Annual Survey of Ruthenium and Osmium for the Year 1986

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Contents:

I. Mononuclear Complexes

(a) Organometallic Porphyrin and Carborane Complexes

New organometallic porphyrin derivatives were reported. The conversion of diethyl[2,3,7,8,12,13,17,18-octaethylporphyrinato]-ruthenium to the corresponding ethylidene(OEP)ruthenium complex was studied. The rate expression for the decomposition of the diethyl complex and the metal-carbon bond dissociation energy were determined. The kinetics as well as the effect of a radical trap on the reaction lead to a proposed mechanism involving homolysis of a ruthenium-carbon bond.[1]
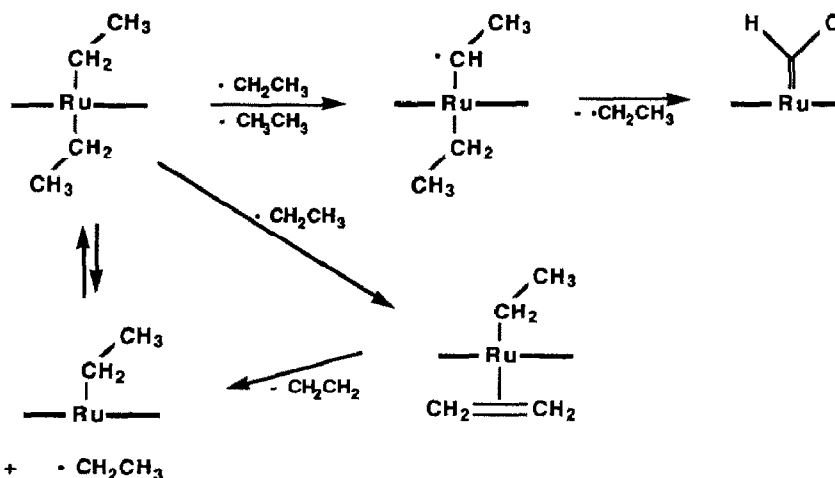
The oxidation of bis(rutheniumoctaethylporphyrin) with HX (X=F, Cl, Br) resulted in the formation of dihaloruthenium(IV) complexes of octaethylporphyrin. Reactions with phenyl lithium and methyl lithium gave diphenyl and dimethyl ruthenium porphyrin species.[2] A monomeric, tetramesitylporphyrin ruthenium complex was prepared by pyrolysis of [Ru(TMP)(MeCN)]$_2$. Adducts with a variety of ligands were prepared. A bis(dinitrogen) complex, Ru(TMP)(N$_2$)$_2$, was formed from Ru(TMP) under a nitrogen atmosphere.[3]

Electrochemical and spectroscopic techniques have been used to investigate the electronic structure of osmium and ruthenium porphyrin complexes. Electrochemistry of the ruthenium and osmium octaethylporphyrin dimers, [M(OEP)]$_2$, was studied. The voltammogram of each compound exhibits four reversible oxidations and two reversible reductions. The first two oxidations are metal centered. The resulting oxidized complexes, [M(OEP)]$_2$ and [M(OEP)]$_2$, can be isolated by chemical oxidations. The metal-metal bond order increases on oxidation from 2, in the starting materials, to 2.5 and 3, for the oxidized species.[4] The resonance Raman spectra for octaethylporphyrin and tetraphenylporphyrin ruthenium complexes with

pyridine, methanol and carbon monoxide axial ligands were reported. The carbonyl group effectively competes with the porphyrin for metal back-bonding and greatly effected the spectra obtained with both 407 nm and 531 nm excitation.[5]
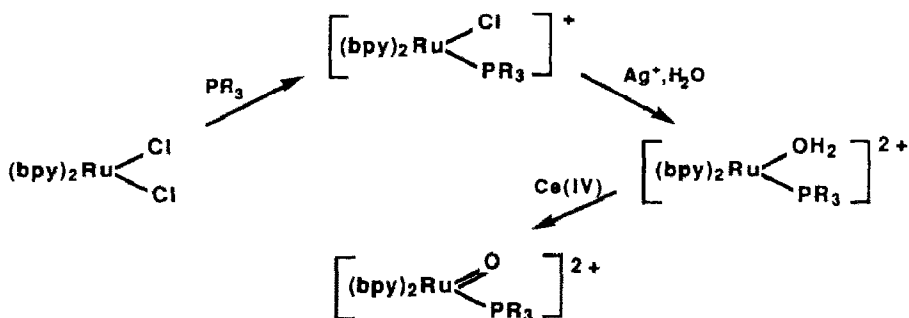
A ruthenium carbonyl complex of a new macrocyclic ligand was synthesized and structurally characterized.The chloride and carbonyl ligands were in a *cis* configuration in [RuCl(CO)L][BPh$_4$] (L= 2,7,12-trimethyl-3,7,11, 17-tetra-azabicyclo[11.3.1]heptadeca-1, (17), 13, 15-triene).[6]

A number of papers reported new osmium and ruthenium metallaboranes. A series of metallaboranes was synthesized from [(η^6-C$_6$Me$_6$)MCl$_2$]$_2$ (M= Ru, Os). Examples of arachno-, nido-, and closo- type clusters with four, five, six, ten, and eleven vertices were described.[7] One of the products of the reaction between *arachno*-[B$_6$H$_{11}$]$^-$ with [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ is [(η^6-C$_6$Me$_6$)RuB$_8$H$_{14}$] which has the same framework as *nido*-[B$_9$H$_{15}$].[8] The *nido* 6-metalladecaboranes of osmium and ruthenium were prepared and an X-ray crystal structure of (PMe$_2$Ph)$_3$OsB$_9$H$_{13}$ was published.[9] The eleven vertex *closo*-osmaundecaborane, [(PPhMe$_2$)$_2$OsB$_{10}$H$_8$(OEt)$_2$] was prepared in 42% yield from OsCl$_3$(PPhMe$_2$)$_3$ and *closo*-B$_{10}$H$_{10}$$^{2-}$.[10]

(b) Complexes of Phosphorus Ligands

Ruthenium and osmium complexes MHCl(CO)(PPr$^i_3$)$_2$ were prepared from MCl$_3$ and tri(isopropyl)phosphine in methanol. A variety of neutral donors add to these complexes to form the six-coordinate molecules, MLHCl(CO)(PPr$^i_3$)$_2$ (L= PMe$_3$, P(OMe)$_3$, CH$_2$=CHR).[11]

The synthesis of a stable ruthenium(VI) oxo complex with a tertiary phosphine ligand, *cis*-[(bpy)$_2$Ru(O)(PR$_3$)]$^{+2}$, was reported. The reaction of *cis*-[(bpy)$_2$RuCl$_2$] with triethylphosphine gave *cis*-[(bpy)$_2$RuCl(PEt$_3$)]. Abstraction of the halide with silver perchlorate in acetone/water, followed by oxidation with cerium(IV) produced the oxoruthenium phosphine complex. Reversible reductions to Ru(III) and Ru(II) complexes were observed by cyclic voltammetry in aqueous solution. The oxo complex, *cis*-[(bpy)$_2$Ru(O)(PR$_3$)]$^{+2}$, was found to oxidize isopropyl alcohol, propionaldehyde and triphenylphosphine.[12]

$$[(bpy)_2Ru(Cl)(PR_3)]^+$$

$$[(bpy)_2Ru(OH_2)(PR_3)]^{2+}$$

$$(bpy)_2Ru(Cl)(Cl) \xrightarrow{PR_3}$$
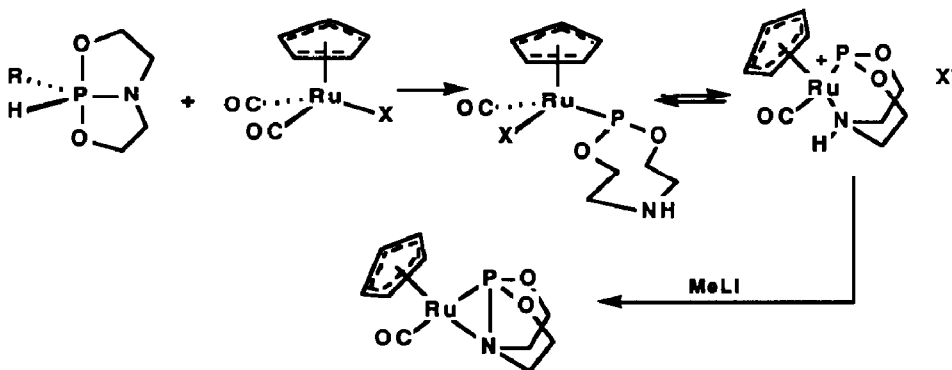
$$Ag^+, H_2O$$

$$Ce(IV)$$

$$[(bpy)_2Ru(O)(PR_3)]^{2+}$$

Ruthenium complexes of diphenylphosphinomethane and diphenylphosphino-ethane were synthesized. Several synthetic methods were used to prepare $RuCl_2(dppm)(PMe_2Ph)_2$, $RuCl_2(dppm)(PMePh_2)_2$, $RuCl_2(dppe)(PMe_2Ph)_2$ and $RuCl_2(dppe)(PMePh_2)_2$.[13] The ruthenium(0) phosphine complex $Ru(dmpe)_2(PMe_3)$ was prepared from $Ru(dmpe)_2(naphthyl)H$ and trimethylphosphine. The complex was shown to be square pyramidal with an axial trimethylphosphine by an X-ray crystal structure. Carbon monoxide and neopentylisocyanide displace PMe_3, producing other zero valent derivatives. The geometry of the carbonyl complex is trigonal bipyramidal with the carbonyl equatorial.[14]

PMe_3 ... Ru ... Me_2P ... PMe_2 ... PMe_2 ... Me_2P $\xrightarrow{CO}$ Me_2P ... Ru—CO ... PMe_2 ... PMe_2

Addition of the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n= 1-3) to the ruthenium carboxylate dimers $Ru_2(O_2CR)_4Cl$ (R= Me, Et, Ph) gave cis and trans isomers of $Ru(O_2CR)_2L_2$. Hydrido and carbonyl derivatives were obtained with $NaBH_4$ and CO.[15]

Complexes of polydentate phosphorus-nitrogen donor ligands were reported. Ruthenium complexes of the new terdentate ligands, bis(2-(diphenylphosphino)ethyl)benzylamine and bis(2-(diphenylarsino)ethyl)-benzylamine, were prepared and characterized. A variety of ruthenium(II) and ruthenium(III) complexes were prepared by reaction of these ligands with $RuCl_2(PPh_3)_3$, $RuX_3(AsPh_3)_2MeOH$ (X= Cl, Br), and $RuCl_2(Me_2SO)_4$.[16] A ruthenium complex containing the coordinated bicycloaminophosphorane, $[Ph(H)P[(OCH_2CH_2)_2N]$, was prepared. Reaction of $CpRu(CO)_2X$ (X= Cl, Br) with $[Ph(H)P[(OCH_2CH_2)_2N]$ gave $[Cp(CO)Ru\{\eta^2\text{-}PhP(OCH_2CH_2)_2NH\}]X$. Deprotonation of the coordinated nitrogen produced a ruthenium phosphoranide.[17]

Neutral and cationic complexes of phenyl and diphenylphosphine of ruthenium and osmium were prepared. These phosphines readily substitute for carbon monoxide or triphenylphosphine in $MHCl(CO)(PPh_3)_3$ (M= Ru, Os) and $M(CO)_3(PPh_3)_2$. Oxidative addition to give terminal phosphide complexes was not observed during the substitution reactions.[18] The terminal phosphido complexes $M(PRPh)Cl(CO)_2(PPh_3)_2$ (M= Os, R= H, Ph, I, OMe,; M= Ru, R= H) were prepared by deprotonation of $[M(PRPh)Cl(CO)_2(PPh_3)_2]^+$ by DBU. The structure of $Os(PHPh)Cl(CO)_2(PPh_3)_2$ was determined.[19]

The reaction of $RuCl_2(\eta^1\text{-}PPh_2CH_2COOEt)_2(\eta^2\text{-}PPh_2CH_2COOEt)$ with CO under oxidizing conditions produced $RuCl_2(\eta^1\text{-}PPh_2CH_2COOEt)_2(CO)_2$.[20]

(c) Hydrides

The photolysis of cis-$[MH_2L_2]$ (M= Ru, Os; L_2= dmpe, dppe) in toluene results in the formation of H_2. Labelling studies showed the reaction to be intramolecular. The highly reactive organometallic intermediates, $[ML_2]$, oxidatively added tetracyanoethylene in a free radical process. These primary photoproducts were also trapped with carbon monoxide or ethylene.[21]

Ruthenium and osmium complexes containing aluminohydride or borohydride and tertiary phosphine ligands were synthesized. The reaction between MX_2L_n (L= PMe_3, $PEtPh_2$, PPh_3, X= halide) and $LiAlH_4$ gave $L_3HM(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2MHL_3$. Treatment of this with TMEDA gave $[L_3HRu]_2AlH_5$.[22] The treatment of $RuH(BH_4)(tripod)$ (tripod= $MeC(CH_2PPh_2)_3$) with methanol produced a bimetallic ruthenium hydride borohydride complex, $[H(tripod)Ru(\mu\text{-}\eta^2\text{-}BH_4)RuH(tripod)]^+$. NMR spectra suggest fluxionality around the boron center. The product has been structurally characterized and found to have very short Ru-B distances.[23]

$$2 \text{ RuH(BH}_4)\text{(tripod)} \longrightarrow \left[\begin{array}{c} \end{array} \right]^+ BH_4^-$$
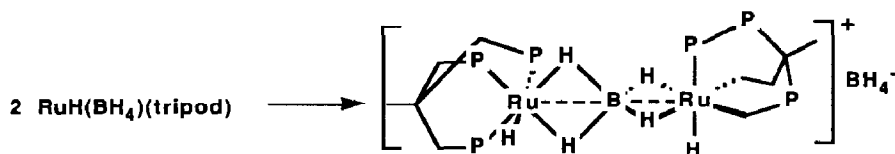
The thermodynamic acidity of some common mononuclear carbonyl hydrides was measured in acetonitrile by IR measurements of the deprotonation equilibria with various bases. The pKa values of $H_2Ru(CO)_4$, $H_2Os(CO)_4$, and $CpRu(CO)_2H$ were found to be 16.6, 18.5, and 19.6.[24]

