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SUBSTITUTED RUTHENIUM CARBONYL HALIDES

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CONTENTS

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ABBREVIATIONS

acac	acetylacetone
bpy	2,2′-bipyridyl
Bu	butyl
C_5H_5	cyclopentadienyl
C_7H_8	bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)
COD	cycloocta-1,5-diene
Cy	cyclohexyl
diphos	bis(diphenylphosphino)ethane
dma	dimethylacetamide
dmf	dimethylformamide
dmso	dimethylsulfoxide
Et	ethyl
EtOH	ethanol
L,L′	unidentate ligand
L″	bidentate ligand
L‴	tridentate ligand
L⁗	tetradentate ligand
Me	methyl
MeCN	acetonitrile
Me_3NO	trimethylamine-*N*-oxide
MeOH	methanol
Ph	phenyl
phen	1,10-phenanthroline
Pr	propyl
PPh_3	triphenylphosphine
py	pyridine
THF	tetrahydrofuran
tpy	2,2′;6′,2″-terpyridyl
X	halogen

A. INTRODUCTION

This review describes the preparation and reactions of substituted ruthenium carbonyl halides. These compounds all contain at least one CO group and one halide (X) ligand and may be generally formulated $Ru(CO)_mX_nL$ (m, $n = 1$, 2, 3 or 4; $m + n = 2$, 3, 4 or 5). In addition, at least one "substituted" ligand (L) is present which contains one or more Group III–VIA donor atoms. Cyclopentadienyl and related ligands are treated as single uninegative ligands since their bonding cannot be regarded

as unidentate. Complexes containing hydrides (L = H) are also included in this review.

The compounds occur as neutral, cationic or anionic complexes and in most cases the oxidation state of the ruthenium in 2 + . The coordination numbers of four, five and six generally correspond to pseudo-tetrahedral, trigonal bipyramidal and octahedral geometries respectively.

The chemistry of substituted ruthenium carbonyl halides has not been reviewed previously, although certain aspects of this area have been encompassed within other more general reviews [1,2].

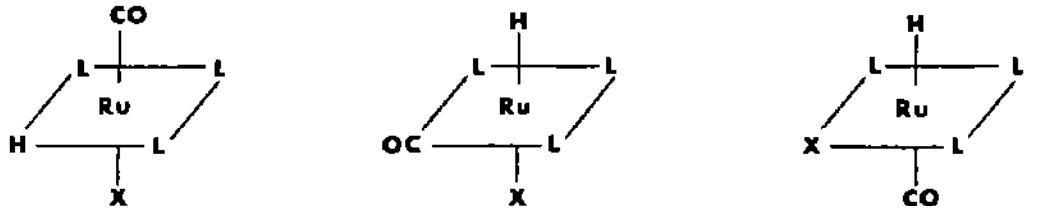
B. Ru(CO)X COMPOUNDS

(i) $Ru(CO)XL_3L'$ ($L \neq L' =$ unidentate)

The first compound of this type to be isolated was the hydrido species $RuH(CO)ClL_3$ ($L = PPh_3$, PEt_2Ph) prepared by Chatt and Shaw [3–5] via decarbonylation of ethanol using $[Ru_2Cl_3L_6]Cl$. Vaska et al. [6,7] independently showed that boiling $RuCl_3$ in ethylene glycol solutions containing phosphines also results in abstraction of hydride and CO from the solvent to give $RuH(CO)Cl(PPh_3)_3$. Similar decarbonylation reactions have been observed for $RuCl_3$ in a variety of solvents, particularly alcohols [8–11] as well as for other ruthenium halide complexes [12].

The proposed mechanism [3,13] for the decarbonylation of alcohols involves the initial formation of an alkoxo complex followed by hydride transfer to the alkyl group. The resultant O-bonded aldehyde complex then decomposes to give alkane and the ruthenium carbonyl hydride (Fig. 1).

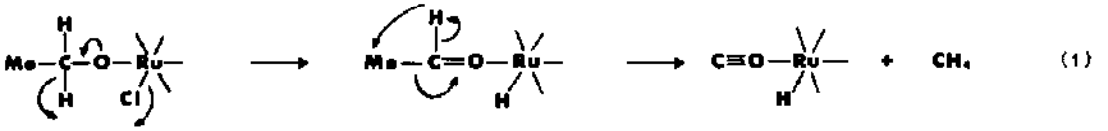
Three isomeric forms of $RuH(CO)XL_3$ have been reported **Ia** [14], **Ib**



Ia **Ib** **Ic**

[9,15], and **Ic** [9,15]. In all cases the phosphine ligands adopt a *mer*-configuration which is presumably preferred to the *fac*-isomers on steric grounds.

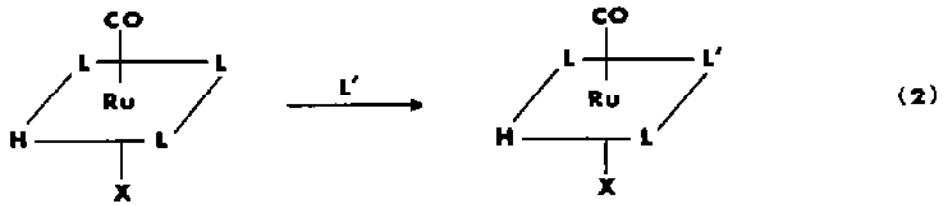
Most reactions involving $RuH(CO)XL_3$ complexes involve **Ia**, the stereochemistry of which is based on the crystal structure of an analogous osmium



(1)

Fig. 1. Proposed mechanism for the decarbonylation of alcohols by chlororuthenium complexes.

complex $OsH(CO)Br(PPh_3)_3$ [16] and by the similarity of the IR spectra of the ruthenium and osmium derivatives [17]. The strong *trans*-labilizing effect of the hydride ligand in **Ia** has been used to effect substitution by a variety of unidentate N-, P- or As-donor ligands [14,18] (reaction (2)). The high



(2)

reactivity of $RuH(CO)XL_3$ complexes is reflected in the variety of reactions they undergo and these are summarized in Table 1.

The hydride ligand is replaced by unidentate anions when $RuH(CO)Cl(PMe_2Ph)_3$ reacts with acids HR (R = NO_3, $MeCO_2$, $EtCO_2$, $PhCO_2$) [19]

$$2\ RuH(CO)ClL_3 + 2\ HR \rightarrow 2\ Ru(CO)ClL_3R + 2\ H_2 \quad (3)$$

A similar product $Ru(CO)ClL_2R$ is formed from the reaction of $RuH(CO)Cl(PPh_3)_3$ and HgR_2 (R = *p*-MeC_6H_4) [51].

The dicarbonyl complexes $Ru(CO)_2XL_2L'$ undergo thermal CO replacement by PMe_2Ph [58] to form $Ru(CO)XL_3L'$

$$Ru(CO)_2Cl(PMe_2Ph)_2Ph + PMe_2Ph \overset{56°C}{\rightarrow} Ru(CO)Cl(PMe_2Ph)_3Ph + CO \quad (4)$$

However, at lower temperatures combination of CO and Me groups gives an acetyl ligand [59,60].

$$Ru(CO)_2Cl(PMe_2Ph)_2Me + PMe_2Ph \overset{-33°C}{\rightarrow} Ru(CO)Cl(PMe_2Ph)_3(COMe) \quad (5)$$

At 0°C $Ru(CO)Cl_2L_2(\eta^2\text{-}C_2H_4)$ (L = PMe_2Ph) reacts with L [61]

$$Ru(CO)Cl_2L_2(\eta^2\text{-}C_2H_4) + 2\ L \rightarrow [Ru(CO)ClL_3(CH_2CH_2L)]Cl \quad (6)$$

This reaction involves initial nucleophilic attack on the ethene and displace-

TABLE 1

Reactions of $RuH(CO)XL_3$ complexes

$RuH(CO)XL_3$ complex [a]	Other reactant	Product	Ref.
$L = PEt_2Ph$	HCl	$Ru(CO)X_2L_3$	3
$L = PMe_2Ph$	RH ($R = MeCO_2$, $EtCO_2$, $PhCO_2$)	$Ru(CO)XL_3R$	19
$L = PMe_2Ph$	HNO_3	$Ru(CO)XL_3(NO_3)$	19
$L = PR_2Ph$ (R = Et, n-Pr, n-Bu)	L′ (L′ = tertiary phosphine or arsine)	$RuH(CO)XL_2L'$	14
$L = PPh_3$	p-$MeC_6H_4SO_2NMe(NO)$	$Ru(CO)XL_2(NO)$	20, 21
$L = PPh_3$	$P(OPh)_3$	$RuH(CO)XL_2\{P(OPh)_3\}$	18
$L = PPh_3$	RCHO (R = Me, Et)	$Ru(CO)XL_2(\pi\text{-COR})$	22
$L = PPh_3$	RNC (R = Me, i-Pr, t-Bu)	$RuH(CO)XL_2(CNR)$	23, 24
$L = PPh_3$, PCy_3 X = Cl, Br	CS_2	$Ru(CO)XL_2(HCS_2)$	25–27
$L = PPh_3$	RCO_2H (R = Me, Et, Ph)	$Ru(CO)XL_2(OCOR)$	28, 29
$L = PPh_3$	Diazonium salts	$Ru(CO)XL_2(NH{=}NR)(FBF_3)$ ($R = p$-MeC_6H_4)	30
$L = PPh_3$	$[RN_2]PF_6$ ($R = MeOC_6H_4$)	$[Ru(CO)X(NCMe)L_2(RN{=}NH)](PF_6)$	24
$L = PPh_3$	HNO_2	$RuX_3L_2(NO)$	24
$L = PPh_3$	HCl(g)	$Ru(CO)_2X_2L_2$ + $Ru_2(CO)_2X_4L_3$	24
$L = PPh_3$	$(Me_2NCS_2)_2$	$Ru(CO)(S_2CNMe_2)_2L$	31
$L = PPh_3$	RNCS (R = Me, Et, Ph)	$Ru(CO)XL_2(RN{=}CH{=}S)$	32, 33
$L = PPh_3$ X = Cl, Br	RN=C=NR (R = i-Pr, p-MeC_6H_4)	$Ru(CO)XL_2(RN{=}CH{=}NR)$	34–37
$L = PPh_3$	UV light	$RuH(CO)_2XL_2 + RuHXL_3$	38
$L = PPh_3$	$L' = PhN_4CS$	$Ru(CO)XLL'_2$	9
$L = PPh_3$	$L'' = CH_3COCH_2COCH_3$, $CF_3COCH_2COCF_3$, $CF_3COCH_2COCH_3$, $H_2C{=}CHCN$	$Ru(CO)XL_2L''$	39, 40 41
$L = PPh_3$	PhN=NC(Ph)=NNHPh	$Ru[(\sigma\text{-}C_6H_4)N{=}NC(Ph){=}NNPh](CO)L_2$	42
$L = PPh_3$	RNCO ($R = p$-MeC_6H_4)	$Ru(CO)X(RN{=}CH{=}O)L_2$	43, 44
$L = PPh_3$	PdL''_2 ($L'' = CF_3COCH_2COCF_3$)	$Ru(CO)XL_2L''$	45
$L = PPh_3$	L′ = 1,8-diazabicyclo (5,4,0)undec-7-ene	$Ru(CO)_3L'_2$	46
$L = PPh_3$	$Na[Co(CO)_4]$	$RuCo(\mu\text{-}PPh_2)(CO)_5L_2$ + $RuH(CO)_2XL_2$	47
$L = PPh_3$	$NOCl + Ru(CO)_3L_2$	$Ru(CO)_3L_2(NO)$	48
$L = PPh_3$	RHC=CHCN (R = H, CN)	$[Ru(CO)XL_2(RCH_2CHCN)]_2$	49

