, 2015s, 1995w, 1981m and 1974m cm^{-1} respectively) D_{4d} symmetry has been inferred. The proton NMR spectra of the two complexes show a single peak, indicating the presence of only one isomer.

A C_8H_8 substituted derivative, $C_8H_8FeRu(CO)_5$, has been obtained by the action[77] of $Ru_3(CO)_{12}$ on $C_8H_8Fe(CO)_3$ in xylene for 12 h. Ir measurements show that the bridging CO groups of the iron and ruthenium atoms are retained in the new complex (Structure VI). Proton spectrum indicates that the complex is a fluxional system.



(VI)

The cyclopentadienyl derivative of mixed ruthenium–cobalt carbonyl, which was obtained by the action[78, 79] of $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ on $NaCo(CO)_4$ in THF in 1:3 mole ratio, is a light orange crystalline solid. Unlike the analogous iron derivative,[78] which exists in both bridged and non-bridged forms (VII, VIIIa, b), $(C_5H_5)Ru(CO)_2Co(CO)_4$ exists in only non-bridged form (VII).



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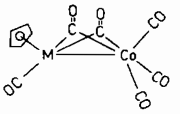
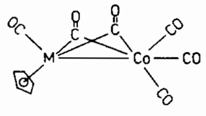


(VIII a)



(VIII b)

The derivative, $(\pi\text{-}C_5H_5)RuRe(CO)_7$, which was prepared by the action of $Re(CO)_5^-$ anion on $(\pi\text{-}C_5H_5)Ru(CO)_2X$ (X = Cl or I), may also have the similar structure with no bridging group as evidenced by its ir spectrum (νCO: 2101s, 2025m, 1993vs, 1964vs, 1938s cm^{-1}). The structure of the nickel derivative, $(\pi\text{-}C_5H_5)RuNi(CO)_3$, which was prepared[79] by the action of $Ru_3(CO)_{12}$ on nickelocene, has not been established finally. One terminal CO and one bridging CO bands were observed in the ir spectrum of this compound.

Several tertiary phosphine substituted derivatives of ruthenium–platinum mixed carbonyls[80, 81] (Structure IX–XI) have also been synthesised. The methods of their preparations are summarised as:

$$PtL_4 + Ru_3(CO)_{12} \xrightarrow[25^\circ C]{\text{benzene}} RuPt_2(CO)_5L_3$$

$$\text{or } Pt(Ph_3P)_2(\text{Stilbene}) + Ru_3(CO)_{12} \xrightarrow{25^\circ C} RuPt_2(CO)_5L_3$$

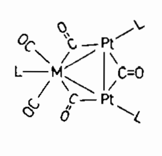
$(L = PPh_2Me, PMe_2Ph, Ph_3As, Ph_3P, P(OMe)Ph_2)$

$$cis\text{-}H_2Os(CO)_4 + Pt(Ph_3P)_2(C_2H_4) \rightarrow H_2Os(CO)_3(Ph_3P),\ OsPt_2(CO)_5(Ph_3P)_3,\ HOsPt(CO)_4(Ph_3P)$$

$$Pt(PPh_2Me)_4 + Ru_3(CO)_{12} \xrightarrow[25^\circ C]{\text{benzene}} Ru_2Pt(CO)_7(PPh_2Me)_3 + RuPt_2(CO)_5(PPh_2Me)$$

$$PtL_4 + Ru_3(CO)_{12} \rightarrow RuPt_2(CO)_4L_4$$

$(L = P(OPh)_3, PPh(OMe)_2)$



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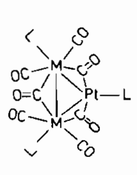
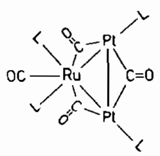


(X)



(XI)

The infrared spectra[80, 81] of the compounds having structure IX contain two strong bands at *ca.* 2020 and 1950 cm^{-1} indicating terminal CO groups and a strong band at 1785 cm^{-1} suggesting the presence of bridging CO. Weak bands at about 1850 cm^{-1} have also been recorded. NMR data[80, 81] suggest a structure in which one phosphine ligand is coordinated to each metal atom and the simple νCO spectrum indicates the high degree symmetry of the molecule. The ir spectra of the compounds (X) show two strong terminal and two bridging CO stretching frequencies. In these molecules one phosphine ligand is coordinated to each metal atom. The NMR spectra of the complexes having structure XI reveal that two phosphine or phosphite ligands are bonded to platinum while the third and fourth are attached to ruthenium. In the ir spectra only one terminal CO and three bridging CO bands have been recorded.

4. Substituted Derivatives

A large number of substituted derivatives of these carbonyls are known. Only in a few cases they have been obtained by the direct displacement of CO molecules from metal carbonyls. Indirect methods are used to prepare most of the complexes.

A. Complexes with Group V Donors

(i) Mononuclear

In this class the derivatives of the types $M(CO)_4L$, $M(CO)_3L_2$, $M(CO)_3L'$, $M(CO)_2L'_2$ and $M(CO)L''$ (L, L′ and L″ are monodentate, bidentate and quadridentate respectively) are known. Preparative details of these compounds have been summarised in Table IV. It has been observed that several ligands cleave the Ru–Ru bond in $Ru_3(CO)_{12}$ with the formation of mononuclear substituted derivatives. Thus on refluxing 2-vinylphenyl(diphenylphosphine) with $Ru_3(CO)_{12}$ in octane, $Ru(CO)_3(o\text{-}CH_2{=}CHC_6H_4PPh_2)$ and $Ru(CO)_3(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$ were obtained. When

TABLE IV. Substituted Mononuclear Ru and Os Carbonyls.

Compound	Preparation	Reference
$Ru(CO)_4(Ph_3P)$	a, b	40, 82, 83
$Ru(CO)_3L_2$ (L = Ph_3P, Bu_3P, $(MeO)_3P$, $(EtO)_3P$, $PPhMe_2$, $(C_6H_4Me)_3P$, $\{(MeO)C_6H_4\}_3P$, (o-$CH_2{=}CHC_6H_4PPh_2$), Ph_3As)	a, b, c, d, e, f	82–84, 87–89, 91, 92, 94
$Ru(CO)_3\{(CF_2)_3(PPh_2)C{=}C(PPh_2)\}$	f	95
$Os(CO)_4(Ph_3P)$	a, g	82, 83, 93
$Os(CO)_3L_2$ (L = Ph_3P, $PPhMe_2$, $(MeO)_3P$)	a, d, g, h	82, 83, 85, 86, 90, 93

[a] Action of ligands on $M(CO)_5$. [b] Carbonylation of $M_3(CO)_9L_3$. [c] Action of CO on $M(CH_3C_3H_4)_2L_2$. [d] Reduction of $M(CO)_2L_2Cl_2$ with Zn. [e] Action of HCHO on alk. solution of MX_3 and subsequent reaction of ligands. [f] Action of ligands on $Ru_3(CO)_{12}$. [g] Action of ligands on $HMeM(CO)_4$. [h] Action of ligands on $C_8H_8Os(CO)_3$.

the ligand acts as a monodentate one, donation takes place through only phosphorus atom and when it behaves as a bidentate ligand, donation is through phosphorus atom as well as through the double bond of the vinyl group. In the similar manner 1,2-bis(diphenylphosphine)-3,3,4,4,5,5-hexafluorocyclopentene also cleaves[95] the metal–metal bond in $Ru_3(CO)_{12}$ to form $Ru(CO)_3$(1,2-bis(diphenylphosphine)-3,3,4,4,5,5-hexafluorocyclopentene). Evidences have also been obtained[2] that the quadridentate ligands, $(o\text{-}Ph_2C_6H_4P)_3P$ and $(o\text{-}Ph_2C_6H_4As)_3As$, break down the $Ru_3(CO)_{12}$ cluster to form compounds of the type Ru(CO)(L–L–L). A few nitrogen donors like mesoporphyrine IX dimethylester[96] and tetraphenylporphine[96] also react with $Ru_3(CO)_{12}$ to form similar compounds. The ir spectra of these compounds showed a single band at 1940 or 1945 cm^{-1}, respectively, in the $\nu C{\equiv}O$ region. It has been indicated[96] that the sixth coordination site in both the above compounds is either empty or at least in some sort of equilibrium with a five coordinate species, because imidazole and similar bases immediately complex with both the compounds upon simple mixing in benzene to form red crystalline diamagnetic solids, Ru(CO)L(imidazole) (H_2L = mesoporphyrine dimethyl ester and tetraphenylporphine). Besides neutral complexes a few unstable cationic species like $[Ru(NH_3)_5CO]^{++}$ and $[Os(CO)_4(PR_3)_2]^{++}$ have also been investigated. The cation $[Ru(NH_3)_5CO]^{++}$ has been obtained by the following methods:[31, 97]

(i) Ammination of the anion $[Ru(H_2O)Cl_4CO]^{--}$ under mild condition

$$[Ru(H_2O)Cl_4CO]^{--} \xrightarrow{\text{Ammination}} [Ru(NH_3)_5CO]Cl_2$$

(ii) Reaction of hydrazine on $[Ru(CO)_3Cl_2]_2$

$$[Ru(CO)_3Cl_2]_2 \xrightarrow{N_2H_4} [Ru(NH_3)_5CO]Cl_2$$

(iii) Reaction of hydroxylamine on $[Ru(CO)_2Cl_2]_n$

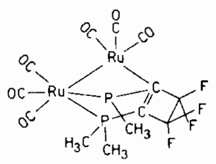
$$[Ru(CO)_2Cl_2]_n + NH_2OH \xrightarrow{\text{6 h/room temp.}} [Ru(NH_3)_5CO]Cl_2$$

The ir spectrum of $[Ru(NH_3)_5CO]^{++}$ shows a single CO band at 1930 cm^{-1} (KBr) and the bands at 3200(br) and 1620 cm^{-1} have been assigned for coordinated ammonia molecules.

Two unstable, substituted osmium carbonyl cations,[98] $[Os(CO)_4(PR_3)_2]^{++}$ (R = phenyl or cyclohexyl), have been identified as a result of the reaction between $AlCl_3$ and $Os(CO)_2(PR_3)_2Cl_2$ in CO atm.

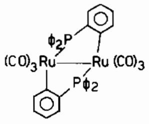
(ii) Dinuclear

Dinuclear complexes are obtained either by the reactions of bidentate ligands on $M_3(CO)_{12}$ or by the pyrolysis of $Ru_3(CO)_9L_3$ derivatives. Tetrakis(pentafluorophenyl)diphosphine, tetrakis(pentafluorophenyl)diarsine, 1,2-bis(diphenylphosphino)-3,3,4,4-tetrafluorocyclobutene, 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene and 1,2-bis(diphenylphosphino)-3,3,4,4,5,5-hexafluorocyclopentene react[95, 99] with $Ru_3(CO)_{12}$ to form the corresponding $Ru_2(CO)_6L$ derivatives. Similarly 1,2-bis(diphenylphosphino)-3,3,4,4-tetrafluorocyclobutene reacts with $Os_3(CO)_{12}$ in a 2:1 molar ratio to yield $Os_2(CO)_6L$.[100] In the complexes $M_2(CO)_6L$ (L = 1,2-bis(diphenylphosphino)-3,3,4,4-tetrafluorocyclobutene) the phosphines of the ligand are coordinated to one metal atom and the cyclobutene ring is bonded to the other metal atom (XII).

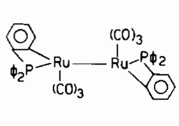


(XII)

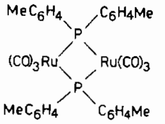
Controlled pyrolytic reactions in an inert solvent, such as decalin, are more useful for the preparation of these complexes. Refluxing of $Ru_3(CO)_9L_3$ (L = Ph_3P, $P(m\text{-}MeC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$ or $PMePh_2$) in decalin[101] affords a variety of complexes, $Ru_2(CO)_6(PPh_2)_2(C_6H_4)_2$, $Ru_2(CO)_6(PAr_2)_2$ (Ar = phenyl or *m*-tolyl) and $Ru_2(CO)_6(PPhR)(C_6H_4)(PPhR)$ (R = Me or Ph), which have been separated on alumina. In the complex $Ru_2(CO)_6(PPh_2)_2(C_6H_4)_2$ the presence of *ortho*-metallated phosphine ligands and six carbonyls attached to two metal atoms[101] has been concluded on the basis of NMR and mass spectroscopy (XIII, XIV).



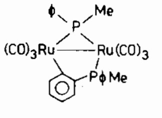
(XIII)



(XIV)



(XV)



(XVI)

^1H NMR spectra of another complex $Ru_2(CO)_6\{P(m\text{-}MeC_6H_4)_2\}_2$ indicated that metallation of the ring did not occur in this complex (Structure XV).

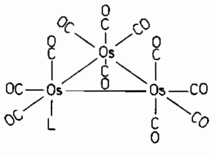
A heterobridged dinuclear complex, $Ru_2(CO)_6(PMePh)(C_6H_4)(PMePh)$, (XVI) has been obtained by the pyrolysis of $Ru_3(CO)_9(PMePh_2)_3$.

Phenylthiodiphenylphosphine after reaction with $Ru_3(CO)_{12}$ yields[102] another complex $Ru_2(CO)_6PPh_2(SPh)$. Dinuclear complexes containing semidine and azobenzene as ligands alongwith a trinuclear compound $Ru_3(CO)_9(C_{12}H_{10}N_2)$ have been synthesised by the reaction of $Ru_3(CO)_{12}$ with azobenzene while the similar reaction[103] between *o*-semidine and $Ru_3(CO)_{12}$ gave $Ru_2(CO)_4(\text{semidine})_3$, $Ru_2(CO)_4(\text{semidine})_2$ and $Ru_3(CO)_8(\text{semidine})_3$.

(iii) Trinuclear

Substituted trinuclear ruthenium and osmium carbonyl clusters have been prepared mainly by using phosphorus and rarely arsenic, antimony and nitric oxide donors. The investigated species are: $M_3(CO)_{11}L$, $M_3(CO)_{10}L_2$, $M_3(CO)_{10}(L\text{–}L)$, $M_3(CO)_9L_3$ and $M_3(CO)_6(L\text{–}L)_3$ (M = Ru and Os) and $M_3(CO)_8L_4$ and $M_3(CO)_7L$ (M = Ru), (Table V).

In several investigations[81, 100, 101, 105, 106] the derivatives $M_3(CO)_{11}L$, $M_3(CO)_{10}L_2$ and $M_3(CO)_9L_3$ have been obtained simultaneously as mixtures. Their separations have been carried out mainly by chromatography. In a recent communication[107] several unusual carbonyl hydrides alongwith normal complexes have been reported to form when the reaction between $Os_3(CO)_{12}$ and Ph_3 P is performed in a mole ratio of 1:2. The single species $Os_3(CO)_{11}L$ (XVII) could be isolated[108] when $Os_3(CO)_{12}$ was refluxed with



(XVII)

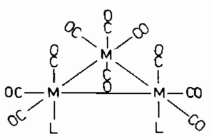
TABLE V. Substituted Trinuclear Ru and Os Carbonyls.

Compound	Preparation	Reference
$Ru_3(CO)_{11}L$ (L = Ph_3P, $PPhMe_2$, Ph_3As)	a	101, 108
$Ru_3(CO)_{10}L_2$ or (L–L) (L = $PPhMe_2$, PPh_2Me, $P(OMe)_2Ph$, Ph_3As; L–L = $Ph_2PCH_2CH_2PPh_2$, $(CF_2)_2Ph_2PC{=}CPPh_2$, $(CF_2)Ph_2AsC{=}CAsPh_2$)	a	95, 101, 109, 115
$Ru_3(CO)_9L_3$ (L = Ph_3P, Bu_3P, Et_3P, $PPhMe_2$, $PPhEt_2$, PPh_2Me, PPh_2Et, $(p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$, PMe_2PhCH_2, $(Me_2N)_3P$, $P(OMe)_3$, $P(OPh)_3$, $AsMe_2Ph$, Ph_3Sb)	a	2, 84, 101, 104, 112, 115–117
$Ru_3(CO)_8L_4$ (L = PH_3, $PPh(OMe)_2$)	a	101, 118
$Ru_3(CO)_8(L\text{–}L)_2$(L–L= $(CF_2)_2Ph_2PC{=}CPPh_2$, $(CF_2)_2Ph_2As\text{–}C{=}CAsPh_2$)	a	95, 119
$Ru_3(CO)_7L$ (L = $(C_6H_4)(Ph_2P)_2$, $\{(m\text{-}MeC_6H_4)_2P\}_2MeC_6H_3$, $\{(p\text{-}MeC_6H_4)_2P\}_2MeC_6H_3$)	b	101
$Ru_3(CO)_6(L\text{–}L)_3$ (L–L = $Ph_2PCH_2CH_2PPh_2$, $(C_6H_4)(AsMe_2)_2$)	a	2
$Os_3(CO)_{11}L$ (L = Ph_3P, Et_3P, PEt_2Ph, PMe_2Ph, $(CF_2)_2Ph_2PC{=}CPPh_2$, Ph_3As)	a, c	100, 105, 106, 108
$Os_3(CO)_{10}L_2$ (L = Ph_3P, Et_3P, PEt_2Ph, PMe_2Ph, $(CF_2)_2Ph_2PC{=}CPPh_2$)	a	100, 105, 106
$Os_3(CO)_9L_3$ (L = Ph_3P, Et_3P, PPh_2Me, $PPhEt_2$, $(p\text{-}MeC_6H_4)_3P$, $(CF_2)_2Ph_2PC{=}CPPh_2$)	a, d	37, 38, 85, 100, 105, 106
$Os_2(CO)_6\{(C_6H_4)AsMe_2)_2\}_3$	a	37, 100

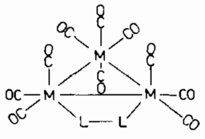
[a] Reactions of ligands with $M_3(CO)_{12}$. [b] Pyrolysis of $Ru_3(CO)_9(PAr_3)$. [c] Refluxing $Os_3(CO)_{12}$ with bromo(triphenylphosphine or triphenylarsine)gold. [d] Reactions of ligands with $Os_4O_4(CO)_{12}$.

bromo(triphenylphosphine)gold or bromo(triphenylarsine)gold in xylene for 15 minutes, yellow crystals of $Os_3(CO)_{11}(Ph_3P)$ or $Os_3(CO)_{11}(Ph_3As)$ being obtained.

$M_3(CO)_{10}L_2$ (L = monodentate) or $M_3(CO)_{10}$ (L–L) derivatives have been prepared both by reflux and UV irradiation methods. With the help of X-ray diffraction[95,109] it has been concluded that two carbonyl groups, attached to different metal atoms, are displaced with these donors (XVIII a,b). The short and long metal–metal bond distances become the measure of the bonding characteristic of the ligand.



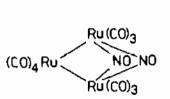
(XVIII a)



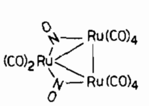
(XVIII b)

Apart from the phosphorus and arsenic donor atoms, nitric oxide plays an important role in the formation of the complexes of this class. Except mononuclear $Os(CO)_2(NO)_2$ which has been identified in argon matrix[110] as a result of the photochemical reaction between $Os(CO)_5$ and NO, all the known nitrosyl carbonyls are polynuclear in nature. Nitric oxide and moist nitrogen peroxide react with dichloromethane solution of $Ru_3(CO)_{12}$ to form $Ru_3(CO)_{10}(NO)_2$[111] and insoluble polymeric $[Ru(CO)_2(NO_2)_2]_n$.[112]

The solution[111] and matrix[54,55] spectra of $Ru_3(CO)_{10}(NO)_2$ are almost identical. These measurements clearly indicate the presence of bridging NO[113] (νNO: 1524w, 1508m cm^{-1} in n-hexane; 1533w, 1530w, 1516m and 1513m cm^{-1} in argon) and the absence of bridging CO groups. The structures (XIXa) and (XIXb) are consistent[111] with the analysis and the spectroscopic data while crystal data[114] favour the structure (XIXa).



(XIX a)



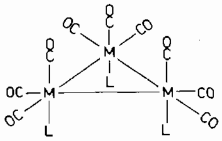
(XIX b)

For terminal carbonyl groups, there are nine ir bands ($4A_1 + 2B_1 + 3B_2$) predicted for C_{2v} symmetry if there is coupling between the vibrations and seven bands $M(CO)_4$ $2A_1 + B_1 + B_2$ and $M(CO)_3$ $2A' + A''$ for the uncoupled case. In the solution[111] and matrix[54] spectra of $Ru_3(CO)_{10}(NO)_2$ there are more bands (νCO: 2110w, 2077s, 2068s, 2061sh, 2039s, 2030s, 2026sh, 2015w and 2000m cm^{-1} in n-hexane; 2115w, 2083vw, 2071s, 2066sh, 2044vs, 2033s, 2028m, 2017w and 2001m cm^{-1} in argon matrix) than might be expected for totally uncoupled vibrations.

Straight forward reaction between $Os_3(CO)_{12}$ and NO at 60 psi of NO/100° C for 24 h produced the osmium analogue,[114] $Os_3(CO)_{10}(NO)_2$, in 13% yield. The ir spectrum[114] (νCO: 2108m, 2068s, 2063s, 2054sh, 2025s, 2017w, 2008w and 1996m cm^{-1}; νNO: 1500 cm^{-1} in tetrachloroethylene) suggested the presence of bridged nitrosyl ligands.

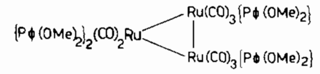
$M_3(CO)_9L_3$ derivatives are the most common species[37,38,84,85,100,101,104–108,112,115–118] among substituted trinuclear ruthenium and osmium carbonyl clusters. These derivatives are obtained by strainghtforward thermal reactions between ligands and $M_3(CO)_{12}$. The osmium analogues have also been synthesised by the action of ligands on $Os_4O_4(CO)_{12}$.

In these derivatives the trinuclear skeleton is retained and the ligands displace three carbonyl groups attached to different metal atoms (XX).



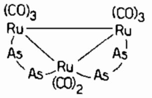
(XX)

Considerably, a smaller number of $M_3(CO)_8L_4$ derivatives are known. PH_3 reacted[118] with a suspension of $Ru(CO)_2Cl_2$ in common organic solvents at (25–80° C) to form $Ru_3(CO)_8(PH_3)_4$. $Ru_3(CO)_8\{PhP(OMe)_2\}_4$ was obtained when $PPh(OMe)_2$ reacted[101] with $Ru_3(CO)_{12}$. Ir and NMR studies suggest structure (XXI) with two ligands attached in a relative *cis* configuration on one metal atom.



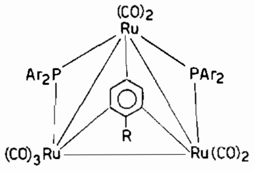
(XXI)

$Ru_3(CO)_8(L–L)_2$ (L–L = 1,2-bis(diphenylphosphino)-3,3,4,4-tetrafluorocyclobutene or 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene) are isolated as one of the reaction products[95] when these ligands react with $Ru_3(CO)_{12}$. The structure (XXII) of the arsenic derivative has been confirmed by ir, NMR and crystal data.[119]



(XXII)

Controlled pyrolysis[101] of some of the $Ru_3(CO)_9(PAr_3)_3$ derivatives in decalin yielded the products of the type $Ru_3(CO)_7(PAr_3)(PAr_2)$ with other dinuclear species. The trinuclear compounds, $Ru_3(CO)_7(Ph_2P)_2(C_6H_4)$, $Ru_3(CO)_7\{P(m\text{-}MeC_6H_4)_2\}_2(MeC_6H_3)$ and $Ru_3(CO)_7\{P(p\text{-}MeC_6H_4)_2\}_2(MeC_6H_3)$, have been separated by chromatography. On the basis of NMR studies the structure of these derivatives has been assigned as (XXIII).



