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SUBSTITUTED OSMIUM CARBONYL HALIDES

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CONTENTS

ABBREVIATIONS

bpy	2,2′-bipyridyl
Bu	*n*-butyl
Cp	cyclopentadienyl
Cy	cyclohexyl
diars	$Ph_2AsCH_2CH_2AsPh_2$

dmnp	dimethyl(1-naphthyl)phosphine
dpp	$Ph_2P(CH_2)_3PPh_2$
dppb	1,2-bis(diphenylphosphino)benzene
dppe	$Ph_2PCH_2CH_2PPh_2$
dppene	*cis*-1,2-bis(diphenylphosphino)ethylene
dppm	$Ph_2PCH_2PPh_2$
DBU	1,8-diazabicyclo[5.4.0.]undec-7-ene
DME	dimethoxyethane
DMF	dimethylformamide
Et	ethyl
Et_3N	triethylamine
EtOH	ethanol
hmp	2-hydroxy-6-methylpyridine
i-Pr	isopropyl
L or L′	unidentate ligand
L″	bidentate ligand
Me	methyl
MeCN	acetonitrile
Me_5Cp	pentamethylcyclopentadienyl
Me_3NO	trimethylamine-*N*-oxide
ox	oxalate
pdma	*o*-phenylenebis(dimethylarsine)
py	pyridine
Ph	phenyl
Phen	1,10-phenanthroline
PPh_3	triphenylphosphine
Pr	*n*-propyl
triphos	$PhP[CH_2CH_2PPh_2]_2$
X	halogen or halide

A. INTRODUCTION

The chemistry of substituted osmium carbonyl halides has only been briefly mentioned in earlier reviews [1,2], and in the present article the preparations and reactions of these compounds are described up to 1987. The complexes may be generally formulated as $OsX_m(CO)_nL$ ($m,n = 1$, 2, 3 or 4; $m + n = 2$, 3, 4 or 5) and they contain at least one "substituted" ligand (L) having one or more donor atoms (generally a group V atom). In addition, many organoosmium and hydrido complexes have been described and are included in this review.

The compounds occur most commonly as neutral osmium(II) complexes, generally with a coordination number of six and hence octahedral geometry.

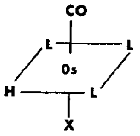
Less common are cationic and anionic complexes, coordination numbers of four and five and complexes with +3 oxidation states.

B. OSMIUM(II) HYDRIDO COMPOUNDS

(i) Octahedral complexes

The hydrido complexes $OsHX(CO)L_3$ ($X = Cl$, Br; $L = PPh_3$) were first prepared by reacting the $[OsX_6]^{2-}$ salts with L in alcoholic solvents [3,4]. Although originally formulated as $OsXL_3$ [5], it was subsequently apparent from IR data that Os–H and Os–CO groups were present in these complexes [3] and originated by hydride and CO extraction from the solvent. Similar solvent decarbonylation reactions by $[OsX_6]^{2-}$ salts have been observed in a variety of alcohols (e.g. 2-methoxyethanol [3,6,7], ethylene glycol [3,8] and 2-(β-methoxy)ethanol [9]) and in DMF [10] in the presence of phosphine and arsine ligands (e.g. $L = PPh_3$ [3,6,9,10], $AsPh_3$ [6,7], $As(CH_2Ph)_3$ [8]). The presence of a weak base (e.g. Et_3N) has been shown to assist hydride abstraction from solvents [7] by removing the alcoholic protons to give an alkoxo intermediate which rearranges to form the OsH(CO) species by a mechanism presumably similar to that previously described for ruthenium [11]. The complexes OsX_2L_3 and $OsX_2(O_2)L_2$ ($X = Cl$; $L = PPh_3$) also react with solvents (e.g. 2-methoxyethanol–HCHO) to give $OsHX(CO)L_3$ [12], while $OsX_2(CO)_3$ extracts H^- from ethanol [12] or a methanol–$NaBH_4$ mixture to give the same product [12(a)].

Only the *mer*-$OsHX(CO)L_3$ isomer has been described [7,9,13] in which the CO and X ligands are mutually *trans* (**I**). This assignment is based on



I

early measurements of the $\nu(Os–H)/\nu(Os–D)$ ratio [13] which indicate that the CO and H ligands are *cis* to each other. In addition, unsuccessful attempts to convert **I** ($X = Cl$, $L = AsPh_3$) into the corresponding dihydro complex $OsH_2(CO)L_3$ by reaction with borohydride [7] support the presence of halide *trans* to CO, which is also consistent with the weak *trans* effect of CO in this complex.

$OsHX(CO)L_3$ complexes undergo a variety of reactions leading to the formation of many monocarbonyl monohalogeno osmium(II) compounds (Table 1), but few examples exist of direct hydride replacement by ligands