TABLE 1 (continued)

$RuH(CO)XL_3$ complex [a]	Other reactant	Product	Ref.
$L = PPh_3$	$EtCO_2COEt$	$Ru(CO)XL_2(COEt)$	50
$L = PPh_3$	HgR_2 ($R = p\text{-}MeC_6H_4$)	$Ru(CO)XL_2R$	51
$L = PPh_3$	CO	$RuH(CO)_2XL_2$	38
$L = PCy_3$	CS_2	$Ru(CO)L_2H(S_2CL)^+$	52
$L = PPh_3$	$RCO_2CH{=}CH_2$ (R = Me, Et, n-Bu)	$Ru(CO)XL_2(CH_2CH_2CO_2R)$	53
$L = PPh_3$	HL″ (HL″ = 8-hydroxyquinoline, 2-hydroxyphenones, *N*-benzoyl-*N*-phenylhydroxylamine)	$Ru(CO)XL_2L''$	54
$L = PCy_3$	$RC{\equiv}CH$ (R = H, Ph)	$Ru(CO)XL_2(RC{\equiv}CH)$	55
$L = PPh_3$	$CH_2{=}CHCH_2OPF_2$	$RuH(CO)XL_2(C_3H_5OPF_2)$	56
$L = PPh_3$	$RN{=}N{-}NHR$ ($R = p\text{-}MeC_6H_4$)	$Ru(CO)XL_2(RN_3R)$	57

[a] Unless otherwise indicated, X = Cl.

ment of Cl^- with subsequent substitution of the halide ion *trans* to the newly formed alkyl ligand.

(ii) $Ru(CO)XL_3$ (L = unidentate)

The five coordinate cation $[Ru(CO)Cl(PMe_2Ph)_3]^+$ has been prepared by halide abstraction of the neutral dichloro compound $Ru(CO)Cl_2(PMe_2Ph)_3$ [61]

$$Ru(CO)Cl_2(PMe_2Ph)_3 + AgClO_4 \rightarrow [Ru(CO)Cl(PMe_2Ph)_3]ClO_4 + AgCl \quad (7)$$

A similar reaction with $NaBPh_4$ gives a product analysing for $[Ru(CO)ClL_3]BPh_4$ where $L = PPh_2(OMe)$; however, spectroscopic evidence suggests formation of a dimeric species [62].

(iii) $Ru(CO)XL_2L'$ ($L \neq L'$ = unidentate)

The reaction between $RuH(CO)ClL_3$ and $MeCO_2H$ [29], $Hg(MeC_6H_4)_2$ [51] or $p\text{-}MeC_6H_4SO_2NMe(NO)$ [20] leads to loss of an L group and formation of $Ru(CO)ClL_2L'$ compounds ($L = PPh_3$; $L' = MeCO_2$, $p\text{-}MeC_6H_4$, NO).

Direct carbonylation of $RuCl(PPh_3)_3L'$ (L' = EtCO) [50] or $RuCl_3(Ph_2PCH_2Ph)_2L'$ (L' = NO) [63] gives the corresponding $Ru(CO)ClL_2L'$ complex. The nitrosyl compounds, $Ru(CO)X(PR_3)_2(NO)$ (R = Ph, Cy) are also formed by CO abstraction of HCOF by $RuCl(PPh_3)_3(NO)$ [64], by the reaction of $RuH(CO)Cl(PCy_3)_2$ with p-$MeC_6H_4SO_2NMe(NO)$ [65], or by halide abstraction of $PhCH_2Br$ by $Ru(NO)_2(PPh_3)_2$ in the presence of CO [66].

The dimer $[Ru(CO)Cl_2(PMe_2Ph)_2]_2$ reacts with allyl tin reagents to give the corresponding allyl ruthenium complexes

$$[Ru(CO)Cl_2L_2]_2 + 2\ SnBu_3R \rightarrow 2\ Ru(CO)ClL_2R + 2\ SnBu_3Cl \quad (8)$$

where R = η^3-C_3H_5, η^5-C_5H_7 and L = PMe_2Ph [67,68].

Oxidative addition of halogens to $Ru(CO)(PR_3)_2L'$ complexes gives cationic compounds

$$Ru(CO)(PR_3)_2L' + X_2 \rightarrow [Ru(CO)X(PR_3)_2L']X \quad (9)$$

where R = OMe, L' = η^4-C_4Ph_4 and X = Cl, Br, I [69].

(iv) Ru(CO)XLL' (L = unidentate, L' = C_5H_5)

Complexes with this formulation generally contain a cyclopentadienyl group (L' = C_5H_5) or substituted cyclopentadienyl and are formed by substitution reactions of dicarbonyl-C_5H_5 complexes [70–73]

$$Ru(CO)_2Cl(C_5H_5) + PPh_3 \rightarrow Ru(CO)Cl(PPh_3)(C_5H_5) + CO \quad (10)$$

Carbonylation of $RuCl(PPh_3)_2(C_5H_5)$ in the presence of sulfur also gives $Ru(CO)Cl(PPh_3)(C_5H_5)$. In this novel reaction sulfur is used to convert free PPh_3 to PPh_3S. Since substitution reactions of $RuCl(PPh_3)_2(C_5H_5)$ are dissociative the formation of PPh_3S enables CO to coordinate [74].

Treatment of dichlororuthenium compounds with BPh_4^- or PF_6^- salts generally leads to cationic species [75–77]

$$Ru(CO)Cl_2(C_6Me_6) + PPh_3 + NH_4PF_6$$
$$\rightarrow [Ru(CO)Cl(C_6Me_6)(PPh_3)]PF_6 + NH_4Cl \quad (11)$$

UV irradiation of $Ru(CO)_2I(PMe_3)(C_5H_5)$ [78], carbonylation of $RuCl(PPh_3)_2(C_5H_5)$ [75], ligand substitution of $Ru_2(CO)_4(C_5H_5)_2$ [79], and halogenation of $RuH(CO)(PMe_2Ph)(C_5H_5)$ [80] all give $Ru(CO)X(C_5H_5)L$ complexes.

(v) Ru(CO)XL$_n$L'' (L = unidentate, L'' = bidentate; n = 2, 1)

The reactivity of $RuH(CO)Cl(PPh_3)_3$, alluded to earlier, accounts for the formation of a number of $Ru(CO)ClL_2L''$ complexes. For instance,

$RuH(CO)Cl(PPh_3)_3$ reacts with RCHO [22], CS_2 [25–27], $MeCO_2H$ [28], $P(OPh)_3$ [18], $MeCOCH_2COMe$ [39,40], 2-formylpyridine [81] or $Pd(CF_3COCH_2COCF_3)_2$ [45] (Table 1) to give the corresponding $Ru(CO)Cl(PPh_3)_2L''$ complexes.

Methyl iodide rapidly methylates CS_2 complexes forming cationic species containing a bidentate dithiomethyl ester group. Addition of halide ions gives the neutral complexes [82,83]

$$Ru(CO)_2(PPh_3)_2(CS_2) + MeI \xrightarrow{X^-} Ru(CO)X(PPh_3)_2(CS_2Me) \quad (12)$$

where X = Cl, Br, I. Methylation of $Ru(CO)_2(PPh_3)_3$ forms the bidentate dihaptoacyl group [84]

$$Ru(CO)_2(PPh_3)_3 \xrightarrow{+MeHgI} Ru(CO)I(PPh_3)_2[\eta^2\text{-}C(O)Me] \quad (13)$$

Complexes containing bidentate metallated ligands (L'' = 2-phenylpyridine, benzo-h-quinoline [85]; dimethyl(1-naphthyl)phosphine [86]; $(MeC_6H_4)_2CO$ [87]) are also known.

Carbonylation of the monochloro complexes RuClLL'' gives Ru(CO)XLL'' compounds

$$RuClLL'' + CO \rightarrow Ru(CO)ClLL'' \quad (14)$$

where $L = \eta^5\text{-}C_5H_5$, $L'' = CH_2(PPh_2)_2$ [88]; L = NO,

$L'' = Ph_2PCH_2C_{18}H_{10}CH_2PPh_2$ [63]; $L = PPh_3$, $L'' = o\text{-}C_6H_4PPh_2$ [89].

Thermal decarbonylation of $Ru(CO)_2Cl_2L_2$ ($L = o\text{-}CH_2{=}CHC_6H_4PPh_2$) yields $Ru(CO)Cl(o\text{-}MeCHC_6H_4PPh_2)L$ in which one *o*-styryldiphenylphosphine retains its unidentate nature while the other is bonded through both P and C atoms [90].

(vi) $Ru(CO)XL''_2$ (L'' = bidentate)

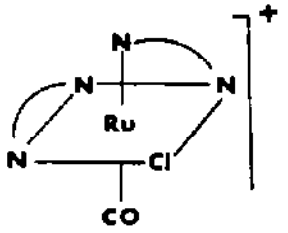
$[Ru(CO)Cl(bpy)_2]Cl$, first isolated from the reaction of $[Ru(CO)Cl_3(norbornadiene)]^-$ with bpy [91], has also been prepared as a by-product during the preparation of $RuCl_2(bpy)_2$ [92,93]

$$RuCl_3 \xrightarrow{bpy} RuCl_2(bpy)_2 + [Ru(CO)Cl(bpy)_2]Cl \quad (15)$$

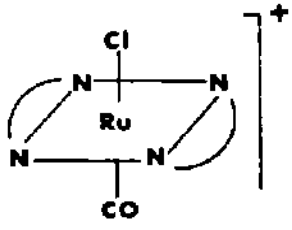
More recently direct carbonylation of $RuCl_2(bpy)_2$ with CO has been shown to form $[Ru(CO)Cl(bpy)_2]^+$ [94,95].

