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ICA Reviews

Advances in Platinum Metal Carbonyls and Their Substituted Derivatives.
II. Rhodium, Iridium, Palladium and Platinum Carbonyls

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Contents

1. Introduction

In Part I of this publication[1] we have reviewed different aspects of ruthenium and osmium carbonyls. In this part several aspects of rhodium, iridium, palladium and platinum carbonyls and their substituted derivatives have been described.

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

2. Rhodium and Iridium

A. Binary Carbonyls

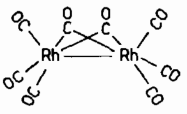
Rhodium and iridium form three types of binary carbonyls, namely, $M_2(CO)_8$, $M_4(CO)_{12}$ and $M_6(CO)_{16}$.

$M_2(CO)_8$ Class

In 1943, Hieber and Lagally[2] reported the preparation of dirhodium octacarbonyl (orange, m.p. 76° C d) by the reaction of carbon monoxide on freshly prepared rhodium metal at 460 atm pressure and 200° C. There has been no subsequent confirmatory evidence[3] to support the existence of this compound. However, IR spectral evidence[4] for the reversible formation of bridged form of $Rh_2(CO)_8$ from $Rh_4(CO)_{12}$ under high pressure of carbon monoxide (490 atm) and low temperature (–19° C) has been presented:

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

The band maxima at 2086s, 2061s, 1860mw and 1845s cm^{-1} suggest that probably the bridged form of $Rh_2(CO)_8$ (I) is stabilised under these conditions. No evidence has been obtained for the formation of a non-bridged isomer of $Rh_2(CO)_8$ in contrast to the $Co_2(CO)_8$[5] system.



(I)

A similar attempt to prepare $Ir_2(CO)_8$ from $Ir_4(CO)_{12}$ was unsuccessful[6], although its formation (yellow green solid) by heating the trihalide at 100 to 140° C with CO at 350 atm pressure has already been claimed by Hieber and Lagally[7]. Structural details are not available for this compound.

$M_4(CO)_{12}$ Class

Originally $Rh_4(CO)_{12}$ was prepared by Hieber and Lagally[2] by the action of CO on anhydrous binary halides of rhodium at high temperature and pressure in presence of Cu or Ag.

The improved method of preparation of this compound is by the carbonylation of $[Rh(CO)_2Cl]_2$ in presence of different catalysts like Ullmann Cu-bronze powder,[8,9] alkali[10] or water[11,12] under varying conditions of temperature and pressure. The carbonylation of aqueous solution of $RhCl_3$ at room temperature and pressure also yields[13] this product.

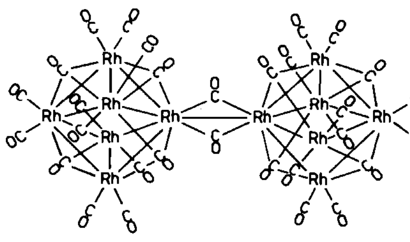
On reducing[14] $[Rh(CO)_2Cl]_2$ with CO in presence of alkali solution the evidence for the formation of anions has also been obtained:

$$Rh_2(CO)_4Cl_2 \xrightarrow[H_2O]{CO} Rh_4(CO)_{12} \xrightarrow[OH^-]{CO} [Rh_{12}(CO)_{30}]^{2-}$$

$$\xrightarrow[OH^-]{CO} [Rh_7(CO)_{16}]^{3-} \xrightarrow[OH^-]{CO} [Rh_6(CO)_{14}]^{4-}$$

$$\xrightarrow[Na]{CO} [Rh(CO)_4]^-$$

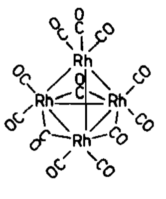
X-ray and ^{13}C NMR spectral measurements[15] of $[Rh_{12}(CO)_{30}]^{2-}$ show the presence of three inequivalent terminal carbonyls, one type of doubly bridging carbonyls and two types of inequivalent triply bridging carbonyls (II)



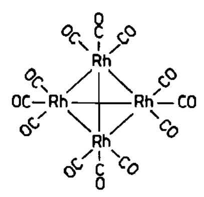
(II)

Firstly, $Ir_4(CO)_{12}$ was prepared by Hieber and Lagally[7] by heating iridium trihalides with CO at 200 atm in a Cu vessel. Later on it was obtained by the carbonylation of iridium halides[9,16] or alkali metal hexachloroiridates[6,17,18] under 40–100 atm pressure and 60 to 100° C in alcohols.

Different experimental techniques like vibrational spectra,[19,20] NMR[21] and X-ray[22–24] have been employed for the structural determination of $Rh_4(CO)_{12}$. It has a C_{3v} symmetry (IIIa) based on a tetrahedron of four Rh atoms with three bridging and two terminal CO groups for each of the three Rh atoms. The fourth metal atom is bonded through three terminal CO groups. Five terminal $(2A_1+3E)$ and two bridging (A_1+E) CO stretching frequencies are expected in the IR and Raman spectra. Of these only three terminal (2109, 2066 and 2026 cm^{-1}) and two bridging (1828 and 1817 cm^{-1}) frequencies have been obtained in the Raman spectrum.[19] In the far-infrared spectrum[20] four bands have been assigned as 225 cm^{-1}, E; 200 cm^{-1}, E; 176 cm^{-1}, A_1; and 128 cm^{-1}, A_1. Griffith and Wickham[19] have reported absorptions at 221, 173 and 134 cm^{-1} in the Raman spectra but no assignments have been given. In the crystal of $Rh_4(CO)_{12}$ the six Rh–Rh bond distances[23] range from 2.70 to 2.80 Å with no apparent difference in lengths between three carbonyl-bridged basal–basal Rh–Rh bonds and the three apical–basal Rh–Rh bonds. A ^{13}C NMR[21,25] study of $Rh_4(CO)_{12}$ shows that rapid scrambling of CO groups does occur at higher temperature (T_d symmetry) by a single process. It has the same structure in solution as in the crystal.[21] These observations are important in demonstrating the generality of rapid permutational isomerization reactions through the agency of bridge–terminal interconversion of CO groups (IIIb).

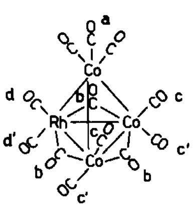


(IIIa)



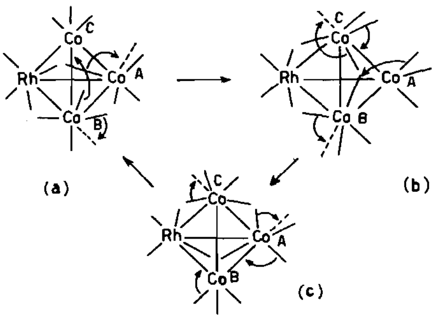
(IIIb)

In a recent communication evidence has been presented[26] for the bridge–terminal site exchange in case of a mixed metal carbonyl, $RhCo_3(CO)_{12}$[27], (IV) via two distinct and independent processes:



(IV)

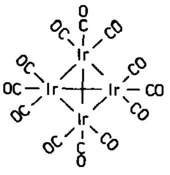
At low temperatures (–60 to –30° C) rearrangements (IVa), (IVb) and (IVc) combined lead to site exchange within the three triangular metal faces $RhCo^ACo^B$, $RhCo^BCo^C$ and $RhCo^CCo^A$ and imply a concerted interchange of bridging and terminal CO groups. These rearrangements make the carbonyl resonances due to groups a, b, b′, c and c′ to coalesce. Carbonyl groups d and d′ do not participate in this rearrangement process, however, since the process causes all cobalt atoms to become equivalent. Carbonyl groups d and d′ also become equivalent. At higher temperature (>–30° C) interconversion of all carbonyl groups occurs leading to bridge formation in any of the four triangular metal faces $RhCo^ACo^B$, $RhCo^BCo^C$, $RhCo^CCo^A$ and Co^A Co^BCo^C. These observations clearly indicate that carbonyl site exchange in carbonyl clusters is not necessarily a simple one-stage process and that such exchanges are very dependent on the disposition of the metal ions within a cluster unit:



(IV a-c)

A mixed metal carbonyl, $Co_2Rh_2(CO)_{12}$, has also been synthesised.[28]

The structure of $Ir_4(CO)_{12}$ has been investigated by vibrational spectra[6, 29–31] and X-ray crystallography.[32] The vibrational spectrum[30] of this compound suggests a T_d symmetry with no bridging CO group (ν_{CO}: 2072, 2032 cm^{-1}). The twelve CO groups are disposed around the four iridium atoms to form a cubooctahedral structure (V). The Ir–Ir distances[32] are 2.68 Å.



(V)

The low frequency Raman spectrum[29] of $Ir_4(CO)_{12}$ has been obtained by using He–Ne laser source. Three strong equally intense emissions are obtained at 208, 164 and 105 cm^{-1} which may be assigned to the A_1, F_2 and E modes of the Ir_4 cluster. Another strong band at 458 cm^{-1} is assigned to the Ir–C stretching mode. Kettle[33] has used a topological equivalent orbital treatment on $Ir_4(CO)_{12}$. This approach is based on a number of assumptions such as the fixed presence of metal–metal bonds in edge and face positions. While it does include the electrons formally involved in metal–CO π bonding, it appears that the questionable assumptions make the treatment unreliable.

$M_6(CO)_{16}$ Class

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

(i) By the action[8] of $Fe(CO)_5$ on $RhCl_3$ or $[Rh(CO)_2Cl]_2$ at atmospheric pressure in methanol.

(ii) By the CO reduction of $[Rh(CO)_2Cl]_2$ in presence of alkali[3, 10] or water[11, 12]:

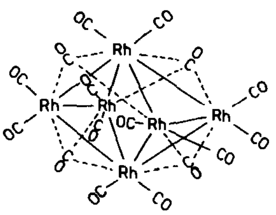
$$Rh_2(CO)_4Cl_2 \rightarrow Rh_4(CO)_{12} \rightarrow [Rh_{12}(CO)_{30}]^{2-} \xrightarrow{CO} [Rh_{12}(CO)_{34}]^{2-} \xrightarrow{\text{acid}} Rh_6(CO)_{16}$$

(iii) By the reaction[4] of CO on $Rh_4(CO)_{12}$ in a mixture of liquid paraffin and heptane at 760° C/600 atm.

(iv) By the treatment of protonated aqueous solution[13] of $Rh_2(OAc)_4$ and HBF_4 with CO (1 atm).

(v) By the action[34] of a mixture of propene and hydrogen to a toluene solution of $Rh_4(CO)_{12}$ at room temperature and pressure.

It is a black air stable solid which decomposes above 220° C. Its structure has been examined by IR[19, 35–37] and three dimensional X-ray crystal[38] studies. Vibrational spectra of $Rh_6(CO)_{16}$ suggest an overall T_d symmetry based on an octahedron of six Rh atoms with two terminal CO groups per metal atom and four bridging CO groups (VI).



(VI)

Except the F_2 mode which is IR active all the modes are Raman active. In fact, four terminal (2077, 2074, 2041 and 2016 cm^{-1}) and one bridging (1770 cm^{-1}) CO stretching frequencies appear in the IR spectra, so one of the expected Raman stretches may have been activated by crystal effects. In the IR region, absorptions at 199 and 172 cm^{-1} have been noted[19] but no attempt has been made at their assignments. X-ray crystallography[38] of the molecule is in accord with the T_d symmetry. The average Rh–Rh bond distance is 2.776 ± 0.001 Å.

Kettle has used a topological equivalent orbital treatment[39] on $Rh_6(CO)_{16}$ and found that it should be two electron deficient owing to the destabilization of an orbital of A_2 symmetry relative to an isolated metal orbital, but no experimental evidence has been obtained so far to support this view. A mixed metal carbonyl, $Co_2Rh_4(CO)_{16}$, has also been reported.[40]

$Ir_6(CO)_{16}$ has been prepared as a red crystalline substance by the carbonylation[41] of a suspension of $(Et_4N)_2[Ir_6(CO)_{15}]$ in acetic acid:

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

It is a very stable substance and has been identified by analytical data and also by the close similarity of its IR spectrum to those of the well known $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ (ν_{CO}: 2103, 2061, 2057, 2026, 2022, 2018, 1806 and 1772 cm^{-1} for $Co_6(CO)_{16}$; 2105, 2070, 2047, 2040, 2022, 2020, 1833 and 1798 cm^{-1} for $Rh_6(CO)_{16}$; 2115, 2070, 2057, 2047, 2034, 2009, 1800 and 1765 cm^{-1} for $Ir_6(CO)_{16}$).

B. *Substituted Derivatives*

A large number of substituted derivatives, which contain N, P, As, Sb, O and S donors, have been prepared. Except a few O and S donor containing products most of the mononuclear derivatives occur in cationic forms Rhodium forms substituted metal carbonyl anions also.

Group V and VI donors

Phosphine and arsine ligands react with $Rh_4(CO)_{12}$ or $Ir_4(CO)_{12}$ to give $Rh_4(CO)_{11}L$[14,42,43] (L = Ph_3P,P(p-$MeC_6H_4)_3$, P(p-$FC_6H_4)_3$, Ph_3As), $M_4(CO)_{10}L_2$[14,42–46] (M = Rh, L = Ph_3P, P(p-$MeC_6H_4)_3$, P(p-$FC_6H_4)_3$, Et_3P, $P(OCH_2)_3CEt$, $^1/_2(Ph_2PCH_2)_2$, Ph_3As; M = Ir, L = Ph_3P, Et_3P, Pr^n_3 P, Bu_3P, Pr^i_3P), $M_4(CO)_9L_3$[14,44–46] (M = Rh, L = Ph_3P, $P(OCH_2)_3CEt$; M = Ir, L = Ph_3P, Et_3P, Pr^n_3 P, Bu_3P, Pr^i_3P, P(p-$C_6H_4Me)_3$), $M_4(CO)_8$ L_4[44,45 47 48] (M = Rh, L = Ph_3P; M = Ir, L = Ph_3P, Et_3P, Bu_3P, Pr_3P, PPh_2Me, $PPhMe_2$, PPh_2Et; $AsPh_2Me$, $AsPhMe_2$, $(OPh)_3P$, $^1/_2(Ph_2PCH_2)_2$) and $Ir_4(CO)_6$ (triphosphine)$_2$[18] under varying conditions. $Ir_4(CO)_{10}$ L_2 and $Ir_4(CO)_9L_3$ have also been obtained[46] by the action of ligands (L = Ph_3P, PPh_2Me, PPh_2Et) on the salts $(Me_3PhCH_2N)_2HIr_4(CO)_{11}$ and $(Me_3PhCH_2N)_2$ $[Ir_4(CO)_{10}]_2$.

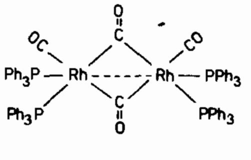
The IR spectra of $Rh_4(CO)_{11}L$ and $Rh_4(CO)_{10}L_2$ (in hexane) in the C–O region are more complex than that of the parent $Rh_4(CO)_{12}$, as would be expected because of the lowering of the molecular symmetry on replacement of one or two C–O groups by the ligands. There is, however, a similarity between the species of monosubstituted derivatives, $Rh_4(CO)_{11}L$ (L = Ph_3P, ν_{CO}: 2087, 2058, 2053, 2031, 2020, 2009, 1902, 1871 and 1857 cm^{-1}) and $Rh_4(CO)_{12}$ (ν_{CO}: 2075vs, 2070vs, 2044s and 1882 cm^{-1}) (in hexane). Thus the very strong doublet at 2075, 2070 cm^{-1} shifts to *ca.* 2058, 2053 cm^{-1} in $Rh_4(CO)_{11}(Ph_3P)$ and the bridging carbonyl frequency at 1882 cm^{-1} is split and shifts to *ca.* 1871 and 1857 cm^{-1}. This is similar to the behaviour observed with the analogous cobalt system[49] $Co_4(CO)_{11}(Ph_3P)$, (ν_{CO}: 2084, 2045, 2039, 2030, 1854.5, and 1837.5 cm^{-1}) and it seems likely that a similar species is present.

The spectra of $Rh_4(CO)_{10}L_2$ are very similar to that of $Ir_4(CO)_{10}(Ph_3P)_2$[46] (ν_{CO}: 2060s, 2030s, 2000s, 1830s and 1790s cm^{-1}). In dichloromethane spectra of $Rh_4(CO)_{10}L_2$ additional peaks at *ca.* 2087 and 2058 cm^{-1} appeared and increased slowly in intensity with time. These peaks correspond with the bands observed in the spectra of $Rh_4(CO)_{11}L$ and presumably are due to the slow rearrangement in solution to form some of the monosubstituted species. Such a rearrangement may well explain the discrepancy between the IR data for $Rh_4(CO)_{10}(Ph_3P)_2$ reported by Whyman[43] and Haszeldine *et al.*[45] The ν_{CO} frequencies reported by Haszeldine *et al*[45] are 10–15 cm^{-1} higher than those described by Whyman[43].

A crystal structure study[50] of $Ir_4(CO)_{10}(Ph_3P)_2$ shows it to consist of a tetrahedron of four iridium atoms joined by metal–metal bonds in which three basal iridium atoms are additionally supported by bridging carbonyl groups. The triphenylphosphine ligands are bonded to two of the basal iridium atoms and the remaining coordination sites are occupied by seven terminal carbonyl groups. In view of the close similarity between the IR spectra of the disubstituted Rh and Ir derivatives, it seems likely that the Rh complexes are of the same structure and this in turn suggests that initial substitution in $Rh_4(CO)_{12}$ by a phosphine or arsine occurs at one of the basal Rh atoms rather than at the apical one.

Reactions of $Rh_4(CO)_{10}L_2$ with CO under pressure, preferably in the presence of excess ligand, yield the unstable dinuclear $Rh_2(CO)_6L_2$[42,43,51] (L = Ph_3P, P(p-$MeC_6H_4)_3$, P(p-$FC_6H_4)_3$), which readily revert to the tetranuclear ones. $Ir_2(CO)_6L_2$ (L = Ph_3P, Pr_3P, P(p-$C_6H_4Me)_3$) compounds have been obtained by the treatment[44,47] of $Ir_4(CO)_9L_3$ with CO. $Ir_2(CO)_6L_2$ on further carbonylation[44,47] yield $Ir_2(CO)_7L$. Polymeric carbonyl halide, $[Ir(CO)_3Cl]_n$, on refluxing[52] with $Ph_2PK \cdot 2$Dioxane gives $[Ir(CO)_3PPh_2]_2$. The IR spectra of $Rh_2(CO)_6L_2$ in the CO region consist predominantly of a very strong band at *ca.* 1960 cm^{-1} together with shoulder at *ca.* 1980 and 1910 cm^{-1}, and the absorption patterns are very similar[53] to that observed for the dimeric non-bridged phosphine-substituted complexes of dicobalt octacarbonyl.

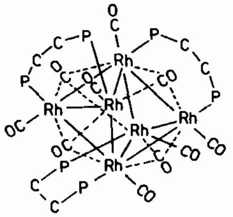
Several t-phosphine and t-arsine ligands break[43,45,54,55] the Rh_4 cluster in $Rh_4(CO)_{12}$ to form the dinuclear $L_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)L_2$ (VII) (ν_{CO} for Ph_3P complex: 2018s, 1985s, 1791s and 1766vs cm^{-1} in mull phase). These derivatives have also been prepared by the treatment[43] of $Rh_2(CO)_6L_2$ with two equivalents of L (L = t-phosphines). Carbonylation[54] of $HRh(CO)L_3$ yields similar derivatives. Similar compounds of iridium are not known.