(XXIII)

On heating[2,37] $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ with several bidentate ligands (L) *viz.*, bis(diphenylphosphino) ethane, *o*-phenylenebis(dimethylarsine) in inert solvents like xylene, derivatives of the class $M_3(CO)_6(L{-}L)_3$ have been prepared.

C–O stretching frequencies of some of the important substituted derivatives have been given in Table VI.

B. Complexes with Group VI Donors

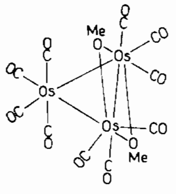
Methoxy, acetato and dionato complexes of ruthenium and osmium carbonyls which contain oxygen donors are of significant importance due to their peculiar structures. On treating OsO_4 in methanol with CO at 125° C for 12 h, a mixture of $Os_3(CO)_{10}(OMe)_2$ and $HOs_3(CO)_{10}(OMe)$ was obtained. $Os_3(CO)_{10}(OMe)_2$ was separated from the hydride complex by thin layer chromatography. Structure (XXIV) of $Os_3(CO)_{10}(OMe)_2$ has been established by X-ray dif-

TABLE VI. CO Frequencies of Substituted Carbonyl Compounds of Ru and Os.

Compound	νCO (cm^{-1})	References
$Ru(CO)_3(Ph_3P)_2$	1895^a	84
$Ru(CO)_3\{(C_6H_4Me)_3P\}_2$	1890^a	91
$Ru(CO)_3(Bu_3P)_2$	1895^a	84
$Ru(CO)_3\{(MeO)_3P\}_2$	2006, 1931, 1923^b	88
$Ru(CO)_3\{(EtO)_3P\}_2$	1991, 1917, 1905^b	88
$Ru(CO)_3(o\text{-}CH_2{=}CHC_6H_4PPh_2)$	2060, 1990, 1968^c	94
$Ru(CO)_3(Ph_3As)_2$	1890^a	89
$Ru(CO)_3(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$	1978, 1917^b	94
$Os(CO)_3(Ph_3P)_2$	1840^b	90
$Os(CO)_3(PhPMe_2)_2$	1889^b	86
$Os(CO)_3\{(MeO)_3P\}_2$	1924, 1914^b	85
$Ru_2(CO)_6(Ph_2P)_2$	2072, 2041, 2011, 2007, 1983, 1975^b	101
$Ru_2(CO)_6\{(m\text{-}MeC_6H_4)_2P\}_2$	2070, 2067, 2039, 2009, 2004, 1981, 1972^b	101
$Ru_2(CO)_6\{P(C_6H_4)(PhMe)(PPhMe)\}$	2068, 2033, 2008, 2003, 1987, 1977, 1965^b	101
$Ru_2(CO)_6\{P(C_6H_4)(Ph_2)(PPh_2)\}$	2071, 2037, 2010, 1991, 1987, 1969	101
$Ru_3(CO)_{11}(PhPMe_2)$	2092, 2039, 2026, 2010, 1998, 1991, 1980, 1973, 1956^b	101
$Ru_3(CO)_{10}(PhMe_2)_2$	2069, 2013, 1989, 1969^b	101
$Ru_3(CO)_{10}(Ph_2PMe)_2$	2070, 2016, 1991, 1969^b	101
$Ru_3(CO)_{10}\{(MeO)_2PPh\}_2$	2080, 2029, 2005, 1984, 1972^b	101
$Ru_3(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$	2082, 2021, 2016, 2001, 1983, 1965, 1935^b	101
$Ru_3(CO)_{10}\{(CF_2)_2Ph_2PC{=}CPPh_2\}$	2087, 2027, 2019, 2007, 1989, 1974, 1960, 1950^b	95
$Ru_3(CO)_{10}\{(CF_2)_2Ph_2AsC{=}CAsPh_2\}$	2087, 2024, 2014, 2007, 1980, 1967, 1950, 1938^b	109
$Ru_3(CO)_9(Ph_3P)_3$	2060, 2040, 2020, 1980, 1965, 1958^a	101
$Ru_3(CO)_9(Bu_3P)_3$	2035, 1960, 1927^b	84
$Ru_3(CO)_9(Ph_2PMe)_3$	2042, 1966, 1939	101
$Ru_3(CO)_9(PhPMe_2)_3$	2040, 1972, 1966, 1938^b	101
$Ru_3(CO)_9\{(MeO)_3P\}_3$	2054, 2001, 1988, 1963^b	101
$Ru_3(CO)_9\{(OPh)_3P\}_3$	2001, 1985, 1970, 1945^d	101
$Ru_3(CO)_8\{Ph(OMe)_2\}_4$	2031, 1983, 1965, 1913^e	101
$Ru_3(CO)_8\{(CF_2)_2Ph_2PC{=}CPPh_2\}_2$	2048, 1996, 1978, 1972, 1944, 1898^f	101
$Ru_3(CO)_7\{(C_6H_4)(Ph_2P)_2\}$	2057, 2020, 2009, 1998, 1968, 1955^b	101
$Ru_3(CO)_7\{(m\text{-}MeC_6H_4)_2P\}_2MeC_6H_3$	2054, 2017, 2006, 1996, 1965, 1950^b	101
$Os_3(CO)_{11}(Ph_3P)$	2108, 2055, 2035, 2019, 2000, 1989, 1978, 1956^g	108
$Os_3(CO)_{11}(Ph_3As)$	2109, 2056, 2036, 2020, 2001, 1991, 1977, 1957^g	108
$Os_3(CO)_{10}(Ph_3P)_2$	2085, 2012, 1998, 1969, 1951^e	105, 106
$Os_3(CO)_9(Ph_3P)_3$	2053, 1999, 1990, 1976, 1944^f	38, 108
$Os_3(CO)_9\{p\text{-}MeC_6H_4)_3P\}_3$	1997, 1989, 1974, 1941^g	108
$Os_3(CO)_9(Ph_2PMe)_3$	1987, 1976, 1938, 1922^g	85

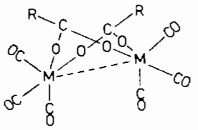
[a] Dichloromethane. [b] Cyclohexane. [c] n-octane. [d] Nujol. [e] Chloroform. [f] Carbon disulphide. [g] Carbon tetrachloride.

fraction (R. Mason and V. Duckworth, Notes added in proof of ref. 33).



(XXIV)

Acetato complexes have been obtained under different conditions. Polymeric, $[Ru(CO)_2(RCOO)]_n$[120], derivatives were obtained by the reaction of $Ru_3(CO)_{12}$ with RCOOH in benzene, which reversibly change into $Ru_2(CO)_6(RCOO)_2$ on treatment with CO. The osmium[120] analogue was obtained in a similar manner. The polymeric ruthenium dicarbonyl compounds are yellow orange amorphous solids, insoluble in nondonor solvents and are completely nonvolatile. The ir spectra show four strong and several other weaker bands in CO stretching region. Other bands in the region 700–1800 cm^{-1} are assigned to the various vibrations associated with bridging carboxylate ligands. The possibility that these compounds are hydrido derivatives of the type $[HRu(CO)_2(RCOO)_2]_n$ and that one or more of the bands in the region 1800–2200 cm^{-1} are due to a Ru–H stretching vibration has been ruled out[120] since no signal is observed in the region 10–40, which is normally associated with metal hydride irrespective of the method of coordination of the hydrogen. Bands normally associated with bridging carbonyl groups have not been observed. A mass spectrometric study on $Os_2(CO)_6(RCOO)_2$ was possible due to the sufficient volatility of the compound and the dimeric formulation has been established. A crystal study[121] on $Os_2(CO)_6(OAc)_2$ shows it to be composed of dinuclear molecular units with no crystallographic imposed symmetry (Structure XXV).



(XXV)

The two independent units are identical within their established standard deviations and each has approximately C_{2v} symmetry with *cisoid* bridging acetate groups. The coordination about each Os atom is roughly octahedral and the Os–Os distance is 2.731 Å. The dionato derivative $Ru(CO)_2$(2,4-pentanedionato)$_2$[122] was obtained by the carbonylation of tris(β-dionato) ruthenium complexes at elevated temperature.

Sulphur containing ligands[116, 123–125] like thiols,[116] thiophenol,[125] aniline sulphide[125] and alkyldithiocarbamates[124] have been used in the synthesis of substituted ruthenium carbonyl derivatives. Thus methyl-, ethyl-, butyl- and phenylthiols react[116] with $Ru_3(CO)_{12}$ to yield the derivatives of the type $Ru_2(CO)_6(S_2R_2)$ and $[Ru_2(CO)_6(S_2R_2)]_n$. The interaction of CO containing ruthenium solution, reported by Chatt[123] with a solution of sodium diethyldithiocarbamate produces an immediate colour change from red to green with the formation of yellow pentacoordinated Ru $(CO)(Et_2NCS_2)_2$.[124] In the similar manner another pentacoordinated derivative $Ru(CO)(Me_2NCS_2)_2$ has been prepared[124] by using tetramethylthiuram disulphide as ligand. The hexacoordinate $Ru(CO)_2$ $(R_2NCS_2)_2$ complexes[124] in which the CO groups are *cis* to each other have been prepared by using the corresponding dialkyldithiocarbamates. Only one CO band in the yellow complex, $Ru(CO)_2\{(CH_2Ph)_2NCS_2\}_2$, indicates the presence of *trans* CO groups.

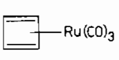
Derivatives containing Se and Te donors are less familiar.[126] Diphenyldiselenide and diphenylditelluride react with Ru_3CO_{12} to produce two polymeric derivatives $[Ru(CO)_3(EPh)_2]_n$ (E = Se, Te), (n = 6–7 and 12–14) alongwith minor amounts of dimeric $[Ru(CO)_3(EPh)]_2$ derivatives.

C. Complexes with Hydrocarbon Donors

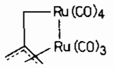
Unsaturated organic molecules like mono-, di-, tri- and tetra-olefins and acetylenes which behave as both σ and π donors react with these carbonyls to yield the compounds having different nuclearities (Table VII).

(i) Monoolefins

Only a few reactions of these olefins with triruthenium dodecacarbonyl are known. Dichlorocyclobutene reacts with the reduction product of $Ru_3(CO)_{12}$ (by Na/Hg in THF) to give (π-cyclobutadienyl)ruthenium tricarbonyl[127] (XXVI) while 1,1-bis(chloromethyl) ethylene under similar condition yields a dinuclear derivative[128] (XXVIa). Ethylene has been found to produce[129, 130] hydrocarbon bonded carbonyl hydrides (see Carbonyl Hydride section).



(XXVI)



(XXVIa)

(ii) Diolefins

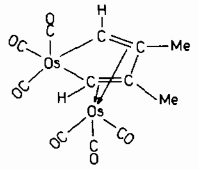
$Ru_3(CO)_{12}$ reacts with tetraphenylcyclobutadiene palladium(II) bromide to give $(C_4Ph_4)Ru(CO)_3$.[131] Treatment of 1,3-dimethyl-1,3-butadiene[35] with Os_3 $(CO)_{12}$ yields a dinuclear product $C_6H_8Os_2(CO)_6$. It was erroneously reported as $C_6H_{10}Os_2(CO)_6$ by Fischer *et al.* but a crystal study[132] showed it to have the structure (XXVII).

Other dienes like cyclohexa-1,3-diene[133] or cycloocta-1,5-diene[133, 136] when refluxed with $Ru_3(CO)_{12}$

TABLE VII. Hydrocarbon Derivatives of Ru and Os Carbonyls.

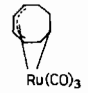
Compound	Preparation	References
$Ru(CO)_4(C_2Ph_2)$	a	178, 180
$Ru(CO)_3L$ (L = C_8H_8, C_8H_{12}, $ClCH_2C_7H_7$, $C_8H_{17}C_7H_7$, C_6H_8, C_7H_8, C_7H_{10}, 1,5-$C_8H_{11}CN$, 1,3,5-C_6H_8, C_5H_4CO, 3,5,7-$C_{10}H_{16}$, C_5Ph_4CO, $C_5(CF_3)_4CO$, C_4H_4, C_4Ph_4, 1,2,3,5,6-$Bu_5C_8H_3$)	a, b, c, d	127, 131, 133–137 155–157, 163, 172
$[Ru(CO)_3L]^+$ (L = C_8H_{11}, C_8H_9, C_5H_5, C_6H_7)	a, e, f	79, 133, 136, 173
$[Ru(CO)_2(C_5H_5)]^-$	g	79
$Ru(CO)_2(C_3H_5)_2$	h	88
$Ru(CO)_2(C_7H_8)$	a	135
$Ru_2(CO)_7(C_2Ph_2)_2$	a	180
$Ru_2(CO)_6L$ (L = C_8H_8, C_7H_8, C_4Ph_4)	a	131, 135, 164, 180
$Ru_2(CO)_5(C_8H_8)$	i	164
$Ru_2(CO)_4L_2$ (L = C_5H_5, MeC_5H_4, C_9H_7)	j	138, 139, 147
$Ru_3(CO)_{10}L$ (L = C_8H_{12}, C_4Ph_4)	a	112, 180
$Ru_3(CO)_9L$ (L = $(C_2Ph_2)_2CO$, *p,p'*-$(C_6H_4Cl)_2C_2$)	a	131, 180
$Ru_3(CO)_9(C_2Ph_2)_n$ (n = 2 or 3)	a	131, 180
$Ru_3(CO)_8L_2$ (L = C_2Ph_2, *p,p'*-$(C_6H_4Cl)_2C_2$)	a	131, 180
$Ru_3(CO)_6(C_7H_7)(C_7H_9)$	a	135
$Ru_3(CO)_4(C_8H_8)_2$	a	164
$Ru_4(CO)_{10}(C_{12}H_{16})$	a	158, 159
$Ru_4(CO)_9(Me_3C_{10}H_5)$	a	160, 161
$Ru_4(CO)_4(C_5H_5)_4$	g	79
$Ru_5(CO)_7(C_5H_5)_4$	g	79
$Os(CO)_4(C_2Me_2)_2$	a	85, 179
$Os(CO)_3L$ (L = C_8H_8, C_8H_{12}, MeC_7H_7, 3-Me-2,4,6-C_7H_7, *p*-$C_6H_4Me_3C_8H_7$)	a, b	136, 156, 157, 172
$[Os(CO)_3(C_8H_9)]^+$	i	173
$Os_2(CO)_6L$ (L = C_8H_8, C_6H_8, C_4Me_4)	a	35, 85, 170, 179
$Os_2(CO)_4(C_5H_5)_2$	j	140
$Os_3(CO)_9(Ph_2C_2)_3$	a	184
$Os_3(CO)_8(Ph_2C_2)_2$	a	182

[a] Reaction of hydrocarbon ligands with $M_3(CO)_{12}$. [b] Reaction of ligands with $M(CO)_5$. [c] Ligand displacement from $(C_8H_{12})M(CO)_3$. [d] Treatment of $C_8H_{12}Ru(CO)_3$ with Ph_3CBF_4 and CN^-. [e] Protonation of $(C_8H_8)M(CO)_3$ with acids. [f] Carbonylation of $(C_8H_8)M(CO)_3$. [g] Reaction of ligands with $[C_5H_5M(CO)_2]_2$. [h] Reduction of $(\pi\text{-}C_3H_5)M(CO)_3$ with Na/Hg. [i] Pyrolysis of $(C_8H_8)M_2(CO)_6$. [j] Reaction of metal carbonyl halides with sodium cyclopentadienide.



(XXVII)

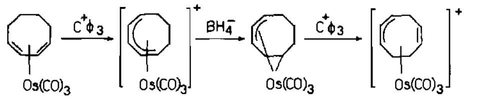
in benzene yield $(C_6H_8)Ru(CO)_3$ and $(C_8H_{12})Ru(CO)_3$, respectively. Several other isomeric products are also obtained in case of cycloocta-1,5-diene substitution. The product $(C_8H_{12})Ru(CO)_3$ appears to involve a C–Ru σ and a π-allyl bond. $(C_6H_8)Ru(CO)_3$ and $(C_8H_{12})Ru(CO)_3$ on treatment with triphenylmethyltetrafluoroborate[133–136] yield the tetrafluoroborate salts of the cations $[(C_6H_7)Ru(CO)_3]^+$ and $[C_8H_{11}Ru(CO)_3]^+$ respectively with the abstraction of hydride ion. The latter on reduction with sodium borohydride[136] yields the complex (XXVIII).



(XXVIII)

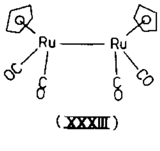
Both $(C_6H_8)Ru(CO)_3$ and $(C_8H_{12})Ru(CO)_3$ react with nucleophiles[133] (Y) to yield the products $(C_6H_7Y)Ru(CO)_3$ and $(C_8H_{11}Y)Ru(CO)_3$ respectively *via* $(C_6H_7)Ru(CO)_2(COY)$ and $(C_8H_{11})Ru(CO)_2(COY)$ intermediates and then by subsequent rearrangements.

Unlike cycloocta-1,5-diene, cycloocta-1,3-diene on reaction with $Ru_3(CO)_{12}$ yields a different product, $C_8H_{12}Ru_3(CO)_9$, which retains the triruthenium skeleton. Both cycloocta-1,3-diene and cycloocta-1,5-diene on refluxing with $Os_3(CO)_{12}$ in benzene yield the products which retain the triosmium skeleton while the UV irradiation of a mixture of $Os_3(CO)_{12}$ and cycloocta-1,5-diene in benzene for 90 hr gives a mixture of two mononuclear products[136, 137] (cycloocta-1,5-diene)$Os(CO)_3$ and (cycloocta-1,3-diene)$Os(CO)_3$. (Cycloocta-1,3-diene)$Os(CO)_3$ (XXIX) gives 1,2,3,5,6-*pentahapto* ion (XXXII) by the following mechanism.



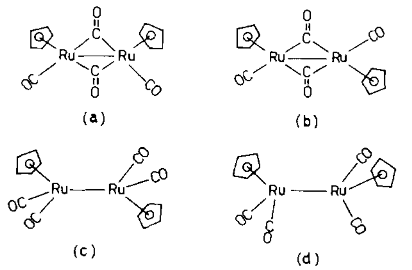
(XXIX) (XXX) (XXXI) (XXXII)

Dimeric cyclopentadienylmetal dicarbonyls, $[C_5H_5M(CO)_2]_2$, which occupy an important position in this class of compounds, can be prepared by refluxing 2:1 mixtures of sodium cyclopentadienide and ruthenium[138, 139] or osmium[140] carbonyl halides. On the basis of ir and NMR spectra it has been concluded that the osmium compound exists entirely in the nonbridged form[140, 141] under all conditions, the cyclopentadienyl ligands being symmetrical and all the carbonyl groups terminal. For $[C_5H_5Ru(CO)_2]_2$, both bridged and nonbridged forms have been identified. The enthalpy (1.56 Kcal/mol) and entropy (5.5 cal/mol) differences[142] for the equilibrium of bridged and nonbridged structures in CS_2 at 30° C indicates the presence of 45% bridged and 55% nonbridged forms in equilibrium. It is also concluded that the bridged isomer is more stable than the nonbridged one. A detailed spectroscopic study[145] of $[(C_5H_5)Ru(CO)_2]_2$ in the C–O stretching region (temperature range −100° to + 100° C) has shown that in solution both complexes exist as an equimixture of two structurally isomeric molecular forms. At low temperatures the configuration with two C–O bridges appears to be more stable, whereas at high temperatures the isomeric form with a pure metal–metal bond and four terminal C–O groups is favoured. The rotational configuration of the nonbridged $[C_5H_5Ru(CO)_2]_2$ has not been established definitely but it appears to be *cis* rather than the *gauche* or staggered but definitely not *trans*.[141] The measurements[141] of the C–O stretching fundamentals, overtones and combination bands in CS_2 and heptane solutions show the presence of equimolar mixture of the products having structure (XXXIVa) and some noncentrosymmetric nonbridged isomer (XXXIII) probably of C_{2v} or C_2 symmetry.



(XXXIII)

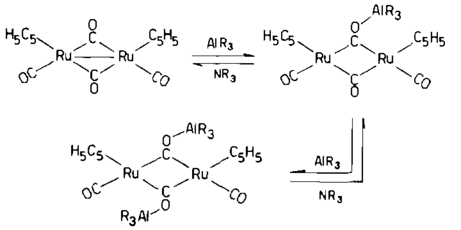
The remarkable tendency of the free molecules to adopt only the *cis* configuration may be ascribed to some participation of π and δ contribution[143] in the metal–metal bond. Recently[144] on the basis of ir and pmr spectroscopy in solution a four configuration model (XXXIVa–d) (*cis*-bridged, *trans*-bridged, *trans*-nonbridged and polar nonbridged) has been suggested.



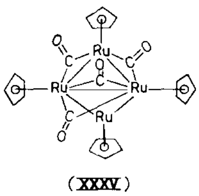
(XXXIV a-d)

Mass spectrometric[145] and X-ray studies[146] have also been performed for the ruthenium compound. In the solid state $[C_5H_5Ru(CO)_2]_2$ exists in the centrosymmetric structure with Ru–Ru 2.70 Å, Ru–C(CO) 1.86 Å, Ru–C(bridged CO) 1.99 Å and Ru–C(ring) 2.26 Å. The methylcyclopentadienyl and indenyl analogues have also been synthesised.[147, 148]

$[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ after reaction with isobutylaluminium[149] yields an adduct in which the isobutylaluminium coordinates the oxygen of the bridging carbonyl only (1:1 adduct νCO: 2006, 1988, 1831 and 1680 cm^{-1}; 1:2 adduct, νCO: 2045, 2006 and 1680 cm^{-1}). Treatment of the 1:2 adduct with triethylamine regenerates $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$.



A deep purple tetrameric derivative[79] $[\pi\text{-}C_5H_5Ru(CO)]_4$ (XXXV) analogous to $[\pi\text{-}C_5H_5Fe(CO)]_4$[150] was obtained on refluxing a solution of $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ in xylene under nitrogen for four weeks. A single ir band at 1616 cm^{-1} for νCO is observed which is believed to be the lowest yet recorded for a transition metal carbonyl. A brown solid[79] which was separated chromatographically from the tetrameric product was found to be $(C_5H_5)_4Ru_5(CO)_7$ (XXXVI).



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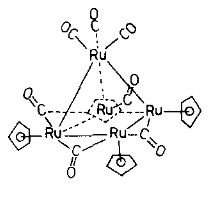


(XXXVI)

Spectroscopic evidence[79] for the formation of complexes by the reaction of the anion $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$ and Me_2SnCl_2, $N(C_4H_9)_2SnCl_2$ or Me_3SnCl has also been obtained although the products have not been isolated. Treatment of $[\pi\text{-}C_5H_5Ru(CO)_2]_2$ with trichlorosilane[79] at 140° C gave white $(\pi\text{-}C_5H_5)Ru(CO)_2SiCl_3$.

