

Annual Survey of Ruthenium and Osmium for the Year 1984

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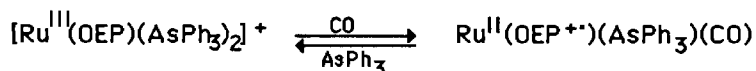
*Previous review see p. 297.

I. Mononuclear Complexes

Organometallic Porphyrin Complexes

The preparation of ruthenium(II) porphyrin complexes with axial phosphine ligands was reported. The axial ligands in the octaethylporphyrin and tetraphenylporphyrin complexes, Ru(porphyrin)(CO)(EtOH), can be substituted for a variety of phosphines to yield Ru(porphyrin)L₂.¹ These ruthenium phosphine porphyrin complexes and the related carbonyl phosphine complexes, Ru(porphyrin)(CO)L, have been oxidized to form the ruthenium(III) porphyrin complexes [Ru(porphyrin)L₂]X and Ru(porphyrin)LX, where X = Br or Cl.² The oxidation of Ru(porphyrin)(CO)(ROH) by t-butyl hydroperoxide produces dimeric ruthenium(IV) porphyrin complexes with bridging oxo ligands, [Ru(porphyrin)(OR)]₂O and [Ru(porphyrin)X]₂O.³ A dioxoruthenium tetramesitylporphyrin complex was reported.⁴ The oxidation of ruthenium octaethylporphyrin triphenylphosphine complexes with O₂ produces RuO₂ and the phosphine oxide. It is proposed that this occurs through an inner sphere mechanism, while the oxidation of PPh₃ by O₂ catalyzed by Ru(OEP)(PPh₃)₂ proceeds by an outer sphere mechanism.⁵ The synthesis and structure of other binuclear ruthenium and osmium porphyrin complexes has been reported.^{6,7} The preparation of an oxo ruthenium(IV) complex of a saturated macrocyclic tetramine⁸ and oxo osmium complexes with a multianionic chelating ligand^{9,10} were reported.

A reversible, intramolecular electron transfer between ruthenium and the octaethylporphyrin ligand was observed. The displacement of carbon monoxide by triphenylarsine in a ruthenium(II) porphyrin π -cation radical complex results in the formation of a ruthenium(III) porphyrin complex.¹¹



The ¹H NMR spectrum of a ruthenium(II) porphyrin π -cation radical complex, [Ru(OEP)(CO)][ClO₄], was obtained.¹² The photolysis of a carbonyl complexes of ruthenium(II) porphyrin π -cation radicals was observed with picosecond transient absorption techniques.¹³ The lifetime of the products was less than 35 picoseconds in most cases.

The metallation of an N,N'-vinyl bridged tetraphenylporphyrin with Ru₃(CO)₁₂

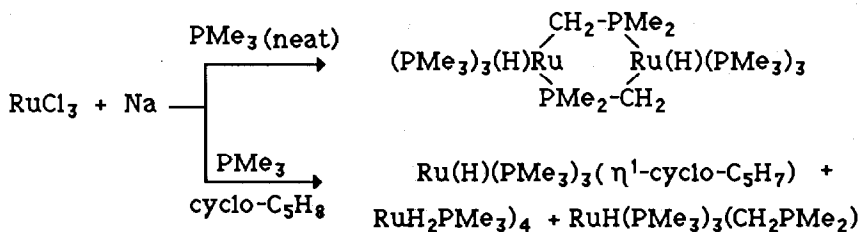
gives two products. The major product, previously characterized, is $\text{Ru}(\text{TPP})(\text{C}=\text{CR}_2)$. An alkyl-ruthenium(II) amido complex, resulting from the insertion of a ruthenium atom into a pyrrole C-N bond, was isolated in 30% yield and characterized by X-ray crystallography.¹⁴

Organometallic Carborane Complexes

The metallocarborane, $\text{closo-1-Os}(\text{CO})_3\text{-2,3-}[\text{CSiMe}_3]_2\text{-B}_4\text{H}_4$, has been prepared by the reaction of $\text{Os}_3(\text{CO})_{12}$ with either $\text{closo-Sn}[\text{CSiMe}_3]_2\text{B}_4\text{H}_4$ or $\text{nido-}[\text{CSiMe}_3]_2\text{B}_4\text{H}_4$.¹⁵ The carbonyl ligands on the ruthenium vertex of another metallocarborane, $1\text{-Ru}(\text{CO})_3\text{-2,3-}[\text{CH}]_2\text{B}_8\text{H}_8$, react with a variety of nucleophiles, including H- , OH- , MeO- and MeLi .¹⁶ A $\text{closo-ruthenaundecaborane}$, $[1,1\text{-}(\text{PPh}_3)_2\text{-1,5-}(\text{OEt})_2\text{-1-RuB}_{10}\text{H}_8]$, was prepared in 40% yield from $\text{closo-B}_{10}\text{H}_{10}^{2-}$ and $\text{RuCl}_2(\text{PPh}_3)_3$.¹⁷ Homo- and hetero-bimetallic metallaboranes, $(\text{PPh}_3)\text{Cl M'ClMB}_{10}\text{H}_8(\text{OEt})_2$ where M and M' are either Ru or Os, have been prepared by the reaction of $\text{M'Cl}_2(\text{PPh}_3)_2$ with $\text{closo-}(\text{PPh}_3)_2\text{MB}_{10}\text{H}_8(\text{OEt})_2$.¹⁸

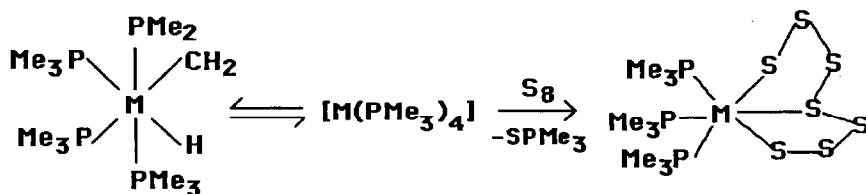
Complexes of Phosphorus Ligands

Several groups have prepared new complexes of Os(II) and Ru(II) with the trimethylphosphine ligand. The reduction of RuCl_3 with sodium sand in neat PMe_3 leads to a ruthenium dimer, isolated in 36% yield, in which a C-H bond of the phosphine has been oxidatively added to the metal. When the reduction is carried out in the presence of PMe_3 and cyclopentene, a mixture of mononuclear products are formed. C-H bonds from either the phosphine or the C_5 ring are activated at the reduced metal.¹⁹



The metallated phosphine complex, $(\text{PMe}_3)_3\text{M}(\text{H})(\text{CH}_2\text{PMe}_2)$ where M = Os or Ru, reacts with S_8 to form the first polysulfido metal complex with a tridentate S_7^{2-} ligand.

The unstable tetraphosphine complex is an intermediate in the reaction.²⁰



Another metallated phosphine complex, $(\text{PMe}_3)_3\text{Ru}(\text{CH}_2\text{PMe}_2)\text{Cl}$, was prepared from *cis*- $\text{Ru}(\text{O}_2\text{CMe})\text{Cl}(\text{PMe}_3)_4$ and $\text{LiN}(\text{SiMe}_3)_2$. The bistrimethylsilylamide acts as a base rather than as a nucleophile in the reaction. Similarly, *cis*- $\text{Ru}(\text{O}_2\text{CMe})_2(\text{PMe}_3)_4$ and two equivalents of $\text{LiN}(\text{SiMe}_3)_2$ give $(\text{PMe}_3)_2\text{Ru}(\text{CH}_2\text{PMe}_2)_2$. Both the mono- and bis-metallated phosphine complexes react with hydrogen to cleave the metal carbon bond and form the corresponding hydrido ruthenium trimethylphosphine complexes.²¹ The osmium(II) trimethylphosphine complexes, $\text{Os}(\text{O}_2\text{CMe})_2(\text{PMe}_3)_4$ and $\text{OsCl}_2(\text{PMe}_3)_4$, are alkylated with magnesium alkyls. The methyl complex *cis*- $\text{Me}_2\text{Os}(\text{PMe}_3)_4$ is formed from MgMe_2 . Metallo-cycles are isolated from the reactions of $\text{Os}(\text{O}_2\text{CMe})_2(\text{PMe}_3)_4$ with bis-trimethylsilylmethylmagnesium and benzylmagnesium chloride, presumably from gamma-hydride activation and loss of alkane from a dialkyl intermediate. The reaction of $\text{OsCl}_2(\text{PMe}_3)_4$ and $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ forms the metallated phosphine complex $(\text{PMe}_3)_3\text{Os}(\text{CH}_2\text{PMe}_2)\text{Cl}$.²²

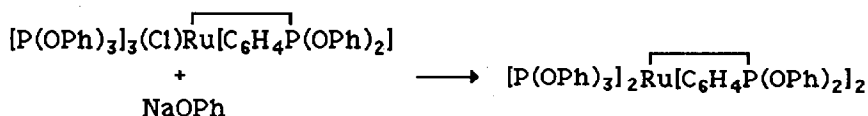
The preparation of alkyl, hydride and borohydride complexes of ruthenium(II) has been described. The complex $\text{RuClMe}(\text{PMe}_3)_4$ was converted to $\text{RuXMe}(\text{PMe}_3)_4$, where $X = \text{Me}, \text{H}, \text{MeCO}_2$, and *mer*- $\text{RuH}(\text{BH}_4)(\text{PMe}_3)_3$ was prepared from the ruthenium dichloride or hydrido-chloride complexes. As with the osmium complex, alkylation of $\text{RuCl}_2(\text{PMe}_3)_4$ with benzylmagnesium chloride or neopentylmagnesium chloride gives five-membered metalocycles.²³ Reaction of R_2Mg ($\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) with $\text{RuCl}_2(\text{PMe}_3)_4$ gives alkyl-hydride complexes, *cis*- $\text{Ru}(\text{H})\text{R}(\text{PMe}_3)_4$.²⁴ The complexes $(\text{C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2\text{X}$, where X is an alkyl, hydride or a halide ligand, were prepared.²⁵

It was found that $[\text{CpFe}(\text{CO})_2]_2$ catalyzed substitution reactions on $\text{CpRu}(\text{CO})_2\text{I}$ with

a variety of phosphine and phosphite groups. L. The complexes $\text{CpRu}(\text{CO})\text{LI}$ and $[\text{CpRu}(\text{CO})_2\text{L}_2]\text{I}$ were produced.²⁶

The synthesis of new phosphine complexes was reported. Two isomers of bis(anilinopyridine)bis(triphenylphosphine)ruthenium were prepared and characterized by X-ray diffraction.²⁷ Another new triphenylphosphine complex, $\text{OsBr}_3(\text{PPh}_3)_2(\text{MeCN})$, was prepared from $[\text{OsBr}_6]^{2-}$.²⁸ The preparation, structure and electronic spectra of tricyclohexylphosphine complexes of ruthenium(II) and osmium(II) were discussed.²⁹

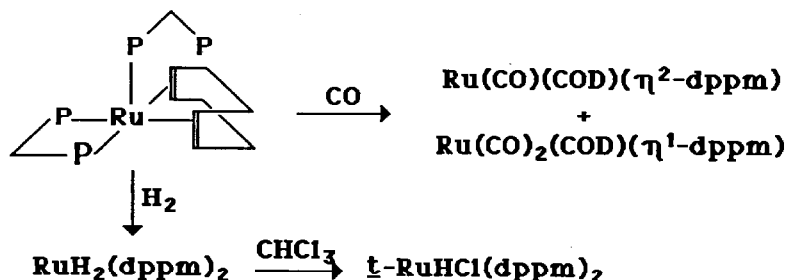
Deuteration of various phosphines coordinated to ruthenium in the complexes RuH_4L_3 was observed. The solvents C_6D_6 or C_7D_8 were the deuterium sources. It was found that $\text{P}(\text{NEt}_2)_3$ was deuterated more rapidly than $\text{P}(\text{C}_6\text{H}_{11})_3$ which was deuterated more rapidly than $\text{P}(\text{Pr}^i)_3$.³⁰ The phosphine complexes $\text{RuHCl}(\text{C}_6\text{Me}_6)\text{L}$, where L is a trialkyl or triarylphosphine, were prepared from $[\text{RuCl}_2(\text{C}_6\text{Me}_6)]_2$. C-H activation of the phosphine ligands resulted in cyclometallated products.³¹ Orthometallation of triphenylphosphine by an osmium dimer resulted in the isolation of a binuclear complex with bridging metallated phosphines. The structure was determined.^{32,33} Sodium phenoxide induced ortho-metallation of a second triphenylphosphite ligand in $[\text{P}(\text{OPh})_3]_3(\text{Cl})\text{Ru}[\text{C}_6\text{H}_5\text{OP}(\text{OPh})_2]$. An X-ray crystal structure was obtained on the product.³⁴



Cyclometallation of a variety of trialkyl and triaryl phosphines was observed when $[\text{RuCl}_2(\eta\text{-C}_6\text{Me}_6)]_2$ was treated with PR_3 in the presence of sodium carbonate and isopropanol.³¹

A ruthenium complex with a monodentate diphenylphosphinomethane group, $\text{RuCl}(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$, was prepared from $\text{RuCl}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ and dppm. The unbound phosphorus can be methylated by methyl iodide. Displacement of either chloride or triphenylphosphine from the metal coordination sphere produces the dihapto dppm complexes $[\text{Ru}(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)\text{-}$

$(\eta^2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^+$ and $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$ respectively.³⁵ Mono- and di-hapto diphenylphosphinomethane complexes of ruthenium(0) and ruthenium(II) were prepared by treatment of $\text{Ru}(\text{COD})(\text{COT})$ with dppm .³⁶ Carbonyl and hydrido derivatives were prepared by reaction of $\text{Ru}(\text{COD})(\eta^1\text{-dppm})(\eta^2\text{-dppm})$ with CO and hydrogen.



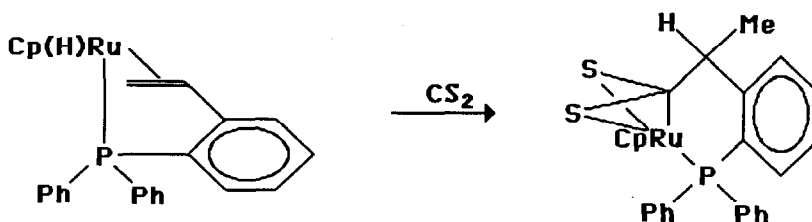
Reduction of OsCl_6^{4-} and $\text{Ru}_2\text{OCl}_{10}^{4-}$ followed by treatment with dppm results in the formation of *cis*- $\text{MCl}_2(\text{dppm})_2$ and *trans*- $\text{RuCl}_2(\text{dppm})_2$.³⁷

A diphenylphosphinoethane complex, $\text{Ru}(\text{dppe})_2(\eta^2\text{-CH}_2=\text{CHPh})$, was prepared by reaction of dppe with $\text{Ru}(\text{PPh}_3)_2(\eta^2\text{-CH}_2=\text{CHPh})_2$.³⁸ The styrene ligand can be displaced with CO or $\text{P}(\text{OR})_3$. Thermolysis of trialkylphosphite complexes, $\text{Ru}(\text{dppe})_2(\text{P}(\text{OR})_3)$, forms $\text{Ru}(\text{dppe})_2(\text{H})(\text{O}=\text{P}(\text{OR})_2)$ while ortho-metallation of one or both dppe ligands results from the heating of $\text{Ru}(\text{PPh}_3)_2(\eta^2\text{-CH}_2=\text{CHPh})_2$. The all *trans* octahedral complexes: $\text{RuCl}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PMe}_2\}_2$, $\text{RuHCl}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PMe}_2\}_2$, and $[\text{RuX}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PMe}_2\}_2]^+$ and trigonal bipyramidal complexes: $[\text{RuX}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PMe}_2\}_2]^+$, where $\text{X} = \text{H}$ or Cl , were reported.³⁹ A diphenylphosphinobutane complex, $\text{RuCl}_2(\text{PPh}_3)(\text{dppb})$ was isolated. ³¹P NMR suggests that this molecule is in equilibrium with a dimer, $[\text{RuCl}(\text{dppb})(\mu\text{-Cl})]_2$.⁴⁰

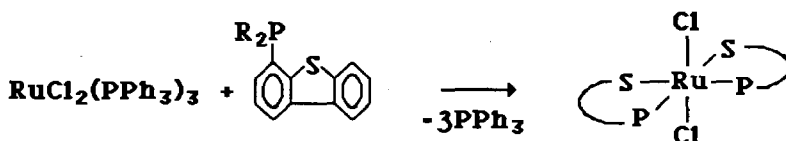
The substitution of chloride for acetonitrile in the diastereomers of $\text{CpRuCl}[(R)\text{-Ph}_2\text{PCHCH}_3\text{CH}_2\text{PPh}_2]$ was found to proceed with retention of configuration at ruthenium. A crystal structure of the (*S*)-diastereomer was determined.⁴¹

Complexes of ruthenium and osmium with chelating ligands containing one

phosphine unit were reported. A ruthenium complex of an unsaturated phosphine ligand was prepared.⁴² An X-ray structure of *trans*- $\text{Ru}(\text{CO})\text{Cl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{PPh}_2)$ showed that the metal is six-coordinate, bound to the C-C double bond as well as to both phosphorus atoms of the ligand. Ruthenium and osmium complexes of another unsaturated phosphine were prepared.⁴³ The complex $(\eta^5\text{-C}_5\text{H}_5)\text{OsBr}(\text{sp})$, where $\text{sp} = 2\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$, was characterized by its X-ray crystal structure. The complexes $\text{RuBr}_2(\text{sp})_2$, $\text{CpRuCl}(\text{sp})$, and $\text{CpRuH}(\text{sp})$ were also prepared and the reaction of $\text{CpRuH}(\text{sp})$ with CS_2 was reported.



Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPhCH}_2\text{CH}_2\text{C}_5\text{H}_5$, where $n = 3$ or 4 , gave complexes $\text{RuCl}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPhCH}_2\text{CH}_2\text{C}_5\text{H}_4)$ having penta-hapto coordination of the C_5 ring as well as coordination of both phosphorus atoms to the metal.⁴⁴ The first coordination complex of a dibenzothiophene was prepared. $\text{RuCl}_2(\text{PPh}_3)_3$ reacts with 4- R_2P -dibenzothiophene to give $\text{RuCl}_2(4\text{-R}_2\text{P}(\text{DBT}))_2$.⁴⁵ An X-ray crystal structure shows that the dibenzothiophene ligand is coordinated through both sulfur and phosphorus.



The phenylphosphine complex $[\text{Os}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}(\text{PH}_2\text{Ph})]^+$ can be deprotonated to form a phenylphosphido complex. This complex, $\text{Os}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}(\text{PPh})$, will add methyl iodide or methanol to form $[\text{Os}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}(\text{PHMePh})]^+$ and $\text{Os}(\text{PPh}_3)_2(\text{CO})_2\{\text{PH}(\text{OMe})\text{Ph}\}$.⁴⁶ An osmium(II) complex with an iodophenylphosphide ligand was prepared. The reaction of $\text{Os}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}(\text{PIPh})$

with AgSbF_6 in the presence of methanol gives $[\text{Os}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}\{\text{PH}(\text{OMe})\text{Ph}\}]^+$. A phosphinidine intermediate was proposed.⁴⁷

Hydrides

A molecular orbital study of structural and electronic effects in organometallic hydride complexes predicted that $\text{CpOs}(\text{CO})_2\text{H}$ and related species should function as hydride donors rather than proton donors in their reactions.⁴⁸

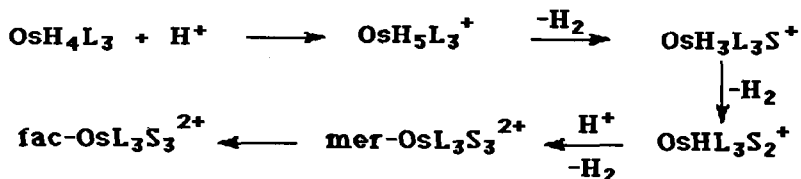
The preparation of hydrido carbonyl complexes of ruthenium and osmium with polypyridyl ligands, including $\text{cis-}[M(\text{chelate})_2(\text{CO})\text{H}]^+$, $\text{trans-}[\text{Os}(\text{chelate})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$, and $[\text{Os}(\text{chelate})(\text{diphos})(\text{PR}_3)\text{H}]^+$, was reported.⁴⁹ The carbonyl hydride complexes $\text{cis,mer- RuH}_2(\text{CO})(\text{PMe}_2\text{Ph})_3$ and $\text{mer- RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3$ were prepared from $\text{mer- RuH}(\eta^2\text{-BH}_4)(\text{PMe}_2\text{Ph})_3$, NaBH_4 and Cl^- in ethanol.⁵⁰ Also reported were the synthesis and ligand exchange reactions of some cyclopentadienyl hydride complexes of ruthenium and osmium including: $\text{CpM}(\text{H})(\text{PPh}_3)_2$, $\text{CpRu}(\text{H})\text{L}_2$, and $\text{CpRu}(\text{H})\text{L}'(\text{PPh}_3)$ where $\text{M} = \text{Os, Ru}$; $\text{L} = 1/2 \text{ dppe}$, $1/2 \text{ dppm}$, $1/2 \text{ dpae}$ or AsPh_3 , and $\text{L}' = \text{CNBu}^\dagger$ or $\text{P}(\text{OPh})_3$.⁵¹ The bond dissociation energy for Ru-H in the gas phase was found to be $41 \pm 3 \text{ kcal/mol}$, a value similar to that found for Rh-H and Pd-H . This compares with the Ru-CH_3 bond dissociation energy of $54 \pm 5 \text{ kcal/mol}$.⁵²

The reaction of $\text{RuH}_2(\text{PPh}_3)_4$ with either S_8 or H_2S yielded $\text{RuH}(\text{SH})(\text{PPh}_3)_3$. The intramolecular rearrangement and intermolecular SH exchange reactions of this complex were studied by ^1H NMR.⁵³

The reactions of anionic transition metal hydrido complexes, including $\text{HRu}(\text{CO})_4^-$, with alkyl halides was studied. The reactivity of $\text{HRu}(\text{CO})_4^-$ for halide displacement from alkyl halides was found to be low relative to anionic hydrido complexes of the Cr and V triads.⁵⁴

The reaction chemistry of some ruthenium and osmium polyhydrides has been studied. A ruthenium polyhydride was found to activate C-H bonds in saturated hydrocarbons. The dehydrogenation of cyclooctane to cyclooctene was catalyzed by $\text{RuH}_4[\text{P}(\text{p-C}_6\text{H}_4\text{F})_3]_3$. 3,3-Dimethyl-1-butene was used as the hydrogen acceptor. The triphenylphosphine complex $\text{RuH}_4(\text{PPh}_3)_3$ was less active.⁵⁵ A dihydrido arene complex, $\text{Ru}(\text{C}_6\text{Me}_6)\{\text{PH}(\text{C}_6\text{H}_{11})_2\}_2\text{H}_2$, was found to activate the C-H bonds in

benzene.⁵⁶ The osmium polyhydride complex, $\text{OsH}_4(\text{PPh}_3)_3$, can be protonated at low temperature by HBF_4 in acetonitrile. Hydrogen loss follows protonation and the product, *fac*- $[\text{Os}(\text{PPh}_3)_3(\text{NCMe})_3]^{2+}$, was characterized by ^{31}P NMR.⁵⁷ Hydrogen is also lost from $(\text{PPh}_3)_3\text{MH}_2(\text{CO})$, where $\text{M} = \text{Ru}$ or Os , after reaction with $(\text{CF}_3\text{SO}_2)_2\text{CHPh}$. The product of the reaction was $[(\text{Ph}_3\text{P})_3\text{MH}(\text{CO})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$.⁵⁸ The step-wise, reductive acidolysis of $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ was observed by ^1H and ^{31}P NMR.⁵⁹



The osmium polyhydride, $\text{OsH}_6(\text{PPhPr}^i_2)_2$, reacts with mercury dichloride to form an adduct, $\text{OsH}_6(\text{PPhPr}^i_2)_2(\text{HgCl}_2)$.⁶⁰ The reaction between $\text{OsH}_6[\text{P}(\text{cyclopentyl})_3]_2$ and $\text{BH}_3\cdot\text{THF}$ produces $\text{H}_2\text{B}(\mu\text{-H}_2)\text{OsH}_3[\text{P}(\text{cyclopentyl})_3]_2$ in quantitative yield. The product has been structurally characterized.⁶¹

Carbonyls

Treatment of $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ with S_8 under a CO atmosphere gives $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{Cl}$. Addition of L, where $\text{L} = \text{CO}$, PMe_3 or $\text{P}(\text{OPh})_3$, displaces the chloride from the coordination sphere to form $[\text{CpRu}(\text{PPh}_3)(\text{CO})\text{L}]\text{Cl}$.⁶²

Photosubstitution reactions of $[\text{Ru}(\text{bpy})_2\text{XY}]^{n+}$ were studied. The ligands XY included $(\text{PPh}_2\text{Me})_2$, $(\text{CO})\text{Cl}$, and $(\text{CO})_2$ as well as various nitrogen donor ligands.⁶³ Carbonized coconut shell was used to store CO for the preparation of red ruthenium carbonyl.⁶⁴

The electrochemistry of some carbonyl ruthenium catecholates and semiquinone complexes was reported.⁶⁵

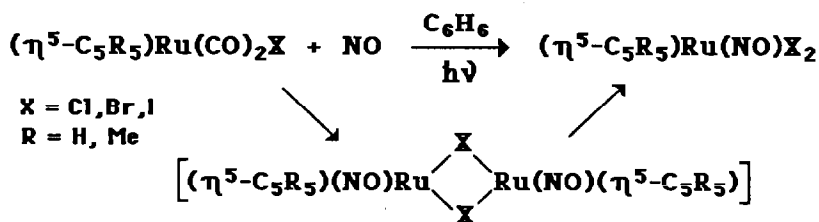
Reactions of ruthenium(II) carbonyl complexes have been reported. The reaction of polymeric $\text{Ru}(\text{CO})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) with 2,2':6',2''-terpyridine gave $\text{Ru}(\text{CO})_2\text{X}_2(\text{tpy})$. An X-ray crystal structure of $\text{Ru}(\text{CO})_2\text{Br}_2(\text{tpy})$ shows that the terpyridine ligand is

bidentate. A tridentate terpyridine ligand is found in $\text{Ru}(\text{CO})\text{X}_2(\text{tpy})$. The *cis* form of this molecule is prepared by treating $\text{Ru}(\text{CO})_2\text{X}_2$ with Me_3NO , while the *trans* form is prepared from the terpyridine and RuCl_3 in DMF. Both were structurally characterized.⁶⁶ A variety of bidentate donor ligands, L, (where L = N-benzoyl-N-phenylhydroxylamine, 2-hydroxy-phenones, salicylaldehyde, hydrazone, and β -diketones) react with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ to form $\text{RuCl}(\text{CO})(\text{PPh}_3)_2\text{L}$.⁶⁷

The preparation of ruthenium and osmium complexes with other donor ligands has been reported. Osmium(III) and osmium(IV) complexes of a variety of bi- and polydentate thioethers have been prepared from OsX_6^{2-} and excess thioether in 2-ethoxyethanol.⁶⁸ Mixed isocyanide-halide complex of osmium, $\text{t-Os}(\text{CNR})_4\text{X}_2$, can be prepared from $\text{OsO}_2\text{X}_2(\text{PPh}_3)_2$, $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2\text{X}_4(\text{PPh}_3)_2$ or from $[\text{OsBr}_6][\text{NH}_4]_2$.^{69,70} Open-chain polyether carboxylic acids, HL, react with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ to give $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{L}_2$. One of these has been characterized by X-ray crystallography.⁷¹

Nitrosyls and Other Nitrogen Ligands

Evidence for the rapid intramolecular interconversion of linear and bent nitrosyl in $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2][\text{BF}_4]$ was obtained by ^{15}N NMR.⁷² Another nitrosyl complex, $\text{Na}_2\text{Ru}(\text{CN})_5(\text{NO})$, was prepared by the reaction of RuCl_3 with NaCN and HNO_3 . It was characterized by X-ray crystallography.⁷³ The formation of a mononuclear ruthenium nitrosyl from the nitrosylation of $(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{CO})_2\text{X}$ was proposed to result from the disproportionation of a binuclear intermediate.⁷⁴

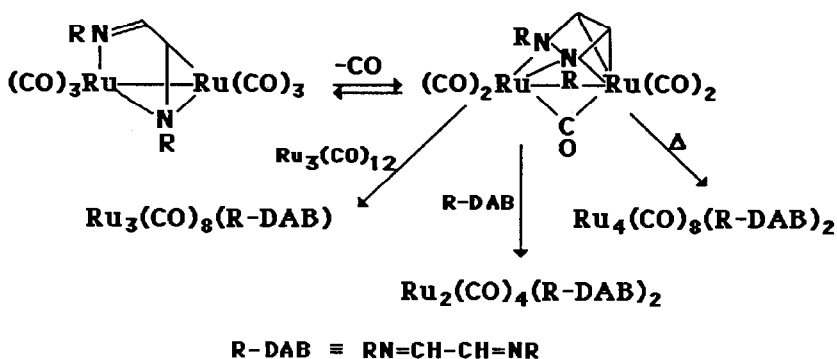


The reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NO})\text{Cl}_2$ with either AlMe_3 or AlEt_3 in the presence of added ligand ultimately forms either a cyanide complex, $(\eta^5\text{-C}_5\text{Me}_5)\text{RuL}_2(\text{CN})$, or a carboxamide complex, $(\eta^5\text{-C}_5\text{Me}_5)\text{RuL}_2\{\text{NHC}(\text{O})\text{CH}_3\}$, respectively. It was proposed

that these products form from the thermally induced insertion of nitrosyl into a Ru-C bond of the initially formed dialkyl-nitrosyl complex, $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NO})\text{R}_2$.⁷⁵ Coupling of the nitrosyl group in $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ with $\text{IC}(\text{N}_2)\text{CO}_2\text{Et}$ gave, after treatment with HCl , $\text{Os}(\text{PPh}_3)_2\text{Cl}_2(\text{N}_2)\{\text{N}(\text{OH})\text{CHCO}_2\text{Et}\}$. The aldoxime group was converted to a nitrile with a dehydrating agent.⁷⁶

Thionitrosyl complexes, $\text{M}(\text{NS})\text{Cl}_3(\text{PPh}_3)_2$ where $\text{M} = \text{Os}$ or Ru , was prepared by the reaction of $(\text{NSCl})_3$ with $\text{MCl}_2(\text{PPh}_3)_3$. The thionitrosyl group was found to be linear by X-ray diffraction in the osmium complex.⁷⁷ Another thionitrosyl complex, $[\text{Os}(\text{NS})\text{Cl}_4]^-$, was prepared from the nitride, $[\text{Os}(\text{N})\text{Cl}_4]^-$, and KCNS . The structure of $[\text{PPh}_4][\text{Os}(\text{H}_2\text{O})(\text{NS})\text{Cl}_4]$ was determined.⁷⁸

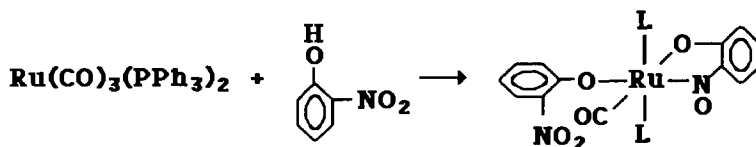
A ruthenium(VI) complex of triazene-1-oxide was reported.⁷⁹ The reaction of *cis*- $\text{RuMe}_2(\text{PMe}_3)_4$ with trimethylsilylazide produces *cis*- $\text{Ru}(\text{N}_3)_2(\text{PMe}_3)_4$ in 75% yield.⁸⁰ A diazabutadiene complex of ruthenium was prepared from $(\text{PhCN})_4\text{RuCl}_2$ and $\text{RN}=\text{CR}-\text{CR}=\text{NR}$. The green *trans*- $(\text{RN}=\text{CR}-\text{CR}=\text{NR})_2\text{RuCl}_2$ isomerized to the violet *cis* complex at 130° .⁸¹ Reactions of binuclear diazobutadiene complexes were reported.⁸²



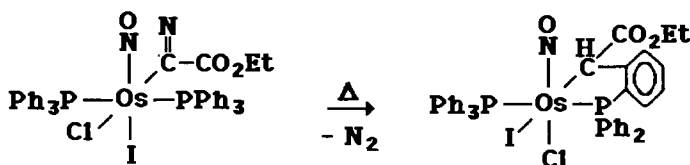
The ^{15}N NMR and ^{31}P NMR spectra of a series of terminal N_2 complexes of Mo , W , Re , Fe , Ru , Os , and Rh were obtained. The nitrogen shielding constant increased with atomic number in a series and down in a group. Among the complexes studied were $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Br}$, and *mer*- $[\text{OsXY}(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$ where $\text{X} = \text{Cl}$, Br , H and $\text{Y} = \text{Cl}$, Br .⁸³

The reaction of 2-nitrophenol with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ produces

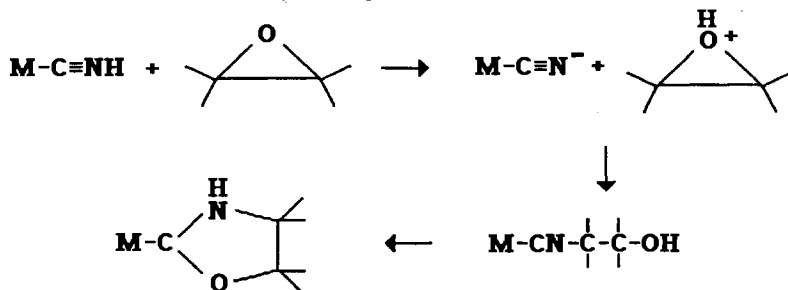
$\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{OC}_6\text{H}_4\text{NO}_2)(\text{OC}_6\text{H}_4\text{NO})$. The product, in which one nitro group has been deoxygenated, was characterized by X-ray diffraction.⁸⁴



An α -diazoalkylosmium complex, was prepared from $\text{OsCl}(\text{NO})\text{L}_3$ where $\text{L} = \text{PPh}_3$, $\text{Hg}(\text{CN}_2\text{CO}_2\text{Et})$, and I_2 . *trans*- $\text{OsL}_2\text{Cl}(\text{NO})\text{I}\{\text{C}(\text{N})\text{CO}_2\text{Et}\}$ loses N_2 . The carbyne complex inserts into the ortho C-H bond of a PPh_3 to give a metallocycle which was characterized by X-ray crystallography.⁸⁵



Osmium hydrazine complexes $[\text{OsCl}(\text{COD})(\text{NH}_2\text{NR}_2)_3]\text{X}$ ($\text{R}=\text{H}, \text{Me}$; $\text{X}=\text{BPh}_4, \text{PF}_6$) can be prepared from $[\text{OsCl}_2(\text{COD})]_x$ and the hydrazine. These complexes can be converted to a variety of hydrazine and hydrazone complexes of osmium.⁸⁶ The metal stabilized isocyanic acids, $\text{H}_4\text{M}(\text{CN})_6$ where $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$, react with epoxides.⁸⁷