(VII)

Tributylphosphine yields $[(Bu_3P)_3(CO)Rh]_2$ under similar conditions.[45]

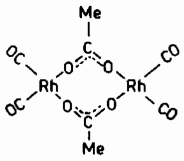
$Rh_6(CO)_{16}$ reacts with excess of t-phosphines or t-arsines in chloroform when heated under reflux to give yellow compounds, $Rh_6(CO)_7L_9$[56]. The IR spectra of these compounds are very similar in the CO streching region, with one broad band at *ca.* 1980 cm^{-1}. In contrast to $Rh_6(CO)_{16}$, no band is observed in the region 1800–1850 cm^{-1}, showing the absence of any bridging group in these molecules. Under similar conditions $Ph_2P(CH_2)_2PPh_2$ (diphos) forms[45,56] ctystals of $Rh_6(CO)_{10}(diphos)_3$. A possible structure for the complex is shown in (VIII). The presence of a diphosphine group bridging two metal atoms is not usual. An absorption band at a 1776 cm^{-1} in the IR spectrum is consistent with the presence of bridging CO groups in the molecule. $Rh_6(CO)_{10}L_6$ (L = Ph_3P, $(OMe)_3P$, $P(OCH_2)_3CEt$) has also been prepared[45] in a similar manner.



(VIII)

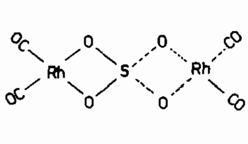
Thiols react[56] with $Rh_6(CO)_{16}$ in boiling toluene to give red solutions of thiolato bridged dimers, $Rh_2(CO)_4(SR)_2$ (R = Et, Bu or Ph). $Rh_2(CO)_4Cl_2$ or $Rh_4(CO)_{12}$ at room temperature yields identical products after the reaction with thiols.[57–59] Prolonged reactions yield red, polymeric and insoluble compounds of the type $[Rh(SR)_3]_n$.

Acetic, phthalic, benzoic and p-fluorobenzoic acids or their silver salts react[56,60] slowly with $Rh_6(CO)_{16}$ or $Rh_2(CO)_4Cl_2$ to give $Rh_2(CO)_4(RCOO)_2$ (IX).

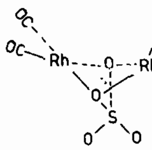


(IX)

The carboxylate compounds are stable in dry air, but are sensitive to moisture. In the solid state they are generally dichroic, suggesting the presence of metal–metal bonds as in rhodium carbonyl chloride itself. Under similar conditions, with silver nitrate, sulphate and thiocyanate, binuclear species are formed. They dissolve in polar solvents giving stable yellow-orange non-conducting solutions. They are also very sensitive to moisture. The IR spectrum[60] of the sulphato complex, $Rh_2(CO)_4SO_4$, has no bridging CO band and therefore there must be some form of sulphate bridge (Xa and Xb) between the Rh atoms. Structure (Xa) is supported by the resemblance of a single, very broad band (1130 cm^{-1}) observed for ionic (tetrahedral) sulphates (1104 cm^{-1}).



(Xa)

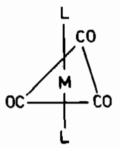


(Xb)

The mononuclear $Rh(CO)_2L$ (L = 8-quinolinolate, 8-mercaptoquinolinate, thiosalicylate, anilide of thioglycollic acid, acetylacetonate, trifluoroacetylacetonate, hexafluoroacetylacetonate and dithizone) complexes have been prepared by the action of the anionic ligands[61–63] on $Rh_2(CO)_4Cl_2$ or by the displacement of the propionate group[64] in $Rh(CO)_2$(Propionate) by the β-diketones ($MeCOCH_2COPh$, $PhCOCH_2COPh$, $MeCOCH_2COCF_3$, $CF_3COCH_2COCF_3$,$PhCOCH_2COCF_3$, $ButCOCH_2COBut$). Generally two CO bands appear in their IR spectra. Additional weak bands around 2085 cm^{-1} have also been noted in some cases. A crystallographic study[65] of $Rh(CO)_2$(acetylacetonate) shows it to be square planar. The analogous iridium complexes, $Ir(CO)_2L$ (L = 2,4-pentanedionate; 1,1,1-trifluoropentane-2,4-dionate; 1,1,1,5,5,5-hexafluoropentane-2,4-dionate;1-phenylbutane-1-3-dionate, acetylacetonate) have been obtained by the action[66] of β-diketones on $Na_2Ir_2(CO)_4Cl_{4.8}$ in presence of isopropylamine. IR, NMR and dipole moment studies are in agreement with an electronic delocalization of the chelate ring.

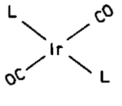
A dinuclear bridged complex, $Rh_2(CO)_4(\mu_2\text{-}S_2PF_2)$, has also been isolated[67] as a result of the reaction between S_2PF_2 and $Rh_2(CO)_4Cl_2$.

Several substituted carbonyl cations like $[M(CO)_3L_2]^+$, $[M(CO)_2L_2]^+$, $[M(CO)_2L_3]^+$, $[M(CO)L_4]^+$, $[M(CO)(L\text{–}L)_2]^+$ and $[M(CO)L_3]^+$ have also been identified. $[Rh(CO)_3(Ph_3P)_2]^+$ is obtained by the hydrocarbon diplacement[68] in [Rh(1,5-cyclooctadiene)$(Ph_3P)_2]^+$ when CO is bubbled through its solution. Identical $[Ir(CO)_3L_2]^+$ cations (L = Ph_3P, PMe_2Ph, PPh_2Me, PPh_2Et, $PPhEt_2$, Et_3P, Pr_3P, $(C_6H_{11})_3P$, Ph_3As, $AsPhMe_2$) have been obtained by the action[69–71] of CO on $Ir(CO)L_2X$ in presence of $NaBPh_4$. The cations $[M(CO)_3L_2]^+$ have D_{3h} symmetry and have probably distorted bipyramidal structures (XI).



(XI)

In cationic dicarbonyls, the metal atoms are either tetra or pentacoordinate. The tetracoordinate [M$(CO)_2L_2$ or (L–L)]$^+$ (M = Rh, L = Ph_3P; L–L = o-phen, 2,2′-bipy; M = Ir, L = $(C_6H_{11})_3P$, Pr_3P, L–L = $Ph_2As(CH_2)_2AsPh_2$) have been obtained by bubbling CO through the solutions of Rh or Ir perchlorates[72] in presence of ligands. Another method[73] of preparation of $[Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)]^+$ is by the action of sodium tetraphenylborate on $Ir(CO)_2(Ph_2AsCH_2CH_2AsPh_2)Cl$. It has also been observed that the cations $[M(CO)_3L_2]^+$ in presence of excess of the ligands change[68,71,74] to $[M(CO)_2L_2]^+$ in solution. IR evidence has been provided for the *trans*-planar configuration (XII) of $[Ir(CO)_2L_2]^+$.

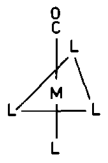


(XII)

The pentacoordinate cations $[Rh(CO)_2L_3]^+$ (L = Ph_3P, PPh_2Me, Ph_3As) have been isolated as their perchlorates. The corresponding iridium cations are obtained as their tetrachloroaluminate or tetrachloroferrate salts by the action[53,70,74] or dry CO on $Ir(CO)L_3X$ in benzene in presence of $AlCl_3$ or $FeCl_3$. The geometry of $[M(CO)_2L_3]^+$ is a distorted trigonal bipyramid as evidenced by the two strong CO bands in their IR spectra.[70] Both penta and tetracoordinate cationic monocarbonyls of Rh and Ir, [M(CO)L_4 or $(L–L)_2]^+$ (M = Rh, L = $PPhMe_2$, L–L = o-$C_6H_4(AsMe_2)_2$; M = Ir, L = $PPhMe_2$, Ph_2PH, L–L = CH_2 (Ph_2P_2), $Me_2P(CH_2)_2PMe_2$, o-$C_6H_4(AsMe_2)_2$) and $[M(CO)L_3]^+$ (M = Rh, L = Ph_3P, PPh_2Me, $PPhEt_2$; M = Ir, L = $PPhMe_2$, $AsPhMe_2$, p-MeC_6H_4NC, 1,1,3,3′-tetramethyl-2,2′-biimidazolidinylidene) are known. These cations have been prepared by the action of the ligands on $M(CO)L_2X$ in methanol:[52,68,70,75–82]

$$M(CO)L_2X + L\ (\text{in excess}) \rightarrow [M(CO)L_3]^+ + [M(CO)L_4]^+$$

The cation $[Rh(CO)(Ph_3P)_3]^+$ shows a single ν_{CO} absorption[68] at 2029 cm^{-1}. The pentacoordinate cations, $[M(CO)L_4]^+$ (XIII) show only one strong CO band in the region 1900–1930 cm^{-1}.



(XIII)

The reactions[83] of $Rh_2(CO)_4Cl_2$ with *cis*-1,2-dithiolato salt, 2,2′-dithiolato isomer, disodium toluene-3,4-dithiolate or dipotassium tetrachlorobenzene-1,2-dithiolate led to the formation of $[Rh(CO)_2S_2C_2(CN)_2]^-$, $[Rh(CO)_2S_2C{:}C(CN)_2]^-$, $[Rh(CO)_2S_2C_6H_3Me]^-$ and $[Rh(CO)_2S_2C_6Cl_4]^-$ respectively, which were isolated as diamagnetic salts with Bu_4N^+ cation. In the IR spectra of these species two strong CO absorptions were obtained in the region 2060–1960 cm^{-1}. The relative positions of these bands depend on the nature of the sulphur ligands in the expected way, *i.e.* ν_{CO} decreases in the order: $S_2C_2(CN)_2 > S_2C{:}C(CN)_2 > S_2C_6H_3Me$. Several other isolated anionic species known are $[Rh(CO)_2(NCS)_2]^-$[84], $[Rh(CO)_2S_2CNEt_2]^-$[85] and $[Rh(CO)_2S_2C_2(CF_3)_2]^-$[83].

Hydrocarbon donors

Acetylene, π-allyl-, and π-cyclopentadienyl complexes of Rh and Ir carbonyls are well investigated. $Rh_4(CO)_{12}$ reacts with PhC≡CPh or $CF_3C{\equiv}CCF_3$ to yield[45] $Rh_4(CO)_{10}(RC{\equiv}CR)$ (R = Ph or CF_3). In these compounds acetylenes are π-bonded with two rhodium atoms in a bridged form. π-allyl and π-cyclopentadienyl derivatives have been obtained by the action of allyl magnesium bromide[86] and sodium cyclopentadienide[87,88] respectively, on metal carbonyl halides:

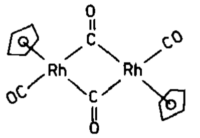
$$Rh_2(CO)_4X_2 + NaC_5H_5 \rightarrow Rh(CO)_2(\pi\text{-}C_5H_5)$$

$$Rh_2(CO)_4X_2 + C_3H_5MgBr \rightarrow Rh(CO)_2(\pi\text{-}C_3H_5)$$

$$Ir(CO)_3X + NaC_5H_5 \rightarrow Ir(CO)_2(\pi\text{-}C_5H_5)$$

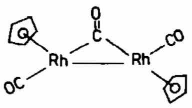
Pentamethylcyclopentadienyliridium dichloride dimer when reacting with $Fe_3(CO)_{12}$ in boiling benzene or with CO and $NaHCO_3$ in ethanol at 80° C yields $(C_5Me_5)Ir(CO)_2$.[89] It is a volatile, stable yellow solid. Attempts to prepare the analogous rhodium compound by this method were unsuccessful.

$(\pi\text{-}C_5H_5)Rh(CO)_2$ dimerizes in air[90] to yield $[(\pi\text{-}C_5H_5)Rh(CO)_2]_2$ (XIV). The complex, $[(\pi\text{-}C_5H_5)Rh(CO)_2]_2$ appears (based on IR spectrum) to have a structure similar to that of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, with both bridging and terminal carbonyl groups, although it may not have a metal–metal bond.



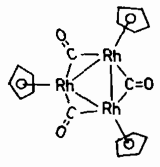
(XIV)

Ultraviolet irradiation[91,92] of $(\pi\text{-}C_5H_5)Rh(CO)_2$ yielded $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ and two isomeric forms of $[(\pi\text{-}C_5H_5)Rh(CO)]_3$. The former has only one bridging CO group[92] (ν_{CO}: 1841 cm^{-1}) and a metal–metal bond (2.68Å) (XV). ^{13}C NMR[93] chemical shifts of bridging and terminal CO carbons in $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ have been established from[103] Rh–^{13}C coupling data at −80° C; at 20° C the spectrum showed rapid intramolecular interconversion of all CO groups.

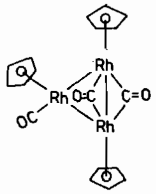


(XV)

The structure of one isomer of $[(\pi\text{-}C_5H_5)Rh(CO)]_3$ consists of a triangular cluster of rhodium atoms, also joined by bridging carbonyl groups[70, 94] and metal–metal bonds (2.62 Å) (XVIa). All the carbonyl groups lie on one side of the plane of the metal atoms with the cyclopentadienyl groups being on the other side. The second isomer (XVIb) has only two bridging carbonyl groups[95, 96] with Rh–Rh distances 2.620, 2.663, 2.705 Å.



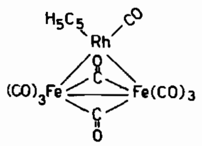
(XVI a)



(XVI b)

Several reaction products of varying nuclearities, $(\pi\text{-}C_5H_5)RhFe_2(CO)_9$, $(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$, $(\pi\text{-}C_5H_5)_2Rh_2Fe(CO)_6$ and $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$, which contain Rh–Fe bonds have been obtained[97] as a result of the reaction between $(\pi\text{-}C_5H_5)Rh(CO)_2$ and $Fe_2(CO)_9$. All the complexes are black crystalline solids. They have been separated by chromatography on silica gel.

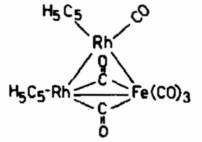
The IR spectrum[97] of $(\pi\text{-}C_5H_5)RhFe_2(CO)_9$ reveals the presence of both bridging and terminal CO groups (ν_{CO}: 2079, 2037, 2032, 2015, 1999, 1982, 1844 and 1803 cm^{-1}). The Mössbauer spectrum indicates the equivalence of both Fe atoms. It has been assigned the structure (XVII).



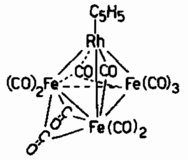
(XVII)

IR and Mössbauer spectra[97] of $(\pi\text{-}C_5H_5)_2Rh_2Fe(CO)_6$ (XVIII) showed the presence of both terminal and bridging CO groups (ν_{CO}: 2054, 2002, 1989, 1980, 1839 and 1792 cm^{-1}).

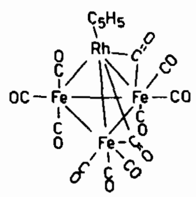
On the basis of IR[97] (ν_{CO}: 2069, 2033, 2025, 1993, 1977, 1957, 1945, 1873 and 1826 cm^{-1}) only the structure of $(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$ was suggested as (XIX) but a later study of its crystal structure[98] showed it to consist of three $Fe(CO)_3$ groups and a $(\pi\text{-}C_5H_5)$-Rh moiety which are mutually connected via metal–metal bonds (Fe–Fe 2.553–2.594 and Fe–Rh 2.568 to 2.615 Å) along with two bridging Rh–(CO)–Fe carbonyl groups (XX).



(XVIII)

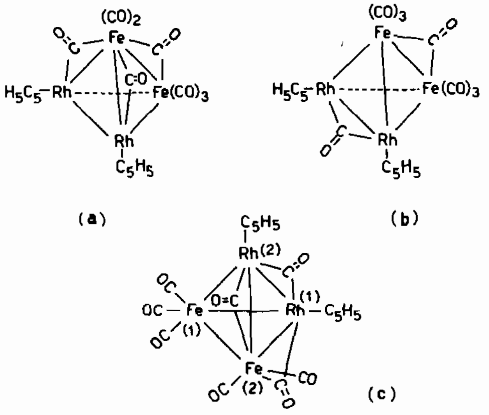


(XIX)



(XX)

Out of the possible structures (XXIa, b, c) of $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$, structures (XXIa, b) have been suggested on the basis of IR and NMR studies.[97] Two absorptions and the relatively large half-widths in the Mössbauer spectrum are consistent with two different iron sites favouring the structure (XXIa). Structure (XXIb) can be regarded as derived from $Fe_2(CO)_9$ by replacement of two of the bridging CO groups by Rh fragments just as the structure of $(\pi\text{-}C_5H_5)RhFe_2(CO)_9$ is derived by replacement of one bridging CO group. A crystallographic study[99] of this compound showed it to have C_s symmetry with the four metal atoms defining an irregular tetrahedron with Rh–Rh 2.648, Rh–Fe 2.570–2.598 and Fe–Fe 2.539 Å (XXIc). Two π-C_5H_5 ligands and one bridging



(XXI a-c)

CO group are associated with the two Rh atoms, while three terminal CO groups are at Fe(1) and two terminal groups at Fe(2). An unusual feature of the structure (XXIc) is the presence of two asymmetric carbonyl bridges Fe(2)–CO–Rh(1) and Fe(2)–CO–Rh(2). The overall disposition of the ligands around the tetrahedral metal atom core is such that it becomes impossible to assign 18 outer valence electrons to each metal atom.

C. Mixed Ligand Carbonyls

In addition to simple substitution products a large number of substituted derivatives which contain two or more ligands (other than CO) have been synthesised (Table I) using different experimental techniques. Most of these derivatives are mononuclear; a few are di- or trinuclear. Although several cationic complexes have been prepared, anionic derivatives are of very rare occurence.

TABLE I. Mixed Ligand Carbonyls of Rhodium and Iridium.

