Annual Survey of Ruthenium and Osmium for the Year 1985

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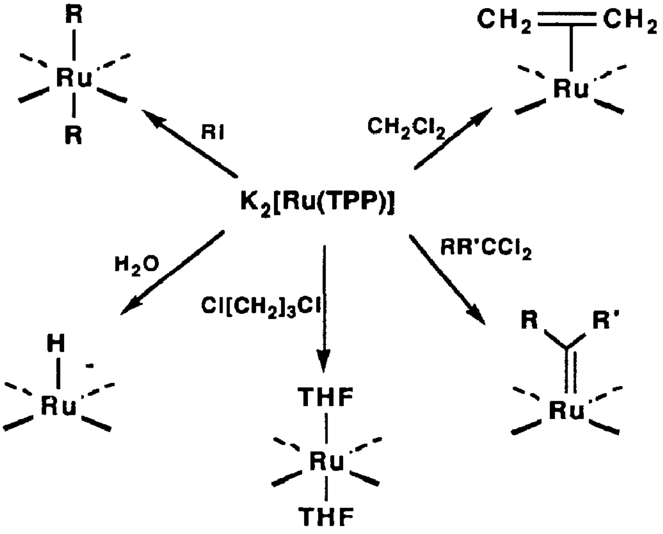
I. Mononuclear Complexes

This section includes published material on the synthesis, reaction chemistry, and physical properties of mononuclear organometallic complexes of osmium and ruthenium. Metal carbonyl and metal phosphine complexes are included along with complexes having sigma or pi bonds between the metal center and carbon atoms of an organic moiety. Applications of known mononuclear complexes in synthesis or in homogeneous catalysis are covered in section four.

(a) Organometallic Porphyrin and Carborane Complexes

Organometallic complexes of metal porphyrins were reported. The reactions of a zero valent ruthenium porphyrin complex with organic electrophiles were investigated. The dipotassium salt of tetraphenylporphyrin ruthenium(0), K_2[(TPP)Ru], reacted with alkyl iodides to form the dialkyltetraphenylporphyrin ruthenium(IV) complexes. There are few alkyl complexes of ruthenium in this oxidation state. The reactions with 1,1-dichloroalkanes produced tetraphenylporphyrin ruthenium alkylidene complexes. An ethylene complex was formed upon reaction of K_2[(TPP)Ru] with methylene chloride or with 1,2-dibromoethane. Reaction with water or with benzoic acid gave an anionic hydride complex of ruthenium.[1]

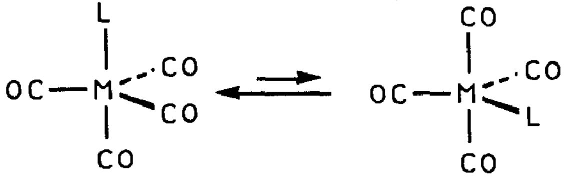


Picosecond transient absorption and emission measurements on the octaethylporphyrin complexes were reported. The complexes [Ru(OEP)(CO)(L)] (where L = ethanol, pyridine or 1-methylimidazole) are similar with the lowest excited state being ring 3T(π-π^*) while the lowest excited state for [Ru(OEP)(PBu$_3$)$_2$ was assigned as a metal to ring charge transfer state.[2]

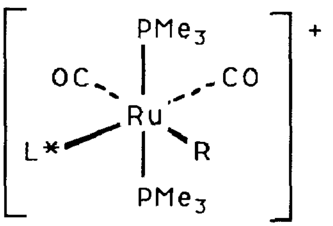
The synthesis and crystal structure of 2,5,6,-(η-C_6H_6)$RuC_2B_7H_{11}$, a π-arene rutheniumcarborane, was reported. The compound was prepared by the polyhedral contraction of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$.[3]

(b) Complexes of Phosphorus Ligands

The syntheses of ruthenium(II) complexes with mono-dentate phosphine and arsine ligands were reported. The triphenylphosphine and triphenylarsine complexes $Ru(EPh_3)(C_6H_5CHO)_2Cl_2$, $Ru(CO)(EPh_3)_2Cl_2$, $Ru(AsPh_3)(py)_3Cl_2$, $Ru(EPh_3)(DMF)_3Cl_2$, and $Ru(CO)(py)_2(EPh_3)Cl_2$ were prepared and characterized by IR, electronic spectroscopy, ^1H NMR, magnetic susceptibility and molecular weight.[4] Cationic complexes of ruthenium(II) with phosphines and carboxylato or nitrato ligands were prepared by substitution reactions on a ruthenium cyclooctadiene complex. Reaction of $[(\eta\text{-}C_8H_{12})RuH(NH_2NMe_2)_3][PF_6]$ with HX (X= RCO_2, NO_3; R= H, CF_3, Ph) followed by treatment with diphenylphosphinomethane (dppm), diphenylphosphinopropane, or dimethylphenylphosphine gave $[RuXL_4\}PF_6$.[5] Substitution of chloride on $[OsCl_3(PMe_2Ph)_3]$ by a variety of donor solvents or available ligands can be induced by electrochemical reduction. The initially formed osmium(II) anion, $[OsCl_3(PMe_2Ph)_3]$, loses Cl^- to form a five coordinate intermediate. Both of these osmium intermediates were spectoscopically characterized. Under certain conditions, binuclear osmium complexes are formed.[6] Substitution of a carbonyl ligand on $M(CO)_5$ (M=Ru or Os) for a variety of trisubstituted phosphines, arsines and stibines produced $M(CO)_4L$. In solution, an equilibrium between isomers with L axial or equatorial was observed for many of these complexes. It was concluded that weaker sigma donors prefer the equatorial site.[7]

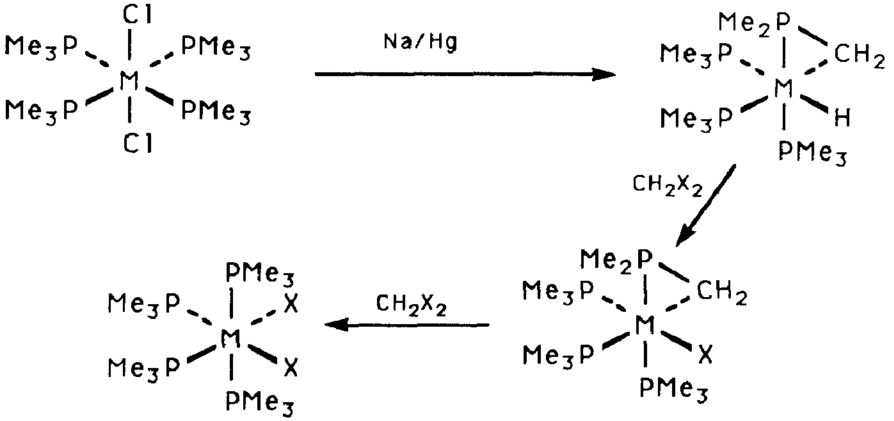


A series of chiral ruthenium complexes was prepared. The complexes $[RuX(CO)L(triphos)]X'$ (X= Br, I, Me, H; X'= halide; L=CO, t-BuNC, s-BuNC, $P(OMe)_3$, PMe_2Ph) are chiral at the metal atom. The crystal structure $[RuMe(CO)(t\text{-}BuNC)(triphos)]^+$ was obtained.[8] Asymmetric phosphines, PhP(R')R", were synthesized and used to prepare chiral ruthenium complexes, $[RuR(CO)_2\{PhP(R')R''\}(PMe_3)_2]^+$. The two axial PMe_3 groups are diastereotopic in these complexes. The phosphorus-phosphorus coupling constant between these chemically equivalent phosphines was determined.[9]



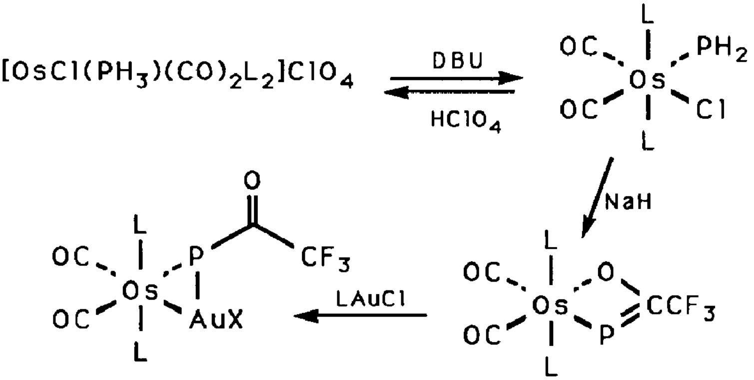
L^* = PhP(Me)(o-C_6H_4OMe),
PhP(Me)(OBu^t),
R = Me, CH_2Ph

The stereochemistry of substitution reactions at the chiral ruthenium atom in [Ru(η^5-$C_5H_5R^*$)(CO)(PPh_3)L]$^{n+}$ (where R*= menthyl, neomenthyl; n= 0, L= Cl; n= 1, L= $NCCH_3$ or $NCCD_3$) was studied by a number of spectroscopic techniques. The substitution reactions occur with retention of configuration at ruthenium.[10] The synthesis of diphosphine complexes of ruthenium was reported. A variety of diphosphines, L_2, react quantitatively with CpRu$(CO)_2$H to give CpRuL_2H.[11] The diphosphines are chelating in these complexes. Bis(dimethylphosphino)methane, dmpm, complexes of iron and ruthenium were prepared. The species [Ru$(dmpm)_3$]X_2 (X= Cl, PF_6) and *trans*-[RuH(η^1-dmpm)$(dmpm)_2$]PF_6 were prepared. The latter complex was characterized by X-ray crystal structure. The hydride was found to be *trans* to the η^1-dmpm ligand.[12] Activation of C-H bonds in phosphine ligands by the metal was reported. Reduction of *trans*-$MCl_2(PMe_3)_4$ (M= Ru, Os) with Na/Hg produces MH(η^2-CH_2PMe_2)$(PMe_3)_3$. The reactions of the complexes MH(η^2-CH_2PMe_2)$(PMe_3)_3$ with dihalomethanes, Bronsted acids, and with water were described. The hydrolysis of OsH(η^2-CH_2PMe_2)$(PMe_3)_3$ yields the hydroxy hydride complex *cis*- MH(OH)$(PMe_3)_4$.[13]

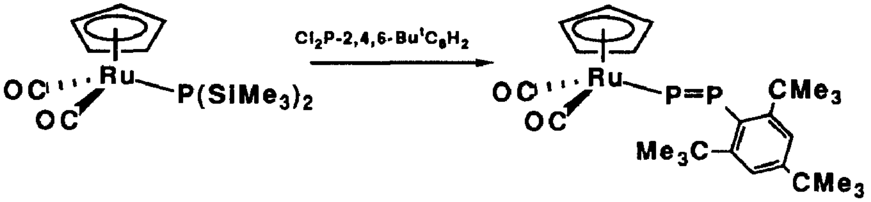


The orthometallated complex $RuCl[P(C_6H_4)Ph_2](PPh_3)_2 \cdot CH_2Cl_2$ was formed in the reaction of $RuHCl(PPh_3)_3$ with alkynes. The orthometallated ruthenium complex is not, however, an intermediate in the hydrogenation of these alkynes catalyzed by $RuHCl(PPh_3)_3$.[14]

Substitution of phosphine for triphenylphosphine in $MHCl(CO)(PPh_3)_3$ produced the osmium and ruthenium phosphine complexes, $MHCl(CO)(PPh_3)_2(PH_3)$. These complexes were used to prepare the terminal phosphide complexes, $MCl(CO)_2(PPh_3)_2(PH_2)$. Acylation of $OsCl(CO)_2(PPh_3)_2(PH_2)$ followed by deprotonation gave a P-metallated phospha-alkene, $[Os(P{=}C(O)CF_3)(CO)_2(PPh_3)_2]$ rather than a phosphinidene complex. The phospha-alkene complex was structurally characterized. A 1:1 adduct is formed between this complex and gold(I) complexes.[15]



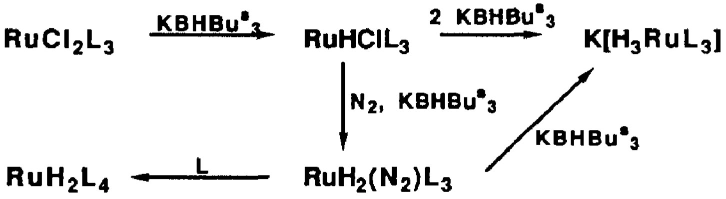
Trimethylsilylphosphido complexes of ruthenium were prepared and used to prepared metal complexes with novel phosphorus-containing ligands. The first diacylphosphido complex with metal-phosphorus coordination, $(C_5Me_5)(CO)_2RuP(COCMe_3)_2$ was synthesized by the reaction of pivaloyl chloride with $(C_5Me_5)(CO)_2RuP(SiMe_3)_2$. The structure was confirmed by X-ray crystallography.[16] A study was made on the reaction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3][BF_4]$ with silylated lithium phosphides. The ruthenium carbonyl complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3][BF_4]$ reacted with silylated lithium phosphides, $Li[PR(SiMe_3)]$, to form the corresponding phosphinocarbonyl complexes. Only $(\eta^5\text{-}C_5Me_5)Ru(CO)_2[C(O)P(t\text{-}Bu)(SiMe_3)]$ could be isolated as a stable crystalline complex. Products from $Li[PPh(SiMe_3)]$ and from $Li[P(SiMe_3)_2]$ were unstable and decomposed to the phosphide complexes, $(\eta^5\text{-}C_5Me_5)Ru(CO)_2PR(SiMe_3)$, upon work-up.[17] The first diphosphenyl complexes, $(C_5Me_5)(CO)_2M\text{-}P{=}P(2,4,6\text{-}{}^tBu_3C_6H_2)$, (M=Fe,Ru) were prepared by the reaction of bis(trimethylsilyl)phosphido complexes with an aryldichlorophosphine. The structure of the iron complex was confirmed by X-ray crystallography.[18]



(c) Hydrides

The dinuclear hydrido complex $Ru_2H_4Cl_2(PR_3)_4$, where PR_3 is a triaryl phosphine, reacts with excess phosphine to form the monomer $RuHClL_3$.[19] The geometry of the five coordinate complexes $[RuH(PMe_2Ph)_4]^+$ and $[Ru(C_2Ph)(PMe_2Ph)_4]^+$ was found to be square pyramidal in solution by ^{31}P NMR. One of the phosphine ligands is apical.[20]

Polyhydride complexes of both ruthenium and osmium were reported. An improved synthesis of trihydridotri(triphenylphosphine)ruthenate was reported. Treatment of $RuHCl(PPh_3)$ with $KBHBu^s_3$ in thf gave $K[H_3Ru(PPh_3)_3]$. An X-ray crystal structure of the product complexed with 18-crown-6 ether was obtained. This showed a facial distribution of hydrides. The structure is severely distorted from octahedral due to the bulk of the phosphine ligands. Other ruthenium hydrides can be prepared by this route as well.[21]



The related osmium trihydride, $KOsH_3(PMe_2Ph)_3$, was prepared by deprotonation of $OsH_4(PMe_2Ph)_3$ by KH in thf. The hydrides are in a facial arrangement in this complex as well, as shown by NMR spectroscopy. The potassium salt is quite soluble in toluene and other aromatic solvents. This unexpected solubility results from the formation of a dimer in non-polar solvents in which the potassium cations bridge between the hydrides. The structure of the dimer was determined by X-ray crystallography.[22] Polyhydride complexes of ruthenium were prepared by the direct hydrogenation of zero valent olefin complexes of the metal. Mononuclear complexes were of the type RuH_6L_2 and RuH_4L_3, where L is a tertiary phosphine ligand. The tetrahydride complex catalyzed the H-D exchange between the phosphine protons and the deuterated solvent. This reaction requires intramolecular C-H activation of the phosphine C-H bonds and intermolecular C-H activation of the solvent. A mechanism involving the intermediacy of ruthenium(IV) alkyl complexes was proposed to account for the results.[23]

Some polyhydride complexes are now known to be complexes of molecular hydrogen. Two molecular hydrogen complexes of iron and ruthenium with diphenylphosphinoethane ligands, *trans* -$[M(\eta^2-H_2)(H)(dppe)_2]^+$ were prepared. Even though the X-ray crystal structure shows the the hydride and dihydrogen ligands to be oriented *trans* to one another, an intramolecular exchange of the hydride and the hydrogens of the dihydrogen ligand is observed. The dihydrogen ligand of the ruthenium complex is readily displaced by dinitrogen in a nitrogen atmosphere.[24]

(d) Carbonyls

A theoretical study of one aspect of the reactiviy of metal carbonyl complexes was done. Hartree-Fock-Slater calculations on the protonation energies of $Ru(CO)_5$ and $Os(CO)_5$ as well as other d^8 and d^{10} metal carbonyls were reported.[25]

The metal atom vaporization technique has been employed in the synthesis of metal carbonyl compounds. Co-condensation of ruthenium atoms with oxalyl chloride gave ruthenium chloro carbonyl derivatives. These were used as precursors to $Ru(PMe_3)_3(CO)Cl_2$, $[Ru(CO)_3Cl(\mu-Cl)]_2$, and $Ru(PPh_3)_2(CO)_2Cl_2$.[26]