Alkyl, Aryl Complexes

A review was published on the chemistry of μ -alkanediyl complexes of transition metals, including ruthenium and osmium complexes of the type $\text{L}_x\text{M}-(\text{CH}_2)_n-\text{M}'\text{L}_y$ ($n \geq 2$).⁸⁸ Another review concerned cyclometallated complexes incorporating a

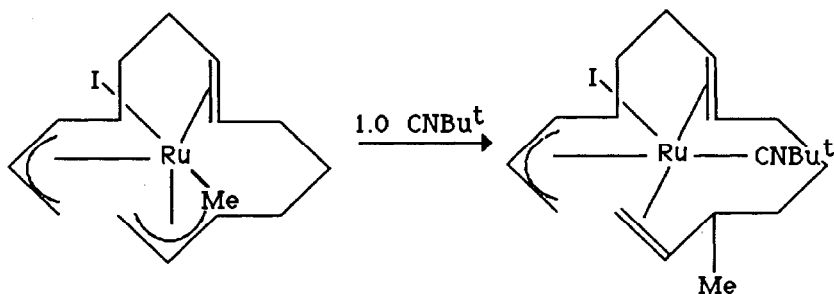
heterocyclic donor atom.⁸⁹

The syntheses and reactions of dialkyl complexes of ruthenium(II) were reported. Dialkyl, diaryl and mixed alkyl-aryl complexes of ruthenium(II) were prepared from *cis*- or *trans*- [Ru(CO)₂Cl₂L₂] and LiR or HgR₂.⁹⁰ The reductive elimination of the ketone, R₂CO, from Ru(CO)₂R₂(PMe₂Ph) was found to be intramolecular. The kinetics were first order for the reaction.⁹¹ The diaryl complex, RuL₂(CO)₂R₂ where R = 4-MeC₆H₄, decomposes in CHCl₃. A product resulting from CO insertion, C-C bond formation, and ortho C-H activation was isolated.⁹² The kinetics of the reaction between Ru(CO)₂MeR(PMe₂Ph)₂, where R = Ph, COMe or Me, and *t*-butylisocyanide were studied. Migration of Me to CO is followed by migration of R to the isocyanide.⁹³ Similar migration reactions were observed with *t*-butylisocyanide and Ru(CO)₂RR'(PMe₂Ph)₂, where R and R' are substituted aryl groups. Migration of aryl to CO was found to be rate determining. The more electron releasing aryl group migrated to CO.⁹⁴ Oxidative cleavage reactions of the Ru-C bond in CpRuLL'R (L,L'=CO, PPh₃; R=Me,PhCH₂) with halogens, HCl, mercury(II) halides and copper(II) halides were studied. The ruthenium alkyls were found to be less susceptible to oxidative cleavage than the analogous iron complexes.⁹⁵ Ruthenium(II) alkyl complexes were prepared by the insertion of unsaturated organic molecules into the Ru-H bond of hydride complexes. Methyl, ethyl and butyl acrylates insert into the Ru-H bond of HRuCl(CO)(PPh₃)₃ to give *b*-carboalkoxy complexes of ruthenium(II), RuCl(CO)(PPh₃)₂(CH₂CH₂COOR).⁹⁶ Ethylene reacts with HRuCl(CO)₂(PPh₃)₂ to give Ru{C(O)Et}Cl(CO)(PPh₃)₂. The reactions of this propionyl complex with CO, isocyanides, HCl and Ag⁺ were studied.⁹⁷ Loss of alkane from CpRu(PPh₃)R, where R is a variety of alkyl or aryl groups, gives an orthometallated phosphine product. Ethylene inserts into the Ru-C bond of the metallocycle. Ethylene can also insert into the Ru-C bond of CpRu(PPh₃)Ph.⁹⁸

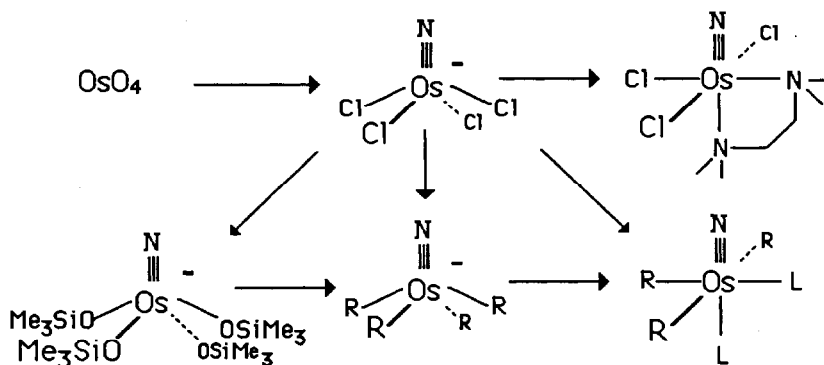
The UV-Vis absorption spectra of some carbon-bound ruthenium(II) imidazole complexes was reported. The LMCT band in copper(II) and ruthenium(II) imidazoles can be correlated.⁹⁹

A phosphorus ylide, CH₂PMe₃, was found to react with a carbonyl ligand on [(η⁵-C₅Me₅)Ru(CO)₃][BF₄] or (η⁵-C₅Me₅)Ru(CO)₃X, where X = Cl or I, to form (η⁵-C₅Me₅)Ru(CO)₂{C(O)CH=PMe₃}.¹⁰⁰

Alkyl complexes of ruthenium and osmium in high oxidation states were reported. The first ruthenium(IV) alkyl complexes were prepared. The reaction between (1-3-6-7:10-12- η -C₁₂H₁₈)RuCl₂ and LiMe produced the dimethyl complex. (1-3-6-7:10-12- η -C₁₂H₁₈)RuI₂Me was also synthesized.¹⁰¹ Reductive elimination from these complexes is observed upon reaction with neutral ligands, including CO, phosphites and isocyanides. An intermediate can be isolated in the reaction of Me₃CNC with (1-3-6-7:10-12- η -C₁₂H₁₈)RuI₂Me.¹⁰²



The synthesis of a series of osmium(VI) alkyl complexes, [Os(N)R₄][NBu₄], where R = Me, CH₂SiMe₃, CH₂CMe₃, and CH₂Ph, was reported.¹⁰³



Formyl and Related C₁ Ligands

The syntheses and reactions of several formyl complexes was reported. The reaction of a copper hydride, [(PPh₃)CuH]₆, with CpRu(CO)₃⁺ gives a one to one mixture of a ruthenium hydride, CpRu(CO)₂H, and a neutral formyl complex, CpRu(CO)₂(CHO). The formyl complex decomposes in a radical initiated reaction.¹⁰⁴

Lithium aluminum hydride addition to $\text{CpRu}(\text{CO})\text{L}_2^+$ ($\text{L}=\text{PPh}_3$ or $1/2$ dppe) produces a mixture of $(\text{CpH})\text{Ru}(\text{CO})\text{L}_2$, $\text{CpRu}(\text{CO})\text{HL}$, and CpRuMeL_2 . The reaction is proposed to proceed through a formyl intermediate.¹⁰⁵ A cationic formyl complex of ruthenium(II) was prepared.¹⁰⁶ The cationic formyl complex *trans*- $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$ decomposes in methylene chloride with first order kinetics to give *cis*- $[\text{RuH}(\text{CO})(\text{dppe})_2][\text{SbF}_6]$. This isomerizes to the *trans* isomer. No free radicals are involved in the reaction.¹⁰⁷ Nitroxide spin traps react with *trans*- $[\text{Ru}(\text{CHO})(\text{CO})(\text{dppe})_2][\text{SbF}_6]$ to form a radical species from which $\text{CHO}\cdot$ is lost.¹⁰⁸

Thermolysis of the iron and ruthenium metallocarboxylic acids, $\text{CpM}(\text{CO})(\text{PPh}_3)(\text{COOH})$, gave CO_2 and the metal hydride complexes.¹⁰⁹

The electron-rich cyano complexes $\text{CpRu}(\text{dppe})(\text{CN})$ and $\text{CpRu}(\text{PPh}_3)_2(\text{CN})$ were prepared from KCN and $\text{CpRu}(\text{dppe})\text{Cl}$ or $\text{CpRu}(\text{PPh}_3)_2$, respectively. The cyano group can be alkylated with organic electrophiles.¹¹⁰

Si, Sn Complexes

Trichlorotin complexes of ruthenium(II), osmium(II), and iridium(III) were prepared. Among these were *trans*- $[\text{RuCl}_2(\text{SnCl}_3)_4][\text{NMe}_4]$ and $[\text{M}(\text{SnCl}_3)_6][\text{PPh}_4]$, where $\text{M} = \text{Ru}, \text{Os}$. In the ^{119}Sn NMR of these complexes, it was found that the resonance for the SnCl_3 group went to lower field as the number of SnCl_3 groups bound to a metal increased. ^{119}Sn - ^{99}Ru and ^{119}Sn - ^{187}Os coupling constants were reported.¹¹¹

Both loss of CO and reductive elimination of Et_3SiH were observed in the photolysis of *cis-mer*- $\text{RuH}(\text{SiEt}_3)(\text{CO})_3(\text{PPh}_3)$. The photolysis was done both in solution at room temperature and in a low temperature glass (100⁰K).¹¹²

The presence of a "cis effect" of the phosphite was used to explain the preferential substitution of two carbonyls on *cis*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ with $\text{P}(\text{OMe})_3$.¹¹³

Alkylidene, Alkylidyne Complexes

A fluorochlorocarbene complex of osmium, $\text{OsCl}_2(\text{CFCI})(\text{CO})(\text{PPh}_3)_2$, was prepared from $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{Cd}(\text{CF}_3)_2(\text{DME})$. The chloride in the -CFCI unit can be replaced by SEt (from NaSEt) or by NMe_2 (from Me_2NH). The structure of a related fluorocarbene complex of ruthenium, $\text{RuCl}_2(\text{CFOCH}_2\text{CMe}_3)(\text{CO})(\text{PPh}_3)_2$, was determined by X-ray diffraction.¹¹⁴

Carbene complexes of ruthenium can be prepared by the reaction of $\text{CpRu}(\text{CO})_3^+$ with aziridine or oxirane.¹¹⁵

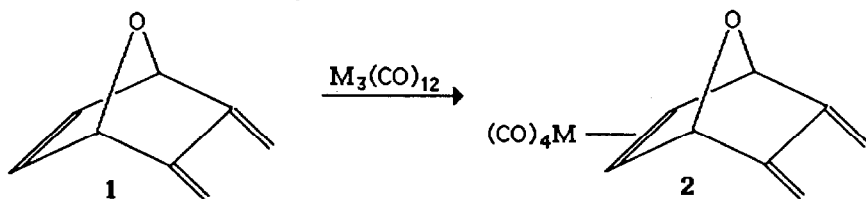
A sulfene complex was obtained from the addition of SO_2 to *trans*- $[\text{Os}(\text{PPh}_3)_2(\text{NO})\text{Cl}(\text{CH}_2)]$.¹¹⁶

Insertion of a chloromethylene group on osmium into the ortho C-H bond of an osmium coordinated PPh_3 was observed.¹¹⁷

π -Complexes

The chemistry of reactive organometallic compounds prepared from metallocenes has been reviewed.¹¹⁸ Evidence for the existence of dimeric forms of ruthenocene and osmocene in the gas phase was reviewed.¹¹⁹

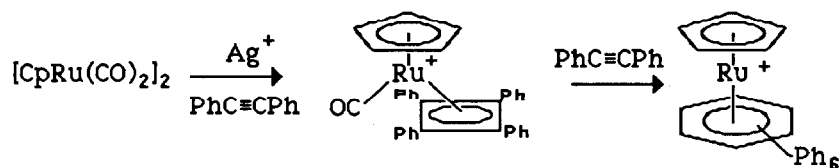
Ruthenium and osmium tetracarbonyl fragments bind to the endocyclic double bond of **1** under photolysis of $\text{M}_3(\text{CO})_{12}$. An additional carbonyl group can be displaced from ruthenium to give a $\text{Ru}(\text{CO})_3(\text{olefin})_2$ complex. The exocyclic diene unit is more active for the Diels-Alder reaction when either ruthenium or osmium is coordinated to the endocyclic double bond.¹²⁰



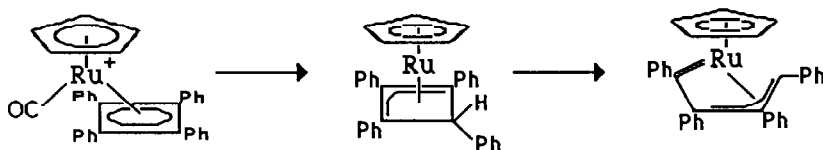
Reactions of cyclooctadiene complexes of ruthenium were reported. The migration of hydride to COD in $[\text{RuH}(\text{PR}_3)_3(\text{COD})]^+$ forms $[\text{Ru}(\text{PR}_3)_3(\eta^3\text{-cyclooctenyl})]^+$. As the size of PR_3 increases, the rate of reaction increases.^{121,122} The reaction of $[\text{RuH}(\text{PR}_3)_3(\text{COD})]^+$ with 1,3-dienes produces $[\text{Ru}(\text{PR}_3)_3(\eta^3\text{-eny1})]^+$. These complexes contain an agostic hydrogen.¹²³ The reduction of RuCl_3 with zinc in the presence of 1,5-COD gives $(1\text{-}3\text{-}5\text{-}6\text{-}\eta^5\text{-COD})_2\text{Ru}$. This rearranges at 70° to $(\eta^6\text{-}1,3,5\text{-cyclooctatriene})(\eta^4\text{-}1,5\text{-COD})\text{Ru}$.¹²⁴

Cyclobutadiene complexes were prepared. The oxidation of $[\text{CpRu}(\text{CO})_2]_2$ with Ag^+ in the presence of diphenylacetylene results in the formation of a cationic ruthenium cyclobutadiene complex. Under photolytic conditions, olefins and

acetylenes insert into the cyclobutadiene, forming cyclohexadienes and substituted benzene rings.¹²⁵



The reaction of $\text{KHB}(\text{Bu}^s)_4$ with $[(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_4\text{Ph}_4)\text{Ru}(\text{CO})]^+$ gives a product in which the cyclobutadiene ligand has been opened.¹²⁶



The reaction of ruthenium atoms with 1,3- or 1,4-cyclohexadiene and carbon monoxide produces $\text{Ru}(\text{CO})(\text{diene})_2$.¹²⁷

Cyclooctatetrene reacts with a ruthenium(II) hydride, $[\text{RuH}(\text{COD})(\text{PMe}_2\text{Ph})][\text{PF}_6]$, to form an η^5 -bicyclo[5.1.0]octadienyl complex of ruthenium.¹²⁸

A series of ruthenium(0) arene complexes have been prepared by arene exchange with $(\eta^4\text{-COD})\text{Ru}(\eta^6\text{-naphthalene})$.¹²⁹ The effects of arene substitution and temperature on the photochemical arene substitution in $[\text{CpRu}(\eta^6\text{-arene})]^+$ has been studied.¹³⁰

Addition and substitution reactions of nucleophiles with π -arene complexes have been reported by several workers. Bis-arene complexes of ruthenium have been converted into bis-cyclohexadienylruthenium complexes by sequential additions of hydride and acid. The products are cyclohexadienyl analogs of ruthenocene.¹³¹ The chemistry of $[(\text{arene})\text{RuCp}]^+$ complexes has been studied. Nucleophilic substitution of halogens on the ring and nucleophilic addition of hydride and Ph^- has been observed. Substituents on the ring can be readily oxidized.¹³² A variety of carbanions, LiR , add to the benzene ring of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{PMe}_3)_2][\text{PF}_6]$ and $[(\eta^6\text{-C}_6\text{H}_6)\text{OsI}(\text{PMe}_3)_2][\text{PF}_6]$ forming η^5 -hexadienyl complexes.¹³³ Hydride abstraction of $(\eta^5\text{-C}_6\text{H}_5\text{R})\text{OsI}(\text{PMe}_3)_2$ with $[\text{CPh}_3][\text{PF}_6]$ generates the alkyl substituted

arene complex, $[(\eta^6\text{-C}_6\text{H}_5\text{R})\text{OsI}(\text{PMe}_3)_2][\text{PF}_6]$ in quantitative yield.¹³⁴ Trialkyl, and aryl phosphines attack the coordinated benzene ring of several η^6 -benzene complexes of ruthenium(II) to give (6-phosphonio- η^5 -cyclohexadienyl)-ruthenium(II) complexes. Addition of CF_3COOH converts the hexadienyl ligand to benzene.¹³⁵

Chloride can be extracted from $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2\text{L}$ with AgPF_6 in acetone to give $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{Me}_2\text{CO})][\text{PF}_6]$. The coordinated acetone is readily lost to give $\{[(\eta^6\text{-C}_6\text{Me}_6)\text{RuL}]_2(\mu\text{-Cl})_2\}[\text{PF}_6]$, for $\text{L} = \text{PMe}_3$ or PMePh_2 . When $\text{L} = \text{PPh}_3$, one of the several products resulting from loss of acetone is a bis-arene complex of ruthenium(II) in which a phenyl ring of PPh_3 is π bonded to the metal.¹³⁶