Compound	Preparation†	Reference
$Rh(CO)(Ph_3P)(S_2CNMe_2)$	a	100
$Rh(CO)(Ph_3P)(S_2PF_2)$	b	67
$Rh(CO)(Me_2PhP)(N_3)$	a	101
$Rh(CO)(L)(C_5H_5)$ ($L = Ph_3P$, $Bu^n{}_3$ P, $P(OCH_2)_3CMe$, $P(OMe)_3$, CNC_6H_{11})	b	102
$Rh(CO)(Ph_3P)(L)$ (L = 8-quinolinate, 8-quinolinethiolate)	b	62
$[Rh(CO)(Ph_3P)(S_2C_2(CN)_2)]^-$	b	83
$Rh(CO)(Ph_3P)(S_2CNMe_2)_3$	a	100
$Rh(CO)(L_2)(NCS)$ ($L = Ph_3P$, Ph_3As, Ph_3Sb, $(OPh)_3P$)	a	84
$Rh(CO)(Ph_3P)_2(L)$ ($L = NCO^-$, $NCSe^-$)	a	103, 104
$Rh(CO)(Ph_3P)_2(C_3H_5)$	b	86
$Rh(CO)(Ph_3P)_2(L)$ (L = PhS, Ph, SC_6F_5, EtS, MeS, *p*-FC_6F_4)	a,b,c	57–59, 105–107
$Rh(CO)(L)_2(L')$ ($L = Ph_3P$, $L' = H_2BH_2$, $NCBH_3$; $L' = (C_6H_{11})_3P$, $L' = H_2BH_2$)	a	108
$Rh(CO)(Ph_3P)_2(COOR)$ (R = Me, Et, Pr, CH_2Cl, $CClF_2$, CF_3, C_2F_5)	c	109
$Rh(CO)(Ph_3P)_2(C{\equiv}CR)$ (R = Me, Et, Bu^n, Bu^t)	d	110
$Rh(CO)(L_2)(L')$ ($L = Ph_2MeP$, Ph_3P; L′ = norbornadiene, 1,3-butadiene)	c	68
$Rh(CO)(Ph_3P)_2(L)$ (L = 1,3-diphenyltriazene, 1.3-di-*p*-tolyltriazene, 1,3-di-p-chlorophenyltriazene, 1-*p*-tolyl-3-*p*-methoxyphenyltriazene)	d	111, 112
$Rh(CO)(Ph_3P)_2(C_2F_4H)$	d	105
$Rh(CO)(Ph_3P)L(C_2(CN)_4)$ (L = acetylacetonate, 8-quinolinolate)	e	62, 113
$Rh(CO)(Ph_3P)L(Ph_3As)$ ($L = NCS^-$, $MeCOO^-$)	a	114
$Rh(CO)(Ph_3P)_2L(C_2(CN)_4)$ ($L = SCN^-$, $NO_3{}^-$)	a	113
$Rh(CO)(Ph_3P)_2(O_2)(OCOCF_3)$	e	109
$Rh(CO)(Ph_3P)_2(C{\equiv}CR)L$ (R = Me, Et; $L = C_2(CN)_4$, SO_2)	e	110
$Rh(CO)(Ph_3P)_2(SO_2)(SC_6F_5)$	e	107
$Rh(CO)(Ph_3P)_2(OH)(CO_2)$	e	115
$[Rh(CO)(L_2)(2,2'\text{-}bipy)]^+$ ($L = Ph_3P$, Ph_3As)	b	72
$[Rh(CO)(Ph_3P)_2(o\text{-}phen)]^+$	b	72
$[Rh(CO)(Ph_3P)_2\{CN(Me)C(Me)CHS\}]^+$	b	116
$Rh(CO)(Ph_3P)_3(C \equiv CR)$ (R = Me, Et, Bu^n)	e	110
$[Rh(CO)(Ph_3P)_3(\pi\text{-}CS_2)]^+$	a	117
$Rh(CO)_2C_2(CN)_4L$ (L = acetylacetonate, 8-quinolinolate)	f	62, 113
$Rh(CO)_2(Ph_3P)_2(C_6H_4PPh_2)$	e	106
$Rh(CO)_2(Ph_3P)_2(COR)$ (R = Et, Ph)	a	105
$Rh(CO)_2(Ph_3P)_2(C_2F_4H)$	a	105
$Rh(CO)_2(Ph_3P)_2L$ ($L = C_6F_5$, NCC_6F_4, $EtO_2CC_6F_4$, $C_6F_3(NC)_2$, C_5F_4N, 4–(2–(NC)C_5F_3N), 3–(6–(NC)C_5F_3N)	b	118
$Rh(CO)_3(Ph_3P)L$ ($L = C_2F_4H$, COPh)	e	105
$[Rh(CO)(Ph_3P)L]_2$ ($L = SCN^-$, $MeCOO^-$)	a	114
$Rh_2(CO)_3(Ph_3P)(PhC \equiv CPh)_2$	g	119
$[Rh(CO)(Ph_3P)_2(Solvent)]_2$ (Solvent = EtOH, CH_2Cl_2)	d	54, 120
$[Rh_3(CO)(Ph_3P)_2\{S_2C_2(CF_3)_2\}_4]^-$	a	83
$Ir(CO)(Ph_3P)L$ (L = pentane-2,4-dionate, 1,1,1-trifluoropentane-2,4-dionate, 1-phenylbutane-1,3-dionate)	b	121
Ir(CO)(1,2-bis(diphenylphosphino)ethane)(pentane-2,4-dionate)	b	121
$Ir(CO)(Ph_3P)(C_5H_5)$	a	122
$Ir(CO)(Ph_3P)_2(\pi\text{-}C_4H_7)$	a,d	123
$Ir(CO)\{(C_6H_{11})_3P\}_2L$ ($L = H_2BH_2$, $NCBH_3$)	a	108

TABLE I. (Cont.)

Compound	Preparation[†]	Reference
$Ir(CO)(Ph_3P)_2(NO)$	–	124
$Ir(CO)(Ph_3P)_2(C \equiv CR)$ (R = Me, Et, Bu^t)	d	110, 125
$Ir(CO)(Ph_3P)_2(O_2)$	–	126
$Ir(CO)(Ph_3P)_2L$ ($L = N_3^-, NCS^-$)	a	127
$Ir(CO)(Ph_3P)_2L$ ($L = OH^-, NCO^-, NCS^-, SH^-$, *p*-toluenesulphonate)	b	103, 128
$Ir(CO)(Ph_3P)_2\{(CN)C_2H_3\}$	d	129
$[Ir(CO)(PhMe_2P)_2L_2]^+$ ($L = C_2H_4, PhC \equiv CPh, C_4H_6, C_5H_8, C_6H_{10}$)	a	130
$[Ir(CO)(Me_2PhAs)_2(PhMe_2P)_2]^+$	a	70
$Ir(CO)(Ph_3P)_2L$ (L = EtCO orPh)	d	105
$Ir(CO)(Ph_3P)_2(SC_6F_5)$	a	113
$[Ir(CO)(Ph_3P)(C_5H_5)R]^+$ ($R = Me, Et, C_6H_{13}, CH_2Ph_2, C_3F_7$)	h	122
$Ir(CO)(Ph_3P)_2(NCSe)$(Acetone)	a	104
$Ir(CO)(Ph_3P)_2(R)(O_2)$ ($R = NCS^-, NCO^-, CF_3COO^-, SH^-, HCOO^-, C{\equiv}CPh^-, OEt^-, CN^-$)	e	128
$Ir(CO)(Ph_3P)_2(C \equiv CR)L$ ($L = O_2$, R = Me, Et, Bu^n, Bu^t; $L = SO_2$, R = Me, Et, Bu^n; $L = SO_4^=$, R = Me, Et; $L = C_2(CN)_4$, R = Me, Bu^n; $L = C_2(COOMe)_2, C_2(CF_3)_2, CF_2CFCFCF_2, CF_3CFCFCF_3, (CF_3)_2CO$, R = Me)	e	110, 125
$Ir(CO)(Ph_3P)_2(O_2)(FC_6H_4)$	e	107
$Ir(CO)(Ph_3P)_2L(SC_6F_5)$ ($L = SO_4^=, SO_2$)	e	107
$Ir(CO)(Ph_3P)_2(OH)(CO_2)$	e	115
$[Ir(CO)(Ph_3P)_2solvent)]^+$ (Solvent = MeCN, PhCN, Me_2SO)	a	110, 131
$[Ir(CO)(Ph_2MeP)_2L_2]^+$ ($L = (OPh)_3P, (OMe)_3P$)	a	71
$Ir(CO)(Ph_3P)_2(C \equiv CR)$ (R = Me, Et, Bu^n, Bu^t, C_6H_{11}, CH_2OH, $C(OH)Me_2$, $C_6H_{10}OH$)	e	110, 125
$[Ir(CO)(Ph_3P)_3(\pi\text{-}CS_2)]^+$	a	117
$Ir(CO)(Ph_3P)_2L(NO_3)_2$ ($L = N_3^-, NCO^-, NCS^-, NO_2^-$)	a	132
$Ir(CO)_2(Ph_3P)(\sigma \text{ or } \pi\text{-}C_4H_7)$	e	123
$Ir(CO)_2(Ph_3P)_2(C \equiv CMe)$	e	110
$Ir(CO)_2(Ph_3P)_2(RCO)$ (R = Me, Et, Pr, Ph)	a, i	105, 133
$Ir(CO)_2(Ph_3P)_2(R)$ (R = Et, Ph)	a	105
$Ir(CO)_2(Ph_3P)_2(COC_4H_7)$	e	123
$[Ir(CO)_2(CS)L_2]^+$ ($L = Ph_3P, (C_6H_{11})_3P$)	c	134
$[Ir(CO)_2(Ph_2MeP)_2(OMe)_3P]^+$	a	71
$[Ir(CO)_2(Ph_3P)_2(C_2(COOMe)_2)]^+$	a	71
$Ir(CO)_3(Ph_3P)(\sigma\text{-}C_4H_7)$	e	123
$Ir(CO)_3(Ph_3P)(COR)$ (R = Et, Ph)	e	105
$Ir_3(CO)(Ph_3P)_2\{S_2C_2(CF_3)_2\}_3$	a	83

[†] Preparative methods are the same as described in section 2C of the text.

(a) Bis(t-phosphine)metal carbonyl halides have been found to be very good starting materials to prepare these derivatives. Scheme (I) represents the reactions of several ligands on these carbonyl halides. Perchlorate complexes, $M(ClO_4)(CO)L_2$ (M = Rh, Ir; $L = Ph_3P, (C_6H_{11})_3P$), have also been used to prepare neutral complexes[108] with anionic ligands:

$$trans\text{-}[M(ClO_4)(CO)L_2] \xrightarrow{L'} trans\text{-}[M(CO)L_2L']$$
$$(L' = BH_4^-, BH_3CN^-)$$

(b) Tertiary phosphines react[57,59,62,67,72,102,118,121,128] with $[Rh(CO)_2L]_2$, $Rh(CO)_2L$, $Rh_2(CO)_4L$, $[Rh(CO)_2L_2]^-$, $[Rh(CO)_2L_2L']^+$ to form derivatives of different stoichiometries:

$$[Rh(CO)_2(SR)]_2 \xrightarrow{Ph_3P} Rh(CO)(Ph_3P)_2(SR)$$

$$Rh(CO)_2L \xrightarrow{L'} Rh(CO)LL'_2 \text{ or } Rh(CO)LL'$$

$$RH_2(CO)_4(S_2PF_2) \xrightarrow{Ph_3P} Rh(CO)(Ph_3P)(S_2PF_2)$$

$$[Rh(CO)_2L_2]^- \xrightarrow{L'} Rh(CO)_2L_2L'$$

$$[Ir(CO)(Ph_3P)(MeCN)]^+ \xrightarrow{\text{Na salts of } L'} Ir(CO)(Ph_3P)_2L'$$

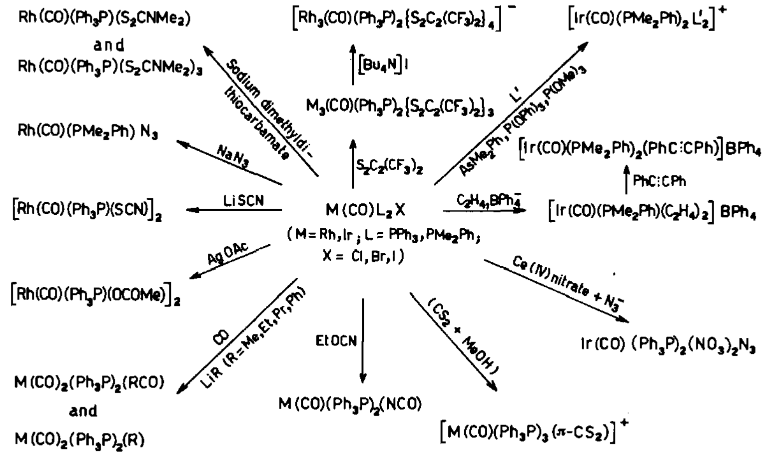
(c) Carbonylation reactions[68,105,106,109,134] of different noncarbonyl substances like ML_3L', $[ML_2(diene)]^+$ or $ML_2L'X$ yield mixed ligand carbonyls of different types:

$$ML_3L' \xrightarrow{CO} M(CO)L_2L'$$

$$[ML_2(diene)]^+ \xrightarrow{CO} [M(CO)L_2(diene)]^+$$

$$ML_2L'X \xrightarrow{CO} [M(CO)L_2L']^+$$

(d) $HM(CO)L_3$ (M = Rh, Ir; $L = Ph_3P$) derivatives react[54,105,110,123,125,129] with suitable ligands (L') like



Scheme I

alkynes or CO in different solvents to yield M(CO)(Ph$_3$P)$_2$L', [M(CO)L$_2$(solvent)]$_2$:

$$\mathrm{M(CO)L_2(C{=}CR)} \xleftarrow{\text{alkynes}} \mathrm{HM(CO)L_3} \xrightarrow[\text{solvent}]{\text{CO}} [\mathrm{M(CO)L_2\,(solvent)}]_2$$

The solvent bonded compounds have CO bridged structures[120] with terminally bonded phosphine ligand and solvent molecules.

(e) M(CO)L(L'–L') and M(CO)L$_2$L' undergo addition[63, 108–110, 125, 132] and carbonylation[105, 106, 123] reactions to form adducts like M(CO)L(L'–L')A or M(CO)L$_2$L'A or other derivatives like M(CO)$_2$LL', M(CO)$_3$LL' or M(CO)$_2$L$_2$L':

$$\mathrm{M(CO)L(L'{-}L') + A\ (O_2\ or\ SO_2) \rightarrow M(CO)L(L'{-}L')A}$$

$$\mathrm{M(CO)L_2L'} \xrightarrow{\mathrm{CO}} \mathrm{M(CO)_2LL',\ M(CO)_2L_2L',\ M(CO)_3LL'}$$

$$\downarrow \mathrm{A(O_2\ or\ SO_2)}$$

$$\mathrm{M(CO)L_2L'A}$$

$$\mathrm{M(CO)L_3L'} \xrightarrow{\mathrm{L''}} \mathrm{M(CO)L_2L'L''}$$

(f) Tetracyanoethylene readily reacts with Rh(CO)$_2$(L'–L') (L'–L' = singly charged acetylacetonate or 8-quinolinate) to form addition compounds Rh(CO)$_2$(L'–L')(TCNE).[62, 113]

(g) Two or more ligands react simultaneously with Rh$_4$(CO)$_{12}$ to form mixed ligand carbonyl derivatives.[119]

$$\mathrm{Rh_4(CO)_{12} + Ph_2C_2 + Ph_3P \rightarrow Rh_2(CO)_3(Ph_3P)(PhC{\equiv}CPh)_2}$$

(h) Cationic complexes of iridium have been obtained by the action[122] of alkyl halides on (C$_5$H$_5$)Ir(CO)(Ph$_3$P):

$$\mathrm{(C_5H_5)Ir(CO)(Ph_3P) + RX \rightarrow [(C_5H_5)Ir(CO)(Ph_3P)\,R]^+}$$

(i) Metal carbonyl perchlorates react with alkaline methanol[133] to form methoxy carbonyl derivatives:

$$\mathrm{[Ir(CO)_3(Ph_3P)_2]^+\ ClO_4^-} \xrightarrow{\mathrm{KOH}} \mathrm{Ir(CO)_2(Ph_3P)_2(COOMe)}$$

D. Si, Ge and Sn Bonded Carbonyls

In comparison to Si, Ge, and Sn bonded ruthenium and osmium carbonyls the chemistry of rhodium and iridium derivatives is less investigated. Table II lists

TABLE II. Si, Ge and Sn Bonded Rhodium and Iridium Carbonyls.

Compound	Preparation	Reference
$\mathrm{Rh(CO)(C_5H_5)(SiCl_3)_2}$	a	135
$\mathrm{Rh(CO)(Ph_3P)_2(GeCl_3)}$	b	136
$\mathrm{Rh(CO)_2(Ph_3P)_2(GeEt_3)}$	b	137
$\mathrm{[Rh(CO)Cl(GeCl_3)_2]^{2-}}$	c	136
$\mathrm{Rh(CO)(C_5H_5)\times(GeX_3)}$ (X = Cl, Br, I)	a	135
$\mathrm{Ir(CO)(Ph_3P)_2(GeMe_3)}$	d	138
$\mathrm{Ir(CO)(Ph_3P)_2(GeEt_3)}$	d	138
$\mathrm{Rh(CO)_2(Ph_3P)_2(SnMe_3)}$	d	139
$\mathrm{Rh(CO)(C_5H_5)X(SnX_3)}$ (X = Cl, Br, I)	a	135
$\mathrm{Ir(CO)_3(Ph_3P)(SnMe_3)}$	b	139
$\mathrm{Ir(CO)_3(Ph_3P)(SnPh_3)}$	b	139
$\mathrm{Ir(CO)(Ph_3P)_2Cl(SnCl_3)}$	e	140
$\mathrm{Ir(CO)(Ph_3P)_2Cl(SnCl_2)}$	e	141
$\mathrm{Ir(CO)(Ph_3P)_2(C_2H_2)(SnCl_3)}$	f	141
$\mathrm{Ir(CO)(Ph_3P)_2(C_2H_4)(SnCl_3)}$	f	141
$\mathrm{Ir(CO)_2(Bu_3P)_2(SnCl_3)}$	b	142
$\mathrm{Ir(CO)_2(Ph_3P)_2(SnCl_3)}$	b	142

[a] Action of trichlorosilane or group IV halides on (C$_5$H$_5$)Rh(CO)$_2$. [b] Action of R$_3$GeX or R$_3$SnX on M(CO)L$_2$X and subsequent carbonylation of the sodium salt. [c] Action of GeCl$_3^-$ on Rh(CO)(Ph$_3$P)$_2$Cl. [d] Action of C$_2$H$_4$ on H$_2$Ir(CO)(Ph$_3$P)$_2$(GeR$_3$). [e] Action of SnCl$_4$ on Ir(CO)(Ph$_3$P)$_2$Cl. [f] Action of C$_2$H$_4$ or C$_2$H$_2$ on Ir(CO)Cl(Ph$_3$P)$_2$SnCl$_3$.

the known Si, Ge and Sn bonded Rh and Ir carbonyls along with their preparative methods. Ge and Sn bonded derivatives are more numerous than the analogous Si bonded compounds.

Silicon bonded compounds have been prepared by using trichlorosilane while germanium and tin bonded compounds are prepared with the help of their corresponding halides:[135]

$$C_5H_5Rh(CO)_2 + Cl_3SiH \rightarrow C_5H_5Rh(CO)(SiCl_3)_2$$

$$C_5H_5Rh(CO)_2 + \text{Ge(IV) or Sn(IV) halides} \rightarrow C_5H_5(CO)XRh\,M'X_3$$

$(M' = Ge, Sn; X = Cl, Br, I)$

Bis(triphenylphosphine)metal carbonyl halides are effective starting materials to prepare Si and Ge bonded complexes.[136, 139–142]

A novel method for the preparation of these derivatives is abstraction of hydrogen by ethylene[138] from derivatives to produce hydrogen free products:

$$H_2Ir(CO)(Ph_3P)_2(GeR_3) + C_2H_4 \rightarrow Ir(CO)(Ph_3P)_2(GeR_3)$$

E. Cu, Au, Zn, Hg, Tl, Mo and W Bonded Derivatives

Considerably little attention has been paid to the investigations of this class of compounds; however, some important methods have been developed for their syntheses. Cu and Au bonded complexes have been prepared[139, 143] by the reactions of $Ph_3PM'Cl$ (M' = Cu, Au) with *trans*-$M(CO)(Ph_3P)_2Cl$ (M = Rh, Ir) or $Ir(CO)_3(Ph_3P)^-$:

$$\textit{trans}\text{-}M(CO)(Ph_3P)_2Cl + M'(Ph_3P)Cl \rightarrow M(CO)(Ph_3P)_2(M'Ph_3P)Cl_2$$

$(M = Rh, Ir; M' = Cu; M = Ir, M' = Au)$

$$[Ir(CO)_3(Ph_3P)]^-Na^+ + Au(Ph_3P)Cl \rightarrow Ir(CO)_3(Ph_3P)(AuPh_3P)$$

Use of the hydridocarbonyl cation $[HIr(CO)(Ph_3P)(C_5H_5)]^+$ has been made[122] for the preparation of Zn, Hg and Tl bonded products:

$$[HIr(CO)(Ph_3P)(C_5H_5)]^+\,BPh_4^- + M'X_n \rightarrow Ir(CO)(Ph_3P)(C_5H_5)(M'X_n)$$

$(M' = Zn, X = Br, n = 2; M' = Hg, X = Cl, n = 2; M' = Tl, X = Cl, n = 3)$

Formation of addition products[144–148] takes place when HgX_2 reacts with $(\pi\text{-}C_5H_5)Rh(CO)_2$ or *trans*-$Ir(CO)(Ph_3P)_2Cl$. In the latter case one of the halide groups (X) migrates to the iridium atom to form $Ir(CO)(Ph_3P)_2ClX \cdot HgX$:

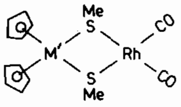
$$(\pi\text{-}C_5H_5)Rh(CO)_2 + HgX_2 \rightarrow (\pi\text{-}C_5H_5)Rh(CO)_2HgX_2 \quad (X = Cl, Br)$$

$$\textit{trans}\text{-}Ir(CO)(Ph_3P)_2Cl + HgX_2 \rightarrow Ir(CO)(Ph_3P)_2ClX \cdot HgX$$

$(X = Cl, Br, I, OAc, CN, SCN)$

Three C–O bands appeared in the IR spectra[148] of $(\pi\text{-}C_5H_5)Rh(CO)_2HgX_2$ around 2090, 2020 and 1990 cm^{-1} while only a single band ($\sim$2080 cm^{-1}) was observed in case of $Ir(CO)(Ph_3P)_2ClX \cdot HgX$.