The behavior in solution of some ruthenium carbonyl complexes was studied. The interaction of solvent with of the ruthenium carbonyl carboxylates $Ru_4(CO)_8(OAc)_4(PBu_3)_2$, $Ru(CO)_2(OAc)_2(PBu_3)_2$, $Ru_2(CO)_4(OAc)_2(PBu_3)_2$ was investigated by NMR and IR.[27] The reaction of triruthenium dodecacarbonyl with ethylene and water results in the formation of another ruthenium carbonyl carboxylate complex, $[Ru(CO)_2(\mu-OOCC_2H_5)]_2$. The propionato carboxylate ligand was found to be derived from a ruthenium carbonyl and water.[28]

The synthesis, IR spectrum and X-ray crystal structure of $[S_5N_5]^+[RuCl_3(CO)_3]^- \cdot 0.5CH_2Cl_2$ was reported. This anionic ruthenium carbonyl complex was prepared by the reaction of $Ru_3(CO)_{12}$ with $(NSCl)_3$. The cation consists of an S_5N_5 ring.[29]

The kinetics of the nucleophilic attack of methoxide and hydroxide on $Ru(CO)_5$ and $Os(CO)_5$ were studied. The product of reaction of the metal carbonyls with sodium methoxide was always the methoxycarbonyl adduct, $[M(CO)_4(COMe)][Na]$. The sodium cation was shown by IR spectroscopy to form an ion pair with the methoxycarbonyl ligand specifically. Reaction of the metal carbonyls with sodium hydroxide gave the hydroxycarbonyl complexes, $[M(CO)_4(COOH)][Na]$. The rate of these reactions depended on solvent and on the central metal.[30]

Homoleptic carbonyls of transition metals such as ruthenium and osmium are well known. Although isonitriles are isoelectronic with carbon monoxide, homoleptic isonitriles are more difficult to prepare. A general synthesis of osmium(II) and ruthenium(II) homoleptic isocyanide complexes was reported. The acetate dimers, $Ru_2(O_2CCH_3)_4Cl$ and $Os_2(O_2CCH_3)_4Cl_2$, react with alkyl isocyanides to form $[M(CNR)_6][PF_6]_2$. Certain of these complexes readily dealkylate to give the corresponding cyanide complexes, $[M(CNR)_5(CN)][PF_6]$.[31]

(e) Nitrosyls and Other Nitrogen Ligands

The dinitrogen ligand is usually assumed to be only weakly bonded in transition metal complexes. A recent report disputes this. Thermolysis of $[Ru(NH_3)_5(N_2)]^{+2}$ in the solid state produces NH_3 before N_2 is released. The dinitrogen ligand is labile in solution, but must be bonded fairly strongly to the metal in the solid. Thermolysis of ruthenium(II) pentaamminecomplexes containing other ligands was also investigated. The cleavage temperature under isobaric conditions was found to increase along the series $CH_3CN < N_2 < CO < CH_3NC < NO$.[32] The ^{15}N NMR spectra and longitudinal relaxation times were reported for the osmium dinitrogen complex, *trans*- $[OsCl_2(^{15}N_2)(PMe_2Ph)_3]$.[33]

A series of cationic ruthenium(II) carbonyl complexes with nitrile ligands was prepared and characterized. Complexes of acetonitrile and acrylonitrile, $[Ru(CO)(PPh_3)_2L(RCN)][ClO_4]$, were synthesized where L is the anion derived from deprotonation of acetylacetone, benzoylacetone, dibenzoylmethane, trifluoromethenylacetone, or 8-hydroxyquinoline.[34]

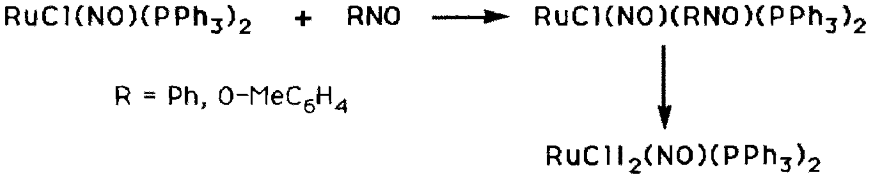
Cationic hydrazine and hydrazone complexes of osmium were prepared from the polymer $[OsCl_2(COD)]_x$. The crystal structure obtained of $[Os(COD)(CNBu^t)_2(NH_2N{=}CMe_2)_2][BPh_4]_2$ shows the hydrazone ligands to be *trans* to one another and bound to the metal through the amino nitrogen atoms.[35]

Reaction of $RuCl_2(CO)_3$ with 2-(*p*-toluidino)pyridine gave $RuCl(CO)_2(tpf)$, a complex with the N-(*p*-tolyl)-N-(2-pyridyl)formamide anion (tpf) coordinated to the ruthenium through the pyridine nitrogen and the amide carbonyl carbon atoms.[36]

Nitrosyl halides were used to prepare some osmium and ruthenium nitrosyl complexes. The reactions of CpRu(II) complexes, $[CpRu(PPh_3)L]X$ and $[CpRu(PPh_3)LX']$, (L= bpy or phen; X= halide; X'= halide, H, CN, NCS, $SnCl_3$) with NOCl and NOBr gave nitrosyl complexes.[37] The reactivity of the ruthenium (II) complexes $[CpRu(PPh_3)L]X$ and $[CpRu(PPh_3)L'X']$ with nitrosyl tribromide and dinitrogentrioxide was studied (L= bpy, 1,10-phen; X= Cl, Br; L'= PPh_3, py, 3- or 4-picoline, 1/2 bpy, 1/2 phen; X'= Cl, Br, I, CN, NCS, H, $SnCl_3$). The nitrosyl complex $Ru(NO)(PPh_3)_2Br_3$ was obtained in over 90 percent yield.[38] The synthesis of the monomeric, low valent osmium nitrosyl complexes $Os(NO)X_2(PPh_3)_2$, $Os(NO)Br_3(PPh_3)_3$, and $Os(NO)X(PPh_3)_3$ (X=Cl, Br) was reported.[39]

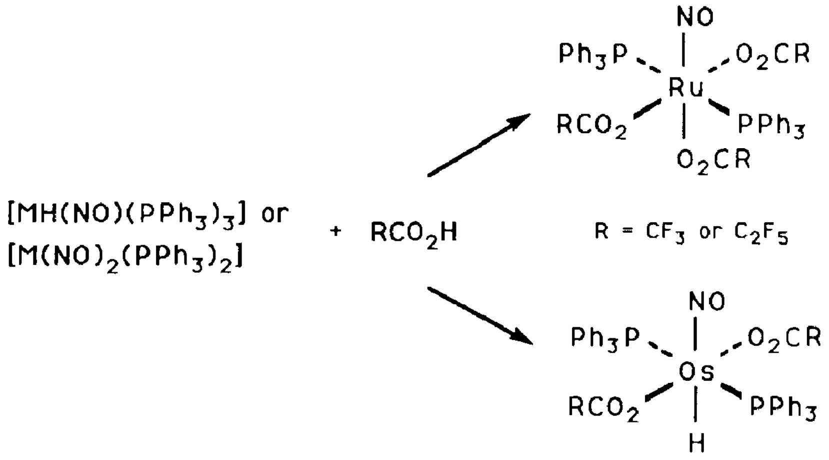
NMR and mass spectroscopy techniques have been applied to the physical characterization of metal complexes with nitrogen containing ligands. Nitrogen-15 NMR was used in the characterization of bent and linear nitrosyl ligands in complexes of ruthenium. Spectra were obtained in the solid state by cross polarisation magic angle spinning spectroscopy. A large chemical shift anisotropy for the bent NO, as compared with linear nitrosyl in $[RuCl(NO)_2(PPh_3)_2][BF_4]$. The resonances are found at 303 and 26 ppm respectively relative to nitromethane. In solution, ^{15}N NMR clearly shows that the molecule is fluxional with an averaged resonance at 130 ppm. The nitrosyls in $[Ru(NO)_2(PPh_3)_2]$, which differ only by 7^0 in the Ru-N-O angle, can also be distinguished by this technique.[40] Two techniques of mass spectroscopy, fast atom bombardment and field desorption mass spectrometry, were used to characterize a series of ruthenium(II) and osmium(II) complexes. All were cationic complexes containing bipyridyl ligands as well as η^2-alkene, η^2-alkyne, carbonyl, alkyl, or hydrido ligands.[41]

Nitrosoarene complexes of ruthenium, $RuCl(NO)(RNO)(PPh_3)_2$, were prepared and their reactions with NO and NO^+ were studied. Although double insertions of NO into metal alkyl bonds are known, the insertion of a nitrosyl into a nitrosoalkyl-metal bond has not been observed. These nitrosoarene ruthenium complexes were found to be rather reactive. They were unstable to oxygen and formed $O{=}PPh_3$ in the presence of either CO or PPh_3. No coupling of the nitrosyl and nitrosoarene groups was observed however.[42]

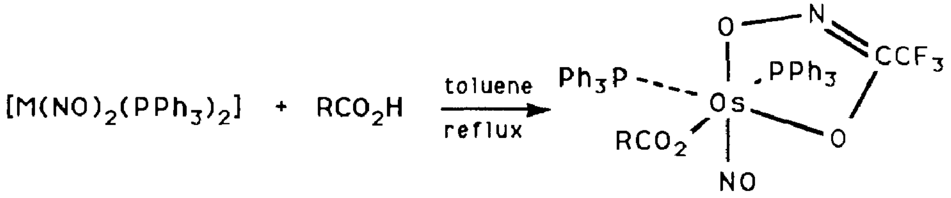


$$\begin{tikzcd}
RuCl(NO)(PPh_3)_2 + RNO \arrow[r] & RuCl(NO)(RNO)(PPh_3)_2 \arrow[d] \\
R = Ph,\ O\text{-}MeC_6H_4 & RuClI_2(NO)(PPh_3)_2
\end{tikzcd}$$

The reactions of nitrosyl complexes with acids were reported. Osmium and ruthenium hydridonitrosyls react with perfluorocarboxylic acids to produce the corresponding perfluorocarboxylate complexes. The reactions proceed by protonation of the metal center followed by coordination of the carboxylate.[43]



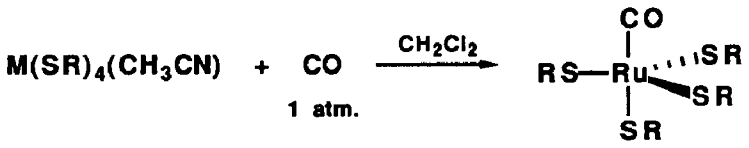
Both a hydroximate complex, $[Os\{ON{=}C(O)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$, and a metal hydride, $[OsH(O_2CCF_3)(NO)(PPh_3)_2]$, resulted from the reaction of $[Os(NO)_2(PPh_3)_2]$ with perfluoroacetic acid. The structure of the hydroximate complex was determined by X-ray crystallography.



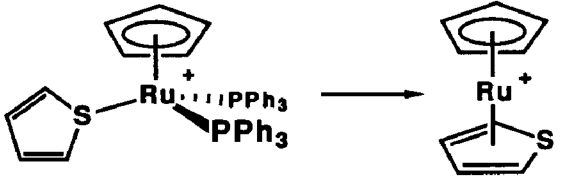
(f) Sulfur Donors

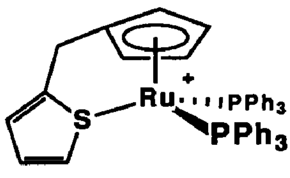
A ruthenium complex of 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecanediol (dttd), was reported. The diazene complex μ-$N_2H_2[Ru(PPh_3)(dttd)]_2$ is the first diazene complex with sulfur coordination to the metal center. It was prepared by oxidation of $Ru(N_2H_4)(PPh_3)(dttd)$.[44]

Several new complexes containing thiolato ligands have been synthesized. Pyridine-2-thiolato complexes of osmium and ruthenium were prepared from pyridine-2-thiol or dipyridyl-2,2'-disulphide and osmium(II) and ruthenium(II) precursors. The structures of $[Ru(C_5H_4NS)_2(CO)_2(PPh_3)]$ and $[Ru(C_5H_4NS)_2(CO)(PPh_3)]$ were determined by X-ray diffraction.[45] Carbonyl complexes of osmium(IV) and ruthenium(IV) were prepared by substitution of CO for acetonitrile in the complexes $M(SR)_4(CH_3CN)$. An X-ray crystal structure of the ruthenium carbonyl complex shows the CO to be axial in the trigonal bipyramidal complex.[46]



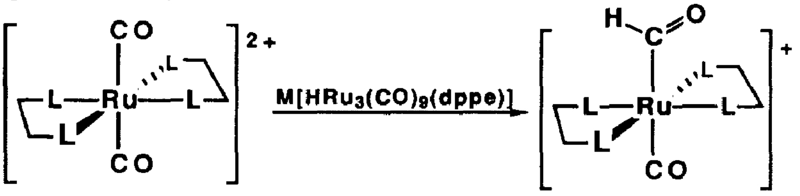
Thiophene has been used as a model for the sulfur containing molecules in fuels which are the substrates in the catalytic hydrodesulfurization of petroleum products. Two groups have published studies on thiophene binding to ruthenium and discussed the implications of the binding mode to HDS catalysts. A ruthenium complex with a π-bonded thiophene ligand, $[(\eta^5\text{-}C_4H_4S)Ru(\eta^5\text{-}Cp)][BF_4]$, was prepared from $(\eta\text{-}Cp)Ru(PPh_3)Cl$, $AgBF_4$ and thiophene. The thiophene is displaced slowly from the metal center by tributylphosphine. Protons on the 2 and 5 positions of the thiophene ring were exchanged for deuterium in a base catalyzed exchange reaction.[47] The unstable sulfur bound thiophene complex $[(\eta^1\text{-}C_4H_4S)Ru(\eta^5\text{-}Cp)]^+$ was characterized in solution by ^1H NMR. This compound rearranged to the η^5-thiophene complex. A stabilized monohapto thiophene complex was prepared. An X-ray crystal structure of $[\eta^1, \eta^5\text{-}(Cyclo\text{-}SC_4H_3\text{-}CH_2\text{-}Cp)Ru(PPh_3)_2]^+$ was obtained. The methylene bridge between the cyclopentadienyl ring and the thiophene prevents the thiophene from rearranging to the π-bonded form.[48]





(g) Formyl and Related C_1 Ligands

Formyl complexes of both ruthenium and osmium were prepared by hydride reduction of cationic carbonyl complexes. The reduction of *cis* or *trans*-$[Os(CO)_2(L_2)][SbF_6]_2$, where L_2 is either of the diphosphines dppe or dppm, with borohydride reducing agents produced $[Os(CO)(CHO)(L_2)][SbF_6]$. The *trans* isomer of the formyl complex was more thermally stable than the *cis* isomer. The structure of *trans*-$[Os(CO)(CHO)(dppe)][SbF_6]$ was determined by X-ray crystallography.[49] Ruthenium formyl complexes *trans*-$[Ru(CHO)(CO)L_2]K$ were isolated in quantitative yield from the reaction of $K[HRu_3(CO)_9(dppe)]$ with *trans*-$[Ru(CO)_2L_2][SbF_6]_2$. No reaction was observed with the sodium salt, $Na[HRu_3(CO)_9(dppe)]$ until 18-crown-6 ether was added to the reaction mixture. The difference in reactivity was attributed to the strength of the ion pair.[50]

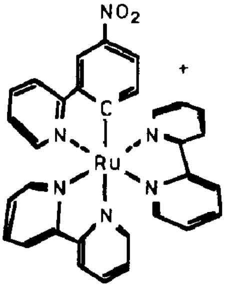


M= K, Na/crown ether
L_2= dppe, 1/2 $1,2\text{-}(PPh_2)_2C_6H_4$

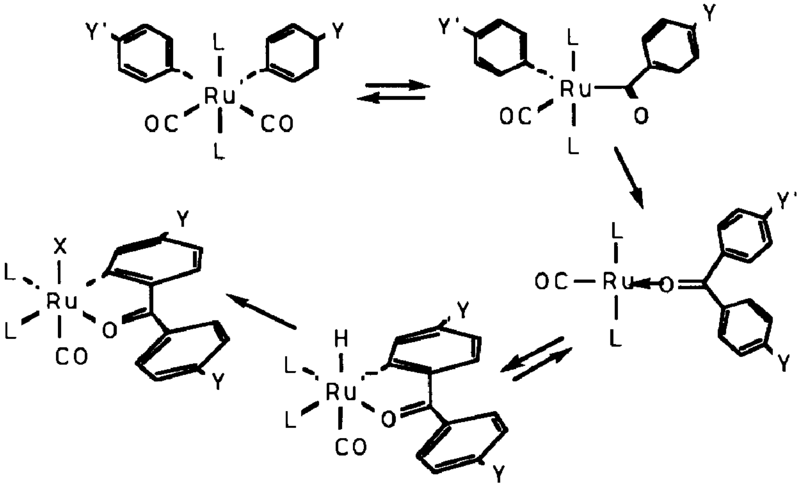
Their is some evidence for a homolytic cleavage of the ruthenium-formyl bond in *trans*-$[Ru(CHO)(CO)(dp)_2][SbF_6]$, where dp is 1,2-bis(diphenylphosphino)benzene. The kinetics for the decomposition of *trans*- $[Ru(CHO)(CO)(dp)_2][SbF_6]$ to *trans*-$[RuH(CO)(dp)_2][SbF_6]$ is first order. No crossover of label occurs in a mixture of $[Ru(^{13}CHO)(^{13}CO)(dp)_2][SbF_6]$ and $[Ru(CDO)(CO)(dp)_2][SbF_6]$, but methyl methacrylate is polymerized under reaction conditions. The authors propose a homolytic cleavage of the Ru-CHO bond, followed by transfer of hydrogen atom to the metal from the formyl radical within a solvent cage.[51]