Tin(II) chloride reacts[79] with $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ to give $(\pi\text{-}C_5H_5)Ru(CO)_2SnCl_3$ formed by the insertion of Sn into the Ru–Cl bond in a reaction similar to the synthesis of the iron analogue.[151] Reaction between $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ and tin(II) chloride or germanium(II) iodide gives the insertion products $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2SnCl_2$ and $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2GeI_2$ respectively. Treatment of the former product with methyl Grignard reagent affords pale cream coloured $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2SnMe_2$. The ir spectra of the tin and germanium complexes of the type $[(\pi\text{-}C_5H_5)Ru(CO)_3]_2MX_2$ (M = Sn or Ge; X = Cl, I or Me) show bands in the carbonyl stretching region of similar pattern as those of the corresponding iron complexes[152] suggesting that in solution these compounds have similar structures. The mercury complex of the anion $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$ has been isolated.[141] Its structure, in solution may be discussed on the basis of *cis*-C_{2v} structure[79] with three terminal νCO bands, whereas in the solid state only two bands are found, presumably arising from a *trans*-C_{2h} structure,[143] similar to that found for $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ in solid state by X-ray.[146]

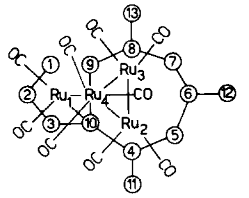
The tetraphenylborate salt of the cation $[(\pi\text{-}C_5H_5)Ru(CO)_3]^+$ has been obtained by the carbonylation[79] of the chloride $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ in acetone under pressure. The method of preparation and properties of this compound are similar to those of the analogous iron compound.[153] The carbonyl stretching frequencies of the ruthenium complexes are some 10–20 cm^{-1} higher than their iron analogues.

Reactions of tetraphenylcyclopentadinone and $Ru_3(CO)_{12}$ have been investigated both kinetically[154] and also by isolation[155] of the products. In the kinetic study the formation of diphenyl acetylene derivatives of triruthenium clusters has been proposed. The tetraphenylcyclopentadinone derivative, $(C_5Ph_4CO)Ru(CO)_3$, has been prepared in good yield by refluxing tetracyclone[155] with $Ru_3(CO)_{12}$ in benzene. It was characterized by ir and mass spectrometry.

(iii) Triolefins

Acyclic and cyclic trienes, *viz.*, 1,3,5-hexatriene, 3-methyl-2,4,6-heptatriene, chloromethylcycloheptatriene, acetylcycloheptatriene, methylcycloheptatriene, trimethylcycloheptatriene, 3,5,7-decatriene, react[156, 157] with Ru and Os pentacarbonyls to yield the products $(triene)M(CO)_3$. It indicates that the trienes act as bidentate π-donors. No structural information is available except for the product (cyclododeca-1,5,9-triene) $Ru_4(CO)_{10}$.[158, 159] It may be prepared either by the action of $Ru_3(CO)_{12}$ on cyclododeca-1,5,9-triene or by treating $HRu_3(CO)_9(C_{12}H_{15})$ with $Ru_3(CO)_{12}$. The electron deficient complex $(C_{12}H_{16})Ru_4(CO)_{10}$ has been shown to contain an open Ru_4 cluster; the monocyclic C_{12} ring is attached to the cluster by a conventional π-allyl bond to one ruthenium atom, and by a novel bridging C_3 unit, which is π-bonded to the two apical metal atoms and σ-bonded to each of the "hingal" metal atoms.

Bonding with azulene is important in the sense that metal atoms may bond either to unsaturated seven membered or to the five membered ring or to both. $Ru_3(CO)_{12}$ reacts with 4,6,8-trimethylazulene to give $(C_{10}H_5Me_3)Ru_4(CO)_9$[160, 161] along with $Ru_6(CO)_{17}C$. $(C_{10}H_5Me_3)Ru_4(CO)_9$ crystallizes[161] in two forms – a monoclinic and a triclinic. The monoclinic crystals are obtained as small red parallelopippeds and the triclinic crystals as red platelets. The two crystal forms contain experimentally indistinguishable molecular units of 4,6,8-trimethylazulenetetraruthenium enneacarbonyl separated by normal Van der Waal's distances. The molecule possesses approximately C_s symmetry with four Ru atoms[161] defining a distorted tetrahedron (Structure XXXVII) in which the interatomic distances range from 2.702 to 2.902 Å (± 0.005 Å) in the monoclinic determination and 2.698 to 2.908 Å (± 0.003 Å) in the triclinic study. The 4,6,8-trimethylazulene ligand is arched across the largest face of the tetrahedral Ru cluster (directly bonded to three Ru atoms) and is best across C(9)–C(10), C(8)...C(4) and C(7)...C(5) such that there is a dihedral angle of 120° between the planar 5-membered ring and the plane defined by C(5), C(6) and C(7). The three Ru atoms that are associated with the azulene are each bonded to 2 terminal CO while the apical Ru is bonded to 3 terminal CO groups. The bonding between the 4,6,8-trimethylazulene and the adjacent three Ru atoms is best considered in terms of delocalized "ligand-to-cluster" bonding.



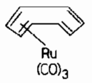
(XXXVII)

In a later investigation, Churchill *et al.*[162] isolated azulenetriruthenium heptacarbonyl by the reaction between azulene and $Ru_3(CO)_{12}$. It crystallizes as a monoclinic crystal. The crystal study[162] suggests that one Ru atom is associated with the five membered carbocyclic system, whereas the other 2 Ru atoms lie below the seven membered ring. The structure of the molecule suggests that it is an intermediate in the formation of azulenetetraruthenium nonacarbonyl.

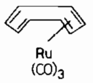
(iv) Tetraolefins

Cyclooctatetraene and their derivatives are the only unsaturated organic molecules in this class which have been investigated in the substitution reactions with ruthenium and osmium carbonyls. Derivates of the type $M(CO)_3L$ (M = Ru, Os), $M_2(CO)_6L$ (M = Ru), $M_2(CO)_5L$ (M = Ru), and $M_3(CO)_4L_2$ (M = Ru) have been obtained.

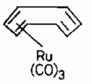
A number of reaction products[163–168] of cyclooctatetraene and $Ru_3(CO)_{12}$ have been isolated. The ir spectrum of $(C_8H_8)Ru(CO)_3$ in heptane indicates three terminal CO(νCO: 2070, 2010 and 2096 cm^{-1}) but no bridging CO. It is isostructural with its Fe analogue,[169] and exhibits a valence tautomerism, similar to that shown by the Fe complex, resulting in an equivalence of all eight protons. Two peaks obtained at –95° and –109° C suggested rapid isomerization between (XXXVIIIa) and (XXXVIIIb). Further cooling suggested the situation XXXIXa $\rightleftharpoons$ XXXIXb, where the 5,7-diene group is no longer involved in bonding to the metal, and is free to oscillate between the chair and boat forms of the ligand.



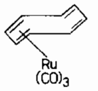
(XXXVIII a)



(XXXVIII b)

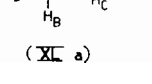


(XXXIX a)

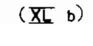


(XXXIX b)

The Os derivative, $(C_8H_8)Os(CO)_3$, which is structurally different from the corresponding Ru derivative was prepared by irradiating with UV light[85, 170] a solution of $Os_3(CO)_{12}$ and cyclooctatetraene in benzene as a pale yellow crystalline solid (XLa). In this complex the hydrocarbon is bonded to the $Os(CO)_3$ group by both a π-allyl system and a metal–carbon σ-bond assuming a boat configuration. On gentle warming in hexane solution it isomerizes to an orange yellow complex (XLb) which is analogous to the ruthenium cyclooctatetraene complexes.[163, 165] The ^1H NMR spectra[170, 171] of this complex exhibits the characteristic singlet at τ 4.78, as observed in the spectra of tricarbonylcyclooctatetraene iron and ruthenium complexes. The chemical shifts, coupling requirements and ir spectrum (of XLa) are in agreement with the suggested structure. A band at 1640 cm^{-1} has been assigned to a ν(C:C) frequency, and one at 775 cm^{-1} to a *cis* double bond. Formation of complex (XLb) has been suggested by a simple electron shift resulting in 1,3-diene formation.



(XL a)

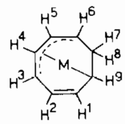


(XL b)

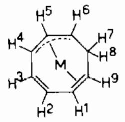
The substituted cyclooctatetraene complexes,[172] (1,2,3,5,6-pentabutylcyclooctatetraene)$Ru(CO)_3$, (*p*-tolylcyclooctatetraene)$Os(CO)_3$, of Ru and Os tricarbonyls have already been prepared to use as antiknock compounds. No structural details are available.

Protonation[173] of tricarbonyl(cyclooctatetraene)-ruthenium has also been studied. Tricarbonyl(bicyclo-5,1,0-octadieneium)ruthenium cation isomerizes to h^5-1,2,5,6,7-$[C_8H_9Ru(CO)_3]^+$. Unlike Fe the initially formed bicyclic cation undergoes a ring opening to give cations containing the C_8H_9 moiety bonded to the metal in a novel way.

A white solid compound $[(C_8H_9)Ru(CO)_3]^+PF_6^-$ (XLI) was isolated by similar protonation[173] in diethylether with HPF_6. The NMR spectrum reveals that in this solvent an initially formed bicyclic ion rapidly isomerises. In HBF_4–Ac_2O system, $[(C_8H_9)Ru(CO)_3]^+$ BF_4^- (XLII) was isolated (νCO: 2125vs, 2060vs cm^{-1}) and except for the difference in the anion, (XLII) is identical to (XLI).



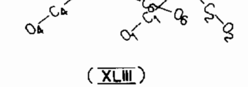
(XLI)



(XLII)

The action of protonic acids on α-$C_8H_8Os(CO)_3$ generates two isomeric forms of the protonated species $[(C_8H_9)Os(CO)_3]^+$. One is isostructural with the Ru complex.

The dinuclear species $(C_8H_8)Ru_2(CO)_6$, (νCO:[164] 2078vs, 2048vs, 2011sh, 1988 and 1978 cm^{-1}) and $(C_8H_8)Ru_2(CO)_5$, (νCO:[164] 2058vw, 2035vs, 2011vs, 1968vs, 1813m cm^{-1}) are also known. The latter compound has been obtained by the thermal decomposition of the first. The ir spectrum indicates the absence of any bridging CO group in the first compound while one bridging CO group is present in the second. These complexes are isostructural with their corresponding Fe analogues.[174, 175] The molecule $(C_8H_8)Ru_2(CO)_6$ (Structure XLIII) consists[176] of two $Ru(CO)_3$ moieties lying on the same side of the C_8H_8 ring and connected to each other by a metal–metal bond. The $Ru_2(CO)_6$ groups are bonded to the other six carbon atoms of ring. Two C atoms remain uncoordinated to olefinic protons of the ring. The $Ru_2(CO)_6$ group by itself has *mm* symmetry, consisting of a "sawhorse" arrangement, $Ru_2(CO)_4$, with the two additional CO groups (C_3–O_3, C_5–O_5) lying almost collinear with the



(XLIII)

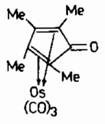
pair of Ru atoms. The Ru–Ru distance, 2.865 Å, indicates the existence of M–M single bond and may be compared with the average Ru–Ru bond length, 2.85 Å, in $Ru_3(CO)_{12}$.

The trinuclear species $(C_8H_8)_2Ru_3(CO)_4$[164] is obtained by refluxing C_8H_8 and $Ru_3(CO)_{12}$ in octane. The ir spectrum shows four terminal bands (νCO: 2032vw, 1996vs, 1956m, and 1920vs cm^{-1}) with no bridging carbonyl groups. The molecule is asymmetric but it has approximately C_2 symmetry.[177] The structure is derived from that of $Ru_3(CO)_{12}$ with π-electron density of the cyclooctatetraene rings replacing that of eight CO groups. The reported structure accounts for the characteristic ir spectrum in the C–O stretching region. In C_2 symmetry four ir-active normal modes are to be expected with the one consisting mainly of in phase stretching of the two CO groups approximately perpendicular to the Ru_3 plane being very weak.

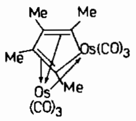
(v) *Acetylenes*

In this class the reactions of several substituted alkynes[178–180] have been described. Hexyne-3 yielded the (cyclopentadienone)$Ru(CO)_3$[131] when it reacted with $Ru_3(CO)_{12}$. Several reaction products, $\{(PhC_2Ph)_2CO\}Ru_3(CO)_9$, $(PhC{:}CPh)_3Ru_3(CO)_9$, $(PhC{:}CPh)_2Ru_3(CO)_9$, $(PhC{:}CPh)_2Ru_3(CO)_8$, $(PhC{:}CPh)_2Ru_2(CO)_7$, $(PhC{:}CPh)_2Ru_2(CO)_6$ and $(PhC{:}CPh)_2Ru(CO)_4$ have been isolated as a result of the reactions between diphenylacetylene and $Ru_3(CO)_{12}$ under varying conditions.[131, 178, 180] The derivative $(PhC_2Ph)_2Ru_3(CO)_8$ exhibited isomerism in methanol solution,[180] yielding two products. The first (violet) shows only terminal carbonyls in the ir spectrum while the second (orange yellow) shows bridging CO groups. The reaction[181] between trinuclear acetylenic carbonyls of Ru and an excess of diphenylacetylene has also been studied in an attempt to determine the order in which the trinuclear intermediates are formed.

The chemistry of acetylene derivatives of osmium carbonyl is considerably recent.[85, 182–184] Thermal reactions of $Os_3(CO)_{12}$ with but-2-yne yield two complexes characterised as $(MeC_2Me)_2Os(CO)_4$ (XLIV) and $(MeC_2Me)_2Os_2(CO)_6$ (XLV).[85, 179] The ir spectrum of (XLIV) shows three terminal CO stretching absorptions at 2101, 2041 and 1987 cm^{-1} suggesting the presence of an $Os(CO)_3$ group and the fourth strong peak at 1673 cm^{-1} for ketonic carbonyl group. These data suggest that (XLIV) should be formulated as the cyclopentadienone derivative. The identity of second complex (XLV) is more certain. The CO stretching frequencies 2076, 2006, 1990, 1972 and 1964 cm^{-1} and the two absorptions at τ 7.26 and 7.39 assigned to the two different methyl groups, are consistent with the isostructural Fe complex, $(RC_2R)_2Fe_2(CO)_6$,[185] in which a ferrocyclopentadiene ring bonded to a tricarbonyl iron moiety has been assumed.

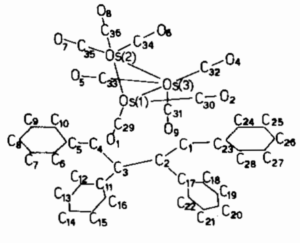


(XLIV)



(XLV)

The reaction of diphenylacetylene with $Os_3(CO)_{12}$ yielded various products; the structure[186] (XLVI) of one of the products, $(PhC{:}CPh)_2Os_3(CO)_8$[182] has been studied by X-rays. It is built up of a cluster of three Os atoms at the corners of an almost equilateral triangle and by the organic ligand. The chelation between the two parts of the molecule is partially attained by μ bonds.



(XLVI)

The reaction[184] of $(PhC{:}CPh)_2Os_3(CO)_8$ with CO was investigated and a structure suggested for $(PhC{:}CPh)_2Os_3(CO)_9$ consists of an Os_3 cluster, in which one of the Os atoms belongs to an osmacyclopentadiene ring, and to which only terminal CO groups are bonded. The formation of $(PhC{:}CPh)_2Os_3(CO)_9$ from $(PhC{:}CPh)_2Os_3(CO)_8$ and CO is a second order process.

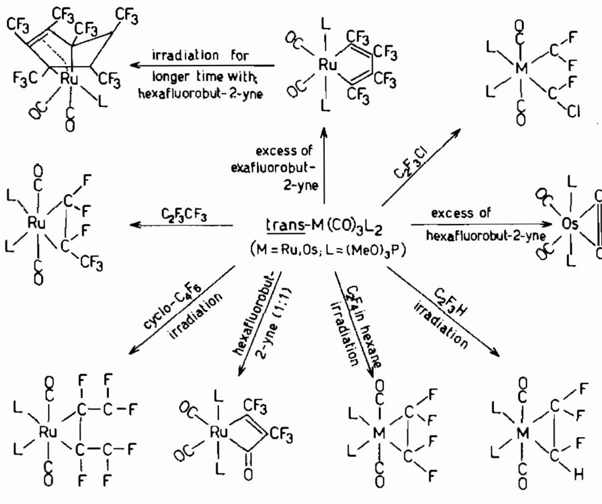
5. Mixed Ligand Carbonyls

Besides these simple substitution products a number of mixed ligand derivatives have been investigated. A brief description of several isolated species is given below.

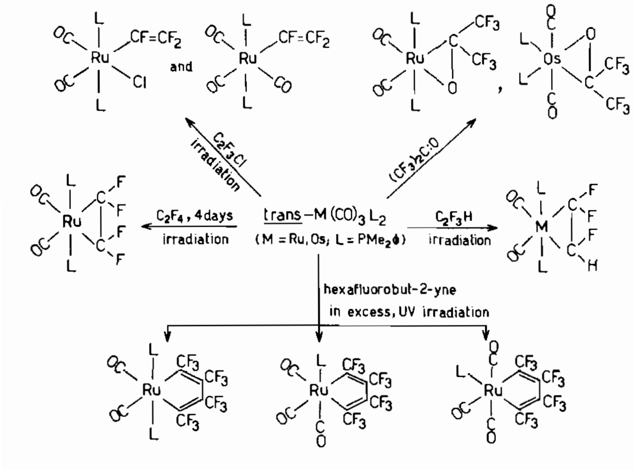
A. Complexes Containing Fluoroolefins and Fluoroacetylenes

Fluorocarbon ligands[86, 187–191] react with substituted ruthenium and osmium carbonyl derivatives to form mixed ligand complexes (scheme 1–3).

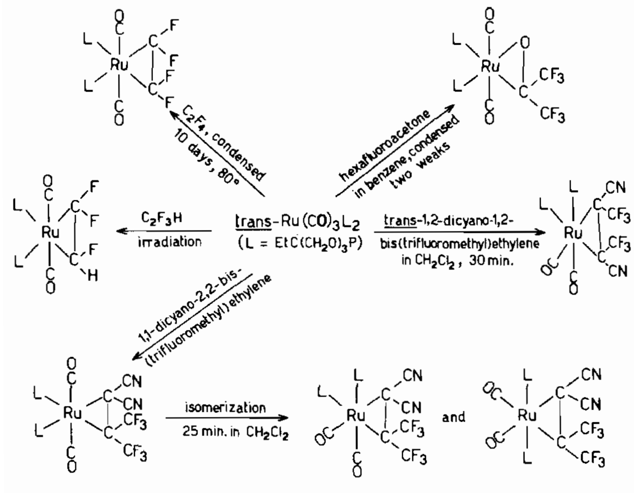
The photochemical reactions of fluoroolefins with the zerovalent ruthenium complexes, *trans*-$M(CO)_3L_2$ (L = phosphite or phosphine), lead to the oxidative elimination of CO and the formation of stable compounds, $M(CO)_2L_2$(fluoroolefin) (fluoroolefin = C_2F_4, C_2F_3H, $C_2F_3CF_3$, C_2F_3Cl or cyclo-C_4F_6), It is seen that phosphite ligands adopt a *cis* configuration whereas phosphines retain their relative *trans* configuration on reaction with fluoroolefins. In the similar manner both hexafluoroacetone and 1,1-dicyano-2,2-



SCHEME I



SCHEME II



SCHEME III

bis(trifluoromethyl)ethylene displace carbon monoxide from $Ru(CO)_3\{EtC(CH_2O)_3P\}_2$ to form $Ru(CO)_2\{EtC(CH_2O)_3P\}_2\{(CF_3)_2(CO)\}$ and $Ru(CO)_2\{EtC(CH_2O)_3P\}_2\{(CF_3)_2CC(CN)_2\}$ respectively, in which the CO ligands occupy a relative *trans*-configuration. The latter complex rapidly isomerizes in solution; one phosphite ligand exchanging coordination position with a CO. A similar reaction occurs with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene forming $Ru(CO)_2\{EtC(CH_2O)_3P\}_2\{CF_3(CN)CC(CF_3)CN\}$ in which the olefin retains its original stereochemistry.

On irradiating a hexane solution of *trans*-$Ru(CO)_3\{(McO)_3P\}_2$ with hexafluoro-1-butyne a metallocyclopentadiene $Ru(CO)_2\{(MeO)_3P\}_2RR^1$ was obtained, whereas *trans*-$Ru(CO)_3(PhPMe_2)_2$ affords $Ru(CO)_2(PhPMe_2)_2RR^1$ and $Ru(CO)_3(PhPMe_2)RR^1$; the latter being a mixture of stereoisomers ($RR^1 = C(CF_3){:}C(CF_3)C(CF_3){:}C(CF_3)$). Reactions of *trans*-$Ru(CO)_3\{(MeO)_3P\}_2$ with one mole equivalent of hexafluoro-2-butyne gave metallocyclobutenones, $Ru(CO)_2\{(MeO)_3P\}_2ZZ^1$ ($ZZ^1 = COC(CF_3){:}C(CF_3)$). The metallocyclopentadiene, $Ru(CO)_2\{(MeO)_3P\}_2RR^1$, reacts with more hexafluoro-2-butyne to afford dicarbonyl(trimethyl phosphite)-1,2,3,4-*tetrahapto*-hexakis-(trifluoromethyl)benzene ruthenium. *Trans*-$Os(CO)_3\{(MeO)_3P\}_2$ reacts with an excess of hexafluoro-2-butyne to give only $Os(CO)_2\{(MeO)_3P\}_2(CF_3C_2CF_3)$.

B. Complexes Containing Nitriles

Direct substitution of a CO group by an isonitrile is a poor route to obtain nitrile substituted compounds. A different approach has been explored[192] to synthesise the isonitrile substituted derivatives. The route for the preparation is summarized as follows:

$$RuHCl(CO)(Ph_3P)_3 \xrightarrow{RNC} RuHCl(CO)(CNR)(Ph_3P)_2 \xrightarrow{AgClO_4} RuH(OClO_3)(CO)(CNR)(Ph_3P)_2$$

$$RuH(OClO_3)(CO)(CNR)(Ph_3P)_2 \xrightarrow{CO} [RuH(CO)(CNR)L(Ph_3P)_2]ClO_4 \xrightarrow{NaOH} Ru(CO)_2(CNR)(Ph_3P)_2$$

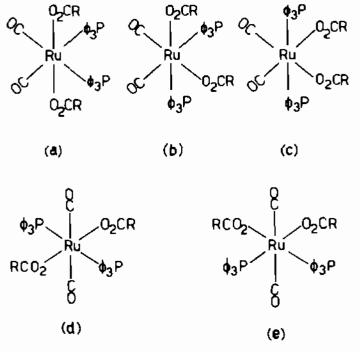
$Ru(CO)_2(CNR)(Ph_3P)_2$ has the same geometry (νCO: 1899, 1865 cm^{-1} in nujol) as $Ru(CO)_3(Ph_3P)_2$ and $Os(CO)_3(Ph_3P)_2$[193] with an isocyanide replacing one equatorial carbonyl group. The observed ir spectrum showing two CO bands of equal intensity is compatible with this structure. When $HRu(CO)(Ph_3P)_3(CNR)$ is treated with NaOH, orange crystals[192] of $Ru(CO)(Ph_3P)_3(CNR)$ are produced. If the reaction is carried out in the presence of dioxygen,[192] the complex $Ru(CO)(O_2)(Ph_3P)_2(CNR)$ results. Both νCO and νCN for $Ru(CO)(Ph_3P)_3(CNR)$ are higher than the corresponding absorptions for $Ru(CO)_2(Ph_3P)_2(CNR)$ and are indicative of a *trans*-arrangement[192] of carbonyl and isocyanide having the three phosphines at equatorial site in a trigonal bipyramid. Reaction of

$Ru(CO)_2(Ph_3P)_2(CNR)$ with dioxygen results in the oxidation[192] of one carbonyl group with the formation of $Ru(CO)(CO_3)(CNR)(Ph_3P)_2$.