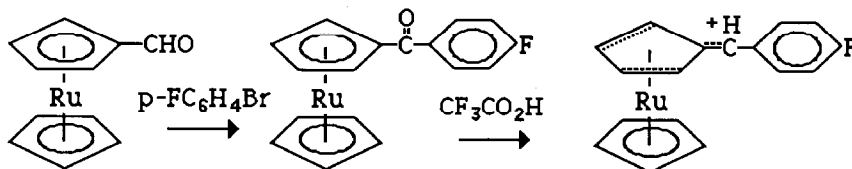
The reaction of the ruthenium and osmium arene complexes, $[\text{M}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$, with excess aqueous sodium hydroxide or sodium carbonate produces hydroxide complexes previously characterized as $[\text{M}_2(\eta^6\text{-C}_6\text{H}_6)_2(\text{OH})_3]^+$. A crystal structure shows it to be a tetramer with an oxo group bridging all four metal atoms, $[\text{M}_4(\eta^6\text{-C}_6\text{H}_6)_4(\mu_2\text{-OH})_4(\mu_4\text{-O})]^{2+}$.¹³⁷ An improved synthesis of $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2(\text{OMe})_3][\text{BPh}_4]$ was reported. Treatment of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$ with NaNH_2 followed by $\text{ROH}/\text{NaBPh}_4$ gives the bridging alkoxide complexes. The structure of one of these was determined by X-ray diffraction.¹³⁸

An η^4 -octamethylnaphthalene complex of ruthenium has been prepared and characterized by X-ray crystallography. $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ will add to $[\text{Ru}(\eta^4\text{-OMN})(\eta^6\text{-arene})]$ to give a product with $\text{Cr}(\text{CO})_3$ coordinating in an η^6 fashion to one ring of OMN and $\text{Ru}(\eta^6\text{-arene})$ coordinating in an η^4 fashion to the other.¹³⁹

The absolute configuration of chiral ruthenium complexes, $(\eta^5\text{-C}_5\text{H}_4\text{R}^*)\text{Ru}(\text{CO})_2\text{L}$ where R^* is menthyl or neomenthyl, was determined by X-ray diffraction.¹⁴⁰

Several reports have been published on the chemistry of cyclopentadienyl complexes of ruthenium. Syntheses of several homologous series of CpRu complexes were reported. Displacement of X (where $\text{X} = \text{Br}^-$, SCN^- , OCN^-) from CpRuXL_2 occurred in ethanol, acetonitrile and dimethylsulfoxide solvents.¹⁴¹ The

haloruthenocene(IV) complexes, $[\text{Cp}_2\text{RuX}][\text{PF}_6]$ where $\text{X} = \text{Cl}$ or Br , react with water to form $(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_4\text{O})\text{RuX}$ in 30% yield. This constitutes an oxidation of a cyclopentadienyl ligand to a cyclopentadienone.¹⁴² Protonation of *p*-fluorophenylcyclopentadienyl ketone complex of ruthenium gave a complex in which charge is extensively delocalized.¹⁴³



The pentamethylcyclopentadienyl ruthenium oligomer, $[(\text{C}_5\text{Me}_5)\text{RuCl}_2]_n$ was prepared from RuCl_3 and $\text{C}_5\text{Me}_5\text{H}$ in ethanol. Reaction with cyclic dienes or α,ω -diphosphines displaced two chloride ligands and formed monomeric derivatives.¹⁴⁴ The reaction of $\text{K}[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2]$ with HCl , MeI , MeOCH_2Cl , HSiCl_3 and t-BuPCl_2 has been studied. $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2\text{X}$ is formed where $\text{X} = \text{H}$, Me , CH_2OMe , SiHCl_2 or $\text{P}(\text{t-Bu})\text{Cl}$, respectively.¹⁴⁵ Allyl halides oxidatively add to $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})_2\text{X}$ (where $\text{X} = \text{halide}$) to produce ruthenium(IV) complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta^3\text{-C}_3\text{H}_5)\text{X}_2$. Carbon monoxide reverses the reaction.¹⁴⁶

The synthesis of polythiaruthenocenophanes has been accomplished. The products are thiacycrocrown ethers with ruthenocene subunits.¹⁴⁷ The synthesis of $[3](1,1')[3](3,3')$ and $[4](1,1')[4](3,3')$ ruthenocenophanes was reported.¹⁴⁸ The structure of cryptands incorporating ruthenocene units has been studied by NMR, using INEPT and DEPT polarization transfer sequences and 2-D NMR.¹⁴⁹ Ruthenocenophanes were prepared in 17-48% yield from $(\eta^5\text{-C}_5\text{H}_4\text{SNa})_2\text{Ru}$ and $\text{BrCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{Br}$, where $n=2-4$.¹⁵⁰ The synthesis and some chemistry of the dication of hexamethyl $[3]$ dibenzeneruthenophane were reported.¹⁵¹

A substituted pentafulvene reacts with $\text{CpRu}(\text{MeCN})_3^+$ to form functionalized ruthenocenes.¹⁵² An azaborolanyl ruthenium sandwich was synthesized by the reaction of ruthenium dichloride with $[\text{cyclo-C}_3\text{H}_3\text{B}(\text{Me})\text{N}(\text{CMe}_3)]\text{Li}$. The structure of the product was determined by X-ray diffraction.¹⁵³ A metastable ruthenocenium was

observed in the photolysis of ruthenocene.¹⁵⁴

A trimethylenemethane complex of osmium was synthesized by the reaction of $(\text{Me}_3\text{SiCH}_2)(\text{CH}_2\text{X})\text{C}=\text{CH}_2$, where $\text{X} = \text{CH}_3\text{C}(\text{O})\text{O}$ or Cl , with $\text{Os}(\text{CO})_2(\text{PPh}_3)_2$. HCl protonates the trimethylenemethane ligand, converting it to η^3 -2-methyl allyl.¹⁵⁵

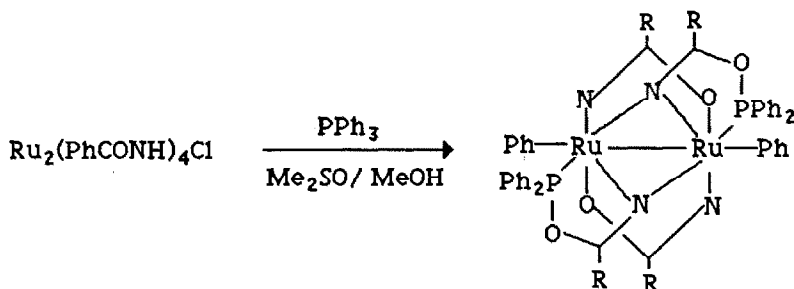
II. Dinuclear Complexes

Homodinuclear Complexes

The organic chemistry of di-ruthenium and tri-ruthenium complexes has been reviewed.¹⁵⁶

The reaction of osmium atoms with mesitylene produces $[\{(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Os}\}_2(\mu\text{-H})_2(\mu\text{-CHC}_6\text{H}_3\text{Me}_2)]$ in 15% yield and a dimer with a metal-metal triple bond, $[\{(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Os}\}_2(\mu\text{-CHC}_6\text{H}_3\text{Me}_2)]$, in 3% yield.¹⁵⁷

The peralkyl metal complexes, M_2R_6 , (where $\text{M} = \text{Ru}$ or Os and $\text{R} = \text{CH}_2\text{SiMe}_3$, CH_2Ph or CH_2CMe_3) have been prepared by the alkylation of $\text{Ru}_2(\text{O}_2\text{CMe})_4\text{Cl}$ or $\text{Os}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ with RMgCl . The crystal structure of $\text{Ru}_2(\text{CH}_2\text{CMe}_3)_6$ shows the two ruthenium atoms to be joined by a triple bond.¹⁵⁸ $\text{Ru}_2(\text{O}_2\text{CMe})_4\text{Cl}$ reacts with molten PhCONH_2 to form the bridging amide complex, $\text{Ru}_2(\text{PhCONH})_4\text{Cl}$. Addition of PPh_3 to this complex gives a phenyl substituted ruthenium dimer, $\text{Ru}_2\text{Ph}_2(\text{PhCONH})_2[\text{Ph}_2\text{POC}(\text{Ph})\text{N}]$.¹⁵⁹



Dimeric ruthenium(II) complexes with bridging carboxylato and aquo ligands have been prepared from $\text{Ru}(\eta^3\text{-C}_3\text{H}_4\text{R})(\text{COD})$ and $\text{R}'\text{COOH}$, where $\text{R}' = \text{CF}_3$, CCl_3 or CH_2Cl . The reactions of $[\text{Ru}(\text{O}_2\text{CR}')_2(\text{COD})]_2$ with phosphines and CO have been studied.¹⁶⁰

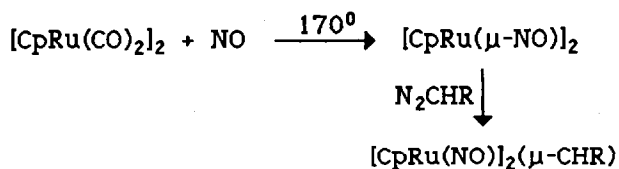
Dinuclear complexes can be stabilized by bridging diphosphorus ligands.

Dehalogenation of $[(\eta^6\text{-C}_6\text{H}_4\text{-1-Me,4-CHMe}_2)\text{RuCl}_2]_2$ in the presence of dppe or dppm forms new ruthenium dimers with bridging diphosphine groups. A Ru_2Fe cluster can be formed by the reaction of one of the bridging diphosphine complexes and $\text{Fe}_2(\text{CO})_9$.¹⁶¹ The complexes $\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-L})_2$, where $\text{L} = (\text{RO})_2\text{PN}(\text{R}')\text{P}(\text{OR})_2$, can be formed by the photolysis of $\text{Ru}_3(\text{CO})_{12}$ with excess L.¹⁶² 1,3',4,4'-Tetramethyl-1,1'-diphosphaferrocene (DPF) will displace triphenylphosphine from $(\text{PPh}_3)_3\text{RuCl}_2$ to form a ruthenium dimer with bridging chlorides and bridging DPF ligands. Excess DPF reacts with RuCl_3 to form a monomeric complex, *trans*- $\text{RuCl}_2(\text{DPF})_4$.¹⁶³

Dinuclear hydride complexes were reported. The reaction of $[(\eta^6\text{-arene})\text{RuX}_2]_2$ with H_2 and NEt_3 gives a μ -monohydride complex, $[(\eta^6\text{-arene})\text{RuX}]_2(\mu\text{-H})(\mu\text{-X})$. Similar μ -monohydrides are produced in the reaction with 2-propanol.¹⁶⁴ The X-ray crystal structure of $\{\text{RuH}(\text{COD})\}_2(\text{pyazoyl})_2(\text{H})$ shows that this complex has a semibridging hydride. ^1H and ^{13}C NMR spectra show that this structure persists in solution.¹⁶⁵

The dimeric ruthenium complex, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_4$, reacts with ethylene under irradiation to produce an ethylene complex, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})(\text{C}_2\text{H}_4)(\mu\text{-CO})$, and two bridging alkylidene complexes, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHMe})$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{Me})\text{CHCH}_2\}$.¹⁶⁶ A series of bridging alkylidene complexes, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHR})$ where $\text{R} = \text{H, Me, Et, Ph}$ or $\text{C H} = \text{C H}_2$, can be synthesized by reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{C}(=\text{O})\}$ with phosphorus ylides, Ph_3PCHR .¹⁶⁷ The bridging methylene ligands in the complexes $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{dppe})(\mu\text{-CO})(\mu\text{-CH}_2)$ can be protonated to form bridging agostic methyl groups. A methyne complex, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{dppe})(\mu\text{-CO})(\mu\text{-CH})]^+$, has been formed from $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\text{dppe})(\mu\text{-CO})(\mu\text{-CH}_3)]^+$ and characterized by X-ray diffraction.¹⁶⁸ A cyclopentadienyl ruthenium nitrosyl dimer with bridging methylene or propylidene

groups has been prepared.¹⁶⁹

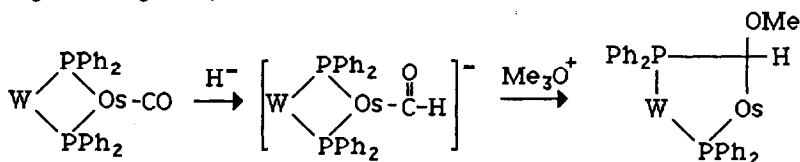


The fulvalene bridged ruthenium carbonyl complex, $(\text{C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_4$, can be prepared efficiently from fulvalene and $\text{Ru}_3(\text{CO})_{12}$. The related mixed metal complex $(\text{C}_{10}\text{H}_8)\text{RuMo}(\text{CO})_4$ can be prepared from fulvalene, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Mo}(\text{CO})_6$.¹⁷⁰ These fulvalene-bridged complexes, $(\text{C}_{10}\text{H}_8)\text{M}^1\text{M}^2(\text{CO})_4$ where $\text{M}^1 = \text{Ru}$ and $\text{M}^2 = \text{Ru}$ or Mo , react photochemically with alkynes. For example, $(\text{C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_4$ and C_2H_2 form a dimetalocyclobutene complex.¹⁷¹

Heterodinuclear Complexes

The heterobimetallic complex, $(\text{CO})_5\text{OsRu}(\text{CO})_3(\text{SiCl}_3)\text{Br}$, having an osmium to ruthenium donor-acceptor bond, dissociates in solution. Isomerization and recombination gives $\text{Br}(\text{CO})_4\text{OsRu}(\text{CO})_4(\text{SiCl}_3)$.¹⁷² The reaction between $\text{W}(\text{CO})_5(\text{THF})$ and $\text{Os}(\text{CO})_4(\text{PMe}_3)$ forms $(\text{CO})_4(\text{PMe}_3)\text{OsW}(\text{CO})_5$ in 55% yield. The product has an osmium to tungsten donor-acceptor bond. The CO ligands were found to scramble between the two metals.¹⁷³

A carbene ligand formed on $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)\text{Os}(\text{CO})_3(\text{PMePh}_2)$ by treating it with LiHBEt_3 and Me_3OBF_4 , inserts into one of the bridging phosphido ligands.^{174,175}



A Ru-Co dimetallic complex, $(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$, can be prepared from $(\eta^6\text{-p-cymene})\text{RuCl}_2(\text{PPh}_2\text{X})$ and $\text{Co}_2(\text{CO})_8$.¹⁷⁶ One carbonyl group on ruthenium can be substituted for hydride with NaBH_4 . The product, $[(\text{CO})_3\text{HRu}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$, has been characterized by X-ray diffraction.¹⁷⁷ CO

and diphenyl acetylene insert into the P-Co bond of the bridging phosphide in $(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ to give $(\text{CO})_3\text{Ru}(\mu\text{-CO})\{\mu\text{-PPh}_2\text{C}(\text{O})\text{C}(\text{PH})=\text{CPh}\}\text{Co}(\text{CO})_2$. Carbon monoxide is lost thermally to give $(\text{CO})_3\text{Ru}(\mu\text{-CO})\{\mu\text{-PPh}_2\text{C}(\text{Ph})=\text{CPh}\}\text{Co}(\text{CO})_2$.¹⁷⁸

$[\text{K}][\text{OsH}_3(\text{PMe}_2\text{Ph})]$ reacts with $\text{Cp}_2\text{Zr}(\text{X})\text{Cl}$, where $\text{X} = \text{Cl}$ or H , to give $\text{Cp}_2\text{Zr}(\text{X})(\mu\text{-H})_3\text{Os}(\text{PMe}_2\text{Ph})_3$. The product with $\text{X} = \text{Cl}$ has been structurally characterized.¹⁷⁹ $(\text{C}_5\text{Me}_5)_2\text{ZrH}_2$ reacts with $\text{CpRuH}(\text{CO})_2$ and $\text{CpRuH}(\text{CO})(\text{PMe}_3)$ to form the heterobimetallic complexes $\text{CpRuH}(\mu\text{-CO})_2\text{Zr}(\text{C}_5\text{Me}_5)_2$ and $\text{Cp}(\text{PMe}_3)_2\text{Ru}(\mu\text{-CH}_2\text{O})\text{Zr}(\text{C}_5\text{Me}_5)_2$. While $\text{CpRu}(\text{CH}_3)(\text{CO})_2$ reacts with $(\text{C}_5\text{Me}_5)_2\text{ZrH}_2$ in the presence of PMe_3 to give $(\text{C}_5\text{Me}_5)_2\text{ZrH}(\text{OCH}=\text{CH}_2)$ and $\text{CpRu}(\text{CO})(\text{PMe}_3)\text{H}$.¹⁸⁰

$\text{NaFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ reacts with $\text{CpRuI}(\text{CO})_2$ to give $\text{Cp}(\text{CO})\text{Ru}(\mu\text{-CO})_2\text{Fe}(\text{CO})\text{Cp}$ in 80% yield. Photochemical substitution reactions on this complex occur without Ru-Fe bond breaking. Reactions with alkynes occur faster than with the dimers $[\text{CpM}(\text{CO})_2]_2$, $\text{M} = \text{Fe}$ or Ru .¹⁸¹

III. Polynuclear Complexes

There have been several recent reviews of particular aspects of the chemistry of cluster compounds of osmium and ruthenium. Electron counting procedures for clusters of the iron triad were reviewed.¹⁸² A review of transition metal clusters containing main group heteroatoms also extensively discussed complexes of ruthenium and osmium.¹⁸³ The reactions of tri-osmium clusters with a wide range of organic compounds were summarized.¹⁸⁴ A review appeared on aspects of clusters $\text{M}_3\text{-M}_{10}$ derived from $\text{M}_3(\text{CO})_{12}$.¹⁸⁵

Ru₃ and Os₃ Complexes

Theoretical and Spectroscopic Studies

A theoretical study discussed the preference of Os and Ru toward forming clusters of the type $\text{M}_3(\text{CO})_{12}$ rather than forming one dimensional polymer ribbon aggregates.¹⁸⁶

A number of reports dealt with spectroscopy of the M_3 clusters. C_2 hydrocarbon fragments on tri-osmium and di- and tri-ruthenium clusters were investigated by ^{13}C