(h) Alkyl, Aryl Complexes

Cyclometallation of ligands bound to ruthenium is a route to the formation of aryl complexes of the metal. Spectral and electrochemical properties of several cyclometallated complexes of ruthenium(II), $[Ru(bpy)_2L]^+$, were reported. The cyclometallated ligands include 2-(3-nitrophenyl)pyridine, benzo[h]quinoline, azobenzene, and p-(dimethylamino)-azobenzene. The nitrophenylpyridine complex was structurally characterized.[52]



Two dimensional heteronuclear decoupled autocorrelated NMR(HDCOSY) was used to assign all 23 non-equivalent protons in the cyclometallated ruthenium complex $[Ru(bpy)_2\mathbf{1}]^+$, where $\mathbf{1}$ is cyclometallated 2-(4-nitrophenyl)pyridine.[53] Ruthenium diaryl complexes $[Ru(CO)_2(C_6H_4Y\text{-}4)(C_6H_4Y'\text{-}4)L_2]$ are converted into *ortho*-metallated ketones in the presence of certain alkyl halides. The structure of one of these, $[Ru(CO)\{C_6H_3MeC(O)C_6H_4Me\}Cl(PMe_2Ph)_2]$, was determined by X-ray crystallography. A mechanism to explain this transformation was proposed.[54]



The first neutral, homoleptic tetraalkyls of the platinum group metals have been prepared. Tetrakis(cyclohexyl)osmium(IV) and tetrakis(o-methylphenyl)osmium(IV) were prepared by treatment of osmium tetroxide or the acetate complex, $Os_2(\mu\text{-}O_2CMe)_4Cl_2$, with the appropriate Grignard reagent. Both compounds were structurally characterized and have tetrahedral geometry about the metal center.[55]

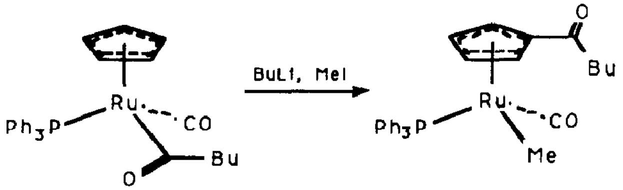
The mechanism of intra- and intermolecular decomposition of alkyl complexes has been examined in chiral metal alkyl complexes and with labelling studies. The chiral ruthenium complexes (R_{Ru},R_C)- and (S_{Ru},R_C)-$CpRuCl(PPh_2CHMeCH_2PPh_2)$ react with MeMgBr to give the corresponding methyl complexes with retention of configuration. Alkylation with EtMgBr gives a mixture of the ethyl complexes and the hydrido complexes, both with retention of configuration. Formation of the hydride was found to be competitive with ethyl formation and does not occur by β-hydride elimination from the alkyl. Diazomethane reacts with the hydride complexes to form the corresponding methyl complexes with retention of configuration at ruthenium.[56] Alkane elimination from $Os(CO)_4(H)R$ and $Os(CO)_4R_2$ has been examined by kinetic and labeling studies. The elimination of R-H from $Os(CO)_4(H)R$ was shown to proceed through an activated complex and involved either an intra- or intermolecular reaction pathway depending on reaction conditions.

Elimination of methane from $Os(CO)_4(CH_3)_2$ was proposed to proceed through a radical pathway.[57]

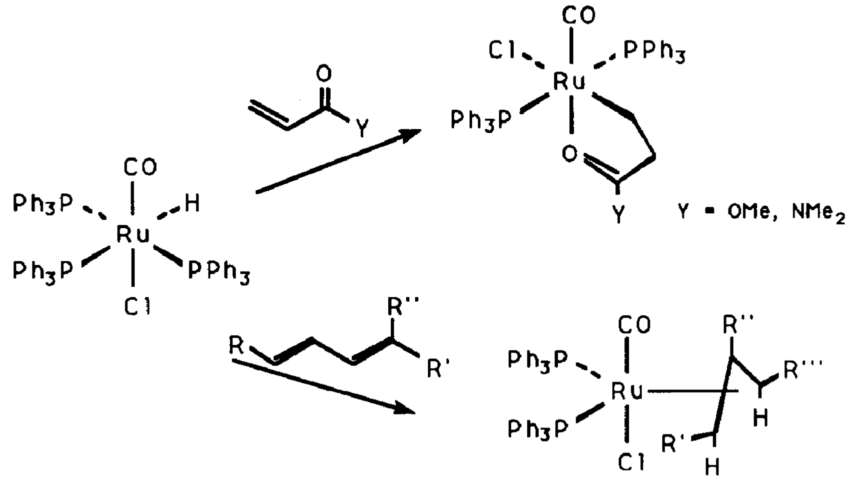
The photochemistry of $Ru(\eta^5\text{-}C_5H_5)(CO)_2R$, R = Me or Et, was studied in solution at -30° and in frozen gas matrices at 12K. The primary process is loss of CO. Depending on conditions, the ruthenium dimers $[CpRu(CO)_2]_2$ and $[CpRu(CO)]_2(\mu\text{-}H)_2$ are formed. The coordinatively unsaturated intermediate can also be trapped by external ligands in either the solution reactions or in doped matrices.[58]

An osmium complex containing both hydrido and allyl ligands was prepared. Alkylation of $[OsHCl(CO)(PPh_3)_3]$ with 2-methallylmagnesium chloride or allyl magnesium chloride gives the π-allyl osmium complexes $[OsH(\eta^3\text{-}CH_2CRCH_2)(CO)(PPh_3)_2]$. Acid hydrolysis in the presence of L (L= CO, PPh_3) gives the cationic complexes $[OsH(H_2O)L(CO)(PPh_3)_2]^+$. The crystal structure of $[OsH(H_2O)(CO)_2(PPh_3)_2]^+$ was obtained.[59]

Stable products can be obtained in reactions involving the insertion of unsaturated ligands into metal-alkyl and metal-acyl bonds. The mechanism of sulfur dioxide insertion reactions in alkyl ruthenium compounds was examined. The reaction of CpRuLL'R (L,L'= CO, PPh_3; R= Me, CH_2Ph) with sulfur dioxide gives the S-sulfinato complex, $CpRuLL'SO_2R$. Consistent with the proposed S_E2 mechanism, the less electron rich carbonyl complex, $CpRu(CO)_2Me$, is inert to reaction with sulfur dioxide.[60] Treatment of an cyclopentadienyl ruthenium acyl complex, $CpRu(CO)(PPh_3)\{C(O)Bu\}$, with n-butyl lithium followed by methyl iodide resulted in the migration of the acyl moiety to the cyclopentadienyl ring.[61]



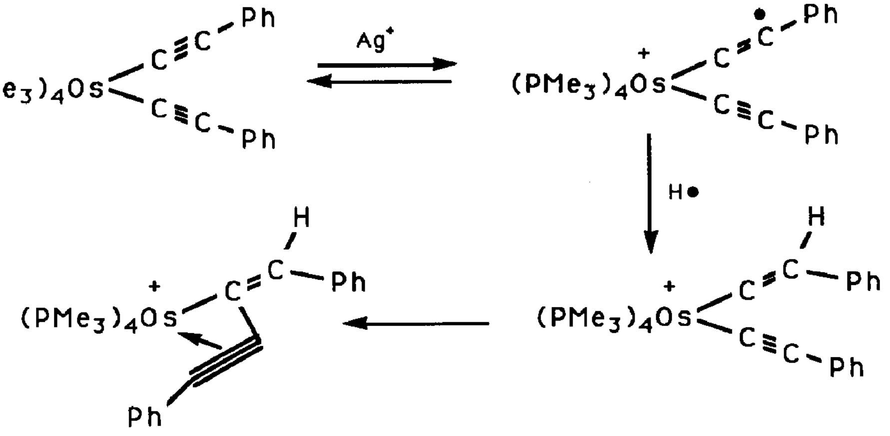
Insertion of unsaturated organic molecules into metal-hydride bonds produces metal alkyl complexes. Reaction of methyl acrylate and N,N-dimethylacrylamide with $[RuCl(CO)H(PPh_3)_3]$ gave the products of insertion into the metal-hydride bond. Conjugated dienes reacted with $[RuCl(CO)H(PPh_3)_3]$ to give η^3-allyl ruthenium complexes.[62]



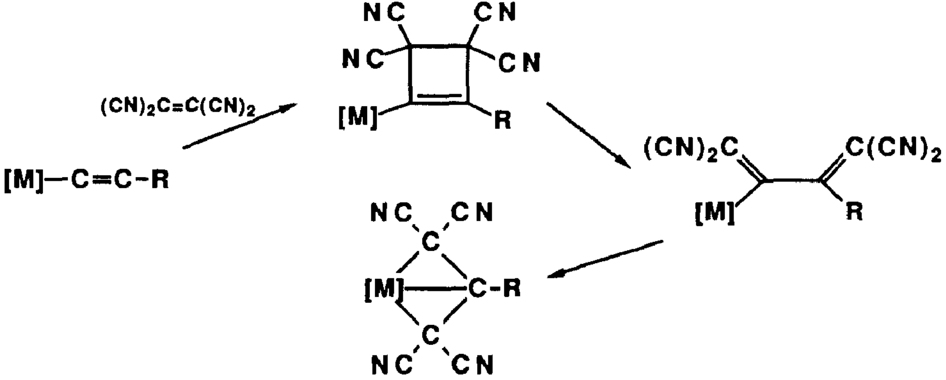
$R'=R'''=Me$, $R''=H$; $R'=R''=Me$, $R'''=H$; $R'=Et$, $R''=H$, $R'''=CO_2Me$

The hydrides $[MH(O_2CCF_3)(CO)(PPh_3)_2]$ (M= Ru,Os) react with the disubstituted acetylenes PhCCR (R=Ph, Me) to give the vinylic products $[M\{C(Ph)=CHR\}(O_2CCF_3)(CO)(PPh_3)_2]$. The osmium hydride and the vinylic compounds are all catalysts for the oligomerization of phenyl acetylene.[63]

Reactions of acetylide complexes have been studied. The oxidation of *cis*-$[Os(C_2Ph)_2(PMe_3)_4]$ by $AgPF_6$ produces $[Os(\eta^3\text{-}PhC_3{=}CHPh)(PMe_3)_4][PF_6]$ which was characterized by X-ray crystallography. A mechanism for this coupling reaction is proposed.[64]



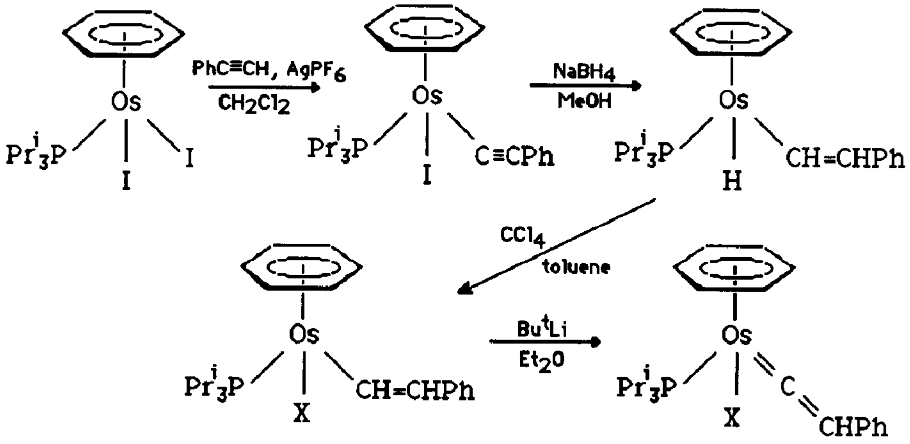
Tetracyanoethylene reacts with some ruthenium acetylide complexes, $CpRuLL'(C_2R)$ (where R=Me, Ph; L=PPh_3; L'=CO, PPh_3, $P(OPh)_3$; LL'=dppe) to give cyclobutenyl, butadienyl, or allyl complexes.



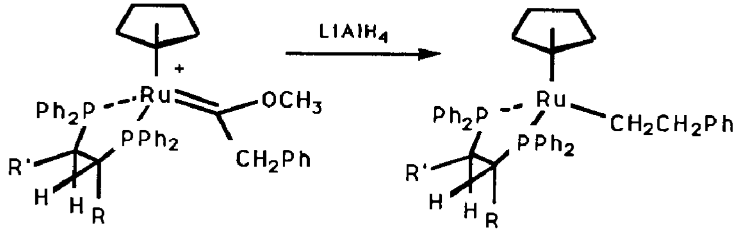
The structure of $CpRu\{C[=CC(CN)_2]CPh=C(CN)_2\}(dppe)$ was determined by X-ray diffraction.[65]

(I) Alkylidene, Alkylidyne Complexes

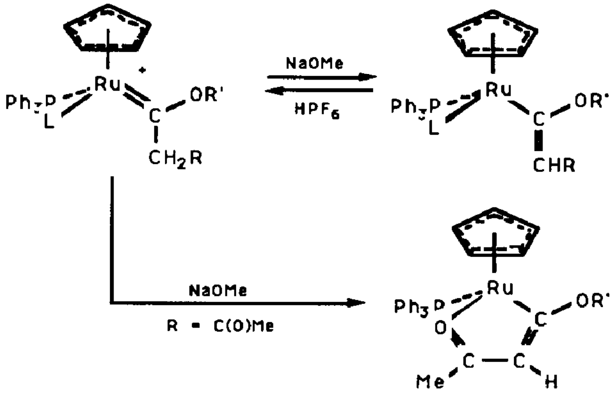
Ruthenium and osmium acetylide complexes have been employed as precursors to vinylidene complexes. The addition of arenediazonium salts and tropylium salts to the ruthenium acetylide complex, $CpRu(C_2Ph)L_2$ (L= PPh_3 or 1/2 dppe), was reported. The reactions produce cationic aryldiazovinylidene and cycloheptatrienylvinylidene complexes, respectively. The crystal structures of $[Ru(C=CPhN=NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]\cdot 0.67CH_2Cl_2$ and $[Ru\{C=CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]\cdot 0.63CH_2Cl_2$ were obtained.[66] Halovinylidene complexes of ruthenium resulted from the reaction of halogens with ruthenium acetylide complexes. Liquid bromine reacted with $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ to give a quantitative yield of $[Ru\{C=CBr(C_6H_4Br\text{-}4)\}(PPh_3)_2(\eta\text{-}C_5H_5)][Br_3]$ in which both the acetylide and the phenyl ring were brominated. The structure of this molecule was determined by an X-ray crystal structure.[67] Novel benzene osmium complexes containing alkynyl, vinyl, and vinylidene groups as ligands were synthesized. A four step synthesis of the first neutral vinylidene complex of osmium from the acetylide complex was reported. This vinylidene complex, $(\eta^6\text{-}C_6H_6)Os(CCHPh)(PPr_3{}^i)$, reacts with sulfur, selenium and with CuCl by electrophilic addition to the osmium-carbon double bond.[68]



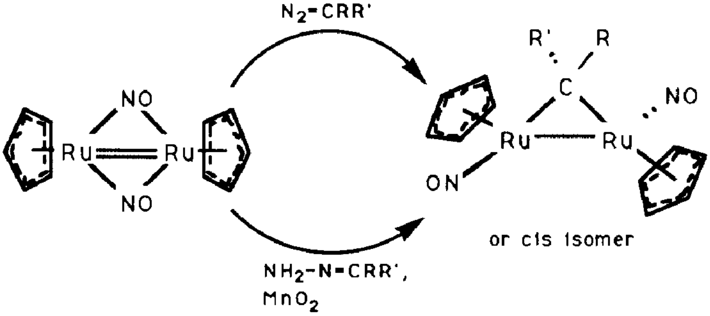
Alkoxycarbene complexes are electrophilic and react with hydride donors and other basic reagents. Hydride addition to the chiral, cationic ruthenium carbene complexes $[(\eta^5\text{-}C_5H_5)Ru\{Ph_2CHRCHR'PPh_2\}\{C(OMe)CH_2Ph\}][PF_6]$ proceeds with retention of configuration at ruthenium. 2-Phenylethyl complexes are formed.[69]



Deprotonation of several cationic alkoxy(alkyl)carbene complexes of ruthenium gave vinyl ether derivatives. Deprotonation at the ß position of the carbene was reversible.[70]

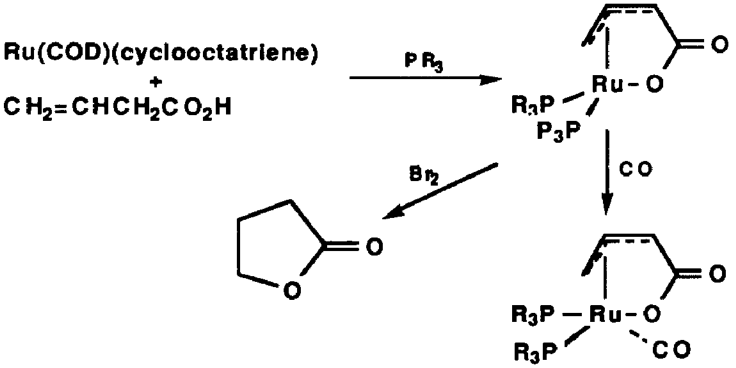


New μ-alkylidene complexes of ruthenium were prepared by treating the nitrosyl dimer, $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}NO)]_2$ with diazoalkanes or with hydrazones plus an oxidizing agent such as MnO_2. The nitrosyls are bound in a terminal fashion in the products. Sulfur dioxide adds cleanly to $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}NO)]_2$ to give a $\mu\text{-}SO_2$ complex. The alkylidene complexes add acid to initially form μ_2-hydride complexes.[71]