C. Complexes Containing Carboxylato Groups

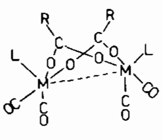
The other mixed ligand complexes containing formato-, acetato- and propionato groups have been synthesised by the action of corresponding acids[194] on $Ru(CO)_3(Ph_3P)_2$ in benzene. The ir spectra of the complexes exhibit bands in the region normally associated with the coordinated carbonyls, carboxylato groups and triphenylphosphine ligands. Two strong bands appearing in the region 1800–2200 cm^{-1} are assigned to terminal CO stretching vibrations. These spectra indicate that the two CO groups are in a *cis*-arrangement in all the complexes, $Ru(CO)_2(Ph_3P)_2(HCOO)_2$, $Ru(CO)_2(Ph_3P)_2(AcO)_2$, $Ru(CO)_2(Ph_3P)_2(EtCO_2)_2$ and $Ru(CO)_2(Ph_3P)_2(AcO)_2 \cdot C_6H_6$.

There could be five possible structures (XLVIIa–e) of $Ru(CO)_2(Ph_3P)_2(RCO_2)_2$. The structures involving a *trans*-arrangement of the CO groups may be eliminated as these would be expected to exhibit one strong CO stretching frequency. Of the three *cis*-arrangements structure (XLVIIb) is preferable due to structural reasons.



(XLVII a-e)

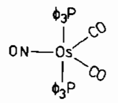
Dimeric complexes of the type $M_2(CO)_4(RCO_2)L_2$ (M = Ru, Os) are formed when the polymer $[M(CO)_2(RCOO)]_n$ or the dimer $M_2(CO)_6(RCOO)_2$ reacts[120] with t-phosphines, t-arsines, pyridine, or acetonitrile. This dimeric formulation has been confirmed by mass spectroscopic studies on some of the derivatives (M = Ru, R = Me, L = Ph_3P; M = Os, R = Me, L = Ph_3P or Ph_3As). NMR and ir data[120] are consistent with structure (XLVIII).



(XLVIII)

D. Complexes Containing Nitrite and Nitro Groups

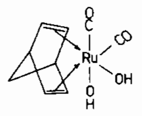
The introduction of nitrite group[195] into the substituted carbonyl complexes is rendered possible by sodium nitrite in dimethylformamide. Thus $M(ONO)_2(CO)_2(Ph_3P)_2$ is prepared by the action of sodium nitrite in dimethylformamide on $RuCl_2(CO)_2(Ph_3P)_2$ or $OsCl_2(CO)_2(Ph_3P)_2$. These nitrito compounds isomerize into the dinitro compounds, $M(NO_2)_2(CO)_2(Ph_3P)_2$. The preparation of a dinitrato complex, $Ru(NO_3)_2(CO)_2(Ph_3P)_2$, has been described as a result of the reaction of CO on $Ru(O_2)(NO_3)(NO)(Ph_3P)_2$. The compound $Ru(O_2)(NO_3)(NO)(Ph_3P)_2$ is obtained by the oxygenation of $Ru(NO)_2(Ph_3P)_2$.[196, 197] The five coordinate complexes $M(CO)_2(NO)L_2$ (L = Ph_3P, Cy_3P; M = Ru, Os) have been obtained either by the elimination of hydrogen from $OsH(CO)(NO)(Ph_3P)_2$, when treated with acids like $HClO_4$, HBF_4 or HPF_6 in presence of CO, or by the reaction[197, 198] of CO on $M(CO)(NO)(Ph_3P)_2Cl$ (M = Ru, Os). $Ru(CO)_2(NO)(Ph_3P)_2$ has also been obtained by the action of nitrosyl ion[198] on $Ru_3(CO)_9(Ph_3P)_3$ in methanol. The species $[M(CO)_2(NO)(Ph_3P)_2]^+$ and $[M(CO)(NO)L_3]^+$ have also been prepared[197] with $M(CO)(NO)(Ph_3P)_2Cl$ by the addition of ligand in CH_2Cl_2/acetone and $AgPF_6$. X-ray structure determination studies reveal the trigonal bipyramidal geometry (XLIX) of the cation with a linear M–N–O group.[196]



(XLIX)

E. Complexes Containing Hydroxyl Groups

A mixed Ru carbonyl complex $C_7H_8Ru(CO)_2(OH)_2$ containing norbornadiene and hydroxyl groups has been obtained by reducing[31] $[C_7H_8RuCl_2]_n$ with Zn in aliphatic alcohols. The compound is diamagnetic showing it to be the octahedral[31] Ru(II) derivative (L).

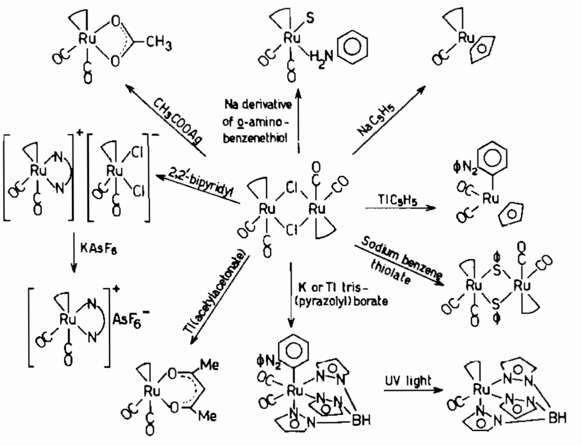


(L)

This structure is in agreement with its ir data (νCO: 2047, 1970 cm^{-1} in $CHCl_3$ solution) which suggests the presence of two CO groups in *cis* position.

F. Complexes Containing Azobenzene, Azide Ion, Carbamate and Thiocarbamate Groups

Sodium or thallium salts of cyclopentadiene, *o*-aminobenzenethiol, acetylacetonate, tris(pyrazolyl) borate or silver acetate[199] react with $[(azobenzene)Ru(CO)_2Cl]_2$ to yield monomeric complexes (azobenzene)Ru$(CO)_2$L with the cleavage of halogen bridges (Scheme IV). 2,2′-Bipyridyl gives the ionic complex [(azobenzene)Ru$(CO)_2$(bipyridyl)][(azobenzene)Ru$(CO)_2Cl_2$]. This complex is a rare example of a cationic Ru–C σ-bond. In all the complexes, the CO groups are in the *cis*-positions as evidenced by CO stretching frequencies.



SCHEME IV

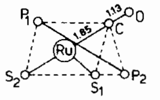
Mixed derivatives have also been prepared by nucleophilic attack[200] on one of the carbonyl groups of the cation $[C_5H_5Ru(CO)_3]^+$. Primary amines, hydrazine, azide ion, methoxy and isothiocyanate groups yield the derivatives $C_5H_5Ru(CO)_2(CONHR)$, $C_5H_5Ru(CO)_2(CONHNH_2)$, $C_5H_5Ru(CO)_2(NCO)$, $C_5H_5Ru(CO)_2(COOMe)$ and $C_5H_5Ru(CO)_2(NCS)$, respectively. Several derivatives, $Ru(CO)NO(Ph_3P)_2L$ ($L = OH^-$, N_3^-, NCO^-, or $HCOO^-$) have been synthesised by the halogen displacement[201] of Ru(CO)(NO)$(Ph_3P)_2$Cl. In contrast to the lability of the anionic ligands, the neutral CO group in the above (νCO: 1925 cm^{-1} for all compounds) is not displaced by an excess of triphenylphosphine.

G. *Complexes Containing* σ-acetyl and σ-allyl Groups

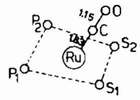
A σ-acetyl derivative,[202] dicarbonyl(σ-acetyl)-π-cyclopentadienylruthenium, has been prepared by the addition of acetylchloride in a cooled (–78° C) solution of Na^+ $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$. The two CO frequencies (1972, 1935 cm^{-1}) are characteristic of the two *cis* carbonyls. The analogous allyl derivative[203] $[(\sigma\text{-}C_3H_5)Ru(CO)_2(\pi\text{-}C_5H_5)]$ may be obtained by irradiating a mixture of Na^+ $[Ru(CO)_2C_5H_5]^-$ with allylchloride in hexane. PMR and ir spectra of π-allyl derivative in solution indicate the presence of two stereoisomers in a 4:1 ratio. Substituted hydridocarbonyl halides like $HRu(Ph_3P)_2Cl$ or $HRu(CO)(Ph_3P)_3$ Cl react with EtCHO and MeCHO to give $Ru(CO)_2$ $(Ph_3P)_2(OCR)$[204] (R = Et, Me) which contain π-bonded acyl groups.

H. *Complexes Containing Bis(perfluoromethyl)dithietene as Ligand*

Reactions of the Group V bases with the orange coloured solution obtained by the reaction of $Ru_3(CO)_{12}$ and bis(perfluoromethyl)dithietene,[205] yield the products $\{(CF_3)_2C_2S_2\}Ru(CO)_n(ER_3)_{3-n}$. The crystal and molecular structure[206] of one of the compounds, $\{(CF_3)_2C_2S_2\}Ru(CO)(Ph_3P)_2$, of this class have been examined. This compound exhibits two isomeric forms (LIa, LIb). Both forms coexist in solution and can be isolated in pure crystalline states. In both the cases, the coordination around the central atom is square pyramidal with no evidence of a trigonal bipyramidal species.



(LI a)



(LI b)

I. *Complexes Containing* β*-diketones*

Ruthenium Carbonyls which contain both Group V donors and the acetylacetonate group are prepared[207] by two methods. The first method is the direct reaction between the ligands like MeCN and $[(diket)_2Ru(CO)]_2$ to yield $(diket)_2Ru(CO)(MeCN)$. The second method of preparation uses a ligand L with greater electron donor ability than MeCN. The other products synthesised are $Ru(CO)(diket)_2L$ ($L = Ph_3P$, Ph_3As, Ph_3Sb, C_5H_5N, C_2H_5CN and CH_2CHCN).

TABLE VIII. Si, Ge, Sn and Pb Bonded Ru and Os Carbonyls.

Compound	Preparation	Colour, m.p. (b.p./10^{-2}mm)° C	νCO (cm^{-1})	Reference
$(Me_3Si)_2Ru(CO)_4$	a	Yellow (50°/10^{-2})	2094, 2031, 2015, 2009	74
cis-$(Cl_3Si)_2Ru(CO)_4$	a			221
trans-$(Cl_3Si)_2Ru(CO)_4$	a			221
$(Me_3Ge)_2Ru(CO)_4$	b	Yellow (75°/10^{-2})	2093, 2035, 2029, 2014	76
$(Me_3Sn)_2Ru(CO)_4$	a, b	Yellow (80°/10^{-2})	2084, 2024, 2021, 2003	208, 209–211

TABLE VIII. (Cont.)

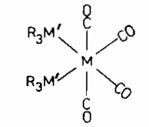
Compound	Preparation	Colour, m.p.(b.p./10^{-2}mm)° C	νCO(cm^{-1})	Reference
$(Me_3Pb)_2Ru(CO)_4$	b	Yellow	2078, 2023, 2018, 2004	209
$(Cl_3Ge)_2Ru(CO)_4$	a	White, 90–100° d	2162, 2117, 2104	76, 220
$(Et_3Sn)_2Ru(CO)_4$	a, b	Yellow (100°/10^{-2})	2079, 2019, 2009, 1998	208, 209
$(Cl_3Sn)_2Ru(CO)_4$	a			222
$(Ph_3Sn)_2Ru(CO)_4$	a, b	Yellow, 180–182°	2097, 2055, 2029	208, 209
$\{(PhCH_2)_3Sn\}_2Ru(CO)_4$	a, b	Yellow, 99–101°	2089, 2050, 2021	208, 209
$(Bu_3Sn)_2Ru(CO)_4$	a	Yellow (150°/10^{-2})	2077, 2017, 2007, 1996	208, 209
$(Pr_3Sn)_2Ru(CO)_4$	a	Yellow (150°/10^{-2})	2078, 2018, 2008, 1997	208, 209
$(SnCl_6)Ru_2(CO)_5$	a	178°		222
$[(Me_3Si)Ru(CO)_4]_2$	a	Yellow, 129–131°	2041, 2014, 2005	74, 212
$[(Me_3Ge)Ru(CO)_4]_2$	a	Yellow, 126–127°	2046, 2017, 2008	76
$[(Me_3Sn)Ru(CO)_4]_2$	c	Orange–Yellow, 130°	2082, 2022, 2010, 2002	74
$[(Et_3Si)Ru(CO)_4]_2$	a	Yellow, 150–152°	2041, 2014, 2005	74
$[(Pr_3Si)Ru(CO)_4]_2$	a	Yellow, 79–81°	2040, 2014, 2004	74
$[(EtO)_3SiRu(CO)_4]_2$	a		2057, 2028, 2018	74
$[(Ph_3Si)Ru(CO)_4]_2$	a		2055, 2026, 2016	74
$[(MeCl_2Si)Ru(CO)_4]_2$	a	Yellow, 136–141°	2073, 2044, 2035	74
$[(Cl_3Si)Ru(CO)_4]_2$	a	Yellow, 145–150°	2086, 2056, 2050	74
$[(Me_3Si)Ru(CO)_3(\mu\text{-}SiMe_2)]_2$	d, e			215
$[(Me_3Ge)Ru(CO)_3(\mu\text{-}GeMe_2)]_2$	a	Yellow, 180–190°	2046, 2008, 1994	74
$[(Me_3Sn)Ru(CO)_3(\mu\text{-}SnMe_2)]_2$	a, e	Yellow, 190–192°	2036, 2000, 1982	208, 209
$[(Bu_3Sn)Ru(CO)_3(\mu\text{-}SnBu_2)]_2$	a	Yellow	2029, 1994, 1975	208, 209
$Ru_2(CO)_6(\mu\text{-}SiMe_2)_3$	f		2033, 2000	215
$Ru_2(CO)_6(\mu\text{-}GeMe_2)_3$	g	Yellow, 150–169°	2029, 1991	76
$[(Me_2Ge)Ru(CO)_3]_3$	g	Orange, 140–150°	2046, 2038, 2017, 2011, 1986	76
$Ru_3(CO)_{12}(SnCl_4)$				222
$[(Cl_3Si)Ru(CO)_4]^-$	i	Yellow		74
cis-$(Me_3Si)_2Os(CO)_4$	a	Yellow, 25°	2099, 2031, 2020, 2011	85, 213
trans-$(Me_3Si)_2Os(CO)_4$	a	White, 26°	2008	85
$(Me_3Ge)_2Os(CO)_4$	a	Yellow (60/10^{-2})	2096, 2031, 2017, 2021	76
$(H_3Ge)_2Os(CO)_4$	a			210
$(Ph_3Sn)_2Os(CO)_4$	a			210
$(Me_3Pb)_2Os(CO)_4$	a			210
$(Ph_3PAu)_2Os(CO)_4$	a			210
$(Me_3Sn)_2Os(CO)_4$	g	Yellow	2088, 2025, 2014, 2007	213
$(Et_3Si)_2Os(CO)_4$	a	Cream	2007	213
$[(Me_3Si)Os(CO)_4]_2$	a	Yellow	2052, 2012, 2003	213
$[(Et_3Si)Os(CO)_4]_2$	a	Yellow	2051, 2011, 2002	213
$[(Me_3Si)Os(CO)_3(\mu\text{-}SiMe_2)]_2$	d, f		2049, 2004, 1949	215
$[(Me_3Ge)Os(CO)_3(\mu\text{-}GeMe_2)]_2$	a	Yellow, 150–160°	2048, 2002, 1988	76
$Os_2(CO)_6(\mu\text{-}GeMe_2)_3$	h	Yellow	2021, 1990	76
$[(\mu\text{-}Me_2Si)Os(CO)_3]_3$	j		2054, 2039, 2016, 2008, 1984	215
$[(\mu\text{-}Me_2Ge)Os(CO)_3]_3$	h	Yellow, 220–240°	2052, 2043, 2014, 2008, 1984	76

Reactions of [a] $M_3(CO)_{12}$ with $R_3M'H$ or $M'Cl_4$. [b] $[M(CO)_4]^{-2}$ with $R_3M'Cl$. [c] $[(R_3M')Ru(CO)_4]^-$ with R_2SnCl_2. [d] $M_3(CO)_{12}$ with $Me_5M'_2H$. [e] $(R_3M')_2M(CO)_4$ with $R_5M'_2H$. [f] $M_3(CO)_{12}$ with $R_2M'H_2$. [g] $[(R_3M')Ru(CO)_4]_2$ with $R_5M'_2H$. [h] $M(CO)_4(GeMe_3)_2$ on pyrolysis. [i] $[(R_3M')M(CO)_4]_2$ reduction with Na/Hg. [j] $M(CO)_4H_2$ with $R_5M'_2H$. M = Ru, Os; M′ = Si, Ge, Sn, Pb; R = Alkyl or Aryl group.

6. C, Si, Ge, Sn, Pb and Hg Bonded Carbonyls

The chemistry of Si, Ge and Sn bonded Ru and Os carbonyls starts from 1967. Several carbonyl derivatives which contain trialkylsilyl, -germyl, -stannyl, trihalosilyl, trihalogermyl and trihalostannyl groups have been synthesised since then (Table VIII).

Most of the mononuclear derivatives $(R_3M')_2M(CO)_4$ are of C_{2v} symmetry (except)$(Me_3Si)_2Os(CO)_4$, $(Et_3Si)_2Os(CO)_4$ and $(Cl_3Si)_2Ru(CO)_4$; the latter two compounds were obtained as an isomeric mixture of *cis* and *trans*-derivatives) with two R_3M' groups in the *cis*-positions (LII) as evidenced by the appearance of four ir active carbonyl bands due to the modes $2A_1 + B_1 + B_2$.



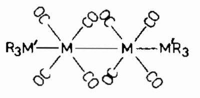
(LII)

The spectrum of $(Me_3Si)_2Os(CO)_4$ showed one strong and three weak CO bands suggesting the presence of both *cis* and *trans*-isomers. The observation of four carbonyl absorptions for a *cis*-isomer ($2A_1 + B_1 + B_2$) and one for a *trans*-isomer (E_u) mode requires that the E_u mode coincides with one of the bands of the *cis*-isomer. Since the strongest CO absorption for $(Me_3Si)_2Os(CO)_4$ is at thc lowest energy, the E_u mode of the *trans*-isomer is degenerate with the lowest energy absorption B_1 of the *cis*-isomer. The similar energy of these two modes is consistent with their nature as the antisymmetric stretching of two mutually *trans* CO groups. The triethylsilyl analogue $(Et_3Si)_2Os(CO)_4$, has only a single strong carbonyl absorption in its ir spectrum, typical of a *trans*-isomer. In case of $(SiCl_3)_2Ru(CO)_4$ the conversion of *cis*-isomer into *trans*-isomer has been investigated kinetically.[214] The negative entropy $\Delta S = -6.9 \pm 3.0$ suggests that the isomerisation proceeds by a nondissociative process.

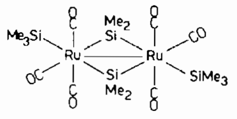
The dinuclear derivatives, $[(R_3M')M(CO)_4]_2$, contain a linear sequence M′–M–M–M′ with the structure (LIII).

These derivatives possess the effective molecular symmetry[74,213] D_{4d} or D_{4h} which is in agreement with their observed spectra.

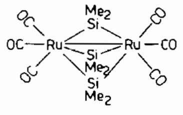
The bridged complexes $[(Me_3Si)M(CO)_3(\mu\text{-}SiMe_2)]_2$ (LIV) have been obtained when pentamethyldisilane reacts[215] with $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ under reflux or UV irradiation. These derivatives are also obtained when $(Me_3Si)_2M(CO)_4$ and pentamethyldisilane are irradiated with UV light. The crystal structure of the ruthenium compounds have been studied recently.[216]



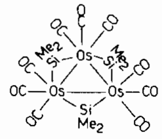
(LIII)



(LIV)



(LV)



(LVI)

The monomeric units based on octahedral coordination polyhedra share an edge to form the dimer. The central Ru atom of each monomer unit is bonded to three terminal carbonyls, one terminal trimethylsilyl group and two bridging dimethylsilylene groups. The Ru_2Si_2 bridge plane contains the crystallographic centre of symmetry, although the molecular symmetry deviates only slightly from C_{2h}. The germanium[76] and tin[208,209,217] analogues possess identical structures.

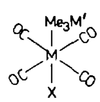
Silicon bridged Ru and Os complexes $Ru_2(CO)_6(\mu\text{-}SiMe_2)_3$ (LV) and $[(\mu\text{-}SiMe_2)Os(CO)_3]_3$ (LVI) have been obtained by treatment[215] of pentamethyldisilane with $[(Me_3Si)Ru(CO)_4]_2$ or $H_2Os(CO)_4$ under UV irradiation or reflux for a longer period. Two CO bands have been recorded for the former and five bands for the latter in their ir spectra. The trimers can be considered as examples of the main group transitional metal compounds containing six membered heterocyclic ring.

Ge-bonded compounds, $M_2(CO)_6(\mu\text{-}GeMe_2)_3$ and $[(\mu\text{-}GeMe_2)M(CO)_3]_3$, have been obtained by different methods. Thermal decomposition[76] of the complexes, $(Me_3Ge)_2M(CO)_4$, at about 160° C yields the clusters $[(\mu\text{-}GeMe_2)M(CO)_3]_3$ (M = Ru, Os) along with dinuclear species $M_2(CO)_6(\mu\text{-}GeMe_2)_3$. These derivatives possess identical structures[218,219] as their silicon analogues.

Several halogenated products of the Si, Ge, Sn bonded Ru and Os carbonyls have been obtained. Products of the type $(R_3M')M(CO)_4X$ (R = Me, M′ = Si, Ge, Sn; M = Ru, Os; X = Br, I) are obtained by direct reactions[75] of bromine or iodine on $[(R_3M')M(CO)_4]_2$ at low or ordinary temperatures. The dimers, $[(R_3M')M(CO)_3X]_2$, are obtained by refluxing[75] $(R_3M')M(CO)_4X$ for a short time at low temperature. Triphenylphosphine after reaction with these dimers yields[75] the products $(R_3M')M(CO)_3(Ph_3P)X$.

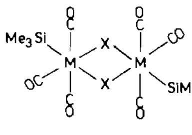
Only two CO stretching bands, one strong and the other weak, in the spectra of $(R_3M')M(CO)_4X$ indicate that the four carbonyl groups are in the *cis*-positions, the halogen and Me_3M' or $SiCl_3$ groups being in *trans*-positions (LVII).

The presence of two isomers (LVIIIa,b) (*fac-* and *mer-*) has been established for the dimeric derivatives

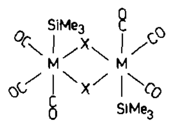


(LVII)

$[(Me_3Si)M(CO)_3X]_2$ both by ir and crystal data. The CO frequencies for these isomers are assigned below (cm^{-1}). Three CO bands may be attributed to *mer*-$M(CO)_3$ and two to *fac*-$M(CO)_3$.



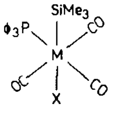
(LVIII a)



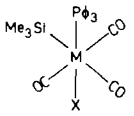
(LVIII b)

	mer-$Ru(CO)_3$	*fac*-$Ru(CO)_3$
M = Ru, X = I	2102w, 2041s, 2011m	2072vw, 2016sh
M = Ru, X = Br	2113w, 2046s, 2009m	2081vw, 2015sh
M = Os, X = I	2109w, 2029s, 2003m	2056vw, 2008sh

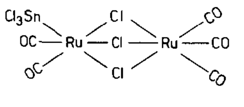
It is evident from ir data[75] that two structures (LIXa,b) are possible for $(R_3M')M(CO)_3(Ph_3P)X$ derivatives in which two CO groups are in the *trans*-positions.