NMR and IR spectroscopy. The organic fragments included $\eta^2\text{-C}_2\text{H}_4$, $\mu\text{-CMe}$, $\mu_3\text{-}\eta^2\text{-HCCH}$, $\mu_3\text{-CCH}$, and $\mu\text{-CHMe}$. The results were compared with spectra obtained from the rearrangement of acetylene on Ni(111) and Fe(110) surfaces.¹⁸⁷ The intramolecular rearrangement of the $\sigma\text{-}\pi$ -acetylide ligand in $\text{Os}_3\text{H}(\text{CO})_{10}(\text{CCC}_6\text{H}_5)$ was studied by ^{13}C NMR.¹⁸⁸ The Raman spectra of $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_4\text{H}_4(\text{CO})_{12}$ were obtained in solution.¹⁸⁹ The Raman and IR spectra of a single crystal of $\text{Ru}_3(\text{CO})_{12}$ was also obtained. The cluster retains D_{3h} vibrational identity in the crystal.¹⁹⁰ The dynamics of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ in solution were studied by ^{13}C and ^{17}O NMR. This molecule has a C_{2v} structure in the crystalline state and in solution at low temperature. ^{13}C magnetisation transfer was used to study slow carbonyl exchange processes in solution.¹⁹¹ The kinetic deuterium isotope effect on μ -hydride and carbonyl ligand migrations in osmium and ruthenium clusters was studied.¹⁹²

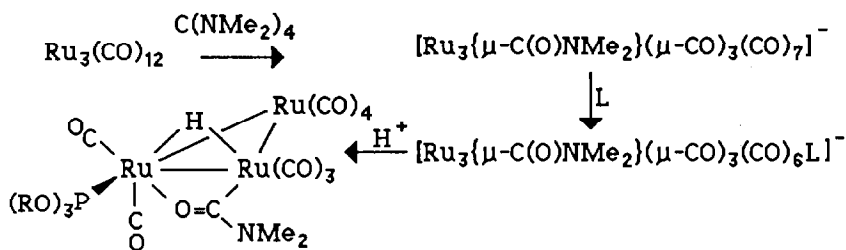
An electrochemical investigation of the ruthenium clusters, $\text{HRu}_3(\text{CO})_9(\mu_3\text{-allenyl})$, $\text{HRu}_3(\text{CO})_9(\mu_3\text{-allyl})$, and $\text{HRu}_3(\text{CO})_9(\mu_3\text{-alkynyl})$ was carried out. Delocalized π systems coordinated to the clusters caused both reduction and oxidation to be more difficult. The cluster framework was retained on reduction of these complexes.¹⁹³ The electrochemistry of 24 mixed metal clusters was studied. Variations in the redox potential of metal clusters was brought about by variations in both the metals and the ligands.¹⁹⁴

M_3 Complexes with Simple Ligands

Complexes containing bridging hydride and bridging halide ligands were prepared. Ion pairing in salts of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-CO})(\text{CO})_{10}]^-$ was studied.¹⁹⁵ Highly dissociated salts, such as $[\text{PPN}][\text{Cl}]$ were found to catalyze substitution reactions on $\text{Ru}_3(\text{CO})_{12}$. Triaryl phosphines, phosphites and arsines readily substitute for Cl^- in the anionic intermediate, $[\text{PPN}][\text{Ru}_3(\mu\text{-Cl})(\text{CO})_{10}]$, to form $\text{Ru}_3(\text{CO})_{11}\text{L}$.¹⁹⁶ The synthesis and characterization of the halide-bridged complexes, $\text{Ru}_3(\mu\text{-H},\mu\text{-X})(\text{CO})_{10}$ and $\text{Ru}_3(\mu\text{-H},\mu_3\text{-I})$ where $\text{X} = \text{Cl}, \text{Br}$ or I , was reported.¹⁹⁷ The addition of HX to $\text{Os}_3(\text{CO})_{11}\text{L}$ and $\text{Os}_3(\text{CO})_{10}\text{L}_2$ gives $[\text{Os}_3(\mu\text{-H})(\text{CO})_{11}\text{L}]\text{X}$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\text{L}_2]\text{X}$ respectively. The reaction of $\text{Os}_3(\text{CO})_{10}\text{L}_2$ with HCl yields $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\text{L}_2][\text{Os}(\text{CO})_3\text{Cl}_3]$. The

structure of this complex was determined X-ray diffraction.¹⁹⁸

Selectivity in CO substitution reactions has been observed in trinuclear metal clusters with bridging ligands. A site specific enrichment of the dimer, $\text{Ru}_2\{\mu\text{-C}(\text{O})\text{Et}\}_2$, with ^{13}CO was observed.¹⁹⁹ A similar site specific ligand substitution occurs in the reaction of $[\text{C}(\text{NMe}_2)_3][\text{Ru}_3\{\mu\text{-C}(\text{O})\text{NMe}_2\}\{\mu\text{-CO}\}_3(\text{CO})_7]$ with phosphites. Treatment of the product with HSO_3CF_3 produces $\text{Ru}_3\{\mu\text{-C}(\text{O})\text{NMe}_2\}\{\mu\text{-H}\}(\text{CO})_9\text{L}$, having a phosphite ligand on a double-bridged ruthenium atom.²⁰⁰

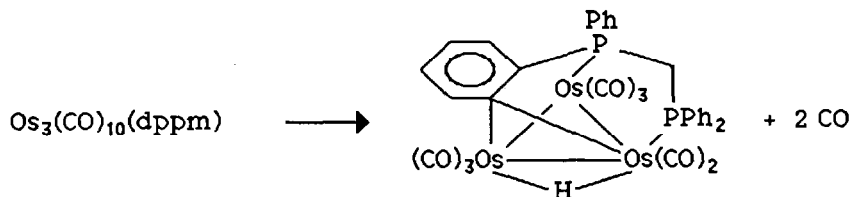


Phosphine substitution in $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})$ with PPh_3 produces $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-OH})(\text{PPh}_3)$ with the phosphine coordinated to one of the doubly-bridged osmium atoms.²⁰¹

Substitution reactions of carbonyl ligands on $\text{Ru}_3(\text{CO})_{12}$ were reported. Substitution of the carbonyls with ^{13}CO is enhanced by the presence of KOME . A methoxycarbonyl intermediate was postulated since such an adduct is in equilibrium with $\text{Ru}_3(\text{CO})_{12}$ in methanol.²⁰² Dimethylphenyl phosphine substitution of a carbonyl group in $\text{Ru}_3(\text{CO})_{12}$ is facilitated by prior reduction of the cluster with an organometallic radical.²⁰³ Reaction of $\text{Ru}_3(\text{CO})_{12}$ with PPh_2H gives a wide range of products depending on reaction conditions. Some of these, including $\text{Ru}_3(\mu_2\text{-PPh}_2)_2(\mu\text{-H})_2(\text{CO})_8$, $\text{Ru}_3(\mu_2\text{-PPh}_2)_3(\mu\text{-H})(\text{CO})_7$, and $\text{Ru}_5(\mu_4\text{-PPh})(\text{CO})_{15}$, have been characterized by X-ray diffraction.²⁰⁴

The kinetics of the formation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})$ from $\text{Os}_3(\text{CO})_{11}(\eta^1\text{-dppm})$ has been studied. The value found for the entropy of activation, $\Delta S^\ddagger = -9.6$ cal, suggests an associative mechanism for this intramolecular bridge forming reaction.²⁰⁵ Tri-osmium diphosphine complexes, $\text{Os}_3(\text{CO})_{10}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}$ where $n = 2-4$,

have been prepared from $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ or $\text{Os}_3(\text{CO})_{10}(\text{C}_4\text{H}_6)$ and the appropriate diphosphine. Isomers with both bridging and chelating diphosphine ligands were characterized.²⁰⁶ $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ loses 2 equivalents of CO in refluxing toluene to give $\text{Os}_3(\text{CO})_8\text{H}\{\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}_2\}$.²⁰⁷



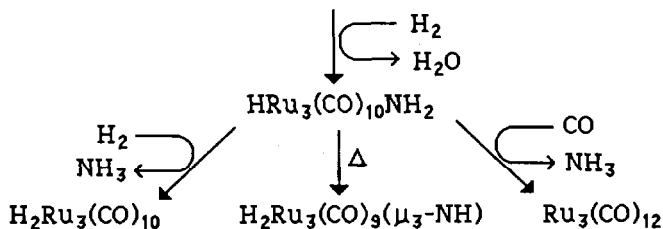
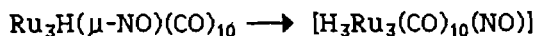
M₃ Clusters with Sulfur-Containing Ligands

A sulfur dioxide complex of osmium, $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\mu\text{-SO}_2)$, was obtained in 30% yield by the reaction of SO_2 with $\text{Os}_3\text{H}_2(\text{CO})_{10}$.²⁰⁸ The structure of this complex is similar to that of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\mu\text{-CH}_2)$. The photochemical decomposition of $\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-SPh})$ produces $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$.²⁰⁹

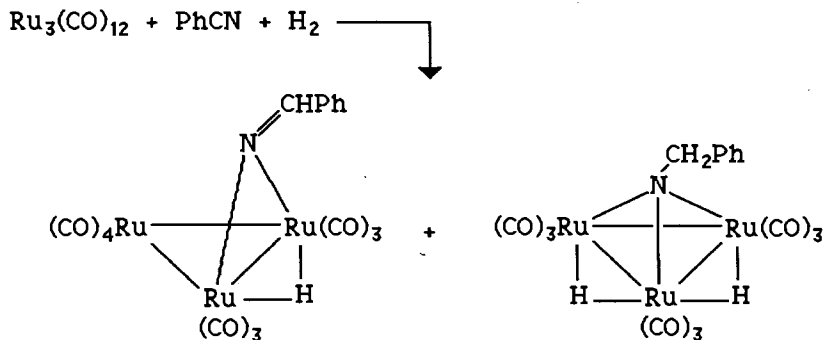
M₃ Clusters with Nitrogen-Containing Ligands

Osmium clusters with μ -carboxamido, μ -formamido, and μ -iminyl groups were synthesized by the reaction of $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3\text{H}_2(\text{CO})_{10}$ with amines and isocyanates.²¹⁰

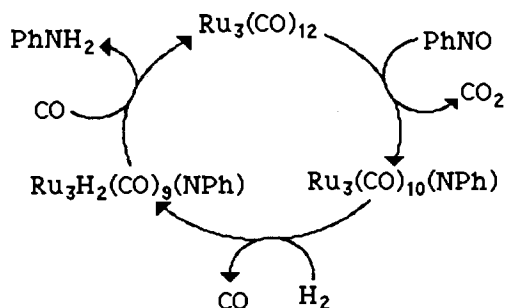
The fluxional properties of $[\text{Os}_3(\mu\text{-NO})(\text{CO})_{10}][\text{PPN}]$ were studied by ^{13}C NMR. At -90° , 6 CO resonances are observed. At 75° , the axial and equatorial carbonyls on each metal exchange rapidly, but there is still no exchange between metal atoms and two CO resonances are observed.²¹¹ The nitrosyl group in $\text{Ru}_3\text{H}(\mu\text{-NO})(\text{CO})_{10}$ can be reduced to NH and NH_2 groups by H_2 .²¹²



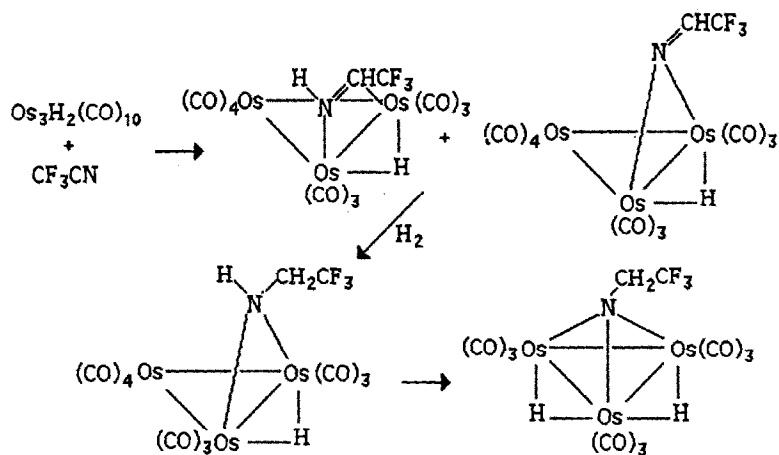
The reduction of PhCN on a ruthenium cluster can be carried out at 130⁰ under 1 atmosphere of H₂.²¹³



A closely related phenylimido complex, Ru₃H₂(CO)₉(μ₃-NPh), was characterized by X-ray diffraction. This species is an intermediate in the catalytic reduction of PhNO to PhNH₂ catalyzed by Ru₃(CO)₁₂.²¹⁴



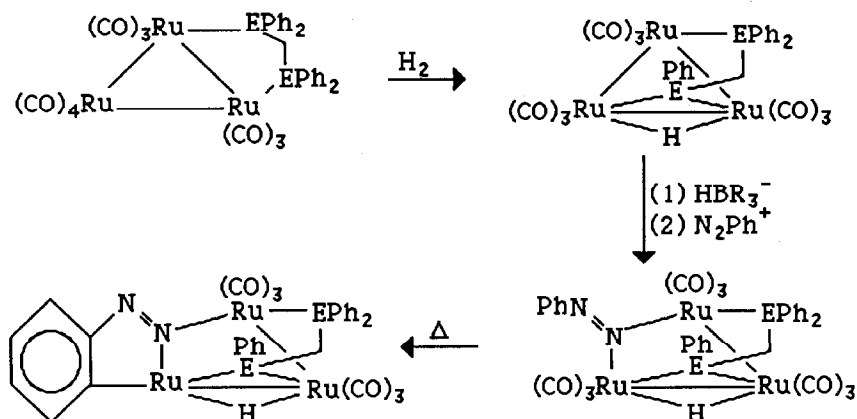
Intermediates in the reduction of CF₃CN on a tri-osmium cluster were identified. Free amine could not be obtained from this reaction, even at 49 atmospheres H₂ and 140⁰.²¹⁵



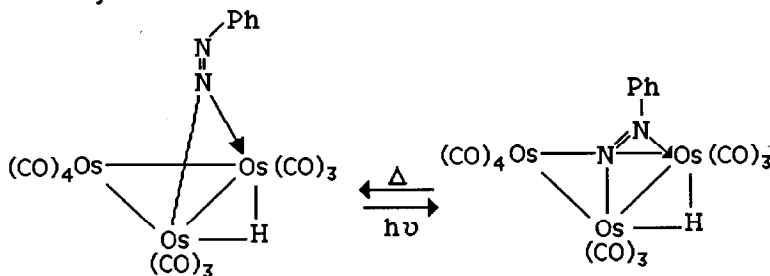
The reaction of $\text{Ru}_3(\text{CO})_{12}$ with PhCN and CH_3COOH formed three products: $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, $\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CHPh})(\text{CO})_{12}$, and $\text{Ru}_3(\mu\text{-H})(\mu\text{-NHCH}_2\text{Ph})(\text{CO})_{10}$. Only $\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CHPh})(\text{CO})_{12}$ is formed when $\text{Ru}_3(\text{CO})_{12}$ and PhCN are treated with H_2 .²¹⁶

Trinuclear osmium clusters $\text{Os}_3(\text{MeCN})(\text{CO})_{11}$ and $\text{Os}_3\text{H}(\text{OH})(\text{CO})_{10}$ reacted with the amino acid esters $\text{NH}_2\text{CHRC}(\text{O})\text{OEt}$, where $\text{R} = \text{H}$ or Me , to give complexes with deprotonated, bridging amino acid groups. The complexes $\text{Os}_3\text{H}(\text{CO})_{10}[\text{C}(\text{O})\text{NHCHRC}(\text{O})\text{OEt}]$ and $\text{Os}_3\text{H}(\text{CO})_{10}[\text{NHCHRC}(\text{O})\text{OEt}]$ were characterized by IR, NMR, mass spectroscopy and X-ray diffraction.²¹⁷

The reactions of a ruthenium complex containing diphenylphosphino-methane or diphenylarsinomethane ligands with H_2 and $[\text{PhN}_2][\text{PF}_6]$ were studied.²¹⁸



The osmium phenyldiazonium cluster, $\text{HOs}_3(\text{CO})_{10}(\text{N}_2\text{Ph})$, was found to interconvert between two isomers. The structures of both isomers have been determined by single crystal X-ray diffraction.²¹⁹



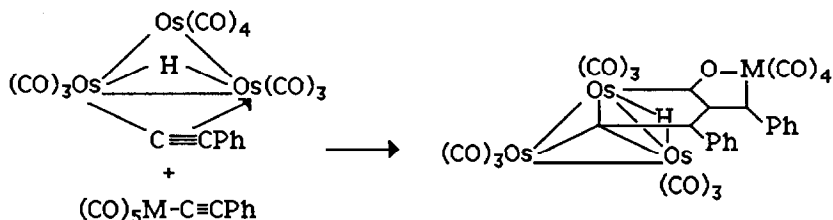
M_3 Clusters with Hydrocarbon Ligands

Tri-ruthenium and tri-osmium clusters containing hydrocarbon ligands were prepared and their reactions studied.