New ruthenium and osmium complexes containing hydride, carboxylate and phosphine ligands were prepared. The reaction of $RuH(OCOMe)(CO)(PPh_3)_2$ with HBr followed by treatment with hydrogen, excess phosphine, and an amine base produced $RuHBr(CO)(PPh_3)_3$. A variety of carboxylate complexes, $MX(OCOR)(CO)(PPh_3)_2$, were synthesized from carboxylic acids and osmium and ruthenium hydride complexes, $MHX(CO)(PPh_3)_2$. A distorted octahedral geometry with *cis* phosphine ligands was found in the X-ray crystal structure of $RuBr(OCOMe)(CO)(PPh_3)_2$. The structure of the related chloride complex, $RuCl(OCOMe)(CO)(PPh_3)_2$, shows the phosphine ligands to have a *trans* orientation.[25]

Protonation of the osmium and ruthenium hydrides, $M(H)_2(CO)(PPh_3)_3$, with $H_2C(SO_2CF_3)_2$ produces the cationic hydride complexes $[(PPh_3)_3MH(CO)][HC(SO_2CF_3)_2]$. Similarly, protonation of the polyhydido complex $(PPh_3)_3OsH_4$ in the presence of triphenylphosphine results in the formation of a fluxional, seven-coordinate hydride complex, $[(PPh_3)_4OsH_3][HC(SO_2CF_3)_2]$. An X-ray crystal structure of $[(PPh_3)_4OsH_3][HC(SO_2CF_3)_2]$ showed that the molecule has a distorted, capped octahedral structure.[26] Protonation of $Ru(H)_2(PPh)_4$ with the fluorocarbon acid $H_2C(SO_2CF_3)_2$ in arene solvents produced (π-arene)$Ru(H)(PPh_3)_2^+$ derivatives. A crystal structure of $[(\eta^6\text{-toluene})Ru(H)(PPh_3)_2]^+$ was obtained and extended Hückel molecular orbital calculations were carried out to explain structural distortions including "ring slippage" in the molecule.[27] The fluorocarbon acids $H_2C(SO_2CF_3)_2$ or $PhCH(SO_2CF_3)_2$ also react with $Ru(H)_2(CO)(PPh_3)_3$ to form a diruthenium complex with bridging hydrides and a bridging trifluoromethylsulfinate ligand, $[(PPh_3)_4Ru_2(\mu\text{-H})_2(\mu\text{-CF}_3SO_2)(CO)_2]^+$. Reaction with lithium triethylborohydride gives a thermally unstable, purple crystalline complex which has been formulated as $(PPh_3)_4Ru_2(H)_2(\mu\text{-H})(\mu\text{-CF}_3SO_2)(CO)_2$. Solvolysis of $[(PPh_3)_4Ru_2(\mu\text{-H})_2(\mu\text{-CF}_3SO_2)(CO)_2]^+$ proceeds readily in acetonitrile to give $[(PPh_3)_2RuH(MeCN)_2(CO)]^+$. Both of these complexes have been structurally characterized.[28]

RuH$_2$(CO)(PPh$_3$)$_3$

+

CHR(SO$_2$CF$_3$)$_2$

$\longrightarrow$

Ph$_3$P, CO, H, CO, PPh$_3$ — Ru — Ru — O—S—O / CF$_3$ (bridged dimer structure)

$\xrightarrow{\text{MeCN}}$

Ph$_3$P — Ru — PPh$_3$ with NCMe, H, MeCN, CO (mononuclear complex)
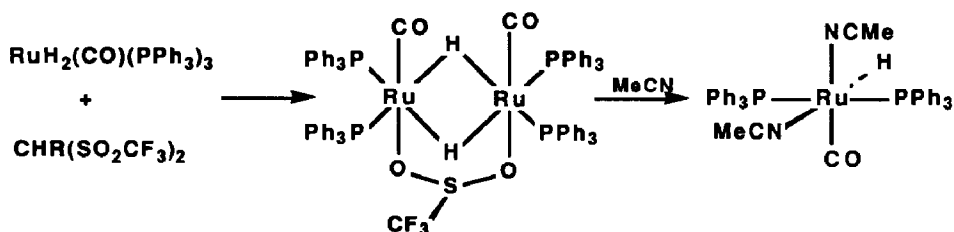
Terminal alkynes inserted into the metal-hydride bonds in MHCl(CO)(PPr$^i_3$)$_2$ (M= Os, Ru) to give five coordinate vinyl complexes, M(CH=CHR)Cl(CO)(PPr$^i_3$)$_2$. The X-ray crystal structure of Os(CH=CHPh)Cl(CO)(PPr$^i_3$)$_2$ shows the molecule to have a square pyramidal geometry with an axial vinyl group. Six-coordinate complexes were produced by the addition of carbon monoxide or by the substitution of chloride for the chelating acetate or acetylacetate ligands.[29] Acetylenes, including phenylacetylene, pent-1-yne, and diphenylacetylene, inserted into the Ru-H bond of RuHCl(CO)(PPh$_3$)$_3$ to generate Ru(RC=HR')Cl(CO)(PPh$_3$)$_2$. The structure of Ru(PhC=CHPh)Cl(CO)(PPh$_3$)$_2$, as determined by X-ray diffraction, consists of a distorted trigonal bipyramid with axial phosphines.[30]

Cationic hydrido complexes of ruthenium with nitrogen donor ligands were synthesized. Substitution of the chloride in Ru(CO)ClH(CO)(PR$_3$)$_3$ for nitrogen bases (L$_2$= 2 py, bpy, phen, Cy-DAB) produces a series of cationic hydrido complexes of ruthenium, [Ru(CO)L$_2$H(PR$_3$)$_2$]$^+$.[31] The reaction of [Ru(NCMe)$_2$H(CO)(PPh$_3$)$_2$]$^+$ with 1-hydroxymethyl-3,5-dimethylpyrazole gives the amidine complex, [Ru(NH=CMe(Me$_2$pz))H(CO)(PPh$_3$)$_2$]$^+$. The X-ray structure shows a distorted trigonal bipyramid with axial phosphines.[32] Amidine complexes of ruthenium, [Ru(η^6-C$_6$H$_6$){NH=CMe(R$_2$Hpz)}-(R$_2$Hpz)]$^{2+}$(R= H, Me), were prepared by the interaction of {Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$ with pyrazole, 3,5-dimethylpyrazole or potassium tris(3,5-dimethyl)pyrazoylborate in acetonitrile. When methanol was used as solvent, only pyrazol complexes were formed.[33] The reaction of (η^6-C$_6$Me$_6$)RuH$_2$(PMe$_3$) with NH$_4$PF$_6$ in acetone gives [(η^6-C$_6$Me$_6$)RuH(NH$_2$Pr^i)(PMe$_3$)]PF$_6$ by the amination of acetone solvent. The X-ray crystal structure of the ruthenium amine complex was obtained.[34]

Certain polyhydrido complexes actually contained η^2-dihydrogen ligands. Since classical hydrido complexes have longer ^{1}H NMR relaxation times than do complexes of molecular hydrogen, NMR studies can be used to provide information on the bonding mode of hydrogen in metal complexes. A series of polyhydride complexes of iron, ruthenium and osmium, MH$_4$(PR$_3$)$_3$, were studied by NMR. The T$_1$ times for the hydride resonance in iron and ruthenium complexes was found to be 24 and 38 ms, respectively. This is consistent with the presence of coordinated dihydrogen in these molecules. The T$_1$ for the hydride resonance in the osmium complex was 820 ms, consistent with the classical structure determined by neutron

diffraction.[35] The protonation of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CNCMe_3)H$ with HPF_6 produced $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)\text{-}(CNCMe_3)(\eta^2\text{-}H_2)]PF_6$. The product was characterized as a cationic molecular hydrogen complex on the basis of NMR spectroscopy (coupling to the phosphorus atom was not observed) and on the exchange reaction with deuterium gas.[36]

The reaction of the polyhydridoruthenium tricyclohexylphosphine complex, $RuH_6(Pcy_3)_2$, with cyclopentene produced $(\eta^5\text{-}C_5H_5)Ru(Pcy_3)_2H$ and $(\eta^4\text{-}C_5H_6)Ru(Pcy_3)_2H_2$. The new trihydrido complex, $(\eta^5\text{-}C_5Me_5)RuLH_3$ (L= PMe_3, PPh_3, PPr^i_3, Pcy_3), was prepared from $(\eta^5\text{-}C_5H_5)RuLCl_2$ and $LiBHEt_3$.[37] A borohydride complex can be isolated in the reaction of $(\eta^5\text{-}C_5H_5)RuLCl_2$ with $NaBH_4$. Hydrogen/deuterium exchange between $(\eta^5\text{-}C_5Me_5)RuLH_3$ and solvent was observed with UV irradiation.[38] The osmium dihydrido complexes, $[CpOsH_2(PPh_3)_2]X$ (X= Cl, Br, I), were prepared either by the oxidative addition of HX to $CpOsH(PPh_3)_2$ or by the thermal dehydrogenation of ethylene glycol by $CpOsBr(PPh_3)_2$. The dihydrido complexes are converted to the neutral halide complexes, $CpOsBr(PPh_3)_2$, by halocarbons.[39]

(d) Carbonyls

A theoretical study by the Hartree-Fock-Slater transition state method of the binding energies, geometries, and relative donor-acceptor properties of a series of ligands on a $Ru(CO)_4$ center was reported. The ligands studied included CX, X_2, H_2CY, and CY_2 (X= O, S, Se, Te; Y= O, S). Bond energies were related to the electronegativity. They were found to strongly increase from the oxygen-containing ligands to the analogous sulfur-containing ligands and then increase only slightly in going to selenium and tellurium-containing ligands.[40]

Strong π-donors, such as CO or Me_3CNC, coordinate to the metal in osmium(VI) complexes of 1,2-bis(2-hydroxybenzamido)benzene and 1,2-bis(2-hydroxy-3,5-dichlorobenzamido)benzene. An internal redox reaction, forming an osmium(IV) complex, and rearrangement of the chelating ligands occurs. The products have the ligand in the *cis* geometry, achieved by rearrangement about the amide C-N bonds.[41]
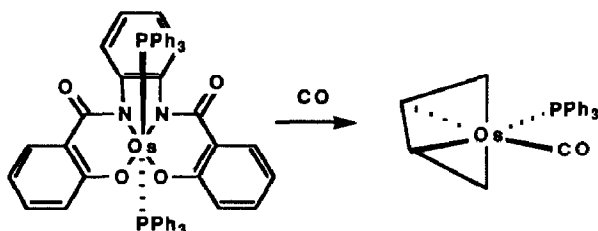
Photolysis of concentrated solutions of $Ru_3(CO)_{12}$ led to the formation of $Ru(CO)_5$ and a ruthenium carbonyl proposed to be an oligomeric form of $Ru(CO)_4$. The reaction of this new carbonyl complex with CO gave a mixture of $Ru_3(CO)_{12}$ and $Ru(CO)_5$. Reactions with halogens, hydrogen, and certain phosphines were similar to reaction chemistry of $Ru_3(CO)_{12}$.[42]
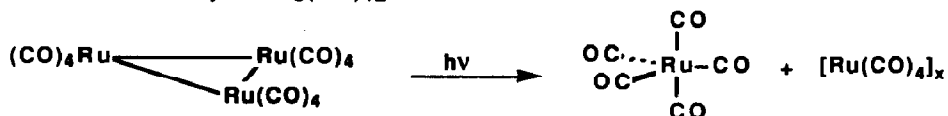
Anionic iodo carbonyl complexes of ruthenium were prepared. The facial and meridional isomers of $[Ru(CO)_3I_3]^-$ were characterized spectroscopically, while a binuclear complex, $Ru_2I_6(CO)_4]^{2-}$, was also structurally characterized.[43]

A series of bipyridine complexes of ruthenium(II) was reported. The complexes prepared were of the formula cis-$[Ru(bpy)(CO)L]^{n+}$ (n=1, L= H, Cl, NCS; n= 2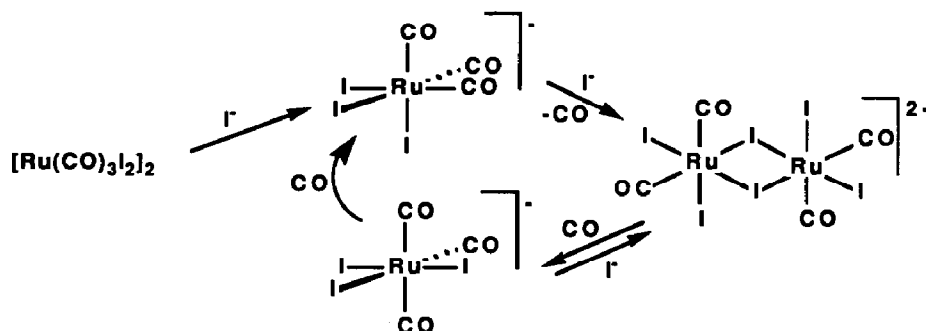, L= H_2O, MeCN, CO, py).[44] The electrochemistry and photochemistry of $[Ru(bpy)HL]^+$ (L= CO, PPh_3, $AsPh_3$) were studied. The phosphine derivative was found to be more photoreactive and the arsine complex.[45] The isolation of intermediates in the water gas shift reactions catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ was reported.[46] The X-ray crystal structure was obtained of one possible intermediate. The hydrido and carbonyl ligands in $[Ru(bpy)_2(CO)H]^+$ are in a cis configuration in this pseudo octahedral complex.[47]

Chelated ruthenium(II) carbonyl complexes of 2-hydroxyphenones were prepared.[48]

(e) Nitrosyls and Other Nitrogen Ligands

The synthesis of thionitrosodimethylamine complexes of ruthenium and osmium, $M(CO)(Me_2NN=S)ClH(PPh_3)_2$, was effected by treatment of $M(CO)ClH(PPh_3)_3$ with $Me_2NN=S$. Cationic complexes were prepared by substitution reactions on $[Ru(NCMe)_2(CO)(PPh_3)_2]^+$ and $[Os(CO)(H_2O)H(PPh_3)_3]^+$.