(LIX a)



(LIX b)



(LX)

The structure of tri-μ-chloropentacarbonyl(trichlorostannyl)diruthenium, $(SnCl_3)Ru_2(CO)_5Cl_3$ (prepared by the reaction of $Ru_3(CO)_{12}$ with $SnCl_4$) has been determined by X-ray single crystal[223] method. Both Ru atoms have positions in the distorted octahedral configuration (LX). The two octahedra share a common face defined by three Cl atoms.

By refluxing octane or heptane solution of *cis*-$(GeMe_3)_2Ru(CO)_4$ and cyclooctatetraene,[224] $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$ derivative is obtained. Other similar derivatives have been given in Table IX.

Several Hg–Ru and Hg–Os bonded carbonyl complexes have been prepared by refluxing[227] the parent carbonyls with mercuric halides in ethanol or xylene for varying time intervals. These are white to pale yellow substances with the composition $M(CO)_4(HgX)_2$. While using mercuric chloride[227] in xylene, another pale cream solid, $Os(CO)_4(HgCl)Cl_3$, was also isolated. All the compounds show one strong band in the range 2118–2075 cm^{-1} and a very strong band in the range 2040–2004 cm^{-1}. All the four observed CO bands are considered to be fundamentals and the *cis*-octahedral configuration may be inferred for these compounds. Following the arguments by Orgel,[228] the band at highest frequency in each spectrum is assigned to the $a_1^{(2)}$ vibration. This mode of vibration involves the symmetric stretching of the mutually *trans*-CO groups. The intensity of the $a_1^{(2)}$ vibration relative to the other CO stretching vibrations in the ir increases in the order Cl < Br < I for each metal series. The most reasonable assignments for the very strong band is due to the b_1 vibration corresponding to the antisymmetric stretching vibration of the *trans*-CO groups. According to Orgel's arguments, the shoulders at 2052 and 2022 cm^{-1} in the spectra of the Os compounds are then assigned to $a_1^{(1)}$ and b_2 vibrations, the symmetric and antisymmetric vibrations of the mutually *cis*-CO groups. It must be concluded that the b_1 and b_2 vibrations are sufficiently close to each other.

Assuming $Os(CO)_4(HgCl)Cl$ in the *cis*-octahedral configuration,[227] the four ir active CO stretching vibrations expected are in agreement to the experimentally observed bands.

$M(CO)_3L_2$ (M = Ru or Os) derivatives react[229] with mercuric halides to form the cationic species $[M(CO)_3L_2(HgX)]^+$ (associated with the anion HgX_3^- (X = Cl, Br or I). The ir spectra of these derivatives show resemblance with those of other cationic tricarbonyl complexes $[M(CO)_3LX]^+$ with a shift of CO frequencies to lower wavenumbers which is consistent with the difference in electronegativity of the mercury anion compared to halide ion. $[Ru(CO)_3(HgX)X]_2$ was obtained by the action[37,38] of HgX_2 (X = Cl^-, Br^- or SCN^-) on $(C_8H_8)Ru(CO)_3$. It reacts[163] with pyridine to form the mixed carbonyl complex, $Ru(CO)_3(C_5H_5N)(HgX)X$. The mixed complex undergoes bridge splitting reaction without breaking the Ru–Hg bond. The similar complex $Os(CO)_3(Ph_3P)(HgCl)Cl$ was obtained by the reaction[37,38] of Hg (II) chloride on $Os_3(CO)_9(Ph_3P)_3$ in cold benzene.

A mercury–ruthenium bonded derivative, $Hg[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$, was obtained in a peculiar way. The anion $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$ which is obtained by reduction[79] of $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ with NaHg, reacts with $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ to yield a number of derivatives along with $Hg[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ (νCO: 2007, 1984, 1978, 1952 and 1946 cm^{-1} in cyclohexane; 2002, 1978 and 1937 cm^{-1} in carbon disulphide). In the formation of this complex mercury of the amalgam is utilized. The ir data for these compounds show that in solution an equilibrium exists between two isomers, one with C_{2v} and the other with

TABLE IX. Si, Ge and Sn Bonded Mixed Ligand Ru and Os Carbonyls.

Compound	Preparation	Colour, m.p. (b.p.), °C	νCO Frequency (cm^{-1})	Reference
$(Me_3Si)_2Ru(CO)_2(Ph_3P)_2$	a, b	Yellow	2046, 1997, 1990, 1970*	74
$(Me_3Ge)_2Ru(CO)_2(Ph_3P)_2$	c	White, 112–114°	2047, 1998, 1990, 1976*	76
$(Cl_3Si)_2Ru(CO)_2(Ph_3P)_2$	b		2113, 2067, 2060, 2047*	74
$(Cl_3Sn)_2Ru(CO)_2(C_5H_5N)_2$	d		2071, 2005**	125
$(Br_3Sn)_2Ru(CO)_2(C_5H_5N)_2$	e		2058, 1992**	125
$(Cl_3Si)Ru(CO)_2(\pi\text{-}C_5H_5)$	f	White	2054, 2006*	79
$(Cl_3Sn)Ru(CO)_2(\pi\text{-}C_5H_5)$	g		2068, 2016**	79
$(Cl_2Sn)Ru(CO)_2(\pi\text{-}C_5H_5)$	g	Yellow	2040, 2015, 1984, 1965**	79
$(I_2Ge)Ru(CO)_2(\pi\text{-}C_5H_5)$	g	245–248°	2043, 2019, 1990, 1969**	79
$(Me_2Sn)Ru(CO)_2(\pi\text{-}C_5H_5)$	h	Yellow	2004, 1994, 1952, 1942**	79
$(Me_3Si)Ru(CO)_4(Me_3Sn)$	i	Yellow	2089, 2031, 2026, 2015, 2006*	74
$(Me_3Si)Ru(CO)_4(Ph_3Sn)$	i	Yellow	2089, 2029, 2024, 2013, 2007*	74
$(Me_3Si)Ru(CO)_4(Ph_3PAu)$	i	Yellow	2059, 1996, 1989, 1970*	74
$(Me_3Ge)Ru(CO)_4(Ph_3PAu)$	i	Orange, 95–105°	2060, 1996, 1991, 1975*	76
$(Me_3Si)Ru(CO)_4Mn(CO)_5$	i	Yellow	2041, 2027, 1996, 1977, 1973*	74
$(Me_3Si)Ru(CO)_4(Bu_3Ge)$	i	Yellow		74
$(Et_3Si)Ru(CO)_4(Me_3Sn)$	i		2088, 2030, 2025, 2014, 2005*	74
$(Me_3Ge)Ru(CO)_4(Me_3Sn)$	i	Yellow ($70/10^{-2}$)	2089, 2028, 2017, 2010*	76
$(Me_3Sn)Ru(CO)_4(Bu_3Sn)$	j	Yellow, 100–102°	2082, 2022, 2010, 2002*	74
$(Me_3Si)Ru(CO)_4 \cdot Os(CO)_4(Me_3Si)$	i			213
$(Me_3Si)Ru(CO)_4Br$	a	Yellow	2058, 2027*	75
$(Me_3Si)Ru(CO)_4I$	a	Yellow	2056, 2024*	75
$(Me_3Ge)Ru(CO)_4I$	a	Orange, 63–65°	2054, 2012*	75
$(Me_3Sn)Ru(CO)_4I$	a	Orange	2051*	75
$(Cl_3Si)Ru(CO)_4Br$	a		2097, 2060*	75
$(Cl_3Sn)Ru(CO)_4Cl$				222
$[(Me_3Si)Ru(CO)_3Br]_2$	k	Red	2113, 2081, 2046, 2015, 2009	75
$[(Me_3Si)Ru(CO)_3I]_2$	k	Red	2102, 2072, 2041, 2016, 2011	75
$[(Me_3Ge)Ru(CO)_3I]_2$	k	Cream, 69–71°	2089, 2064, 2038, 2013, 2009	75
$[(Me_3Sn)Ru(CO)_3I]_2$	k	Orange, 69–71°	2092, 2060, 2034, 2012, 2007	75
$(Me_3Si)Ru(CO)_3(Ph_3P)I$	l	Yellow	2088, 2022, 1999*	75
$(Me_3Ge)Ru(CO)_3(Ph_3P)I$	l	Orange, 83–85°	2088, 2023, 2001*	75
$(Me_3Sn)Ru(CO)_3(Ph_3P)I$	l	Yellow, 108–110°	2092, 2016, 1989*	75
$(Me_3Ge)_2Ru_2(CO)_4(C_8H_6)$	c		2029, 2033, 1995, 1977	224
$(Me_3Si)Ru_2(CO)_5(C_7H_6R)$ ($R = H, Me, Ph, C_6F_5$)	a		2063, 2007, 2003, 1984, 1958	225
$(Me_3Ge)_2Os(CO)_2(Ph_3P)_2$	c	White, 112–117°	2049, 1994, 1981, 1971*	76

TABLE IX. (Cont.)

Compound	Preparation	Colour, m.p. (b.p.), °C	νCO Frequency (cm^{-1})	Reference
$(Me_3Si)(Me_3Sn)Os(CO)_4$	a	Yellow	2093, 2028, 2017, 2009*	213
$(Me_3Si)Os(CO)_4(AuPPh_3)$	a	Yellow		212
$(Me_3Si)Os(CO)_4Br$	a	Yellow	2046, 2014*	75
$(Me_3Ge)Os(CO)_4Br$	a	Yellow, 89–91°	2044, 2012*	75
$(Me_3Si)Os(CO)_4I$	a	Yellow	2045, 2013*	75
$(Me_3Ge)Os(CO)_4I$	a	Yellow	2043, 2011*	75
$[(Me_3Si)Os(CO)_3Br]_2$	k	Yellow	2108, 2057, 2032, 2006, 2001*	75
$[(Me_3Ge)Os(CO)_3Br]_2$	l	Yellow, 88–90°	2107, 2060, 2031, 2007, 2000*	75
$[(Me_3Si)Os(CO)_3I]_2$	l	Yellow	2110, 2056, 2029, 2008, 2003*	75
$[(Me_3Ge)Os(CO)_3I_2$	k	Orange, 69–71°	2098, 2084, 2038, 2013, 2009	75
$(Cl_3Sn)Os_2(CO)_8Cl$	m			226
$(Cl_3Sn)Os_2(CO)_8Br$	m			226
$(Cl_3Sn)Os_3(CO)_{12}Cl$	n			226
$(Me_3Si)Os(CO)_3(Ph_3P)Br$	l		2092, 2016, 1986	75
$(Me_3Ge)Os(CO)_3(Ph_3P)Br$	l	Yellow–Orange, 164°	2090, 2016, 1986	75
$(Me_3Si)Os(CO)_3(Ph_3P)I$	l		2088, 2014, 1989	75
$(Me_3Si)(Me)Os(CO)_3(Ph_3P)$	o			213

* Cyclohexane. ** Carbon disulfide.

Reactions of [a] Phosphines or halogen or other ligands with $(R_3M')M(CO)_4$. [b] $(R_3M'H)$ with $M(CO)_3L_2$. [c] Phosphines or hydrocarbon donor ligands with $(R_3M')_2M(CO)_4$. [d] Pyridine with $[M(CO)_2(SnCl_3)Cl_2]^{2-}$. [e] $M'X_2$ with $M(CO)_2(C_6H_7N)_2Br_2$. [f] Cl_3SiH with $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$. [g] $M'X_2$ with $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$. [h] Grignard reagent with $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2SnCl_2$. [i] Halides with $[(Me_3Si)Ru(CO)_4]^-$. [j] Bu_3SnH with $(Me_3Si)Ru(CO)_4(SnMe_3)$. [k] Refluxing $(Me_3R)Ru(CO)_4X$. [l] Phosphines with $[(Me_3R)Ru(CO)_3]_2$. [m] CX_4 with $HOs_2(CO)_8SnCl_3$. [n] $SnCl_4$ with $Os_3(CO)_{12}$. [o] Phosphines with $(Me_3Si)Os(CO)_4Me$. (M = Ru, Os; M′ = Si, Ge and Sn).

C_s symmetry. On the basis of relative intensities, the bands at 2007, 1984 and 1946 cm^{-1} are assigned to the isomer of C_{2v} symmetry and those at 2011, 1978 and 1952 cm^{-1} to that of C_s symmetry. There is also a shift of *ca.* 6 cm^{-1} when CS_2 is used in place of cyclohexane as solvent.

The complex, $Hg[Ru(CO)_4(GeMe_3)]_2$, containing Hg–Ru–Ge bonds has been prepared by the reaction[76] of the anion $[(Me_3Ge)Ru(CO)_4]^-$ on $(\pi\text{-}C_5H_5)Fe(CO)_2I$ in tetrahydrofuran/NaHg at 0° C. Its ir spectrum is similar in pattern to those of $Hg[Mn(CO)_4L]_2$ (L = t-phosphine) which has been interpreted[230] as consistent with a basically D_{4d} structure distorted through some bending on the Mn–Hg–Mn chain.

7. Carbonyl Halides

Halogenocarbonyl compounds of ruthenium and osmium were first reported by Manchot and König.[231,232] They obtained the compounds $Ru(CO)_2X_2$ (X = Cl, Br, I) by the reactions of CO on anhydrous ruthenium trihalides at 210–290° C. Since then there has been a great expansion in the chemistry of Ru and Os carbonyl halides. Several neutral, anionic and cationic species have been identified. The neutral species may be divided into following classes.

A. M(CO)₄X₂

These derivatives have been prepared by the action of halogens on metal pentacarbonyls or trimetal dodecacarbonyls or metal carbonyl hydrides. $Ru(CO)_4X_2$ (X = Cl, Br, I) were prepared by the action of halogens on $Ru(CO)_5$[233] or $Ru_3(CO)_{12}$.[116,234]

$$\begin{tikzcd}
Ru(CO)_4Br_2 & Ru_3(CO)_{12} \arrow[l, "Br_2"', "-40^\circ C"] \arrow[r, "I_2", "-15^\circ C"'] \arrow[d, "Cl_2"', "-80^\circ C"] & Ru(CO)_4I_2 \\
 & Ru(CO)_4Cl_2 &
\end{tikzcd}$$

Osmium carbonyl hydride, $Os(CO)_4H_2$, also yields $Os(CO)_4X_2$ when it reacts with halogens[235] or CX_4 (X = Cl, Br, I).[236] In the similar manner bromine reacts with *cis*-$Os(CO)_4Et_2$[13] to yield *cis*-$Os(CO)_4Br_2$. In case of $Os(CO)_4Me_2$ only one Os–C bond is broken and the formation of *cis*-$Os(CO)_4MeBr$ is observed.

$Ru(CO)_4Cl_2$ can be prepared by CO insertion[237] in a dichloromethane solution of dichloro(2,7-dimethylocta-2,6-diene-1,8-dienyl)Ru(II).

The formation of $Os(CO)_4Br_2$ or $Os(CO)_4I_2$ has been carried out by the carbonylation of osmium halides.[238]

The ir spectra of $M(CO)_4X_2$ species (M = Ru, Os; X = halogen) show four CO bands; this is in accordance with X-ray structural data[145] and the compounds have a *cis*-configuration with C_{2v} symmetry.[234,239,240] These molecules are expected to show four ir active ν(MC) vibrations and six ir active δ(MCO) vibrations (Table X). Unfortunately, there has been no study in the low frequency region except for $Os(CO)_4Cl_2$[241] and $Os(CO)_4Br_2$[241] where only one band has been observed for ν(MC) and δ(MCO).

Although both *cis* and *trans* derivatives[242] of $Os(CO)_4I_2$ have been synthesised and characterized by their ir spectra, the *trans* derivatives of ruthenium could not be isolated in a pure state. All these compounds exist in *cis* and *trans* forms in solid state as well as in solution.[241] The ir spectra of *cis*-$Os(CO)_4X_2$ derivatives in various solvents[243] like cyclohexane, tetracycloethylene, carbon tetrachloride, chloroform, dichloromethane and nitrobenzene indicate that vibrations involving mutually *trans* CO groups are affected more by change in halogen than those for mutually *cis*-CO groups. The reverse is true for change in polarity of the solvent. The CO stretching frequency decreases and solvent sensitivity increases with increasing replacement of CO by neutral ligands.

From a simple valence theory it is expected that the CO groups *cis* to the halogens should have higher stretching force constants than CO groups *trans* to ligands. It is due to the lower π-acceptor ability of halogens compared to CO. The force constants calculated with the help of frequencies show that the same order of frequencies prevails throughout, *i.e.*, $A_1(2) > B_1 > A_1(1) > B_2$. This follows the same pattern as the amine substituted *cis*-$M(CO)_4L_2$ derivatives[244–246] (M = Cr, Mo or W) of Group VI metal hexacarbonyls but differs in respect to the position and intensity of CO bands.

It has been observed that the CO stretching frequencies decrease as $Cl < Br < I$, the metal remaining the same. The π-bonding capabilities of the halogens are considered to increase along this series and inductive effect to decrease.

The relative strengths of metal–carbon and metal–halogen bonds have been described by the mass spectrum[145] of $Ru(CO)_4I_2$. Under mild conditions $Ru(CO)_4X_2$ (X = Br, I) in chloroform dimerizes[247–249] to form halogen bridged complexes which could be isolated in only one of the possible isomeric forms. Kinetic studies[247] in various solvents indicate that the dimerization process follows the first order rate law.

B. M(CO)$_3$*X*$_2$

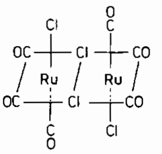
$Os(CO)_3Cl_2$ was first reported by Manchot and König in 1925. Later in the year 1967, Hales and Irving[238] reported the existence of three carbonyl halides. These products prove to be the major products in the reactions of CO at 100 atm on osmium trichloride, diosmium enneabromide or osmium oxyiodide. They are considerably less volatile than the $M(CO)_4X_2$ and are considered to be dimeric, although their molecular weights could not be measured due to their low solubility. The corresponding Ru derivatives[234] are obtained when the trinuclear $Ru_3(CO)_{12}X_2$ compounds are extracted with polar solvents; CO is evolved and dihalogeno tricarbonyl ruthenium compounds are formed. These compounds can also be prepared directly by the reaction of halogens with $Ru_3(CO)_{12}$ at room temperature in polar solvents or when heated in non-polar solvents. $Ru_2(CO)_6Br_4$[250] has been prepared by the action of bromoform on $Ru_3(CO)_{12}$. $[Ru(CO)_3X_2]_2$ and $[Os(CO)_3X_2]_2$ (X = Cl, Br) have also been prepared[251] by the action of formic acid on the metal halides. They are all soluble in common organic solvents and are nonelectrolytes in solutions.

They are formulated as halogen bridged binuclear compounds. The ir spectrum of each of the carbonyl halides in the CO stretching region showed six bands for ruthenium compounds (only two bands have been reported for their osmium derivatives in CCl_4[238]) but variation of relative band intensities in different solvents revealed that the spectra were composed of two overlapping sets of three bands.[27,234] Two isomeric forms in each case from the chloro,[234] bromo,[234] and

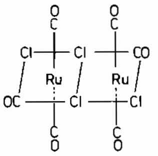
TABLE X. Ir Spectra of $M(CO)_4X_2$.

	νM–X		νC–O or νM–C	δM–C–O	No. of ir active bands		
					MX	CO or MC	MCO
trans-$M(CO)_4X_2$	D_{4h}	$a_{1g} + a_{2u}$	$a_{1g} + b_{1g} + e_u$	$a_{2g} + b_{2g} + e_g + a_{2u} + b_{2u} + e_u$	1	1	2
cis-$M(CO)_4X_2$	C_{2v}	$a_1 + b_2$	$2a_1 + b_1 + b_2$	$2a_1 + 2a_2 + 2b_1 + 2b_2$	2	4	6

iodotricarbonyl[234] compounds have been separated by chromatography. Bruce and Stone[27] have reported the spectra of mixtures of chloro complexes each having three bands in the ν(CO) region.[234] There are a number of possible isomers of $Ru_2(CO)_6X_4$ but the symmetry treatment shows that the two structures (LXIa, b) would have three ir active carbonyl stretching modes.



(LXI a)



(LXI b)

The consideration of the relative intensities of the expected bands by means of oscillating dipoles leads to the expectation that for isomer (a), the A_u and B_u (radial) modes will be stronger than the B_u (axial); for isomer (b), the A_u and B_u (radial) will again be strong but in this case the B_u (axial) would be of medium intensity. Therefore, the bands at 2144, 2084, 2009 cm^{-1} have been attributed to A_u, B_u (radial) and B_u (axial) respectively for the *trans* form and those at 2138, 2063 and 2021 cm^{-1} to the A_u, B_u (radial) and the B_u (axial) for the *cis* form. This simple treatment is not able to distinguish completely between the A_u and B_u (axial) modes.

Structural determination[252] of $Ru_2(CO)_6Br_4$ has shown it to have the structure (LXIa). The molecule possesses molecular point group symmetry C_{2h}; the Ru atoms are not bonded to each other directly but by means of two bromine bridges. The observed lengthening of nonbridging metal halide bond was interpreted as due to the *trans*-effect of the carbonyl ligand.

Only one tetrameric unit of $Ru(CO)_3X_2$ has been reported so far. The carbonylation[253] of $Ru(CO)F_{3.5}$ (obtained by the reaction of CO on RuF_5) at 100 atm pressure yields a pale yellow crystalline solid with ir absorption bands in the CO region at 2141, 2058 and 2000 cm^{-1}. Positions of ruthenium atoms were obtained from Patterson synthesis, and the electron density synthesis phased by ruthenium showed the molecule to be a fluorine-bridged tetramer $[Ru(CO)_3F_2]_4$.

C. $M(CO)_2X_2$

Both monomeric and polymeric forms of the species $M(CO)_2X_2$ have been reported.

$Ru(CO)_2Cl_2$ was prepared as fine yellow crystals in 100% yield by refluxing $RuCl_3$ in 1 : 1 mixture[254] of HCl and HCOOH at 150° C for 10 hr. In the similar manner the bromide and iodide analogues can also be prepared. The analogous osmium derivative is known only with iodine.[238]

Polymeric products, $[Ru(CO)_2Cl_2]_n$, have also been identified[255,256] by the reactions of metal halides or halo complexes with 90% HCOOH. These products have also been obtained[116,234] by the halogen oxidation of $Ru_3(CO)_{12}$. The polymeric derivatives have been prepared either by the reactions of CO on ruthenium trihalide at high temperature or by the pyrolysis[234] of solid *cis*-$Ru(CO)_4X_2$ and $Ru_2(CO)_6X_4$ *in vacuo* at 200° C. These are highly insoluble and each has two bands in the ν(CO) region. These compounds have halogen-bridged structures but in contrast to earlier suggestions,[257,258] the ir spectra clearly indicate that the carbonyl groups are in a *cis*-arrangement giving a kinked form of the chain structure.[257]

D. $M(CO)X_3$

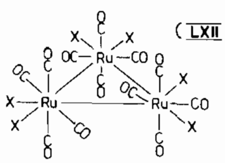
Only $Ru(CO)Cl_3$ and $Ru(CO)Br_3$ have been identified in this category. These products along with several anionic species have been prepared by the direct reaction[259,260] between CO and $RuCl_3$ or $RuBr_3$ in methanol.