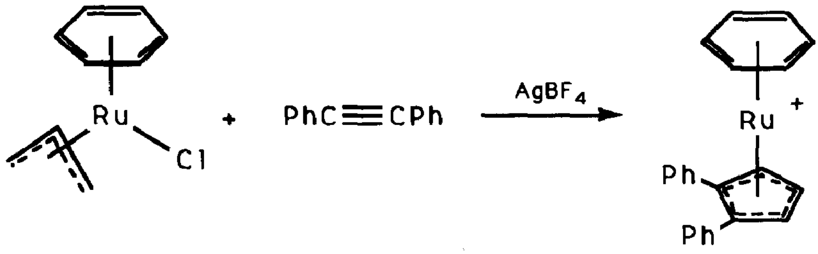


(j) π-Complexes

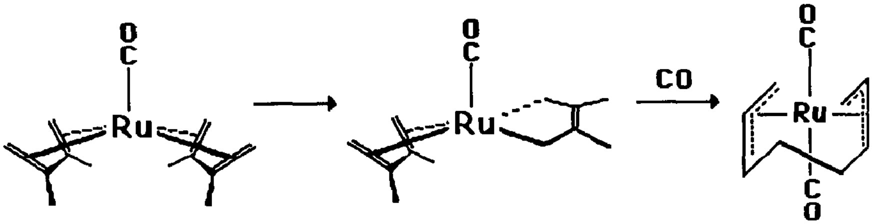
The synthesis and reaction chemistry of several ruthenium π-allyl complexes was investigated. An improved procedure was developed for the synthesis of ruthenium(IV) allyl complexes, $(C_5Me_5)RuCl_2(\eta^3\text{-allyl})$, from allylic halides, alcohol, ethers, acetate, or sulfides and $[(C_5Me_5)RuCl_2]_2$.[72] The thermal decomposition of $(C_5R_5)Ru(CH_3)X(\eta^3\text{-}C_3H_5)$ in the presence of neutral ligands, L, was found to gives $(C_5R_5)RuL_2X$ (R= H, CH_3; X=, Cl, Br).[73] Substitution of cyclooctadiene and cyclooctatriene on ruthenium by 3-butenoic acid and triaryl phosphines gave η^3-allylcarboxylato ruthenium(II) complexes. The reactions of these complexes with carbon monoxide and bromine were studied.[74]



Condensation of a π-allyl ligands and alkynes on a ruthenium center produced π-cyclopentadienyl complexes. The structure of one of these, [(η-C_6H_6)Ru(η-$C_5H_3Ph_2$-1,2)][BF_4], was determined by X-ray.[75]



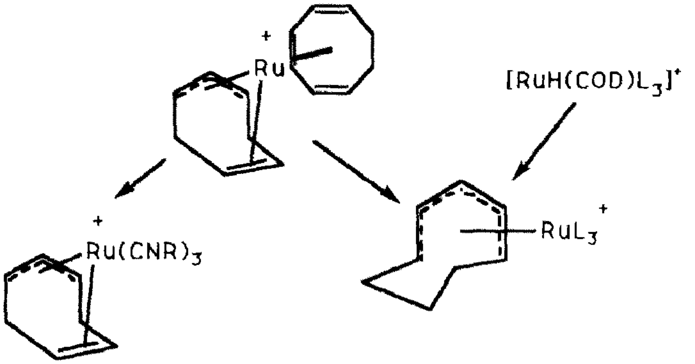
The diene complex Ru(CO)(η^4-C_6H_{10})$_2$ was synthesized by condensation of 2,3-dimethylbutadiene and ruthenium atoms, followed by addition of CO. Heating this complex under CO gave Ru(CO)$_2$(η^3:η^3-$C_{12}H_{20}$) in which the diene groups had coupled to an octadienediyl moiety.[76]



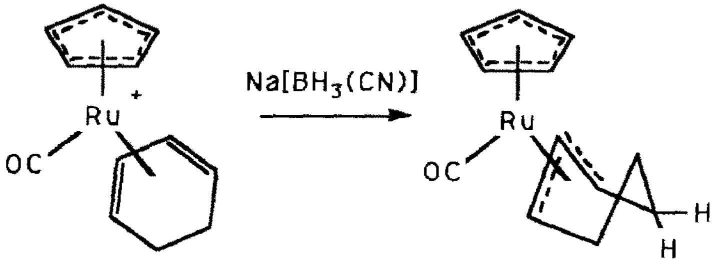
NMR spectroscopy shows four separate fluxional processes in (η^6-cyclooctatetraene)(η^4-cycloocta-1,5-diene)osmium. The ^{13}C NMR spectra of Os(η^6-C_8H_8)(η^4-C_8H_{12}) provide evidence for a metal [1,5] shift on a π-coordinated polyene ligand.[77]

Reactions of 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene with low valent complexes of ruthenium, osmium, and iridium provided a new synthetic route to the η^4-trimethylenemethane complexes. The new η^4-trimethylenemethane complexes of ruthenium and osmium, [MCl(NO)(PPh_3)(tmm)] and [Os(CO)$_2$(PPh_3)(tmm)], were prepared in 20-35% yield from the reactions of [RuCl(NO)(PPh_3)$_2$] or [OsCl(NO)(PPh_3)$_3$].[78]

A variety of ruthenium complexes were obtained by the substitution of cyclooctadiene for other ligands. Substitution of cyclooctadiene from [(η^5-C_5H_5)Ru(C_8H_{12})Cl] by various ligands produced cyclopentadienylruthenium(II) complexes under very mild conditions. The complex [(η^5-C_5H_5)Ru(C_8H_{12})Cl] was prepared from [(η^5-C_5H_5)Ru(C_8H_{12})H] and carbon tetrachloride. Cationic complexes of the type $[(\eta^5\text{-}C_5H_5)RuL_2Cl]$ were prepared with dppe, 3,4,7,8-tetramethyl-1,10-phenanthroline, t-BuNC, and $2,6\text{-}Me_2C_6H_3NC$. Triolefins displace both the cyclooctadiene and the chloride ligand to produce neutral complexes of the type $(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-triene})$.[79] The ruthenium η^3-enyl cations $[Ru(\eta^3\text{-heptenyl})L_3]^+$, $[Ru(\eta^3\text{-hexenyl})L_3]^+$, and $[Ru(\eta^3\text{-butenyl})L_3]^+$ were prepared from $[RuH(COD)L_3][PF_6]$ or $[Ru(\eta^3\text{-}C_8H_{13})L_3][PF_6]$ and the appropriate 1,3-diene. NMR studies show that an aliphatic C-H···Ru exists in each of these dienyl complexes.[80] Dienyl complexes of ruthenium were synthesized from the cations $[Ru(1\text{-}3{:}5\text{-}6\text{-}\eta\text{-}C_8H_{11})(\eta^6\text{-}1,3,5,\text{-cyclooctatriene})]^+$ and $[RuH(COD)L_3]^+$. The crystal structure of $[Ru(\eta^5\text{-cyclooctadienyl})(PMe_2Ph)_3][PF_6]$ was obtained.[81]



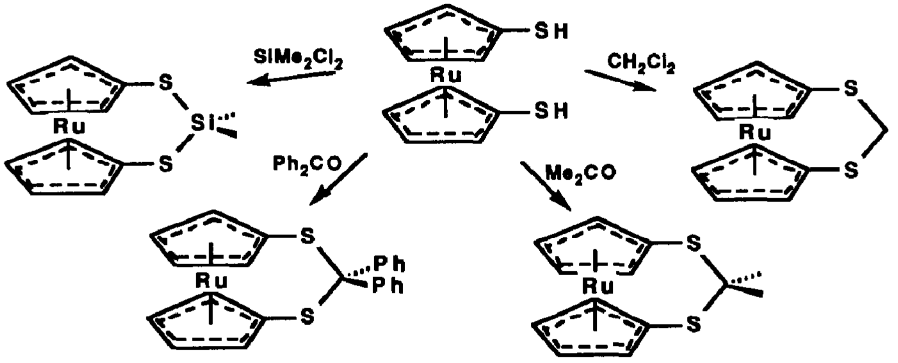
Substitution of the labile acetonitrile ligands on $[Ru(NCMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ by dienes gives cationic ruthenium diene complexes. Complexes of buta-1,3-diene, isoprene, 1,4-diphenylbuta-1,3-diene, and cyclohexa-1,3-diene were isolated and characterized. Addition of nucleophiles to the diene produced π-allyl complexes of ruthenium. Crystal structures of $[Ru(\eta^4\text{-}C_6H_8)(CO)(\eta\text{-}C_5H_5)][BF_4]$ and $[Ru(\eta^3\text{-}C_6H_9)(CO)(\eta\text{-}C_5H_5)]$ were obtained.[82]



Decamethylruthenicenium undergoes a facile deprotonation/oxidation to give a cationic tetramethylfulvene complex, $[Ru(\eta^5\text{-}C_5Me_5)(C_5Me_4\text{-}\textit{exo}\text{-}CH_2)]^+$, and ruthenocene. The fulvene complex can also be prepared by hydride abstraction by Ph_3CBF_4 on ruthenocene.[83]

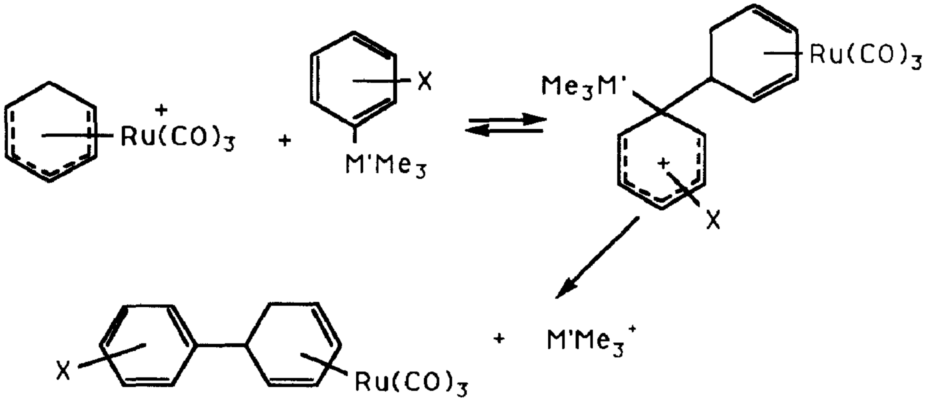
The syntheses of complexes with substituted cyclopentadienyl groups was the subject of several papers. A ruthenium indenyl complex, $RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)$, was prepared from $RuCl_2(PPh_3)_3$, indene, and KOH. A variety of neutral and anionic ligands can be exchanged for the chloride in this complex. An X-ray crystal structure of one derivative, $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)][ClO_4]$, was obtained.[84] The metallocenes and decamethylmetallocenes of osmium and ruthenium have been prepared by the reaction of $[MCl_2(COD)]_x$ and $SnBu_3(C_5R_5)$ (R= H, Me).[85] The synthesis of ruthenocenoyl-1,1'-diglycine ethyl ester via exchange of ferrocenoylglycine ester with ruthenium trichloride was reported.[86]

New ruthenocenphanes were prepared and the bridge reversal process studied by variable temperature NMR spectroscopy.[87]

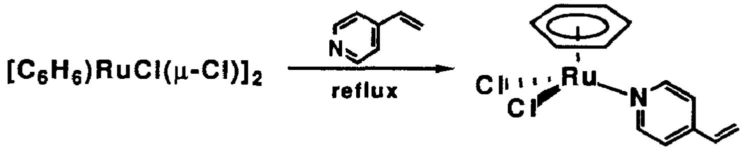


Electron transfer reactions occurred between Ag(I) and the ruthenium atom in polyoxa[n]- and 1,n-dioxathia[n]ruthenocenophanes.[88]

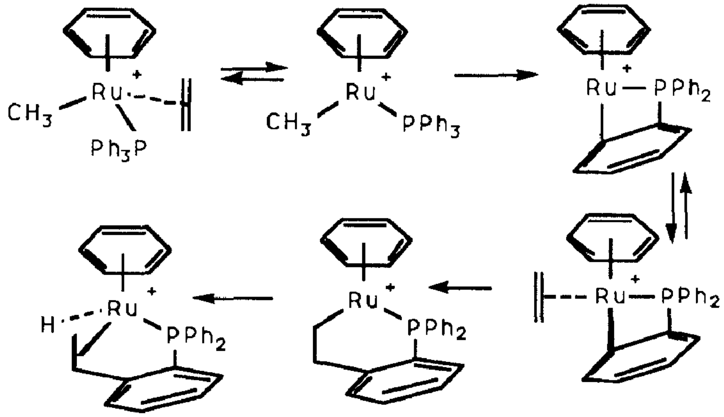
Kinetics of the reaction between a cyclohexatrienyl complex of ruthenium(II) and aryltrimethyl-silanes or stannanes have been studied. Aryl-substituted cyclohexadiene complexes of ruthenium(0) are produced. A mechanism based on this data was proposed in which an electrophilic attack by the ruthenium complex on the aryltrimethyl-silanes or stannanes is the first step.[89]



Synthetic procedures for the preparation of new arene complexes of ruthenium have been developed. Eleven new arene-ruthenium(II) complexes with activated ligands were prepared. These complexes will be use for protein labeling. One example is shown below.[90]

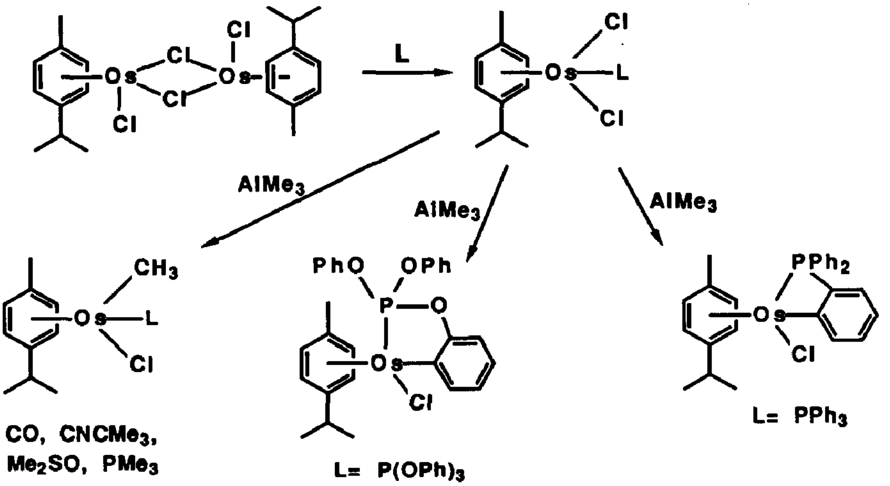


Protonation of $Ru(C_6Me_6)(CH_3)_2(PR_3)$ in the presence of L (L= CO or C_2H_4) gives $[Ru(C_6Me_6)(CH_3)(PR_3)L]^+$. One ethylene adduct, $[Ru(C_6Me_6)(CH_3)(PPh_3)(CH_2{=}CH_2)]^+$ loses methane at room temperature to form a styrenyl-diphenylphosphine complex.[91]

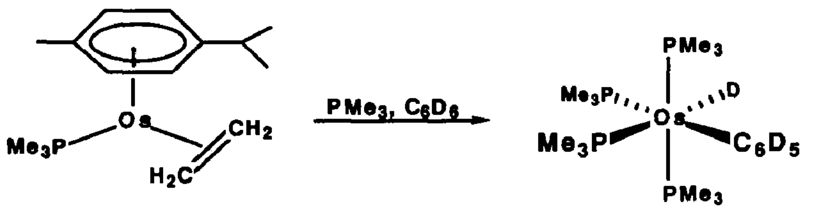


A synthetic procedure for the preparation of ruthenium arene cations $[(\eta^6\text{-arene})Ru(\eta^5\text{-}C_5H_5)]^+$ was published. Treatment of ruthenocene with the arene, $AlCl_3$, Al, NaX, and water in an autoclave gave good yields of the arene complexes.[92]

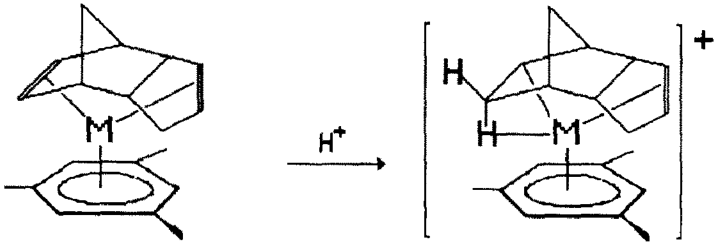
Few π-arene complexes of osmium have been studied due to the lability of the arene-metal unit. Osmium *p*- cymene complexes have recently been prepared in which the osmium *p*- cymene bond is relatively inert. The complexes (*p*-cymene)$OsCl_2L$ were prepared from the dimers $[(p\text{- cymene})OsCl_2]_2$ and excess ligand. Some of these can be alkylated with trimethylaluminum.[93]