Spectroscopic data supports a linear $\eta^1(S)$ coordination mode for the thionitrosodimethylamine ligand.[49]

Ruthenium complexes containing ethylcyanoacetate and 4-vinylpyridine were synthesized.[50,51]

The formation of nitrogen-carbon bonds was observed in ruthenium and osmium complexes. The reaction of a ruthenium nitrosyl complex, $Ru(NO)_2(PPh_3)_3$, with benzyl bromide produced a phenyl nitrile complex, $RuBr_2(NCPh)_2(PPh_3)_2$, along with $RuBr_3(NO)(PPh_3)_2$. When the reaction was performed under a carbon monoxide atmosphere, organic products resulting from C-N bond formation were liberated. The mechanism proposed for the reaction involves initial alkylation of the ruthenium center followed by migration of the benzyl group to the nitrosyl nitrogen.[52] The reaction of phenyl azide with an osmium(IV) complex, $trans\text{-}Os(PPh_3)(\eta^4\text{-}OC_6H_4C(O)NC_6H_4NC(O)C_6H_4O)$, produced a product in which a nitrogen insertion into a phenyl C-H bond has occurred. The intermediate formation of an osmium(VIII) bis(phenylimido) complex was proposed. The structure of $Os(\eta^2\text{-}C_6H_5NC_6H_4NH)(\eta^4\text{-}OC_6H_4C(O)NC_6H_4NC(O)C_6H_4O)$ was determined by X-ray diffraction.[53]

(f) Sulfur and Oxygen Donor Ligands

Complexes with coordinated oxyanions have been isolated and characterized. Osmium and ruthenium complexes with O-coordinated perrhenate groups were prepared. Substitution of the halides (X= Cl or Br) in $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2X$ and $Os(PPh_3)_3(CO)(H)X$ with $AgReO_4$ gave $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(ReO_4)$ and $Os(PPh_3)_3(CO)(H)(ReO_4)$, respectively.[54] Although sulfonate anions are usually considered to be a most weakly coordinating to transition metals, a series of O-bonded sulfonato complexes of ruthenium and osmium has been synthesized. These new complexes have been characterized spectroscopically. Some have been isolated in analytically pure form. The x-ray crystal structure of one of these, aquacarbonylbis(p-toluenesulfonato)-bis(triphenylphosphine)ruthenium shows that both sulfonate groups are monodentate and bonded to ruthenium through oxygen. The sulfonate group is readily displaced by carbon monoxide and other good ligands.[55] Covalent trifluoromethanesulfonato complexes $CpRu(CO)_2L(OSO_2CF_3)$ (L= CO, PMe_3) were prepared from $CpRu(CO)_2LX$ (X= H, halogen, alkyl) and $HOSO_2CF_3$. The trifluoromethanesulfonate ligand was easily displaced by neutral donors.[56]

Organometallic derivatives of tetrathiometallates were also prepared. The reaction of $(RC_5H_4)Ru(PPh_3)_2Cl$ (R= H, CH_3) with $[PPh_4][MS_4]$ (M= Mo, W) in acetonitrile produced $MS_4[CpRu(PPh_3)]_2$. These complexes are configurationally stable and react with carbon monoxide to produce mono-carbonyl complexes. The

electrochemistry of these complexes indicated electron delocalization within the Ru_2M units.[57]
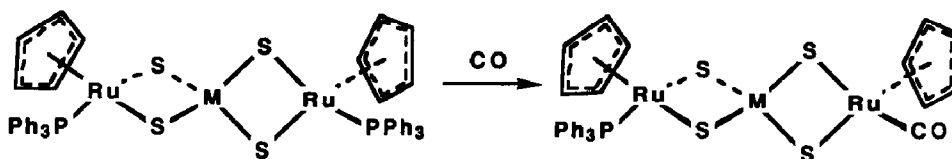
The carbon disulfide ligand in $OsCl(NO)(CS_2)(PPh_3)_2$ can be methylated to give a cationic dithiomethoxycarbonyl complex, $[OsI(NO)\{C(SMe)S\}(PPh_3)_2]^+$. Treatment with either sodium hydrotelluride or with sodium borohydride followed by an electrophilic reagent (HCl, HI, I_2) produced $OsX(NO)(CH_2S)(PPh_3)_2$.[58] Oxidation of the thioformaldehyde complex $OsCl(NO)(CH_2S)(PPh_3)_2$ with 3-chloroperbenzoic acid produced the first metal complex of an unsubstituted sulfine, $OsCl(NO)(CH_2SO)(PPh_3)_2$.[59]

Cyclopentadienylruthenium complexes of dithiolate and other S-S bidentate ligands were prepared from $(\eta^5\text{-}C_5H_4R)RuCl(PPh_3)_2$ (R= H, OMe). Electronic and steric factors determine whether the sulfur ligand is mono- or bi-dentate.[60]

Ruthenium complexes of the tetradentate ligands 2,3-bis(2-mercapto-anilino)butane (bmab) and 1,2-bis(2-mercapto-anilino)ethane (bmae) were synthesized. The complexes $[RuL_2(bmae)]$ and $[RuL_2(bmab)]$ were prepared from the appropriate tetradentate ligand and either $Ru(CO)_3(THF)Cl_2$, $Ru(PMe_3)_4Cl_2$, or $Ru(PPh_3)_2(MeCN)_2Cl_2$.[61]

Structures were reported of two new ruthenium(II) complexes involving two different chelation modes of partially chlorinated 2-(benzylthio)azobenzene.[62]

The crystal structure of a tetraphenylarsonium salt of tetrachloro(D,L-2,5-diselenahexane-Se,Se')ruthenate(III) was obtained.[63]

(g) Formyl and Related C_1 Ligands

Pentamethylcyclopentadienyl ruthenium formyl and hydroxymethyl complexes were synthesized by the reduction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_3][BF_4]$ or $[(\eta^5\text{-}C_5H_5)Ru(PMe_2Ph)(CO)_2][BF_4]$ with borohydrides. The formyl complexes $[(\eta^5\text{-}C_5H_5)Ru(CHO)L(CO)$ decomposed by a radical chain mechanism.[64]

A series of osmium and ruthenium formyl complexes, trans-$[M(CHO)(CO)L_2]^+$, were found to react rapidly with electrophiles (CF_3SO_2Me or CF_3SO_2H) to give methoxy- or hydroxy-carbene complexes, trans-$[M(CHOR)(CO)L_2]^{+2}$.[65]

(h) Alkyl, Aryl Complexes

Oxidative addition reactions of $Ru(CO)_2(triphos)$ with halogens, hydrogen chloride, and alkyl halides produced $[Ru(CO)_2(triphos)X]^+$ (X= Cl, Br, I, Me, Et, CH_2Ph, $\eta^1\text{-}C_3H_5$). The acetyl complex formed from the oxidative addition of acetyl

chloride is unstable. It eliminates ketene and forms [Ru(CO)$_2$-(triphos)H]+.[66] Substitution of a carbonyl ligand in the alkyl complexes [Ru(CO)$_2$(triphos)X]+ for isocyanides or tertiary phosphines produced the chiral octahedral complexes [Ru(CO)L(triphos)R]+. The enantiomers of [Ru(CO)(CNBu^t)(triphos)Me]+ were resolved and structurally characterized.[67]

New alkyl and aryl complexes were formed by intramolecular oxidative addition reactions. A cyclometallated complex of ruthenium, Ru(bpy)$_2$(2-C$_6$H$_4$C$_5$H$_4$N), was prepared by treating Ru(bpy)$_2$Cl$_2$ with 2-phenylpyridine and silver tetrafluoroborate.[68] Spectral, electrochemical and two-dimensional proton NMR data of cyclometallated complexes of ruthenium was reported.[69] A crystal structure of a ruthenium complex of an orthometallated phosphite, Ru{P(OC$_6$H$_3$Me)OC$_6$H$_4$Me-4)$_2$}$_2$(CO)$_2$, was obtained. The geometry around ruthenium is distorted octahedral with *cis* carbonyls.[70]

The reactions of Ru+ and other metal cations with alkanes was studied in the gas phase. Activation of alkanes by ruthenium is dominated by dehydrogenation. While C-H insertions and ß-hydrogen transfers are facile, no evidence was found for C-C insertions or ß-methyl transfers.[71]

Intermolecular activation of carbon-hydrogen bonds in benzene by a tetrakis(trimethylphosphine)osmium(II) system was studied.[72] For the complexes *cis*-(PMe$_3$)$_4$Os(R)H (R= CH$_3$, CH$_2$CMe$_3$, CH$_2$SiMe$_3$), C-H activation was found to be inhibited by excess phosphine. A labeling study showed that the phosphines *cis* to the alkyl and hydride ligands were exchanged faster than those *trans* to these ligands. A rapid γ-hydrogen activation was observed in the unsaturated neopentyl and trimethylsilylmethyl complexes. Kinetic and isotopic labeling evidence was presented to support an osmium(VI) intermediate in the activation of arene carbon-hydrogen bonds.[73]
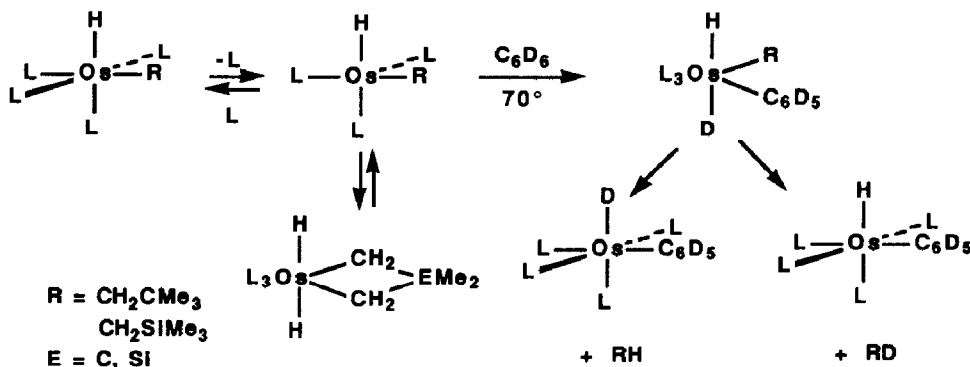
Hydride abstraction of (C$_6$R$_6$)M(CH$_3$)$_2$(PR'$_3$) (M= Ru, R= Me; M= Os, R= H) by [CPh$_3$]PF$_6$ led to the formation of ethylene(hydrido)metal complexes, [(C$_6$R$_6$)MH(C$_2$H$_4$)(PR'$_3$)]PF$_6$. The structure of the ruthenium complex was

determined by X-ray diffraction. Since no radical intermediates were observed, it was proposed that the products result from $M(=CH_2)(CH_3)$ intermediate.[74] Treatment of $(C_6R_6)Os(CH_3)H(PPr^i_3)$ with $[CPh_3]PF_6$ gave the heterometallacycle $(C_6R_6)Os(CH_3)(CH_2CHMePPr^i_2)$. A deuterium labelling study implicates the intermediacy of a cationic $Os(=CH_2)H$ species.[75]

A *cis*-dimetalla-alkene complex formed by the reaction of a ruthenium(II) complex, *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, with bis(phenylethynyl)mercury(II). The X-ray crystal structure of $[Ru(CO)_2\{C(C\equiv CPh)=CPhHgCl\}Cl(PMe_2Ph)_2]$ was obtained. The free diyne was released from the complex by heating. A methyl substituted derivative was synthesized from $Hg(C\equiv CMe)_2$ but was found to be less thermally stable than the phenyl substituted complex.[76]

The syntheses were reported of new alkyl and aryl complexes of osmium, $(\eta^5-C_5Me_5)Os(CO)LR$ (L= CO, R= Me, Bu, Ph; L= PMe_3, R= Me) by the alkylation of $(\eta^5-C_5Me_5)Os(CO)LI$ with the appropriate lithium reagents. Photolysis of $(\eta^5-C_5Me_5)Os(CO)_2Me$ in benzene provided another route to $(\eta^5-C_5Me_5)Os(CO)_2Ph$ by C-H activation of solvent followed by loss of methane. Ethylene displaced one carbonyl ligand from $(\eta^5-C_5Me_5)Os(CO)_2Me$. A diphenylacetylene complex, $[(\eta^5-C_5Me_5)Os(CO)(PPh_3)(\eta^2-C_2Ph_2)]^+$, was formed by treatment of $(\eta^5-C_5Me_5)Os(CO)(PPh_3)I$ with $AgBF_4$ and the acetylene. Terminal acetylenes gave vinylidene complexes in similar reactions, which could be deprotonated to the acetylides.[77]

Oxidation of $(\eta^5-C_5Me_5)Os(CO)(PMe_2Ph)Me$ with either bromine or mercury(II) bromide gave $(\eta^5-C_5Me_5)Os(CO)(PMe_2Ph)Br$. Intermediate osmium(IV) alkyl complexes, $[(\eta^5-C_5Me_5)Os(CO)(PMe_2Ph)(Me)Br][Br]$ and $[(\eta^5-C_5Me_5)Os(CO)(PMe_2Ph)(Me)(HgBr)][Br]$, were isolated from the reaction mixture.[78]

The reaction of the ruthenium carbene complex, $CpRu(Ph_2PCHMeCHMePPh_2)-\{=C(OMe)CH_2Ph\}$, with excess methylmagnesium bromide produced an acetylide complex, $CpRu(Ph_2PCHMeCHMePPh_2)(C\equiv CPh)$. The stereochemistry about the metal atom is retained in the reaction.[79] X-ray crystal structures of the acetylide complex $CpRu(C\equiv CPh)(dppe)$ and the vinylidene complex $[CpRu(C=CMePh)(PPh_3)_2]I$ were obtained. The ruthenium-carbon bond distances were compared.[80] The addition of styrene and styrene derivatives to the acetylide ligand in $CpRu(C_2R)L_2$ (R= Me, Ph; L_2 = CO, PPh_3, 1/2 dppe) was reported. Allylic, butadienyl, and cyclobutenyl complexes were formed. [81]