Hexafluorophosphate salts of Mo and W containing rhodium carbonyl cations, $[Rh(CO)_2(\pi\text{-}C_5H_5)_2(SMe)_2M']^+$ (XXII), have been prepared by the action[149] of $[Rh(CO)_2Cl]_2$ with $(\pi\text{-}C_5H_5)M'(SMe)_2$ (M' = Mo, w). Cleavage of dihalo-bridge and displacement of a chloro ligand occur simultaneously in these reactions. These complexes show three C–O absorptions around 2085, 2025 and 1990 cm^{-1} in their IR spectra:



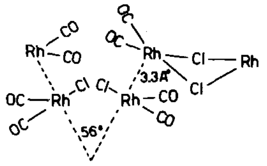
(XXII)

F. Carbonyl Halides

Numerous neutral and anionic carbonyl halides of rhodium and iridium have been reported as intermediates in the formation of carbonyls compounds from the trihalides. First of all two different groups of workers, Manchot *et al.*[150, 151] and Hieber *et al.*[152], reported the formation of $Rh(CO)_2Cl$, $Ir(CO)_3X$ and $Ir(CO)_2X_2$ (X = Cl, Br, I).

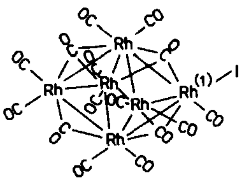
Since then several neutral as well as anionic carbonyl halide complexes of Rh and Ir have been synthesised by the reactions of halides, MX_3, MX_4, MX_6^{3-}, with CO or formic acid in presence of a suitable halogen acid. The species reported are $Rh(CO)X_3$[153] (X = Cl, Br, I), $[Ir(CO)Br_3]^-$,[154] $[M(CO)X_4]^-$ [154–157] (M = Rh, Ir; X = Cl, Br, I), $[M(CO)X_5]^{-2}$ [153, 156–161] (M = Rh, Ir; X = Cl, Br, I), $[M(CO)_2X_2]^-$ [16, 153, 155–157, 159, 161–167] (M = Rh, Ir; X = Cl, Br, I), $[Ir(CO)_2X_3]^-$ [156, 159, 168] (X = F, I), $[M(CO)_2X_4]^-$ [156, 159, 169, 170] (M = Rh, Ir; X = Cl, Br, I), $Ir(CO)_3X$[156, 171] (X = Cl, I), $Ir(CO)_3I_3$,[156, 157] $[Rh_2(CO)_2X_4]^{2-}$ [155] (X = Br, I), $Ir_2(CO)_3I_6$,[156, 157] $Rh_2(CO)_4X_2$[153, 172–175] (X = Cl, Br, I), $[Ir_2(CO)_4Br_3]^-$,[164] $M_2(CO)_4X_6$[156, 157, 168] (M = Rh, Ir; X = F, I), $[Ir_2(CO)_4X_6]^{2-}$ [157, 159] (X = Cl, Br, I), $[Rh_6(CO)_{15}I]^-$ [176, 177] and $Ir(CO)_2Br_2I_2$.[170]

The structures of most of the above mentioned species have been studied by IR as well as X-ray crystallography and had become the subject of an earlier review.[178] Structural details of two important classes, $Rh_2(CO)_4X_2$ and $[Rh_6(CO)_{15}I]^-$, need special emphasis. The X-ray crystal structure of $Rh_2(CO)_4Cl_2$, which is best prepared by the action of CO on $RhCl_3$, shows that two essentially planar $Rh(CO)_2Cl$ groups are joined by two bridging CO ligands, the dihedral angle between two planes being 124° (XXIII). The Rh–Rh distance is 3.31 Å and it appears that in the solid the dimers are held together by weaker intermolecular metal–metal bonds. In solution the bent structure is apparently maintained since the chloride has a dipole moment of 1.64D, and the bromide has a moment of 2.23D.



(XXIII)

The structure of $[Rh_6(CO)_{15}I]^-$[177] has been also determined by X-ray crystallography.[176] The anion is made up of an octahedral cluster of six metal atoms surrounded by 15 carbonyl groups and one iodine atom. Four carbonyl groups bridge four metal atoms and the remaining eleven carbonyl groups are linearly bonded, two to each Rh atom with the exception of Rh(1) which is bonded to one terminal CO group and to the iodine atom. The T_d symmetry of the purely carbonyl complex $Rh_6(CO)_{16}$ is reduced to C_s by the substitution of one CO with iodine (XXIV).



(XXIV)

G. Substituted Derivatives of Carbonyl Halides

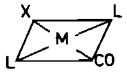
Substituted carbonyl halides are the key reagents to prepare several Rh and Ir carbonyl derivatives. An attempt has been made below to classify these derivatives into different groups.

$M(CO)L_2X$

These are well known compounds and their methods of preparation have been given in Table III.

They react with electron deficient molecules like BF_3, BCl_3 or BBr_3 to form adducts[228,229] of the type $M(CO)L_2X \cdot BX'_3$ (M = Rh, L = Ph_3P, Ph_3As, X = X' = Cl, Br; M = Ir, L = Ph_3P, X = Cl, X' = F).

These compounds possess square planar geometry (XXV) with two ligands in *trans*-positions.



(XXV)

The variation of CO as a function of ligand has been studied[230] for $Rh(CO)L_2X$ (L = $(C_6H_{11})_3P$, $(iso\text{-}Pr)_3P$, $PBuPh_2$, $(p\text{-}C_6H_4Me)_3P$ or $(OPh)_3P$, X = Cl; L = Ph_3P, X = Cl, Br, I). The electron density at the central atom decreases with increasing π-acceptor strength of L independently of the solvent (PhMe, $CHCl_3$, CS_2), whereas on changing X, ν_{CO} does not vary. An order in the CO stretching vibration with variation of halogen (X = F, Cl, Br, I) has been established earlier.[182]

In addition to $Rh(CO)L_2X$, some Rh(CO)(L–L)X (L–L = phenylbis(*o*-vinylphenyl)phosphine, X = Cl, Br, I; L–L = tris(*o*-vinylphenyl)arsine, X = Cl, I) complexes have also been synthesised[231] by the carbonylation of $[Rh(L\text{–}L)X]_2$.

A polymeric derivative, $[Rh(CO)(Ph_2PPPh_2)Cl]_n$, is obtained[52] on keeping a benzene or dichloromethane solution of $Rh(CO)(Ph_2PPPh_2)_2Cl$ at room temperature. In several cases the value of n is two; the compounds are obtained by the action of bidentate ligands (L–L) on $[M(CO)_2X]_2$.

A crystal study of $[Rh(CO)(Ph_2AsCH_2AsPh_2)Cl]_2$[232] shows that the bidentate ligands are in bridged form

TABLE III. Substituted Carbonyl Halides of Rhodium and Iridium [$M(CO)L_2X$ Class].

M	L	X	Preparation	Reference
Rh	Group V donor	Cl	a,b,c	36, 56, 101, 155, 174, 179–207
	Group V donor	Br	a,b	56, 101, 182, 185, 191, 202, 204, 205, 208, 209
	Group V donor	I	a,b,d	101, 169, 179, 182, 191, 204, 210
	Group V donor	F	e	182, 211
	Group VI donor	Cl	a	212
	Tetraphenylcyclopentadienone	Cl	a	213
Ir	Group V donor	Cl	b,c	143–145, 205, 206, 214–224
	Group V donor	Br	c,d	205, 214, 218, 219, 221, 222, 225
	Group V donor	I	c,d	214, 218, 219, 221, 225–227
	Group V donor	F	e	211

[a] Action of ligands on$[M(CO)_2X]_2$, $M(CO)_2X_3$ or$[M(CO)_2X_2]^-$. [b] Carbonylation of ML_3X, $M_2L_4X_2$, $ML_2L'X$, $M(CO)L_2L'X$ or $M(CO)L_2L'L''X$. [c] Action of $CH_3COONa/NaOH$ or ethanol on ML_2X_2. [d] Action of sodium halides on $M(CO)L_2X_3$. [e] Action of NH_4F/Ag_2CO_3 on $M(CO)L_2X$.

in this molecule. The Rh–Rh distance within the dimer is 3.396 Å and appears to be more the result of the steric requirements of the diarsine molecules than of any significant M–M interaction. The coordination about each Rh atom is approximately square pyramidal. The centrosymmetrically related Rh atom occupies the apical position while the basal plane consists of a terminal Cl atom, a terminal CO group and two As atoms, one from each of the two bridging diarsine molecules in a *trans* configuration.

M(CO)LL'X derivatives[183,184,233–238] (M = Rh, Ir; L = group V or hydrocarbon donor; L' = hydrocarbon or other group V donor, X = Cl, Br, I) are derived by the substitution of one ligand L in $M(CO)L_2X$ by L. These derivatives have been prepared by the following methods:

(i) by the treatment of $M(CO)L_2X$ (L = Ph_3P, X = Cl) with the ligands[183,234,236] L' (L' = Ph_3As, Ph_3Sb, C_5H_5N, $PMePh_2$, PMe_2Ph); (ii) by the oxidative addition of RSO_2Cl (R = Me, Ph, *p*-MeC_6H_4, *p*-BrC_6H_4) with $Ir(CO)_2(C_5Me_5)$; (iii) by the treatment of ligands (C_5H_5N, Ph_3P, Ph_3As) on $Ir(CO)(C_4H_7)(C_8H_{14})Cl_2$.[233]

These complexes show a single absorption around 1960 cm^{-1} in their IR spectra. The crystal structure of one compound, $(\pi\text{-}C_5H_5)Rh(CO)(C_2F_5)I$, of this class has been determined.[239]

$M(CO)L_3X$ and $M(CO)(L\text{–}L\text{–}L)X$

These compounds are not very common, although they have been isolated during with the preparation of $M(CO)L_2X$ in a few cases. Rh(I) and Ir(I) complexes, M(CO)(TDPME)Cl, of the tripodal ligand, 1,1-1-tri(diphenylphosphinomethyl)ethane (TDPME),[240] come into this category. The Ir(I) complex is five coordinate in the solid state but capable of dissociating a phosphine ligand in solution. The Rh(I) complex is apparently a mixture of four and five coordinate isomers (with TDPME either as a bidentate or a terdentate ligand) both in solid state and in solution.

Diphenylketene has been found a suitable carbonylating agent[241] for ML_3X. It reacts with $Rh(Ph_3P)_3Cl$ to yield $Rh(CO)(Ph_3P)_3Cl$. On the basis of analytical evidence and electronic spectra it has been concluded that Ph_3Sb on reaction with $[Rh(CO)_2X]_2$ (X = Cl, Br) in benzene yields $Rh(CO)(RC_6H_4)_3SbPh_3X \cdot C_6H_6$[242] with the benzene molecule strongly clathrated in the lattice. Dry HCl with $Rh(CO)L_3(MeCOO)$ gave the derivatives[243] of this class. These compounds[244] with cycloheptene or cyclooctene have been obtained by the action of these hydrocarbons on $H_2IrCl_6 \cdot 6H_2O$ in water–methanol mixture.

$M(CO)L_4X$

These compounds are of very rare occurrence[245] and probably exist as salts[246,247] of cations $[M(CO)L_4]^+$ with halogen anions (M = Rh, L = Ph_3Sb, X = Cl, Br; M = Rh, Ir, L = bis(ethylene-bis(dimethylphosphine)). A six coordinate cation $[Ir(CO)(Ph_2PCH_2CH_2PPh_2)_2Cl]^+$ has been obtained by the action[248] of $Ph_2PCH_2CH_2PPh_2$ on $Ir(CO)(Ph_3P)_2Cl$. It loses CO under vacuum at 150° C to give $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$.

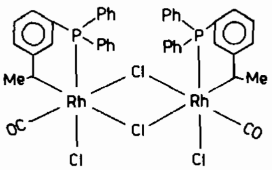
$M(CO)L_2L'_2X$ and $M(CO)L_3L'X$

These derivatives are considered to originate from $M(CO)L_4X$. In some complexes two of the four ligands L are replaced by two other ligands L' to give $M(CO)L_2L'_2X$; in others one L is replaced by L' to give $M(CO)L_3L'X$. The hexacoordinate $Ir(CO)(Ph_3P)_2(NO_3)_2X$[132,249] (X = Cl, Br, I) is prepared by the reactions of Ce(IV), Fe(III) or Cu(II) nitrates with $Ir(CO)(Ph_3P)_2X$. A similar compound $Ir(CO)(Ph_3P)_2(BF_3)_2Cl$ has been prepared by the direct action of BF_3 on $Ir(CO)(Ph_3P)_2Cl$. The pentacoordinate $Ir(CO)(Ph_3P)Cl$ also form (1:1) adduct[250] with BF_3. A sulphato–carbonyl complex, $Ir(CO)(Ph_3P)_3(SO_4)X$, was prepared by the reaction of $Ir(CO)(Ph_3P)(SO_2)X$ (X = Cl, Br, I) with molecular oxygen.

$M(CO)LX_2$

These compounds have been prepared by two methods: (i) by the treatment of ethereal solution of iodine[251,252] with $M(CO)_2L$ (M = Rh, Ir, and L = π-cyclopentadienyl); (ii) by the carbonylation[185,253] of MLX_2 dimers (L = C_5H_5 or C_5Me_5; M = Rh, Ir).

A boiling ethanolic solution of hydrated $RhCl_3$ when treated with CO and then refluxed in the presence of *o*-CH_2:$CHC_6H_4PPh_2$ gave the Cl-bridged Rh dimer[234] (XXVI). It reacted with t-phosphines to give $Rh(CO)Cl_2L'R$ (L' = Ph_3P, $PMePh_2$, PMe_2Ph; R = *o*-$MeCHC_6H_4PPh_2$). Rh(CO)Cl and *o*-CH_2:$CHC_6H_4PPh_2$ reacted to give [Rh(CO)(*o*-CH_2:CHC_6H_4)PPh_2]Cl which on treatment with Ph_3P gave $Rh(CO)(Ph_3P)$(*o*-CH_2:$CHC_6H_4PPh_2$)Cl.



(XXVI)

A polymeric compound, $[Rh(CO)C_2H_4)Cl_2]_x$[254] (ν_{CO}: 2090, 2030 cm^{-1}) has been prepared by saturating $[Rh(CO)(C_2H_4)Cl]_2$ with dry HCl. Dimeric allylic carbonyl complexes[255] of Rh were obtained by the action of $Rh_2(CO)_4Cl_2$ on $Rh_2(allyl)_4Cl_2$. 2- and 1-methylallyl complexes were also prepared similarly. These complexes show two strong CO bands (one ~2105–2109 cm^{-1} and the other 2088–2092 cm^{-1}).

$M(CO)L_2X_3$ and $M(CO)L_2XX'_2$

This is the most widely studied class. Methods of preparation of these complexes are given in Table IV.

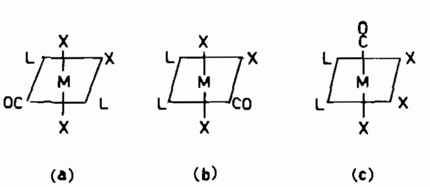
TABLE IV. Substituted Carbonyl Halides of Rhodium and Iridium [$M(CO)L_2X_3$ and $M(CO)L_2XX'_2$ Class].

M	L	X_3 or XX'_2	Preparation	Reference
Rh	Group V donor	Cl_3	a, b, c	36, 56, 143, 179, 183, 190, 191, 208, 214, 256
	Group V donor	Br_3	a, c	56, 130, 209, 214
	Group V donor	I_3	a, c	56, 75, 169, 214, 256
	Group V donor	$ClBr_2$, ClI_2	a	190, 214, 256
	Group V donor	BrF_2, $BrCl_2$, BrI_2	a	214, 215
	Group V donor	ICl_2, IBr_2	a	214
	Group V donor	FCl_2, FBr_2	a	214, 257
Ir	Group V donor	Cl_3	a, b, c	145, 161, 205, 214, 222, 258, 259–263
	Group V donor	Br_3	a	205, 214, 258, 261
	Group V donor	I_3	a	214, 226, 258, 261
	Group V donor	$ClBr_2$, ClI_2	a, b	145, 205
	Group V donor	$BrCl_2$	a	205
	Group V donor	FCl_2	a	257

[a] Halogenation of $M(CO)L_2L'X_2$, $[M(CO)L_3]^+$ or $M(CO)L_2X$. [b] Carbonylation of ML_3X_3. [c] Reaction of alcoholic solution of ligands with MX_3, $M(CO)_2X_3$ or MX_6^{3-}.

Three octahedral arrangements (XXVIIa, b, c)[258,259] are possible for $M(CO)L_2X_3$ compounds and all the three forms have been obtained under different conditions:

$\nu_{CO} = 2073\ cm^{-1}$ $\nu_{CO} = 2105\ cm^{-1}$ $\nu_{CO} = 2073\ cm^{-1}$
$L = Ph_3P, X = Cl$ $L = Ph_3P, X = Cl$ $L = Ph_3P, X = Cl$



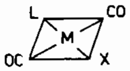
(a) (b) (c)

(XXVII a-c)

$M(CO)LL'X_3$ derivatives are known for Rh only and they may be obtained by displacing one CO group in $M(CO)_2LX_3$ with L′ (L′ = group V donor or hydrocarbon ligand). A single band (~2080 cm^{-1}) in the C–O region is observed in their IR spectra. The transition metal carbene complexes, $L(CO)Cl_3Rh$–C(R)NHR′ (L = Ph_3P, R = Ph, R′ = Me, Et, Pr^i, R = Me, R′ = o-C_6H_4Me; L = PPh_2Me, R = Ph, R′ = Me), which also come into this category, have been obtained[264,265] by the addition of RC(Cl):NR′ in benzene solution of $Rh(CO)_2LCl$ and subsequent passage of HCl gas through the mixture.

$M(CO)_2LX$

Both *cis*- and *trans*-complexes[164,266–270] are known in this class. These derivatives are of square planar geometry with two CO groups in the *trans*[266] (XXVIIIa) or in the *cis*[267,269] (XXVIIIb) positions. The rhodium complexes are prepared by the treatment of dimeric metal dicarbonyl halides with the ligands[266–270] (Ph_3P, Me_3P, 3-5-7-triphenyl-4-H-1-2-diazepine, PhCH:CHCH:NPh, PhCH:CHCH:N(p-MeC_6H_4), PhCN, p-ClC_6H_4CN, o-, m- and p-MeC_6H_4CN; α-$C_{10}H_7CN$, β-$C_{10}H_7CN$, $PhCH_2CN$, halogen = Cl, Br, I). The iridium complexes are prepared by the treatment[164] of $K_2[M_2(CO)_4X_5]^{2-}$ (X = Cl, Br, I) with isopropylamine or p-toluidine.