Both *cis* [92,93] and *trans* [96] isomers (**IIa** and **IIb** respectively) have

been reported for $[Ru(CO)ClL''_2]^+$ complexes containing bpy or phen ligands. It was originally believed that steric crowding between hydrogen atoms on



IIa



IIb

adjacent ligand rings precluded formation of the *trans* isomer. However Meyer and co-workers [96] have prepared a series of $[RuXY(bpy)_2]$ (X, Y = unidentate) complexes with a *trans* configuration. The *trans* isomer is observed for complexes containing bidentate P or As donor ligands [97–100].

One of the few known examples of a substituted ruthenium carbonyl fluoride is $[Ru(CO)F(diphos)_2](BF_4)$. This compound has been obtained from the reaction of $RuCl_2(diphos)_2$ with CO and $AgBF_4$ by fluoride abstraction of BF_4^- [100].

(vii) Ru(CO)XL''' and Ru(CO)XL'''' (L''' = tridentate; L'''' = tetradentate)

Carbonylation of chloro complexes, containing tridentate and tetradentate P-donor ligands, $RuCl_2L'''$ ($L''' = PhP[CH_2CH_2PPh_2]_2$) and $[Ru(Cl)L'''']Cl$ ($L'''' = Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$, $P[CH_2CH_2PPh_2]_3$, $C_6H_4[CH_2P(CH_2CH_2AsPh_2)_2]_2$) gives the monocarbonyl monochloro compounds $[Ru(CO)ClL''']Cl$ and $[Ru(CO)ClL'''']Cl$ respectively [101,102]. A similar reaction between CO and $[Ru(Cl)L'''']Cl$ ($L'''' = P,P,P'P'$-tetrakis(2-diphenylarsinoethyl),α,α'-diphospha-*p*-xylene) is also known [102]. In this complex the tetradentate ligand is believed to coordinate through three As and one P atoms rather than all four As atoms since phosphorus has better donor properties than arsenic.

Bromination of Ru(CO)(OEP) (OEP = octaethylporphyrin) [103] gives Ru(CO)Br(OEP).

(viii) Miscellaneous compounds

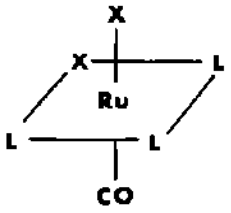
Other monocarbonyl monochloro ruthenium compounds reported are $Ru(CO)Cl(PPh_3)_2(NH_3)(CN)$ [104], $[Ru(CO)Clpy_2L_2]^+$ (L = $CN(Me)CH_2CH_2N(Me)$) [105], $[Ru(CO)Cl(PPh_3)_2(CS)(CNR)]^+$ (R = Me, *p*-

MeC_6H_4) [106], $Ru(CO)Cl(COMe_2)(SnCl_3)(PPh_3)_2$ [107], $RuH(CO)Cl(C_6H_8NOH)(PPh_3)_2$ [108], and $RuH(CO)I(CNR)(PPh_3)_2$ ($R = p\text{-}MeC_6H_4$) [109].

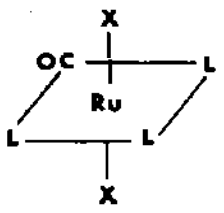
C. $Ru(CO)X_2$ COMPOUNDS

(i) $Ru(CO)X_2L_n$ (L = unidentate; n = 3, 2, 1)

$Ru(CO)Cl_2L_3$ complexes can be conveniently prepared by carbonylation of alcoholic solutions of $RuCl_3$ followed by addition of ligand to the solution [13,19,110–114]. The corresponding bromo or iodo compounds may be obtained by treatment of the solutions prior to carbonylation with halide salts [13,110,113] or by direct reaction of $Ru(CO)Cl_2L_3$ with halides [110]. Generally, this method yields the *cis* isomer, **IIIa** [13,19,110,111], but under more vigorous conditions, e.g. in higher boiling alcohols, the *trans* isomer



IIIa



IIIb

IIIb may be isolated [112]. When heated, solutions of **IIIb** isomerize to **IIIa** [30,110,112,116,117] and this isomerism can be reversed by UV irradiation of **IIIa** [118].

Compounds prepared by the above method as well as other routes are summarized in Table 2. These methods include carbonylation of the tetrakis-substituted complexes RuX_2L_4 [120,124] or the related five-coordinate RuX_2L_3 complexes [86] and ligand substitution of various neutral ruthenium carbonyl halides such as $Ru(CO)_2X_2L_2$ [19,116,117] and $[Ru(CO)_2X_2]_n$ [116,125].

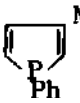
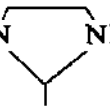
The lability of the hydride ligand in $RuH(CO)ClL_3$ complexes is evident by their reactivity towards acids [13,19]. With HCl hydrogen is evolved forming **IIIa**. The reaction is reversible and with KOH/ethanol the hydride complex is regenerated

$$RuH(CO)ClL_3 \underset{OH^-}{\overset{HCl}{\rightleftharpoons}} Ru(CO)Cl_2L_3 \qquad (16)$$

Carbonylation of $RuCl_2(PPh_3)_3$ with CO_2 in the presence of silicon hydrides gives $Ru(CO)Cl_2(PPh_3)_3$ [129]. This reaction is a rare example of

TABLE 2

Preparation of $Ru(CO)X_2L_3$ complexes

Method of preparation [a]	$Ru(CO)X_2L_3$ product	Ref.
Carbonylation of $RuCl_3$, followed by addition of L	$L = PEt_2Ph$, $PMePh$	13, 110, 112
	$L = AsMe_2Ph$, $AsPh_2Et$, $AsPh_2Me$	19, 114
	$L = MPh_3$ (M = P, As, Sb); X = Cl, I	113, 115
	$L = Ph_2MCH{=}CHPh$ (M = P, As); $Ph_2PC{\equiv}CPh$	111
	L = 	119
$RuX_2L_4 + CO$	$L = MMe_2(CH_2Ph)$ (M = P, As)	120
	$L = SbPh_3$	121
	$L = P(OR)_3$ (R = Ph, p-ClC_6H_4, p-MeC_6H_4); X = Cl, Br, I	122
	L = RCN (R = Me, Et, n-Pr, Ph)	123
	L = 	124
$RuX_2L_3 + CO$	L = dimethyl(1-napthyl) phosphine, $PPh_2(OMe)$	62, 86
$RuX_2(dmso)L_3 + CO$	$L = SbPh_3$	98
$Ru(CO)_2X_2L_2 + L$	$L = PEt_3$	19
	L = PR_3 (R = Et, Ph, OPh); X = I	116
$[Ru(CO)X_2L_2]_2 + L$	$L = PMe_2Ph$	117
$[Ru(CO)_2X_2]_n + L$	$L = MR_2$ (M = Te, Se, S; R = Et, n-Bu, Ph); X = I	116
	$L = P(OEt)_2Ph$	125
$RuH(CO)XL_3 + HX$	$L = MMe_2Ph$ (M = P, As)	13, 19
$[Ru(CO)X_4(H_2O)]^{2-} + L$	$L = PPh_3$	126, 127
$[Ru(CO)X_3(C_7H_8)]^- + L$	$L = MPh_3$ (M = P, Sb)	91, 128
$[Ru_2X_3L_6]Cl$ + alcohol	$L = PR_2Ph$ (R = Et, n-Bu, Pr)	13, 19
$RuX_2L_3 + CO_2$	$L = PPh_3$	129
Ru atoms + oxalylchloride + L	$L = PMe_3$	130
$RuCl_3 + HCHO + L$	$L = AsPh_3$	131
$Ru_2(CO)_2Cl_4(C_7H_8)_2 + L$	L = py, Mepy	132

[a] Unless otherwise indicated, X = Cl.

carbonylation of a transition metal–phosphine complex by CO_2 under mild conditions.

The mixed ligand complex $Ru(CO)I_2[CHN(R)Me](CNR)(PPh_3)$ ($R = p$-MeC_6H_4) has been prepared by reacting MeI with $Ru(CO)(CH{=}NR)(CNR)(MeCO_2)(PPh_3)_2$ [133].

$Ru(CO)Cl_2(PCy_3)_2$ has been prepared by reacting $RuCl_3$ with PCy_3 in 2-methoxyethanol or by addition of the ligand to carbonylated solutions of $RuCl_3$ in ethanol [25]. This complex and the corresponding dibromo analogue [134] have a distorted square-pyramidal geometry and, as in the case

TABLE 3

Preparation of $Ru(CO)X_2L_2L'$ complexes

Method of preparation [a]	$Ru(CO)X_2L_2L'$ product	Ref.
$[RuX_2L_2L']_2 + CO$	L = PPh_3; L' = CS	140
$RuX_2L_2L'_2 + CO$	L = PPh_3; L' = $PhNHNH_2$, pyN_3, RNH_2 (R = p-MeC_6H_4)	141, 142
$RuX_2L_3 + CO + L'$	L = PPh_2Et, P(p-$MeC_6H_4)_3$; L' = dmf, MeOH	143, 144
$Ru(CO)_2X_2L_2 + L'$	L = PMe_2Ph; L' = py, MeCN, PhCN, Me_2SO, Me_2S, C_2H_4	117
$Ru(CO)_2X_2L_2 + L' + Me_3NO$	L = PPh_3; L' = py; X = Cl, Br	145
$RuH(CO)XL_3 + L' + HCl$	L = PPh_3; L' = NH=NAr	30
$RuH(CO)XL_2 + L' + HCl$	L = py; L' = P(t-Bu)$_2$Me	146
$Ru(CO)X_2L_2 + L'$	L = PCy_3; L' = NCCH=CHCN, H_2C=CHCN	147
	L = $Ph_2PC_6H_4OMe$; L' = t-BuNC	148
$Ru(CO)X_2(H_2O) + L$	L = PPh_3; L' = H_2O	149
$Ru_2(CO)_2X_4L_3 + L'$	L = PPh_3; L' = PF_3	150
$Ru(CO)X_2L_2(\eta^2\text{-}C_2H_4) + L'$	L = PMe_2Ph; L' = $AsMe_2Ph$, NH_2CH_2Ph, 4-Mepy, Me_2S, $P(OMe)_2Ph$	147
$Ru(CO)XL_2(CMMe) + HX$	L = PPh_3; L' = CM (M = S, Se); X = Cl, I	82, 83
$Ru(CO)(CH{=}NR)(O_2CMe)L_2 + HX$	L = PPh_3; L' = CHNHR (R = p-MeC_6H_4)	151
$Ru(CO)XL_2[\eta^1\text{-}C(NR)R] + HX$	L = PPh_3; L' = C(NHR)R (R = p-MeC_6H_4)	152
$Ru(CO)XL_2(CF_3)(MeCN) + HX$	L = PPh_3; L' = CF_2	153
$Ru(CO)XL_2(FBF_3)(NH{=}NR) + LiX$	L = PPh_3; L' = NH=NR (R = p-MeC_6H_4)	30
$RuH(CO)XL_2 + Hg(CCl_3)_2$	L = PPh_3; L' = CCl_2	104
$Ru(CO)X_2(CX_2)L_2 + H_2R$	L = PPh_3; L' = CR (R = O, S, Se)	104
$Ru(CO)X_2(CX_2)L_2 + H_2NNMe_2$	L = PPh_3; L' = $CNNMe_2$	104
RuX_2L_2 + 4-vinylcyclohexane	L = PPh_3; L' = C_8H_{12}	154
$RuH(CO)XL_2L' + HX$	L = PR_2Ph (R = Et, Pr, n-Bu), PEt_3, $P(OEt)_3$, AsR_2Et (R = Me, Et); L' = $P(OMe)_2Ph$	14
$[Ru(CO)_2L_2(N_2C_6H_4R)]^+ + HX$	L = PPh_3; L' = p-$N_2HC_6H_4R$ (R = Me, F)	155
$Ru(CO)_3L_2 + NMe_2(CHX)X$	L = PPh_3; L' = $CH(NMe_2)$	156
$Ru(CO)_2XL_2L' + X^-$	L = PPh_3; L' = $CSeCH_2CH_2Se$ X = Br	157
$Ru(CO)XL_2[C(O)Et] + HX$	L = PPh_3; L' = C(OH)Et	158