The S,S and R,R isomers of the pseudotetrahedral molecule $CpRu\{Ph_2PCHMeCHMePPh_2\}Cl$ were used in stereochemical studies. Formation of the vinylidene complex, $CpRu(=C=CPhH)-\{Ph_2PCHMeCHMePPh_2\}$, occurred with retention of configuration when $CpRu\{Ph_2PCHMeCHMePPh_2\}Cl$ was treated with phenylacetylene. Interconversion of this with acetylide, carbene, and alkyl species

occurred with retention of configuration in the chiral cyclopentadienyl ruthenium complexes.[82]
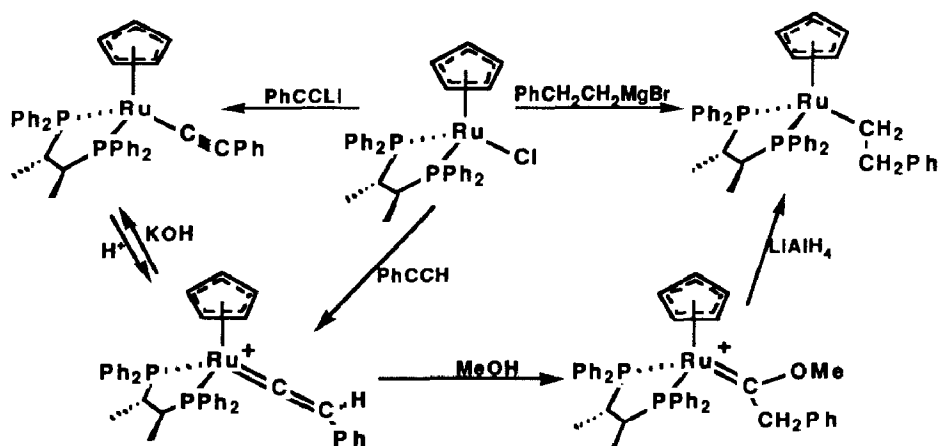
Heterometallacycles were formed when $(\eta^6\text{-}C_6H_6)Os(PPr^i_3)I_2$ was treated with $AgPF_6$ in the presence of methylcarboxylate substituted alkynes. The structure of $[(\eta^6\text{-}C_6H_6)Os(PPr^i_3)(\eta^2\text{-}CH=CIC(OMe)O)]^+$ was determined by X-ray diffraction.[83] An osmium metallacyclobutane-3-one complex, $[Os\{CH_2C(O)CH_2\}(CO)_2(PPh_3)_3]$, was prepared from $[Os(CO)_2(PPh_3)_3]$ with the silyenol ether, $CH_2=C(OSiMe_3)CH_2Cl$.[84]

Restricted rotation in phenyl complexes of ruthenium(II) was studied by NMR. The rotation rate was found to be dependent on the nature of the other ligands on the metal.[85]

A paper concerned the mechanism of decomposition of methyl derivatives of transition metals including ruthenium and osmium.[86]

The syntheses of the first alkyl complexes of ruthenium in the +6 oxidation state were reported. Alkylation of either $[NBu^n_4][Ru(N)Cl_4]$ or $[NBu^n_4][Ru(N)(OSiMe_3)_4]$ with magnesium or aluminum alkyls produced $[NBu^n_4][Ru(N)R_2R'_2]$ (R, R'= Me, CH_2SiMe_3) in high yield.[87]

Alkylation of the osmium(VI) nitrido alkyl complex $[NBu^n_4][Os(N)(CH_2SiMe_3)_4]$ with MeI, Me_3OBF_4, or $MeOSO_2CF_3$ produced the corresponding methylimido complex, $Os(NMe)(CH_2SiMe_3)_4$. X-ray crystal structures of both the reactant and product were obtained. The square pyramidal coordination around osmium in $[Os(N)(CH_2SiMe_3)_4]^-$ is somewhat distorted in the methylimido complex. Methylimido complexes were synthesized from $[Os(N)R_4]^-$ (R=Me, CH_2Ph) and Me_3OBF_4.Trimethylsilylimido, and ethylimido complexes $Os(NR')(CH_2SiMe_3)_4$ (R'=$SiMe_3$, CH_2CH_3) were also prepared.[88]

R= Me, CH₂Ph, CH₂SiMe₃;
R'= Me, Et, SiMe₃
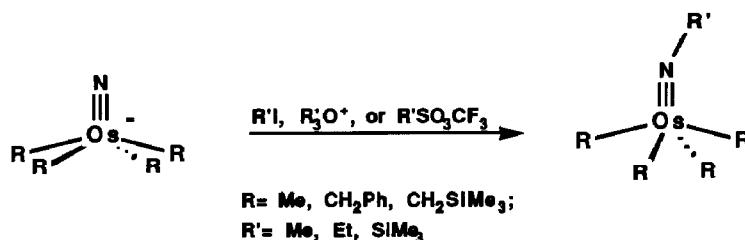
The ruthenium triphenylsilane complex $HRu(SiPh_3)(CO)_3(PPh_3)$, formed from photolysis of $M(CO)_4PPh_3$ in the presence of triphenylsilane, was structurally characterized.[89]

(i) Alkylidene, Alkylidyne Complexes

A review of Roper's work in the formation of metal-carbon multiple bonds appeared. This included the methylene complexes, dihalocarbene, and carbyne complexes of osmium and ruthenium.[90]

An osmium complex with a terminal carbyne ligand, $Os(\equiv CR)Cl(CO)(PPh_3)_2$, was prepared by alkylation of the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ with p-tolyl lithium. The α-carbon of the alkylidyne is nucleophilic. Reactions with HCl and Cl_2 produced carbene complexes. Chalcogens added to the α-carbon to form dihapto-chalcoacyls. Copper, silver and gold halides also added to the α-carbon. X-ray crystal structures of the carbyne complex and of the silver chloride adduct were obtained.[91]

The vinylideneosmium complex, $(C_6H_6)Os(=C=CHPh)PPr^i_3)$ reacts with benzoylazide to form a five-membered metalla heterocycle.[92]
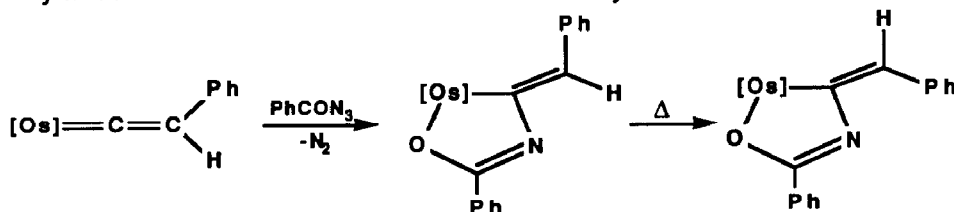
Terminal acetylenes displace chloride on $(\eta^6-C_6Me_6)RuCl_2L_2$ (L= PMe_3, PMe_2Ph) and rearrange to give vinylidene complexes. In methanol, alkoxy(alkylcarbeneruthenium complexes are formed. The use of a hydroxyacetylene in the reaction, such as 4-hydroxybutyne-1, leads to intramolecular cyclisation and formation of the carbene complex, $[(\eta^6-C_6Me_6)Ru(=CCH_2CH_2CH_2O-)Cl(PMe_3)]^+$.[93]

R—C≡CH

R—Ru—Cl (L, Cl) → [Ru=C=C(H)(R) Cl L]⁺ → [Ru=C(CH₂R)(OMe) Cl L]⁺ MeOH
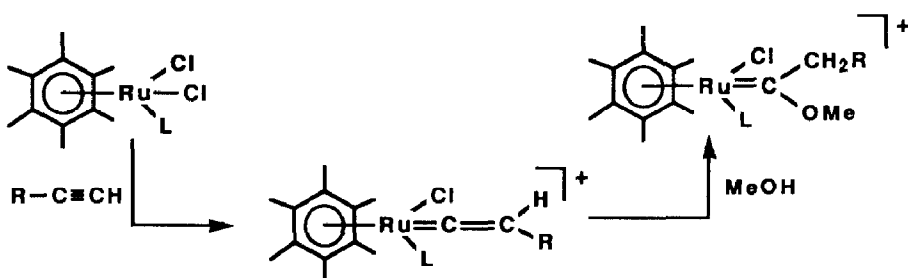
The electronic structure for a ruthenium-methylene complex, $(Ru=CH_2)^+$, was calculated by ab initio methods. These calculations gave a ruthenium-carbon bond energy of 68.0 kcal/mol for the unsaturated complex and a estimate of 83.0 kcal/mol for a saturated analog. The ground state of $(Ru=CH_2)^+$ should have the methylene bonded to ruthenium through a sigma and a pi bond (alkylidene type bonding), but low lying excited states are σ-donor/π-acceptor in character (singlet carbene type bonding).[94] A comparison of the electronic structures of $(Ru=CH_2)^+$ with $(Cr=CH_2)^+$ allowed separation of the donor/acceptor bond strengths.[95] Spectral characterization and measurement of the barrier to methylene rotation by variable temperature ^{13}C and ^1H NMR in $[(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2PPh_2)Ru=CH_2][AsF_6]$ was reported to be 10.9 kcal/mol.[96]

Dicarbonyl(η5-cyclopentadienyl)ruthenium complexes of cycloheptatrienylidene were prepared by reacting $CpRu(CO)_2Br$ with lithium cycloheptatrienide, followed by hydride abstraction with $[Ph_3C][PF_6]$. The salts are similar to the previously prepared iron complexes.[97]

(j) π-Complexes

The reactivity of several ruthenium and osmium π-ethylene and π-benzene complexes towards nucleophiles was related to $k_{CO}^{\bullet}$. This parameter is the C-O force constant for a molecule with CO in place of the unsaturated hydrocarbon.[98]

The ability of the $M(NH_3)_5^{2+}$ moiety to act as a good π-donor has led to the formation of new π-complexes of osmium and ruthenium. Reduction of $[Os(NH_3)_5(CF_3SO_3)]^{2+}$ in acetone produces a thermally stable osmium(0) complex with a π-bonded acetone ligand. An X-ray crystal structure of $[Os(NH_3)_5(\eta^2\text{-}Me_2C=O)]^{2+}$ shows a distortion of the acetone ligand with the carbonyl bent towards the plane of the two methyl groups. The osmium-acetone complex undergoes substitution reactions very slowly. Electron transfer reactions were compared to cyclic voltammetry of the molecule. Thermolysis leads to the formation of a carbonyl species, $[Os(NH_3)_5(CO)]^{2+}$.[99] A ruthenium complex of dimethylacetylenedicarboxylate, $[(NH_3)_5Ru(DMAD)][PF_6]_2$, was prepared by the zinc amalgam reduction of $(NH_3)_5RuCl_3$ in the presence of dimethylacetylenedicarboxylate and ammonium hexafluorophosphate. The product

was characterized spectroscopically and by an X-ray crystal structure. Electrochemistry of the complex showed that the dimethylacetylenedicarboxyalate ligand stabilizes the Ru(II) oxidation state through the π-backbonding of the metal to this ligand.[100] Reactivity of olefins coordinated to pentaamminruthenium(II) was examined in aqueous solutions.[101]

The initial product from the condensation of ruthenium atoms with CO and cyclohexadiene was found to be $Ru(CO)(\eta^5\text{-}C_6H_7)(\eta^3\text{-}C_6H_9)$. Rearrangement of the initial product to $Ru(CO)(\eta^4\text{-}C_6H_8)_2$ occurred at room temperature, while prolonged heating produced $Ru(CO)_2(\eta^3:\eta^3\text{-}C_{12}H_{16})$.[102]
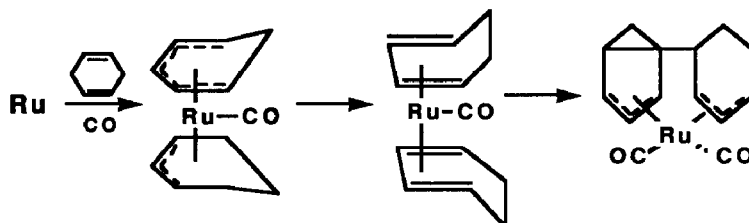
An osmium complex with an η^4 bonded benzene group is formed when osmium atoms are co-condensed with benzene. The complex $Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$ was shown to be fluxional by NMR studies, with interconversion of the two arene rings. Acids react with $Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$ to form $[Os(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$, while the addition of trimethylphosphine gives the C-H activation product, $Os(\eta^6\text{-}C_6H_6)Ph(H)(PMe_3)$.[103]

Addition of excess trimethylphosphine to $(\eta^5:\eta^5\text{-fulvalene})$diruthenium tetracarbonyl at 120° produces a mononuclear ruthenium complex, $(\eta\text{-}C_{10}H_8)Ru(PMe_3)_2CO$. Spectroscopic data and an X-ray crystal structure show some "ring slipage" with η^4 and η^5 -fulvalene-ruthenium resonance forms.[104]

New derivatives of the metallocenes were reported. The functionalized decamethylruthenocenes, $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_5Me_4CHO)$ and $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}C_5Me_4CH_2OH)$, were synthesized. The latter complex was protonated to give nonamethylruthenicenylcarbenium cations, where the carbenium fragment is stabilized by direct interaction with the ruthenium center.[105] The reaction of 1,1'-dilithioruthenocene with elemental selenium produces 1,2,3-triselena[3]ruthenocenophane, which has been structurally characterized.[106] Chromatographic behavior of substituted ruthenocenes, osmacenes and dithiocarbamate derivatives of ruthenium and osmium was described.[107] Isodicyclopentadienide anion reacted with $RuCl_3$ and $OsCl_4$ to form the corresponding metallocene derivatives. The ruthenium complex was shown to have exo complexation of both ligands. A mixed sandwich complex of ruthenium was prepared from $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]^{2+}$ and 4-(dimethylamino)-isodicyclopentafulvene.[108]
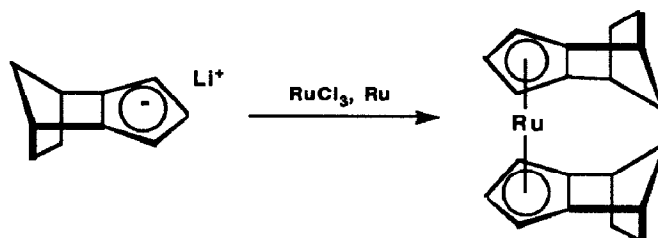
The reaction of $[\{Ru(\eta^4\text{-COD})Cl_2\}_x]$ with $[SnBu^n_3(C_5Me_5)]$ provided an improved high yield synthesis of decamethylruthenocene. Decamethylosmacene was obtained by the direct reaction of $[OsCl_6]^{2-}$ with pentamethylcyclopentadiene. X-ray crystal structures of both permethylmetallocenes were obtained.[109] The crystal structure of osmocene, $Os(\eta^5\text{-}C_5H_5)_2$, was reported.[110]