The synthesis and reaction chemistry of another series of η^6-*p*-cymene complexes of osmium(0) and osmium(II) was reported. One of these complexes, (η^6-*p*-cymene)$Os(C_2H_4)(PMe_3)$, was found to undergo intermolecular C-H activation in C_6D_6 when treated with excess PMe_3. The corresponding π-benzene complex was previously found to undergo an intramolecular C-H addition under these conditions.[94]



Protonation of arene*endo*-dicyclopentadiene complexes of ruthenium and osmium, $M(\eta^6\text{-arene})(\eta^4\text{-}C_{10}H_{12})$, with HPF_6 gave the mono-protonated salts $[M(\eta^6\text{-arene})(C_{10}H_{13})][PF_6]$. Spectroscopic studies support structures with a M-H-C agostic interaction. The crystal structure of $[Os(2,3,5\text{-}\eta\text{-}C_{10}H_{13})(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)][PF_6]$ was reported.[95]

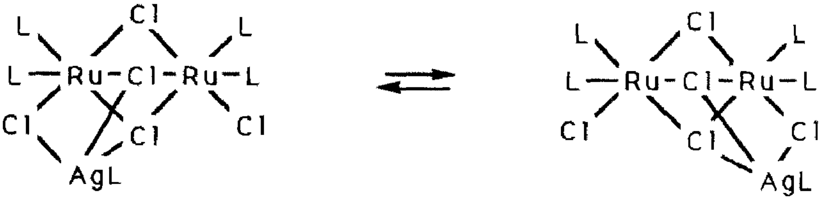


II. Dinuclear Complexes

(a) Homodinuclear Complexes

Binuclear halide bridged ruthenium complexes containing terminal alkene, alkyne, and dinitrogen ligands were prepared. The reaction of $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ with $M[BF_4]$ (where M= Ag, Na, Tl) in the presence of L (where L= N_2, C_2H_4, PhCCPh, MeO_2CCCCO_2Me, MeCN, $MeNO_2$ or PEt_2Ph) produced $[(PEt_2Ph)_3RuCl_3RuL(PEt_2Ph)_2][BF_4]$. The dinitrogen and ethylene complexes can be reversibly interconverted. The cyclic voltammogram of the ethylene complex was obtained.[96]

The reaction of $[Ru_2Cl_4(PEtPh_2)_5]$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$, or $[RuCl_2(PEtPh_2)_3]$ with AgCl produces a trimetallic complex, $[Ru_2Cl_5(PEtPh_2)_4 \cdot Ag(PEtPh_2)]$. The structure of this product was determined by X-ray crystallography. Variable temperature ^{31}P NMR show the molecule to be fluxional.[97]



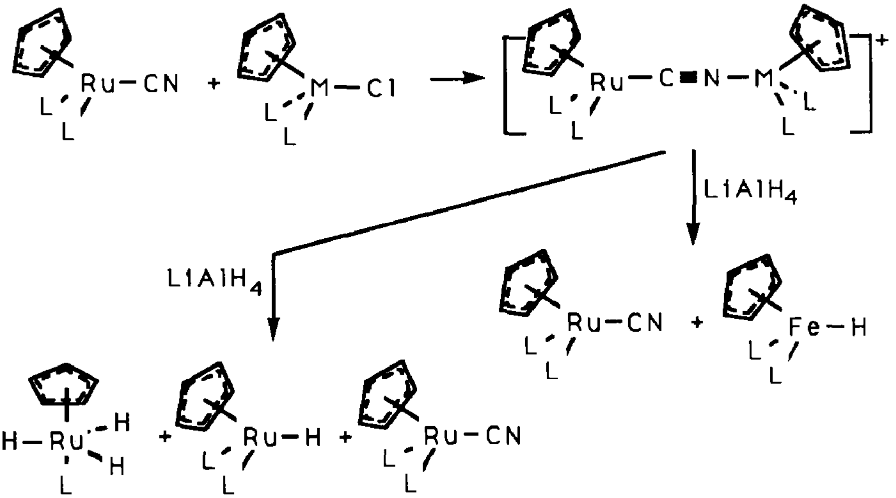
Polyhydride complexes of ruthenium, $RuH_6(PPh_3)_2$ and $Ru_2H_6(PPh_3)_4$, were prepared by the direct hydrogenation of $Ru(styrene)_2(PPh_3)_2$. A dinitrogen complex was formed when these complexes were recrystallized under N_2. An X-ray crystal structure of $Ru_2H_4N_2(PPh_3)_4$ shows a short Ru-Ru distance and three bridging hydrides.[98]

The ^{187}Os chemical shifts of a series of dinuclear p-cymeneosmium hydride complexes were measured using $^1H\text{-}\{^{187}Os\}$ two dimensional NMR spectroscopy. Chemical shifts of osmium and $^{187}Os\text{-}^1H$ coupling constants were determined. The complexes used in this study included $[(\eta^6\text{-}1\text{-}Me,\ 4\text{-}Pr^i\text{-}C_6H_4)_2Os_2(\mu\text{-}H)(\mu\text{-}X)(\mu\text{-}Y)]^+$

(where X=Y=H; X=H, Y=OAc; and X=OAc, Y=Cl). These were prepared from $[(\eta^6\text{-1-Me, 4-Pr}^i\text{-}C_6H_4)_2Os_2Cl_4]$.[99]

The reaction of carbon dioxide with $[M(CO)_4]^{-2}$ (M=Ru,Os) results in the formation of the osmium and ruthenium carbonyl dimers $[M_2(CO)_8]^{-2}$. Both of these complexes have been characterized by X-ray.[100]

Bimetallic complexes with linear cyanide bridges were prepared by the reactions of $[Ru(\eta^5\text{-}C_5H_5)L_2]$ (L=PPh_3 or 1/2dppe) with $Ru(\eta^5\text{-}C_5H_5)Cl$ or $Fe(\eta^5\text{-}C_5H_5)Cl$. Reduction of the dimer regenerated the cyanide complex as well as forming metal-hydrides. A mechanism for the reduction involving initial attack at the carbon of the bridging cyanide ligand followed by ß-hydride elimination was proposed.[101]



A dinuclear ruthenium complex with both terminal and bridging mercapto ligands was reported. The ruthenium(II) hydrido phosphine complex $RuH_2(PMe_2Ph)_4$ reacted with hydrogen sulfide at 50° to give $L_3Ru(\mu\text{-}SH)_3Ru(SH)L_2$. The product was characterized by IR and NMR spectroscopy.[102]

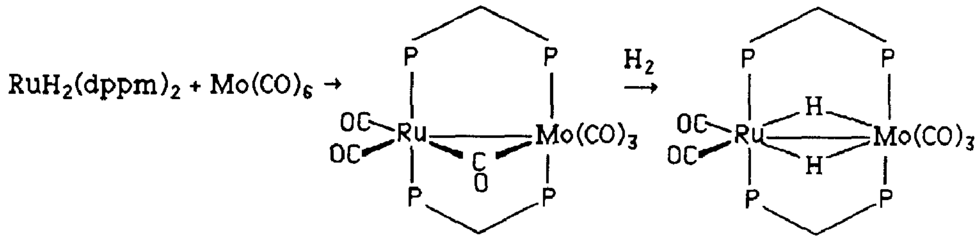
Oxidation of a bridging methylene complex of ruthenium, $Cp_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_2)$, with ferricenium salts followed by deprotonation with the hindered base 2,6-dimethylpyridine produced the bridging methyne complex, $[Cp_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH)]^+$. The μ-methyne complex reacted with a variety of nucleophiles to produce alkylidenes. The bridging methyl complex, $[Cp_2Ru_2(\mu\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$ was formed with H_2 at 150 atmospheres pressure.[103]

The ruthenium cyclooctenyl complex $[Ru_2(1\text{-}2,5\text{-}\eta\text{-}C_8H_{13})(CN\text{-}2,6\text{-}C_6H_3Me_2)_4][PF_6]$ decomposes by homolysis of the metal carbon bond to give 10-40% yields of a homoleptic metal-metal bonded isocyanide dimer of ruthenium(I). The structure of the tetraphenylborate salt, $[Ru_2(CN\text{-}2,6\text{-}C_6H_3Me_2)_{10}][BPh_4]_2$, was determined by X-ray. The metal-metal bond is unbridged and the 2,6-dimethylphenyl isocyanide groups are eclipsed.[104]

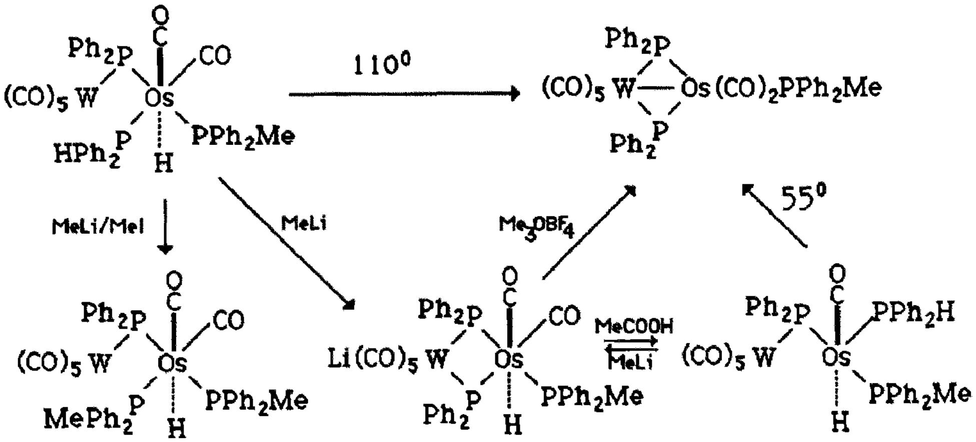
(b) Heterodinuclear Complexes

A number of researchers have investigated the chemistry of heterometallic complexes containing both an early and later transition metal. One paper reported the reactions of $Cp_2Zr[Ru(CO)_2Cp]_2$. This complex reacts reversibly with carbon monoxide to extrude a mononuclear ruthenium hydride, $CpRu(CO)_2H$, and form a ruthenium-zirconium complex having a cyclopentadienyl group which is monohapto-bonded to zirconium and pentahapto-bonded to ruthenium. The complex $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ was stucturally characterized. A similar complex, $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)(PMe_3)$, can be prepared from $Cp_2Zr[Ru(CO)_2Cp]_2$ and trimethylphosphine. Ethylene inserts into the zirconium-η^1-Cp bond.[105]

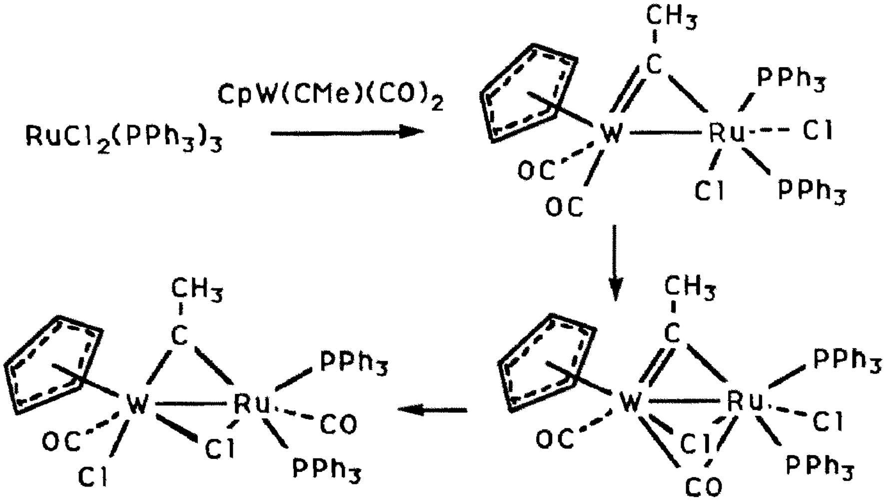
A number of new complexes were prepared with osmium or ruthenium bonded to tungsten or molybdenum. A bis(diphenylphosphino)methane bridged molybdenum-ruthenium complex was prepared, $MoRu(CO)_6(dppm)_2$, which was found to crystallize with either 0, 1, or 2 bridging carbonyls. Hydrogen and carbon monoxide readily add to the molecule.[106]



Heterobimetallic complexes were prepared by the reactions between transition metal anions and ruthenium halides. The complex $MoRu(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)$ was synthesized from $[CpMo(CO)_3]^-$ and $RuCl_2(PPh_3)_3$. A manganese-ruthenium complex, $MnRuCl(\mu\text{-}CO)_2(CO)_3(\mu\text{-}dppm)_2$, was prepared by treatment of the anion $[Mn(CO)_5]^-$ with $RuCl_2(dppm)_2$. The reaction between $[Mn(CO)_5]^-$ and $RuCl_2(PPh_3)_3$ formed a bimetallic complex with a bridging phosphido group, $MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$.[107] A new osmium-tungsten complex was prepared by the protonation of $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)]$ and was structurally characterized. Thermolysis and reactions with MeLi, MeI, Me_3OBF_4, H_2, and $MeCO_2H$ give products which retain the Os-W unit. The most stable of the complexes formed in these reactions is $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)$.[108]

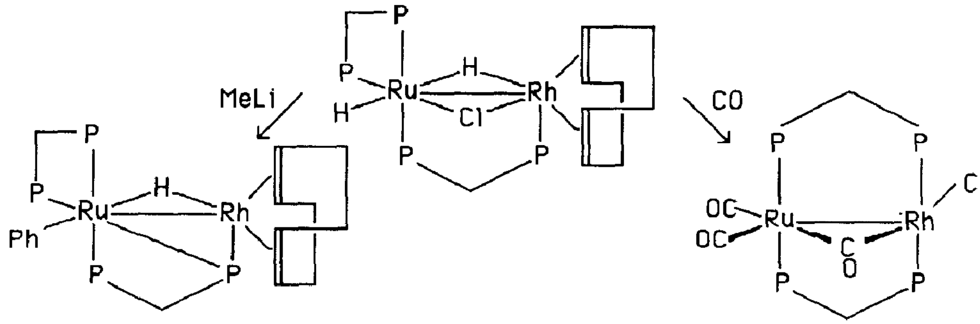


The reaction of the alkylidyne tungsten complex $[W(CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and the ruthenium complexes $Ru(CO)_2(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ produces heterobimetallic complexes. The crystal structures of $[RuW(\mu\text{-}Cl)(\mu\text{-}CMe)(Cl)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $[RuW_2(\mu_3\text{-}C_2Me_2)(CO)_7(\eta\text{-}C_5H_5)_2]$ were determined.[109]

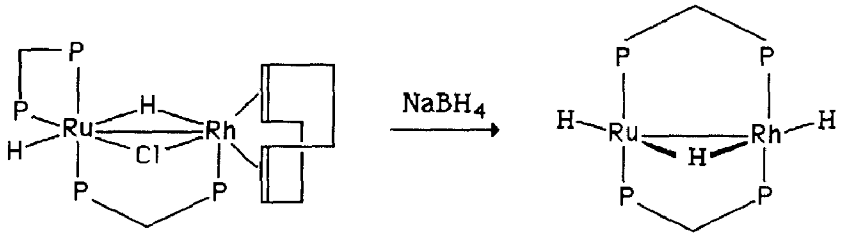


One product resulting from the reaction of $CpRu(PPh_3)_2Cl$ with $Co(CO)_4^-$ was isolated and structurally characterized. The complex consists of a $CpRu(PPh_3)_2$ cation and a $Co(CO)_4$ anion.[110]

Several complexes mixed metal complexes containing ruthenium and rhodium were prepared. A heterobimetallic complex, $RuRhH_2Cl(COD)(dppm)_2$, is formed from the reaction of $RuH_2(dppm)_2$ with $[RhCl(COD)]_2$. A chloride, hydride and dppm ligand bridge the two metal centers. Although reaction with trimethylphosphite gives only mononuclear products, the bimetallic product $RuRhCl(CO)_3(dppm)_2$ can be isolated upon reaction with CO. Reaction with methyllithium produced $RuRhHPh(COD)(PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)$, which has been characterized by X-ray diffraction.[111]



Treatment of $RuRhH_2Cl(COD)(dppm)_2$ with $NaBH_4$ in thf gives a trihydride complex $RuRhH_3(dppm)_2$ which has been structurally characterized. It has an "A-frame" type structure with one bridging and two terminal hydrides.[112]



A heterobinuclear complex of ruthenium and rhodium bridged by a pyrazolate group have been synthesized and its structure determined by X-ray crystal structure. The complex $[(p\text{-}cymene)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)Rh(tfb)]$, where tfb is tetrafluorobenzo[5.6]bicyclo[2.2.2]octan-2,5,7-triene, was prepared from $(p\text{-}cymene)RuCl_2(Hpz)$ and $Rh(acac)(tfb)$.[113] Heterobimetallic complexes $[(\eta$-

arene)MCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (M= Ru, Os) were synthesized from NEt$_2$H$_2$[Pt(S$_2$CNEt$_2$)(Ph$_2$PS)$_2$] with the arene complexes [M(η-arene)Cl$_2$]$_2$. Reaction with additional [Pt(S$_2$CNEt$_2$)(Ph$_2$PS)$_2$]$^+$ produced tri- and penta-metallic complexes.[114]