[a] Unless otherwise indicated, X = Cl.

of the related five-coordinate complex $RuCl_2(PPh_3)_3$ [135], X-ray crystallography indicates that a hydrogen atom from the PPh_3 blocks the sixth octahedral position [136]. Replacement of the hydrogen is readily achieved by reaction with CO [25] or Me_2SO [137]

$$Ru(CO)Cl_2(PPh_3)_2 + CO \rightarrow Ru(CO)_2Cl_2(PPh_3)_2 \quad (17)$$

Mixed ligand complexes such as $Ru(CO)Cl_2(AsPh_3)(C_7H_8)$ [128], $Ru(CO)Cl_2(PPh_3)(CS)$ [138] and $Ru(CO)Cl_2(MeCN)(COD)$ [139a] are also known.

Complexes of the type $Ru(CO)X_2L$ containing a single ligand have been prepared by carbonylation of the chloro-bridged dimers $[RuCl_2L]_2$

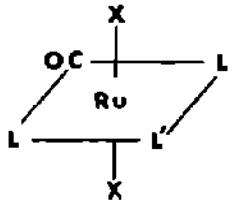
$$[RuCl_2L]_2 + 2\ CO \rightarrow 2\ Ru(CO)Cl_2L \quad (18)$$

where $L = C_{10}H_{16}$ [139b], C_6Me_6 [76,77].

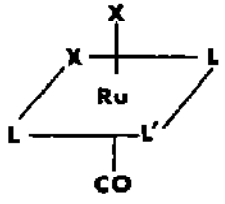
(ii) $Ru(CO)X_2L_2L'$ ($L \neq L'$ = unidentate)

Table 3 shows the variety of these mixed-ligand compounds reported. The more general preparative methods include carbonylation of ruthenium halides such as $[RuX_2L_2L']_2$ [140], RuX_2L_2L' [141,142], and RuX_3L_3 [143], ligand substitution of ruthenium carbonyl halides [61,117,145,149,150,155] and reaction of haloacids with monocarbonylmonohalogenoruthenium complexes [30,82,83,146,151–153].

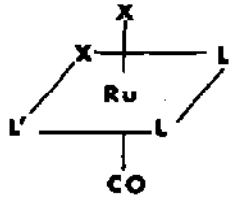
The three isomers reported for these compounds **IVa–c** are prepared by ligand substitution reactions of dicarbonyl complexes **Va–c**.



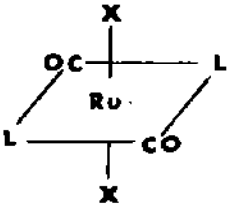
IV a



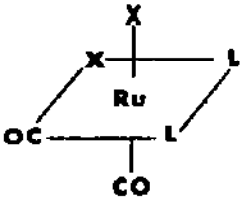
IV b



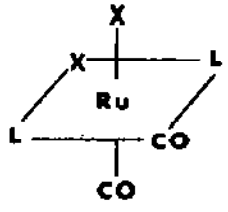
IV c



V a



V b



V c

The stereochemistry of the $Ru(CO)X_2L_2L'$ complexes often depends on the nature of the incoming ligand, L'. For instance the all-*trans* isomer **Va** ($L = PMe_2Ph$, $X = Cl$) reacts with a variety of ligands ($L' = py$, NH_3, piperidine, PMe_2Ph) to give the monosubstituted product **IVa**, whereas with $L' = MeCN$, PhCN, Me_2SO or Me_2S, **IVb** is formed [117]. The stereochemistry of these reaction products appears to be kinetically controlled since studies indicate the complexes rearrange on heating in solution from **IVa** to **IVb** when the incoming ligand contains a phosphorus ligand [117].

Substitution of the all-*cis* isomer **Vb** ($L = PMe_2Ph$, $X = Cl$) results in straightforward replacement of CO by pyridine giving **IVc** ($L = py$) [117]. The third $Ru(CO)_2X_2L_2$ isomer **Vc** is inert to further substitution by pyridine [145], but in the presence of Me_3NO decarbonylates and rearranges to form **IVa** ($L' = py$) [145].

(iii) $Ru(CO)X_2LL''$ (L = unidentate, L'' = bidentate)

Displacement of RCN by CO occurs during carbonylation of $RuCl_2(RCN)_2$(diphos) (R = Me, Et, Pr, Ph) forming $Ru(CO)Cl_2$(RCN)(diphos) [123]. Carbonylation of $RuCl_2L''_2$ ($L'' = o\text{-}MeOC_6H_4PPh_2$) gives $Ru(CO)Cl_2LL''$ in which one L'' ligand retains its bidentate nature while the other, L, functions as a unidentate ligand binding through the P atom only [159].

Carbon monoxide displacement in $Ru(CO)_2Cl_2L_2$ ($L = Ph_2PCH_2CO_2Et$) forms a related complex containing P,O-bonded bidentate and P-bonded unidentate ligands [160].

$$Ru(CO)_2Cl_2L_2 \rightarrow Ru(CO)Cl_2\left[Ph_2PCH_2C(O)OEt\right]L \qquad (19)$$

where $L = Ph_2PCH_2CO_2Et$.

In other reactions decarbonylation of $Ru(CO)_2Cl_2L''$ or $[Ru(CO)_2Cl_2L'']_2$ ($L'' = o\text{-}C_6H_4(MPhMe)_2$ in which M = As, P) can be induced thermally in Me_2SO [161] or by trimethylamine oxide in pyridine [145]

$$Ru(CO)_2Cl_2L'' + Me_2SO \rightarrow Ru(CO)Cl_2(Me_2SO)L'' + CO \qquad (20)$$

where $L'' = o\text{-}C_6H_4(MPhMe)_2$ and M = As, P.

$$Ru(CO)_2Cl_2L'' + py + Me_3NO \rightarrow Ru(CO)Cl_2(py)L'' + Me_3N + CO_2 \qquad (21)$$

where L'' = bpy, phen.

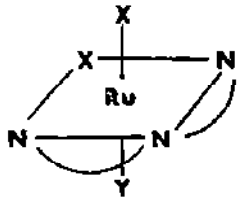
Decarbonylation of benzoylacetylacetone by $RuCl_3(PPh_3)_3$ forms $Ru(CO)Cl_2(PPh_3)(MeCOCH_2COMe)$ [162].

(iv) $Ru(CO)X_2L'''$ (L''' = tridentate)

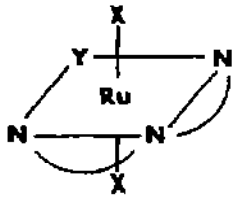
In the presence of tridentate ligands dimethylformamide solutions of $RuCl_3$ result in solvent decarbonylation and the formation of *cis*-

$Ru(CO)Cl_2L'''$ (L''' = tpy [93], $MeC(CH_2SEt)_3$ [163], $PhP(CH_2CH_2PPh_2)_2$ [101]). Solvent decarbonylation also occurs when *fac*-$RuCl_3[MeC(CH_2SEt)_3]$ is heated in dmf [163]. Carbonylation of $RuCl_3$ followed by addition of L''' or direct carbonylation of $RuCl_2L'''$ also gives $Ru(CO)Cl_2L'''$ (L''' = $PhP[CH_2CH_2CH_2PR_2]_2$; R = Ph, Cy).

Both isomeric forms of $Ru(CO)X_2(tpy)$ **VIa, b** (X = Cl; Y = CO) are formed by carbonylation of the corresponding PPh_3 complexes **VIa, b**



VIa



VIb

(X = Cl; Y = PPh_3) [164]. Treatment of $Ru(CO)_2X_2(N,N'$-tpy), which contains bidentate tpy, with Me_3NO also gives **VIa** (X = Cl, Br; Y = CO) [165].

The tripodal P-donor ligand $MeC(CH_2PPh_2)_3$ forms $Ru(CO)X_2[MeC(CH_2PPh_2)_3]$ complexes which have been prepared by a number of routes (Fig. 2) [166].

The five coordinate complex $Ru(CO)(o\text{-}Ph_2PC_6H_4CH{=}CHCH{=}CHC_6H_4PPh_2\text{-}o)$ undergoes addition of HX (X = Cl, Br) to form $Ru(CO)X_2(o\text{-}Ph_2PC_6H_4CH{=}CHCH_2C_6H_4PPh_2\text{-}o)$ which contains the tridentate olefinic ligand bis-1,4-[*o*-(diphenylphosphino)phenyl]-*cis*-2-butene [167].