TABLE 1

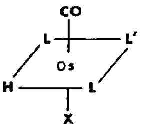
Reactions of $OsHX(CO)L_3$ complexes

$OsHX(CO)L_3$ complex [a]	Other reactants	Product	Ref.
$L = PPh_3$	RCO_2H ($R = CF_3$, C_2H_5, C_6F_5)	$OsX(CO)L_3(RCO_2)$	14–16
$L = PPh_3$	$MeC_6H_4SO_2CH_2NC$	$OsHX(CO)L_2(CNCH_2SO_2R)$ ($R = p$-MeC_6H_4)	17
$L = PPh_3$; $X = Cl, Br$	CS_2	$OsX(CO)L_2(HCS_2)$	18, 19
$L = PPh_3$; $X = Cl, Br$	RNCS ($R = Me, Ph$, p-MeC_6H_4, Et)	$OsX(CO)L_2(S\overset{\cdots}{-}CH\overset{\cdots}{-}NR)$	20, 22
$L = PPh_3$	HgR_2 ($R = p$-MeC_6H_4)	$OsX(CO)L_2R$	21
$L = PPh_3$; $X = Cl, Br$	RNCNR ($R = p$-MeC_6H_4)	$OsX(CO)L_2(RN\overset{\cdots}{-}CH\overset{\cdots}{-}NR)$	23
$L = PPh_3$; $X = Cl, Br$	RNCO ($R = p$-McC_6H_4)	$OsX(CO)L_2(RN\overset{\cdots}{-}CH\overset{\cdots}{-}O)$	24, 25
$L = PPh_3, AsPh_3$ $X = Cl, Br, I$	RNC ($R = p$-MeC_6H_4)	$OsHX(CO)L_2(RNC)$	26
$L = PPh_3$; $X = Cl, Br$	$MeCO_2H$	$OsX(CO)L_2(MeCO_2)$	27
$L = PPh_3$	$L' = PH_2Ph$, $PHPh_2$	$OsHX(CO)L_2L'$	28, 29
$L = PPh_3$	CNR ($R = p$-MeC_6H_4)	$OsHX(CO)L_2(CNR)$	9
$L = AsPhR_2$ ($R = Me$, Et) $X = Cl, Br$	CNR ($R = p$-MeC_6H_4)	$OsHX(CO)L_2(CNR)$	30
$L = PPh_3$	$L' = PR_3, PR_2Ph$, $PRPh_2$ ($R = OMe, OEt$)	$OsHX(CO)L_2L'$	31
$L = PPh_3$	pyXH ($X = O, S$)	$OsCl(CO)L_2(pyX)$	32, 33
$L = PPh_3$	$L' = p$-MeC_6H_4CN	$OsHX(CO)L_2L'$	12
$L = PCy_3$	$L' = CH{\equiv}CR$ ($R = H, Ph$)	$OsHX(CO)L_2L'$	34
$L = PPh_3$	o-$HOC_6H_4CH{=}NPh$	$OsX(CO)(o$-$C_6H_4CH{=}NPh)L_2$	35
$L = PPh_3$	Diazonium salts	$OsX(CO)(FBF_3)L_2(NH{=}NR)$ ($R = p$-MeC_6H_4)	36
$L = PPh_3, AsPh_3$	$P(OPh)_3$	$OsHX(CO)L_{3-y}[P(OPh)_3]_y$ ($y = 1$ or 2)	37
$L = PPh_3$	$MeSO_3H$	$Os(MeSO_3)Cl(CO)L_2$	38(a)

[a] Unless otherwise indicated, $X = Cl$.

(L') to form other $OsX(CO)L_3L'$ complexes. While **I** reacts with HR ($R = CF_3CO_2$, $C_2F_5CO_2$, $C_6F_5CO_2$) to give $OsX(CO)L_3R$ [14–16], more frequently when **I** is treated with L' the strong *trans*-labilizing effect of the hydride ligand results in formation of $OsHX(CO)L_2L'$ (e.g. $L' = P(OPh)_3$

[37], $MeC_6H_4SO_2CH_2NC$ [9,17,26,30], PH_2Ph [28,29], PR_3, PR_2Ph, $PRPh_2$ (R = OMe, OEt) [31], RC≡CH (R = H, Ph) [34]). $OsHX(CO)L_2L'$ complexes are stable with respect to further substitution by neutral ligands and do not react when subjected to prolonged and/or vigorous treatment with excess L′ [31]. The *trans*-labilizing effect of the hydride ligand generally yields $OsHX(CO)L_2L'$ complexes which have structure **II** [12,17,26,30,31,37]. Direct carbonylation of **I** yields the dicarbonyl complex $OsHCl(CO)_2(PPh_3)_2$ [38]. The mixed-ligand hydrido compounds $OsHX(CO)L_2L'$ have also been obtained by ligand substitution of the five-coordinate $OsHX(CO)L_2$ complexes by L′ (L′ = py [39], SO_2, O_2, $CH_2{=}CH_2$ [40,41], $CH_2{=}CHCN$, $(CN)_2C{=}C(CN)_2$ [42]) or by ligand displacement from the octahedral $OsHX(CO)L_3$ complexes by L′ (L′ = $P(OPh)_3$ [37], *p*-$MeC_6H_4SO_2CH_2NC$ [9,26,30,43], PH_2Ph [28], PR_3, PR_2Ph, $PRPh_2$ (R = Me, Et) [31], *p*-MeC_6H_4CN [12], RC≡CH (R = H, Ph) [34]).



II

TABLE 2

Reactions of $OsHX(CO)L_2$ complexes

$OsHX(CO)L_2$ complex [a]	Other reactants	Product	Ref.
L = PCy_3	L′ = py	$OsHX(CO)L_2L'$	39
L = PCy_3, PPh_3	$MeC_6H_4SO_2N(Me)NO$	$OsX(CO)L_2(NO)$	43, 46
L = PCy_3 X = Cl, Br	L′ = SO_2, O_2, $CH_2{=}CH_2$	$OsHX(CO)L_2L'$	40, 41
L = PCy_3 X = Cl, Br	CS_2	$OsX(CO)L_2(HCS_2)$	40, 47
L = PPh_3	L′ = $CH_2{=}CHCN$, $(CN)_2C{=}C(CN)_2$	$OsHX(CO)L_2L'$	42
L = $P(i\text{-}Pr)_3$	L′ = PR_3 (R = Me, OMe), CO, $CH_2{=}CH_2$ $H_2C{=}CHCO_2CH_3$, $H_2C{=}CHCN$	$OsHX(CO)L_2L'$	44
	RC≡CH (R = H, Ph)		48
L = $P(i\text{-}Pr)_3$	$NaBH_4$	$OsH(\eta^2\text{-}BH_4)(CO)L_2$	49

[a] Unless otherwise indicated, X = Cl.