E. $M_2(CO)_8X_2$

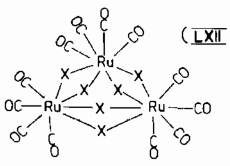
$Os_2(CO)_8Cl_2$[261] and $Os_2(CO)_8Br_2$[261] have been synthesized by the reactions of carbon tetrachloride or tetrabromide on $H_2Os_2(CO)_8$ in quantitative yields. The spectra show six strong CO stretching bands (νCO for $Os_2(CO)_8Cl_2$: 2121, 2082, 2069, 2064, 2054, 2032 cm^{-1}; νCO for $Os_2(CO)_8Br_2$: 2118, 2080, 2068, 2063, 2052, 2031 cm^{-1}). The thermal decomposition of $Os_3(CO)_{12}X_2$ also yields $Os_2(CO)_8X_2$ along with $Os_2(CO)_6X_4$. Mass spectral evidence[36] has been presented for its formation.

F. $M_3(CO)_{12}X_6$

The mononuclear halogenocarbonyls, $M(CO)_4X_2$, rapidly decompose in solution above room temperature to give the trimeric derivatives $M_3(CO)_{12}X_6$.[234] These trimers also remain as residues after sublimation of the mononuclear compounds. By these methods, red-brown $Ru_3(CO)_{12}I_6$ and pale-yellow $Ru_3(CO)_{12}Br_6$ have been prepared. The yellow chloro-derivative, $Ru_3(CO)_{12}Cl_6$, is more conveniently prepared by the action of chlorine on $Ru_3(CO)_{12}$ refluxed in chloroform. In the similar manner analogous bromo and iodo derivatives have also been obtained.[73,116] The corresponding Os derivatives are not known. They are of low volatility and insoluble in nonpolar solvents at room temperature, stable for a short period in solid state but decompose rapidly in solution. The mass spectral evidence suggests that they are nonelectrolytes and have a cyclic rather than a linear structure.[234] Three terminal CO bands in the ir spectra suggest that these molecules are of high symmetry and contain no bridging CO ligand. Two possible structures (LXIIa, b) have been proposed.[234]



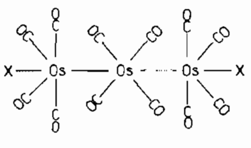
(LXII a)



(LXII b)

G $M_3(CO)_{12}X_2$

$H_2Os_3(CO)_{12}$ (which may be obtained by the reaction between OsO_4 and CO and H_2) when reacting with CCl_4 or CBr_4 yields[262] $Os_3(CO)_{12}Cl_2$ or $Os_3(CO)_{12}Br_2$ All the three carbonyl halides have also been obtained by the halogen oxidation[36 73] of $Os_3(CO)_{12}$ The analogous ruthenium compounds are not known These compounds have been characterised by Raman [58] ir[36 58] and mass spectral[36] techniques The vibrational spectra of dihalide provide strong evidences for a linear X–Os–Os–X molecular structure[36 58] with a point group of $D_{\infty h}$ or D_{4h} if the C–O ligands are included The mass spectral data favour the linear arrangement of the three metal atoms with an overall molecular symmetry (D_{4h}) The structure (LXIII) has been proposed for $Os_3(CO)_{12}X_2$ molecules



(LXIII)

H $M_3(CO)_{10}X_2$

Prolonged heating[105 106] in C_6H_6 converts the linear complexes $Os_3(CO)_{12}X_2$ (X = Cl Br I) to cyclic derivatives $Os_3(CO)_{10}X_2$

(i) Anionic Derivatives

All the known mononuclear anionic halogenocarbonyls $[M(CO)X_5]^{-n}$ (n = 1 [259] 2 [251 259 263 264] and 3 [251 255]) $[M(CO)_2X_4]^{-2}$ [251 254–256 259 263] and $[M(CO)_3X_3]^{-1}$ [251 255 256 259] are of octahedral geometry they have been prepared either by the action of formic acid[251 255 256 259] or by HCl and CO[259 263] on metal halides or on sodium hexahalometallates [251 255 256 264] These anions have been isolated in form of their ammonium and caesium salts

Anions $[M(CO)X_5]^{-n}$ possess C_{4v} symmetry having 13 modes of symmetry species $5A_1+2B_1+B_2+5E$ with A_1 mode of $\nu(CO)$ and $\nu(MC)$

The anionic species $[M(CO)_2X_4]^{-2}$ possess C_{2v} symmetry with 21 modes of symmetry species $8A_1+3A_2+6B_1+4B_2$ (with two CO bands for A_1+B_2 modes) The corresponding *trans* derivatives are not known at present

Anions, $[M(CO)_3X_3]^{-1}$ possess C_{3v} symmetry (*cis* structure) with 16 modes of symmetry species $6A_1+2A_2+8E$ The corresponding *trans* derivatives are uninvestigated The CO stretching frequencies due to modes (A_1+E) of the isolated compounds are M = Ru X = Cl νCO 2137 2074 2061 2047 cm^{-1} X = Br νCO 2126, 2119 2069 2045 cm^{-1} X = I νCO 2114 2110 2048, 2035 cm^{-1}, M = Os, X = Cl, νCO 2125 2046 2014 1992 cm^{-1} X = Br νCO 2120, 2010 2045 2016 cm^{-1} X = I νCO 2109 2105, 2040 2011 cm^{-1}

Evidence has been obtained[265] for the existence of only one dinuclear anion $[Ru_2(CO)_4I_6]^{-2}$ Conductivity measurements[265] on $[NEt_4]^+[Ru(CO)_2I_3]^-$ support its formulation as the iodobridged dimer $[NEt_4]^+_2[Ru_2(CO)_4I_6]^{2-}$ The occurence of only two CO bands (2023 and 1975 cm^{-1}) suggests that each Ru atom must have the same arrangement of substituents more bands would be expected for an unsymmetrically substituted dimer

TABLE XI Substituted Carbonyl Halides $M(CO)_3LX_2$

Metal	X	L	Preparation	Reference
Ru	Cl	Ph_3P	a b	115 234
	Br	Ph_3P	b	115
	I	Ph_3P	b	115 234
	Br	$OPPh_3$	c	248
	I	$OPPh_3$	c	248
	Br	$C_5H_5NO_2$	c	248
	Cl	C_4H_8O	d	27
Os	Cl	Ph_3P	e	255
	Br	Ph_3P	e	251 255
	Br	C_5H_5N	c	247
	I	C_5H_5N	c	247
	Br	3 $CH_3C_5H_4N$	c	247
	Br	3 4 lutidine	c	247

Reaction of [a]Triphenylphosphine with $Ru_3(CO)_{12}$ in $CHCl_3$ [b]Halogens with $Ru_3(CO)_9(Ph_3P)_3$ [c]Group V and VI donor ligands with the complex $Ru(CO)_4X_2$ [d]C_4H_8O with $[Ru(CO)_3Cl_2]_2$ [e]Triphenylphosphine with $Cs[Os(CO)_3X_3]$ in HCOOH

TABLE XII. Substituted Carbonyl Halides $M(CO)_2L_2X_2$.

Metal	X	L	Preparation	References
Ru	Cl	Ph_3P	a, b, c, d, e	198, 251, 255, 263, 266, 268
	Cl	$(OPh)_3P$, $(p\text{-}C_6H_4MeO)_3P$, $(o\text{-}C_6H_4MeO)_3P$, $(2{,}4\text{-}C_6H_3Me_2O)_3P$	f	269
	Cl	PMe_2Ph, PPr_2Ph	g, h	270
	Cl	PMe_2Bu^t, PEt_2Bu^t, $PBu^n{}_2Bu^t$, $PPhBu^t{}_2$, $PMeBu^t{}_2$, $P(p\text{-tolyl})Bu^t{}_2$, $PPr^nBu^t{}_2$	h	271
	Cl	PEt_2Ph	e, g, h	266, 267, 270, 273
	Cl	Et_3P	e, g, h	267, 270, 272
	Cl	Bu_3P	i	274
	Cl	$PPh_2CH_2CH_2Ph_2P$	e	266
	Cl	PBu_2H		275
	Cl	Ph_3As, Et_3As, Ph_3SbS, $S(CH_2)_4$, Ph_2Se, Et_2Se, $PhSeCH_2CH_2SePh$, Ph_2Te, C_5H_5N, $p\text{-}MeC_6H_4NH_2$, $C_5H_{11}N$, C_4H_9N, $C_{12}H_8N_2$	e	262, 266, 267
	Cl	Ph_3Sb	c, e	276
	Cl	$PhNH_2$, $PhCH_2NH_2$, $C_{12}H_8N_2$, $C_{10}N_8N_2$	k	125
	Br	Ph_3P	a, e	251, 255, 266, 267
	Br	$(OPh)_3P$, $P(o\text{-}C_6H_4MeO)_3$	f	269
	Br	$PEtPh_2$, PEt_2Ph, $P(C_6H_{11})_3$, Ph_3As, Et_3As, $S(CH_2)_4$, 1,4-Dithiane, $S_2Et_2(CH_2)_2$, Et_2Se, $PhSeCH_2CH_2SePh$, Ph_2Te, C_5H_5N, $H_2NCH_2CH_2NH_2$, $p\text{-}C_6H_4MeNH_2$, $C_5H_{11}N$, C_4H_9N, $C_{12}H_8N_2$	e	266, 267
	Br	Et_3P, PPr_2Ph	e, h	266, 267, 270
	Br	$PhCH_2NH_2$, $PhNH_2$, $C_{12}H_8N_2$	l	125
	I	Ph_3P, $PEtPh_2$, PEt_2Ph, PPr_2Ph, Et_3P, $(OEt)_3P$, $(C_6H_{11})_3P$, $PPh_2CH_2CH_2Ph_2P$	e, h	265, 266, 267
	I	PPh_2Me	j	191
	I	Ph_3As, Et_3As, Et_3Sb, Et_2S, $S(CH_2)_4$, $HSCH_2CH_2SH$, 1,4-Dithiane, $EtSCH_2CH_2SEt$, $PhSCH_2CH_2SPh$, Ph_2Se, Et_2Se, $PhSeCH_2CH_2SePh$, Ph_2Te, Bu_2Te, $C_5H_{11}N$, C_4H_9N, $C_{12}H_8N_2$, $H_2NCH_2CH_2NH_2$, C_5H_5N, $Me_2NCH_2CH_2NMe_2$, $p\text{-}MeC_6H_4NH_2$	e	265, 266, 267
Os	Cl	Ph_3P	a, d, h, m, n, o	90, 198, 238, 243, 251, 277
	Cl	$(OPh)_3P$, $(p\text{-}C_6H_4MeO)_3P$	h	269
	Cl	$PMePh_2$, $PEtPh_2$, PEt_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$, $PhAsMe_2$	p	278
	Cl	Ph_3As, Ph_3Sb	n	238, 243, 279
	Br	Ph_3P	a, h, m, n	90, 238, 243, 251, 256
	Br	$(OPh)_3P$, $(p\text{-}C_6H_4MeO)_3P$	h	269
	Br	Ph_3As, Ph_3Sb	n	238, 243
	I	Ph_3P	h, n	90, 238, 243
	I	$(OPh)_3P$, Ph_2PCl, $PPhCl_2$, Cl_3P, $Ph_2PCH_2CH_2PPh_2$, $o\text{-}C_6H_4\{As(Me_3)_2\}_2$, C_5H_5N	n, p, q	238
	I	Ph_3As, Ph_3Sb	n	238, 243

Reaction of [a]*t*-phosphines with $Cs_2[M(CO)_2X_4]$ in HCOOH. [b] Alkene substrates with $HM(CO)_2L_2X$. [c] CO with ML_2X_2 or ML_3X_3 or ML_4X_2 in DMF. [d] Refluxing $[M(CO)_2(NO)(Ph_3P)_2]^+$ in $CHCl_3$. [e] Various group V, VI donor ligands with $M(CO)_2L_2X_2$. [f] Group V ligands with di-μ-halodicarbonylruthenium(II). [g] CO with $[M_2L_6X_3X]$. [h] CO with hydrated metal halides or halometallates and ligands in 2-methoxyethanol. [i] CO with $M_2L_4X_5$ in EtOH. [j] Halogens with $M(CO)_3L_2$. [k] Ligands with deep red solution (passing CO on $RuCl_3$ in EtOH). [l] LiBr with the complex obtained by method k. [m] CO with $M(CO)L_3X_2$. [n] Group V donor ligands with $M(CO)_3X_2$. [o] HCl with $M(CO)(NO)L_2X$. [p] Zn reduction of $Os(R_3P)_3X_3$ in presence of CO. [q] Group V donor ligands with $M(CO)_4X_2$.

TABLE XIII. Substituted Carbonyl Halides $M(CO)L_3X_2$.

Metal	X	L	Preparation	Reference
Ru	Cl	Ph_3P	a	255, 263
	Cl	$PPhMe_2$	b	280, 281
	Cl	$PPhEt_2$, $PPhPr_2$, $PPhBu_2$, Et_3P, $AsMe_2Ph$	c	270
	Cl	$P(OPh)_3$, $P(p\text{-}C_6H_4MeO)_3$, $P(p\text{-}C_6H_4ClO)_3$	d	269
	Cl	tetraphenylporphine	b	282
	Cl	Ph_3Sb	a	276
	Br	$PPhMe_2$	b	280
	Br	$PPhPr_2$, $PPhBu_2$	c	270
	I	$PPhMe_2$	b	172
	I	$P(OPh)_3$	d	269
	I	Ph_3Sb	e	265
Os	Cl	Et_3P, PMe_2Ph, PEt_2Ph, PPr_2Ph	d, f	278, 285
	Cl	Ph_3Sb	d	279
	Br	PMe_2Ph	d	278

Reaction of [a] Group V donor ligands with $[M(CO)X_5]^{3-}$ or $[M(CO)H_2OX_4]^{2-}$. [b] Group V donor ligands and CO with MX_3 in alcohols. [c] Group V donor ligands with $M(CO)_2L_2X_2$. [d] CO with ML_4X_2 or ML_3X_3. [e] NaI on carbonylated $RuCl_3$ solution and subsequent addition of Ph_3Sb. [f] CO with Os $(PMe_2Ph)_3(N_2)Cl_2$.

8. Substituted Derivatives of Carbonyl Halides

Substituted derivatives of Ru and Os carbonyl halides of varying stoichiometries have been investigated for a wide range of ligands. Neutral mononuclear $M(CO)_3LX_2$, $M(CO)_2L_2X_2$, $M(CO)L_3X_2$ and dinuclear $M_2(CO)_4L_2X_4$ species along with cationic $[M(CO)_3L_2X]^+$ have been characterised. Their methods of preparations and references have been cited in Tables XI, XII, and XIII.

A. $M(CO)_3LX_2$

These derivatives (Table XI) have been prepared by refluxing $Ru_3(CO)_{12}$ and ligands in chloroform[115] or by the action of ligands on the anion $[M(CO)_3X_3]^-$ in formic acid,[251, 255] or by the action[247] of ligands on $Ru(CO)_4X_2$ or by oxidising[115] $Ru_3(CO)_9L_3$ with halogens. By measuring the C–O frequencies (Table XIV) a structure in which the halogen groups are *cis* to one another has been proposed.

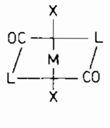
B. $M(CO)_3LX$

$Ru_3(CO)_{12}$ in iso-octane on treating with allyl bromide,[249] at 60–70° C under nitrogen gives $(\pi\text{-}C_3H_5)Ru(CO)_3Br$. Chloro- and iodo-derivatives have been prepared similarly.

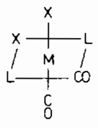
C. $M(CO)_2L_2X_2$

This is a well investigated class and a number of compounds of this class have been prepared using different experimental techniques. In most cases these derivatives have been obtained by the action of ligands on metal carbonyl halides. Other methods that have been used are given in Table XII.

Two configurations (LXIVa, b) are proposed[270, 278] for these derivatives. The C–O frequencies (Table XIV) are in full agreement with these structures.



(LXIV a)



(LXIV b)

Generally two strong bands have been recorded in the CO region for the complexes in which the two carbonyl groups are in the *cis*-positions while only one CO band has been recorded in the ir spectra of the derivatives in which the two carbonyl groups are in the *trans*-positions. The complexes having configuration LXIVa change into complexes of configuration LXIVb on simple heating. Ir spectra have also been recorded in the lower region to examine the Ru–X and Os–X frequencies. Complexes of configuration LXIVa where X is *trans* to X show the expected single M–X band (Ru–Cl, ~320–347 cm^{-1}; Os–Cl, ~308–313 cm^{-1}; Os–Br, 234 cm^{-1}). The isomer (LXIVb) where one halogen is *trans* to CO gives two νM–X bands {ν(Ru–Cl), one between 303–311 cm^{-1} and the other between 276–287 cm^{-1}; νOs–Cl ~305 and 277 cm^{-1}, Os–Br, 212 and 193 cm^{-1}). The lower νOs–X values than the corresponding νRu–X values are due to the higher mass of osmium than ruthenium.

D. $M(CO)L_3X_2$

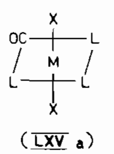
Individual methods of preparations of various derivatives of this class have been given in Table XIII. These complexes possess[270] two configurations (LXVa, b).

The compounds of the configuration LXVa change into the compounds of configuration LXVb on simple heating. The ir spectra of these derivatives (Table XIV) show a single νCO band as is expected. The νCO va-

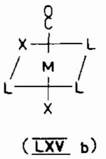
TABLE XIV. CO Stretching Frequencies of $M(CO)_3LX_2$, $M(CO)_2L_2X_2$ and $M(CO)L_3X_2$.

Compound	νCO (cm^{-1})	Reference
$Ru(CO)_3(Ph_3P)Cl_2$	2133, 2075, 2033[a]	234
$Ru(CO)_3(Ph_3P)Br_2$	2128, 2073, 2036[a]	234
$Ru(CO)_3(Ph_3P)I_2$	2116, 2060, 2037[a]	234
$Ru(CO)_2(Ph_3P)_2Cl_2$	2069, 2041, 2004, 1939[b]	251
cis-$Ru(CO)_2(PhMe_2P)_2Cl_2$	2055, 1990[c]	270
trans-$Ru(CO)_2(PhMe_2P)_2Cl_2$	2008[c]	270
cis-$Ru(CO)_2(PhEt_2P)_2Cl_2$	2048, 1975[c]	270
trans-$Ru(CO)_2(PhEt_2P)_2Cl_2$	1997[c]	270
$Ru(CO)_2(Ph_3P)_2Br_2$	2054, 2025, 1978, 1919[b]	251
$Ru(CO)_2\{P(PhO)_3\}_2Br_2$	2081, 2027[c]	269
$Ru(CO)_2(Et_3P)_2Br_2$	2049, 1980[c]	270
$Ru(CO)_2(Ph_3P)_2I_2$	2051, 1982[c]	265
$Ru(CO)_2(Ph_3As)_2I_2$	2050, 1990[c]	265
$Ru(CO)_2(Ph_3Sb)_2Cl_2$	2060, 2000[c]	276
$Ru(CO)_2(C_5H_5N)_2I_2$	2050, 1989, 1964[c]	265
$Ru(CO)_2(C_{12}H_8N_2)Cl_2$	2066, 2005[d]	125
$Ru(CO)_2(C_6H_5NH_2)_2Cl_2$	2070, 2004, 1988[d]	125
$Ru(CO)_2(C_{12}H_8N_2)Br_2$	2066, 2005[d]	125
$Ru(CO)_2(C_6H_5NH_2)_2Br_2$	2070, 2005, 1955[d]	125
$Os(CO)_2(Ph_3P)_2Cl_2$	2040, 1975	90
$Os(CO)_2(Ph_3P)_2Br_2$	2035, 1970	90
$Os(CO)_2(Ph_3P)_2I_2$	2035, 1970	90
$Os(CO)_2\{P(OPh)_3\}_2Cl_2$	2069, 2002	269
$Os(CO)_2\{P(OPh)_3\}_2I_2$	2065, 2004	269
cis-$Os(CO)_2(PEtPh_2)_2Cl_2$	2043, 1971[c]	278
trans-$Os(CO)_2(PEtPh_2)_2Cl_2$	1982[c]	278
cis-$Os(CO)_2(PEtPh_2)_2Br_2$	2046, 1977[c]	278
trans-$Os(CO)_2(PEtPh_2)_2Br_2$	1982[c]	278
$Os(CO)_2(Cl_3P)_2I_2$	2074, 2023[c]	238
$Os(CO)_2(Ph_3As)_2Cl_2$	2038, 1967[c]	238
$Os(CO)_2(Ph_3As)_2Br_2$	2040, 1971[c]	238
$Os(CO)_2(Ph_3As)_2I_2$	2037, 1971[d]	238
$Os(CO)_2(Ph_3Sb)_2Cl_2$	2032, 1964[d]	238
$Os(CO)_2(Ph_3Sb)_2Br_2$	2032, 1966[d]	238
$Os(CO)_2(Ph_3Sb)_2I_2$	2031, 1966[d]	238
$Os(CO)_2(C_5H_5N)_2I_2$	2041, 1974[c]	238
$Ru(CO)(PhMe_2P)_3Cl_2$	1949[d]	281
$Ru(CO)(PhPr_2P)_3Cl_2$	1934[d]	270
$Ru(CO)(PhPr_2P)_3Br_2$	1958[d]	270
$Ru(CO)\{(PhO)_3P\}_3I_2$	2044	269
$Ru(CO)(Ph_3Sb)_3Cl_2$	1980	276
$Os(CO)(PhMe_2P)_3Cl_2$	1957[c]	278
$Os(CO)(PhMe_2P)_3Br_2$	1962[c]	278

[a] Cyclohexane. [b] KBr. [c] Chloroform. [d] Dichloromethane.



(LXV a)



(LXV b)

lues for the (LXVb) isomer are lower than for (LXVa) isomer suggesting a greater overlap of metal non-bonding *d*-orbitals with π^* CO orbitals when CO is *trans* to the weaker *trans* influenced ligand. Only one metal–halogen band (νRu–Cl 311 cm^{-1}; νOs–Cl, ~300 cm^{-1}; νOs–Br, ~200 cm^{-1}) of strong intensity has been recorded in the far ir spectra of the compounds having configuration LXVa while the spectra of the compounds of configuration LXVb show two M–Cl bands (νRu–Cl, one between 279–294 cm^{-1} and the other between 241–270 cm^{-1}; νOs–Cl, 290–261 cm^{-1}). In case of bromo complexes only one Os–Br band at 173 cm^{-1} of medium intensity has been recorded.

Besides these complexes, a few hexa- and penta-coordinated, $Ru(CO)(Ph_3P)_2(CS)Cl_2$, $Ru(CO)(Ph_3P)_2(NO)Cl$, $Os(CO)(Ph_3P)_2(NO)Cl$, compounds have also been synthesised.[283,284] The latter two compounds possess either trigonal bipyramidal or tetragonal pyramidal geometry.