(XXVIII a)

(XXVIII b)

$M(CO)_2LX_2$

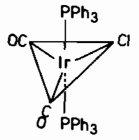
These derivatives are of very rare occurrence. A rhodium complex, $Rh(CO)_2(C_{12}H_{19})Cl_2$[271], is prepared by the action of $RhCl_3$ on *trans, trans, trans*-1,5,9-cyclododecatriene in boiling ethanol. It is a polymeric, red, diamagnetic solid insoluble in all common organic solvents. The iridium compound, $Ir(CO)_2$(p-$MeC_6H_4NH_2)I_2$, is obtained by the reaction[222] of p-toluidine on $K[Ir(CO)_2I_4]$.

$M(CO)_2LX_3$

Both rhodium[56,266] and iridium[222] form this class of compounds. The rhodium compounds may be prepared either by the halogenation of $Rh(CO)_2LX$ (L = Ph_3P, X = Cl, Br, I) or by the treatment of Ph_3P with $Rh(CO)_2X_3$ (X = Cl, Br). The iridium complex, $Ir(CO)_2(Ph_3As)I_3$, is obtained by the treatment of Ph_3As with $K[M(CO)_2I_4]$ in chloroform. In the IR spectra of $Rh(CO)_2LX_3$ (L = Ph_3P, X = Cl, Br) two absorption bands have been observed in the CO region (chloro derivative: ν_{CO} 2100, 2073 cm^{-1}; bromo derivative: ν_{CO} 2070, 2055 cm^{-1}).

$M(CO)_2L_2X$ and $M(CO)_2(L–L)X$

t-Phosphines or arsines react[164,222] with $Ir(CO)_2$ (amine)X or $[Ir(CO)_2I_4]^-$ to give $Ir(CO)_2L_2X$ derivatives. Carbonylation[272] or $Ir(CO)(Ph_3P)_2Cl$ also yielded the similar product. IR spectra[222] and X-ray studies[273] of $Ir(CO)_2(Ph_3P)_2Cl$ suggest the trigonal bipyramidal structure (XXIX). Two CO stretching bands at 1990 and 1930 cm^{-1} have been observed suggesting the *cis* carbonyl groups in the molecule.

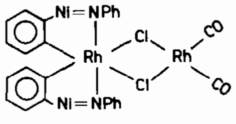


(XXIX)

Bidentate ligands like *o*-phenanthroline,[274] 2,2′-bipyridine,[274] *p*-toluidine,[274] bis(diphenylphosphino)ethane[73] and bis(diphenylarsino)ethane[73] with $Ir(CO)_2$ LX, $[Ir(CO)_2X]_2$ or $[Ir(CO)_3Cl]_n$ yield derivatives of the type $Ir(CO)_2(L–L)Cl$. An analogous rhodium derivative, $Rh(CO)_2$(*o*-phenylenediamine)X (X = Cl, Br), has been obtained by the action[275] of *o*-phenylenediamine on $[Rh(CO)_2X_2]^-$. Two C–O bands at 2048, 1962 cm^{-1} and three bands at 2050, 1965 and 1932 cm^{-1} have been recorded in the IR spectra of $Ir(CO)_2$(diphos)Cl and $Ir(CO)_2$(diars)Cl respectively. $Rh(CO)_2(Ph_3P)\{C_2(CN)_4\}Cl$,[276] which may also be grouped in this class, is obtained as 1 : 1 adduct of tetracyanomethylene and $Rh(CO)_2(Ph_3P)Cl$.

$M_2(CO)_2L_2X_2$

t-Phosphines, $Rh_2(PhN{=}NPh)_4Cl_2$, $[Rh(PF_3)_2Cl]_2$ or $[RhClC_2H_4]_2$ with $[Rh(CO)_2Cl]_2$ yield[52,114,189,267,277] $Rh_2(CO)_2L_2Cl_2$ (L = t-phosphines, PF_3, azobenzene, C_2H_4). The IR spectra of phosphine and ethylene substituted complexes display only one CO band at 1980 and 2008 cm^{-1} respectively, showing the *trans* isomeric nature. The structure of the azobenzene substituted complex may be represented as (XXX):



(XXX)

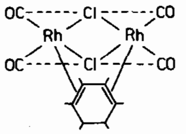
$M(CO)LX_3$ or $[M(CO)LX_3]_n$

A number of Rh(III) carbene complexes are known in this class. The complexes, $[(CO)Cl_3Rh–C(Ph)NR–CPh{=}NMe_2]_2$ (R = Me, Et), have been prepared[264] by the action of a number of imidoyl chlorides, PhC(=NR)Cl, on $[Rh(CO)_2Cl]_2$ in which organic fragments are attached to the metal atom as carbene moieties. The corresponding bromo and iodo derivatives have been prepared by the action of lithium halides on these Rh(III) carbene complexes. A single carbonyl stretching band (2080–2120 cm^{-1}) has been observed in their IR spectra. Polymeric derivatives, $[(CO)Cl_3Rh–C(Ph)NHR]_n$ (R = Me, Pr^i, *o*-MeC_6H_4), have also been synthesised[264,265]; they showed a single CO band in the region 2120–2125 cm^{-1}. On performing the reactions of imidoyl chlorides, R′(Cl)=NR″, with $[Rh(CO)_2Cl]_2$ in rigorous absence of HCl, the Rh(III) carbene chelates, $Cl_3(CO)Rh–CR'(NR'')CR'{=}NR''$ (R′ = Ph, R″ = Me, Et), have been obtained.[278] The corresponding bromo and iodo derivatives were prepared by the action of lithium halides on $Cl_3(CO)Rh–CR'(NR'')CR'{=}NR''$. Dimeric compounds of iridium, $[Ir(CO)P(OR)_3I_3]_2$, have been prepared[18] by the reaction of iodine with $[Ir(CO)P(OR)_3]_2$ (R = Ph, MeC_6H_4).

$M_2(CO)_3LX_2$ and $M_2(CO)_4LX_2$

Dinuclear compounds have been prepared[189] by the reaction of $Rh(CO)_2Cl_2$ with t-phosphines (Me_3P, Et_3P, Ph_3P, PMe_2Ph, $P(NMe_2)_3$). The Ph_3P derivative has also been obtained[279] by the interaction of $[Rh(CO)_2Cl]_2$ with $[Rh(Ph_3P)_2Cl]_2$ in dry petroleum.

1,3-cyclohexadiene reacted[162] with $[Rh(CO)_2Cl]_2$ to yield the derivative $Rh_2(CO)_4$(1,3-cyclohexadiene)Cl_2. X-ray[162] analysis suggests that the olefinic ligand is present as a bridge (XXXI):

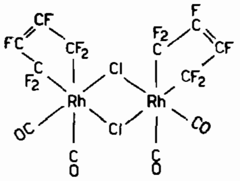


(XXXI)

IR and NMR spectra also favour the same structure. Other complexes were synthesised[280] with ligands $(CH_2)_6(NH_2)_2$, $(CH_2)_{10}(NH_2)_2$, (*o*-$H_2NC_6H_4)_2$, $C_{12}H_8N_2$ and 8,8′-dihydroxy-5,5′-biquinoline. Their IR spectra[280] showed two intense bands in the CO region indicating the presence of *cis* carbonyls.

$M_2(CO)_4(L–L)X_2$ and $[M(CO)_2LX]_2$

$[Rh(CO)_2Cl]_2$ reacted[281] with *α,α′*-bipyridyl to give $Rh_2(CO)_4Cl_2(bipy)_n$ (n = 1, 2, 3) with Rh–dipy–Rh bridges. Similar reaction with perfluorobutadiene gave $[Rh(CO)_2(C_4F_6)Cl]_2$. The IR spectrum[282] of this compound suggested the bridging chloro groups (XXXII):

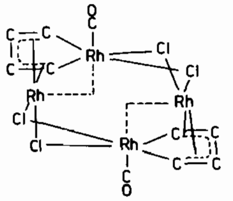


(XXXII)

Three CO bands (2110, 2096 and 2029 cm^{-1}) were observed in chloroform solution. A carbomethoxy compound[161], $[Ir(CO)_2(OAc)Cl]_2$, has also been reported.

$[M_2(CO)L_2X_2]_2$

A tetranuclear derivative,[283,284] $[Rh_2(CO)(EtC{\equiv}CEt)_2Cl_2]_2$, has been synthesised by the treatment of diethylacetylene with $[Rh(CO)_2Cl]_2$. X-ray study[284] suggested the presence of bridging halogen group and overall C_{2h} symmetry (XXXIII):



(XXXIII)

$M(CO)L_2L'X$

A large number of compounds of this class have been synthesised (Table V).

The structure of two peculiar compounds, $Ir(CO)(Ph_3P)_2(O_2)Cl$[295] and $Ir(CO)(Ph_3P)_2(SO_2Cl$,[293] which have been prepared by the action of O_2 or SO_2 on $Ir(CO)(Ph_3P)_2Cl$, are interesting in the sense that they differ considerably in their geometries. In the former the Ir atom, the two oxygen atoms, the carbonyl group and the Cl atom lie in the basal plane with P atoms above and below this plane. The two oxygen atoms are equidistant from the Ir atom, with an average Ir–O distance of 2.07 Å. The partial bond between the two oxygen atoms is retained[318] in this complex, although in similar H_2 HCl, MeI, I_2 and Cl_2 adducts the bond in the diatomic molecule is broken[318] and the constituent atoms form bonds with the central Ir(III). The basic geometry of the SO_2 complex differs

TABLE V. Substituted Carbonyl Halides of Rhodium and Iridium [$M(CO)_2L_2L'X$ Class].

M	L	L′	X	Preparation	Reference
Rh	Ph_3P	SO_2	Cl, Br, I	a	107, 182, 285–287
	Ph_3P	SO_2	F	a	182
	Ph_3P	MeI	Cl	a	288
	Ph_3P	SO_4^{2-}	Cl	b	107
	Ph_3P	$C_2(CN)_4$	Cl, Br	a, c	113, 143, 289
	Ph_3P	$C_6H_4O_2$	Cl	a	290
	Ph_3P, Ph_2MeP	1,2–$O_2C_6Cl_4$, 1,2–$O_2C_6Br_4$, $C_{14}H_8O_2$	Cl	a	291
	Ph_3P, Ph_2MeP	CF_3COCN	Cl	a	292
	Ph_3Sb	$C_2(CN)_4$	Cl, Br, I	a	113
	p-$CH_3C_6H_4NH_2$	dimethylmaleyl	Cl	d	201
Ir	Ph_3P	SO_2, $SC_6H_4COO^-$	Cl, Br, I	a	107, 249, 286, 287, 293, 294
	Ph_3P	SO_4^{2-}	Cl	b	107
	Ph_3P	O_2	Cl, Br, I	a	295–300, 316
	Ph_3P	H_2, MeI	Cl, Br, I	a	299
	Ph_3P	$C_2(CN)_4$	Cl, Br, I	a, c	143, 289, 301–303
	Ph_3P	CS_2	I	–	304
	Ph_3P	toluene-3,4-dithiolate	Cl	a	305
	Ph_3P	C_2F_4, $(CF_3)_2(CN)_2C_2$, CF_3COCN, $(NCO)_2NPh$	Cl	a	292, 302, 306, 307
	Ph_3P, Ph_2MeP	$C_6H_4O_2$, 1,2–$O_2C_6Cl_4$, 1,2–$O_2C_6Br_4$, $C_{14}H_8O_2$	Cl	a	290, 291
	Ph_3P, Ph_2MeP	$(CF_3)_2CCS$	Cl	a	308
	Ph_2MeP	CF_3COCN, $C_2(CF_3)_2$, NCF_3, C_6F_6	Cl	a, e	223, 292, 309–311
	Me_2PhP	C_3H_5	Cl	d	312
	Et_3P	C_2F_4	Cl	a	313
	Me_3P	*trans*-1-bromo-2-fluorocyclohexane*	Cl	a	314
	Ph_3As	O_2	Br	a	297
	Ph_3As	SO_4^{2-}	Cl, I	b	249
	Ph_3As	$C_2(CN)_4$	Cl	a	315
	Me_2PhAs	C_3H_5	Cl	d	312

* A reinvestigation shows that the oxidative addition of *trans*-1-bromo-2-fluorocyclohexane to *trans*-$Ir(CO)(Me_3P)_2Cl$ is unsuccessful.[317]

[a] Action of ligands on $M(CO)L_2X$. [b] Bubbling of O_2 in $M(CO)(Ph_3P)_2(SO_2)X$. [c] Action of Ph_3PAuCl or Ph_3PCuCl on $M(CO)L_2X$ and subsequent treatment with tetracyanoethylene. [d] Action of allyl halides on $M(CO)L_2X$. [e] Action of CF_3NNCF_3 on $Ir(CO)L_2X$.

considerably from that of the analogous O_2 complex in the sense that the iridium is in a trigonal bipyramidal configuration with *trans*-phosphorus atoms at the apices. The mechanism of the reaction of *trans*-$Ir(CO)(Ph_3P)_2(O_2)X$ (X = halides) with SO_2 has also been studied. It involves the formation of a peroxysulphate intermediate[319] where the two oxygen atoms in the peroxy group are those originating from molecular oxygen. The peroxide bond breaks up so that one of the peroxy atoms migrates to the external position and the other remains attached to the metal.

A nitric oxide coordinated cation, $[Ir(CO)(Ph_3P)_2(NO)Cl]^+$, has been obtained by the action[320,321] of $NOBF_4$ on $Ir(CO)(Ph_3P)_2Cl$ or by the carbonylation[322] of $[Ir(Ph_3P)_2(NO)Cl^+ ClO_4^-$ in CH_2Cl_2. The coordination polyhedron of this compound is a tetragonal pyramid[323] with *trans*-P, Cl and CO in the basal plane and N of the NO at the apex. The Cl and CO are slightly below the basal plane with NO as the bent group. Similar is the geoemetry of the cation[324] $[Ir(CO)(Ph_3P)_2(NO)I]^+$ in $[Ir(CO)(Ph_3P)_2(NO)I^+[BF_4]^- \cdot C_6H_6$. A similar derivative, $[Ir(CO)(Me_3P)_2(C_3Ph_3)Cl]^+[BF_4]^- \cdot CH_2Cl_2$, has been obtained[325] by reaction of $[\pi\text{-}C_3Ph_3]^+BF_4^-$ with *trans*-$Ir(CO)(PMe_3)_2Cl$ in MeOH.

M(CO)L₂L′X₂

The preparations of derivatives of this class are described in Table VI.

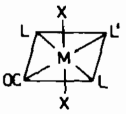
In addition, cationic carbene Ir(III) complexes, $[Ir(CO)(PMe_2Ph)L'Cl_2]^+$ [334] (L′ = $\overline{\text{CNHCHC(Me)S}}$, $\overline{\text{CNHC}_6\text{H}_4\text{S}}$, $\overline{\text{CNHC}_6\text{H}_4\text{O}}$), which may also be placed in this class, have been obtained by the reaction of 2-chloro derivatives of 5-methyl-1,3-thiazole or benzthiazole and benzoxazole with $Ir(CO)(PMe_2Ph)Cl$ and subsequent protonation.

The geometry of the molecules, $M(CO)L_2L'X_2$, is a distorted octahedron with both ligands (L) *trans* to each other (XXXIV).

TABLE VI. Substituted Carbonyl Halides of Rhodium and Iridium [$M(CO)L_2L'X_2$ and $M(CO)L_2L'XX'$ Class].

M	L	L′	X_2 or XX′	Preparation	Reference
Rh	Ph_3P	Me, Ph, CH_2Ph, $C_6H_4CH_2Cl$	Cl_2	a, b	195, 326
	Ph_3P	Me, MeCO, σ-C_3H_5	I_2	a	210, 288
	Ph_3P	Me	ClI	c	114
	Ph_3P	SCN^-	Cl_2, I_2	d	214
	Bu_3P	MeCO, $MeOCOCH_2$	I_2	b	190
	Bu_3P	Me, MeCO, $MeOCOCH_2$	ClI	b	190
	Et_2PhP	MeCO	Br_2	b	191
	Me_2PhP	Me, Et, MeCO, $MeSO_2$, $CH_2CMe = CH_2$	Cl_2, Br_2	b	101, 254
	Me_2PhAs	Me_2CHCO, C_3H_5CO, $MeSO_2$, $CH_2CMe = CH_2$, $MeC_6H_4SO_2$	Cl_2	b	101
Ir	Ph_3P	Me, EtCO, PrCO, AmCO, CSSEt, SO_2Me, SO_2Et, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$, CH_2CH_2Ph, CH_2Ph, $C_6H_4CH_2Cl$, C_3H_5	Cl_2, Br_2	a, b	190, 218, 326–329
	Ph_3P	$MeCO_2^-$, $EtCO_2^-$	I_2	e	226
	Ph_3P	Me, $MeOCOCH_2$, $CH_2 = CHCH_2$	ClI	b	190
	Et_2PhP	$CH_2CH(Cl)CH_3$, $CH_2CH(OAc)CH_3$, $CH_2CH(OMe)CH_3$, EtCO, PrCO, AmCO	Cl_2	b	218, 330
	Me_2PhP	CH_2CH_2Br, CH_2CH_2OMe, $CH_2CH_2PMe_2Ph$, $MeCO_2^-$, $EtCO_2^-$, $PhCO_2^-$, $CH_2CH(OMe)CH_3$, $CH_2CH(OEt)CH_3$, $CH_2CH(OAc)CH_3$, $CH_2CH(OH)CH_3$, $CH_2CHMeCH_2$, $CH_3CHClCH_2$, Me_2CClCH_2, MeCO	Cl_2	b, d, f, g	130, 233, 330–332
	Me_2PhP	σ-C_3H_5	ClBr	b	333
	$Me_2(o\text{-}MeC_6H_4)P$	MeCO, CO, σ-C_3H_5	Cl_2	b	224
	$Me_2(p\text{-}MeC_6H_4)P$	Me	I_2, ICl	b	224
	Et_2PhAs	MeCO	Br_2	b	218
	Me_2PhAs	RCO_2^- (R = Me, Et, Ph)	Cl_2	g	331
	Me_2PhAs	$CH_2CHMeCH_2$	Cl_2, Br_2	b	332

[a] Oxidative addition of alkyl, aryl or acyl halides to ML_3X in presence of CO. [b] Oxidative addition of alkyl, acyl, allyl or sulphonyl halides to $M(CO)L_2X$. [c] Action of Ph_3P on $RhClI(COMe)(Ph_3P)_2$. [d] Action of halogens on $Rh(CO)(Ph_3P)_2(SCN)$ or $[Ir(CO)(PMe_2Ph)_2(C_2H_4)_2]^+$. [e] Action of ligands on $[Ir(CO)_2I_4]^-$ in alcohols. [f] Action of MeOH on $Ir(CO)(PMe_2Ph)_2(CH_2CH_2Br)Br_2$. [g] Action of chloroformate esters on $Ir(CO)L_2X$.

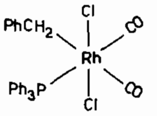


(XXXIV)

The crystal structure[335] of a compound, Ir(CO) $(C_{10}H_8N_2)(CH_3COO)I_2$, of this class has been studied. In this molecule the metal atom displays a distorted octahedral coordination with the two I atoms in *trans* positions. On the basis of the observed Ir–C distance (2.05 Å), the carbomethoxy group seems to be linked to the metal via a pure σ bond. The observed coplanarity of the –COO group with the metal atom, the carbonyl, and the two N atoms of bipyridine seems to be due to an angulated hydrogen bond concerning the "ketonic" oxygen of the carbomethoxy group with an α-C atom of bipyridine. The Ir–C bond connecting the metal with the CO ligand is rather short (1.80 Å), although the C–O bond (1.11 Å) and the stretching frequency (2050 cm^{-1}) do not indicate a particularly strong metal–carbonyl interactions. Owing to a steric repulsion of 2 hydrogen atoms, the 2,2'-bipyridine ligand is not planar and consequently, the chelate ring is also not planar.