(ii) Five-coordinate complexes

As with $OsHX(CO)L_3$ complexes, the five-coordinate hydrido compounds $OsHX(CO)L_2$ (III) ($X = Cl$, Br; $L = PCy_3$) have also been prepared from the reaction of $[OsX_6]^{2-}$ salts with L in alcohol solvents, but require longer reaction times, e.g. 48–60 h. Presumably $OsHX(CO)L_3$ is formed initially and undergoes thermal displacement of L yielding the bis(phosphine) complex. Complex **III** will not react with excess phosphines to give **I** owing to steric hindrance by the bulky PCy_3 ligands [39], but does react with some N-donor ligands (e.g. $L' = py$ [39], acrylonitrile [42], CNR ($R = p\text{-}MeC_6H_4$) [43]) and activates small molecules such as SO_2, O_2 and ethylene [40,41] to give coordinatively saturated $OsHX(CO)L_2L'$ complexes. Complex **III** ($X =$ Cl; $L = i\text{-}PPr_3$) has also been isolated by $OsCl_3$ decarbonylation of methanol in the presence of L [44]. The crystal structure of $OsHCl(CO)(PCy_3)_2$ indicates a square-pyramidal geometry for **III** [45]. Table 2 summarizes the known reactions of $OsHX(CO)L_2$ complexes which yield other monocarbonyl monohalogeno compounds.

C. ORGANOMETALLIC COMPOUNDS

(i) Alkyl and aryl osmium(II) complexes

Although metal alkyl and aryl bonds are frequently unstable, several alkyl and aryl osmium(II) carbonyl halide complexes have been prepared. These compounds all contain π-acid ligands such as CO, PPh_3 and/or π-arenes which generally stabilize the σ-alkyl and σ-aryl bonds. The majority of these compounds have the general formula $Os(R)X(CO)_2(PPh_3)_2$ (**IV**) where $R =$ Me, Et, Ph or $p\text{-}MeC_6H_4$. Complex **IV** ($L =$ Me, $X = I$) has been obtained from the reaction of $Os(CH_2I)I(CO)_2(PPh_3)_2$ with $NaBH_4$ [50], while the ethyl derivatives ($L =$ Et, $X =$ Cl, I) are obtained by reacting the ethene complex $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ with HX [51]. Oxidation of the zero-valent phenyl carbyne complex $Os(CPh)Cl(CO)(PPh_3)_2$ with O_2 gives the aryl complex $Os(Ph)Cl(CO)_2(PPh_3)_2$ [52]. The related p-tolyl complex (**IV**) ($R = p\text{-}MeC_6H_4$, $X =$ Cl) has been obtained by hydrolysis and carbonylation of the chlorocarbene complex $Os(CClR)Cl_2(CO)(PPh_3)_2$ [53] and by carbonylation of the five-coordinate $Os(R)Cl(CO)(PPh_3)_2$ complex [21]. The latter coordinatively unsaturated complex is prepared from the reaction of $OsHCl(CO)(PPh_3)_3$ with HgR_2 [21].

The tetracarbonyl alkyl complexes *cis*-$Os(R)X(CO)_4$ have been obtained by oxidative addition of MeI to $[HOs(CO)_4]^-$ [54,55] and by electrophilic attack on $OsMe_2(CO)_4$ [56] or $Os_3Me_2(CO)_{12}$ [57] by X_2 ($X =$ Cl, Br, I).

The alkyl hydrido complex $OsHEt(CO)_4$ reacts with CCl_4, possibly via a radical-chain mechanism, to give the related $OsEtCl(CO)_4$ [58].

A four-coordinate alkyl osmium carbonyl halide complex OsMeCl(CO)L ($L = p\text{-}MeC_6H_4CHMe_2$) has been prepared by methylation of $OsCl_2(CO)L$ with Al_2Me_6 [59].

(ii) Carbene, isocyanide and related complexes

A number of organometallic osmium carbonyl halides containing carbene ligands, of the general type Os = CRR′, and the related compounds Os CR$_3$ are known. The most common neutral complexes have the general formula $Os(CH_2R)X(CO)_2(PPh_3)_2$ (**Va**) (e.g. R = Cl, Br, I, OMe, OH, SMe or $p\text{-}MeC_6H_4$) and are obtained by a number of routes. Addition of excess HX to the η^2-formyl complexes $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ gives the halo compounds **Va** (R = Br, I, X = Cl [60]; R = X = Cl, Br, I [50,61,60]) whereas with equimolar amounts of HX the alkoxo derivatives **Va** (R = OH, X = Cl, Br [60]) are formed. The electrophilic nature of the CR_3 group is evident from the ease with which the carbon undergoes reaction with nucleophilic reagents, e.g. **Va** (R = Cl) reacts with MeOH to give **Va** (R = OMe) [61]. Complex **Va** has also been obtained from the reactions of $Os(C_8H_8)(CO)_2(PPh_3)_2$ with HCl ($R = p\text{-}MeC_6H_4$ [62]), $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ with CF_3SO_3Me (R = OMe [61]), $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]^+$ with LiCl (R = OMe [60]) and $[Os(\eta^2\text{-}CH_2SMe)(CO)_2(PPh_3)_2]^+$ with LiCl (R = SMe [63,64]). The neutral carbene complexes $Os(=CRR')X_2(CO)(PPh_3)_2$ (**Vb**) have been prepared by HCl addition to $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ (R = OH, R′ = Et [65]) or by oxidative addition reactions with the carbyne complexes $Os(CR)Cl(CO)(PPh_3)_2$ to give **Vb** (R = Ph, R′ = H [66]; $R = p\text{-}MeC_6H_4$, R′ = Cl [53]). Complex **Vb** ($R = p\text{-}MeC_6H_4$, R′ = Cl) reacts with $LiEt_3BH$ to form $Os(CHR)Cl_2(CO)(PPh_3)_2$ [53]. The dichlorocarbene complex $Os(CCl_2)Cl_2(CO)L_2$ reacts with $Cd(CF_3)_2$ to give $Os(CFCl)Cl_2(CO)L_2$ which in turn forms $Os(CFR)Cl_2(CO)L_2$ upon reaction with Me_2NH or NaSEt ($R = Me_2N$, SEt; $L = PPh_3$ [67]). The related formyl and thioformyl complexes $Os(CHR)X(CO)_2(PPh_3)_2$ (R = O [60] or S [63] respectively) have also been reported.