III. Polynuclear Complexes

(a) Ru$_3$ and Os$_3$ Complexes

1. Theoretical and Spectroscopic Studies

The photoreactions of organotriruthenium clusters have been surveyed.[115] UV photoelectron spectroscopy and theoretical studies of μ-hydrido-μ_3-allyl and μ-hydrido-μ_3-allenyl triangulo carbonyl clusters of ruthenium and osmium have been reported.[116] H-H coupling in ^{1}H-^{187}Os satellite NMR spectra have been observed and interpreted.[117]

2. M$_3$ Complexes with Simple Ligands

Two reviews of metal carbonyl cluster reactions have appeared.[118,119] A facile and economical synthesis of Ru$_3$(CO)$_{12}$ has been claimed.[120] The nucleophilic activation of coordinated carbon monoxide has been probed by examining hydroxide and methoxide reactions with trinuclear clusters.[121] Electrochemical studies on Ru$_3$(CO)$_{12}$ and K$_2$Ru$_3$(CO)$_{11}$ demonstrated that during reduction of Ru$_3$(CO)$_{12}$, the initially formed triangulo-Ru$_3$(CO)$_{12}^-$ rearranges to a linear form.[122]

Flash photolysis studies of Ru$_3$(CO)$_{12}$ have provided evidence for intermediates in the competing fragmentation and ligand substitution photoreactions.[123] The kinetics of the reaction of bis(diphenylphosphino)methane with dodecacarbonyl triruthenium have been reported.[124] The clusters M$_3$(CO)$_{12-n}$(PBu$_3$)$_n$, where M=Os or Ru, react with PBu$_3$ by a pathway that involves fragmentation; these reactions have been labeled F$_N$2.[125,126] The kinetics and mechanism of dihydrogen addition/elimination and of related ligand substitution reactions with certain alkylidyne triosmium clusters has been reported.[127]

The mechanism of localized site exchange of carbonyl groups in HM$_3$(CO)$_9$L clusters has been considered.[128] The preparation and X-ray structure of Ru$_3$(μ-CO)$_2$(CO)$_6${PPh(OMe)$_2$}$_4$ shows it to be a Ru$_3$(CO)$_{12}$ derivative with an Fe$_3$(CO)$_{12}$-like structure.[129] New isomers of [Os$_3$(CO)$_{10}$(PMe$_2$Ph)$_2$] and [Os$_3$(CO)$_9$(PMe$_2$Ph)$_3$] have been discovered and their pathways of intramolecular carbonyl exchange examined.[130,131] NMR evidence for a trigonal twist mechanism involving a phosphite ligand in Os$_3$(CO)$_7$[P(OMe)$_3$]$_5$ has been presented.[132]

Several papers have dealt with ligands derived from cyclometallated bi- or tridentate phosphines. The transformation of dppm on a triruthenium framework was demonstrated by the synthesis and structural characterization of $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$, $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PPhCH_2PPh_2)$, and $Ru_3(CO)_{10}(\mu\text{-}\eta^2\text{-}PPhCH_2PPh(C_6H_4)$.[133] The complexes $[Ru_3(CO)_9\{Ph_2PCHP(Ph)C_6H_4PPh\}]$, $[Ru_2H(CO)_4(Ph_2PCHPPh_2)\text{-}\{PhPC_6H_4C(O)\}]$, and $[Ru_2(CO)_4Cl(PPh_2)(dppm)]$ have been isolated from the reaction between $Ru_3(CO)_{12}$ and the tridentate phosphine $HC(PPh_2)_3$ and have been characterized by X-ray crystal structures.[134] The preparation of the unsaturated hydrido osmium cluster $Os_3(CO)_8H_2(dppm)$ was achieved by hydrogenolysis of a cyclometallated phosphine; its X-ray structure was determined.[135]

The systematic synthesis and characterisation of phosphido-bridged triosmium carbonyl clusters has been claimed.[136] Reactions of some ruthenium cluster complexes $Ru_3(CO)_{12-n}L_n$ with hydrogen also shows cleavage of element-carbon bonds.[137] The synthesis of an isostructural series of μ-hydrido, μ-phosphido clusters, $(\mu\text{-}H)_2M_3(CO)_8(\mu\text{-}PPh_2)_2$ (where M = Fe, Ru, Os), was reported.[138]

3. M_3 Clusters with Sulfur-Containing Ligands

Two papers have dealt with the products derived from the interaction of phosphino- and arsino-substituted sulfurdiimides with $H_2Os_3(CO)_{10}$; the crystal structures and solution stereodynamics of $H_2Os_3(CO)_{10}(^tBu_2PNSNAs^tBu_2)$ and of $(\mu\text{-}H)Os_3(CO)_8(\mu_3\text{-}As^tBu)[\mu(N,As)\text{-}NSNAs^tBu_2]$ were described.[139,140] The preparation and crystal structure of $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}S\text{-}Et)$ has been reported.[141] The synthesis, structure, bonding, and unusual reactivity of sulfido osmium carbonyl clusters has been reviewed.[142]

4. M_3 Clusters with Nitrogen-Containing Ligands

The reaction of $Ru_3(CO)_{12}$ with 2,2'-bipyridine has been investigated and the X-ray crystal structure of $Ru_3(CO)_{10}(bipy)$ was determined.[143] The preparation, characterization and some general reactions of $[Ru_3(CO)_{11}(NCMe)]$ and $[Ru_3(CO)_{10}(NCMe)_2]$ were reported.[144] Additionally, the *ortho-* metallation reactions of various methylpyridines, quinoline, isoquinoline, diazines, and 2,2'-bipyridine with $[Ru_3(CO)_{10}(NCMe)_2]$ have been described.[145]

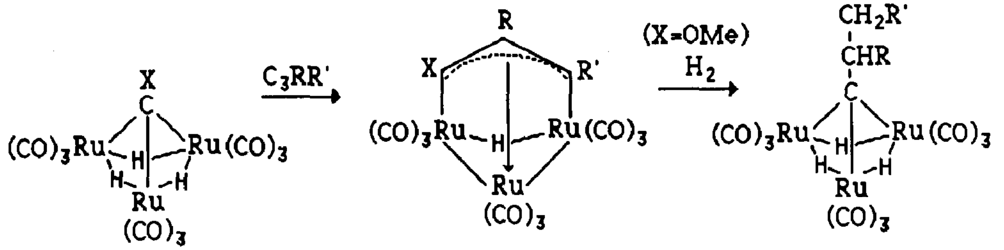
New triosmium clusters derived from the reactions between $[Os_3(CO)_{10}(NCMe)_2]$ and amides have been characterized.[146] The reactions of Os_3 and Ru_3 clusters with nitrogen heterocycles have been explored as potential models of the active sites in heterogeneous HDN catalysts.[147] Direct evidence for the involvement of a coordinated carbene ligand in a triosmium cluster-catalyzed tertiary amine transalkylation reaction has been offered.[148] The reaction of $[Os_3(\mu\text{-}H)_2(CO)_9L]$ (L=CO or PEt_3) with dimethylcyanamide produced $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$;

the X-ray crystal structure and the reaction of this complex with acids were described.[149]

5. M_3 Clusters with Hydrocarbon Ligands

The synthesis and X-ray structure of $[Ru_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3Cp_3][BF_4]$ was reported; the μ_3-ethylidyne ligand was activated through a novel sequence of oxidation-deprotonation steps.[150] The preparation of $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ was described; its X-ray structure showed a new mode of allyl binding to a metal cluster.[151] The synthesis and crystallographic characterization of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}MeCCOMe)$ has been recorded.[152] The synthesis and some reactions of $H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$ have been reported, including the reductive elimination of C-H bonds and insertion of alkynes into Ru-C and Ru-H bonds.[153]

A comprehensive study of methylidyne-alkyne coupling on Ru_3 clusters to produce 1,3-dimetalloallyl clusters and the hydrogenation of these cluster bound 1,3-dimetalloallyl units has been reported. The alkynes C_2R_2 react with $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (where X= OMe, Me, Ph) to produce cis-alkenes and $HRu_3(\mu_3\text{-}\eta^3\text{-}XCCRCR)(CO)_9$. Hydrogenation of those clusters with X=OMe gives μ_3-alkylidyne complexes.[154]



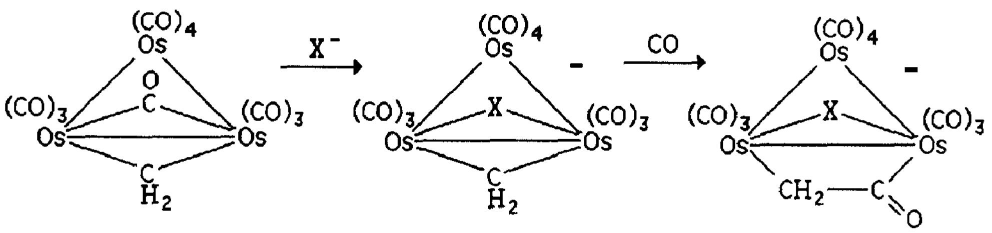
Ligand substitution reactions on $HRu_3(\mu\text{-}CX)(CO)_{10}$,where X = OMe or NMe_2, by L, where L= $AsPh_3$ or PPh_3, produced three isomeric forms $HRu_3(\mu\text{-}CX)(CO)_9L$. The kinetics of the substitution reactions were investigated and indicate a mechanism involving dissociation of CO; however, changes in the coordination mode of the CX ligand were proposed to occur during the substitution reaction.[155] The crystal structures of the derivatives $(\mu\text{-}H)Ru_3[\mu\text{-}CNMe_2](CO)_9py$ and $(\mu\text{-}H)Ru_3[\mu\text{-}CN(CH_2Ph)_2](CO)_9(PPh_3)$ were determined by X-ray diffraction.[156]

Two papers detailed the reactivity of triruthenium carbonyl 1,4-diaza-1,3-butadiene $Ru_3(CO)_8$(R-DAB) complexes.[157,158] Reversible CO addition occurs without rupture of a metal-metal bond, whereas addition of a methylene fragment from diazomethane leads to rupture of one Ru-Ru bond. Crystal structures of $Ru_3(CO)_9$(R-DAB)[R=cyclohexyl] and of $Ru_3(CO)_8$(R-DAB)(CH_2)[R=neopentyl] were determined.

Brief treatment of $Ru_3(CO)_{12}$ with diazomethane in refluxing cyclohexane provided the methylene complex $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.[159] The molecule is fluxional and a bridge to terminal interconversion of the methylene ligand was proposed. Excess diazomethane reacts with $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ to give the coupling product $H_2Ru_3(CO)_9(\mu\text{-}CCH_2)$, whereas rearangement to $H_2Ru_3(CO)_9(CCO)$ occurs upon heating. The related dianion $[Ru_3(CO)_9(CCO)][PPN]_2$ was prepared in 53% yield by acylation of the bridging carbonyl in $[Ru_3(CO)_{11}][PPN]_2$ followed by reductive cleavage of the activated CO bond.[160] The X-ray crystal structure showed the linear CCO fragment to be tipped toward a Ru-Ru bond. Protonation gave $[(\mu\text{-}H)Ru_3(CO)_9(CCO)][PPN]$ and $(\mu\text{-}H)_2Ru_3(CO)_9(CCO)$, and treatment with $Fe_2(CO)_9$ produced a mixed-metal carbide complex, $[Ru_3FeC(CO)_{12}][PPN]_2$.

The crystal structure of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}O_2CCH_3)$ has been recorded.[161] Reversible carbon-carbon bond formation by interconversion of CO and μ-acyl ligands on the face of a triosmium cluster has been reported.[162] The variety of triosmium clusters derived from α,β-unsaturated aldehydes has been described,[163] as has the acid-induced displacement of acetaldehyde from a μ-vinyloxy-triosmium cluster.[164] Metallation of 2-vinylpyridine occurred in the formation of the open trinuclear clusters $[Os_3H(CO)_9L(NC_5H_4CH{=}CH)]$ (L=CO, PMe_2Ph).[165]

The fifty-electron cluster $[PPN][Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]$ was prepared from $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and [PPN]X salts, where X= Cl, Br, or NO_2; $[PPN][Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NCO)]$ was produced with $[PPN]N_3$.[166] X-ray crystal structures of the iodo and isocyanate derivatives show some metal-metal bonding around the triangular array despite the an electon count lower than usual for a *closo* structure. The insertion of CO into Os-μ-methylene bonds is promoted by halides; the rate is faster for X=I than for X=CO.[167]



The benzylidyne complex, $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$, was prepared by treatment of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ with PhLi and $MeSO_2CF_3$; the benzylidyne ligand was characterized as "semi-triply bridging".[168] Hydrogen gas gave $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CPh)$,whereas pyrolysis formed the *ortho*-metalated product, $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}$

CHC_6H_4). A mixed carbene-carbyne cluster complex $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$ was characterized as an intermediate in the formation of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$.[169]

The discovery of benzene in a new face-capping bonding mode was established by the molecular structures of $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$.[170] An osmium atom reaction led to the formation of the trinuclear osmium cluster $[Os(\eta^6\text{-}C_6H_6)(\mu\text{-}H)]_3\{\mu_3\text{-}(CH_2)_3CH\}$, involving activation of the three methyl groups of 2-methylpropane.[171]

6. Supported Os_3 and Ru_3 Clusters

The anionic cluster $HRu_3(CO)_{11}^-$, when adsorbed onto silica modified with quaternary ammonium functions was more active for ethylene hydrogenation (700C) and the water gas shift (1500C) than when adsorbed onto unmodified silica.[172] The water gas shift reaction also can be catalyzed by a supported osmium catalyst. Treatment of $Os_3(CO)_{12}$ supported on a zeolite with base gives $[H_3Os_4(CO)_{10}]^-$ trapped within the zeolite framework. This is active at temperatures above 100°C.[173]

$M_3(CO)_{10}(dppm)$ undergoes selective substitution with phosphine ligands to give $M_3(CO)_9L(dppm)$. This reaction was used to anchor complexes onto phosphinated solica and cross-linked polystyrene.[174] The pyrolysis products of $H_2Os_3(CO)_{10}$ supported on phosphinated or thiolate silica have been examined by EXAFS; evidence was obtained for Os-Os bonds and for Os-S bonds but not for Os-P bonds.[175]

A molecular analog of a triosmium cluster anchored on silica, $(\mu\text{-}H)(\mu\text{-}OSiEt_3)Os_3(CO)_{10}$, has been synthesized and characterized by X-ray diffraction.[176] The chemisorption, reactivity, and decomposition of $Ru_3(CO)_{12}$ on silica has been studied by gas desorption, IR, and Raman techniques; reversible interconversion between intact $Ru_3(CO)_{12}$ and ensembles of $Ru(CO)_n(OSi...)_2$, n=2 or 3, was proposed.[177] The interaction of $HOs_3(CO)_{12}^+$ with the smectite clay hectorite led to deprotonation at the platelet edges, resulting in well-dispersed $Os_3(CO)_{12}$.[178]

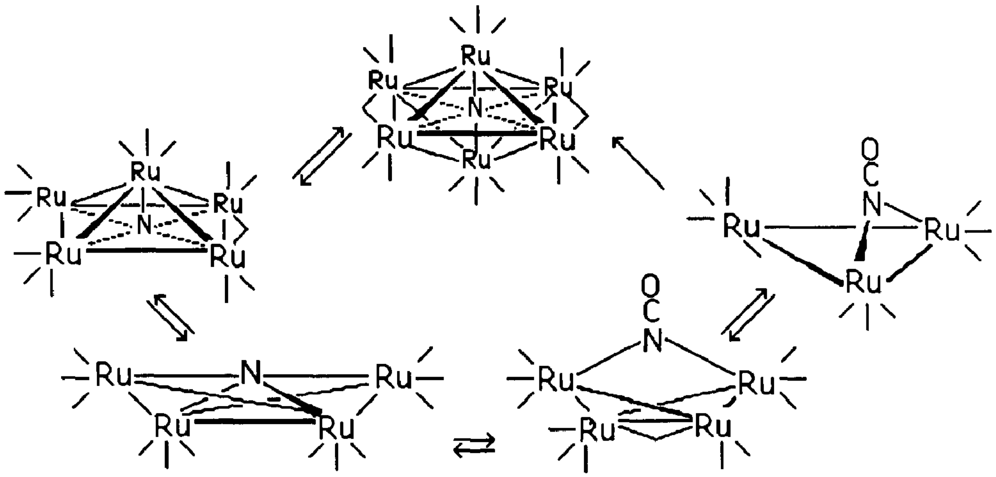
(b) Ru_4, Ru_5, and Ru_6 Complexes

The reaction of $Ru_2(CO)_5(R\text{-}DAB)$ [DAB=1,4-diaza-1,3-butadiene] with H_2 produced $H_2Ru_4(CO)_8(R\text{-}DAB)_2$, which contained a Ru_4 chain.[179] Two new tetranuclear ruthenium complexes have been isolated and structurally characterized: $[Ru_2(CO)_5(PPh_2)(C_2PPh_2)]_2$, with two dinuclear units linked by two phosphinoacetylide bridges, and $[Ru_4(CO)_{10}(PPh)(PhC_2PPh_2)]$, a flattened "butterfly" with β-π-phenyl(diphenylphosphino)acetylene and μ_4-phosphinidene ligands extracted from the bis(diphenylphosphino)acetylene reactant.[180]