$M(CO)_2LL'X_2$

The compounds of this class are less familiar. Ethyl chloroformate, iodobenzene or benzyl chloride react with $Rh(CO)_2(Ph_3P)Cl$ to give $Rh(CO)_2(Ph_3P)(COOEt)Cl_2$[266], $Rh(CO)_2(Ph_3P)PhClI$[266] and $Rh(CO)_2(Ph_3P)(PhCH_2)Cl_2$[326]. The benzyl derivative shows two IR active CO bands (ν_{CO}: 2065 and 1990 cm^{-1}) in agreement with the *cis*-structure (XXXV):



(XXXV)

Similar compounds of iridium have also been investigated.[336] A study of the carbonyl insertion reactions of $Ir(CO)_2L(Et)Cl_2$ in presence of L' giving Ir(CO) L(COEt)L'Cl_2 shows[336] that the rate determining step involves the combination of ethyl and CO to give a five coordinate intermediate of square pyramidal geometry with the propionyl group in the apical position. Subsequent attack by the incoming ligand L' occurs at the vacant octahedral coordination site *trans* to the propionyl group.

$M_2(CO)_2L'_2L'_2X_4$, $M_2(CO)_4L_2L'X_2$ and $M_2(CO)_2L_2L'X_4$

The compounds of these classes are also not common. A dinuclear complex, $[Ir(CO)(PPhMe_2)(COMe)Cl_2]_2$, has been obtained[233] by the reaction of $PPhMe_2$ on $[Ir(CO)_2MeCl_2]_2$. $Ir_2(CO)_4(Ph_3P)_2(COOR)_2X_2$ (X = Br, R = Et; X = I, R = Me, Et; X = Cl, R = Et) complexes have been prepared[226] by the action of bromine or iodine in alcohols or CCl_4 on $[Ir(CO)_3(Ph_3P)]_2$. These compounds show two $\nu_{C=O}$ bands at about 2100 and 2050 cm^{-1} and a $\nu_{C=O}$ band at 1670 cm^{-1} in their IR spectra.

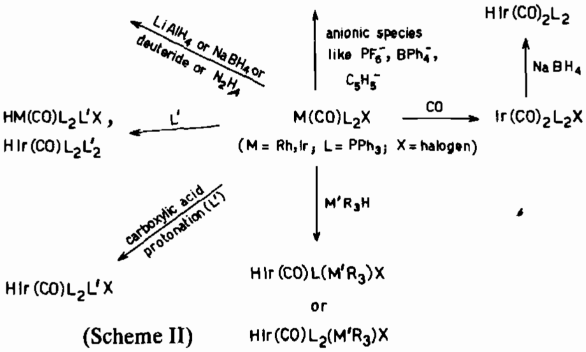
A novel compound[337] with molecular nitrogen $Rh_2(CO)_2(N_2)(Ph_3P)_2Cl_4$ has been synthesised by the treatment of Rh(CO)(Ph_3P)(acac) with excess of N_3H in dichloromethane at –60° C.

H. Carbonyl Hydrides and Their Derivatives

There is no positive evidence for the existence of any neutral carbonyl hydride of rhodium. The protonated species of $Rh_6(CO)_{16}$ in H_2SO_4 shows a singlet[56] at τ 27.4; attempts to isolate the cationic complexes by addition of NH_4PF_6 were unsuccessful. Iridium forms two neutral carbonyl hydrides, namely $HIr(CO)_4$ and $H_2Ir_4(CO)_{11}$. In 1940 Hieber and Lagally[7] reported the preparation of a very volatile compound $HIr(CO)_4$ along with two binary carbonyls. There has been no further positive evidence to support the existence of $HIr(CO)_4$. Recently[6,338] its formation by the direct action of CO and H_2 on $Ir_4(CO)_{12}$ under pressure has been described. The IR spectrum of $HIr(CO)_4$ is identical (ν_{CO}: 2054 m, 2031 s and 1999 w cm^{-1}) to $HCo(CO)_4$.[165] By analogy two bands at 2054 and 2031 cm^{-1} may be assigned to the A_1 and E vibrations respectively. The presence of another weak A_1 vibration at 1999 cm^{-1} could not be confirmed due to the appearance of absorption bands of dissolved CO. Attempts to isolate $HIr(CO)_4$ have been unsuccessful on account of its decomposition into $Ir_4(CO)_{12}$ at low pressure. $H_2Ir_4(CO)_{11}$[46] has been obtained as a very unstable brown-yellow compound when a solution containing $[HIr_4(CO)_{11}]^-$ is acidified under nitrogen.

Several types of substituted hydrido carbonyl complexes of these metals have been reported in the Table VII.

It has been observed that most of the compounds possess t-phosphines as stabilising ligands. They may be prepared by the following methods: (a) by the action of suitable ligands[51,54,75,105,107,108,133,138,271,339–341,343,346,347,354,357,359–363] on $M(CO)L_2X$ ($L = Ph_3P$, X = halogen):



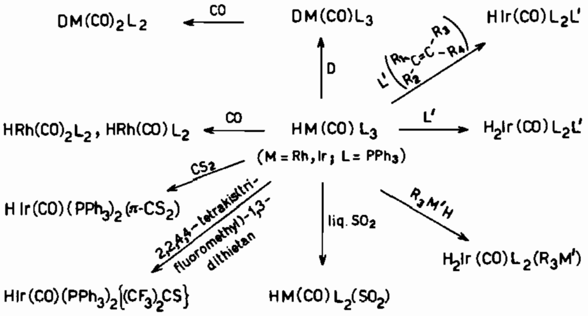
(Scheme II)

TABLE VII. Substituted and Halo–Carbonyl Hydrides of Rhodium and Iridium.

Compound	Preparation†	Reference
$HIr(CO)(Ph_3P)_2$	c	51, 133
$HIr(CO)(Ph_3P)\{(OPh)_3P\}$	b	216
$HRh(CO)(Ph_3P)_3^{*}$	a, b	54, 339, 340
$HIr(CO)(Ph_3P)_3^{*}$	a, b, c	51, 133, 166, 339
$HIr(CO)(Ph_3As)_3$	c	341
$HIr(CO)\{(PhO)_3P\}_3$	b	216
$HRh(CO)(Ph_3P)_2(SO_2)$	b	342
$HIr(CO)(Ph_3P)_2(\pi\text{-}CS_2)$	b	327
$HIr(CO)(Ph_3P)_2L$ ($L = C_2(CN)_2H_2, C_2(CN)_4, C_2CNPhH_2, C_2(COOH)_2H_2, C_2(COOMe)_2H_2, C_2(COOH)PhH_2$)	b	129
$HIr(CO)(Ph_3P)_2\{(CF_3)_2CS\}$	b	327
$HRh(CO)(C_5H_5)L$ ($L = SiPh_3, SiPhCH_2$)	–	135
$HRh(CO)_2(Ph_3P)_2^{*}$	b	54
$HIr(CO)_2L_2$ ($L = Ph_3P,^{*} Ph_2EtP, (FC_6H_4)_3P, PhEt_2P, Ph_3As$)	b, c	51, 343, 344
$HIr(CO)_3L$ ($L = Ph_3P, Et_3P, (p\text{-tol})_3P, Pr^{i}_3P, Bu_3P$)	e	345
$HRh(CO)L_2Cl_2$ ($L = Ph_3P, Pr^{i}_3P$)	a, c	179, 215, 346
$HRh(CO)LX_2$ ($L = C_{12}H_8N_2, C_{10}H_8N_2; X = Cl, Br$)	a	275, 347
$HRh(CO)(Ph_3P)_2(SiCl_3)Cl$	a, b	346
$HRh(CO)(Ph_3P)_2(C_2F_4H)Cl$	a	105
$HIr(CO)L_2Cl_2$ ($L = Ph_3P, Et_2PhP, Me_2BuP, Et_2BuP, Pr_2BuP, Bu^{t}Bu^{n}_2P, Bu_2MeP, Bu_2EtP, Bu_2PrP$)	a, f, c	105, 144, 261, 348–352
$HIr(CO)L_2Br_2$ ($L = Me_2BuP, Et_2BuP, Pr_2BuP, Bu^{n}_2Bu^{t}P$)	a	349
$HIr(CO)(Ph_3P)_2I_2$	f	133
$HIr(CO)L_2X_2$ ($L = Ph_2MeAs, Ph_2EtAs; X = Cl, Br$)	–	353
$HIr(CO)(Ph_3P)_2LCl$ ($L = SiCl_3, SnCl_3^{*}$)	a, g	140, 346, 354
$HIr(CO)(Ph_3P)LCl$ ($L = SiEtCl_2, SiPhCl_2, Si(OEt)_3, SnCl_3$)	a	354, 355
$HIr(CO)(Ph_3P)(GePh_3)Cl\cdot{}^{1}/_{2}C_6H_{12}$	a	138
$HIr(CO)(Ph_3P)_2XX'$ ($XX' = FCl, FBr, ClBr,^{*} ClI,^{*} BrI$)	f	351
$HIr(CO)(Ph_3As)_2X_2$ ($X = Cl, Br$)	f	297
$HIr(CO)(Et_3P)_2Cl_2$	c	356
$HIr(CO)(Ph_3P)_2(CN)Cl^{*}$	a, f	357, 358
$HIr(CO)L_2(COOPh)X$ ($L = PMe_2Ph, X = Cl, Br, I; L = Ph_3P, Ph_2MeP, Me_3P, Ph_3As, Me_2PhAs, Et_2PhP, X = Cl$)	a	359
$HIr(CO)(Ph_3P)_2LCl$ ($L = p\text{-}SC_6H_4NO_2, SC_6H_4Br, SC_6H_4Cl, SC_6H_4F, SC_6H_4Me, SC_6H_4OMe, SC_6H_3SHMe, SH, OOCCF_3, OOCEt, ClO_4$)	a, c	105, 350, 357, 360
$HIr(CO)(Ph_3P)_2LX$ ($L = SnMe_3, X = Cl^{*}, Br; L = SnPh_3, X = Cl^{*}, Br^{*}, I; L = SnEt_3, X = Cl$)	a	361, 362
$HIr(CO)(PPh_2Me)(SNPh_3)Cl$	a	361, 362
$HIr(CO)(Ph_3P)_2(SC_6F_5)_2$	a	107
$HIr(CO)(Ph_3P)_2LX$ ($L = SC_6F_5, X = Cl, Br, I; L = SC_6H_5, X = Cl, Br, I; L = SC_6F_4SH, X = Cl, Br, I$)	a	107
$HIr(CO)(Ph_3Sb)_2Cl_2^{*}$	f	243
$[HIr(CO)L_3X]^{+}$ ($L = PMe_2Ph, AsMe_2Ph$)	a	75
$[HIr(CO)(Ph_3P)(C_5H_5)]^{+}$	d	122
$H_2Ir(CO)(Ph_3P)_2L$ ($L = C_2F_5COO^{-}, SC_6H_5, SnCl_3^{*}$)	b, f, g	107, 140, 327
$H_2Ir(CO)(Ph_3P)_2L$ ($L = SiPh_3, SiEt_3, Si(OEt)_3$)	a, b	138, 354, 363, 364
$H_2Ir(CO)L_2(GeMe_3)$ ($L = PEt_3, PMe_2Ph$)	h	138
$H_2Ir(CO)(Ph_2PCH_2CH_2PPh_2)(GeEt_3)$	h	138
$H_2Ir(CO)L_2X$ ($L = Ph_3P, X = Cl^{*}, Br, I; L = Et_3P, X = Cl, I; L = (C_6H_{11})_3P, X = Br, I; L = Pr_3P, X = Cl, Br, I$)	f	138, 151, 260, 365 366, 367
$[H_2Ir(CO)(Ph_3P)_3]^{+}ClO_4^{-}$	f	133
$[H_2Ir(CO)_2L_2]^{+}BPh_4^{-}$ ($L = Ph_3P, Ph_3As, MePh_2P^{*}, Ph_2EtP, Et_2PhP, Et_3P, (C_6H_{11})_3P, Pr_3P$)	f	71
$H_2Ir_2(CO)_2(Et_3P)_2Cl_4$	–	261
$H_3Ir(CO)L_2$ ($L = Ph_3P^{*}, Bu_2PrP, Et_2PhP, Ph_3As$)	a, c, f	51, 108, 123, 133, 341, 344, 348, 368

* Deuterated derivatives are also known. † Preparative methods are the same as described in section 2H of the text.

(b) by the action of the ligands[51, 54, 129, 133, 166, 216, 327, 339, 342, 343, 364] on $HM(CO)L_3$ (Scheme III) under varying conditions:



Scheme III

Deuterium exchange reactions have also been performed in these derivatives;

(c) by bubbling CO[51, 133, 179, 341, 343, 344, 348, 350, 356, 368] through the reaction mixtures of several non-carbonyl containing substituted metal hydrides:

$$HRhL_4Cl_2 \xrightarrow{CO} HRh(CO)L_2Cl_2$$

$$HIrL_2X_2 \xrightarrow{CO} HIr(CO)L_2Cl_2$$

$$H_5IrL_2 \xrightarrow{CO} H_3Ir(CO)L_2 \text{ and } HIr(CO)_2L_2$$

$$H_3IrL_2 \xrightarrow{CO} HIr(CO)L_2$$

$$H_3IrCl_3 \xrightarrow{CO} HIr(CO)L_2,\ HIr(CO)L_3,\ HIr(CO)_2L_2,\ H_3Ir(CO)L_2$$

$$HML_2L'X \xrightarrow{CO} HM(CO)L_2L'X$$

(d) by the treatment of cyclopentadienyl derivatives of Rh and Ir carbonyls, $(C_5H_5)Rh(CO)_2$ and $(C_5H_5)Ir(Ph_3P)(CO)$, with $M'R_3H$[135] or with acids[122] as indicated below:

$$(C_5H_5)Rh(CO)_2 + M'R_3H \rightarrow HRh(CO)(C_5H_5)(M'R_3)$$

$$(C_5H_5)Ir(CO)(Ph_3P) \xrightarrow{\text{acid protonation}} [HIr(CO)(Ph_3P)(C_5H_5)]^+$$

(e) by the action[44,45] of CO and H_2 (1:1) on $Ir_2(CO)_6L_2$:

$$Ir_2(CO)_6L_2 \xrightarrow{CO + H_2} HIr(CO)_3L$$

(f) by the action[57, 71, 107, 123, 138, 260, 320, 365, 367] of H_2, D_2 or their halides[145, 243, 261, 297, 349, 351] on different substituted metal carbonyl species:

$$M(CO)L_2X \xrightarrow{H_2 \text{ or } D_2 \text{ bubbling}} H_2M(CO)L_2X \text{ or } D_2M(CO)L_2X$$

$$M(CO)L_2X \xrightarrow[DX \text{ or } DX']{HX \text{ or } HX'} HM(CO)L_2X_2 \text{ or}$$

$$HM(CO)L_2XX' \text{ and its deuterium analogue}$$

$$Ir(CO)(Ph_3P)_2(HgCl)Cl_2 + HCl \rightarrow HIr(CO)(Ph_3P)_2Cl_2$$

$$H_3M(CO)L_2 \xrightarrow{HX} HM(CO)L_2X_2$$

$$[M(CO)_2L_3]^+ \xrightarrow{H_2} [H_2M(CO)L_3]^+$$

$$[M(CO)_3L_2]^+ \xrightarrow{H_2 \text{ or } D_2} [H_2M(CO)_2L_2]^+ \text{ or } [D_2M(CO)_2L_2]^+$$

$$M(CO)L_2L' \xrightarrow{H_2} H_2M(CO)L_2L'$$

$$HM(CO)_2L_2 \xrightarrow{H_2} H_3M(CO)L_2$$

(g) by hydride transfer reaction[140] between $Ir(CO)L_2Cl$ (or $HIr(CO)L_2Cl_2$) and H_2O in acetone solution containing $SnCl_2$;

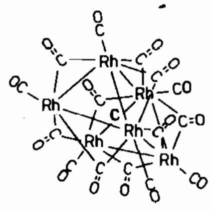
(h) by the displacement[138] of Ph_3P in $H_2Ir(CO)(Ph_3P)_2(GeR_3)$ (R = Me, Et) from other t-phosphines:

$$H_2Ir(CO)(Ph_3P)_2(GeR_3) \xrightarrow{L'} H_2Ir(CO)L'_2(GeR_3)$$

I. Carbonyl Carbide Complexes

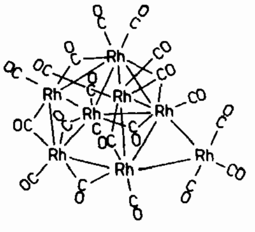
One neutral and two anionic carbido carbonyl clusters of Rh have been reported so far. Iridium does not form such complexes. The anion, $[Rh_6(CO)_{15}C]^{2-}$, proved to be the first carbido complex[369] of the cobalt triad, and at the same time the first hexanuclear metal atom cluster having a trigonal prismatical geometry. Treatment of $Rh_4(CO)_{12}$ with methanolic NaOH under CO for 2h gave a deep green solution of $[Rh_7(CO)_{16}]^{3-}$ which slowly changed into a yellow-green solution after the addition of chloroform. Subsequent addition of solid CO_2 to this solution and evaporation to dryness yielded a residue. It was dissolved in water and saturated with KBr. Pure potassium salt of the anion, $[Rh_6(CO)_{15}C]^{2-}$, was obtained after extraction with tetrahydrofuran (ν_{CO}: 2030sh, 1995vs, 1840s and 1802 cm^{-1} in MeCN). Another salt with benzyltrimethylammonium cation was also prepared.

The crystal structure study[369] suggests for precise C_2 and idealized D_{3h} symmetry (XXXVI) of the anion. The six Rh atoms define a trigonal prism whose edges are associated with symmetrical bridging CO groups; each carbonyl group of the remaining six is linearly bonded one per Rh atom. The carbide atom occupies the centre of the prism. The mean basal and inter-basal Rh–Rh distances are 2.776 and 2.817 Å respectively (mean Ru–C, 2.134 Å).



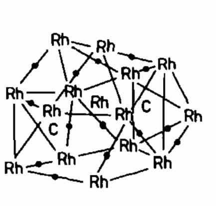
(XXXVI)

On oxidation of $[Rh_6(CO)_{15}C]^{2-}$ in water under CO using ferric ammonium alum as a mild oxidant a brown precipitate was obtained, which changed into black diamagnetic $Rh_8(CO)_{19}C$[370] (XXXVII) after dissolution in toluene or dichloromethane under CO. The molecule contains a metal atom cluster derived from the prismatic unit present in the dianion, $[Rh_6(CO)_{15}C]^{2-}$, to which two extra atoms have been attached, one in a capping position on one rectangular face and the other in a bridging position on one base edge. The Rh–Rh distance ranges from 2.669 to 2.913 Å (mean value 2.81 Å). The carbido carbon atom is situated in the centre of the prism with a mean Rh–C distance of 2.127 Å. Eleven of the nineteen CO groups are linearly bound, six of them are edge bridging, and two are face bridging. This molecule is a rare example of a completely asymmetric cluster, contradicting the common opinion that the clusters are highly symmetrical units of close packed metal atoms:



(XXXVII)

On performing the whole oxidation process of $[Rh_6(CO)_{15}C]^{2-}$ under nitrogen, a new black crystalline, diamagnetic and nonelectrolyte (in dichloromethane) species was obtained. It was tentatively formulated as $[H_3O][Rh_{15}(CO)_{28}C_2]$[370] (XXXVIII). The molecule possesses C_{2v} idealized symmetry and the Rh_{15} cluster can be described as a centred tetracapped pentagonal prism, or alternatively as a system of two octahedra sharing one vertex (the central atom), plus four other atoms forming tetrahedra fused with the octahedra and with themselves; the Rh–Rh distances are scattered in the range 2.738–3.332 Å. It is worthwhile pointing out the highly metallic situation of the central Rh atom, which is linked to twelve other metal atoms (mean distance 2.90 Å) and to both carbide carbon atoms occupying the centres of the octahedra with mean Rh–C distance 2.06 Å. The twenty eight CO ligands are arranged as fourteen in terminal positions, one per metal atom, and the remaining are bridging edges of the metal atom polyhedra:



• represents bridging CO groups
terminal CO groups are not shown

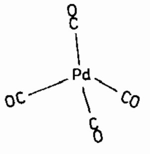
(XXXVIII)

The reaction between $[Rh(CO)_4]^-$ and $Co_3(CO)_9CCl$ gave an anion, $[Co_2Rh_4(CO)_{15}C]^{2-}$[370], the tetramethylbenzylammonium salt of which was isomorphous with the corresponding salt of the anions $[Rh_6(CO)_{15}C]^{2-}$ and $[Co_6(CO)_{15}C]^{2-}$, implying that the three anions were isostructural.