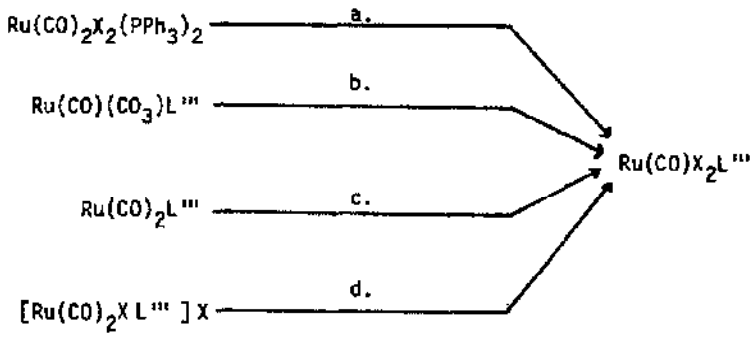


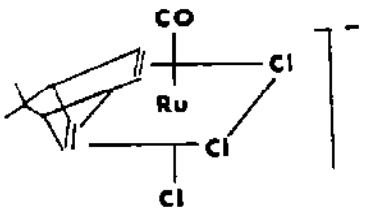
Fig. 2. Preparative routes to $Ru(CO)X_2L'''$ complexes (L''' = $MeC[CH_2PPh_2]_3$): (a) L''' in toluene at 120°C (X = Cl); (b) HX (X = Cl); (c) X_2 (X = Cl, Br); (d) recrystallization.

D. $Ru(CO)X_3$ COMPOUNDS

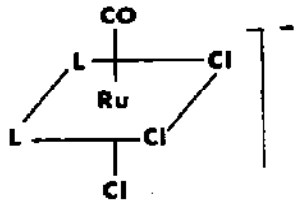
The anionic ruthenium(II) norbornadiene complex $[Ru(CO)Cl_3(C_7H_8)]^-$ is prepared by cleavage of the polymer $[Ru(CO)Cl_2(C_7H_8)]_n$ [168,169]

$$[Ru(CO)Cl_2(C_7H_8)]_n + n\ Ph_3(PhCH_2)PCl \rightarrow n\ [Ph_3(PhCH_2)P][Ru(CO)Cl_3(C_7H_8)] \quad (22)$$

X-ray crystallography shows that the anion is essentially octahedral with facial chlorine ligands **VIIa** [170].



VII a



VII b

Complex **VIIa** reacts with unidentate ligands (L = Me_2SO, Me_2S, CH_2=CHCN, $AsPh_3$, $SbPh_3$, py) to form the anions $[Ru(CO)Cl_3L_2]^-$ [91,128,144,171]. Spectroscopic evidence suggests structure **VIIb** for these compounds. With bpy, $[Ru(CO)Cl_3(bpy)]^-$ is formed [128].

Bromination of $Ru(CO)_2Br(\eta^5\text{-}C_5Me_4Et)$ gives $Ru(CO)Br_3(\eta^5\text{-}C_5Me_4Et)$, the crystal structure of which has also been reported [172].

E. $Ru(CO)X_4$ COMPOUNDS

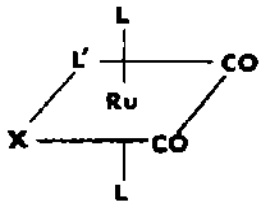
Only two examples of this class of compound appear to have been reported. The complex $[Ph_4As][Ru(CO)Cl_4py]$ is prepared by addition of pyridine to a carbonylated solution of $RuCl_3$ which was allowed to stand in air for 24 h [115]. Acidic aqueous solutions of ruthenium(III) chloride absorb CO to give $[Ru(CO)Cl_4(H_2O)]^{2-}$, isolated as the ammonium salt [127].

F. $Ru(CO)_2X$ COMPOUNDS

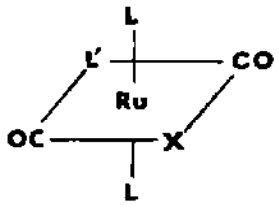
(i) $Ru(CO)_2XL_nL'$ ($L \neq L'$ = unidentate; $n = 2, 1$)

The majority of $Ru(CO)_2XL_2L'$ compounds contain an anionic ligand (L') giving rise to neutral complexes with *cis* CO groups **VIIIa** (e.g.,

L = PPh_3; L′ = NO_3 [173], Me [51,84], $CONH_2$ [174], CF_3 [153], CN [104], CF_2H [175]). The *trans* isomer **VIIIb** is less common [59,60]. Only a few of



VIII a



VIII b

the complexes of this type are cations. The most interesting of these is the novel compound $[Ru(CO)_2Cl(PPh_3)_2(N_2S_2)][AlCl_4]$ which contains coordinated disulfur dinitride, a four membered N-bonded ring [176]

$$Ru(CO)_2Cl_2(PPh_3)_2 \xrightarrow{S_2N_2 \cdot 2AlCl_3} [Ru(CO)_2Cl(PPh_3)_2(N_2S_2)][AlCl_4] \qquad (23)$$

Other cationic complexes all have the *cis* configuration **VIIIa** (X = Cl, I; L = PPh_3; L′ = *p*-$FC_6H_4NH_2$ [155], MeCN [153], NHNPh [177,178], $NHN(MeOC_6H_4)$ [30]).

The hydride complex $RuH(CO)_2ClL_2$ (**VIIIa**, X = Cl, L = PPh_3, $AsPh_3$, PCy_3; L′ = H) has been prepared by a number of reactions, e.g., carbonylation of the hydrides $RuH(CO)Cl(AsPh_3)_3$ [131], $RuH(CO)X(PCy_3)_2$ (X = Cl, Br) [134], $RuHCl(dma)(PPh_3)_2$ [179], $RuHCl(PPh_3)_3$ [180]; hydrogenation of $RuX_2(PPh_3)_3$ (X = Cl, Br) followed by carbonylation [137], and decarbonylation of COS by $RuH(CO)Cl(PCy_3)_3$ [52]. By contrast to $RuH(CO)Cl(PPh_3)_3$ which undergoes numerous reactions (Table 1) the reactivity of $RuH(CO)_2Cl(PPh_3)_2$ is less extensive (see Fig. 3). Reactions leading to other $Ru(CO)_2XL_2L'$ complexes are summarized in Table 4.

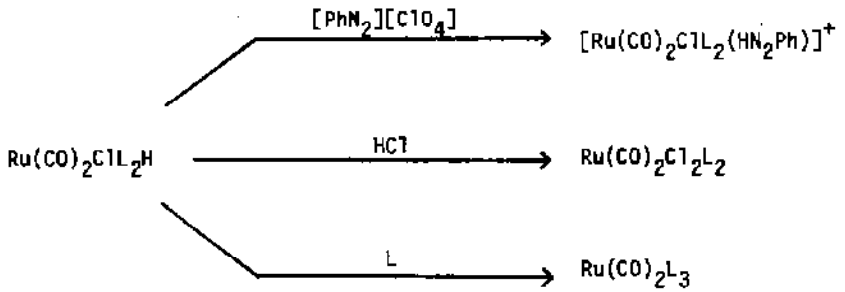


Fig. 3. Reactions of $Ru(CO)_2ClL_2H$ (L = PPh_3).

TABLE 4

Preparation of $Ru(CO)_2XL_2L'$ complexes

Reactants [a]	$Ru(CO)_2XL_2L'$ product	Ref.
$[Ru(CO)_3XL_2]^+ + KOH$	$L' = CO_2Me$; X = I	181
$[Ru(CO)_3XL_2]^+ + NH_3$	$L' = CONH_2$	174
$Ru(CO)_3L_2 + CFCl{=}CF_2$	$L = PMe_2Ph$; $L' = CF{=}CF_2$	182
$[Ru(CO)_3X_2]_2 + RNH_2$	$L = RNH_2$; L' = CONHR (R = t-Bu, *p*-MeC_6H_4)	141
$Ru(CO)_2X_2L_2 + HgL'_2$	$L = PMe_2Ph$, PPh_2Me; L' = Me	58
(or SnL'_4)	$L = PMe_2Ph$; L' = Ph, Et	
$Ru(CO)_2XL_2 + CO$	$L = PMe_2Ph$; L' = COMe; X = Cl, Br, I	59, 60
$[Ru(CO)_2L_2(N_2Ph)]^+ + LiX$	$L' = N_2Ph$; X = Cl, Br, I	183
$Ru(CO)_2X(RNH_2)(CONHR) + L$	L' = CONHR (R = t-Bu, *p*-MeC_6H_4)	141
$Ru(CO)_2(CF_3)(HgCF_3)L_2 + X_2$	$L' = CF_3$	153
$Ru(CO)_2L_3 + MeHgI$	L' = Me; X = I	51, 84
$Ru(CO)X(FBF_3)(NH{=}NR)L_2 + CO$	L' = NH=NR (R = *p*-$MeOC_6H_4$, *p*-MeC_6H_4)	30
$Ru(CO)X(CN)(NH_3)L_2 + CO$	L' = CN	104
$RuX(NO)O_2L_2 + CO$	$L' = NO_3$	173
$Ru(CO)_2XL_2Me + CO$	$L = PMe_3$; L' = MeCO	184
$Ru(CO)_2(=CF_2)L_2 + HX$	$L' = CF_2H$	175
$Ru(CO)_2X_2L_2 + RO_2CC{\equiv}CCO_2R$	$L = PMe_2Ph$; $L' = C(CO_2R){=}C(CO_2R)$; R = Me, Et	26

[a] Unless otherwise indicated, X = Cl, L = PPh_3.

The complexes $Ru(CO)_2Cl(\eta^3\text{-}C_3H_5)L$ ($L = PPh_3$, $AsPh_3$) are formed from the reaction of $[Ru(CO)_2Cl_2L]_2$ with η^3-allyl tin compounds [67].

$$[Ru(CO)_2Cl_2]_2 + 2\ SnBu_3(\eta^3\text{-}C_3H_5) + 2\ L \rightarrow 2\ Ru(CO)_2Cl(\eta^3\text{-}C_3H_5)L + 2\ SnBu_3Cl \quad (24)$$

They are also formed by ligand substitution of $Ru(CO)_3Br(\eta^3\text{-}C_3H_5)$ [185].

The mixed ligand complex $Ru(CO)_2Cl(\sigma\text{-}C_3H_5)(PPh_3)L$ ($L = CH_2{=}CHCN$) is prepared by PPh_3 cleavage of $[Ru(CO)_2Cl(\sigma\text{-}C_3H_5)L]_2$ [185].