Diphenylacetylene adds to $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-PPh}_2)$ without loss of CO to form $\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-C}_2\text{Ph}_2)$.²²⁰

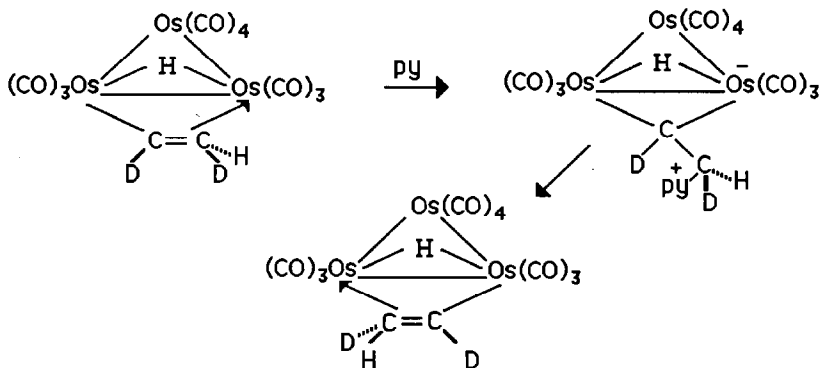
Stoichiometric reduction of CO on the clusters was reported by several workers. The η^1 -acyl complex, $\text{Li}[\text{Os}_3(\text{CO})_{11}(\eta^1\text{-C(O)CH}_3)]$, formed by the reaction of $\text{Os}_3(\text{CO})_{12}$ with LiMe , can be alkylated with $\text{CH}_3\text{OSO}_2\text{CF}_3$. An X-ray crystal structure was obtained for the product, $\text{Os}_3(\text{CO})_9(\eta^1\text{-C(O)CH}_3)(\mu\text{-C(O)CH}_3)$. This complex can be hydrolysed to give Os_3 clusters containing bridging acyl units and either bridging hydrides or hydroxides.²²¹ The stepwise reduction of a carbonyl group on a

were studied and the X-ray crystal structure of one product, $\text{Ru}_3(\mu\text{-H})_3(\mu_3\text{-CPh})(\text{CO})_7(\text{AsPh}_3)_2$, was determined.²²⁶ An acetylide ligand on a tri-osmium cluster has been found to couple with the acetylide ligand on $(\text{CO})_5\text{M}(\text{CCPh})$, where $\text{M} = \text{Mn}$ or Re .²²⁷



Chain growth of an organic fragment bound to a tri-ruthenium cluster has been observed in the reaction of diazomethane with the $\mu_3\text{-}\eta^2$ -acetylide complex, $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-CCCHMe}_2)$, resulting in the formation of an allenyl complex, $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=CCHMe}_2)$. Addition of a second equivalent of CH_2N_2 forms a butadienyl complex, $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu\text{-H})\text{-}\{\mu_3\text{-}\eta^4\text{-CH}_2\text{=CC(CHMe}_2\text{)=CH}\}$ ²²⁸

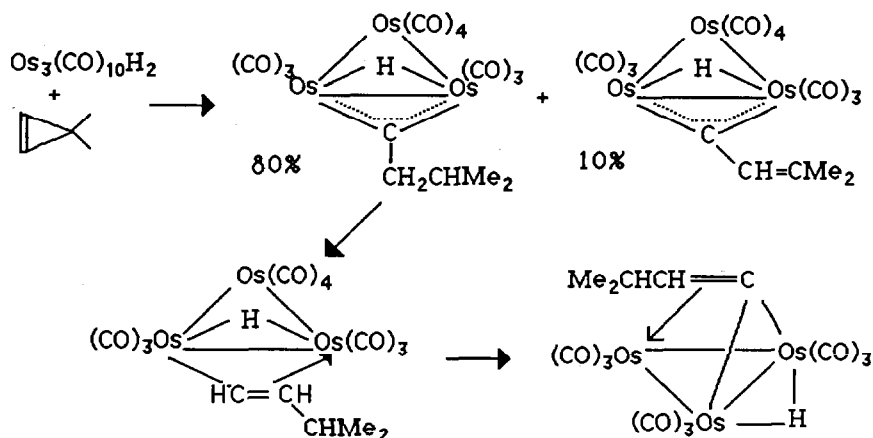
Isomerization and nucleophilic addition to bridging vinyl groups has been observed. Pyridine catalyzes the cis-trans isomerization of the $\mu\text{-}\eta^2$ -vinyl group in $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\eta^2\text{-CD=CDH})$. The intermediate is proposed to be a bridging alkylidene complex.²²⁹



The nucleophiles PMe_2Ph , CN^- , and MeO^- were, also, found to add to the $\mu\text{-}\eta^2$ -vinyl

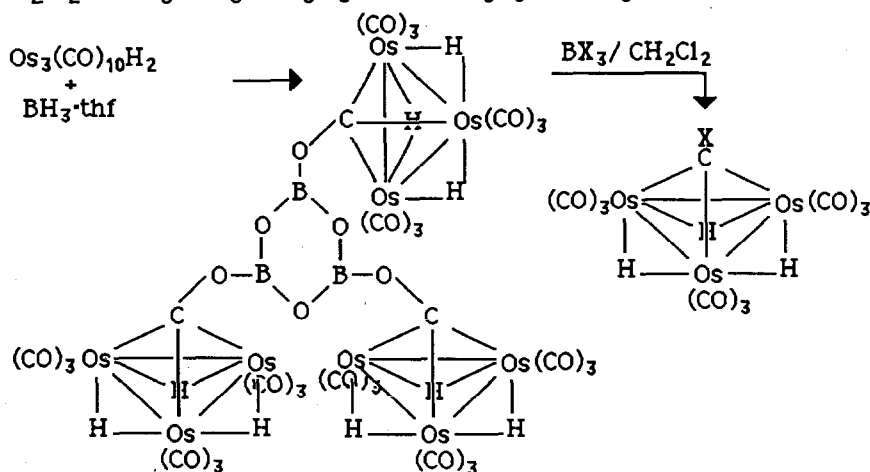
group of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH=CHR})$.²³⁰ A vinyl complex, $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-CH=CHPh})$, was prepared in low yield from $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and $\text{CpMn}(\text{CO})_2(\text{C=CHPh})$.²³¹

New complexes were formed by the insertion of unsaturated organic molecules into the metal-hydride bonds of hydrido carbonyl cluster complexes. A bridging carbyne complex was formed from $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and 3,3-dimethylcyclopropane.²³²



The insertion of $\text{CH}_2=\text{C}(\text{H})\text{OMe}$ into a metal hydride bond of $\text{Os}_3\text{H}_2(\text{CO})_{10}$ forms an alkyl complex stabilized by formation of a donor bond from the oxygen atom of the ether to an osmium. β -Hydride elimination from $\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-MeCHOMe})$ is slow.²³³ The reaction between $\text{Os}_3\text{H}_2(\text{CO})_{10}$ and CF_3CCCF_3 produces $\text{Os}_3(\text{CO})_{10}\text{H}(\mu_3\text{-}\eta^2\text{-CF}_3\text{C=CHCF}_3)$. A variety of two electron donors will react with the product. Treatment of $\text{Os}_3(\text{CO})_{10}\text{H}(\mu_3\text{-}\eta^2\text{-CF}_3\text{C=CHCF}_3)$ with PEt_3 causes an osmium-osmium bond to be cleaved, forming $\text{H}(\text{CO})_4\text{Os-Os}_2(\text{CO})_6(\text{PEt}_3)(\mu\text{-CF}_3\text{CCHCF}_3)$.²³⁴ A major product in the reaction of $[\text{Os}_3(\text{CO})_{10}\text{H}\{\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3\}]^-$ with trimethyl oxonium salts is $\text{Os}_3(\text{CO})_9\text{H}(\mu_3\text{-}\sigma\text{-}\eta^2\text{-CCF}_3)$ in which a carbon-carbon bond has been cleaved.²³⁵ α - β -Unsaturated ketones react with $\text{Os}_3(\text{CO})_{10}\text{H}_2$ or $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$.²³⁶

the oxymethylidyne can be cleaved with BX_3 to give $Os_3(CO)_9(\mu-H)_3(\mu_3-CX)$, in CH_2Cl_2 , or $Os_3(CO)_9(\mu-H)_3(\mu_3-CPh)$, in C_6H_6 with BF_3 .²⁴⁵



The triosmium cluster, $Os_3H_2(CO)_{10}L$, is converted under photolysis at room temperature to $Os_3H_2(CO)_9L$. The ligand, L, can be a phosphine, PPh_3 or PPh_2Et , or it can be silica bound diphenylphosphine.²⁴⁶ The interaction of $Ru_3(CO)_{12}$ with silica, titania and alumina has been studied.²⁴⁷

Ru₄ and Os₄ Complexes

In rigid alkane matrices, photolysis of $Ru_4H_4(CO)_{12}$ results in the loss of CO and formation of $Ru_4H_4(CO)_{11}$.²⁴⁸

An anion exchange resin, IRA 401, was used as a support for the anionic cluster $[Ru_4H_{4-n}(CO)_{12}]^{n-}$. The mobility of the cluster on the support was spectroscopically observed. This material showed little activity in catalytic hydrogenation.²⁴⁹

The X-ray crystal structure of $[Ru_4(CO)_5\{P(OMe)_3\}(\mu_3-C_5H_4)_2(\eta-C_5H_5)_2]$ was reported.²⁵⁰

The Ru_4 carbido cluster, $[Ru_4(CO)_{12}(H)_2C]$, was prepared via ruthenium-gold carbido intermediates. Treatment of $Ru_5(CO)_{14}C(AuPR_3)_2$ with CO produces $Ru_4(CO)_{12}C(AuPR_3)_2$. Iodine and HI react with this complex to form $Ru_4(CO)_{12}C(AuPR_3)(I)$ and $Ru_4(CO)_{12}C(AuPR_3)(H)$, respectively. Reaction with BH_4^-

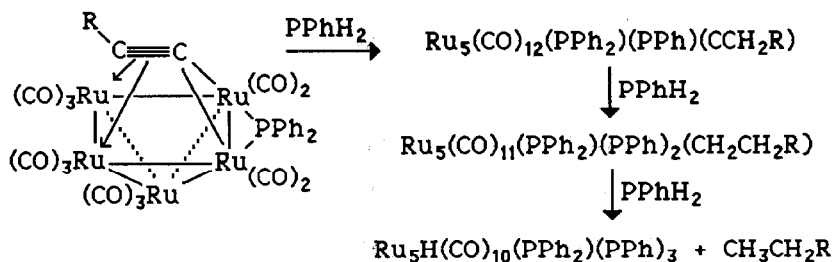
yields $\text{Ru}_4(\text{CO})_{12}(\text{H})_2\text{C}$. The structures of these complexes were determined by single crystal X-ray diffraction.²⁵¹

Reaction chemistry of tetranuclear complexes with bridging sulfido or selenido groups was investigated. Substitution of a carbonyl group for PMe_2Ph or CNCMe_3 in $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})_2$ proceeds through an associative mechanism. Crystal structures of both $\text{Os}_4(\text{CO})_{12}\text{L}(\mu_3\text{-S})_2$ and $\text{Os}_4(\text{CO})_{11}\text{L}(\mu_3\text{-S})_2$ were obtained.²⁵² Photolysis of a mixture of $\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-SePh})$ and $\text{Os}(\text{CO})_5$ produces $\text{Os}_4(\text{CO})_{13}(\mu_3\text{-Se})$ in 33% yield. Heating this complex to 125° quantitatively converts it to $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$. An X-ray crystal structure shows the the osmium atoms in a butterfly-type array.²⁵³ A number of cluster complexes, including tetra-ruthenium clusters containing sulfide, alkylphosphide or carbyne μ_3 -ligands, were found to fragment under CO.²⁵⁴

The cluster complex $\text{Ru}_4(\text{CO})_{12}(\text{MeC}_2\text{Ph})$, which has a butterfly-type core structure, reacts with alkynes to form a bis(alkyne)tetraruthenium complex. A crystal structure of $\text{Ru}_4(\text{CO})_{10}(\text{MeC}_2\text{Ph})_2$ shows that each alkyne is σ -bonded to two ruthenium centers and π -bonded to a third. The ruthenium atoms are arranged in a square.²⁵⁵

Ru₅ and Os₅ Complexes

The stepwise reduction of an acetylide ligand to free alkane was observed in the reactions of $\text{Ru}_5(\text{CO})_{13}(\mu\text{-PPh}_2)(\text{CCPr}^i)$ with PPhH_2 .²⁵⁶



Loss of one equivalent of CO and the cleavage of a Ru-Ru bond results from the reaction of the acetylide complex $\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-CCPh})$ with PhCCCCPh .²⁵⁷

Alcohols add to $\text{Os}_5\text{C}(\text{CO})_{15}$ and $\text{Os}_5\text{C}(\text{CO})_{15}\text{I}_2$ to form $\text{Os}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})\text{H}$ and $\text{Os}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{R})\text{I}$, respectively.²⁵⁸ The nucleophiles LiMe and NaC_5H_5 preferentially attack the unique ruthenium atom in $\text{Ru}_5\text{C}(\text{CO})_{15}$. The complexes

$\text{Ru}_5\text{C}(\text{CO})_{14}(\eta^2\text{-MeCO})(\mu\text{-AuPPh}_3)$ and $\text{Ru}_5\text{C}(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-AuPPh}_3)$ were obtained and characterized by X-ray crystal structures after treatment with AuPPh_3^+ .²⁵⁹

Ru₆ and Os₆ Complexes

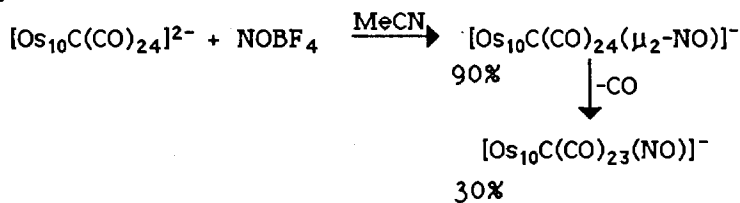
The reaction of $\text{Os}_6(\text{CO})_{18}$ with excess pyridine produces predominantly $[\text{Os}_5(\text{CO})_{15}]^{2-}$ along with some $\text{Os}_6(\text{CO})_{17}\text{Py}_2$.²⁶⁰

Loss of two equivalents of CO from $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2$ causes dimerization through one edge of the osmium triangles forming $\text{Os}_6(\text{CO})_{16}(\mu_3\text{-S})_4$.²⁶¹ Reaction of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ with $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ produces either $\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})$ or $\text{Os}_6(\text{CO})_{17}(\mu_4\text{-S})$, depending on reaction conditions.²⁶² The synthesis and crystal structure of $\text{Os}_6(\text{CO})_{14}(\mu_2\text{-PPh}_2)_2(\mu_3\text{-S})_3(\mu_4\text{-S})$ was also reported.²⁶³

Higher Nuclearity Complexes

$\text{Os}_8\text{H}(\text{CO})_{22}$ and $[\text{Os}_8\text{H}(\text{CO})_{22}]^-$ have been prepared from $\text{Os}_3(\text{CO})_{12}$ in refluxing iso-butanol. The X-ray crystal structure was determined. $\text{Os}_4\text{-Os}_{10}$ carbonyl clusters, including $[\text{Os}_8\text{H}(\text{CO})_{22}]^-$, can also be prepared from $\text{Os}_6(\text{CO})_{18}$ in refluxing butanol.²⁶⁴

The first nitrosyl derivatives of high nuclearity osmium clusters were synthesized.²⁶⁵



The reaction between S_8 and $\text{Os}_3(\text{CO})_{12}$ at high temperature (200-260^o) produced a decaosmium sulfido complex, $\text{Os}_{10}(\text{S})_2(\text{CO})_{23}$, along with several $\text{Os}_3\text{-Os}_7$ sulfido clusters. The core structure of $\text{Os}_{10}(\text{S})_2(\text{CO})_{23}$ is similar to that of $[\text{Ru}_{10}(\text{C})_2(\text{CO})_{24}]^{2-}$.²⁶⁶

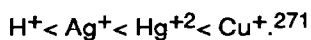
Mixed Metal Cluster Complexes

Clusters Containing Main Group Metals

The structure of $\text{Os}(\text{CO})_4(\text{AuPPh}_3)_2$ was determined by X-ray diffraction. The three

metals are in a triangular array, joined by metal-metal bonds.²⁶⁷

Several cluster containing gold or another main group metal and a triruthenium unit were reported. $\text{Ru}_3(\text{CO})_{12}$ reacts with $\text{Au}(\text{PPh}_3)\text{Cl}$ in refluxing dichloromethane to give $\text{Ru}_3(\mu_2\text{-AuPPh}_3)(\mu\text{-Cl})(\text{CO})_{10}$. The structure of this product, determined by X-ray, is similar to that of $\text{Ru}_3(\mu\text{-H})(\mu\text{-Cl})(\text{CO})_{10}$.²⁶⁸ The anion $\text{Ru}_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9^-$, prepared by deprotonation of $\text{Ru}_3\text{H}(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_9$, reacts with $[\text{O}(\text{AuPPh}_3)_3]^+$ to form $\text{Ru}_3\text{Au}_3(\text{PPh}_3)_3(\mu_3\text{-C}_{12}\text{H}_{15})(\text{CO})_8$.²⁶⁹ The cation of the parent cluster was observed in the fast atom bombardment (FAB) mass spectrum of $\text{HRu}_3\text{Au}(\mu_3\text{-S})(\text{CO})_9(\text{PPh}_3)$, $\text{Ru}_3\text{Au}_2(\mu_3\text{-S})(\text{CO})_9(\text{PPh}_3)_2$, and $\text{Ru}_3\text{Au}_3(\mu_3\text{-S})(\text{CO})_8(\text{PPh}_3)_3$.²⁷⁰ $\text{Ru}_3(\mu\text{-dppm})_2(\text{CO})_8$ forms weak adducts with the Lewis acids: AgO_2CCF_3 , $\text{Hg}(\text{O}_2\text{CCF}_3)_2$, $\text{Cu}(\text{MeCN})\text{BF}_4$, and HO_2CCF_3 . The adducts were characterized by IR and ^{31}P NMR. The equilibrium constant for adduct formation was found to increase in the following manner:



$\text{Au}_3\text{Ru}_4(\mu_3\text{-H})(\text{CO})_{12}(\text{PPh}_3)$ was synthesized from $\text{Au}(\text{CH}_3)(\text{PPh}_3)$ and either $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ or $\text{Au}_2\text{Ru}_4(\mu_3\text{-H})_2(\text{CO})_{12}(\text{PPh}_3)$ in 60% yield. A preliminary communication on this work appeared previously.²⁷²