3. Palladium and Platinum

A. Binary Carbonyls

Although two CO adsorbed palladium compounds,[371,372] PdCO and Pd_2CO, are known since a long time, binary carbonyls have not been reported until recently.[373–375] Earlier, the formation of an unidentified unstable zerovalent palladium carbonyl was observed by the oxidative hydrolysis[376] of the complexes formed by the CO reduction of H_2PdCl_4. In 1972 the existence of an unstable palladium carbonyl, $Pd(CO)_4$, has been established by IR spectroscopic studies.[373,375] It was obtained in argon matrix by vaporising palladium metal at 1800° K and co-condensing with a mixture of argon and CO at 20°K. Other identified species obtained were $Pd(CO)_3$, $Pd(CO)_2$ and PdCO. A single ν_{CO} frequency (2070.3 cm^{-1}) and the calculated band intensity provided the confirmation for $Pd(CO)_4$ and the quintet patterns were characteristic for a tetracarbonyl with T_d symmetry (XXXIX):



(XXXIX)

Diffusion studies[374] indicate that the lower carbonyls readily react with excess of CO to yield $Pd(CO)_4$.

A CO adsorbed platinum compound, $Pt_3(CO)_4$, was obtained[377,378] by vacuum deposition of Pt in CO atmosphere. The nature of the deposit depended[378] to a large extent on the rate of vaporization of platinum. For relatively slow rates of vaporization of platinum a crystal deposit was obtained having cubic lattice with a = 6.16 Å. For relatively rapid rate of vaporization of platinum in CO atmosphere at the same pressure, a brown deposit was obtained but with a = 6.04 Å. These two compounds were nearly isomorphic with the known $Pt_3(O_2)_4$ with a = 6.17 Å.

A binary platinum carbonyl, $Pt(CO)_n$, has been described as a red black product[379] which was obtained in the colloidal state by the action of CO on a dilute aqueous solution of chloroplatinic acid. An unidentified black crystalline by-product[380] was obtained by the action of CO on a solution of K_2PtCl_4 in dil. HCl. Later on two different groups of workers[381–384] reported the preparation of a polymeric binary car-

TABLE VIII. Substituted Derivatives of Platinum and Palladium Carbonyls.

Compound	Preparation	ν_{CO} (cm^{-1})	Reference
$Pd(CO)(Ph_3P)_3$	a		386
$Pd(CO)(Ph_3P)_2(PF_3)$	b		387
$Pt(CO)(Ph_3P)_3$	c, d, e	1930	383, 388–390
$Pt(CO)(Ph_2MeP)_3$	d, e	1923	383, 388
$Pt(CO)(PhMe_2P)_3$	e	1913	388
$Pt(CO)(Ph_2PPhCH_2)_3$	e	1908	388
$Pt(CO)(Ph_2Pr^iP)_3$	e	1912	388
$Pt(CO)\{(p\text{-}ClC_6H_4)_3P\}_3$	e	1922	388
$Pt(CO)(Et_3P)_3$	e	1913	388
$Pt(CO)_2(Ph_3P)_2$	e	1990, 1948	388
$Pt(CO)_2(Ph_2MeP)_2$	e	1985, 1949	388
$Pt(CO)_2(Ph_2EtP)_2$	e	1982, 1940	388
$Pt(CO)_2(Ph_2PrP)_2$	e	1980, 1939	388
$Pt(CO)_2(Me_2PhP)_2$	e	1980, 1937	388
$Pt(CO)_2(Et_3P)_2$	e	1970, 1923	388
$Pt(CO)_2(Bu_3P)_2$	e	1973, 1931	388
$Pt(CO)_2(PF_3)_2$	b		387
$Pt(CO)(Ph_3P)_2(SnCl_3)_2$	f	2050	391, 392
$Pt(CO)(Ph_3P)_2(SnCl_3)_2(MeOH)$	f	2061	391, 392
$Pt(CO)(Ph_3P)_2(SnCl_3)_2(EtOH)$	f	2060	391, 392
$Pt(CO)(C_{10}H_8N_2)(SnCl_3)_2$	f	2041	391, 392
$Pt(CO)(C_{12}H_8N_2)(SnCl_3)_2$	f	2046	391, 392
$Pd_2(CO)_2(C_{12}H_8N_2)_2$	g		393
$Pd_2(CO)_2(C_{10}H_8N_2)_2$	g		393
$Pt_2(CO)S(Ph_3P)_3$	h	1989, 1960	394–396
$Pt_3(CO)_3(Ph_2PPhCH_2)_3$	d, e	1852, 1789	383, 397
$Pd_3(CO)_3(Ph_3P)_4$	k		386
$Pt_3(CO)_3(Ph_3P)_4$	d, e, m	1839, 1784	383, 397, 398
$Pt_3(CO)_3(Ph_2MeP)_4$	d, e	1838, 1775	383, 397
$Pt_3(CO)_3(Ph_2EtP)_4$	e	1835, 1782, 1770	397
$Pt_3(CO)_3(Et_3P)_4$			399
$Pt_4(CO)_5(Ph_3P)_4$	i	1810, 1797	397
$Pt_4(CO)_5(Ph_2PPhCH_2)_4$	e	1993, 1885, 1856, 1800, 1772, 1714	397
$Pt_4(CO)_5(Me_2PhP)_4$	e	1800, 1779	397
$Pt_4(CO)_5(Et_3P)_4$	d	1980, 1975, 1845, 1785, 1755	397
$Pt_4(CO)_5(Ph_3As)_4$	e	1995, 1890, 1860, 1795, 1775	397
$Pt_4(CO)_5(Ph_3As)_3$	e	1995, 1875, 1865, 1800, 1775, 1720	397
$Pt_4(CO)_5(Ph_3P)_4 \cdot C_6H_6$	e	1850, 1822, 1789	400
$Pt_4(CO)_5\{PPh_2(o\text{-}MeC_6H_4)\}_4\ C_6H_6$	e	1855, 1811, 1785	400
$[Pt(CO)(p\text{-}FC_6H_4)(Et_3P)_2]^+$	j	2098	401
$[Pt(CO)(m\text{-}FC_6H_4)(Et_3P)_2]^+$	j	2101	401
$[Pt(CO)(p\text{-}ClC_6H_4)(Et_3P)_2]^+$	j		402
$[Pt_3(CO)(Ph_3P)_4(Ph_2C_2H)]^+$	l	2040	403
$[Pt_3(CO)(Ph_3P)_4(PhC_2HMe)]^+$	l	2040	403
$[Pt_3(CO)(Ph_2MeP)_5(Ph_2C_2H)]^+$	l	2030	403

[a] Reaction of t-phosphines with $Pd(acac)_2$ in presence of CO. [b] Reaction of CO with $M(Ph_3P)_2(PF_3)_2$. [c] Reaction of CO with PtL_4. [d] Reaction of t-phosphines with $Pt_n(CO)_{2n}$. [e] Reaction of Group V donor ligands and CO with Pt(II) halides or Na_2PtCl_4 *in presence of* $N_2H_4 \cdot H_2O$. [f] *Reaction of Group V donor ligands and* $SnCl_2$ *with* Na_2PtCl_4 *in presence of CO.* [g] Reaction of *o*-phen or 2,2′-bipy with $PdCl_2$ in presence of CO. [h] Refluxing of $Pt(COS)(Ph_3P)_2$ in $CHCl_3$. [i] Reaction of CO with $Pt_3(CO)_3(Ph_3P)_4$ in acetone. [j] Reaction of CO and $NaClO_4$ with $Pt(Et_3P)_2LCl$. [k] Heating $Pd(CO)(Ph_3P)_3$. [l] Hydrocarbon ligands with oxalatobis(t-phosphine)Pt(II) in presence of CO and by addition of corresponding anion. [m] Reaction of CO with $Pt(Ph_3P)_2(\pi\text{-}CF_3CN)$ in benzene.

bonyl, $Pt_n(CO)_{2n}$ (n may be 5), by the action of H_2O or D_2O on benzene solutions of $Pt(CO)_2Cl_2$ in CO atmosphere (purple coloured product) or by the CO reduction of an ethanolic solution of Na_2PtCl_4 (brown coloured product). K_2PtCl_4, K_2PtCl_6, K_2PtBr_6, $K_2Pt(SCN)_4$, K_2PtI_4, $Pt(acac)_2$ also react[381,385] with CO to form a similar compound. The brown product has been described to be a pure form. It was air sensitive, diamagnetic and insoluble in most of the organic solvents but soluble in acetone/aq. ammonia. It showed one Pt–C(ν_{Pt-C}: 450 cm^{-1}) and two CO bands (ν_{CO}[384]: 2062 and 1879 cm^{-1} in nujol; ν_{CO}[381]: 2050 and 1870 cm^{-1} in KBr) in its IR spectrum. In the crystal the measured Pt–Pt and Pt–C bond distances[381] are 2.7 Å and 1.6 Å respectively.

B. Substituted Derivatives

Several mono-, di- and trinuclear derivatives which contain N, P and As donors have been reported for, both the metals (Table VIII). Platinum forms tetranuclear derivatives also.

Mononuclear

$Pd(CO)(Ph_3P)_3$ was obtained[386] by bubbling CO through a toluene solution containing one mol of palladium acetylacetonate, 3 mol of triphenylphosphine and triethylaluminium at –50°–10° C. When equimolar quantities of triphenylphosphine and palladium acetylacetonate were taken, the formation of a polynuclear compound, $[Pd(CO)(Ph_3P)]_n$, resulted. A mixed ligand carbonyl derivative, $Pd(CO)(Ph_3P)_2(PF_3)$, was obtained by autoclaving[387] $Pd(Ph_3P)_2(PF_3)_2$ at high pressure of CO.

Similar compounds of platinum were prepared by slow carbonylation[383, 388–390] of PtL_4 or PtL_3 (L = substituted phosphines). By using excess of ligand and reducing with hydrazine followed by the treatment with potassium hydroxide, $Pt(CO)L_3$ were obtained[388] in 80–90% yield. In case of triphenylphosphine derivatives, two different forms of $Pt(CO)(Ph_3P)_3$ have been isolated. $Pt(Ph_3P)_4$ gives a form (A) which in the solid state shows a strong CO stretching band at 1940 cm^{-1} and has approximately a tetrahedral arrangement of ligands.[397] This form easily changes to a more stable form (B), which may be obtained directly by the carbonylation of $Pt(Ph_3P)_3$. It is a colourless solid and the solid state spectrum shows a single CO band at 1908 cm^{-1}. Its crystal structure study showed a more deformed tetrahedral arrangement of the ligands[404] in the molecule, suggesting greater back donation. In solution (THF) both forms absorb at 1930 cm^{-1}.

The CO stretching frequencies in these compounds are a measure of acceptor properties of the phosphine ligands in these complexes. By using two moles of the ligands, $Pt(CO)_2L_2$ derivatives were obtained.[388, 405, 406]

$$K_2PtCl_4 + 2L \rightarrow L_2PtCl_2 + 2KCl$$

$$L_2PtCl_2 + 2NH_2NH_2 \rightarrow L_2PtHCl + NH_4Cl + NH_3 + N_2$$

$$L_2PtHCl + KOH + 2CO \rightarrow Pt(CO)_2L_2 + KCl + H_2O$$

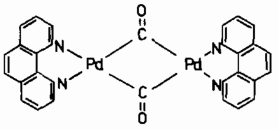
These compounds were air stable and showed two strong carbonyl stretching bands in their IR spectrum in agreement with a tetrahedral arrangement. The relative band intensities of $Pt(CO)_2L_2$ and $Pt(CO)L_3$ decrease in the series $PPh_2Pr^i > Ph_3P > PPh_2Et > PPh_2Me$, the less sterically crowded $Pt(CO)_2(PPh_2R)_2$ being preferred to $Pd(CO)(PPh_2R)_3$ on increasing the steric requirements of the group R in PPh_2R.

In addition to the neutral mononuclear Pt carbonyl complexes, a few cationic, $[Pt(CO)(Et_3P)_2L]^+$ (L = p-FC_6H_4, m-FC_6H_4 or p-ClC_6H_4), complexes have also been prepared. The crystal structure study[407] of one cation, $[Pt(CO)(Et_3P)_2(p\text{-}ClC_6H_4)]^+$, shows that the coordination around the Pt atom is square planar; Pt, the carbonyl group and p-chlorophenyl group lie in a crystallographic mirror plane. The phosphine atoms are above and below the mirror plane.

The tin bonded, $Pt(CO)(Ph_3P)_2(SnCl_3)_2$, $Pt(CO)(o\text{-phen})(SnCl_3)_2$ and $Pt(CO)(py)(SnCl_3)_2$, complexes have been obtained by the reactions[391, 392] of the ligands with a red solution of platinum carbonyl species (prepared by mixing Na_2PtCl_4 and $SnCl_2$ in alcohols under CO). However, when the red solution was treated with Ph_3P in acetone, the complex $Pt(CO)(ROH)(Ph_3P)_2(SnCl_3)_2$ (R = Et, Me) was obtained which contained coordinated alcohols.

Dinuclear

Dinuclear palladium and platinum complexes are very rare. A dimeric compound, $[Pd(CO)(o\text{-phen})]_2$, (XL) was prepared by the action[393] of hot aqueous solution of $PdCl_2$ on excess of o-phenanthroline in presence of a mixture of CO and air. It absorbs at 550 mμ. In the similar manner an analogous, very unstable, 2,2′-bipyridine compound[393] has also been prepared.

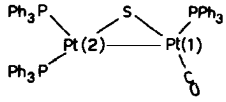


(XL)

$Pt_2S(CO)(Ph_3P)_3$, previously thought[394] to be $Pt_2S(CO)_2(Ph_3P)_3$, was obtained by heating $Pt(COS)(Ph_3P)_2$ in chloroform. The reaction is considered to be the condensation of two molecules of (carbonylsulphide)bis(triphenylphosphine)platinum(II) with the elimination of one molecule of carbonyl sulphide:

$$2Pt(COS)(Ph_3P)_2 \xrightarrow[CHCl_3]{reflux} Pt_2S(CO)(Ph_3P)_3 + COS + Ph_3P$$

Its IR spectrum showed two terminal CO bands.[394] Later on an X-ray structural study[395, 396] revealed the presence of only one carbonyl group. In the crystalline state the complex exists in two conformationally isomeric forms in the ratio *ca.* 67 : 33; the difference between the two isomers is mainly confined to one Ph_3P group in which the phenyl rings adopt two quite different conformations with respect to the rest of the molecule. This also results in a slightly different orientation of the adjacent carbonyl group for each isomer. The IR data (ν_{CO}: 1989 and 1960 cm^{-1}) obtained by Baird and Wilkinson[394] may well be explained with the presence of one carbonyl group per molecule of the complex having slightly different environments in the two conformational forms. In the crystal[396] of $Pt_2S(CO)(Ph_3P)_3$, two platinum atoms with sulphur form a three membered ring (XLI). The Pt–Pt distance is 2.647 Å and Pt(1)–S and Pt(2)–S distances are 2.218 and 2.27 Å, respectively. The angles of the triangle are Pt(1)–Pt(2)–S, 53.3°, Pt(2)–Pt(1)–S, 53.6°, and Pt(1)–S–Pt(2), 73.1°. The Pt atoms and their immediate neighbours are essentially planar. However, the coordination about the metal atom is far from square planar:



(XLI)

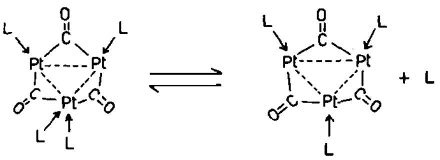
Trinuclear and tetranuclear

Trinuclear palladium carbonyl clusters are of very rare occurrence. The formation of $Pd_3(CO)_3(Ph_3P)_4$ has been reported[386] as a result of the elimination of Ph_3P from $Pd(CO)(Ph_3P)_3$. In case of platinum two different types of compounds, $Pt_3(CO)_3(PPh_2PhCH_2)_3$ and $Pt_3(CO)_3L_4$ (L = Ph_3P, PPh_2Me, PPh_2Et), have been reported. The $Pt_3(CO)_4L_3$ complexes, which were erroneously formulated earlier,[383] were actually found to be tetranuclear, $Pt_4(CO)_5L_4$, in the later studies.[397]

The trinuclear derivatives have been prepared either by the action[383,397] of phosphine ligands on $[Pt(CO)_2]_n$ or by the reduction[384] of $HPtL_2X$ with hydrazine in presence of CO. It is just possible that $Pt(CO)_2L_2$ is an intermediate in all the original preparations:

$$5Pt(CO)_2L_2 \rightleftharpoons Pt_3(CO)_3L_4 + 2PtL_3 + 7CO$$

$Pt_3(CO)_3L_4$ (XLII) loses one ligand molecule to give $Pt_3(CO)_3L_3$ (XLIII).



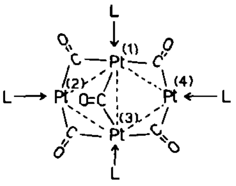
(XLII) (XLIII)

The trinuclear clusters become increasingly unstable as the basicity of the phosphines increases and this is evident in the case of the red $Pt_3(CO)_3(Et_3P)_4$ which has a very limited stability not only in solution but also in the solid state. The IR spectra[397] of $Pt_3(CO)_3L_4$ indicate the presence of only bridging carbonyl groups and are consistent with a C_{2v} structure. For $Pt_3(CO)_3L_3$ complexes (D_{3h}) only one band E′ is expected on symmetry considerations, but the presence of two bands in THF solution is possibly caused by partial reversion to $Pt_3(CO)_3L_3 \cdot$solvent.

The tetranuclear carbonyl clusters are of two types, *viz.*, $Pt_4(CO)_5L_4$ and $Pt_4(CO)_5L_3$. $Pt_4(CO)_5L_4$ are prepared[397] by the action of CO on trinuclear species.