(ii) $Ru(CO)_2XL$ ($L = C_5H_5$ or related ligand)

These compounds, which generally contain a single uninegative cyclopentadienyl ligand, participate in a variety of inorganic and organometallic reactions as indicated by their extensive reactivity shown in Table 5. They are commonly prepared by cleavage of $[Ru(CO)_2L]_2$ with halogens [73,200–202], haloacids [203] or halogenated solvents [72,204,205]

$$[Ru(CO)_2L]_2 + X_2 \rightarrow 2\ Ru(CO)_2XL \quad (25)$$

where $L = C_5R_5$, R being H, Me and X = Cl, Br, I. The corresponding dimer containing a substituted cyclopentadienyl group ($L = \eta^5\text{-}C_5Me_4Et$) is

TABLE 5

Reactions of $Ru(CO)_2XL$ complexes

$Ru(CO)_2XL$ [a] + other reactants	Product	Ref.
RSH	$Ru(CO)_2(SR)L$ (R = Me, C_6F_5)	186
KCN	$Ru(CO)_2(CN)L$	187
L′	$Ru(CO)XLL'$ (X = Cl, Br, I; L′ = PR_3 (R = Me, Ph, n-Bu, OPh))	72, 188
$NaBPh_4$	$Ru(CO)_2(Ph)L$	187
$NaBPh_3CN + AgClO_4$	$Ru(CO)_2(NCBPh_3)L$	187
$AlCl_3$ + L′	$[Ru(CO)_2LL']^+$ (L′ = MeCN, NH_3, PEt_3)	70
$AgBF_4 + PPh_2H$	$[Ru(CO)_2(PPh_2H)L]^+$	189
Na/Hg	$Na[Ru(CO)_2L]$	190
Allylic halides	$Ru(CO)(\eta^3\text{-}C_3H_5)L$ (X = Cl, Br)	191
$[Et_4N][BH_4]$	$RuH(CO)_2L$ (X = Br)	192
$CH_2{=}CHCH_2SnMe_3$	$Ru(CO)(\pi\text{-}C_3H_5)L$	193
$AgBF_4$ + CO	$[Ru(CO)_3L]^+$ (L = $\eta^5\text{-}C_5Me_5$, X = I)	194
L′	$Ru(CO)XLL'$ (L = $\eta^5\text{-}C_5Me_4Et$; L′ = $AsPh_3$, PR_3 (R = Ph, OMe, OPh); X = Cl, Br)	195, 196
L′	$Ru(CO)XLL'$ (L = η^5-menthylcyclopentadienyl, L′ = PPh_3)	71
$AgBF_4$ + L′	$[Ru(CO)_2LL']^+$ (L = 1-5-$\eta^5\text{-}C_7H_9$; X = I; L′ = PPh_3)	197
$Fe(CO)_2(PPh_3)L$	$[Ru(CO)_2L]PPh_2[Fe(CO)_2L]^+$	198
NO + $h\nu$	$RuX_2(NO)L$ (X = Cl, Br, I)	199

[a] Unless otherwise indicated, X = Cl, L = $\eta^5\text{-}C_5H_5$.

also cleaved by halogens forming initially the halogen bridged cation $[Ru(CO)_2L]_2X^+$ which further reacts with X_2 to give $Ru(CO)_2XL$ [172].

Cleavage of $[Ru(CO)_3Cl_2]_2$ by $Tl(\eta^5\text{-}C_5H_5)$ has also been reported [203]

$$[Ru(CO)_3Cl_2]_2 + 2\ Tl(\eta^5\text{-}C_5H_5) \rightarrow 2\ Ru(CO)_2Cl(\eta^5\text{-}C_5H_5) + 2\ TlCl + 2\ CO \quad (26)$$

Other preparations of $Ru(CO)_2XL$ where L is a cyclopentadienyl ligand involve halogenation of $RuH(CO)_2L$ by CCl_4 or MeI [204], carbonylation of $RuX_2(\eta^3\text{-allyl})L$ leading to reductive elimination of allylic halides [206], the reaction of $Ru_3(CO)_{12}$ with $\eta^5\text{-}C_5Ph_4Br$ [158] and the reaction of $Ru(CO)_3Br(C_3H_5)$ with $(C_5H_5)SnMe_3$ [193]. The crystal structures for L = $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5Me_4Et$ have been reported [207] and show no unusual features.

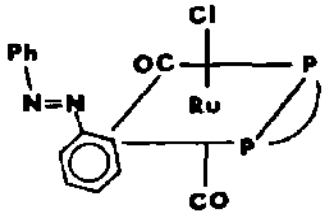
The related $Ru(CO)_2IL$ complexes (L = 1-5-η^5-$C_7H_8GeMe_3$ [208]; 1,2,3,3a,8a-η^5-$C_{10}H_8$(6-$GeMe_3$) [209]) are prepared by iodine cleavage of the Ru–Ge bond in the corresponding $Ru(CO)_2(GeMe_3)L$ compounds. Iodine or CX_4 (X = Cl, Br) also react with the clusters $Ru_3(CO)_6(C_7H_7)L$ (L = η^5-C_8H_9 [210]; 1-5-η^5-C_7H_8R (R = H, Me, Ph) [202]) to give $Ru(CO)_2IL$. The cationic complex $[Ru(CO)_3(COD)]^+$ reacts with I^- to give $Ru(CO)_2I(COD)$ [211].

(iii) $Ru(CO)_2XLL''$ (L = unidentate, L'' = bidentate)

These complexes contain cyclometallated bidentate ligands and are formed by reacting the chloro-bridged dimers $[Ru(CO)_2ClL'']_2$ (L'' = 1-phenylpyrazole, 2-phenylpyridine, benzo-[h]-quinoline [85], azobenzene [212,213]) with unidentate ligands (L = py, PPh_3, $AsPh_3$ [212,213], γ-picoline [85])

$$[Ru(CO)_2ClL'']_2 + 2\ L \rightarrow 2\ Ru(CO)_2ClLL'' \qquad (27)$$

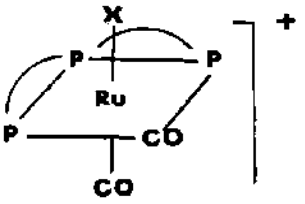
With diphos $[Ru(CO)_2ClL'']_2$ (L'' = azobenzene) gives **IX** [212,213].



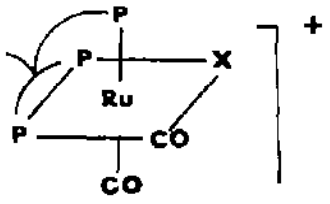
IX

(iv) $Ru(CO_2)XL'''$ (L''' = tridentate)

Both *fac*- and *mer*-$[Ru(CO)_2XL''']^+$ have been prepared. Oxidative addition of HX or X_2 (X = Cl, Br) to $Ru(CO)_2L'''$ gives **Xa** (L''' = $PhP[CH_2CH_2CH_2PCy_2]_2$) [214] or **Xb** (L''' = $MeC[CH_2PPh_2]_3$) [166].

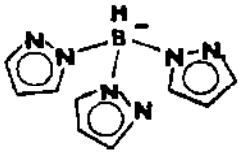


Xa



Xb

In other studies $Ru_3(CO)_{12}$ reacts with the tris(pyrazolyl) borate anion, **XI**, and in the presence of halogens forms a *fac*-isomer similar to **Xb** in which **XI** bonds through three N-atoms [215]



XI

$$Ru_3(CO)_{12} \xrightarrow{K(HBpz_3)} Ru(CO)_2X(HBpz_3) \quad (28)$$

This complex is also formed from $[Ru(CO)_3Cl_2]_2$ [215]

$$[Ru(CO)_3Cl_2]_2 + 2\ Tl(HBpz_3) \rightarrow 2\ Ru(CO)_2Cl(HBpz_3) + 2\ TlCl + 2\ CO \quad (29)$$

When heated in boiling alcohol $Ru(CO)_2Cl_2L_2$ ($L = o\text{-}CH_2{=}CHC_6H_4PPh_2$), which contains two monodentate P-bonded ligands, gives a mixture of products including $Ru(CO)_2Cl[o\text{-}Ph_2PC_6H_4CHCH_2CH(Me)C_6H_4PPh_2\text{-}o]$ in which the two vinyl groups of $Ru(CO)_2Cl_2L_2$ have incorporated one hydrogen atom and coupled to give a tridentate P–C–P grouping containing fused five and seven membered rings [90].

G. $Ru(CO)_2X_2$ COMPOUNDS

(i) $Ru(CO)_2X_2L_2$ (L = unidentate)

The most frequently encountered synthetic routes to these complexes are shown in Table 6 and include ligand substitution or neutral ruthenium carbonyl halides such as $[Ru(CO)_2X_2]_n$ or $[Ru(CO)_3X_2]_2$, and carbonylation of substituted ruthenium halides such as RuX_2L_3 or RuX_2L_4.

Depending on reaction conditions carbonylation of $RuCl_3$ in alcohols yields either red or yellow solutions from which after addition of ligands $Ru(CO)_2Cl_2L_2$ complexes may be isolated (Fig. 4). Using this procedure $Ru(CO)_2Cl_2L_2$ complexes containing a variety of ligands have been prepared (L = PPh_3 [115], PEt_3 [3], $P(Me_3SiCH_2)_3$ [217], $AsPh_3$ [115], $As(p\text{-}MeC_6H_4)_3$ [226], $SbPh_3$ [115], $AsPh_2R$ (R = Me, Et, n-Pr, n-Bu) [114,227, 228], PEt_2Ph [3], PMe_2Ph [110], $P(OR)_2Ph$ (R = Me, Et) [125], $PR_2(t\text{-}Bu)$ (R = Et, n-Pr, n-Bu, Ph, $p\text{-}MeC_6H_4$) [177], $P(t\text{-}Bu)_2R$ (R = Me, n-Pr) [177],

TABLE 6

Preparation of $Ru(CO)_2X_2L_2$ complexes

Reaction [a]	X	L
$[Ru(CO)_2X_2]_n + 2n\ L \rightarrow n\ Ru(CO)_2X_2L_2$	Cl	PPh_3, p-$NH_2C_6H_4$ [216]; $P(OR)_3$ (R = Ph, C_6H_4Me) [122]; $P(OMe)Ph_2$ [125]; $P(CH_2SiMe_3)_2Me$ [217]; MR_3 (M = As, P; R = p-MeC_6H_4) [218]
	Br	$P(OR)_3$ (R = Ph, p-MeC_6H_4) [122]; MR_3 (M = As, P; R = p-MeC_6H_4) [218]
	I	py, MPh_3 (M = P, As, Sb) [116,219,220,221]; NH_3, MeCN, $PhNH_2$, $AsPh_2Me$, p-$NH_2C_6H_5$ [221]; MEt_3 (M = Sb, As), PR_3 (R = OEt, Et), PPh_2Et, PEt_2Ph, MR_2 (M = S, Se; R = Et, Ph), MPh_2, (M = Se, Te), p-$MeC_6H_4NH_2$, $C_5H_{10}NH$ [116]; MR_3 (M = As, P; R = p-MeC_6H_4) [218]
$[Ru(CO)_3X_2]_2 + 4\ L \rightarrow 2\ Ru(CO)_2X_2L_2 + 2\ CO$	Cl	$MeSCH_2Ph$ [222], py [223]; $Ph_2PCH_2CH_2SPh$ (P-bonded) [224]; $PPh_2CH_2SiMe_3$ [225a] PEt_3 [225b]; pyrazole [212,213]; $MMe_2(PhCH_2)$ (M = P, As) [120]
$RuX_2L_3 + 2\ CO \rightarrow Ru(CO)_2X_2L_2 + L$	Cl	PPh_3 [115,179]; $Ph_2PCH_2C(O)OEt$ [160]
	Br	PPh_3 [115]
$RuX_2L_4 + 2\ CO \rightarrow Ru(CO)_2X_2L_2 + 2\ L$	Cl	PPh_3 [115]; $SbPh_3$ [121]; MeCN, EtCN [123,124]

[a] Unless otherwise indicated, X = Cl

PPh_2R (R = Me, Et) [177], $AsEt_2Ph$ [1], C_4H_4PR (R = Me, n-Bu, t-Bu, Ph, $PhCH_2$) [119], $PhCH_2PPh_2$ [229]). Treatment of the carbonylated $RuCl_3$ solution with bromide or iodide salts gives the corresponding $Ru(CO)_2X_2L_2$ complexes [226].