E. $M_2(CO)_4L_2X_4$

Dimeric substituted carbonyl halides, $[M(CO)_2LX_2]_2$, are known for ruthenium only. They may be prepared by the following methods:

(i) Action of ligands[254] like triphenylphosphine on $Ru(CO)_2X_2$ in methanol produces $Ru_2(CO)_4(Ph_3P)_2X_4$:

$Ru(CO)_2Cl_2 + Ph_3P \rightarrow Ru_2(CO)_4(Ph_3P)_2Cl_4$

(ii) Halogens oxidise[40,234] the substituted metal carbonyls like $Ru(CO)_4(Ph_3P)$ and $Ru_3(CO)_9(Ph_3P)_3$ to produce $Ru_2(CO)_4(Ph_3P)_2X_4$:

$Ru(CO)_4(Ph_3P) + X_2 \rightarrow Ru_2(CO)_4(Ph_3P)_2X_4$ (X = Cl, Br, I)

$Ru_3(CO)_9(Ph_3P)_3 + X_2 \rightarrow Ru_2(CO)_4(Ph_3P)_2X_4$ (X = Cl, Br, I)

(iii) $Ru(CO)_4(Ph_3P)$ on refluxing in chloroform[40] yields the corresponding chloro derivative:

$Ru(CO)_4(Ph_3P) + CHCl_3 \rightarrow Ru_2(CO)_4(Ph_3P)_2Cl_4$

(iv) It may also be prepared when $[Ru(CO)_2ClL]_2$ reacts with halogens:[271]

$[Ru(CO)_2ClL]_2 + Cl_2 \rightarrow Ru_2(CO)_4L_2X_4$ ($L = PBu^t_2$) Ph or PBu^t (*p*-tollyl)

In solution the ir spectra[234] of these compounds show two strong bands (νCO for chloro-, bromo-, and iodo-complexes are 2076, 2016; 2079, 2011 and 2059, 2006 cm^{-1} respectively). The structure of these compounds are presumed to be based on a halogen bridged dimer analogous to that of $Ru_2(CO)_6X_4$. Furthermore, in contrast to unsubstituted dimer, there is no evidence for existence of the isomers.

The species $Ru_2(CO)_4(C_7H_7)(X)$ along with $Ru(CO)_2(C_7H_9)(X)$ have also been prepared[135] by the action of iodine on $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ in hexane or with CX_4 (X = Cl, Br).

F. Cationic Derivatives

Reactions of Ru and Os substituted carbonyl halides with halogen acceptors such as $AlCl_3$, AlI_3 or $FeCl_3$ in C_6H_6 under CO atmosphere gave a series of complexes,[90,98] $[M(CO)_3L_2X]^+Y^-$ (M = Ru, L = Ph_3P, $EtPPh_2$, $(C_6H_{11})_3P$, X = Cl, I, Y = $AlCl_3I^-$, $AlCl_4^-$, PF_6^-, $Cl_6IAl_2^-$; M = Os, L = Ph_3P, $(C_6H_{11})_3P$, X = Cl, Br, I, Y = HCl_2^-, $[(CO)_3(NO)Fe]^-$, Cl^-, Br^-, I_3^-). Their stabilities increase by decreasing basicity of the phosphine ligands and increasing the coordination number of the central metal.

G. Anionic Derivatives

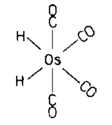
The anion, $[Ru(CO)H_2OCl_4]^{-2}$, was prepared in form of its ammonium salt by the homogeneous reduction[259,263] of $[Ru(CO)Cl_5]^{-2}$ with H_2. It was also prepared when CsCl reacted[260] with $Ru(CO)(H_2O)Cl_2$ (prepared when $RuCl_3$ and 50:50 HCO_2H–HCl were refluxed). Its infrared spectrum exhibited[263] strong peaks at 1950 (assigned to CO), 3140 and 1400 (assigned to NH_4^+) and 3480 and 1610 cm^{-1} (assigned to H_2O). Another anion $[Os(CO)_2Ac_2Br_2]^{-2}$ was prepared by the action[41,93] of methylmagnesium bromide on $Os(CO)_4Br_2$.

9. Carbonyl Hydrides

Ruthenium and Osmium carbonyl hydrides are known since 1943, however their systematic investigation has started from 1966. Since then several neutral, cationic and anionic species have been reported. Table XV lists the known mono-, di-, tri-, tetra- and hexanuclear carbonyl hydrides.

A Mononuclear

The existence of $H_2Ru(CO)_4$ is doubtful, however the osmium analogue has been obtained by a number of methods. $H_2Os(CO)_4$ has a *cis*-octahedral structure (LXVI) with C_{2v} symmetry as evidenced by ir,[236,240,261] NMR[236,261] and mass[261] spectral studies.

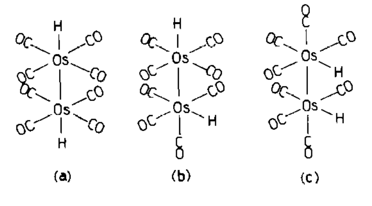


(LXVI)

On reducing[93] $H_2Os(CO)_4$ with sodium sand in THF, the sodium salt, $NaOsH(CO)_4$, is obtained. NMR and ir studies are in close agreement with C_{3v} symmetry of the anion $[HOs(CO)_4]^-$ with a metal hydrogen bond. Any indication for the formation of $[Os(CO)_4]^{2-}$ has not been obtained. The cation $[HOs(CO)_5]^+$ has been prepared as its hexafluorophosphate salt by extracting[286] n-heptane solution of $Os(CO)_5$ with sulphuric acid and further treatment with aqueous solution of ammonium hexafluorophosphate.

B. Dinuclear

$H_2Os_2(CO)_8$ has been isolated[261] in a poor yield (10–15%) in the preparation of $H_2Os(CO)_4$. Its ruthenium analogue is not known. With the help of ^1H NMR spectrum[261] it has been concluded that both hydrogen atoms in the molecule are equivalent. Out of the three possible structures (LXVIIa,b,c) structure (LXVIIc) is in full accordance with ir and NMR data.



(a) (b) (c)

(LXVII a-c)

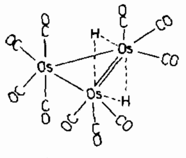
TABLE XV. Hydrido Carbonyls of Ruthenium and Osmium.

Compound	Preparation	νCO (cm^{-1})	References
$H_4Ru_3(CO)_{10}$	a		34
$H_2Ru_3(CO)_{11}$	a		34
α-$H_4Ru_4(CO)_{12}$	b, c	2084, 2067, 2063, 2033, 2026, 2013*	12, 20, 293–295, 321
β-$H_4Ru_4(CO)_{12}$	b, c	2080, 2068, 2056, 2034, 2027, 2008*	12, 20, 293–295, 321
α-$D_4Ru_4(CO)_{12}$			321
β-$D_4Ru_4(CO)_{12}$	b, c	2076, 2064, 2056, 2033, 2019, 2004*	293, 294
$H_2Ru_4(CO)_{13}$	b, d, e	2083, 2068, 2056, 2033, 2026, 2008, 1880*	291, 293, 321
$D_2Ru_4(CO)_{13}$	b	2079, 2063, 2056, 2033, 2019, 2003, 1880*	293
$H_2Ru_6(CO)_{18}$	f	2060, 2054, 2008**	299
$[HRu_3(CO)_{12}]^+PF_6^-$	g	2129, 2102, 2081, 2068, 2030***	288, 289
$H_2Os(CO)_4$	a, h, i	2132, 2093, 2057, 2039, 2037, 2023, 2020, 1988†	235, 236, 261, 262
$D_2Os(CO)_4$	j		235
$H_2Os_2(CO)_8$	h	2132, 2093, 2057, 2039, 2033, 2020, 1988†	261
$H_2Os_3(CO)_{10}$	a	2110, 2076, 2062, 2025, 2009, 1982, 1969, 1956*	36, 39
$H_2Os_3(CO)_{12}$	h		262
$H_4Os_4(CO)_{12}$	a, k	2110, 2070, 2060, 2023, 2001, 1990, 1982*	36, 39, 238, 295
$H_2Os_4(CO)_{13}$	k	2090, 2062, 2041, 2020, 1998, 1987*	36
$[HOs(CO)_5]^+PF_6^-$	l	2141, 2019††	286
$[HOs(CO)_4]^-$	m		93
$[HOs_3(CO)_{12}]^+PF_6^-$	g	2135, 2102, 2080, 2061, 2021***	286–290

*Cyclohexane. **Carbon tetrachloride. ***Nitromethane. †Heptane. †† Sulphuric acid. [a] Reaction of hydrogen with $M_3(CO)_{12}$. [b] Sodium borohydride in THF with $M_3(CO)_{12}$. [c] CO with $Ru_2(OAc)_4$ in water and Pr–OH. [d] Refluxing $Ru_3(CO)_{12}$ in n-octane or n-nonane. [e] CO and hydrogen with ruthenium chloride solution. [f] Mononuclear carbonyl anion with $Ru_3(CO)_{12}$. [g] H_2SO_4 with $M_3(CO)_{12}$ in presence of NH_4PF_6. [h] CO and H_2 with OsO_4. [i] Pyrolysis of $H_2Os_3(CO)_{12}$. [j] D_2 with $H_2Os(CO)_4$. [k] H_3PO_4 and KOH with $Os_3(CO)_{12}$ in CH_3OH. [l] $Os(CO)_5$ in concd. H_2SO_4. [m] Sodium with $H_2Os(CO)_4$.

C. Trinuclear

Only two trinuclear carbonyl hydrides of ruthenium, $H_4Ru_3(CO)_{10}$ and $H_2Ru_3(CO)_{11}$, have been reported. These compounds were obtained as side products[34] in the polymethylene synthesis using carbon monoxide and hydrogen on ruthenium catalyst. No structural information is available for these carbonyl hydrides. A thermally very unstable[211] hydride, $H_2Ru_3(CO)_{12}$, has also been prepared by the treatment of $Ru_3(CO)_{12}$ with Na in liquid ammonia followed by the action of H_3PO_4. The trinuclear osmium carbonyl hydrides, which have been characterised, are $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{12}$. The ir spectrum[36,39] of $H_2Os_3(CO)_{10}$ is very complex and bands due to bridging CO groups are not present. The complicated nature of the spectrum may probably be due to the lower symmetry of the complex. Mass spectral data favour a cyclic configuration (LXVIII) with bridging hydride group and Os=Os double bond.[36]



(LXVIII)

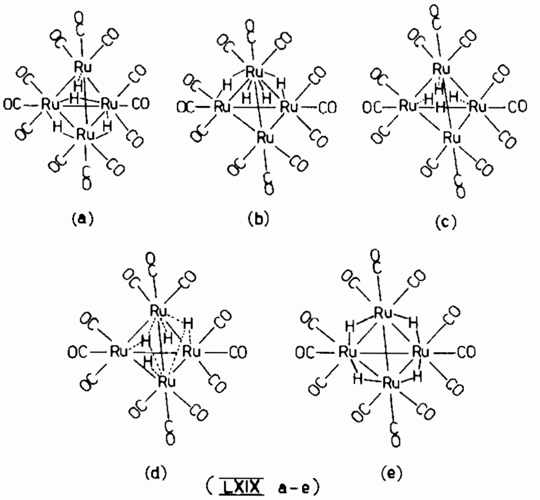
$H_2Os_3(CO)_{12}$ has been isolated[262] by the reaction of OsO_4 with CO and hydrogen. The structure of $H_2Os_3(CO)_{12}$ is not known at present. Pyrolysis of this compound yields other carbonyl hydrides with varying stoichiometries.

Air stable cationic complexes, $[HRu_3(CO)_{12}]^+PF_6^-$ and $[HOs_3(CO)_{12}]^+PF_6^-$, are obtained when NH_4PF_6 is added[286–290] in the solution of $M_3(CO)_{12}$ in 98% sulphuric acid. In the ir spectra[288,289] of these protonated species, increased number of carbonyl absorption bands are observed. It may be attributed to the lowering of symmetry in these molecules than the D_{3h} symmetry of $M_3(CO)_{12}$. No definite evidence for the bridging nature of the hydride ligand has been found. The A′ and E′ vibrations of the D_{3h} symmetry of $M_3(CO)_{12}$ are transformed by the proton into corresponding A_1 and (A_1+B_2) vibrations of C_{2v} symmetry. In the neutron spectrum of the cation, $[HOs_3(CO)_{12}]^+$, two bands one at 160 ± 4 cm^{-1}(s) and the other at 112 ± 5 cm^{-1}(sh), have been recorded. These bands have been assigned[290] to the two A_1 cluster frequencies by analogy with $H_3Mn_3(CO)_{12}$.

D. (d) Tetranuclear

Only two tetranuclear, $H_4M_4(CO)_{12}$ and $H_2M_4(CO)_{13}$, species each of ruthenium[12,20,291–295] and osmium[36,39,238,295] are known. The treatment of $Ru_3(CO)_{12}$ with aqueous methanolic KOH followed by careful acidification produces a mixture of red $H_2Ru_4(CO)_{13}$ and one form (β-form) of $H_4Ru_4(CO)_{12}$. A similar mixture was also obtained by refluxing $Ru_3(CO)_{12}$ with $NaBH_4$ in tetrahydrofuran. These products are volatile, readily soluble in organic solvents and air stable in solid state but decompose in solution. $H_2Ru_4(CO)_{13}$ can be quantitatively converted into β-$H_4Ru_4(CO)_{12}$ when the former is refluxed with $NaBH_4$ in tetrahydrofuran.

For α- and β-$H_4Ru_4(CO)_{12}$, two structures, one with molecular symmetry T_d (LXIXd) and the other with molecular symmetry D_{2d} (LXIXe) may be considered. For structure (LXIXd) two ir active CO bands are expected. The possibility of this structure may be excluded due to the appearance of six ir active CO bands. The structure (LXIXe) appears to be correct because in this structure all the four hydrogen atoms are equivalent and there is close agreement between the observed (six) and calculated (five) CO bands.

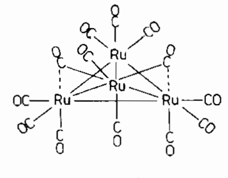


(LXIX a-e)

Recently the report of a simplified spectrum containing five CO bands for the sample[295] favours this structure. Hydrogen modes have been observed[296] in the laser-Raman spectrum of $H_4Ru_4(CO)_{12}$ at 1585 and 1290 cm^{-1}, and for the tetra deuterated derivative at 1153 and 900 cm^{-1} confirming a bridging position for the hydrogen atoms. To explain the existence of two forms, a rapid intramolecular rearrangement of the four hydrogen atoms may be considered and this possibility cannot be excluded. On this basis three structures (LXIXa, b, c) are also possible.

The corresponding osmium derivative, $H_4Os_4(CO)_{12}$, has been obtained along with the trinuclear derivatives $HOs_3(CO)_{10}(OH)$, $H_2Os_3(CO)_{10}$ and $H_2Os_4(CO)_{13}$ when $Os_3(CO)_{12}$ is treated[36,39,238,295] with Na/Hg/CH_3OH or $NaBH_4$/THF and the reaction mixture is acidified. Unlike $H_4Ru_4(CO)_{12}$ it exists in only one form. The spectrum of $H_4Os_4(CO)_{12}$ bears less resemblance to that of α- or β-$H_4Ru_4(CO)_{12}$ although all three compounds exhibit four strong bands in this region.

NMR,[294] ir[294] and mass spectroscopic[292,294,297] data indicate that $H_2Ru_4(CO)_{13}$ also exists in two forms (α and β). Recently[298] the structure of $H_2Ru_4(CO)_{13}$ has been examined and structure (LXX) has been established by crystallographic analysis.

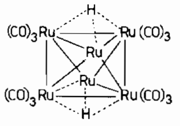


(LXX)

The two crystallographically independent $H_2Ru(CO)_{13}$ molecules have similar configuration with two metal tetrahedrally disposed. Eleven of the thirteen CO groups are terminally bound; the other two CO groups form asymmetric Ru–C–Ru bridges with average Ru–C and Ru····C distances of 1.94 and 2.40 Å respectively. Two different metal–metal distances are observed; each molecule has two long Ru–Ru distances of mean value 2.93 Å and four shorter distances averaging to 2.78 Å. Indirect evidence implies that the hydrogen atoms are situated in bridging configurations on the two long Ru–Ru edges. The ir spectrum of analogous $H_2Os_4(CO)_{13}$ is complicated in the νCO region, however, it closely resembles with the spectrum of $H_2Ru_4(CO)_{13}$ except for the presence[36] of bridging CO groups. No further structural details are known for $H_2Os_4(CO)_{13}$.

E. Hexanuclear

Only one hexanuclear compound, $H_2Ru_6(CO)_{18}$, is known so far. This is the first noncarbide containing octahedral metal carbonyl cluster[299] known, which is outside the cobalt triad. It is prepared by reducing $Ru_3(CO)_{12}$ with mononuclear carbonyl anions, acidifying the mixture, and subsequently extracting with CH_2Cl_2. Its ir spectrum[299] suggests a highly symmetrical structure. It crystallizes in the centrosymmetric monoclinic space group. It has precise C_i and approximately D_{3d} symmetry.[300] The six Ru atoms define an octahedron (LXXI), each Ru atom being associated with three terminal carbonyl groups. A consideration of the symmetrical enlargement of (and distortion of CO groups away from) two opposite faces of each octahedral Ru_6 cluster leads to postulate the presence of triply bridging hydride ligand at mutually *trans* sites.



(LXXI)

10. Substituted Derivatives of Carbonyl Hydrides

A. Derivatives of $H_2M(CO)_4$

The hydrocarbonyls, $H_2M(CO)_4$ (M = Ru, Os), form well characterised derivatives (Table XVI) and they have been classed into three types, $H_2M(CO)_{4-x}L_x$, $HM(CO)_4L$ and $HM(CO)_{4-x}L_xL'$ whose preparative methods are given below:

$H_2Ru(CO)(Ph_3P)_3$ was obtained by the addition of ethanolic solution of $RuCl_3$, HCHO and $NaBH_4$ to a well stirred boiling solution of Ph_3P. Introduction of formaldehyde[92,301] solution to the reaction mixture prior to the addition of $NaBH_4$ is essential and provides simple one stage synthesis.

Monosubstituted derivatives, $H_2M(CO)_3L$, have been obtained by the reaction of hydrogen[82,83,302] on substituted metal carbonyls.

More highly substituted metal carbonyl hydrides are obtained by the carbonylation[303–306] of substituted metal hydrides.

$MH_2L_4 + CO \rightarrow H_2M(CO)L_3$ (M = Ru; L = Ph_3P, $PhPMe_2$; M = Os; L = Ph_3P, Ph_2PMe, Ph_2PEt, $PhPMc_2$, $PhPEt_2$, Ph_2AsEt, $PhAsEt_2$)

$OsH_4L_3 + CO \rightarrow H_2Os(CO)L_3$ (L = $PhPMe_2$, $PhPEt_2$, Ph_2PMe, Ph_2PEt, Ph_2AsEt)

Mono- and disubstituted derivatives in case of osmium have also been obtained by the reactions of suitable ligands[235,236] on $H_2Os(CO)_4$.

The displacement of one hydrido group has been achieved by the reaction[213] of trialkyl-silanes, -germanes and -stannanes on $M_3(CO)_{12}$, $[(R_3M')M(CO)_4]_2$ or $[(R_3M')M(CO)_4]^-$. The compounds formed are trisilyl, trigermyl and tristannyl derivatives of metal carbonyl hydrides, $H(M'R_3)M(CO)_4$ (M' = Si, Ge, Sn; M = Ru, Os). The deuterium[213] analogues have been prepared by using deuterated silanes.

Direct displacement of one of the hydride ligands has been achieved in $H_2Os(CO)_4$ by the reaction[226] of $SnCl_4$ forming $H(SnCl_3)Os(CO)_4$.

$HM(CO)_{4-x}L_xL'$ derivatives have been obtained by the following reaction:

$$(Me_3Sn)Ru(CO)_3(Ph_3P)I + NaBH_4 \rightarrow HRu(CO)_3(Ph_3P)(SnMe_3)$$

Sodium borohydride reacts[75] with $(R_3M')M(CO)_3LX$ to produce $HM(CO)_3(Ph_3P)(R_3M')$.

Metal halides and hexachlorometallates react[307–310] with ligands like tertiary phosphines or arsines in 2-methoxyethanol or ethylene glycol to produce the substituted hydridocarbonyl halides, $HM(CO)L_{3\text{ or }2}X$ (Table XVII). The derivatives, $HM(CO)L_3X$, have also been prepared by the reaction[306] of metal halides with $H_2Os(CO)L_3$.

The five-coordinate complex $HOs(CO)\{P(C_6H_{11})_3\}_2Cl$ reacts with ligands like pyridine to form[301] six-coordinate complex, $HOs(CO)\{P(C_6H_{11})_3\}_2(C_5H_5N)Cl$. The addition of tetrahydrofuran to a mixture of $H_2Os(CO)L_3$ and mercuric chloride gives $HOs(CO)L_3(HgCl)$(L = Ph_2PEt, $PhPMe_2$, $PhPEt_2$). Deuterium analogues of six coordinated species have been obtained by deuterium exchange reactions.[311]

On refluxing substituted ruthenium carbonyl halides with KOH or alkali metal halides in 2-aminoethanol[270] several substituted ruthenium carbonyl hydrides of the type $HM(CO)L_3X$ are formed.

Reactions of sodium borohydride or lithium aluminium deuteride on $Os(CO)(PhPMe_2)_3Cl$ lead to the formation[312] of $HOs(CO)(PhPMe_2)_3Cl$ or $DOs(CO)(PhPMe_2)_3Cl$. Several substituted ruthenium hydrido carbonyl halides containing different ligands have been obtained by direct ligand exchange reaction.[313]

Among the mononuclear substituted metal carbonyl hydrides, in addition to the neutral species described above, only one cationic species $[HOs(CO)_3(Ph_3P)_2]^+$ has been investigated. Strong acids react[302] with $Os(CO)_3(Ph_3P)_2$ to form this cationic hydrido complex. Its salts with anions HCl_2^-, Br^-, ClO_4^-, BF_4^- and PF_6^- are known. The ir spectra of different salts in the CO stretching region indicate a *trans* arrangement of the phosphine ligands. The cation is inert to further exchange of CO by other ligands and can be reconverted to neutral $Os(CO)_3(Ph_3P)_2$ by the action of bases.

B. Derivatives of $H_2M_2(CO)_8$

Only osmium compounds are known in this class (Table XVI). The synthesis of both CO displaced[261] and hydrido ligand displaced[226] derivatives has been carried out.

$$H_2Os_2(CO)_8 + Ph_3P \rightarrow H_2Os(CO)_6(Ph_3P)_2$$

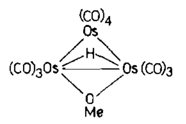
$$H_2Os_2(CO)_8 + SnCl_4 \rightarrow HOs_2(CO)_8SnCl_3$$

C. Derivatives of $H_2M_3(CO)_{10}$

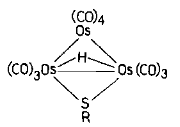
Triruthenium and triosmium dodecarbonyls react with thiols[314] to produce the trinuclear hydridocarbonyl complexes $HM_3(CO)_{10}(SR)$ (Table XVI).

These complexes are volatile and are soluble in organic solvents. A sulphur bridged compound, $HRu_3(CO)_9S$, has been prepared by treating[315] $HRu_3(CO)_{10}(SEt)$ with H_2SO_4 and heating the solution for 30 min. The ir spectra of $HM_3(CO)_{10}SR$ derivative in the CO region indicate that they are of low symmetry. The spectra closely resemble[36,39] the spectrum of $HOs_3(CO)_{10}(OMe)$ indicating that the structures are similar. Bands due to bridging carbonyl groups have not been observed. The NMR, mass spectra and single crystal X-ray diffraction studies indicate the structures (LXXII) and (LXXIII) for $HOs_3(CO)_{10}(OMe)$ and $HOs_3(CO)_{10}(SR)$, respectively.