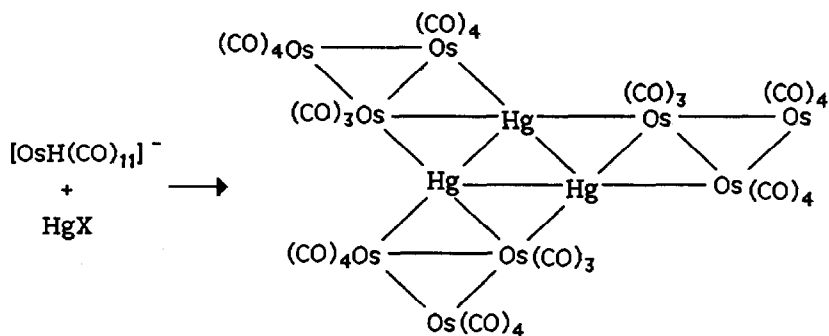
Mixed metal clusters containing Cu, Ag and Au of the formula $\text{H}_3\text{MRu}_4(\text{CO})_{12}(\text{PPh}_3)$ can be prepared from $[\text{Ru}_4\text{H}_3(\text{CO})_{12}][\text{PPN}]$ and $\text{MX}(\text{PPh}_3)$. In the copper and silver complexes, the metal binds to a face of the Ru_4 tetrahedron and the hydrides bridge the M-Ru bonds. Although the molecular formula is the same for all three complexes, the structures are different. In the AuRu_4 cluster, the gold atom bridges one edge to the Ru_4 tetrahedron and hydrides bridge only Ru-Ru bonds.²⁷³

$\text{Au}(\text{PR}_3)\text{Cl}$ reacts with $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ and $[\text{Ru}_5\text{WC}(\text{CO})_{17}]^{2-}$ to form $\text{Ru}_6\text{C}(\text{CO})_{16}(\text{AuPMePh}_2)_2$ and $\text{Ru}_5\text{WC}(\text{CO})_{17}(\text{AuPEt}_3)_2$, respectively. The two gold groups bridge opposite faces of the Ru_6 octahedron in the former complex while a Au-Au bond exists between these two groups in the Ru_5W cluster. Both complexes were shown to be fluxional at room temperature by ^{31}P NMR studies.²⁷⁴

Treatment of the dianion $[\text{Os}_8(\text{CO})_{22}]^{2-}$ with $\text{Au}(\text{PPh}_3)\text{Cl}$ results in the formation of $\text{Os}_8(\text{CO})_{22}(\text{AuPPh}_3)_2$. The core geometry consists of two octahedra sharing an

edge.²⁷⁵

The synthesis and X-ray crystal structure of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}][\text{PPN}]$ was reported. This complex can be reduced electrochemically.²⁷⁶ The synthesis and structure of mercury bridged complex $\{\text{Ru}_3(\text{NO})(\text{CO})_{10}\}_2\text{Hg}$ was reported.²⁷⁷ Heteronuclear complexes, $\{\text{M}_3(\text{CO})_{11}\text{Hg}\}_3$ where $\text{M} = \text{Ru}$ or Os , have been prepared from $[\text{M}_3\text{H}(\text{CO})_{11}]^-$ and $\text{Hg}(\text{I})$ or $\text{Hg}(\text{II})$ salts. The central Hg_3Os_3 core is planar in these complexes.²⁷⁸

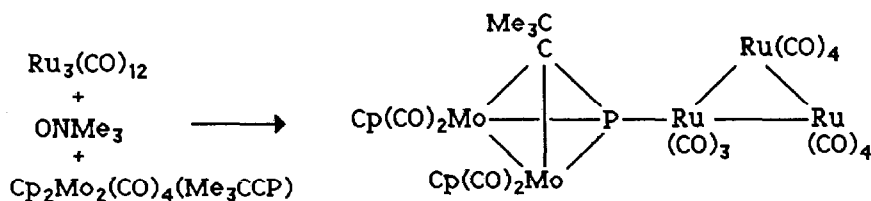


A tin-osmium cluster was prepared by the addition of $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ to $\text{Os}_3\text{H}_2(\text{CO})_{10}$. IR, NMR and X-ray diffraction were used to confirm the structure of $\text{Os}_3\text{SnR}_2\text{H}_2(\text{CO})_{10}$. The dialkyl tin unit and a carbonyl doubly bridge one Os-Os bond. The hydrides bridge a Sn-Os and an Os-Os bond.²⁷⁹

Clusters with Other Transition Metals

$\text{K}[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ reacts with $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrI}_2$ to form the triangular cluster, $\text{Ru}_2\text{ZrCp}_4(\text{CO})_4$.²⁸⁰

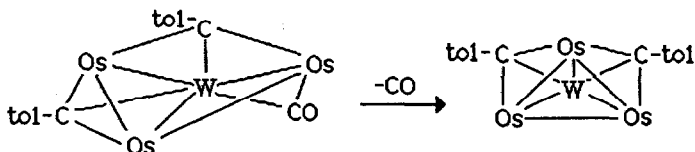
Cluster complexes containing tri-osmium or tri-ruthenium units and two molybdenum atoms, $[\text{Mo}_2\text{M}_3(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_{15}(\text{Me}_3\text{CCP})]$, have been reported. There are no bonds between molybdenum and osmium or ruthenium in these complexes.²⁸¹



The cobalt atom in $\text{RuCoM}(\eta^5\text{-Cp})(\mu_3\text{-S})(\text{CO})_8$, where $\text{M} = \text{Mo}$ or W , can be exchanged for M' , where $\text{M}' = \text{Mo}$ or W . The reaction of $\text{RuCoM}(\eta^5\text{-Cp})(\mu_3\text{-S})(\text{CO})_8$ with $[\text{M}'\text{Cp}(\text{CO})_3]_3$ forms $\text{RuM}'\text{M}(\eta^5\text{-Cp})_2(\mu_3\text{-S})(\text{CO})_7$.²⁸²

The photolysis of a mixture of $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2$ and $\text{W}(\text{CO})_5(\text{PPhMe}_2)$ results in the formation of four mixed metal clusters: $\text{Os}_3\text{W}(\text{CO})_{12}(\text{PPhMe}_2)(\mu_3\text{-S})_2$, $\text{Os}_3\text{W}(\text{CO})_{12}(\text{PPhMe}_2)_2(\mu_3\text{-S})_2$, $\text{Os}_3\text{W}(\text{CO})_{11}(\text{PPhMe}_2)_2(\mu_3\text{-S})_2$, and $\text{Os}_3\text{W}_2(\text{CO})_{14}(\text{PPhMe}_2)_2(\mu_3\text{-S})(\mu_4\text{-S})$.²⁸³ Under similar conditions, $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ reacts with $\text{W}(\text{CO})_5(\text{PPhMe}_2)$ and $\text{Pt}(\text{PPhMe}_2)_4$ to give $\text{Os}_3\text{W}(\text{CO})_{11}(\text{PPhMe}_2)_2(\mu_3\text{-S})$ and $\text{Os}_3\text{Pt}(\text{CO})_8(\text{PPhMe}_2)_3(\mu_3\text{-S})$, respectively.²⁸⁴ The synthesis of the pyramidal cluster complex, $\text{Os}_3\text{W}(\eta^5\text{-Cp})(\mu\text{-H})\text{S}(\text{CO})_{11}$, was reported.²⁸⁵ Interaction of $[\text{Os}_3\text{H}(\text{CO})_{11}]^-$ with $\text{W}(\text{CO})_3(\text{MeCN})_3$ produces $[\text{Os}_3\text{WH}(\mu\text{-CO})(\text{CO})_{13}]^-$. This complex can be deprotonated with KOH , protonated with H_2SO_4 , and oxidized with I_2 , forming $\text{Os}_3\text{WH}(\text{CO})_{14}$.²⁸⁶

The first tetrametallic di-alkylidyne cluster was prepared. The metal atoms in $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CC}_6\text{H}_4\text{CH}_3)_2\text{H}$ form a butterfly type core. This molecule is fluxional in solution. Loss of CO closes the structure.²⁸⁷



Addition of one equivalent of trimethylamine oxide and acetylene to $\text{CpWOs}_3(\text{CO})_{12}\text{H}$ produces a complex with acetylene bridging a Os_2W triangle, $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)\text{H}$. The addition of another equivalent of trimethylamine

oxide forms $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)\text{H}$. The oxide is doubly bound to the tungsten atom and bridge-bonded to an osmium.²⁸⁸ A similar oxo cluster is formed from the thermal C-O bond scission in a $\mu_3\text{-}\eta^2$ -acyl complex. Thermolysis of $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{C}_6\text{H}_4\text{CH}_3)$ yields $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{C}_6\text{H}_4\text{CH}_3)$. Reaction of $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{C}_6\text{H}_4\text{CH}_3)$ with hydrogen reduces the bridging alkylidyne to an alkylidene.²⁸⁹

A manganese-triosmium cluster, $\text{CpMnOs}_3(\mu_2\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(\text{CO})_{11}$, was prepared and structurally characterized.²⁹⁰ A mixed metal acetylide cluster was prepared from $\text{HOs}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CCPh})$ and $(\text{CO})_5\text{M}(\text{CCPh})$, where $\text{M} = \text{Mn}$ or Re . The structure of the product, $\text{HMOs}_3(\text{CO})_{14}(\text{CCPh})_2$, was determined.²²⁷

Several groups have reported the synthesis of new iron-ruthenium clusters. $[\text{FeRu}_3(\text{CO})_{12}(\text{NO})]^-$, prepared from $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ and $\text{Ru}_3(\text{CO})_{12}$, has been shown to lose CO_2 to form the nitrido cluster, $[\text{FeRu}_3(\text{CO})_{12}(\text{N})]^-$. The structures of both mixed metal clusters were determined by single crystal X-ray diffraction and ^{15}N NMR spectra were obtained.²⁹¹ Iron-ruthenium mixed metal clusters containing bridging alkyne ligands have been prepared from $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$ and either diphenyl- or diethyl acetylene. The complexes $\text{Fe}_2\text{Ru}(\text{CO})_9(\text{alkyne})$, $\text{Fe}_2\text{Ru}(\text{CO})_8(\text{alkyne})_2$ and $\text{FeRu}(\text{CO})_6(\text{alkyne})_2$ were isolated and characterized.²⁹² Ligand substitution reactions in the clusters $\text{FeRu}_2(\text{CO})_{12}$ and $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ were found to take place preferentially at the ruthenium centers.²⁹³

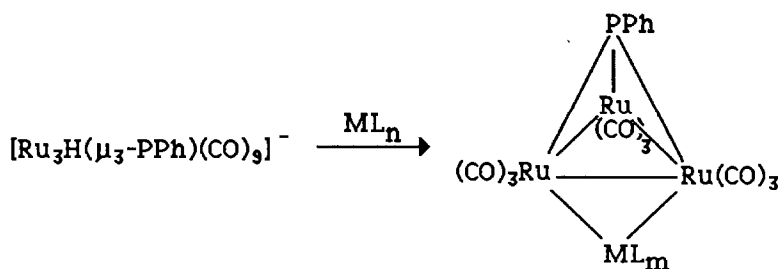
The reaction of $[\text{Fe}_3(\text{CO})_{11}]^-$ and $\text{Os}_3(\text{CO})_{12}$ produces $[\text{FeOs}_3\text{H}(\text{CO})_{12}]^-$. The complex has a distorted tetrahedral geometry. Several other iron-osmium clusters were prepared. The clusters $\text{Fe}_2\text{Os}(\text{CO})_{12}$ and $\text{FeOs}_3\text{H}_2(\text{CO})_{13}$ were synthesized from $\text{OsH}_2(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$. Reaction of $\text{H}_2\text{Os}_2(\text{CO})_8$ with $\text{Fe}_2(\text{CO})_9$ yields $\text{FeOs}_2(\text{CO})_{12}$ and minor amounts of $\text{FeOs}_3\text{H}_2(\text{CO})_{13}$.²⁹⁴ The cobalt-osmium clusters, $\text{Co}_2\text{Os}(\text{CO})_{11}$, $\text{H}_2\text{Co}_2\text{Os}_2(\text{CO})_{12}$, and $\text{Co}_2\text{Os}(\text{CO})_{11}$ can be prepared from $\text{Co}_2(\text{CO})_8$ and either $\text{H}_2\text{Os}(\text{CO})_4$ or $\text{Os}(\text{CO})_5$.²⁹⁵

Cluster complexes containing three or four different metals have recently been prepared and characterized. The synthesis of $\text{MM}'\text{Co}_3\text{L}(\text{CO})_{12}$, where $\text{M} = \text{Fe}$ or Ru

and $M' = \text{Cu}$ or Ag , was reported.²⁹⁶ A cluster with a core consisting of $\text{FeRuCoAu}(\text{PPh}_3)(\mu_3\text{-E})$, where $\text{E} = \text{S}$ or PMe , was prepared from MePCl_2 , $\text{Fe}_2(\text{CO})_9$, $\text{KCo}(\text{CO})_4$, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Au}(\text{PPh}_3)\text{Cl}$.²⁹⁷ Clusters of this type were shown to fragment under CO pressure.²⁵⁴ The crystal structure of $\text{RuCo}_3(\mu\text{-CO})_3(\text{CO})_9[\mu_3\text{-HgCo}(\text{CO})_4]$ showed the mercury atom bound to four cobalt centers.²⁹⁸ The gold-cobalt-ruthenium clusters $\text{CoRu}_3\text{Au}(\text{PPh}_3)(\text{CO})_{13}$, $\text{CoRu}_3\text{Au}_2(\text{PPh}_3)_2\text{H}(\text{CO})_{12}$ and $\text{CoRu}_3\text{Au}_3(\text{PPh}_3)_3(\text{CO})_{12}$, were all prepared from $\text{CoRu}_3\text{H}(\text{CO})_{13}$ and $[(\text{AuPPh}_3)_3\text{O}][\text{BF}_4]$.²⁹⁹ $\text{CpNiOs}_3(\mu\text{-H})_2(\mu_3\text{-MPPh}_3)(\text{CO})_9$ was prepared by the deprotonation of $\text{CpNiOs}_3(\mu\text{-H})_3(\text{CO})_9$ followed by treatment with $\text{M}(\text{PPh}_3)\text{Cl}$, where $\text{M} = \text{Au}$ or Cu . A crystal structure shows that one Os-Os edge of the NiOs_3 tetrahedron is bridged by M .³⁰⁰

Clusters containing metals of the cobalt triad along with ruthenium or osmium have been reported. The isomerization of an acetylene to a vinylidene on a Co_2Ru cluster was observed. Both isomers of $\text{Co}_2\text{Ru}(\text{CO})_9(\text{Me}_3\text{CC}_2\text{H})$ were characterized by X-ray crystal structures.³⁰¹ Heating $\text{Co}_2(\text{CO})_8$ and $\text{Ru}_3(\text{CO})_{12}$ in the presence of ethyl thiol and synthesis gas results in the formation of $\text{SRuCo}_2(\text{CO})_9$. Phosphines and arsines will displace up to three carbonyls.³⁰² The synthesis and crystal structure of $[\text{RuRh}_4(\text{CO})_9(\mu\text{-CO})_6][\text{PPN}]_2$ was reported.³⁰³ The complex $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ was synthesized from $\text{NaRh}(\text{CO})_4$, $\text{Ru}_3(\text{CO})_{12}$ and phosphoric acid. The structure of this Ru_2Rh_2 cluster is similar to that of $\text{Rh}_4(\text{CO})_{12}$.³⁰⁴ The reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{CpRh}(\text{CO})_2$ produces $\text{CpRhOs}_2(\text{CO})_9$ and $\text{H}_2\text{CpRhOs}_3(\text{CO})_{10}$. An X-ray crystal structure was obtained for $\text{CpRhOs}_2(\text{CO})_9$.³⁰⁵

Phosphide-capped clusters $[\text{Ru}_3\text{ML}_m(\text{CO})_9(\mu_3\text{-PPh})]^-$ were prepared, where $\text{ML}_m = \text{Rh}(\text{CO})(\text{PR}_3)$, $\text{Re}(\text{CO})_2(\text{NCMe})$, $\text{Ir}(\text{CO})(\text{PPEt}_3)$, $\text{Cu}(\text{PR}_3)$, $\text{Ag}(\text{PR}_3)$, or $\text{Au}(\text{PR}_3)$.³⁰⁶



The reaction of transition metal hydrides with $\text{Os}_3\text{H}_2(\text{CO})_{10}$ produced tetranuclear mixed metal clusters. Clusters resulting from reaction with $\{\text{CuH}(\text{PPh}_3)\}_6$, $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$, $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ and $\text{Ni}(\text{H})\text{Cl}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2$ were characterized.³⁰⁷

The reactions of $\text{CpNiRu}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-}\eta^2\text{-C=CHCMe}_2)$ with olefins at high temperature were reported.³⁰⁸ This Ru_3Ni cluster was prepared, along with $\text{CpNiRu}_3(\mu\text{-H})_3(\text{CO})_9$, from $[\text{CpNi}\{\text{CHCC}(\text{CH}_2)\text{CH}_3\}]_2$ and $\text{Ru}_3(\text{CO})_{12}$ under an H_2 atmosphere.³⁰⁹ The reaction of $\text{CpNiOs}_3(\mu\text{-H})_3(\text{CO})_9$ with various donor molecules results in the formation of monosubstitution products.³¹⁰ $\text{Cp}_2\text{Ni}_2\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_2(\mu\text{-}\eta^2\text{-C}_2\text{Ph}_2)$ was prepared similarly from $\text{Ru}_3(\text{CO})_{12}$ and $[\text{CpNi}(\text{C}_2\text{Ph}_2)]_2$ under H_2 .³¹¹