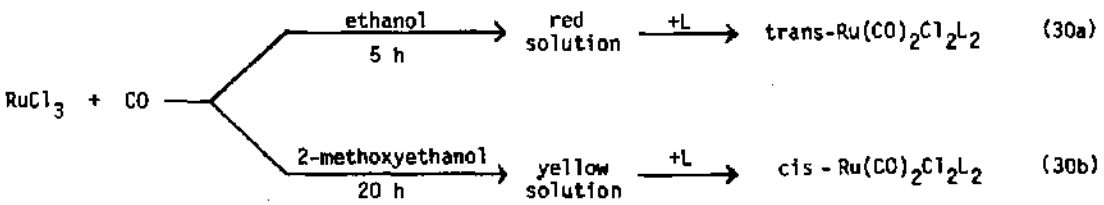
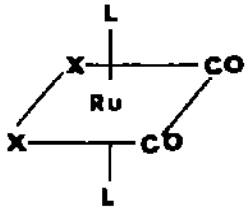
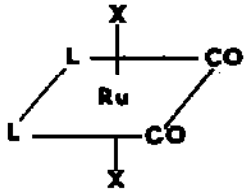


Fig. 4. Preparation of *cis*- and *trans*-$Ru(CO)_2X_2L_2$ complexes from carbonylated solutions of $RuCl_3$.

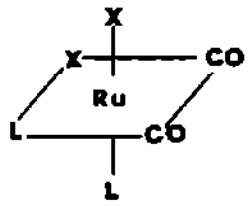
There are five possible isomers for $Ru(CO)_2X_2L_2$ complexes (**XIIa–e**) and



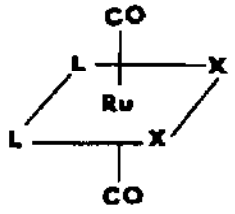
XII a



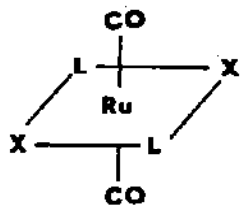
XII b



XII c



XII d



XII e

all have been reported. Addition of ligands to the red carbonylated solution of $RuCl_3$ (reaction (30a)), which forms at low temperatures and short reaction times, usually gives yellow *trans*-$Ru(CO)_2Cl_2L_2$ (**XIIe**) [3,110,119,217]. By contrast, the white *cis* isomer (**XIIa**) generally forms from the yellow carbonylated solution (reaction 30b) produced at higher temperatures and longer reaction times [110,119,227]. This generalisation is based on a limited number of reported reactions involving eqns. (30a) and (30b) since complete spectroscopic or structural data of the final $Ru(CO)_2Cl_2L_2$ product has not always been reported [226,228,230]. In addition, the final color of the carbonylated $RuCl_3$ solution has frequently been omitted from the reported experimental results [114,125,177,228, 231,232].

The complexes have been isolated from many other reactions involving mononuclear ruthenium complexes (Table 7) and dinuclear species (Table 8). Generally the *cis* isomers **XIIa** [3,4,25,65,111,114,116,120,131, 161,179,181,218,225a,232,236,237,240] or **XIIb** [111,116,213,223,240,241] are formed. The remaining isomers **XIIc** [90,224,232], **XIId** [114,179,234] and **XIIe** [115,148,160,179,234] are less common. It should be stressed that some of the above structural assignments are tentative since spectroscopic data alone cannot always distinguish between some configurations (e.g. **XIIa** and

TABLE 7

Miscellaneous reactions leading to $Ru(CO)_2X_2L_2$ complexes

Reaction [a]	L	Ref.
$RuX_2(O_2)L_3^b + CO$	$AsPh_3$	233a
$RuHX(dma)L_2 + CO$	PPh_3	179
$RuX_3(MeOH)L_2 + CO$	$AsPh_3$, PPh_3; (X = Cl, Br)	234
$Ru(CO)X_2L + CO$	PCy_3	25
$RuX_3L_3 + CO$	$AsPh_2Et$	114
$Ru(CO)X_2L_3 + CO$	MPh_3 (M = P, As)	131
$RuX_2L'_2 + CO$	$C_6H_4(OMe)PPh_2$	148
	o-CH_2=$CHC_6H_4MPh_2$ (M = P, As)	232
$Ru(CO)_3X_2(THF) + L$	py, MPh_3 (M = P, As)	235
$[Ru(CO)_2X_4]^{2-} + L$	PPh_3 (X = Cl, Br)	127
$Ru(CO)_3L_2 + X_2$	PPh_3 (X = Cl, Br, I)	231, 236
	Ph_2Ppy	237
$[Ru(CO)_2(NO)L_2]^+ + X_2$	PR_3 (R = Ph, Cy)	65
$Ru(CO)_3L_2 + NOX$	PPh_3 (X = Br)	48
$[Ru(CO)_3XL_2][AlCl_3X] + heat$	PPh_3 (X = Cl, Br)	181
$RuX_3 + HCHO + KOH + L$	PPh_3	238
$Ru(acac)_3 + SbPh_3 + MeX$	$SbMe_3$ (X = I)	239
$Ru(CO)X(o\text{-}MeCHC_6H_4PPh_2)$-$(o\text{-}CH_2$=$CH_2C_6H_4PPh_2) +$ heat	o-$EtC_6H_4PPh_2$	90
$[Ru(CO)_2X(FC_6H_4NH_2)L_2]I_3 + NaBF_4$	PPh_3	155

[a] Unless otherwise indicated, X = Cl.

[b] This compound has been shown to be $RuX_2(O_2)L_2$ [233b].

TABLE 8

Formation of $Ru(CO)_2X_2L_2$ complexes from dimeric ruthenium compounds and $Ru_3(CO)_{12}$

Reactants [a]	L	Ref.
$[Ru_2X_3L_6]X$ + alcohol	PEt_3, PEt_2Ph	3, 5
$[Ru_2X_2L_6]X + CO$	$AsPh_2Et$	114
$[Ru(CO)X_2(C_7H_8)]_2 + L$	Quinoline	132
$[RuX_2L_3]_2 + CO$	PhCN, P(n-Bu)$_3$	240, 241
$[Ru(CO)_2X_2L]_2 + L$	PPh_3	242
$[Ru(CO)_2X(2\text{-phenylazophenyl})]_2 + L$	Pyrazole	212, 213
$[Ru_2X_5L_4] + CO$	P(n-Bu)$_3$	240
$Ru_3(CO)_{12} + L$	$AsPh_3$	243

[a] Unless otherwise indicated, X = Cl.

XIIc [114,224,227]) and in such cases X-ray crystallography can be employed to resolve the structure [114].

The predominance of the *cis* isomers is due to the thermal instability of the *trans* isomers. For instance, **XIIe** rapidly isomerizes on heating or during recrystallization to form the stable *cis* isomer **XIIa** [3,110,177,179]. Irradiation of the *trans* complexes also results in isomerism [244]. **XIIa** is extremely thermally stable and chemically inert. For example treatment of **XIIa** ($L = PEt_3$, $X = Cl$) with an alcohol/base mixture does not form the hydride complex and metathesis of **XIIa** by Br^- or I^- is extremely slow [3,177].

Several anions of the type $[Ru(CO)_2X_2L_2]^{2-}$ ($X = Cl$, I; $L = CN$, $SnCl_3$ [115,219,220,245]) have been prepared by ligand substitution of $[Ru(CO)_2X_2]_n$

$$[Ru(CO)_2Cl_2]_n + SnCl_2 \xrightarrow{HCl} [Ru(CO)_2Cl_2(SnCl_3)_2]^{2-} \qquad (31)$$

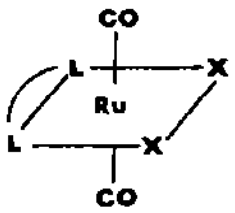
(ii) $Ru(CO)_2X_2LL'$ ($L \neq L'$ = unidentate)

The reaction of $Ru(CO)_3Cl_2(CS)$ with PPh_3 gives the all-*cis* isomer $Ru(CO)_2Cl_2(PPh_3)(CS)$ (**XIIc**) [246]. The coordinated CS is readily displaced by primary amines NRH_2 ($R = Ph$, Cy, p-MeC_6H_4) giving $Ru(CO)_2Cl_2(PPh_3)(NRH_2)$ [246].

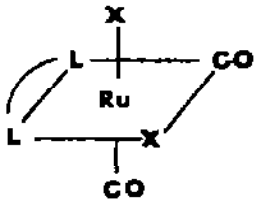
In other reactions carbonylation of $RuCl_3(AsPh_3)_2(OAsPh_3)$ or $RuCl_2(AsPh_3)_2(dmso)$ gives $Ru(CO)_2Cl_2(AsPh_3)L$ ($L = OAsPh_3$ [247], dmso [98]). Pyridines react with the dimer $[Ru(CO)_2Cl_2(R)]_2$ to form $Ru(CO)_2Cl_2(R)L$ ($R = PMe_3$ [248], PBu_2Ph [177]; L = py, Mepy).

(iii) $Ru(CO)_2X_2L''$ (L'' = bidentate)

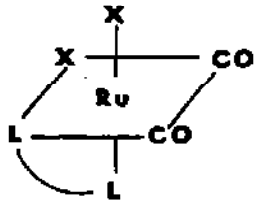
These compounds are obtained by methods outlined in Table 9 and are similar to those described above for $Ru(CO)_2X_2L_2$ compounds. Of the three possible isomers (**XIIIa–c**) only the two *cis* isomers **XIIIc** and **XIIIb** [116,232,237,242,250] have been reported.