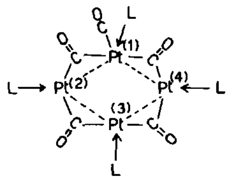
$$2Pt_3(CO)_3L_4 + 3CO \xrightarrow[1\ atm]{25°\ C} Pt_4(CO)_5L_4 + 2Pt(CO)_2L_2$$

They exist in two isomeric forms (brown to black, and red). The IR stretching bands of the brown–black isomers[397] show only bridging carbonyl groups (XLIV):



(XLIV)

The red isomers show both bridging and terminal CO stretching bands (XLV) which may be due to the splitting of Pt(1)–Pt(3) bond in (XLIV) at the central bridging CO groups. $Pt_4(CO)_5L_4$ molecules lose one ligand molecule to yield $Pt_4(CO)_5L_3$ (L = Ph_3As). The IR spectra of the red $Pt_4(CO)_5L_4$ and $Pt_4(CO)_5L_3$ species are very similar; both show a complicated pattern indicating that if structure (XLV) of the red form is correct, the ring is puckered:



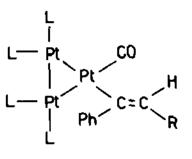
(XLV)

Cationic complexes

Recently, trinuclear cationic clusters of platinum (XLVI, XLVII) have also been reported.[403] The mechanism of their formation is described below:

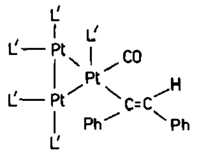
$$Pt(C_2O_4)L_2 + L' \xrightarrow[Stirring]{CO/EtOH} \text{Oily liquid} \xrightarrow{NaX} [Pt_3(CO)L_4L'H]^+X^-$$

($L = Ph_3P$, $L' = C_2Ph_2$ or PhC_2Me; $X = BF_4^-, NO_3^-, PF_6^-$)



(L= PPh_3; R=Ph, Me)

(XLVI)



(L′ = PPh_2Me)

(XLVII)

Cyclopentadienyl derivatives

Sodium cyclopentadienide reacts[408] with a mixture of platinum carbonyl chlorides (obtained by passing a thin stream of CO over $PtCl_2$ at 220°C) in benzene to yield $[(C_5H_5)Pt(CO)]_2$. It is an air stable, diamagnetic, red solid. NMR, IR and dipole moment[408] measurements support a non-centrosymmetric structure involving π-bonded C_5H_5, terminal CO groups and a Pt–Pt bond.

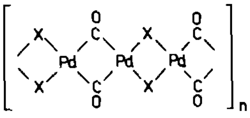
When a solution of iodine[408] in pentane is added dropwise in the absence of air to an ice cooled solution of $[C_5H_5Pt(CO)]_2$ in nitrogen saturated pentane, black needles of $C_5H_5Pt(CO)I$ are isolated.

C. Carbonyl Halides

Carbonyl halide complexes of Pd(II) were first reported by Fink[409] in 1898; but Manchot *et al.*[410] were only able to confirm the stoichiometry of $Pd(CO)Cl_2$. On passing CO through a suspension of palladium(II) chloride at 0° C, they obtained a pale yellow solid, $Pd(CO)Cl_2$, stable when dry but decomposed at once by water. It was suggested to be dimeric or trimeric. Its formation has also been claimed[411] when vapours of methanol or ethanol are passed into the solution of $PdCl_2$. Other mono- and di-carbonyl halides of palladium have been obtained by the reduction[376] of H_2PdCl_4 with CO.

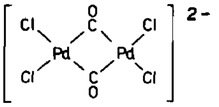
Dent *et al.*[412] on studying the carbonylation of allyl chloride in presence of $PdCl_2$, reported the formation of an insoluble Pd(I) complex, $[Pd(CO)(Cl)]_n$. Fischer and Vogler[413] claimed the formation of $Pd_2(CO)_2Cl$ by allowing the complex $PdCl_2(PhCN)_2$ in $CHCl_3$ to react with CO. Schnabel and Kober[414] reported the formation of yellowish green Pd(CO)Cl by the same reaction. The IR features of both Pd(CO)Cl and $Pd_2(CO)_2Cl$ were identical. Trieber[415] has also confirmed the formation of Pd(CO)Cl.

In their earlier studies Kushnikov *et al.*[416] reported the formation of a polymeric palladium carbonyl bromide, $[Pd(CO)Br_2]_n$, by the reaction of K_2PdBr_4 or $PdBr_2$ dispersed in dioxane containing water and CO. In their later studies[417] they claimed the formation of $[Pd(CO)X]_n$ as a result of the reaction between CO and PdX_2 (X = Cl or Br) in the presence of methanol vapour or dioxane containing known quantities of water. A recent IR study[418] on $[Pd(CO)X]_n$ (X = Cl, ν_{CO}: 2023vvw, 2002vw, 1978vs, br, 1951vvw, sh, 1936vw; X = Br, ν_{CO}: 2008vvw, sh, 1996vw, 1987w, 1953vs, br, 1932sh and 1922w, sh cm^{-1}) shows that the polymeric complexes have CO and X bridges alternatively between Pd atoms (XLVIII).



(XLVIII)

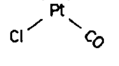
Palladium halo carbonyl anions were investigated[419] in as early as 1942. Recently several anions like $[Pd_2(CO)_2Cl_4]^{2-}$, $[Pd_4(CO)_4Cl_6]^{2-}$ and $[Pd(CO)X_3]^-$ have been isolated[418] as their tetralkylammonium salts. Tetrapropylammonium salt of $[Pd_2(CO)_2Cl_4]^{2-}$ was prepared by the action of CO on hydrated Na_2PdCl_4 in conc. HCl and precipitating it with Pr^n_4NCl. The bromide complex was similarly obtained with K_2PdBr_4. The corresponding NBu_4^+ and NPr_4^+ salts were isolated by the reaction of NBu_4X or NPr_4X on $[Pd(CO)X]_n$ in dichloromethane. From their spectra it has been concluded that they have carbonyl bridged structures (XLIX):



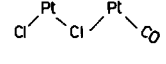
(XLIX)

These anions seem to be essentially planar in the solid Pr_4N^+ salts but in solution and as the salts of the larger cations they appear to be bent about the carbonyl bridges. $(Pr_4N)_2[Pd_2(CO)_2Cl_4]$ is converted into $(Pr_4N)_2[Pd_4(CO)_4Cl_6]$ when soaked in methanol.

The platinum halocarbonyl species, $Pt(CO)Cl_2$, $Pt(CO)_2Cl_2$ and $Pt_2(CO)_3Cl_4$, were first prepared by Schützenberger[420] by the action of CO and Cl_2 on Pt sponge at 250° C. These products were separated by recrystallization from carbon tetrachloride and had different melting points (194°, 142° and 130° C respectively). They were interconvertible. A non volatile residue of uncertain nature was also obtained.[421] Dipole moment studies indicate the *cis* structure (L) of $Pt(CO)_2Cl_2$. $Pt(CO)Cl_2$ is dimeric and is formulated as (LI). The structure of $Pt_2(CO)_3Cl_4$ is not known.

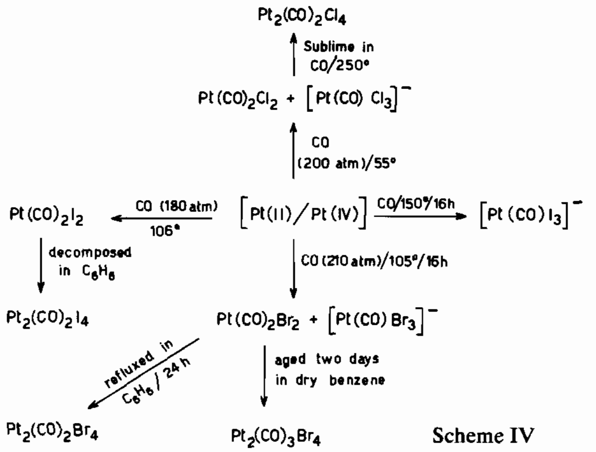


(L)



(LI)

The preparative methods of different neutral and anionic species are described[422–426] in the scheme (IV).



Scheme IV

A peculiar method for the preparation of *cis*-$Pt(CO)_2Br_2$ is by the action of CO on the adduct $PtF_4 \cdot 2BrF_3$ under static pressure.

The anionic species described in scheme IV have been isolated as their H^+, K^+, Cs^+, $C_5H_5NH^+$ and $AsPh_4^+$ salts.[422,423,426–428] Absorption frequencies of these species[422,423] increase in the order I<Br<Cl and $[Pt(CO)X_3]^- < Pt_2(CO)_3X_4 < Pt_2(CO)_2X_4 < Pt(CO)_2X_2$. Bond strength and stability to hydrolysis decrease along the above series. Raman studies[427–429] in aqueous solution together with IR spectra (ν_{CO}: 2120s and 2101wsh cm^{-1}) indicate the C_{2v} symmetry for $[Pt(CO)Cl_3]^-$.

The anion, $[Pt_2(CO)_2X_4]^{2-}$, which has been discovered recently,[430] is known to have metal–metal links, with no bridging groups.

D. Substituted Derivatives of Carbonyl Halides

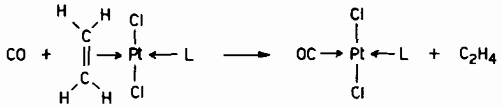
Palladium has a little tendency to form substituted carbonyl halides. Pyridine, 2,6-lutidine, isoquinoline, pyridine-N-oxide and triphenylarsine form the corresponding $Pd(CO)LCl_2$ complexes.[431,432] The derivatives with the former four ligands have been obtained by treating[432] palladium dichloride with the ligands in *o*-dichlorobenzene and then with CO. The triphenylarsine derivative has been obtained by the slow addition[431] of triphenylarsine to a CO swept solution of palladium chloride in methoxyglycol. The last compound was characterized by its IR spectrum (ν_{CO}: 1900s, 1875w cm^{-1}). The band at 1875 cm^{-1} has been attributed to the presence of impurities or to the presence of more than one geometric forms of the same molecule.

Platinum forms three main types of mononuclear substituted carbonyl halides namely, $Pt(CO)LX_2$, $Pt(CO)L'X_2$ and $[Pt(CO)L_2X]^+$ where L is a neutral and L′ an anionic ligand. The neutral species are prepared by the methods given below:

(i) when a benzene suspension[433] of the orange chloro-bridged complexes, $Pt_2Cl_4(PR_3)_2$ (R = Et, Pr or Bu), is treated with CO at 20° C/1 atm, colourless crystals of mononuclear carbonyl complexes, $Pt(CO)Cl_2(PR_3)$, are formed in 70–90% yields after 2 h. A bromo complex, $Pt(CO)(Et_3P)Br_2$, has been prepared[433] from the corresponding chloro complex by treatment with an acetone solution of lithium bromide. The analogous iodo complex has been prepared by fission of the iodo-bridged complex $Pt_2(Et_3P)_2I_4$ with CO;

(ii) $Pt_2(CO)_2X_4$ (X = Cl, Br, I) complexes react[434] with two mol of neutral monodentate ligands to give $Pt(CO)LX_2$; with one mol of neutral bidentate ligands ionic derivatives of the type $[Pt(CO)(dipy)X]^+[Pt(CO)X_3]^-$ have been obtained;

(iii) the discovery[435] that ethylene is readily replaced by CO in $Pt(C_2H_4)LCl_2$, made available[436–439] a large number of substituted Pt(II) carbonyl complexes of the type $Pt(CO)LCl_2$ (L = pyridine, pyridine-N-oxide, their substituted derivatives or RNH_2) (LII):

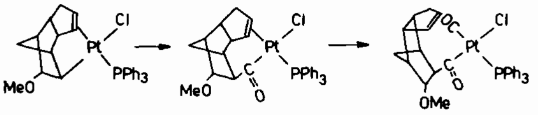


(LII)

(iv) neutral complexes of Pt(II) with anionic ligands[440,441] have been prepared by the action of CO on $Pt(C_2H_4)L'Cl$ (L′ = acetylacetonate or amino-acetyl group):

$$Pt(C_2H_4)(acac)Cl \xrightarrow{CO} Pt(CO)(acac)Cl$$

A mixed ligand carbonyl halide of platinum, $Pt(CO)(C_{10}H_{12}OMe)(Ph_3P)Cl$ (LIII), has been synthesised[442] by passing CO through a stirred solution of $Pt(Ph_3P)(C_{10}H_{12}OMe)Cl$ at room temperature for 2 days and precipitating with hexane. The IR spectrum (in CH_2Cl_2) in the CO stretching region showed two bands at 2060 and 1720 cm^{-1}. The former band was attributed to terminal CO while the latter to the acyl C–O group. The reaction scheme may be summarized as follows:



(LIII)

A few cationic complexes have also been obtained by the methods given below:

(i) cations $[M_2(R_3M')_4X_2]^{2+}$ (M = Pt, Pd; X = Cl, Br, I; R = Et, Ph; M′ = P, As, Sb) react with CO at ordinary temperature to give[443–446] *trans*-$[M(CO)(R_3M')_2X]^{2+}$. These cationic complexes have been isolated as their BF_4^- salts;

(ii) CO reacts with $PtH(R_3M')_2X$[447] or $Pt(M'R_3)_2X_2$[69,401,448] (M′ = P, As) in the presence of $NaBF_4$ or

$NaClO_4$ to yield $[Pt(CO)(M'R_3)_2X]BF_4$ or $[Pt(CO)(M'R_3)_2X]ClO_4$;

(iii) the salt $[Pt(CO)(Et_3P)_2Cl]^+SiF_5^-$ has been obtained[449] by a peculiar reaction between *trans*-$PtHCl(Et_3P)_2$ and C_2F_4 in silica tube. The salts containing SiF_5^- and BF_4^- are formed when reactions are carried out in Pyrex glass tubes.

The anionic complexes[392] $[M(CO)(SnCl_3)_2Cl]^-$ (M = Pd, Pt) have been obtained as a result of the reaction between CO and methanol solution of $PdCl_2$ or Na_2PtCl_4 and $SnCl_2$ followed by the addition of NEt_4Cl:

$$\begin{array}{l} \left.\begin{array}{c} Na_2PtCl_4 \\ \text{or} \\ PdCl_2 \end{array}\right\} + SnCl_2 \xrightarrow[\text{reflux}]{CO,\ MeOH} [M(CO)(SnCl_3)_2Cl]^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad + Cl^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow NEt_4Cl \\ \qquad\qquad [NEt_4]^+[M(CO)(SnCl_3)_2Cl]^- \ (M = Pd, Pt) \end{array}$$

With $AsPh_4Cl$ as the precipitating agent,[392] purple complexes, $[AsPh_4]^+[M(CO)(SnCl_3)_2(ROH)Cl]^-$ (R = Me, Et), have been obtained by refluxing in methanol or ethanol.

The derivatives $Pt(CO)LX_2$ (L = trialkylphosphines) have the *cis*-configuration.[433,450,451] They show a single CO band in their IR spectra both in nujol and in solution. The iodo complexes are thermally less stable than the corresponding chloro or bromo derivatives. It may probably be due to the higher *trans* effect of iodine over chlorine and bromine which would labilize the CO ligand in a *trans* position. The *trans* configuration of dichloro-4-methoxy-pyridine-N-oxide(carbonyl)Pt(II) has been established.[452]

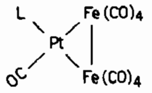
The cations $[M(CO)L_2X]^+$ (M = Pd, Pt; X = halogen; L = P, As, Sb donor ligands) are of square planar configuration and confirm the *trans*-configuration[401,443–449] of the ligand L. Three-dimensional X-ray data[449] for $[Pt(CO)(Et_3P)_2Cl]^+BF_4^-$ suggest that the cation is essentially planar. The small deviations may make the coordination trend towards a flattened tetrahedron rather than a square pyramid.

In the dinuclear derivatives, $Pt_2(CO)_2LX_4$ (L = ethylenediamine, N,N'-dimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine; X = Cl or Br), it has been inferred[453,454] that the diamines are always present in the *trans* form and there is a bridge between the two Pt atoms.

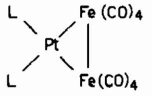
A number of compounds of Pt having stoichiometry $C_nH_{2n+1}Pt(CO)Cl$ have been investigated. They probably posses a dimeric structure. Pd does not form such derivatives. The Pt derivatives, LPt(CO)Cl (L = C_2H_5, n-C_7H_{15}, n-C_8H_{17} or $C_{12}H_{35}$), have been prepared by the interaction[455,456] of $PtCl_2$ on olefins and HCOOH in dimethylformamide containing LiCl.

E. Derivatives Containing Pt–M Bonds

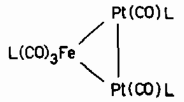
Recently the synthesis and properties of several new carbonyl clusters containing Pt bonded to Fe[457,458] and stabilised by the presence of a variety of t-phosphines, phosphites or arsines have been described. Mainly four types of complexes, $Fe_2Pt(CO)_9L$, $Fe_2Pt(CO)_8L_2$, $Fe_2Pt(CO)_8L'$ and $FePt_2(CO)_5L_3$ (L is monodentate and L' is bidentate), were isolated. When a solution of $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ was treated[457–459] with PtL_4, $Pt(L–L)_2$ or *cis*-PtI_2Cl_2, a mixture of several compounds of the type $Fe_2Pt(CO)_9L$ (L = Ph_3P, PPh_2Me, $PPhMe_2$, Me_3P, Ph_3As) (LIV), $Fe_2Pt(CO)_8L_2$ (L = Ph_3P, PPh_2Me, $PPhMe_2$, Me_3P, $PPh(OMe)_2$, $P(OPh)_3$), $Fe_2Pt(CO)_8(L–L)$ (L–L = diphos or diars) (LV), $FePt_2(CO)_5\{P(OPh)_3\}_3$ (LVI) and $Ru_2Pt(CO)_8(diphos)$ (LVII) was isolated. The structures of these complexes were confirmed by IR and NMR data.[457–459] NMR data of the phosphine substituted complexes further suggest that the phosphorus ligands remained bonded to platinum:



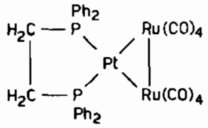
(LIV)



(LV)



(LVI)



(LVII)

A few Pt and Pd derivatives which contain Mn, Co and Mo carbonyls have also been characterized. They have been prepared[460] by the action of $[Mn(CO)_5]^+$, $[Co(CO)_4]^-$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ on *trans*-ML_2Cl_2 (M = Pd, Pt; L = pyridine, 3-methylpyridine, 4-methylpyridine). A crystal study on $Pt(py_2)[Mn(CO)_5]_2$ and $Pt(py_2)[Co(CO)_4]_2$[461] confirmed the *trans* square planar configuration. With the exception of *trans*-$Pt(py_2)Cl[Mo(CO)_3(\pi\text{-}C_5H_5)]$ all the other compounds contain a linear triatomic chain M'–Pt–M' derived from a square planar skeleton, Pt, M'_2, L_2 where L represents the donor atom of the ligand and M' represents $Mn(CO)_5$ or $Co(CO)_4^-$.

F. Substituted Derivatives of Carbonyl Hydrides

Neutral carbonyl hydrides of Pd and Pt are not known, although a few cationic derivatives,[401,446,448] $[HPt(CO)(Et_3P)_2]^+$ and $[HPt(CO)(Et_3As)_2]^+$, have been identified. The deuterium analogue of the triethylphosphine substituted derivative has also been prepared. The methods of preparations are summarised by the following equation:

$$PtHClL_2 + NaClO_4 + CO \rightarrow [HPt(CO)L_2{}^+[ClO_4]^- + NaCl \ (L = Et_3P, Et_3As)$$

$[Pt(CO)_2]_5$ with Cl^- and H_2O in presence of Fe^{3+} yield the hydridocarbonyl halide $H_2Pt(CO)Cl_2$.[462,463] Pyridinium, quinolinium and tetraphenylarsonium salts of the anion, $[HPd(CO)Cl_2]^-$, have been obtained by bubbling[431] CO through a solution of $PdCl_2$ in methoxyglycol at room temperature and subsequent addition of pyridinium, quinolinium, or tetraphenylarsonium salts. A weak band at 1960 cm^{-1} in the IR spectrum[431] of $[HPd(CO)Cl_2]^-[AsPh_4]^+$ was due to the M–H frequency and the strong band at 1900 cm^{-1} was assigned to a terminal CO stretching mode. Conductivity measurements of the complexes suggested uni–univalent electrolyte behaviour in DMF.

The tetraethylammonium salt, $[NEt_4]^+[H_2Pt(CO)Cl_3]^-$, was prepared by the treatment[462,463] of $H_2Pt(CO)Cl_2$ with Et_4NOH in presence of an acid. IR spectra indicated the presence of Pt–Cl bond.

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