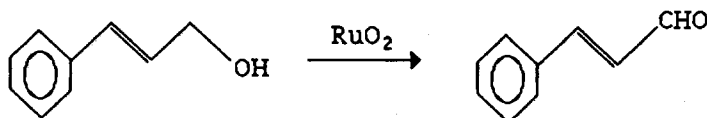
A series of PtOs_3 clusters was prepared. The reaction between $\text{Os}_3(\text{CO})_9(\mu\text{-S})_2$ and $\text{Pt}(\text{PPh}_3)(\text{C}_2\text{H}_2)$ formed $\text{PtOs}_3(\text{CO})_9\text{L}(\text{PPh}_3)(\mu\text{-S})_2$, where $\text{L} = \text{CO}$ or PPh_3 .³¹² The reaction between $\text{Os}_3(\text{CO})_{10}(\mu\text{-S})$ and $\text{Pt}(\text{PMe}_2\text{Ph})_4$ at room temperature produced $\text{PtOs}_3(\mu_3\text{-S})(\text{CO})_{10}\text{L}_2$, $\text{PtOs}_3(\mu_3\text{-S})(\text{CO})_9\text{L}_2$, $\text{PtOs}_3(\mu_3\text{-S})(\text{CO})_9\text{L}_3$, and $\text{PtOs}_3(\mu_3\text{-S})(\text{CO})_8\text{L}_3$.³¹³ Decarbonylation of $\text{PtOs}_3(\mu_3\text{-S})_2(\text{CO})_{10}(\text{PPh}_3)$ by trimethylamine oxide gave $[\text{PtOs}_3(\text{CO})_8(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-H})(\text{PPh}_2\text{C}_6\text{H}_4)]_2$. The X-ray crystal structure showed two trigonal-prismatic PtOs_3S_2 units linked on an edge by quadruply-bridging sulfido groups.³¹⁴

IV. Catalytic and Synthetic Reactions

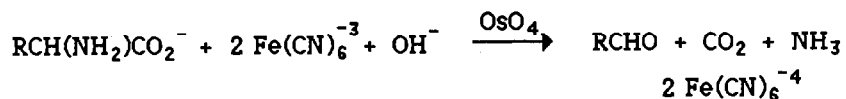
Mechanistic features of hydroformylation and water-gas shift reactions with ruthenium compounds were investigated. The stability of triarylphosphines under hydroformylation conditions was studied. Only trace amounts of C-P bond cleavage products were found for hydroformylations catalyzed by $\text{Ru}_3(\text{CO})_{12}$. With cobalt and

rhodium carbonyl catalysts, greater amounts of phosphine decomposition products were obtained.³¹⁵ Under other conditions, the carbonyl clusters $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ catalyzed exchange of aryl groups in triarylphosphines.³¹⁶ A homogeneous bimetallic catalyst system, consisting of $\text{Co}_2(\text{CO})_8$ and $\text{Ru}_3(\text{CO})_{12}$, showed a much higher catalytic activity for the hydroformylation of cyclohexene than $\text{Co}_2(\text{CO})_8$ alone.³¹⁷ Under conditions commonly used for the water gas shift reaction, the monomeric complexes $[\text{HM}(\text{CO})_4]^-$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) are converted to trinuclear species, $[\text{HM}_3(\text{CO})_{11}]^-$.³¹⁸ Silica, functionalized with tetra-alkylammonium groups, has been used as a support for the anionic ruthenium cluster, $[\text{HRu}_3(\text{CO})_{11}]^-$. The supported cluster is a catalyst for the water gas shift reaction.³¹⁹

Research has continued on the application of high oxidation state osmium and ruthenium complexes to the oxidation of both organic and inorganic substrates. The oxidation of the furan ring of khellin, an antiatherosclerotic drug, with sodium periodate can be catalyzed by osmium tetroxide.³²⁰ The oxidation of phosphite to phosphate with chloramine T has been catalyzed by osmium tetroxide in alkaline aqueous solution. The kinetics and mechanism of this reaction has been investigated.³²¹ Ruthenium dioxide in the presence of dioxygen has been shown to oxidize allylic alcohols to unsaturated carbonyl compounds.³²²



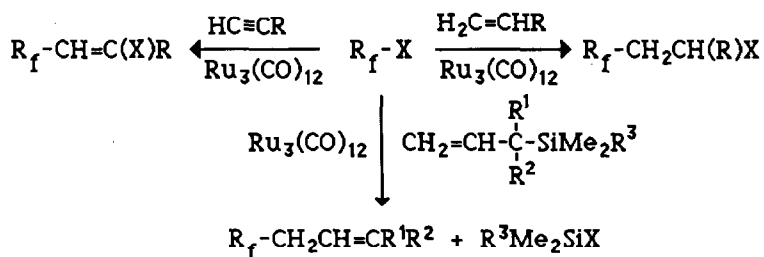
The oxidation of the C-C double bond of cinnamic acid by RuO_4^{2-} and RuO_4^- has been studied. The value of the ΔG^\ddagger for the reaction with RuO_4^{2-} was 7 kcal. higher than for the reaction with RuO_4^- . This was explained by the presence in the latter ruthenium complex of a "spectator oxo group" which does not participate in the reaction but can increase its π bonding to the metal center during the course of the reaction.³²³ Sodium ruthenate has been found to oxidize alcohols to carbonyl compounds. In the oxidation of cyclobutanol with Na_2RuO_4 , cyclobutanone is formed specifically. No ring opening is observed.³²⁴ The kinetics and mechanism of the oxidation of amino acids by $\text{Fe}(\text{III})$ catalyzed by osmium tetroxide has been studied.³²⁵



Sulfides are catalytically oxidized to sulfoxides in alcohol solution by ruthenium(II) complexes. At 100^o and 100 psi of O₂, a rate of up to 170 turnovers per hour is achieved. The reaction is first order in total ruthenium and first order in oxygen gas. A mechanism was proposed involving the oxidation of O₂ to peroxide by ruthenium followed by oxidation of the sulfide by peroxide.³²⁶ The oxidation of alcohols was carried out with Ru₃(CO)₁₂ as the catalyst.³²⁷ The electrochemical oxidation of primary amines coordinated to ruthenium(II) has been reported. The products were characterized by their chemical and electrochemical behavior.³²⁸

Dehydrogenation reactions have been catalyzed by ruthenium complexes. The dehydrogenation of hydroxyesters and cyanohydrins with *tert*-butylhydroperoxide can be catalyzed by various ruthenium complexes including RuCl₂(PPh₃)₃, Ru₃(CO)₁₂, [RuCl₂(CO)₃]₂, (C₆H₆)RuCl₂, RuCl₃, Ru(acac)₃ and ruthenium supported on carbon. α -Keto esters and α -keto nitriles are produced in 40-97.5% yield.³²⁹ For the oxidation of alcohols, RuL(CO)₃ and [RuL(CO)₂]₂ (L = η^4 -tetracyclone) are faster than Ru₃(CO)₁₂.³³⁰ Alcohols and catechols can be oxidized to the corresponding carbonyl compounds with *tert*-butylhydroperoxide. The reaction, catalyzed by RuCl₂(PPh₃)₃, was reported to occur with 90% conversion and 50-100% selectivity.³³¹

A series of papers appeared dealing with ruthenium catalyzed addition and substitution reactions of olefins. Ruthenium, palladium and rhodium complexes catalyze the reactions between trialkylsilanes and trifluoropropene or pentafluorostyrene. The dehydrogenative silylation of R_fCH=CH₂ to R_fCH=CHSiR₃ is favored by Ru₃(CO)₁₂.³³² The triruthenium cluster also catalyzed the addition of polyfluoroalkyl halides to terminal acetylenes and olefins³³³ and to allylsilanes.³³⁴



The reactions of arenesulfonyl chlorides with *cis*- or *trans*- β -methyl- styrene are catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$. The products are β -methyl, β -arylsulfonyl styrenes.³³⁵ The hydrosilation of ketones and alkynes catalyzed by *trans*- RuCl_2L_4 is enhanced in the presence of air or light and may proceed by a radical mechanism.³³⁶

New homogeneous and heterogeneous catalysts for the reduction of olefins and acetylenes were reported. The ruthenium complexes $(\eta^6\text{-arene})(1,5\text{-COD})\text{Ru}$ were found to be homogeneous catalysts for the hydrogenation of α -olefins and cycloolefins.³³⁷ Methanol and ethanol were used as the hydrogen donors in the reduction of cyclohexanone to cyclohexanol. Among the platinum group metals effective as catalysts for this reaction were $\text{OsH}(\text{CO})\text{Br}(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$.³³⁸ The homogeneous hydrogenation of α,β -unsaturated aldehydes catalyzed by Ru and Os complexes³³⁹ and the homogeneous hydrogenation of cyclohexene by Os_3 and Os_4 clusters³⁴⁰ were reported. Ruthenium acetate on a polymer support catalyzed the hydrogenation of olefins.³⁴¹ The hydrogenation of pentynes and pentadienes has been catalyzed by $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}_3(\text{CO})_{12}$ and mixed ruthenium-iron clusters on γ -alumina. The highest activity was observed for $\text{Ru}_3(\text{CO})_{12}$ and the activity of the mixed metal catalysts increased with an increase in the percentage of ruthenium.³⁴² Gold-osmium bimetallic catalysts were prepared from heterometallic cluster complexes. A catalyst was prepared from $(\mu_2\text{-X})\text{AuOs}_3(\text{CO})_{10}\text{L}$ ($\text{X} = \text{H}, \text{Cl}$; $\text{L} = \text{PPh}_3$) and phosphine functionalized silica. At room temperature, metal-metal bonds in the gold-osmium cluster opened reversibly under CO. At higher temperatures, the cluster fragmented.³⁴³ The mixed metal cluster $\text{CpNiOs}_3(\mu\text{-H})(\text{CO})_9$ was supported on chromosorb P in a GC column. Under H_2 flow, the supported cluster was a catalyst for

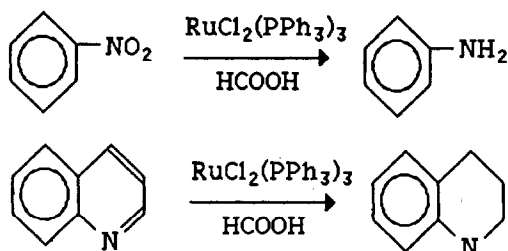
the hydrogenation of 1,3-pentadiene. The presence of metal particles was postulated on the basis of a loss of selectivity in the reaction.³⁴⁴ Ruthenium(II) complexes of sulphonated triphenylphosphine were immobilized on ion exchange materials for use in catalytic reactions.³⁴⁵

The regioselective hydrogenation of unsymmetrical substituted cyclic anhydrides was catalyzed by ruthenium phosphine complexes.³⁴⁶

The homologation of olefins at 250-300⁰ under 1 atmosphere of synthesis gas (CO, H₂) was catalyzed by ruthenium and osmium supported on silica.³⁴⁷ Olefin metathesis of 7-methylnorbornene catalyzed by RuCl₃·3H₂O produced the all trans, atactic polymer.³⁴⁸

The effect of the support was studied in the isomerization of 1-hexene with heterogenous catalysts prepared from Os₃(CO)₁₂ and various oxide supports. The activity of osmium carbonyl on MgO, Al₂O₃, or SiO₂ was greater than that on TiO₂, ZrO₂, CeO₂, Cr₂O₃, or ThO₂. Mononuclear osmium carbonyl complexes were observed by IR.³⁴⁹

Nitroarenes were converted to aminoarenes with formic acid using RuCl₂(PPh₃)₃ as a catalyst. Substituted quinolines and indoles were also reduced under these conditions.³⁵⁰

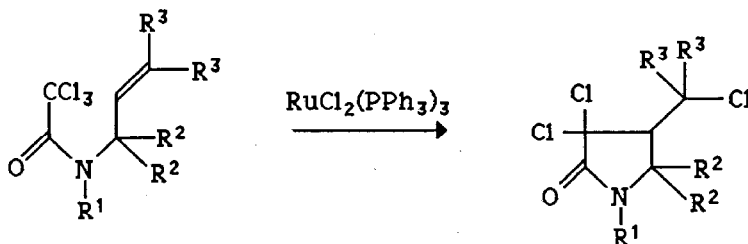


The N-alkylation of aminoarenes with alcohols was catalyzed by RuCl₂(PPh₃)₃ at 150-180⁰. The rate was first order in catalyst and first order in alcohol.³⁵¹ The reductive carbonylation of aromatic nitro compounds to carbamates has been catalyzed by Ru₃(CO)₁₂ or Ru(CO)₃(PPh₃)₂ with tetra-ethylammonium chloride as co-catalyst.³⁵²

O-alkyl aldoximes, RON=CHR, react with (NH₃)₅Ru(H₂O)⁺² to generate the alcohol ROH and a ruthenium nitrile, (NH₃)₅RuNCR⁺².³⁵³

In a study of the alcoholysis of triethylsilane by $\text{RuCl}_2(\text{CO})_2(\text{PMe}_3)_2$, it was found that the active catalyst is a dimeric ruthenium species, $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_3)]_2$.³⁵⁴

The cyclization of N-alkyl-trichloroacetamides to trichlorinated γ -butyrolactams can be catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ in benzene at 140° .³⁵⁵



A number of investigators reported the use of polypyridal complexes of ruthenium as photocatalysts or photosensitizers. It was reported that $\text{Ru}(\text{bpy})_3^{2+}$ photocatalyzed the reduction of various functionalized olefins.³⁵⁶ The photochemical production of H_2 from ascorbic acid was also reported to be photocatalyzed by $\text{Ru}(\text{bpy})_3^{2+}$.³⁵⁷ A platinum catalyzed reduction of water used $\text{Ru}(\text{bpy})_3^{2+}$ as a photosensitizer.³⁵⁸ A ruthenium(II) tris(polypyridyl) complex was found to photocatalyze the oxidations of alcohols to carbonyl compounds.³⁵⁹ Water was oxidized by another bipyridyl ruthenium complex, $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}]_2(\mu\text{-O})^{4+}$.³⁶⁰

Catalysis by supported metal clusters was reviewed with emphasis on catalysis by supported triosmium clusters.³⁶¹

V. Reviews and Theses

Several general review articles on ruthenium and osmium chemistry appeared in 1984. The annual surveys of ruthenium and osmium for the years 1978 and 1982 appeared in *J. Organomet. Chem.*^{362,363} The chemistry of ruthenium was covered in a book by Seddon and Seddon.³⁶⁴ After a historical overview, ruthenium compounds were discussed in order of decreasing oxidation state.

The following theses related to organometallic chemistry of osmium and ruthenium were listed in "Comprehensive Dissertation Index 1984 - Sciences Part 1" published by University Microfilms International or in "Chemical Abstracts".

Theses were published concerning the chemistry of mononuclear ruthenium and osmium complexes with various ligands. Chemistry of ruthenium porphyrin

complexes was discussed in theses by Barley and by Chang.^{365,366} Doeff investigated axial ligand substitution reactions of ruthenium phthalocyanine complexes.³⁶⁷ The solution behavior and reactivity of some triarylphosphine complexes of ruthenium was discussed in a thesis by Dekleva.³⁶⁸ Zubkowski studied the photochemical reactivity of transition metal polyhydrides of osmium and molybdenum.³⁶⁹ Ruthenium oxime complexes were investigated by Geno.³⁷⁰ Wolfgang studied the photophysical and photoredox properties of ruthenium(II) complexes with π acceptor ligands.³⁷¹ The thesis by Joseph reported on the synthesis, electrophilic cleavage reactions, and electrochemistry of CpRuLL'R (where L,L' = CO, PPh₃; R = CH₃, CH₂Ph).³⁷² Electrochemical and physicochemical studies of (hexamethylbenzene)ruthenium cyclophane complexes were investigated by Voegeli.³⁷³

The preparations and crystal structures of dinuclear ruthenium and osmium complexes were the subject of a thesis by Thompson.³⁷⁴ Audett studied the reactivity of osmium tetroxide and peroxy-carboxylic acids with low valent iridium complexes.³⁷⁵

Ruthenium and osmium cluster complexes were the subject of several theses. A thesis by Strickland involved the synthesis and reactivity of alkylidyne triosmium clusters.³⁷⁶ Acyl and Fischer-type carbene derivatives of triosmium and triruthenium clusters was investigated by Jensen.³⁷⁷ A study of edge double-bridged triruthenium clusters was reported by Kampe.³⁷⁸ Hayward studied the synthesis of large carbonyl clusters of ruthenium, osmium and rhenium.³⁷⁹ Yang investigated the synthesis and reactivity of high nuclearity sulfido clusters of osmium and aspects of the reactivity of nitriles with hydrido-osmium carbonyl clusters.³⁸⁰ Mechanistic studies of the photoreactions of Ru₃(CO)₁₂ and its derivatives was reported by Desrosiers.³⁸¹ Park investigated the organometallic chemistry of tungsten-triosmium clusters.³⁸²

Several theses concerned synthetic and catalytic reactions using ruthenium and osmium complexes. Bricker studied the reactivity of ruthenium carbonyl anions with respect to the water-gas shift reaction.³⁸³ A thesis by Murphy concerned the rational design of electrocatalysts based on ruthenium polypyridal complexes.³⁸⁴ The photochemistry and photocatalytic properties of homogeneous and surface confined ruthenium carbonyl complexes was discussed by Liu.³⁸⁵ McGuiggan investigated the synthesis, characterization and catalytic properties of ruthenium and rhodium phosphine complexes.³⁸⁶ Barbachyn reported on β -hydroxysulfoximine-directed cyclopropanations and osmylations.³⁸⁷

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