Several complexes containing cyclic carbene ligands are known and have been prepared by intramolecular cyclization reactions. For instance the methoxycarbonyl complex $Os(MeOCO)(CNR)Cl(CO)L_2$ ($R = p\text{-}MeC_6H_4$, $L = PPh_3$) reacts with 2-chloroethanol and Et_3N giving $[Os(\overline{COCH_2CH_2O})(CNR)Cl(CO)L_2]^+$ [68]. With $NaClO_4$, $Os(CS_2CH_2CH_2Br)Br(CO)_2L_2$ similarly gives $[Os(\overline{CSCH_2CH_2S})Br(CO)_2L_2]^+$ [69]. Nucleophilic attack on coordinated isocyanide complexes also gives similar complexes. Thus $[Os(CNCH_2SO_2R)Cl(CO)_2L_2]^+$ reacts with benzaldehyde and NaOMe to give the oxazo-2-ylidene complex $OsH\{\overline{COC(Ph)CHNH}\}Cl(CO)L_2$. An analogous reaction with acetaldehyde forms $OsH\{\overline{COC(MeO)HC(OMe)HNH}\}Cl(CO)L_2$ ($L = PPh_3$) [17].

The cationic carbene complexes $[Os(CRR')X(CO)_2(PPh_3)_2]^+$ ($R = R' = SMe$, $X = I$ [63]; $R = H$, $R' = SMe$, $X = Cl$ [54]) have also been prepared.

Several isocyanide complexes containing CNR ligands are known. $OsHCl(CO)L_2$ undergoes direct addition of CNR ($R = p\text{-}MeC_6H_4$, $L = PPh_3$) forming $OsH(CNR)Cl(CO)L_2$ [68]. Reaction of the latter with perchloric acid gives $Os(CNR)(OClO_3)Cl(CO)L_2$ which in turn undergoes displacement of the weakly coordinated perchlorate by CO to yield $[Os(CNR)Cl(CO)_2L_2]^+$ (**VI**) [68]. Isocyanide complexes are frequently susceptible to nucleophilic attack; consequently **VI** reacts reversibly with basic methanol to give the methoxycarbonyl complex $Os(CNR)(MeOCO)Cl(CO)L_2$ [68]. The octahedral hydrido complexes $OsHX(CO)L_3$ ($X = Cl$, Br, I; $L = PPh_3$, $AsPh_3$) also react with CNR to give $OsH(CNR)Cl(CO)L_2$ ($R = CH_2SO_2(p\text{-}MeC_6H_4)$ [17] or $p\text{-}MeC_6H_4$ [9,26]) which may also react as above to form **VI** [17]. As noted earlier, **VI** undergoes nucleophilic attack at the coordinated CNR ligand to give cyclic carbene compounds [17,68]. A further example of the electrophilic nature of carbenes is the reaction of $Os(CCl_2)Cl_2(CO)L_2$ with RNH_2 ($R = Me$, Bu, $p\text{-}MeC_6H_4$) to form $Os(CNR)Cl_2(CO)L_2$ [69]. $OsCl_2(CS)L_3$ also reacts with CNR to form $Os(CNR)(CS)Cl_2L_2$ ($L = PPh_3$, $R = p\text{-}MeC_6H_4$), and this complex further reacts with $AgClO_4$ and CO forming $[Os(CNR)(CS)Cl(CO)L_2]^+$ [70].

(iii) Four-coordinate cyclopentadienyl and π-arene complexes

These compounds all have pseudotetrahedral geometries and are carbocyclic π-complexes containing arene or cyclopentadienyl ligands. They have the general formulae $OsX(CO)_2L$ or $OsX_2(CO)L$ and also form the mixed-ligand complexes $OsX(CO)L(L')$ ($L = Cp$ or arene; L' = unidentate).

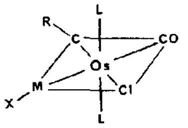
For the $OsX(CO)_2L$ series ($L = Cp$ or Me_5Cp [71,72]) the cyclopentadienyl compounds have been obtained by treating $OsBr_2(CO)_4$ with Cp or TlCp [71] or by reacting $Os_3(CO)_{12}$ with Me_5Cp and I_2 [71,72]. Displacement of $SiMe_3$ by X_2 in the cycloheptadienyl complex $Os(SiMe_3)(CO)_2L$ also yields $OsX(CO)_2L$ complexes ($X = Br$, I; $L = 1\text{-}5\text{-}\eta\text{-}C_7H_9$) [73]. Decarbonylation of the $[Os(Me_5Cp)(CO)_2(PR_3)]I$ salts by Me_3NO gives $Os(Me_5Cp)I(CO)(PR_3)$ [72]. $OsX_2(CO)L$ complexes have been isolated by carbonylation of the monoarene complex $OsCl_2L$ ($L = \eta^6\text{-}C_6H_6$) [74] and by the bridge-splitting reaction of CO with the dimer $Os_2X_4L_2$ ($X = Cl$, $L = \eta^6$-p-cymene [59]; $X = I$, $L = \eta^6\text{-}C_6H_6$ [75]).

The mixed-ligand complexes have been obtained by carbonylation of bis(phosphine) complexes which result in displacement of a PR_3 ligand.

Carbonylation of $Os(Cp)Br(PPh_3)_2$ yields the neutral $Os(Cp)Br(CO)(PPh_3)$ complex [76] while a similar reaction with $Os(C_6H_6)I_2(PPr_3)$ in the presence of $AgPF_6$ gives the cationic complex $[Os(C_6H_6)I(CO)(PPr_3)](PF_6)$ [77,78]. Methylation of $OsCl_2(CO)L$ ($L = p\text{-}MeC_6H_4CHMe_2$) by Al_2Me_6 gives $Os(Me)Cl(CO)L$ [59].