Treatment of a sulphuric acid solution of $Os_3(CO)_9(Et_3P)_3$ with aqueous ammonium hexafluorophosphate[286] gave both $[H_2Os_3(CO)_9(Et_3P)_3](PF_6)_2$ and $[HOs_3(CO)_9(Et_3P)_3](PF_6)$. Conductance measure-



(LXXII)



(LXXIII)

ments of these complexes in nitrobenzene are consistent with their formulation as 2 : 1 and 1 : 1 electrolytes, respectively. Using methyldiphenylphosphine as ligand only the 1 : 1 electrolyte, $[HOs_3(CO)_9(PMe_2Ph)]^+(PF_6)^-$, has been isolated.[286] The complexes $[HOs_3(CO)_9L_3]^+(PF_6)^-$ ($L = PEt_3$ or $PMePh_2$) exist in two forms (yellow and orange).

$HOs_3(CO)_{10}(SPh)$ readily dissolves[287] in conc. H_2SO_4 to produce the cationic hydride species $[H_2Os_3(CO)_{10}(SPh)]^+$ (α-form). In the NMR spectrum[287] two resonances are observed in the high field region and on this basis the hydrido ligands are considered to be nonequivalent. On heating the solution at 100° C for 1 hr, a new isomer is produced (β-form). Reaction of $HOs_3(CO)_{10}(SPh)$ with Et_3P gave three products, $HOs_3(CO)_9(Et_3P)(SPh)$ and $HOs_3(CO)_8(Et_3P)(SPh)$ (two isomers of latter product). With $PMePh_2$ similar

TABLE XVI. Substituted Hydrido Carbonyls of Ru and Os.

Compound	Preparation	νCO (cm^{-1})	Reference
$H_2Ru(CO)(Ph_3P)_3$	a, c	1943	92, 301
$H_2Ru(CO)_2(Ph_3P)_2$	b		83
$H_2Ru(CO)(Ph_2PMe)_3$	c		305
$H_2Ru(CO)_3(Ph_3P)$	b		83
$HRu_3(CO)_9(C_6H_9)$			317
$HRu_3(CO)_7(C_{24}H_{33})$	d	2054, 2018, 1998, 1965	316, 318
$HRu_3(CO)_9(C_{12}H_{15})$	d	2096, 2070, 2045, 2027, 2015, 2007, 1995, 1973	316
$HRu_3(CO)_9(C_{12}H_{17})$	d	2087, 2058, 2033, 2017, 2009, 2002, 1994, 1990, 1982, 1972	316
$HRu_3(CO)_{10}(SC_2H_5)$	e	2105, 2064, 2056, 2026, 2012, 2008, 1994*	314
$HRu_3(CO)_{10}(SC_4H_9)$	e	2105, 2064, 2056, 2025, 2012, 2007, 1994*	314
$HRu_3(CO)_9S$	f	2118, 2085, 2061, 2050, 2020, 2011, 2000, 1995, 1968*	315
$HRu(CO)_3(Ph_3P)(Me_3Sn)$	g	2061, 2009, 1989*	75
$H_4Ru_4(CO)_{11}\{(OMe)_3P\}$		2097, 2068, 2060, 2032, 2030, 2017, 2008, 1974	296
$H_4Ru_4(CO)_{10}\{(OMe)_3P\}_2$		2080, 2059, 2039, 2023, 2001, 1967	296
$H_4Ru_4(CO)_9\{(OMe)_3P\}_3$		2067, 2033, 2014, 1998, 1985, 1976, 1962	296
$H_4Ru_4(CO)_8\{(OMe)_3P\}_4$		2025, 1970	296
$HOs(CO)_4(Me_3Si)$	h	2119, 2050, 2036, 2029	213
$DOs(CO)_4(Me_3Si)$	h	2118, 2045, 2031, 2023	213
$HOs(CO)_4(Et_3Si)$	h	2118, 2050, 2036, 2028	213
$HOs(CO)_4(Me_3Sn)$	h	2113, 2049, 2034, 2026	213
$HOs(CO)_4(Et_3Ge)$	h	2116, 2050, 2033, 2028	213
$HOs(CO)_4(Cl_3Sn)$	i		213
$H_2Os(CO)_2(Ph_3P)_2$	b, i	2015, 1995**	83, 235, 302
$H_2Os(CO)_2(Bu_3P)_2$	i		235
$H_2Os(CO)_3(Ph_3P)$	b, i		82, 83, 235, 236
$H_2Os(CO)(Ph_3P)_3$	c		304
$H_2Os(CO)(PhPMe_2)_3$	c		303, 306
$H_2Os(CO)(PhPEt_2)_3$	c		303, 306
$H_2Os(CO)(PhAsEt_2)_3$	c		303, 306
$H_2Os(CO)(Ph_2PMe)_3$	c		303, 306
$H_2Os(CO)(Ph_2PEt)_3$	c		303, 306
$H_2Os(CO)(Ph_2AsEt)_3$	c		303, 306
$H_2Os_2(CO)_6(Ph_3P)_2$	j	2109, 2073, 2029, 2008, 1979, 1959, 1915***	261
$HOs_3(CO)_{10}(OH)$	k	2110, 2072, 2060, 2027, 2025, 2006, 1989*	36, 39
$HOs_3(CO)_{10}(OMe)$	k	2112, 2071, 2060, 2038, 2025, 2000, 1990, 1985*	36, 39
$HOs_3(CO)_{10}(SC_2H_5)$	e	2105, 2064, 2047, 2031, 2022, 2017, 2001, 1997, 1987, 1981	314
$HOs_3(CO)_{10}(SPh)$	e	2106, 2067, 2057, 2024, 2018, 2000, 1986, 1980	314
$HOs_3(CO)_{10}(SBu)$	e	2104, 2065, 2056, 2022, 2018, 2000, 1997, 1984, 1959, 1947	314

TABLE XVI. (Cont.)

Compound	Preparation	νCO (cm^{-1})	Reference
$HOs_3(CO)_9(Ph_3P)(Ph_2PC_6H_4)$	e		107
$HOs_3(CO)_8(Ph_3P)(Ph_2PC_6H_4)$	e		107
$HOs_3(CO)_7(Ph_3P)(Ph_2P)(C_6H_4)$	e		107
$HOs_3(CO)_7(Ph_2P)\{(Ph_2P(C_6H_4C_6H_3)\}$	e		107
$[HOs(CO)_3(Ph_3P)_2]HCl_2$		2120, 2080, 2030**	302
$[HOs(CO)_3(Ph_3P)_2]Br$		2120, 2080, 2030**	302
$[HOs(CO)_3(Ph_3P)_2]ClO_4$		2125, 2075, 2035**	302
$[HOs(CO)_3(Ph_3P)_2]BF_4$		2125, 2075, 2035**	302
$[HOs(CO)_3(Ph_3P)_2]PF_6$		2125, 2075, 2035**	302
$[H_2Os_3(CO)_9(Et_3P)_3](PF_6)_2$	a	2094, 2069, 2060, 2017, 1993, 1937†	286
$[HOs_3(CO)_9(Et_3P)_3]PF_6$	a	2104, 2075, 2057, 2045, 2026, 1978***	286
$[HOs_3(CO)_9(Ph_2PMe)_3]PF_6$	a	2110, 2081, 2067, 2050, 2028, 1986***	286
$[HOs_3(CO)_9(Et_3P)_3]PF_6$	b	2095, 2058, 2016, 1990, 1954***	286
$[HOs_3(CO)_9(Ph_2PMe)_3]PF_6$	b	2098, 2064, 2020, 1986, 1970, 1959***	286

* Cyclohexane. ** KBr. *** Chloroform. † Acetone.

Reactions of [a] $RuCl_3$ with $NaBH_4$ and Ph_3P in presence of CO. [b] $M(CO)_3(Ph_3P)_2$ with hydrogen. [c] Carbonylation of MH_2L_4. [d] $Ru_3(CO)_{12}$ with cyclododeca-1,5,9-triene. [e] $M_3(CO)_{12}$ with thiols or *t*-phosphines. [f] $HRu_3(CO)_{10}(SEt)$ with H_2SO_4. [g] $NaBH_4$ with $(Me_3Sn)Ru(CO)_3(Ph_3P)I$ at 0° C. [h] $Os_3(CO)_{12}$ with $R_3M'H$. [i] $H_2Os(CO)_4$ with *t*-phosphines or $M'X_4$. [j] $H_2Os_2(CO)_8$ with *t*-phosphines or $M'X_4$. [k] OsO_4 with CO in MeOH. (M = Ru or Os; M' = Si, Ge or Sn; X = halogen; R = alkyl group).

TABLE XVII. Substituted Hydrido Carbonyl Halides of Ru and Os.

Compound	Preparation	Colour, m.p. (b.p.), °C	νCO (cm^{-1})	References
$HRu(CO)(Ph_3P)_3Cl$	a		1916, 1900*	307
$DRu(CO)(Ph_3P)_3Cl$	b			311
$HRu(CO)(PhPPr_2)_3Cl$	c	Colourless, 131–136°	1883**	270
$HRu(CO)(PhPPr_2)_3Br$	c	Colourless, 126–128°	1880**	270
$HRu(CO)(PhPPr_2)_3I$	c	Yellow, 118–127°	1894**	270
$HRu(CO)(PhPBu_2)_3I$	c			270
$HRu(CO)(PhPBu_2)_3Br$	c		1916**	270
$HRu(CO)(PhPMe_2)_3Cl$	c	Cream, 91–92°	1916***	270
$HRu(CO)(PhAsMe_2)_3Cl$	c	Yellow, 183–188°	1913†	270
$HRu(CO)(PhPEt_2)_2(PhPMe_2)Cl$	d	108–112°	1906**	313
$HRu(CO)(PhPPr_2)_2(PhPMe_2)Cl$	d	110–115°	1906**	313
$HRu(CO)(PhPBu_2)_2(PhPMe_2)Cl$	d	110–116°	1905**	313
$HOs(CO)(Ph_3P)_3Cl$	a	Colourless, 179°	1911†	307, 308
$HOs(CO)(Ph_2PMe)_3Cl$	d			306
$HOs(CO)(Ph_3P)_3Br$	a	Colourless, 172°	1915†	307, 308, 309
$HOs(CO)(Ph_3As)_3Cl$	a	Colourless, 200°	1906†	308
$HOs(CO)(Ph_3As)_3Br$	a	Tan, 195°	1910†	308
$HOs(CO)(PhPMe_2)_3Cl$	e	White, 143–145°	1901†	312
$DOs(CO)(PhPMe_2)_3Cl$	e	White, 141–144°	1904†	312
$DOs(CO)(Ph_3P)_3Cl$	b			311
$DOs(CO)(Ph_3P)_3Br$	b			311
$HOs(CO)\{(C_6H_{11})_3P\}_3Cl$	a	Red, 210°	1932, 1887††	310
$HOs(CO)\{(C_6H_{11})_3P\}_2(Py)Cl$	a	Yellow	2119, 1870††	310

* Mull phase. ** Hexane. *** Benzene. † Chloroform. †† KBr.

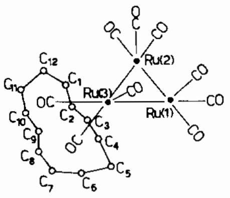
Reactions of [a] *t*-phosphines or pyridine with metal halides or hexahalometallate dianion in presence of 2-methoxyethanol. [b] D_2 with $HM(CO)(Ph_3P)_2X$. [c] KOH and MX with $Ru(CO)L_3Cl_2$ or $Ru_2(CO)_2L_6(\mu\text{-}Cl_3)Cl\cdot H_2O$ respectively. [d] Phosphines or HX with $HRu(CO)(PhPMe_2)_3Cl$ or $H_2Os(CO)L_3$ respectively. [e] Refluxing $NaBH_4$ or $LiAlD_4$ with $Os(CO)(PhPMe_2)_3Cl_2$.

products were observed, but only $HOs_3(CO)_9(PMePh_2)(SPh)$ in two isomeric forms was isolated. Protonation of these derivatives occurs in H_2SO_4 to give $[H_2Os_3(CO)_9(SPh)L]^+$ (L = Et_3P or $PMePh_2$) and $[H_2Os_3(CO)_8(Et_3P)_2(SPh)]^+$ which could be isolated as hexafluorophosphate salts. Evidences for the doubly protonated species $[H_3Os_3(CO)_8(Et_3P)_2(SPh)]^{2+}$ have also been found.

D. Hydrocarbon Bonded Derivatives

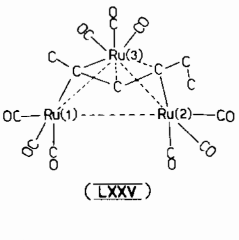
The reaction of cyclopentadiene with $Ru_3(CO)_{12}$ yields $HRu(CO)_2(\pi\text{-}C_5H_5)$ quantitatively, via intermediate formation of $Ru(CO)_3(2\text{-}5\text{-}\eta\text{-cyclopentadiene})$. The osmium analogue was obtained by the action of cyclopentadiene on $H_2Os_3(CO)_{10}$.

Cyclododeca-1,5,9-triene reacts[316] with $Ru_3(CO)_{12}$ to give dehydrogenation and subsequent isomerization of three hydrido–carbonyl cluster compounds, $HRu_3(CO)_9(C_{12}H_{15})$, $HRu_3(CO)_9(C_{12}H_{17})$, $HRu_3(CO)_7(C_{24}H_{33})$ along with the hydrocarbon complex $Ru_4(CO)_{10}(C_{12}H_{16})$. The crystal structure[316] of the first compound has been investigated. Three ruthenium atoms are situated on the apices of a triangle in which Ru(1)–Ru(3) = 2.773 Å, Ru(2)–Ru(3) = 2.779 Å and Ru(1)–Ru(2) = 2.921 Å. Each ruthenium atom carries three CO groups. The mean Ru–C and the C–O bond distances are 1.85 Å and 1.19 Å, respectively. The monocyclic σ-1,3-$h^2\pi$-1,2,3-h^3-cyclododeca-1,6,9-trienyl ligand is attached by an allylic bonding arrangement involving only three carbon atoms (LXXIV).



(LXXIV)

A similar derivative, $HRu_3(CO)_9(C_6H_9)$ (LXXV), has also been prepared by the action[317] of *cis, trans* or *trans, trans*-hexa-2,4-diene on $Ru_3(CO)_{12}$ by another rearrangement.



(LXXV)

Mixed carbonyl hydrides containing one hydrocarbon and one P(III) donor ligands are also known. Thus $HRu_3(CO)_7(C_{12}H_{15})L_2$ (L = $P(OMe)_3$, $P(OCH_2)_3CEt$, PMe_2Ph), $HRu_3(CO)_6(C_{12}H_{15})L_3$ (L = $P(OMe)_3$, $P(OCH_2)_3CEt$) and $HRu_3(CO)_7(C_{12}H_{15})\{P(OMe)_3\}_2$ derivatives have been obtained by the action[318] of substituted phosphines or phosphites on $HRu_3(CO)_9(C_{12}H_{15})$.

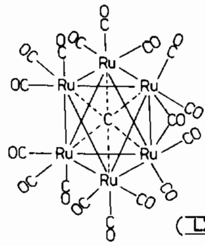
The reaction of ethylene with $Os_3(CO)_{12}$ gives the compound $H_2Os_3(CO)_9(CCH_2)$.[129] By ^1H NMR spectrum, it was suggested that the complex contained vinylidene (CCH_2) rather than coordinated acetylene (HCCH) which would have been analogous to the complex derivatived from cyclic mono-olefins[130] and $M_3(CO)_{12}$ (M = Ru or Os). The conversion into the ethylidene complex $H_3Os_3(CO)_9(CCH_3)$ occurs on bubbling H_2 through a refluxing n-heptane solution of $H_2Os_3(CO)_9(CCH_2)$ for 24 hr. This product is the Os analogue of $H_3Ru_3(CO)_9(CCH_3)$ prepared from α-$H_4Ru_4(CO)_{12}$ and ethylene.[130]

Reaction of $Os_3(CO)_{12}$ with Ph_3P in a mole ratio of 1:2 gave a mixture of products among which were the unusual new compounds,[107] $HOs_3(CO)_9(Ph_3P)(PPh_2C_6H_4)$, $HOs_3(CO)_8(Ph_3P)(PPh_2C_6H_4)$ and $HOs_3(CO)_7(PPh_2)(Ph_3P)(C_6H_4)$. The compounds were separated by fractional crystallization and chromatography on alumina column. Decomposition of $Os_3(CO)_{10}(Ph_3P)_2$ led to a similar mixture which also induced the compound $HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4\cdot C_6H_3)$.

The trisubstituted complexes $Ru_3(CO)_{12-n}\{P(OR)_3\}_n$ (R = Ph, n = 2 or 3), (R = *p*-tolyl, n = 3) undergo intramolecular metallation and degradation reactions in refluxing decalin[319] to give $H_4Ru_4(CO)_9\{P(OPh)_3\}_3$ and $HRu_2(CO)_3\{P(OC_6H_3R)(OC_6H_4R)_2\}_2\{OP(OC_6H_4R)_2\}$ (R = H or Me) along with $Ru(CO)_2\{P(OC_6H_3R)_2\}_2$ (R = H or Me).

11. Carbonyl Carbide Complexes

Only very few polynuclear ruthenium carbonyl compounds containing a cluster of six atoms are known. $Ru_6(CO)_{17}C$ (Structure LXXVI) has been obtained by the treatment of appropriate arene ligands[160,320,321] like toluene, xylene, mesitylene and azulene on triruthenium dodecacarbonyl in aliphatic hydrocarbons. Using the first three arenes, arene substituted carbonyl carbides[320,321] $Ru_6(CO)_{14}C(Ar)$ (Ar = arene) (Structure LXXVII) have also been isolated. Azulene yields[160] only $Ru_6(CO)_{17}C$ along with other hydrocarbon substituted complexes which do not come in this category. Several aliphatic hydrocarbons like n-octane or n-nonane also yield $Ru_6(CO)_{17}C$ along with hydrido complexes,[292,293] $H_2Ru_4(CO)_{13}$ and β-$H_4Ru_4(CO)_{12}$, when $Ru_3(CO)_{12}$ is refluxed in these solvents. It may be due to the hydrogen abstraction from an alkane (solvents, n-octane, n-nonane) by a metal carbonyl to produce a hydrido–carbonyl metal compound. In all these reactions an excess of the solvent was necessary to ensure reasonable yields of the compound. The mesitylene complex has been prepared by the irradiation of $Ru_3(CO)_{12}$ in mesitylene for 24 hr. The source of the carbon atom in these compounds is unknown. However, in view of the comparative ease with which these compounds are produced in both aromatic and aliphatic solvents, it is reasonable to assume that the carbon atom arises from reduction of a carbonyl group, as in case of $Fe_5(CO)_{15}$.[322]



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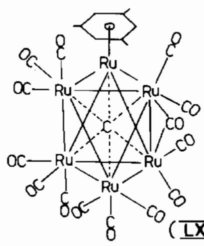


(LXXVII)

The carbide complexes are stable in air and soluble in most of the organic solvents. They are nonvolatile under normal preparative conditions, but sufficiently volatile at 10^{-6} mm of mercury.

In the ir spectrum[320,321] of $Ru_6(CO)_{17}C$ only one bridging and five terminal CO bands (νCO: 1854, 2064, 2049, 2007, 1993 and 1958 cm^{-1}) have been observed, which is in agreement with the C_{2v} symmetry of the molecule. The number of terminal bands increases to seven in case of arene substituted derivatives. This may be due to the lowering of symmetry (C_s). For either of these symmetries at least 13 terminal bands are predicted. Apparently, many of the CO stretching vibrations are accidentally degenerate or have not been resolved.

The mass spectra[321] of these complexes provide the major evidence for their formulation as hexanuclear ruthenium carbonyl carbide compounds. With a simple carbonyl the ion, $[Ru_6(CO)_{17}C]^+$, was observed in high abundance together with the ions $[Ru_6(CO)_xC]^+$ ($x = 0-16$) corresponding to the step-wise loss of 17 CO groups.

The complete crystal structure of the mesitylene derivative, $Ru_6(CO)_{14}(C_6H_3Me_3)C$, has been examined by X-ray diffraction[323] method. The monoclinic unit cells belong to the space groups P_{21} or $P_{21/m}$ with *a* 9.465, *b* 15.825, *c* 10.563 Å. The carbon atom of carbide lies very close to the centre of the slightly distorted octahedron of ruthenium atoms. Three Ru atoms have three terminally coordinated CO groups and 2 Ru atoms are bridged by a single CO group and have 2 terminal CO; the 6th Ru atom is bonded to the arene, the carbide atom, and 4 adjacent Ru atoms. All the Ru atoms are therefore effectively 8-coordinated.

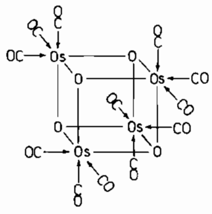
The reactions of $Ru_6(CO)_{17}C$ with donor ligands L (L = Ph_3P, $(C_6H_4F)_3P$ or Ph_3As) have been investigated and the monosubstituted compounds[294] of the type $Ru_6(CO)_{16}(L)C$ have been characterised.

12. Polynuclear Oxocarbonyls

Ruthenium does not form oxocarbonyls. Two polynuclear oxocarbonyls of osmium are known. The first one is tetranuclear while the second is hexanuclear. The formation of tetranuclear compound, $Os_4O_4(CO)_{12}$ (νCO: 2089, 2079, 2019, 1984 and 1953 cm^{-1} in nujol; 2097, and 2012 cm^{-1} in $CHCl_3$), has been observed in the preparation of $Os_3(CO)_{12}$ from OsO_4.

The mass spectrum[48] shows that the ions of the type $[Os_4O_4(CO)_n]^+$ ($n = 0-12$) occur in high abundance, whereas ions corresponding to the breakup of the Os_4 nucleus are not observed until all the CO groups have been removed.

The crystal structure of $Os_4O_4(CO)_{12}$ has been determined by X-ray diffraction[324] and found to contain four equivalent Os atoms (LXXVIII) arranged in the form of a cube with $Os(CO)_3$ groups alternating with the oxygen atoms at the corners. The cube skeleton is slightly distorted by a movement of the oxygen atoms closer to its centre than the osmium atoms.



(LXXVIII)

The Os–C distances, 1.91 and 1.92 Å, are comparable with those found in $Os_3(CO)_{12}$, 1.95 Å, while the two independent Os–Os distances, 3.253 and 3.190 Å, are considerably longer than the Os–Os bond distances of 2.88 Å in $Os_3(CO)_{12}$. This suggests that there is no metal–metal bonding in the oxocarbonyl in contrast to the suggestions of King[325] who assumed it to be an acid–base adduct. Both distances are longer than that reported[326] (3.05 Å for the Os–Os distance in $[Os_2O_6(NO_2)_4]^{4-}$). The O–Os–O angles are 78° and 76°, and the Os–O–Os angles are 100° and 103°.

Another oxocarbonyl, which was hexanuclear, was observed[37] as an orange yellow compound in traces during the preparation of $Os_3(CO)_{12}$ by the reaction of OsO_4 in xylene with CO at 175° C and at 175 atm pressure for 24 hr. It has been identified as $Os_6O_6(CO)_{16}$ by mass spectrometry.[327] The parent ion was observed with the expected isotopic pattern and the predominant fragmentation scheme involved successive loss of sixteen carbon monoxide groups. The doubly charged ions $[Os_6O_6(CO)_n]^{2+}$ ($n = 0-16$) and various fragments of the Os_6O_6 cluster were also observed.

The structure of $Os_6O_6(CO)_{16}$ is based on an octahedral arrangement of six osmium atoms. As there is no indication of bridging carbonyls in the ir spectrum[327] (νCO: 2106s, 2092sh, 2022s, 1993s, 1976sh, 1964sh, 1926s and 1890w cm^{-1} in nujol), it is likely that all the carbonyl groups are terminal, four of the osmium atoms being bound to three carbonyl groups and the remaining two to two carbonyl groups.

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