Borole complexes of osmium and ruthenium, $(\eta^5\text{-}C_4H_4BR)M(CO)_3$ (R= Ph, OMe, Me), were prepared.[111] Ruthenium(II) complexes containing a cyclopentadienyl and a pyrazolylborate ligand were synthesized from $[(\eta^5\text{-}C_5R_5)Ru(MeCN)_3]PF_6$ (R= Me, H) and potassium hydrotrispyrazolylborate or potassium hydrotris(3,5-dimethyl)pyrazolylborate. An X-ray crystal structure of $[CpRu(HBpz_3)]$ was obtained. The electrochemistry of these complexes was compared to that of ruthenocene. The mixed cyclopentadienyl-pyrazolylborate ruthenium complexes were much more reactive chemically and electrochemically than ruthenocene. Both carbon monoxide and trimethylphosphite were able to displace a pyrazole group from the metal center.[112]

Crown ethers containing bound ruthenocene units were prepared from $Ru(\eta^5\text{-}C_5H_4COCl)_2$ and amine substituted crown ethers. The molecules were found to be fluxional.[113] Dynamic ^{1}H and ^{13}C NMR was used to study the fluxional behavior of cryptands containing ruthenocene units.[114]

A general synthesis of $bis(\eta^6\text{-}[2_n]cyclophane)ruthenium(II)$ compounds was reported. The syntheses involved capping a cyclophane with an arene-ruthenium unit, removing the arene by reduction and treatment with acid, and coupling the ruthenium(II) cyclophane complex with another molecule of the cyclophane.[115]
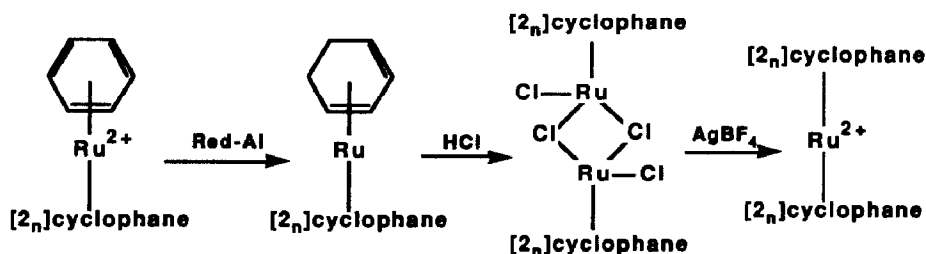
A cyclophane capped by two π-arene ruthenium groups, $[(\eta^6\text{-}C_6Me_6)Ru]_2[\eta^6,\eta^6\text{-}[2_4](1,2,4,5)\text{cyclophane}][BF_4]_4$, was found by cyclic voltammetry to undergo two reversible, two-electron oxidations. A novel mixed-valence ion, $[(\eta^6\text{-}C_6Me_6)Ru]_2[\eta^4,\eta^6\text{-}[2_4](1,2,4,5)\text{cyclophane}][BF_4]_2$, was prepared by chemical oxidation with $(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)Ru$. NMR studies are consistent with a fluxional molecule having localized $Ru^{2+}Ru^0$ sites at low temperature.[116]

Cyclic voltammetry was studied on [m](1,1')- and [m](1,1')[n](3,3')ruthenocenophanes (m, n = 3, 4).[117]

Tin(IV) halide adducts with ruthenocene and with [2]ferrocenophanes were studied by Mössbauer spectroscopy.[118] Tin-119 Mössbauer spectroscopic studies were also performed on tin(IV) chloride adducts of ferrocenylruthenocene and biruthenocene.[119] Structures were obtained of 1,10-(1,1'-ruthenocenediyl)-1,10-dioxa-4,7-dithiadecane and its palladium dichloride complex.[120]

A synthetic procedure was reported for the synthesis of ruthenium phosphazene complexes. The reaction of lithium (1-phenyl-3,3,5,5-tetrachlorocyclotriphosphazen-1-yl)triethylborate with $CpRu(CO)_2I$ gave the 1-phenyl-1-(carbonylcyclopentadienyl-ruthenium)-3,3,5,5-tetrachlorocyclo-triphosphazene.[121] The first bis-transannular metallocenyl cyclophosphazene was prepared from dilithioruthenocene and 1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Ru$ in low yield. The product was structurally characterized.[122] The mechanism for the substitution of fluoride for other anions was discussed.[123]
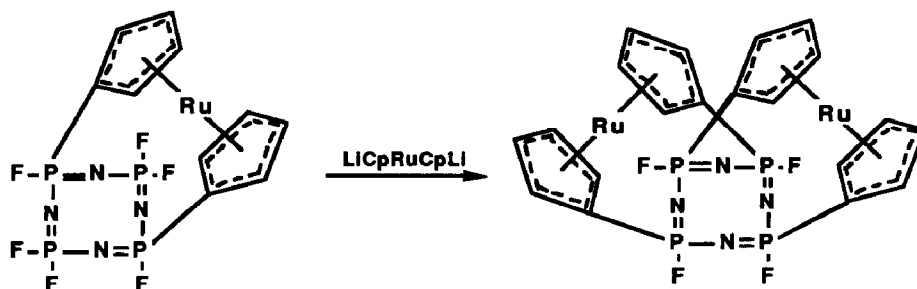
Trihalogeno(pentamethylcyclopentadienyl)ruthenium(IV) complexes were prepared by the oxidative addition of halogen to $[(\eta^5\text{-}C_5Me_5)RuCl_2]_m$ in carbon tetrachloride. Monomeric complexes $(\eta^5\text{-}C_5Me_5)RuX_3L$ (X= Cl, Br, I; L= CO, PPh_3) are formed by addition of the appropriate ligand to $[(\eta^5\text{-}C_5Me_5)RuX_3]_n$ in methylene chloride.[124] Refluxing $CpRuCl(PPh_3)_2$ in ethylene glycol produced $CpRuCl(PPh_3)(CO)$, which was structurally characterized.[125]

Different olefins showed different enantioface selectivity for coordination in the chiral pseudotetrahedral molecules $[CpRu\{(S,S)Ph_2PCHMeCHMePPh_2\}-(CH_2=CHR)]^+$ (R= H, Me, Ph, $CHMe_2$, COOMe, CH_2COMe, $COCH_2Me$). For styrene, only one diastereomer was observed while the diastereomeric ratio is close to unity

for methyl acrylate.[126] The olefin complexes were isolated and the rates of epimerization were found to depend on the structure of the coordinated olefin.[127]

The addition of trimethylphosphite to a σ,η^3-butadienylruthenium complex resulted in rearrangement of the ligand to a σ,η^2-butadienyl coordination mode. The product was structurally characterized. Thermolysis led to ruthenium insertion into a phenyl C-H bond rather than loss of the phosphite ligand.[128]
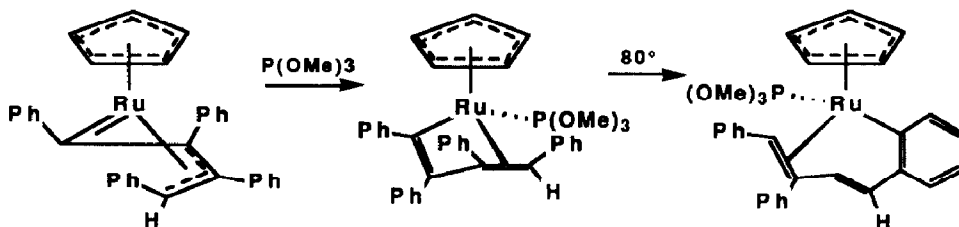
Substitution of acetonitrile for diazadienes (dad= RN=CR'-CR'=NR) in [(η^6-C$_6$H$_6$)Ru(NCMe)$_2$Cl]$^+$ produced [(η^6-C$_6$H$_6$)Ru(dad)Cl]$^+$. Oxidative addition of alkyl iodides gave the alkyl complexes [(η^6-C$_6$H$_6$)Ru(dad)R]$^+$.[129]

Coordinatively saturated, cationic ruthenium(II) complexes were prepared by the reaction of [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ with AgBF$_4$ and the cyclic dienes or trienes: cyclopentadiene, pentamethylcyclopentadienem, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, and 1,3,5-cycloheptriene. Potassium superoxide was reacted at a ligand rather than at the metal. Treatment of [(η^5-C$_6$H$_7$)(η^6-C$_6$H$_6$)Ru][BF$_4$] with KO$_2$ gave a cyclohexadienone complex of ruthenium(0).[130]
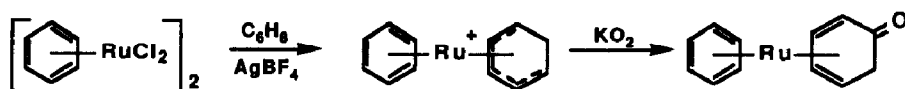
Photosubstitution reactions of the ruthenium(II) arene complexes Ru(η^6-arene)L$_3$$^{2+}$ (L = NH$_3$ or H$_2$O) were studied in aqueous solution. The quantum yields for the formation of Ru(H$_2$O)$_3$L$_3$$^{2+}$ were dependent on the nature of the arene but not on L.[131] Ruthenium cyclopentadienyl complexes of naphthalene, anthracene, pyrene, chrysene and azulene, [(η^5-C$_5$R$_5$)Ru(η^6-arene)]PF$_6$ (R = H, CH$_3$), have been prepared. Kinetic studies of arene displacement reactions in acetonitrile solutions were reported. Two proposed mechanisms for the formation of [(η^5-C$_5$R$_5$)Ru(NCMe)$_3$]PF$_6$ involve preequilibrium of the η^6-arene complex to an η^4-arene, or direct nucleophilic attack at the metal center.[132] Methylation of the cyclopentadienyl and arene rings in the ruthenium complexes [(η^5-C$_5$R$_5$)Ru(η^6-

arene)]+ decreased the quantum yield for the photochemical arene displacement reaction.[133]

$$Ru^+ \quad \xrightarrow[\text{pyrene}]{hV \ , \ MeCN} \quad MeCN \diagdown \overset{MeCN}{\underset{Ru^+}{\big|}} \diagup NCMe$$
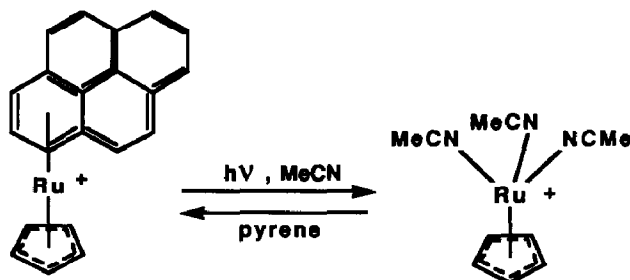
Treatment of [RuH(COD)(NH$_2$NMe$_2$)$_3$]PF$_6$ with thallium cyclopentadienide gave CpRu(COD)H. Treatment with alkyl halides (CCl$_4$, MeI, CH$_3$Br$_2$) gave the halide complexes CpRu(COD)X.[134] Addition of either triphenylphosphine or xylyl isonitrile to the hydrido complex resulted in the migration of the hydride to the cyclooctadiene ligand to form allyl complexes, CpRu(η^3-C$_8$H$_{13}$)L. The addition of chelating diphosphines to the hydido complex gave alkenyl species, CpRu(η^1-C$_8$H$_{13}$)L$_2$.[135]

A number of papers detailed reactions of the ruthenium cyclooctadiene complexes, CpRu(COD)X (X= Br, Cl). The reaction of the ruthenium cyclooctadiene complex, CpRu(COD)X with 3-bromocyclohexene and cis-3,4-dichlorocyclobutene in methanol produced the ruthenium(VI) allyl complexes CpRu(η^3-C$_6$H$_9$)Br$_2$ and CpRu(η^3-C$_4$H$_4$OMe)Cl$_2$. Dehydrohalogenation and dehydrogenation of CpRu(η^3-C$_6$H$_9$)Br$_2$ takes place in refluxing ethanol to produce the arene complex, [CpRu(η^6-C$_6$H$_6$)]+. The X-ray crystal structure of CpRu(η^3-C$_4$H$_4$OMe)Cl$_2$ was obtained.[136] Phenylacetylene reacted with CpRu(COD)Br to form a metallacyclopentatriene complex, CpRu(CPhCH$_2$CH$_2$CPh)Cl. The X-ray crystal structure of the product shows bond lengths in the ruthenacycle to be consistent with a delocalized metallacyclopentatriene unit.[137] The reaction of bidentate amines with (η^5-C$_5$H$_4$R)Ru(COD)Cl gave the ruthenium(II) amine complexes with displacement of the cyclooctadiene.[138] Dehydrogenation of the cyclooctadiene ligand in CpRu(COD)Cl was promoted by NH$_4$PF$_6$. One of the two isomeric products of the reaction, [CpRu(η^6-C$_8$H$_{10}$)]PF$_6$, contains a cyclooctatriene ligand. In the other product, the C$_8$H$_{10}$ unit is bonded as a 1-3-η: 5-7-η-cycloocta-1,5-dienediyl ligand. This structure was confirmed by an X-ray crystal structure.[139]