(iv) Cyclometallated complexes

A small number of cyclometallated osmium carbonyl halides are known and these contain a heterocyclic ring consisting of osmium, carbon and at least one other atom, one of which is coordinated to the metal. Direct interaction between the Os≡C bond in the carbyne complex $Os(CR)Cl(CO)L_2$ and simple transition metal salts, e.g. CuI or AgCl, gives the mixed dimetallocyclopropene complex **VII** ($R = p\text{-}MeC_6H_4$, $L = PPh_3$) [79]. Addition of XH^- ($X = S$, Se, Te) to the chlorocarbene complex $Os(CClR)Cl_2(CO)L_2$ yields the corresponding thioacyl, selenoacyl or telluroacyl compounds $Os(\eta^2\text{-}CXR)Cl(CO)L_2$ ($R = p\text{-}MeC_6H_4$, $L = PPh_3$) [53]. The thioacyl complex is also formed by intramolecular rearrangement when the thiocarbonyl complex $OsR(CS)X(CO)L_2$ is heated [80,81]. The difluoro complex $Os(CHF_2)Cl(CO)_2(PPh_3)_2$ reacts with BCl_3 giving the metallacycle $Os[o\text{-}PPh_2C_6H_4CHCl]Cl(CO)_2L_2$ which is formed by addition of a CHCl to a benzene ring of the ligated PPh_3 [82]. Further reaction with BCl_3 generates the metallabicyclic complex $Os[o\text{-}PPh_2C_6H_4CHC_6H_4PPh_2\text{-}o]Cl(CO)_2$ [82].



VII

In low boiling solvents the hydrido complex $OsHCl(CO)(PPh_3)_3$ reacts with $P(OPh)_3$ forming $OsHCl(CO)(PPh_3)_2\{P(OPh)_3\}$ owing to the *trans*-labilizing effect of the hydride. However, under vigorous reaction conditions (refluxing decalin) the orthometallated complex $Os(C\text{-}P)Cl(CO)(PPh_3)\{P(OPh)_3\}$ ($C\text{-}P = (PhO)_2P(o\text{-}C_6H_4)$) [37] is produced.

Other related organometallic compounds reported are the methallyl complex $Os(\eta^3\text{-}CH_2CMeCH_2)Cl(CO)(PPh_3)$ [83] and the metallabenzene complex $Os\{C(SR)CHCHCHCH\}X(CO)(PPh_3)_2$ ($R = H$, $X = Cl$; $R = Me$, $X = I$) [84]. The σ-alkenyl complex $Os(\eta^1\text{-}PhC{=}CHPh)(CS)ClL_2$ reacts with CO and rapidly rearranges to the η^2-thioacyl $Os\{C(S)CPh{=}CHPh\}Cl(CO)L_2$ ($L = PPh_3$) [85].

(v) *Miscellaneous complexes*

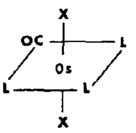
Addition of the alkynes RC≡CH (R = H or Ph) to the coordinatively unsaturated hydrido complex $OsHCl(CO)(PPr_3)_2$ gives the vinyl complexes $Os(CH{=}CHR)Cl(CO)(PPr_3)_2$ [48]. On reaction with CO the latter forms the octahedral dicarbonyl complex [48]. Insertion of HCl in $Os(CCF_3{=}CCF_3)(CO)_2\{P(OMe)_3\}_2$ gives the related $Os(CCF_3{=}CHCF_3)Cl(CO)_2\{P(OMe)_3\}$ complex [87].

Other organometallic compounds include the carbamoyl compounds $Os(CONH_2)Cl(CO)_2L_2$, formed from the reaction of $[OsCl(CO)_3L_2]^+$ (L = PPh_3, PCy_3) and liquid ammonia [88], and the thiocarbonyl complex $Os(CS)Cl_2(CO)(PPh_3)_2$, formed by addition of HCl to $Os(CO)_2(CS_2)(PPh_3)_2$ [86].

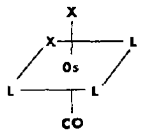
D. NEUTRAL OCTAHEDRAL OSMIUM(II) COMPOUNDS CONTAINING GROUP V DONOR LIGANDS

(i) *$OsX_2(CO)(unidentate)_3$ complexes*

These compounds, which all contain trialkyl phosphines, arsines or stibines, are prepared by carbonylation and reduction of the substituted osmium(III) halides, OsX_3L_3 (L = $SbPh_3$ [89], PMe_2Ph or PEt_2Ph [90–92]. Reduction by solvent [89] or Zn/Hg [90–92] yields the *trans* isomer **VIIIa**, which on heating is converted into **VIIIb**. Direct carbonylation of $OsCl_2L_3$ (L = dmnp [93]) or $OsCl_2L_4$ (L = PMe_3 [30,94]) yields **VIIIb** and **VIIIa** respectively. In HCHO–alcohol, $OsCl_2L_3$ gives **VIIIa** (L = PPh_3 [12]) while under similar conditions the anions $[OsX_6]^{2-}$ react with $AsPhR_2$ (R = Me, Et, Pr) [95] or $AsPh_3$ [7] to give **VIIIb**. Irradiation and carbonylation of the dinitrogen complex $OsCl_2(N_2)L_3$ (L = $PPhEt_2$ [96]) gives **VIIIb**.



VIIIa



VIIIb

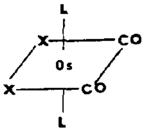
Other reactions leading to **VIII** are the reactions of $OsCl_2(O_2)L_2$ with L in HCHO–alcohol (L = PPh_3) [12], $OsHCl(CO)L_3$ with HCl [12] and substitution of *trans*-$[OsX_4(CO)_2]^-$ (X = Cl, Br, I) by pyridine [97]. Stepwise hydrolysis of $[OsX_5(CO)]^{2-}$ (X = Cl, Br, I) also reportedly gives **VIII** (L = H_2O) [98].

(ii) $OsX_2(CO)_2$(unidentate)$_2$ and $OsX_2(CO)_2$(bidentate) complexes

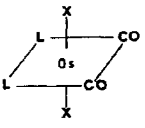
Many examples of $OsX_2(CO)_2$(unidentate)$_2$ complexes are known and they have been obtained by numerous different reactions (Table 3). These include ligand substitution of neutral [12,54,55,102,109,110] or anionic [103–107] osmium carbonyl halides, or by carbonylation of a variety of substituted osmium halides [7,12,89,90,95,96,99] or the hexahalide salts $[OsX_6]^{2-}$ [95,99,100].