Two reports have appeared regarding the synthesis and crystal structure of the open 5-atom cluster, $[Ru_5(CO)_{13}(\mu_2\text{-}PPh_2)(\mu_5\text{-}CCPPh_2)]$, obtained from the reaction of bis(diphenylphosphino)acetylene and triruthenium dodecacarbonyl.[181,182] Further chemistry of this complex has been examined. Carbonylation occured under mild conditions, leading to cleavage of two Ru-Ru bonds and formation of two isomers of $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}]$.[183] Hydrogenation under 10 atm pressure led to excision of a ruthenium carbonyl fragment and formation of $Ru_4(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$.[184] However, hydrogenation at 1 atm allowed the sequential isolation and structural characterization of $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C{=}CHPPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ and $[Ru_5(\mu_5\text{-}C)(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)]$; the overall result on this Ru_5 cluster was stepwise hydrogenation of an acetylide ligand to carbon and methyl.[185]

The reactivity of the phosphinidene cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ toward diphenylacetylene was examined; both *nido-* $Ru_4(CO)_{10}(\mu\text{-}CO)_2[P(Ph)C(Ph)C(Ph)]$ and *closo-* $Ru_4(CO)_9(\mu\text{-}CO)_2(PhP)[C(Ph)C(Ph)]$ were isolated and structurally characterized.[186] Several unusual tetra- and penta-ruthenium complexes were generated from linking of ethylidyne and vinylidene ligands.[187]

In work dealing with the reduction of μ_2-NO in $[Ru_3(CO)_{10}(\mu_2\text{-}NO)_2]$ by carbon monoxide, evidence was provided for the formation of a triruthenium nitrido intermediate; from this system the complexes $[Ru_4N(CO)_{12}(\mu_2\text{-}NO)]$ and $[Ru_4N(CO)_{12}(\mu_2\text{-}NCO)]$ were isolated and structurally characterized.[188] In related work a homologous series of nitrido clusters, $[Ru_4N(CO)_{12}]^-$, $[Ru_5N(CO)_{14}]^-$, and $Ru_6N(CO)_{16}]^-$, were formed. The nitrido group in each new cluster was derived from a coordinated isocyanate. The direct conversion of $[Ru_4(NCO)(CO)_{13}]^-$ to $[Ru_4N(CO)_{12}]^-$ occurred in refluxing THF. The reaction of $Ru_3(CO)_{12}$ with $PPN(N_3)$ proceeded by way of the isocyanate complexes $[Ru_3(NCO)(CO)_{11}]^-$ and $[Ru_3(NCO)(CO)_{12}]^-$ to give $[Ru_6N(CO)_{16}]^-$. The Ru_5 complex, $[Ru_5N(CO)_{14}]^-$, was readily formed from $[Ru_6N(CO)_{16}]^-$. The nitrido complexes were converted back to isocyanates under high CO pressure.[189]



(c) Os_4, Os_5 and Os_6 Complexes

The cluster compound $(PMe_3)(CO)_4OsOs_3(CO)_{11}$ was shown to have an unsupported dative metal-metal bond.[190] The synthesis of tetranuclear osmium clusters by the reaction of trinuclear clusters with $OsH_2(CO)_4$ has been described.[191] The interaction of $H_3Os_4(CO)_{12}I$ with $[PPN][NO_2]$ provided mainly $[PPN][H_2Os_4(CO)_{12}I]$ and a small amount of $H_3Os_4(CO)_{11}(NO)$, the X-ray crystal structure of which was determined.[192] The X-ray structure analysis of $[PPN][H_2Os_4(CO)_{12}I]$ provided evidence for a reversible metal framework rearrangement assisted by coordinated iodide.[193] The reactions of $Os_4(CO)_{12}(\mu_3\text{-}S)$ with terminal alkynes have been described.[194]

The X-ray crystal structures of the hexanuclear osmium cluster alkyne complexes $[Os_6(CO)_{17}(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}CCEt)]$, $[Os_6(CO)_{17}(\mu_4\text{-}\eta^2\text{-}HCCEt)]$, and $[Os_6(CO)_{16}(\mu_3\text{-}\eta^2\text{-}MeCCEt)]$ have been reported.[195] The two-electron reduction of $Os_6(CO)_{18}$ occurs overall with a structural change from bicapped tetrahedron to octahedron; a detailed electrochemical study using polarography and cyclic voltammetry has been published.[196]

(e) Higher Nuclearity Complexes

Examination of some reactions of decaosmium clusters with electrophilic and nucleophilic reagents has led to the isolation and X-ray structure analyses of $[PPN][Os_{10}C(CO)_{24}(\mu\text{-}I)]$, $[Os_{10}C(CO)_{24}(\mu\text{-}I)_2]$, $[PPN]_2[Os_{10}C(CO)_{22}(NO)(I)]$, and $[Os_{10}C(CO)_{24}\{P(OMe)_3\}(\mu\text{-}I)_2]$.[197]

(f) Mixed Metal Cluster Complexes

1. Clusters Containing Main Group Metals

The cluster anion $[HRu_3(CO)_{10}(SiEt_3)_2]^-$ has been examined by cyclic voltammetry, dynamic ^{13}C NMR, and X-ray crystallography.[198] The synthesis and characterisation of new triosmium and triruthenium main-group metal clusters $M_3(H)(CO)_{11}(M'R_3)$ and $Os_3(H)(CO)_{10}(CH_3CN)(M'R_3)$ (M= Os, Ru: M'= Ge, Sn; R, aryl, alkyl) has been reported.[199]

Unusual reactivity of $[Os_3Sn(\mu\text{-}H)_2(CO)_{10}R_2]$ involving the tin atom and the bridging hydride has been observed; the X-ray crystal structures of $[Os_3Sn(\mu\text{-}H)_2(CO)_9\{\mu\text{-}RC(OS)=O(SN)\}R]$ and $[Os_3Sn(\mu\text{-}H)_2(CO)_9\{\mu,\eta^1\text{-}C(CO)_2Me)CH_2C=O(Os)OMe\}R_2]$, (R= $CH(SiMe_3)_2$) have been determined.[200]

A number of mixed metal cluster compounds containing copper, silver, and especially gold atoms have been prepared and characterized. Bidentate phosphine ligands for copper and silver derivatives have been described.[201] The synthesis and structures of the ruthenium-gold-sulfur clusters $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$, $Ru_3Au(\mu_3\text{-}SBu^t)(CO)_9(PPh_3)$, and $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)$ have been reported.[202] The reaction of $[\{Au(PPh_3)\}_3O]^+$ with $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ led to $[Ru_3Au_2(\mu\text{-}C=CHBu^t)(CO)_9(PPh_3)_2]$, containing a t-butylvinylidene ligand attached to a trigonal bipyramidal Ru_3Au_2 core.[203]

Substitution of $[Au(PPh_3)^+]$ for H^+ in $[H_4Ru_4(CO)_{12}]$ increased the rate of catalytic l-pentene isomerization.[204] The synthesis of $[N(PPh_3)_2][Ru_5C(CO)_{13}(NO)]$ and $[Ru_5C(CO)_{13}(NO)(AuPR_3)]$ (R= Et, Ph) has been reported; the X-ray structure analysis of the gold derivative showed the presence of both $[Ru_5C(CO)_{13}(NO)(\mu_3\text{-}AuPEt_3)]$ and $[Ru_5C(CO)_{13}(NO)(\mu_2\text{-}AuPEt_3)]$ forms in one crystal.[205]

The reactions between $M(C_2R)(PR_3')$ (M=Cu, Ag, Au; R= Ph, C_6F_5; R'= Me, Ph) and $H_2Os_3(CO)_{10}$ have been examined and the X-ray structures of $Os_3Au(\mu\text{-}CH=CHR)(CO)_{10}(PPh_3)$ (R= Ph and C_6F_5) reported.[206] The unsaturated osmium-gold clusters $Os_4(CO)_{12}(AuPR_3)_2$, (where PR_3=PEt_3, PPh_3, $PMePh_2$) may be prepared by the thermal decarbonylation of $Os_4(CO)_{13}(AuPR_3)_2$; the unsaturated nature of the complexes is demonstrated by the ease of addition of CO, H_2, $P(OMe)_3$, and t-BuNC.[207]

2. Clusters with Other Transition Metals

A comprehensive review of selective metal-ligand interactions in heterometallic transition metal clusters has appeared.[208] New multinuclear Hg-Co-Ru and Hg-Co-Fe sandwich complexes have been synthesized and the X-ray crystal structure of $Hg[RuCo_3(\mu\text{-}CO)_3(CO)_9]_2$ determined.[209] Carbonylcobalt ruthenium clusters with μ_3-acetylene and μ_3-vinylidene ligands have been characterized.[210] The crystal structures of $HRuRh_3(CO)_{12}$, $HRuRh_3(CO)_{10}(PPh_3)_2$, and $HRuCo_3(CO)_{10}(PPh_3)_2$ have been reported.[211] Two reports of the synthesis and X-ray crystal structure of $\{[Rh(\eta\text{-}C_5Me_5)]_3[Ru(CO)_3](\mu_3\text{-}CO)_2\}$ have been published.[212,213] Reversible syntheses of related cyclopentadienylrhodium triruthenium cluster complexes, including the X-ray structures of $CpRhRu_3\{\mu\text{-}H\}_2\{\mu\text{-}CO\}(CO)_9$, Cp = $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5Me_5$, and $(\eta^5\text{-}C_5Me_5)Rh\{\mu\text{-}H\}_2Ru_3\{\mu\text{-}H\}_2(CO)_9$ have been described.[214,215] The crystal structure of the mixed-metal carbonyl cluster $[PPN][RuIr_3(CO)_9(\mu\text{-}CO)_3]$ has been determined.[216]

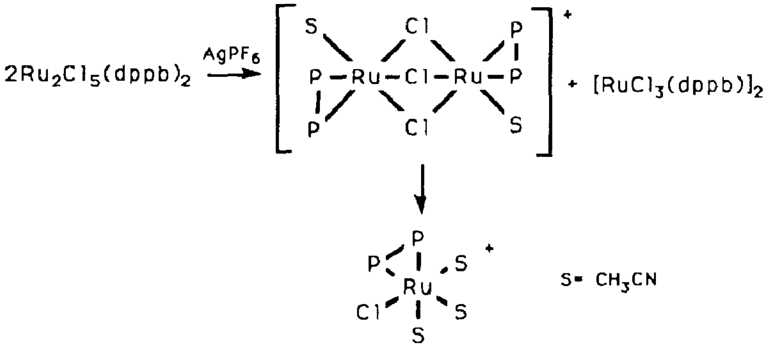
Reversible alkyne ligand scission was demonstrated by the interconversion of $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$ with $Cp_2W_2Os(CO)_5(\mu\text{-}CTol)(\mu_3\text{-}CTol)$.[217] Crystal structures of a tetrahedral oxo-alkylidyne complex, $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$,[218] and of the products resulting from its hydrogenation, $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$,[219] or pyrolysis, $CpWOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}C{=}CHTol)$,[220]have been published. The synthesis and crystal structure of $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$ has been reported.[221]

The reaction of $CpNiOs_3(\mu\text{-}H)_3(CO)_8(Ph_2PCCPr^i)$ with cobalt carbonyl provided $CpNiOs_3(\mu\text{-}H)_3(CO)_8\{(Ph_2PCCPr^i)Co_2(CO)_6\}$; crystal structures were determined.[222] Several mixed transition metal clusters containing the coordinated phosphaalkyne ^tBuCP have been reported.[223]

Dynamic ^{13}C NMR evidence has been presented for unusually facile metal-metal bond reorganization in $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$.[224] Chemistry of the unsaturated cluster compound $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3]$ has been described together with the X-ray structures of $[Os_3Pt(\mu\text{-}H)_2(CO)_{11}\{P(cyclo\text{-}C_6H_{11})_3]$, $[Os_3Pt(\mu\text{-}H)_4(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3]$, and two isomers of $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3]$.[225] The synthesis and X-ray analysis of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$, an unusual high nuclearity osmium-platinum cluster has been published.[226]

IV. Catalytic and Synthetic Reactions

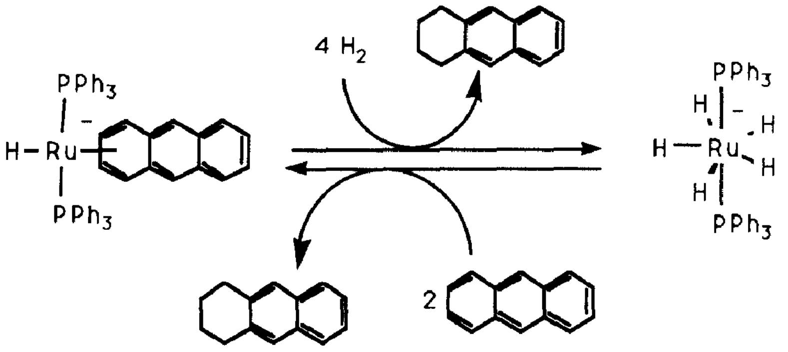
New catalysts for the hydrogenation of olefins were reported. The ruthenium complexes $[Ru_3(CO)_7(PPh_2)_2(C_6H_4)]$ and $[Ru_2(CO)_5(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}O{=}CPh)]$ catalyzed the hydrogenation of cyclohexene and 2-cyclohexen-1-one. A crystal structure of $[Ru_2(CO)_5(PPh_3)(\mu\text{-}PPh_2)(\mu\text{-}O{=}CPh)]$ was obtained.[227] A cationic ruthenium(II) complex containing the diphosphine ligand bis(diphenylphosphino)butane, dppb, was prepared from the dimer $Ru_2Cl_5(dppb)_2$ and $AgPF_6$ in acetonitrile.



Both $[Ru_2Cl_5(dppb)_2(MeCN)_2]^+$ and $[RuCl(dppb)(MeCN)_3]^+$ were effective catalysts for the hydrogenation of hex-1-ene, styrene, and acrylimide.[228] Bromo(carbonyl)hydrido-tris(triphenylphosphine)osmium(II) catalyzes C=C bond migrations, hydrogenation of olefins other unsaturated groups, and the hydroformylation of olefins.[229] Cyclopentadienone ruthenium complexes $[(\eta^4\text{-}R_4C_4CO)(CO)_2Ru]_2$ (where R=Me or Ph) catalyze the hydrogenation of a variety of olefin and acetylene substrates.[230]

The asymmetric reduction of olefins was reported. The hydrogenation of α-acylaminoacrylic acids was achieved by chiral ruthenium catalysts containing the 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ligand.[231] Asymmetric hydrogenation of tiglic acid occurred in the presence of phosphine substituted carbonylruthenium carboxylates. The catalyst precursors were $Ru_4(CO)_8[OOC(CH_2)_nCOO]_2[(\text{-})\text{-}DIOP]_2$ with n=0-3. Tiglic acid was reduced to (+)(S)-2-methylbutanoic acid with an optical purity of ~35%.[232]

Intermediates in the catalytic hydrogenation of anthracene to tetrahydoanthracene by hydrido(phosphine)ruthenate complexes were identified.[233]



The reduction of carbon monoxide was affected by a ruthenium-zeolite catalyst and by a ruthenium-rhodium catalyst. Ethane was selectively synthesized from CO and H_2 in a reaction catalyzed by zeolite entrapped ruthenium carbonyl clusters. Catalysts prepared from $Ru_3(CO)_{12}$ and NaY zeolite were studied as catalysts for the reduction of carbon monoxide with hydrogen. When this catalyst was treated with methyl iodide, up to 60% of the hydrocarbon product consisted of ethane while the product mixture was rich in methane in the absence of MeI. Intermediate formation of methanol from the methyl iodide under reaction conditions was proposed to account for these observations.[234] Hydrogenation of carbon monoxide to ethylene glycol occurs at 400-850 atm., 190-240°C, with a homogeneous ruthenium-rhodium catalyst and an iodide promotor. The selectivity to ethylene glycol increases with the rhodium concentration, but no mixed metal species are directly observed.[235]

Carbon monoxide has been catalytically reduced by ruthenium catalysts. The reduction of carbon dioxide by anionic trinuclear, tetranuclear, and hexanuclear ruthenium carbonyl clusters was reported.[236] Carbon dioxide was reduced to formic acid in a photochemical reaction catalyzed by $Ru(bipy)_3Cl_2$. A ruthenium hydride intermediate was proposed.[237] A polypyridyl complex of ruthenium, $Ru(trpy)(dppene)Cl^+$ (where trpy = 2,2',2"-terpyridine and dppene = *cis*- 1,2-bis(diphenylphosphino)ethylene), was found to be a catalyst for the electrochemical reduction of CO_2.[238]

Ruthenium complexes catalyze reductive bond cleavage reactions. Photosensitized cleavage of acetylene to methane was reported. A ruthenium amine complex, $[Ru(NH_3)_5(H_2O)]^{2+}$, along with $[Ru(Bpy)_3]^{2+}$ as sensitizer and triethanolamine as electron donor, was found to cleave acetylene to methane under visible light illumination. Two moles of methane are formed per mole of $[Ru(NH_3)_5(H_2O)]^{2+}$. IR spectra suggest that $[(NH_3)_5Ru\text{-}CCH]^+$ is formed from photolysis of $[(NH_3)_5Ru(\eta^2\text{-}HCCH)]^{2+}$ in this reaction. The authors propose that the methane results from protonation of the acetylene under reaction conditions.