The syntheses and NMR spectra of mixed sandwich ruthenium(II) η^5-dienyl, η^6-arene complexes were reported. The complexes, [Ru(η^5-dienyl)(η^6-arene)]+ were prepared from [Ru(H$_2$O)$_6$]+^{2} in ethanol with the appropriate diene and arene. An X-ray crystal structure of a cyclooctadienyl ruthenium complex, Ru(η^5-C$_8$H$_{11}$)(η^6-C$_7$H$_7$SO$_3$), was obtained.[140]

Photochemical studies of [η^5-C$_5$R$_5$)Ru(η^6-COT)]PF$_6$ and [(η^5-C$_5$R$_5$)Ru(η^4-1,5-COT)L]PF$_6$ (R= H, Me; L= CO, P(OMe)$_3$) were reported. Irradiation of [η^5-C$_5$H$_5$)Ru(η^6-COT)]PF$_6$ in the presence of a large excess of trimethylphosphite produced [CpRu{P(OMe)$_3$}$_3$]PF$_6$. The η^4-1,5-cyclooctatetraene ligand was more photochemically labile and the η^6-COT group.[141]

The oxidative dimerization of [Ru(CO)$_2$L(η^4-COT)] (L = CO or PPh$_3$, COT = cyclooctatetraene) occurred upon reaction with ferricenium salts. The initially formed radical cation, [Ru(CO)$_2$L(η^4-COT)]$^+$, dimerized via a carbon-carbon bond coupling to form [Ru$_2$(CO)$_4$L$_2$(η^3,η^3:η'^2,η'^3-C$_{16}$H$_{16}$)]$^+$.[142]

[Ru]= Ru(CO)$_2$L
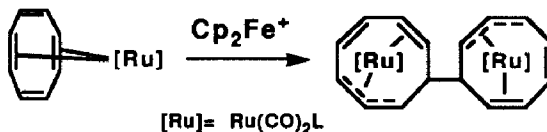
New *p*-cymene derivatives of osmium were prepared and characterized. The X-ray molecular structure of (η^6-p-cymene)(dimethylsulfoxide-S)dichloroosmium(II) was reported.[143] Addition of sodium hydroxide in water to [(η^6-p-MeC$_6$H$_4$Pr^i)OsCl]$_2$ gave a complex with three bridging hydroxides. This complex was active for the catalytic oxidation of acetaldehyde and propionaldehyde to the carboxylic acids in water. Bridging acetate complexes were obtained with one equivalent of the aldehydes and (η^6-p-MeC$_6$H$_4$Pr^i)$_2$Os$_2$(μ-OH)$_3$.[144]

Trimethylenemethane complexes of ruthenium and osmium were prepared by the reaction between metal complexes, OsCl(NO)(PPh$_3$)$_3$ and RuCl$_3$(NO)(PPh$_3$)$_2$, and 2-[(methylsulfonyloxy)methyl]-3-ytrimethylsilylprop-1-ene.[145]

II. Dinuclear Complexes

(a) Homodinuclear Complexes

New homodinuclear complexes were prepared from ruthenium and osmium acetate complexes. The binuclear alkyl complexes M$_2$R$_6$ and M$_2$R$_4$(μ-O$_2$CMe)$_2$ (M= Os, Ru; R= CH$_2$SiMe$_3$, CH$_2$CMe$_3$) were synthesized by the alkylation of Ru$_2$(μ-O$_2$CMe)$_4$Cl or Os$_2$(μ-O$_2$CMe)$_4$Cl$_2$ with alkyl magnesium reagents. Careful air oxidation of the ruthenium alkyl complex provided a ruthenium alkyl dimer with bridging oxo ligands.[146] A homodinuclear, mixed ligand ruthenium complex was prepared from the multiply bonded complex Ru$_2$Cl(O$_2$CCH$_3$)$_4$. Treatment with 2-anilinopyridine followed by reaction with dimethylphosphinomethane and chlorotrimethylsilane produced [Ru$_2$Cl(dmpm)$_2$(PhNpy)$_2$]$^+$. The cyclic voltammetry and X-ray crystal structure of the molecule were reported.[147]

Ru₂Cl(O₂CMe)₄

$Ru_2Cl(O_2CMe)_4$

↓ PhNHpy

$Ru_2Cl(O_2CMe)_2(PhNpy)_2(PhNHpy)$

dmpm, Me₃SiCl →
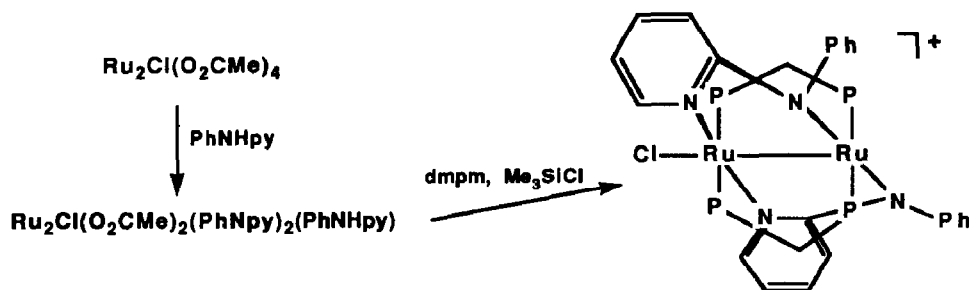
The structure was determined of a dinuclear ruthenium(II) complex containing bridging carboxylato ligands and a bridging aqua ligand, μ-aqua-bis(μ-trichloroacetato-O,O')bis{(η⁴-bicyclo[2.2.1]hepta-2,5-diene)(trichloroacetato)ruthenium(II)}.[148] Substitution of the isocyanides CNR (R= Buᵗ, CH₂Ph, 2,6-Me₂C₆H₃) on the the ruthenium acetate polymer, [Ru(CO)₂(O₂CMe)]ₓ, provides the diruthenium complexes [Ru₂(CO)ₓ(CNR)₁₀₋ₓ]²⁺.[149]

A ruthenium dimer complex containing the chiral diphosphine ligand chiraphos (2(S), 3(S)-bis(diphenylphosphino)butane) was reported. The crystal structure of Ru₂Cl₅(chiraphos)₂ shows that the two ruthenium atoms are bridged by three chlorides, and the diphosphine chelates.[150] Diruthenium complexes bridged by either three chlorides or two chlorides and one carboxylate ligand have been prepared by treatment of RuHCl(CO)(PPh₃)₂ with haloacetic acids.[151]
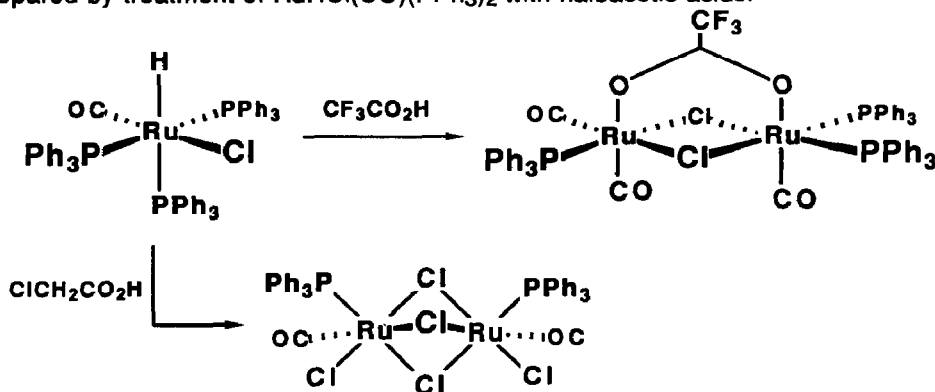
The reaction of aliphatic and aromatic carboxylic acids with Ru₃(CO)₁₂ produced dinuclear carboxylate complexes Ru₂(μ-RCOO)₂(CO)₄. The X-ray crystal structure of Ru₂(μ-4-F-C₆H₄COO)₂(CO)₄ was obtained. Substitution of one carbonyl ligand on each ruthenium atom occurred readily by an associative mechanism.[152]

Oxidation of [Ru₂(CO)₂(μ-CO)(μ-CCH₂)(η⁵-C₅Me₅)₂] with two equivalents of AgBF₄ converted the vinylidene complex to a a μ-ethynyl cation, [Ru₂(CO)₂(μ-CO)(μ-CCH)(η⁵-C₅Me₅)₂]⁺. After chromatography on alumina a μ-ketene complex was obtained, [Ru₂(CO)₂(μ-CO)(μ-C(O)CH₂)(η⁵-C₅Me₅)₂], which was structurally

characterized. Decarboxylation, carbonylation, and reduction reactions of the ketene complex were reported.[153]
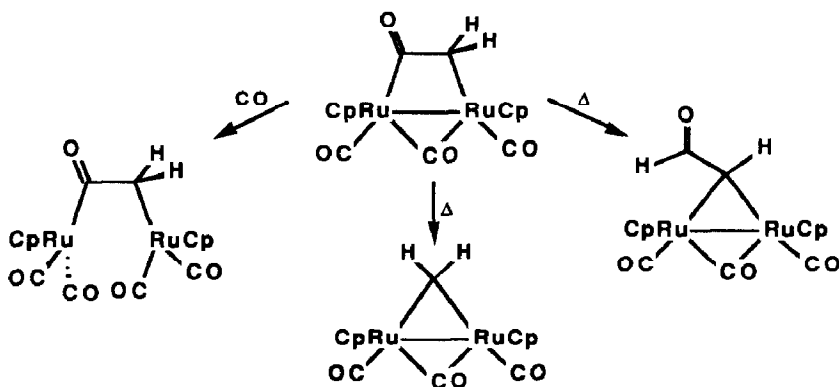
Diruthenium complexes of pyridine-2-carbaldehyde-imines (R-py-2-CR^2=NR) were synthesized. Additional pyridine-2-carbaldehyde-imine reacts with $Ru_2(CO)_6(R$-py-2-CR^2=NR) to form a molecule containing two linked pyridine-2-carbaldehyde-imine ligands. The X-ray crystal structure of [$Ru_2(CO)_5$\{1,2-bis(μ-isopropylamido)-1,2-bis(2-pyridyl)ethane\}] shows the 10 electron ligand bridging the two metal centers which have no metal-metal bond.[154]

The diphosphazane-bridged diruthenium complexes [$Ru_2X(CO)_5$\{μ-$(RO)_2PN(Et)P(OR)_2$\}$_2$]X (R= Me, Pr^i, Ph; X= Cl, Br, I) are readily decarbonylated to [$Ru_2(\mu$-X)(CO)$_4$\{μ-$(RO)_2PN(Et)P(OR)_2$\}$_2$]X. The structure of [$Ru_2(\mu$-I)(CO)$_4$\{μ-$(Pr^iO)_2PN(Et)P(OPr^i)_2$\}$_2$]I was determined by X-ray.[155] Decarbonylation of [$Ru_2(CO)_5$\{μ-$(RO)_2PN(Et)P(OR)_2$\}$_2$] in CCl_4 solution gives [$Ru_2Cl_2(CO)_4$\{μ-$(RO)_2PN(Et)P(OR)_2$\}$_2$] which isomerizes to [$Ru_2(\mu$-Cl)(CO)$_4$\{μ-$(RO)_2PN(Et)P(OR)_2$\}$_2$]Cl. The latter complex can also be readily decarbonylated.[156]

A dimeric ruthenium sulfide complex, [(η^5-$C_5Me_4Et)Ru]_2(\mu,\eta^2$-$S_2)(\mu,\eta^1$-$S_2$), reacts with acetylenes in the presence of tributylphosphine to produce ruthenium dithiolene complexes. The X-ray crystal structures of [(η^5-$C_5Me_4Et)Ru]_2(\mu,\eta^2$-$S_2)(\mu,\eta^1$-$S_2$) and [($\eta^5$-$C_5Me_4Et)Ru]_2(S_2C_2Ph_2$) were obtained.[157]
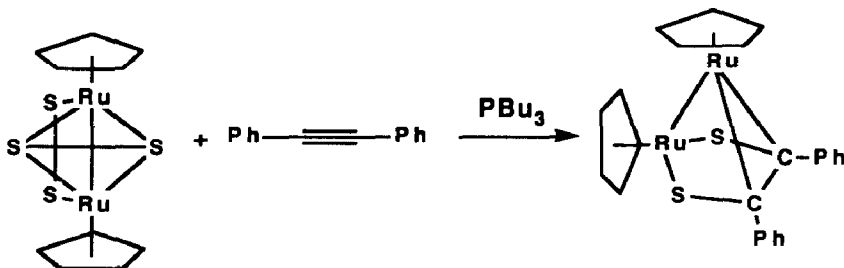
A new group of dinuclear ruthenium cyclopentadienone complexes containing both acidic and hydridic hydrogen atom was reported. The complexes, (η^5-

$C_4R_2R'_2O)(\eta^5\text{-}C_4R_2R'_2OH)Ru_2(CO)_2H$ are catalysts for the dehydration of alcohols and the hydrogenation of ketones. A crystal structure of $(\eta^5\text{-}C_4Ph_2(p\text{-}ClC_6H_4)_2O)(\eta^5\text{-}C_4R_2R'_2OH)Ru_2(CO)_2H$ was obtained and both bridging hydrogen atoms were observed.[158]
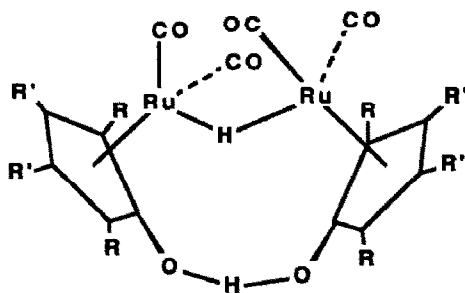
R	R'
Ph	Ph
Ph	p-ClC$_6$H$_4$
Me	Ph
CO$_2$Me	Ph

UV-PES and ab initio calculations on the electronic structure of the bimetallic "flyover-bridge" derivative [cyclic] $Ru_2(CO)_6[(EtC=CEt)_2CO]$. The primary bonding between the unsaturated organic ligand and the $Ru_2(CO)_6$ framework was found to be a sigma interaction between the metals and the terminal carbon atoms.[159] Variable temperature NMR spectra of the flyover bridge complexes $Ru_2(CO)_5L\{\mu\text{-}[C(R)=C(R')]_2CO\}$ (L = CO, PPh$_3$, AsPh$_3$, SbPh$_3$; R, R' = Me, Ph) is consistent with a fluxional process of the dienone ligand with exchange of σ and π bonding of the metal centers to this ligand.[160]