By contrast with $RuCl_3$, which may be readily carbonylated in a variety of alcohol solvents [11], carbonylation of $OsCl_3$ is slow and generally incomplete owing to its poor solubility [99], and it is therefore not a good source of $OsX_2(CO)_2L_2$ complexes. However, carbonylation of the more soluble $[OsX_6]^{2-}$ salts does yield these complexes [95,99,100].

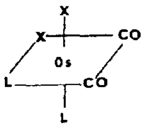
Of the five possible isomers for $OsX_2(CO)_2L_2$ (**IXa–IXe**) all except **IXd** have been reported. Generally the white isomer **IXa** is the thermodynamically stable isomer and is formed under high temperature reaction conditions [7,12,36,69,89,90,95,108,109,111,113]. At lower temperatures the yellow all-*trans* isomer, **IXe**, is the kinetic product [12,89,90,95] which may be converted to **IXa** upon heating [12,90]. Similarly, **IXb** [107,114] thermally reverts to **IXa**. (The all-*cis* isomer **IXc** has only been reported for the anion $[Os(MeCO)_2Br_2(CO)_2]^{2-}$ [10,54,55].) The mixed-halide complex $OsBrCl(CO)_2(NH_3)_2$ has been prepared from the halide exchange of **IX** (X = Br, L = NH_3) with HCl [106].



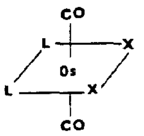
IXa



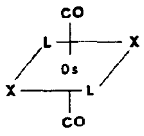
IXb



IXc

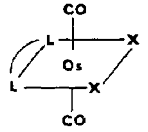


IXd

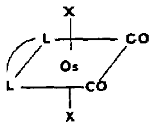


IXe

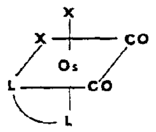
Only a few $OsX_2(CO)_2$(bidentate) complexes have been reported. The *cis,trans* isomer **Xa** has been obtained by treating the anion $[OsX_4(CO)_2]^{2-}$ with pdma at room temperature [115]. At shorter reaction times, $[OsX_6]^{2-}$ or $[OsX_2(CO)_4]^{2-}$ react with pdma in refluxing 2-methoxyethanol to give **Xb**. A similar reaction for longer periods gives the all-*cis* isomer **Xc** [115]. The conversion of **Xb** into **Xc** is achieved in refluxing ethylene glycol [115]. Complex **X** has also been prepared from $[OsX_2(CO)_3]_2$ with pdma or dppe [102].



Xa



Xb



Xc

(iii) $OsX_2(CO)_3$(unidentate) complexes

Oxidative addition of X_2 to the trinuclear complexes $Os_3(CO)_9L_3$ gives $OsX_2(CO)_3L$ (X = Cl, Br, I, L = PPh_3 [116]; X = Cl, L = PEt_3 [117]) which have *cis* halogen ligands [117]. Halide displacement by PPh_3 converts $[OsX_3(CO)_3]^-$ to $OsX_2(CO)_3L$ (X = Cl, Br) [103–105]. With MeCN, the dimer $Os_2Br_4(CO)_6$ yields $OsBr_2(CO)_3$(MeCN) [118].

(iv) $OsX_2(CO)$(tridentate) complexes

As already mentioned, $OsCl_3$ is not generally a convenient starting material for synthesis. However, when it is heated under reflux for long periods in DMF with triphos, *cis*-$OsCl_2(CO)$(triphos) is formed [65].

(v) Miscellaneous mixed-ligand complexes

In addition to halide and carbonyl ligands, these complexes generally also contain PPh_3 and one or more additional neutral or anionic unidentate or bidentate ligands (L′ and L″ respectively). They include $OsX_2(CO)(PPh_3)_2$(L′) (L′ = *p*-MeC_6H_4CN [12], PhNC [119], HNO [43,69,101], NH=N(*p*-MeC_6H_4) [36], $EtCO_2C{\equiv}N$ [120], PH_2Ph or $PHPh_2$ [29]) and $OsX(CO)(PPh_3)_2$(L″) (L″ = HCS_2 [18,19,40,47], $S{\doteq}CH{\doteq}NR$ [20,22], $RN{\doteq}CH{\doteq}NR$ [23], $RN{\doteq}CH{\doteq}O$ [24,25] (R = *p*-MeC_6H_4), $MeCO_2$ [27], pyX (X = O, S) [32,33], *o*-$C_6H_4CH{=}NPh$ [35], S_2CNR_2 (R = Me, Et) [121], MepyO [122]) complexes. Other compounds in this mixed-ligand category include $Os(RCO_2)X(CO)(PPh_3)_3$(R = CF_3, C_2F_5, C_6F_5) [14–16], $OsX(CO)(PPh_3)_2$-