XIII a



XIII b



XIII c

TABLE 9

Preparation of $Ru(CO)_2X_2L''$ complexes

Reaction [a]	L''	Ref.
$[Ru(CO)_2X_2]_n + L''$	phen (X = Cl, I)	116, 219, 220, 249
	bpy (X = Cl, I)	221, 231, 249
	$PhMCH_2CH_2MPh$ (X = I)	116
	$Ph_2MCH{=}CHMPh_2$ (M = As, P; X = Cl, Br, I)	250, 251
$RuX_3 + CO + L''$	phen, bpy	230
	$Ph_2PCH_2CH_2PPh_2$	252
	$o\text{-}CH_2{=}CHC_6H_4MPh_2$ (M = P, As)	232
$Ru(CO)_3X_2(THF) + L''$	bpy, diphos	235
$RuX_2L''_2 + CO$	$PhSCH_2CH_2SPh_2$ (X = Cl, Br)	163
	$Ph_2MCH_2MPh_2$ (M = P, As)	111
$[Ru(CO)_3L'']_3 + X_2$	Ph_2Ppy	237, 253

[a] Unless otherwise indicated, X = Cl.

Complexes such as $Ru(CO)_2Cl_2(bpy)$ were originally believed to be inert to further substitution by neutral donor ligands [230] but recently some reactions of these compounds have been described. Halide replacement reactions of $Ru(CO)_2Cl_2(bpy)$ gives $[Ru(CO)_2(bpy)_2]^{2+}$ [254] and $Ru(CO)_2(bpy)L''$ [255]

$$Ru(CO)_2Cl_2(bpy) + bpy + 2\ NH_4PF_6 \rightarrow [Ru(CO)_2(bpy)_2](PF_6)_2 + 2\ NH_4Cl \quad (32)$$

$$Ru(CO)_2Cl_2(bpy) + 2\ NaL'' \rightarrow Ru(CO)_2(bpy)L'' + 2\ NaCl \quad (33)$$

where L'' = 8-hydroxyquinoline, hydroxy aromatic ketones, β-ketones. Selective monodecarbonylation gives $Ru(CO)Cl_2py(bpy)$ (reaction 21) [145].

The reaction between $[Ru(CO)_2X_2]_n$ and bidentate ligands (L'') leads to $Ru(CO)_2X_2L''$ formation as outlined in Table 9. A similar reaction with terpyridyl gives $Ru(CO)_2X_2(tpy)$ (X = Cl, Br) which has been shown by X-ray crystallography to contain a bidentate terpyridyl ligand [249]. This form of coordination has been proposed for a number of terpyridyl complexes [256–261] largely on the basis of spectroscopic data.

Carbonylation of $RuCl_3[MeC(CH_2SEt)_3]$ reportedly forms $Ru(CO)_2Cl_2[MeC(CH_2SEt)_3]$ tentatively formulated as a seven coordinate complex [163]. However, only spectroscopic evidence is given to support this formulation.

H. $Ru(CO)_2X_3$ COMPOUNDS

The only reported example of this type of complex is the anion $[Ru(CO)_2I_3(PPh_3)]^-$ formed by reacting MeI with $Ru(CO)_2I_2(PPh_3)_2$ [262]

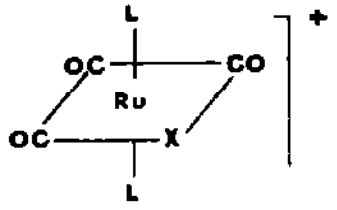
$$Ru(CO)_2I_2(PPh_3)_2 + MeI \rightarrow [PPh_3Me][Ru(CO)_2I_3(PPh_3)] \quad (34)$$

The reaction is reversible since the anion readily reacts with PPh_3 regenerating $Ru(CO)_2I_2(PPh_3)_2$.

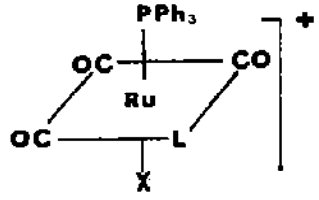
I. $Ru(CO)_3X$ COMPOUNDS

(i) $Ru(CO)_3XL_n$ (L = unidentate; n = 2, 1)

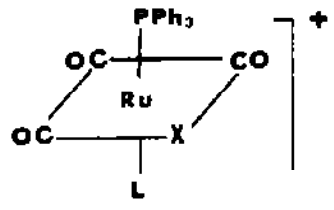
Iodine reacts with $Ru(CO)_3(PPh_3)_2$ to give the tricarbonyl complex *mer*-$[Ru(CO)_3I(PPh_3)_2]I$, **XIVa** (X = I; L = PPh_3) [263]. Complex **XIVa**



XIV a



XIV b



XIV c

reacts with tin or mercury salts and results in anion exchange and formation of $[Ru(CO)_3I(PPh_3)_2](MI_3)$ (M = Sn, Hg) [264]. Carbonylation of $Ru(CO)_2Cl_2(PPh_3)_2$ in the presence of $AlCl_3$ gives the chloro analogue **XIVa** (X = Cl, L = PPh_3) [181]

$$Ru(CO)_2Cl_2(PPh_3)_2 + AlCl_3 + CO \rightarrow [Ru(CO)_3Cl(PPh_3)_2][AlCl_4] \quad (35)$$

In other studies CO transfer from a carbamoyl ligand to the metal gives the tricarbonyl cation [141]

$$Ru(CO)_2Cl(p\text{-}MeC_6H_4NHCO)L_2 \xrightarrow{+2\,HCl} [Ru(CO)_3ClL_2]Cl + L \cdot HCl \quad (36)$$

where L = p-$MeC_6H_4NH_2$.

The monosubstituted tricarbonyls $Ru(CO)_3XL$ have been isolated from the reaction of $Ru_3(CO)_{12}$ with C_3H_5Br (X = Br, L = π-C_3H_5) [265] and by addition of HCl to $Ru(CO)_3(COT)$ (X = Cl, COT = 3-5-η^3-cyclooctatrienyl) [266]. The allyl complex $Ru(CO)_3Cl(C_3H_5)$ reacts with diethylacetylenedicarboxylate to give $Ru(CO)_3Cl[C(CO_2Et)=CHC(OEt)O]$ [185].

A cyclopentadienyl complex $Ru(CO)_3Cl(C_5H_5)$ is formed from $[Ru(CO)_3Cl_2]_2$ [193]

$$[Ru(CO)_3Cl_2]_2 + 2\,C_5H_5SnMe_3 \rightarrow 2\,Ru(CO)_3Cl(C_5H_5) + 2\,SnMe_3Cl \quad (37)$$

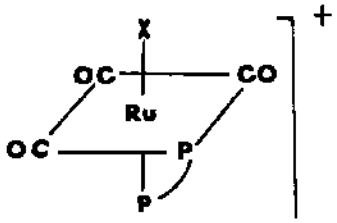
Addition of PPh_3 to $Ru(CO)_4I(SiMe_3)$ [267] or $[Ru(CO)_3XL]_2$ (X = I, L = MMe_3 where M = Si, Ge, Sn) [267]; X = Cl, L = $SiCl_3$ [268]) gives

mixed ligand complexes *mer*-$Ru(CO)_3X(PPh_3)L$. The two alternative geometries for these complexes **XIVb** and **XIVc** can be distinguished by ^{31}P NMR measurements [267,268]. **XIVc** (X = Cl; L = $SiCl_3$) is also obtained when $Ru(CO)_3(PPh_3)(SiCl_3)H$ is heated in a sealed tube with CCl_4 [268].

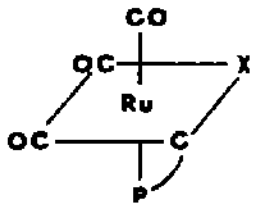
Pyridine splits the halogen bridged dimer $[Ru(CO)_3X(HgX)]_2$ (X = Cl, Br), without breaking the Ru–Hg bond and forms $Ru(CO)_3X(py)(HgX)$ [269].

(ii) $Ru(CO)_3XL''$ (L'' = bidentate)

In the presence of CO, *o*-phenylenebis(methylphenylphosphine) reacts with $[Ru(CO)_3Cl_2]_2$ to give *mer*-$[Ru(CO)_3ClL'']Cl$, **XVa** [161]. A *fac* isomer



XVa



XVb

XVb has also been reported from the reaction of $Ru(CO)_3L''$ (L'' = *o*-$CH_2{=}CHC_6H_4PPh_2$) with HX in which the chelate carbon is σ-bonded to ruthenium [270].

J. $Ru(CO)_3X_2$ COMPOUNDS

$Ru(CO)_3X_2L$ complexes have been isolated from reactions of $Ru(CO)_4X_2$ (X = Br, I) or $[Ru(CO)_3Cl_2]_2$ with a variety of ligands, (e.g., L = py, 3,4-Me_2py, 3-Mepy [223,271]; THF [235]; Et_3N [213]; RCN (R = Et, Ph, $CH_2{=}CH$) [223]; $OPPh_3$, Opy [272]; *o*-$CH_2{=}CHC_6H_4PPh_2$ [232]; $Ph_2PCH_2CH_2SPh$ (P-bonded [224]). Both *fac* [224,232] and *mer* [223] isomers have been reported.

Several trimeric complexes are oxidized by halogens or halogen containing compounds. $Ru_3(CO)_9L_3$ (L = $AsPh_3$, PPh_3 [243,251,273,274]) reacts with X_2 (X = Cl, Br, I), $CHCl_3$ or CCl_4 to give $Ru(CO)_3X_2L$. With $CSCl_2$, $Ru_3(CO)_{12}$ forms $Ru(CO)_3Cl_2(CS)$ [246]. The CS ligand can be displaced by primary amines NRH_2 (R = Ph, Cy, *p*-MeC_6H_4) forming isocyanide complexes $Ru(CO)_3Cl_2(CNR)$ [246].

K. $Ru(CO)_4X$ COMPOUNDS

These *trans*-$Ru(CO)_4XL$ complexes have been isolated from the reaction of $[Ru(CO)_4L]_2$ with halogens (L = $SiMe_3$, $GeMe_3$, $SiMeCl_2$; X = I, Br [267, 268]). Reaction of $RuH(CO)_4(SiCl_3)$ with CBr_4 gives the related complex $Ru(CO)_4Br(SiCl_3)$ [268].

L. CONCLUDING REMARKS

The chemistry of ruthenium carbonyl halides is one example of the rich and expanding area embraced in the general coordination chemistry of ruthenium. Many of the compounds described in this review also function in a variety of catalytic processes, but this area has not been covered in this review which is restricted to synthetic procedures.

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