Diazoalkanes, N_2CR_2 (R= H, Me, Ph), add to the the bridging acetylide ligand in $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C\equiv CPh)(\mu\text{-}PPh_2)$ to form $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}R_2C=C=CPh)(\mu\text{-}PPh_2)$. The product is fluxional at room temperature. A mechanism was proposed involving a flipping of the allenyl unit to equilibrate the σ and π interations to the two metal centers.[161]

The synthesis of $Os_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}I)$ from $Os_2(CO)_6(\mu\text{-}I)_2$ and lithium diphenylphosphide was reported.. The product was structurally characterized. Procedures were also developed for higher yield syntheses of $Os_2(CO)_8I_2$ and $Os_2(CO)_6(\mu\text{-}I)_2$.[162]

(b) Heterodinuclear Complexes

Two zirconoxycarbene complexes of ruthenium were prepared by the insertion of a ruthenium carbonyl ligand into a zirconium-hydrogen or zirconium-carbon bond. Both of the starting complexes, 1 and 2, were prepared from $Cp_2Zr[Ru(CO)_2Cp]$. An X-ray crystal structure of $Cp_2Zr(CHO)(CO)RuCp$ was obtained.[163]
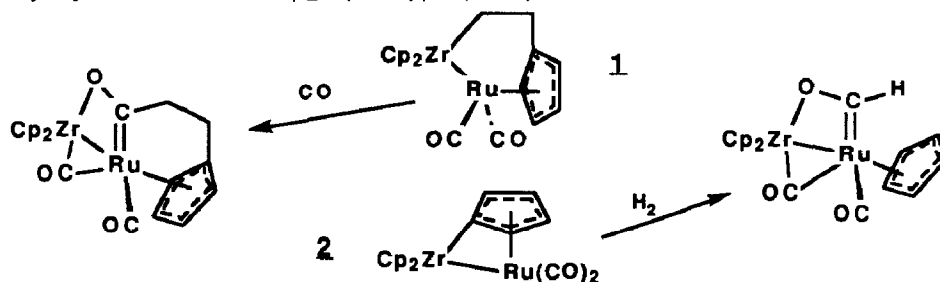
Phosphido bridged Os-Fe and Os-Cr heterobimetallic complexes were prepared. The reactions of $Li_2[Fe(CO)_3(PPh_2)_2]$ or $Li_2[Cr(CO)_4(PPh_2)_2]$ with $Os(CO)_4Br_2$ produced $[FeOs(CO)_6(\mu\text{-}PPh_2)_2]$ or $[CrOs(CO)_7(\mu\text{-}PPh_2)_2]$. The reduction of these complexes with $LiBHEt_3$ resulted in the formation of anionic formyl complexes with the formyl ligand bound to the osmium center.[164]

Several cobalt-ruthenium complexes were prepared. The reaction of $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ with bis(diphenylphosphino)methane gave a complex with a chelating dppm ligand, $(CO)_2(\eta^2\text{-}dppm)Ru(\mu\text{-}PPh_2)Co(CO)_3$, and a product with a bridging dppm group, $(CO)_3Ru(\mu\text{-}PPh_2)(\mu\text{-}dppm)Co(CO)_2$.[165] The substitution of carbon monoxide on $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ by a number of phosphines occurs exclusively at the ruthenium center. Mono and disubstitution products, $L(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ and $L_2(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (L= PPh_2H, PMe_3, PMe_2Ph, $PPhMe_2$, $PPh_2C\equiv CR$), were isolated. The structure of $(PPh_3)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ was determined.[166]

The synthesis and structure of a new phosphido bridged ruthenium-cobalt complex, $[(MeO)_3P]_2(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_2[P(OMe)_3]$, was reported. Two-dimensional shift correlated (COSY) ^{31}P NMR spectra provided information on the network of spin-spin coupled ^{31}P nuclei in the molecule having different stereochemical dispositions.[167] The ruthenium dithiocarbene complex $[Cp(CO)_2Ru=C(SMe)_2]PF_6$ was prepared by alkylation of a ruthenium complex of carbon disulfide. Photochemical displacement of a carbonyl ligand followed by treatment with $NaCo(CO)_4$ produced the heterometallic complex $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Co(CO)_2$.[168]

Heterodimetallic fulvalene complexes with ruthenium along with either iron, chromium, molybdenum, or tungsten, were prepared from $(\eta\text{-}C_{10}H_8)Ru(PMe_3)_2CO$ and $Fe(CO)_5$ or $M(CO)_3(MeCN)_3$ (M= Cr, Mo, W).[169] Electrochemical studies of carbonyl(fulvalene) dimetal complexes were carried out. The complexes

$Ru_2(CO)_4(\mu\text{-}\eta^5C_5H_4\text{-}\eta^5C_5H_4)$ and $MoRu(CO)_5(\mu\text{-}\eta^5C_5H_4\text{-}\eta^5C_5H_4)$ each underwent irreversible two electron oxidation at approximately 1 V, and two electron reduction at -1.65 and -1.25, respectively. An ECE mechanism was proposed for the reduction process. The reactions with iodine and bromine give dihalide products in which the metal-metal bond has been cleaved. Cyclic voltammetry of these compounds showed that reduction occurs at potentials 200-400 mV more positive than in the metal-metal bonded species. [170]

The synthesis of a number of mono- and bis[bis(diphenylphosphino)methane]-bridged ruthenium-rhodium complexes was reported. A heterobimetallic carbonyl bridged complex was prepared from $RuH_2(dppm)$ and $[RhCl(CO)_2]_2$. Reaction of the ruthenium hydrido complex with $[RhCl(COD)]_2$ produced another ruthenium-rhodium complex, $RuRhH_2Cl(COD)(dppm)_2$. Reactions of this complex were discussed. Of particular interest was the migration of a phenyl group from the dppm ligand to ruthenium following alkylation of $RuRhH_2Cl(COD)(dppm)_2$ with methyl lithium. An X-ray crystal structure of $RuRhH(Ph)(PhPCH_2PPh_2)\text{-}(Ph_2PCH_2PPh_2)(C_8H_{12})$ was obtained. [171]
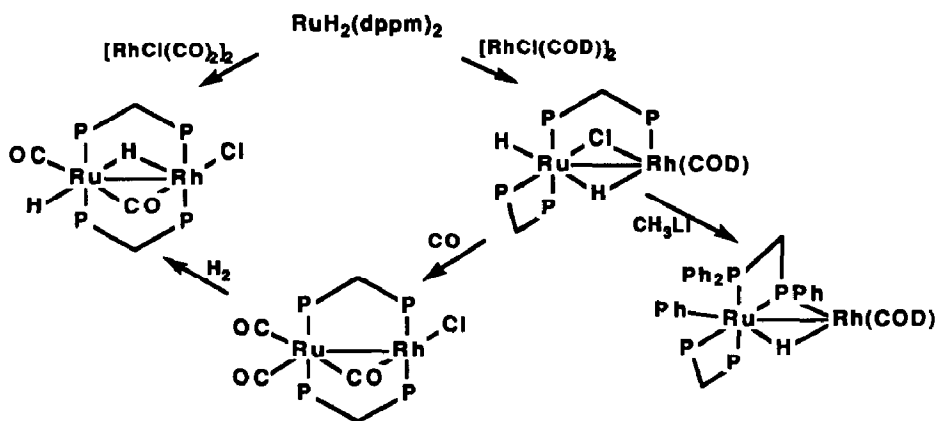
Carbon dioxide is reduced to carbon monoxide on reaction with a heterometallic Rh-Os complex, $(COD)RhH_3Os(PMe_2Ph)_3$. The source of the carbonyl ligand in the product, $H_2Os(CO)(PMe_2Ph)_3$, was confirmed by a labelling study. Another product of this reaction is a heterometallic complex containing both carbon dioxide and hydride ligands. A crystal structure of $(COD)_2Rh_2H_2Os(CO_2)(PMe_2Ph)_3$ was obtained. [172]

$$H_2Os(CO)L_3$$

$$+$$

$$(COD)RhH_3Os(PMe_2Ph)_3 \xrightarrow{CO_2}$$
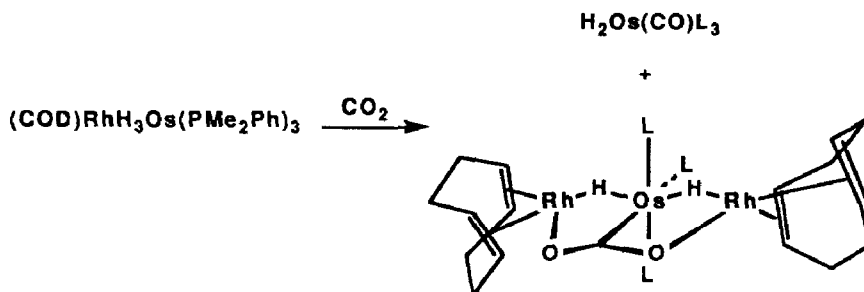
The bridging bis(diphenylphosphino)methane complex $RuRhH_2Cl(COD)(dppm)_2$ was protonated to give,$[RuRhHCl(COD)(dppm)_2]^+$, a complex in which the dppm ligands chelate to ruthenium. Treatment of this with carbon monoxide produced another μ-dppm complex, $[RuRhHCl(CO)_3(dppm)_2]^+$.[173]

A metal-metal bonded pentamethylcyclopentadienyl(dicarbonyl)-ruthenium complex of rhodium octaethylporphyrin was prepared by treating $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ with $[Rh(OEP)]_2$.[174]

New hydrido ruthenium copper complexes were prepared.[175]

III. Polynuclear Complexes
(a) Ru₃ and Os₃ Complexes

Structural information on metal clusters can be obtained directly from the X-ray powder pattern by using the radial distribution method. This technique has been applied to triosmium clusters.[176]

1. M₃ Complexes with Simple Ligands

The X-ray crystal structures of $Ru_3(CO)_{11}(CNBu^t)$ and $Os_3(CO)_{11}(CNBu^t)$ were obtained.[177]

Aldehydes react with $Os_3(CO)_{11}(NCMe)$ to give $Os_3(CO)_{10}(\mu\text{-}H)(COR)$ (R= Me, Ph, CH_2Ph, C_6H_{13}).[178]

The photochemistry from both continuous and flash photolysis of $Ru_3(CO)_{12}$ and the phosphine substituted clusters $Ru_3(CO)_{12-n}(PR_3)_n$ were studied. Irradiation at 350 nm leads to ligand substitution reactions, while irradiation at wavelengths greater than 400 nm leads to photofragmentation. The primary photoproduct in the latter process with $Ru_3(CO)_{12}$ was found to be a non-radical, coordinatively unsaturated isomer. Reaction of this species with ligand, L, leads to $Ru_3(CO)_{12}L$ which is the precursor to the fragmentation products.[179]

The edge double-bridged triruthenium cluster complex $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$ was structurally characterized.[180]

The reactions the $Ru_3(CO)_{12-n}L_n$ with H_2 were studied. Depending on the ligand, L, and the conditions of the reaction, various triruthenium and tetraruthenium hydrido clusters were formed.[181]

The reactions of PH_3, PH_2Me and $PHMe_2$ to $H_2Os_3(CO)_{10}$ produced products resulting from simple substitution of the phosphines for carbon monoxide, as well as complexes containing bridging and capping phosphido groups resulting from insertion of the metal into P-H bonds.[182]

Complexes of osmium and ruthenium with the unsaturated phoshine ligand, sp= $PPh_2(C_6H_4CH=CH_2-2)$, were prepared. Substitution reactions on $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}H_2$ by $PPh_2(C_6H_4CH=CH_2-2)$ gave phosphorus bonded $Os_3(CO)_{11}(sp)$ and $Os_3(CO)_{10}(sp)H_2$, respectively. A similar reaction with $Os_3(CO)_{10}(MeCN)_2$ produced $Os_3(CO)_{10}(sp)$ with phosphorus bound to one metal center and the olefin coordinated to another osmium. Products with chelating $PPh_2(C_6H_4CH=CH_2-2)$ ligands were also formed by substitution on $Ru_3(CO)_{11}(CNBu^t)$.[183]

An osmium cluster complex of 1,1-bis(diphenylphosphino)ethene ligands was prepared from $Os_3(CO)_{12}$ and the phosphine. An X-ray crystal structure determination of $Os_3(CO)_{10}(dppee)$ was obtained.[184]

Water soluble triruthenium clusters were prepared from $Ru_3(CO)_{12}$ and the trisodium salt of tris(m-sulfonatophenyl)phosphine. The mono-, di-, and trisubstituted clusters, $Ru_3(CO)_{12-x}[P(C_6H_4-m-SO_3^-Na^+(H_2O)_3]_x$ (X= 1-3), were isolated.[185]

New osmium and ruthenium cluster complexes with the diphenylphosphinomethane ligand were prepared. Treatment of $Ru_3(CO)_{10}(dppm)$ with trimethylamine oxide and excess diphenylphosphinomethane gave $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$, while the thermal reaction of $Ru_3(CO)_{12}$ with diphenylphosphinomethane produced $Ru_3(CO)_6(dppm)_3$. The osmium complexes $Os_3(CO)_{10}(dppm)$, $Ru_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$, and $Os_3(CO)_8(dppm)_2$ were also synthesized.[186] Iodine was found to cause the declusterification of $Ru_3(CO)_{10}(dppm)$. Both dinuclear, $Ru_2(\mu\text{-I})_2(CO)_4(\mu\text{-dppm})$, and mononuclear, $RuI_2(CO)_2(dppm)$, products were isolated.[187] Treatment of $Ru_3(CO)_{10}(dppm)$ with $KBHBu^s_3$ resulted in the formation of $[Ru_3(CO)_{10}(\mu_3\text{-PPhCH}_2PPh_2)]^-$.[188]