TABLE 3

Preparation of $OsX_2(CO)_2L_2$ complexes

Method of preparation	X	L
$OsX_2(CO)L_3 + CO$	Cl	PPh_3 [12,99] $AsPh_3$ [7]
$OsX_3L_3 + CO$	Cl	PPh_3 [89]
	Cl, Br	$AsPh_2R$ (R = Me, Et, Pr, Bu) [95] PPh_2R, $PPhR_2$, (R = Et, Pr, Bu), $AsPhMe_2$ [90]
$OsX_2L_3 + CO$	Cl	PPh_3 [12]
$[OsX_6]^{2-} + CO + L$	Cl	$P(OPh)_3$ [100]
	Cl, Br	PPh_3 [99] $AsPh_2R$ (R = Me, Et, Pr, Bu) [95]
$OsX_2(CO)(HNO)L_2 + CO$	Cl	PPh_3 [69,101]
$OsX_2(N_2)L_3 + CO + h\nu$	Cl	PEt_2Ph [96]
$OsX_2(O_2)L_2 + CO$	Cl	PPh_3 [12]
$OsX_2(CO)L_2(NH{=}NC_6H_4Me)$	Cl	PPh_3 [36]
$OsHX(CO)L_3 + CO + HX$	Cl	PPh_3 [12]
$[OsX_2(CO)_3]_2 + L$	Cl, Br, I	MPh_3 (M = P, As, Sb), $P(OPh)_3$, py [102]
$[OsX_4(CO)_2]^{2-} + L$	Cl, Br	PPh_3 [103–105] NH_3 [106]
	Cl, Br, I	py [107]
$[OsX_2(CO)_3]_2 + L$	Cl	PR_3 (R = OPh, Ph, C_6H_{11}) [108] PR_2Ph, $PRPh_2$ (R = OMe, OEt) [109]
$Os_3X_2(CO)_{12} + L$	Br	PPh_3, PPh_2Me [110]
$Os_3(CO)_{12} + Au(PPh_3)X$	Cl, Br, I	PPh_3 [111]
$OsX_2(O_2)L_2 + EtOH + L$	Cl	PPh_3 [112]
$[Os(CO)_2(NO)L_2]^+ + X_2$	Cl	PPh_3 [46]
$Os(CO)_3L_2 + HX$	Cl	PPh_3 [99]

(L′) (L′ = NNPh [123], Me [21]), $OsX(CO)(PPh_3)_2L(L')$ (L = NH=N(p-MeC_6H_4), L′ = FBF_3 [36]; L = PH_2Ph, L′ = MeCN [29]), and $OsX(CO)_3(PPh_3)L$ (L = Me_3Si [124], HgCl [116,125]) complexes.

E. CATIONIC OCTAHEDRAL OSMIUM(II) COMPOUNDS CONTAINING GROUP V DONOR LIGANDS

(i) $[OsX(CO)_3(unidentate)_2]^+$ and $[OsX(CO)_2(unidentate)_3]^+$ complexes

Oxidation of the osmium(0) complex $Os(CO)_3L_2$ with X_2 gives $[OsX(CO)_3L_2]^+$ (**XI**) (X = Br, I, L = PPh_3 [99]; X = I, L = PMe_2Ph [87]).

When heated, **XI** decarbonylates if L = PPh_3, but when L is the less bulky PMe_2Ph no decarbonylation occurs [87,99]. **XI** has also been prepared by carbonylation of *trans*-$[OsX(CO)_2L_3]^+$ (L = PPh_3, X = Cl [60]) or $OsX_2(CO)_2L_2$ (L = PR_3 (R = Ph, OPh, C_6H_{11}), X = Cl [108]) and by HCl cleavage of the carboalkoxocarbonyl complex $Os(MeCO_2)Cl(CO)_2L_2$ [126]. A further reference to **XI** (L = PPh_3, X = Br) has been reported with no preparative details [127].

The complex $[OsI(CO)_2L_3]^+$ (L = NH_3) has been obtained by NH_3 substitution of $[OsI_4(CO)_2]^{2-}$. Halide exchange with HX (X = Cl, Br) gives $[OsX(CO)_2L_3]X$ [106,113]. Chlorination of $Os(CO)_2L_3$ (L = PPh_3) by trichloroacetaldehyde in the presence of $NaClO_4$ also gives $[OsCl(CO)_2(PPh_3)_3]^+$ [60].

(ii) $[OsX(CO)(bidentate)_2]^+$ complexes

These cationic complexes have been isolated in both *cis* and *trans* configurations. Direct carbonylation and solvent reduction of $[OsCl_6]^{2-}$ in the presence of pdma for long reflux periods yields *cis*-$[OsCl(CO)(pdma)_2]^+$ [128], while carbonylation of $[OsCl(dpp)_2]^+$ for shorter times gives *trans*-$[OsCl(CO)(dpp)_2]^+$ [129]. The mixed-ligand *trans*-$[OsCl(CO)(phen)(L'')]^+$ complex (L″ = dppb or dppene) is formed by carbonylation of $OsCl_4(phen)$ in the presence of L″ [130]. *Cis*-$OsCl_2(bpy)_2$ decarbonylates formic acid to give the corresponding *cis* isomer [130]. Both isomers of $[Os(CHO)(CO)(L'')_2]^+$ (L″ = dppe or dppm) react with CH_2Cl_2 to give the corresponding $[OsX(CO)(L'')_2]^+$ isomer [131].

(iii) Miscellaneous complexes

Other cationic complexes prepared include $[OsCl(CO)L_3L']^+$ (L = PEt_3 or $PPhMe_2$, L′ = CNR (R = Me, Ph)) obtained from the reduction of $[OsCl_2L_2L']^+$ with ethanol in the presence of CO [119], and $[OsCl(CO)(PPh_3)_2(NH{=}NR)]^+$ (R = *p*-MeC_6H_4, *p*-$MeOC_6H_4$) formed by CO displacement of the weakly bonded BF_4 in $OsCl(FBF_3)(CO)(PPh_3)_2(NH{=}NR)$ [36]. The complexes $[OsX(CO)(PPh_3)_2L']^+$ (e.g. L′ = PHMePh, PH_2Ph, PHIPh, PMeIPh [28,29,131(a),132]) react with the non-nucleophilic base DBU to form terminal phosphido complexes where L′ is PRPh (R = H, OMe, I) [131(a)]. The complex $[OsCl(CO)(PPh_3)_2(phen)]^+$ has been obtained by decarbonylation of ethylene glycol by $OsCl_4(phen)$ in the presence of the phosphine ligand [130].

F. NEUTRAL FIVE-COORDINATE OSMIUM(II) COMPOUNDS

The most important complex in this category is the hydrido complex $OsHX(CO)L_2$ (**III**). As with most five-coordinate complexes of this type, where L is a tertiary phosphine, the sixth octahedral site is generally blocked by the bulky phosphine. Reactions of the hydrides have been outlined in Table 2. Other five-coordinate complexes are $OsX_2(CO)L_2$, prepared from the reaction of **III** ($L = PCy_3$) with acetyl chloride [40] or HCl [133], the square-pyramidal σ-aryl compound $Os(R)Cl(CO)L_2$, prepared by reacting $OsHCl(CO)L_3$ with HgR_2 ($R = p\text{-}MeC_6H_4$, $L = PPh_3$) [21] and the carbyne complex $Os(\equiv CR)Cl(CO)(PPh_3)_2$ referred to in the section on organometallic complexes [53].