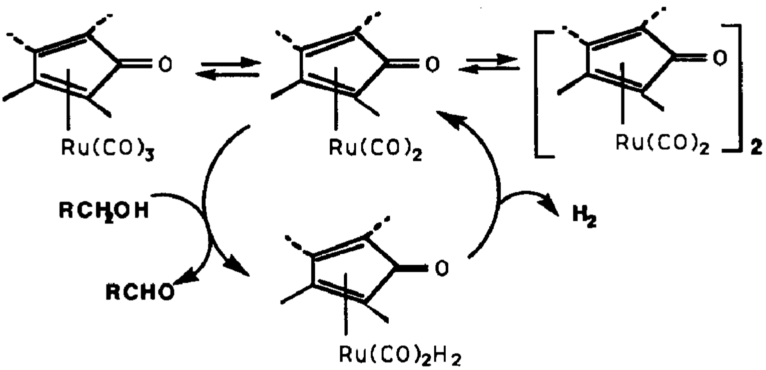
The triple bond in some substituted acetylenes is also reductively cleaved under these conditions.[239] Trimethylsilyl ethers are cleaved by $RuH_2(PPh_3)_4$ at the C-O and the Si-O bonds. Excess triphenylphosphine inhibits the C-O cleavage selectively. Products resulting from the reaction with (2-butenyl)trimethylsilylether include C_3H_6, C_3H_8, C_4H_8, Me_6Si_2O, $RuH_2(CO)L_3$, and $Ru(CO)_3L_2$.[240]

A study on the catalytic hydrogenation of nitrogen containing aromatic compounds by $RuHCl(PPh_3)_3$ appeared. The system was used as a model for catalytic hydrodenitrification.[241]

The ruthenium clusters $H_4Ru_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Ru_3(CO)_{10}(dppe)$ and $Ru_3(CO)_8(dppm)_2$ were studied as catalysts for the water gas shift reaction under conditions where H_2 was allowed to accumulate, or was removed from the mixture. Under all conditions, $[HRu_3(CO)_{11}]^-$ was the predominant ruthenium complex in solution. The tetranuclear cluster, $[H_3Ru_4(CO)_{12}]^-$, was detected only when H_2 was allowed to build up in the reaction system. The anion $[HRu_3(CO)_{11}]^-$ was found to be a hydride donor in the presence of carbon monoxide. The chemistry was discussed in terms of the mechanism of the water gas shift reaction.[242] Isotope labelling studies on the ruthenium catalysed hydroformylation of ethylene: indirect evidence for catalysis at intact clusters.[243]

A homogeneous catalyst for the carbonylation of esters to carboxylic acids was prepared from $RuCl_3$ and methyl iodide. Ester carbonylation was found to be faster than the carbonylation of alcohols.[244] Ruthenium carbonyl iodide complexes catalyze the homologation of ethyl orthoformate with carbon monoxide and hydrogen. The product mixture changes with the temperature of the reaction with diethyloxymethane being the main product at low temperature, while at high temperature, methyl ethyl ether, methanol, and ethyl propionate predominate.[245]

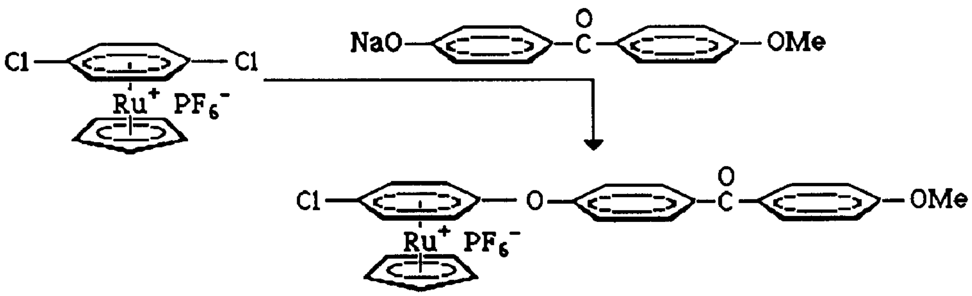
The oxidation of alcohols was investigated. In some cases the hydrogen produced by alcohol dehydrogenation was used to reduce unsaturated molecules. The ruthenium complex $[RuCl_2(PPh_3)_3]$ is a catalyst for the conversion of methanol to methyl formate.[246] Methanol can be used as a hydrogen donor in certain reactions catalyzed by $[Ru(PPh_3)_3Cl_2]$. In the reduction of cyclohexanone to cyclohexanol, methanol is converted to methyl formate.[247] Dehydrogenation of methanol under anhydrous conditions to formaldehyde and hydrogen can be catalyzed by $[Ru_2(OAc)_4Cl]/PR_3$ or by the monometallic complex $[Ru(OAc)Cl(PR_3)_3]$, where $R{=}PPh_3$ or $PEtPh_2$. Addition of moderate amounts of acetic acid increased the rates of reaction.[248] The complex CpL_2RuCl was found to reduce methanol or ethanol to the aldehyde with production of the ruthenium hydride, $Cp(PPh_3)_2RuH$.[249] The direct oxidation of primary alcohols to esters can be effected catalyically using (η^4-tetracyclone)$(CO)_3Ru$ or $[(\eta^4\text{-tetracyclone})(CO)_2Ru]_2$ as catalyst precursors. Hydrogen is evolved in the process. The structure of the catalyst precursor was determined.[250,251]

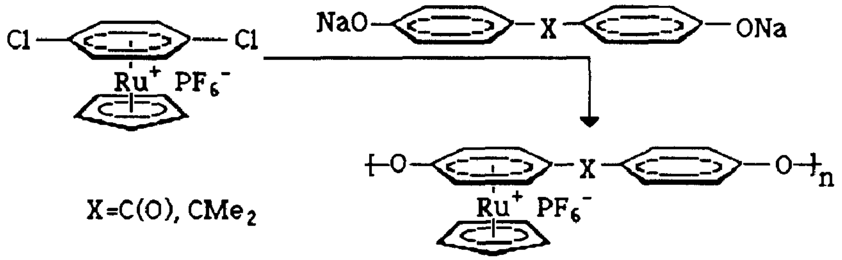


A ruthenium complex, $RuCl_2(PPh_3)_3$, catalysed the oxidation of secondary amines to imines using t-butyl hydroperoxide with isolated yields ranging from 52-98%. A mechanism involving the formation of a ruthenium amide intermediate was proposed.[252]

Osmium and ruthenium complexes were used in the oxidation of olefins. The epoxidation of olefins, such as *cis-* and *trans-* stilbenes, with sodium metaperiodate can be catalyzed by $RuCl_3 \cdot nH_2O$ associated with bipyridal or substituted phenanthrolines. Ratios of products from oxidative double bond cleavage to epoxidation varied from 100:0 to 10:90. The epoxidation reaction was stereospecific.[253] Stereoselective *cis-* osmylation of 5-vinyl-4,5-dihydroisoxazoles with osmium tetroxide gave the *anti:syn* product in ratios of between 73:27 to 92:8.[254]

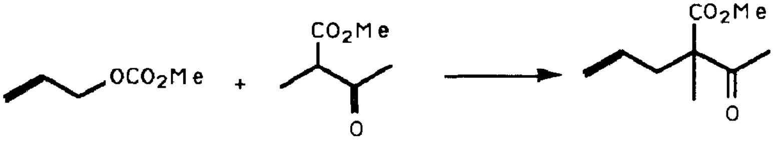
Aromatic polyethers were synthesized via activated substitution in a ruthenium(II) complex of p-dichlorobenzene. Organoruthenium polymers were prepared by nucleophilic substitution of chloride on an η^6-dichlorobenzene complex of ruthenium by bis-aryloxy anions. The free organic polymer can be obtained by treating the complex with dimethylsulfoxide. Mononuclear and dinuclear arene complexes of ruthenium were also prepared by this route.[255]





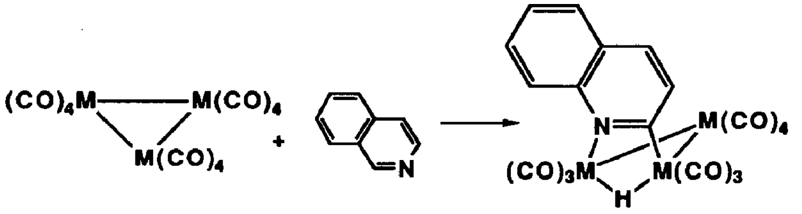
The reactions of unsaturated alcohols with $RuCl_2(PPh_3)_4$ and $RuH_2(PPh_3)_4$ were studied. The ruthenium complexes catalyzed the rearrangement of 1-hexen-3-ol and 2-methylencyclohexanol to the ketones $C_2H_5COC_3H_7$ and 2-methylcyclohexanone, respectively. Treatment of 2-penten-4-ol with the ruthenium catalysts gave mixtures of the ketone, $CH_3COC_3H_7$, and the double bond isomerization product, $CH_3CHOHCH_2CH{=}CH_2$.[256]

The allylation of carbonucleophiles with allylic carbonates catalyzed by $RuH_2(PPh_3)_4$ and other transition metal complexes was studied. The ruthenium catalyst was the most active for the reaction.[257]

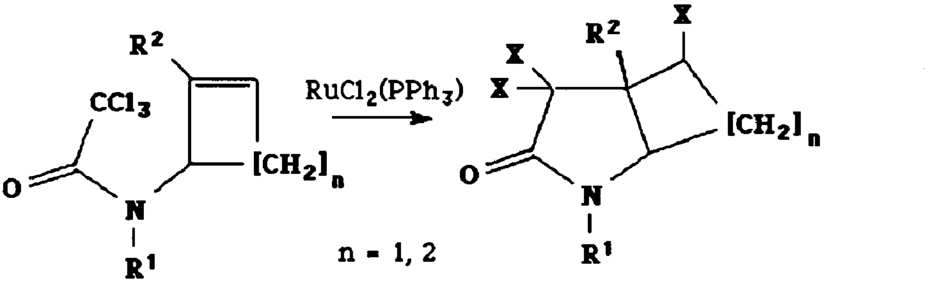


A kinetic and mechanistic study examined the transalkylation of tertiary amines with a catalyst based on $Ru_3(CO)_{12}$. The reaction of a mixture of tripropylamine and triethylamine with the ruthenium catalyst gave ethyldipropylamine and propyldiethylamine.The presence of CO slowed catalyst decomposition and improved yields. The reaction rate is enhanced by the presence of iron carbonyls, although they are not catalysts by themselves, while water decreases rate. C-H activation in the α and ß positions preceeded the transalkylation reaction. This was determined by the rapid H/D interconversion in these positions when D_2O is present in the catalytic system.[258]

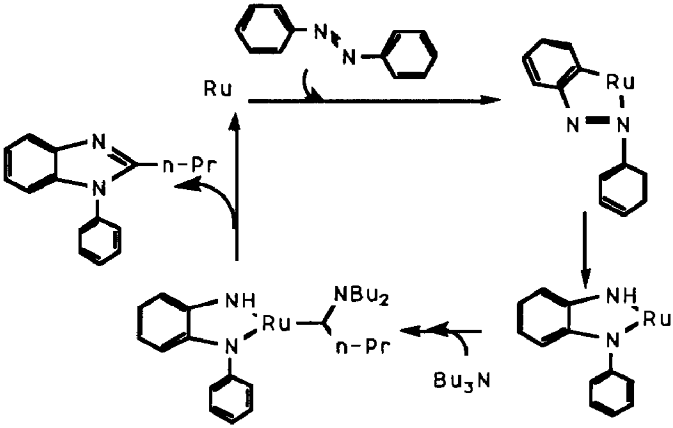
The reaction between $Os_3(CO)_{12}$ or $Ru_3(CO)_{12}$ and heterocyclic amines such as quinoline, pyridine, tetrahydroquinoline and piperidine, gave products in which an α C-H bond had been oxidatively added to the metal. A typical reaction is shown below:[259]



Ruthenium complexes were used in the synthesis of nitrogen containing heterocycles. The heterocyclization reaction between 1,3-propanediol and aminoarenes is catalyzed by $RuCl_3 \cdot 3H_2O$. Quinoline derivatives are produced in yields of 4-50%.[260] The stereoselective preparation of several bicyclic lactams by the cyclization of N-allyltrichloroacetamides was catalyzed by $RuCl_2(PPh_3)_3$.[261]



Ruthenium carbonyl complexes catalyze the preparation of 1-phenylbenzimidazoles from azobenzene derivatives and tertiary amines. The catalyst precursor is $RuCl_3$ and required temperatures are 160-190°C. A mechanism for the reaction was proposed.[262]



1-Phenylbenzimidazoles were prepared from azobenzene derivatives and primary alcohols. The reaction was catalyzed by $RuCl_3$ in the presence of PPh_3 and CO, under basic conditions.[263] In the reaction of azobenzenes with secondary alcohols, N-phenyl-1,2-phenylenediamine, and N^1-phenyl-N^2-(2-propyl)-1,2-phenylenediamine were produced in the ruthenium catalyzed reaction.[264] Azobenzene-d_{10} and 4,4'-disubstituted azobenzene-d_8 were used in the reactions with n-butanol or 2-propanol. NMR studies of the 1-phenylbenzimidazoles and N-phenyl-1,2-phenylenediamines produced in the reactions show that in all cases *ortho*-metallation of the azobenzene derivative has occurred.[265]

The addition of haloalkenes to olefins, the Kharasch addition reaction, can be catalyzed by $RuCl_2(PPh_3)_3$. A kinetic study of the reaction rules out a mechanism involving the ruthenium acting a radical initiator. In the mechanism proposed, the ruthenium(II) center is oxidized by R-X, generating a ruthenium(III) halide complex and an alkyl radical which can add to the olefin. Reaction of the new radical with the ruthenium(III) halide would then regenerate the catalyst and form the observed product.[266]

The selective *o*-deuteration of phenol catalyzed by $RuCl\{P(OPh)_3\}_3\{P(OPh)_2(OC_6H_5)\}$ was found to be much slower than originally reported. The ortho positions on the triphenylphosphite ligands did exchange readily with D_2. Deuteration of the phenol was suggested to occur by transesterification of free, deuterated triphenylphosphite and was found to be accelerated by KOPh.[267]

V. Reviews and Theses

General reviews of the chemistry of ruthenium and of osmium for for the year 1980-1981 were published.[268,269,270] A review of the chemistry of the platinum metals for the year 1984 included sections on chemistry of ruthenium and osmium.[271] The literature for the year 1983 of complexes containing metal carbon sigma bonds of the iron, cobalt and nickel triads was reviewed.[272] A review of alkoxy derivatives of the platinum metals including osmium and ruthenium,appeared.[273]

Information on the following Ph.D theses was taken from Dissertation Abstracts B.

Theses appeared on mononuclear osmium and ruthenium complexes and their application to oxidation of organic and inorganic molecules. Studies in the coordination of bis-hydroxylbenzamido chelating ligands to chromium, iron, and osmium was the subject of a thesis by Spies. The thesis includes a survey of the organometallic chemistry of osmium, and discusses the oxidation of the low valent carbonyl complexes, $Ru(CO)_3L_2$ and $PtL_2(C_2H_4)$ by osmium complexes.[274] Roecker reported on the reactivity of $[(bpy)_2(py)Ru(O)]^{2+}$ in the oxidation of various organic molecules, including the conversion of formate to CO_2, alcohols to aldehydes and ketones, DMSO to sulfone.[275]

Metal phosphine complexes were investigated. A thesis by Hommeltoft on ruthenium complexes of 1,1,1-tris(diphenylphosphinomethyl)ethane included oxidative addition reactions of $Ru(CO)_2$(triphos), and the formation of chiral complexes.[276] Research in the synthesis and characterization of new compounds of osmium in middle oxidation states was reported by Kibala. The thesis concerns chemistry of coordition compounds, as well as organometallic halides and oxides of osmium. An X-ray crystal structure of $OsBr_2(PPh_3)_2(CO)(AcOH)$ was included.[277]

Three theses appeared on dinuclear osmium and ruthenium complexes. Ruthenium complexes containing chelating di-phospines were the subjects of a thesis by Thorburn. The complexes $Ru_2Cl_5(P\text{-}P)_2$ were synthesized from $RuCl_3(PPh_3)_2(DMA)$. With complexes of chiral di-phosphines, asymmetric hydrogenation of olefins was catalyzed.[278] A thesis by Rosenberg reported on phosphido-bridged binuclear complexes of osmium with molybdenum, chromium and tungsten, including $(CO)_4W(\mu\text{-}PPh_2)Os(CO)_3$.[279] A thesis by Feldmann reported the synthesis, characterization and electrochemistry of novel dimeric Ru(II,III) complexes, including ruthenium carboxylate and amide-bridge dimers.[280]

Osmium and ruthenium clusters were studied as models for active catalysts. Taube's thesis included the chemistry of $Ru_3(CO)_{11}(CO_2CH_3)^-$, its substitution reactions with phosphines, and the kinetics of substitution. Reactions of the triruthenium clusters was studied with respect to their relevance to the water gas shift reaction.[281] Triosmium clusters were investigated as models for intermediates in catalytic CO hydrogenation reactions by Morrison. Triosmium carbonyl clusters with methylene and ketene ligands and reduction of these species were discussed.[282]

A thesis by Blohm appeared on the synthesis and reactivity of ruthenium carbonyl nitrido clusters. Hydrogenation and hydroformylation of olefins were catalyzed by certain complexes. Reactivity of the nitrogen atom in $[Ru_3(NCO)(CO)_{10}]^-$, $[Ru_4(N)(CO)_{12}]^-$, $[Ru_5(N)(CO)_{14}]^-$, $[Ru_6(N)(CO)_{16}]^-$ was studied.[283]

Flash photolysis of $Ru_3(CO)_{12}$ and addition of substrates was the subject of a thesis by Wink.[284]

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