G. COMPOUNDS WITH GROUP IV OR GROUP VI DONOR LIGANDS

With the exception of the organometallic compounds described earlier, few substituted osmium carbonyl halides contain only group IV or VI donor ligands. More commonly, mixed-ligand complexes which also contain phosphines or related ligands are known. Only the tetracarbonyl complexes *trans*-$OsX(MMe_3)(CO)_4$ (M = Si or Ge) fall into the former category. They are prepared by electrophilic attack on $Os(MMe_3)_2(CO)_4$ or $Os_2(SiMe_3)_2(CO)_8$ by X_2 (X = Br, I) [134].

A variety of mixed-ligand complexes which contain at least one ligand with a Group IV or VI donor atom have been prepared, and many of these have been referred to in earlier sections. These include complexes containing carboxylates RCO_2 (R = Me, Et [27,108,135], CF_3, C_2F_5, C_6F_5 [14–16]), SO_2 and O_2 [40,41], pyX (X = O, S [32,33], S_2CNR_2 (R = Me, Et [121]), MepyO [122], SMe [63,64], oxalate [136], H_2O [128], MeCO [54,55] or $MeSO_3$ [38(a)].

A series of complexes containing ligands with two donor atoms is formed from the hydrido complexes $OsHX(CO)L_3$ (**I**, $L = PPh_3$). With CS_2 the dithioformato complex $Os(S_2CH)Cl(CO)L_2$ is formed [18,19]. **I** also reacts with alkyl and aryl isocyanates (RNCO) or isothiocyanates (RNCS) to form formamido and thioformamido complexes $Os(RN{\dots}CH{\dots}YR)X(CO)L_2$ ($R = p\text{-}MeC_6H_4$, Y = O, X = Cl, Br [24,25]; R = Me, Et, Ph, Y = S, X = Cl, Br [20,22]) respectively, and with carbodiimides (RN=C=NR) to yield $Os(RN{\dots}CH{\dots}NR)X(CO)L_2$ complexes ($R = p\text{-}MeC_6H_4$, X = Cl, Br [23]). Under mild conditions these complexes form with *cis* L groups and are converted thermally to the *trans* isomer [20,22,23].

H. ANIONIC COMPOUNDS

Only a few anionic complexes have been prepared. The all-*cis* isomer of $[Os(COMe)_2Br_2(CO)_2]^{2-}$ is formed by attack of MeMgBr on the CO groups of $OsBr_2(CO)_4$ [54,55]. A similar complex is obtained by decarbonylation of DMF with $[OsCl_6]^{2-}$ and $AsPh_3$ [10]. Carbonylation of $[OsX_6]^{2-}$ in 2-methoxyethanol gives the aquo anion $[OsX_4(CO)(H_2O)]^-$ [128]. The water is readily displaced by L giving $[OsX_4(CO)L]^-$ (X = Cl, Br, L = PPh_3 or unidentate dpma) [128]. Pyridine displaces a halide from $[OsX_5(CO)]^{2-}$ or CO from $[OsX_4(CO)_2]^{2-}$ to give $[OsX_4(CO)(py)]^-$ [137]. In all cases the CO and L ligands are *trans* to each other. Oxalate also reacts with $[OsX_4(CO)_2]^-$ or $[OsX_5(CO)]^{2-}$ (X = Cl, Br, I) to give *mer*-$[OsX_3(CO)(ox)]^{2-}$ [136].

I. COMPOUNDS WITH OTHER OXIDATION STATES

Several neutral osmium(III) complexes have been prepared and they have the general formulae $OsX_3(CO)(unidentate)_2$ or $OsX_3(CO)(bidentate)$. A variety of chlorinating agents have been used to oxidize hydrido complexes such as $OsHCl(CO)L_3$ or $OsH_2(CO)L_3$ to $OsCl_3(CO)L_2$ (L = PPh_3) [12]. The same product is obtained by carbonylation of $[OsCl_6]^{2-}$ in a basic alcohol solution containing L [12]. $[OsCl_6]^{2-}$ also decarbonylates DMF in the presence of dppe or dppm giving, for example, $OsCl_3(CO)(dppe)_2$ in which the P-donor ligands function as unidentate ligands [10]. CO is also extracted from ethanol during the reaction of $OsCl_2(O_2)L_2$ with hmp giving $OsCl_3(CO)L_2$ (L = PEt_2Ph) [122]. However, when L = PPh_3, this reaction yields $OsCl_2(hmp)L_2$ [122]. Other osmium(III) compounds are the sulfato complex $OsCl(SO_4)(CO)(PCy_3)_2$ isolated from the oxidation of the SO_2 adduct $OsHCl(CO)(PCy_3)_2(SO_2)$ with O_2 [138], $Os(MeCO_2)_2Cl(CO)(py)_2$ [135] and the anions $[OsX_4(CO)L]^-$ [128,137] and $[OsX_3(CO)(L'')]^{2-}$ [136] described above.

The osmium(0) complex $OsI(NO)(PPh_3)_2$ has been isolated from the reaction of $[Os(NO)(CO)_2(PPh_3)_2]^+$ with Bu_4NI [46] or by reacting $OsHCl(CO)(PCy_3)_2$ with *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide [43,46].

J. CONCLUDING REMARKS

This review has described principally the preparative routes to substituted osmium carbonyl halide complexes and, to a lesser extent, the reactivities of these compounds. Although less extensive than the chemistry of the analogous ruthenium compounds, many reactions of the two metals are identical or at least very similar. In many of the reactions, conditions such as temperature, reaction time and steric and basic properties of the ligands are critical in influencing the nature and stereochemistry of the reaction products.

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