Structures and reaction chemistry of new oxo-ruthenium clusters were reported. The complex, $Ru_3(\mu_3\text{-O})(\mu\text{-H})_2(\mu\text{-dppm})_2(CO)_5$, was prepared from $Ru_3(\mu_3\text{-O})(\mu_3\text{-CO})(\mu\text{-dppm})_2(CO)_5$ and hydrogen. Electrophiles, including H^+, $AuPPh_3^+$, and Ag^+, add to $Ru_3(\mu_3\text{-O})(\mu\text{-H})_2(\mu\text{-dppm})_2(CO)_5$ to give $[Ru_3(\mu_3\text{-O})(\mu\text{-E})(\mu\text{-H})_2(\mu\text{-dppm})_2(CO)_5]^+$. Iodine oxidatively adds to $Ru_3(\mu_3\text{-O})(\mu\text{-H})_2(\mu\text{-dppm})_2(CO)_5$ to open the ruthenium triangle and form $[Ru_3(\mu_3\text{-O})(\mu\text{-I})(\mu\text{-H})_2(\mu\text{-dppm})_2(CO)_5][I]$.[189]

Ruthenium and osmium clusters containing a bridging cis-1,2-bis(diphenylphosphino)ethene ligand were prepared by substitution of carbonyl ligands on $M_3(CO)_{12}$. The ruthenium complex, $Ru_3(CO)_{10}(\mu\text{-Ph}_2PCH=CHPPh_2)$,

readily eliminated $Ru(CO)_4$ to give $Ru_2(CO)_6(\mu\text{-}Ph_2PCH=CHPPh_2)$ which has been structurally characterized.[190]
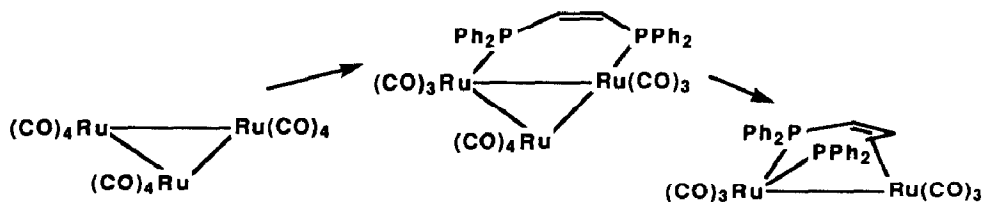
Reactions of the linear triosmium complex, $Br_2Os_3(CO)_{12}$ with phosphines and phosphites gave fragmentation and substitution products. The reactions with PPh_3 and PPh_2Me produced mainly $Os(CO)_4(PR_3)$ along with smaller amounts of $OsBr_2(CO)_2(PR_3)_2$ and $Br_2Os_3(CO)_{10}[P(OPh)_3]_2$. Under the same conditions, addition of triphenylphosphite to the triosmium species resulted mainly in the formation of $Br_2Os_3(CO)_{10}[P(OPh)_3]_2$, which has been structurally characterized.[191]
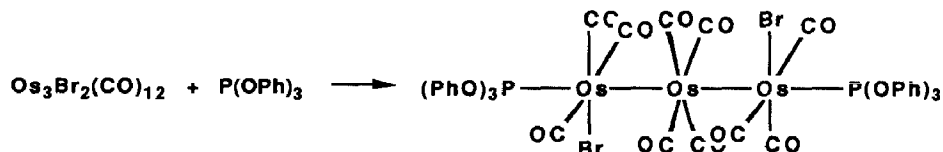
The sulfate and hydrogen phosphate oxyanions coordinate to triosmium carbonyl clusters. Treatment of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ with sulfuric acid produced $H_3Os_3(CO)_9(\mu_3\text{-}O_3SO)$. An X-ray crystal structure of the molecule confirms the tridentate bonding mode of the sulfate ligand. A similar hydrogen phosphate complex was prepared by treatment of $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ with phosphoric acid and trifluoromethanesulfonic acid.[192]

2. M₃ Clusters with Sulfur-Containing Ligands

Substitution reactions of alkynes on $Os_3(CO)_{12}$ were investigated. The kinetics of the reactions of dodecacarbonyltriosmium with diphenylacetylene in decalin or tetradecane have been studied. Two reaction paths have been identified. A bimolecular reaction between the cluster and the acetylene results in fragmentation products. The formation of $Os_3(CO)_{10}(\mu\text{-}C_2Ph_2)$ results from a preequilibrium formation of $Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$ followed by a slow dissociation of carbon monoxide. Additional diphenylacetylene reacts readily with $Os_3(CO)_{11}(\eta^2\text{-}C_2Ph_2)$ to form $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$.[193] Photolysis of $Os_3(CO)_{12}$ in the presence dimethylacetylene dicarboxylate(DMAD) results in the formation of $Os_2(CO)_8(\mu\text{-}\eta^1\text{-}DMAD)$ and $Os_2(CO)_6(DMAD)_4$. A diosmiumcyclobutane structure was found for $Os_2(CO)_8(\mu\text{-}\eta^1\text{-}DMAD)$.[194]

Phosphine substitution reactions on osmium and ruthenium clusters were studied. Ligand substitution kinetics of the triruthenium hydride ion $[HRu_3(CO)_{11}]^-$ were reported. The mechanism of triphenylphosphine substitution for carbon monoxide was proposed to involve unimolecular CO dissociation.[195] The kinetics of phosphorus and arsenic donor substitution reactions on $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$ were studied. A low activation barrier was found for the dissociation of acetonitrile from these complexes.[196]

The kinetics of the intramolecular isomerization of the complexes $(\mu\text{-H})M_3(\mu\text{-}CNMe_2)(CO)_9L$ (M= Ru, L= PR_3, $AsPh_3$, $SbPh_3$; M=Os, L= $AsPh_3$) were investigated. The mechanism for the isomerization was proposed to involve migration of the hydride, methylidyne, and carbonyl ligands through pairwise bridge opening with intermediates having only terminally bound ligands.[197]

Heterocyclic thioamides were found to react with react with $Os_3(CO)_{10}(MeCN)_2$ to give complexes in which the thioamide bridges through sulfur.[198]

The reactions of of osmium and ruthenium carbonyl clusters with dimethylamine were studied. The reaction of $Os_3(CO)_9(\mu_3\text{-S})_2$ with dimethylamine produced $Os_3(CO)_8(\mu_3\text{-S})_2(\mu\text{-Me}_2NC{=}O)(\mu\text{-H})$ as a result of addition of the amine followed by insertion into a metal-carbon bond. The carbamoyl cluster was characterized spectroscopically and by an X-ray crystal structure.[199] The analogous reaction with $Ru_3(CO)_9(\mu_3\text{-S})_2$ produced both $Ru_3(CO)_7(NMe_2H)(\mu_3\text{-S})_2(\mu\text{-}Me_2NC{=}O)(\mu\text{-H})$ and $Ru_3(CO)_6(NMe_2H)(\mu_3\text{-S})_2(\mu\text{-Me}_2NC{=}O)_2$. Ligand substitution and ligand addition occurred in the ruthenium complex. The products were structurally characterized.[200]

The reaction of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ with bis(dimethylamino)methane produces a carbene complex, $Os_3(CO)_9(CHNMe_2)(\mu\text{-SPh})(\mu\text{-H})$. Photolysis of the carbene cluster results in dissociation of CO, α-C-H activation of the carbene ligand, and formation of $Os_3(CO)_8(\mu\text{-C}{=}NMe_2)(\mu\text{-SPh})(\mu\text{-H})$.[201]

The reactions of either $Os_3H_2(CO)_{10}$ or $Os_3(MeCN)_2(CO)_{10}$ with phenylvinylsulfide produced $Os_3H(\mu\text{-SPhCHMe})(CO)_{10}$. Thermolysis or photolysis of the complex resulted in C-H bond cleavage and formation of $Os_3(\mu\text{-SPh})(\mu\text{-}CH{=}CH_2)(CO)_{10}$.[202]

Thioformaldehyde complexes, $Os_3(CO)_{11}(\mu\text{-SCH}_2)$ and $Os_3(CO)_{10}(\mu_3\text{-SCH}_2)$, were synthesized from $Os_3(CO)_{11}(\mu\text{-CH}_2)$ and ethylene sulfide.[203]

The reactivity and catalytic activity of dissolved and tethered thiolate-bridged triosmium and triruthenium cluster complexes was compared.[204]

Structures were determined of $[Ru_3(\mu\text{-H})\{\mu\text{-SC(CH}_3)_3\}(dppm)(CO)_8]$ and $[Ru_3(\mu\text{-H})\{\mu_3\text{-SC(CH}_3)_3\}(dppm)(CO)_7]\cdot 0.5\ CH_2Cl_2$.[205]

3. M₃ Clusters with Nitrogen-Containing Ligands

The osmium and ruthenium carbonyl clusters $M_3(CO)_{12}$ react with nitrosoarenes, p-XC_6H_4NO, to give the arylimido clusters $M_3(CO)_{10}(p$-$XC_6H_4N)$ and $M_3(CO)_9(p$-$XC_6H_4N)_2$.[206] Azoarenes react with the ruthenium monoimido cluster, $Ru_3(CO)_{10}(NAr)$, to form $Ru_3(CO)_9(NAr)(NAr')$. The yield of the bis(imido) cluster improved when $para$-electron withdrawing groups were present on the azoarene. Addition of hydrogen gave $Ru_3(CO)_8H_2(NAr)(NAr')$ which was used as an olefin hydrogenation catalyst.[207]

Diphenylacetylene fragments the imido cluster, $Ru_3(CO)_{10}(NPh)$. Three bimetallic products were isolated from the reaction mixture.[208]
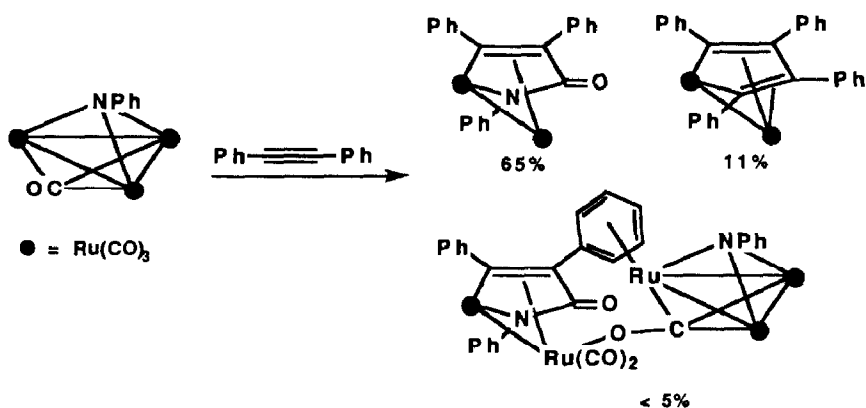
The reaction between tert-butyldiazomethane and $Os_3H_2(CO)_{10}$ produced $Os_3H(Bu^tCH=NNH)(CO)_{10}$, by insertion of the diazoalkane into an osmium-hydrogen bond. Reaction of the diazoalkane with $Os_3H_2(CO)_9(PMe_2Ph)$ resulted in carbon-nitrogen bond formation and the production of an isocyanate complex, $Os_3H_2(Bu^tCH=NNCO)(CO)_8(PMe_2Ph)$. An X-ray crystal structure was obtained which showed the η^2, μ_3-bonding mode of the isocyanate ligand. Protonation cleaved the carbon-nitrogen bond to form $[Os_3H_2(Bu^tCH=NNH)(CO)_9(PMe_2Ph)]^+$.[209]

The reactions of arylazides with triruthenium dodecacarbonyl produced arylimido ruthenium clusters. An X-ray structure was obtained of one of these, $Ru_3(\mu_3$-$NPh)_2(\mu$-$dppm)(CO)_7$.[210]

Aryldiazo-triruthenium complexes, $Ru_3(\mu_3$-$EPhCH_2EPh_2)(\mu$-η^1-$N=NAr)(CO)_9$ (E= P, As; Ar= Ph, 2,4-$Cl_2C_6H_3$), were obtained by treatment of the anions $[Ru_3(\mu_3$-$EPhCH_2EPh_2)(CO)_9]^-$ with aryldiazonium salts. X-ray structure of $Ru_3(\mu_3$-$PPhCH_2PPh_2)(\mu$-η^1-$N=NC_6H_3Cl_2$-$2,4)(CO)_9$ was obtained. Loss of a carbonyl ligand and insertion of a ruthenium atom into and aryl C-H bond occurs on heating.[211]

● = Ru(CO)₃
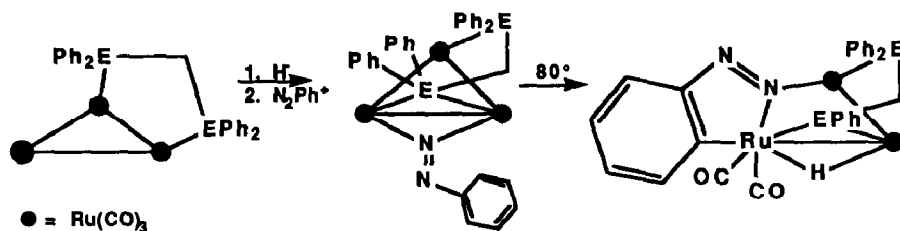
The ruthenium cluster $Ru_3(CO)_{12}$ reacted with nitrogen heterocycles to give either substitution products or cyclometallated species. Reactions with 2,2'-bipyridine gave the simple substitution product while reaction with pyridine gave the cyclometallated complexes $Ru_3(\mu-H)(\mu-NC_5H_4)(CO)_{10}$ and $Ru_3(\mu-H)_2(\mu-NC_5H_4)_2(CO)_8$. Pyrazole and substituted pyrazoles reacted with $Ru_3(CO)_{12}$ to give $Ru_3(\mu-H)(\mu-N_2C_3R_2H)(CO)_{10}$ (R= H, Me, CF₃).[212]

4. M₃ Clusters with Hydrocarbon Ligands

A triosmium cluster containing hydrido and ethyl groups, $HOs_3(CO)_{10}(C_2H_5)$, has been prepared. NMR studies show that a ß-proton of the ethyl moiety interacts with another osmium center in the molecule. Reversible α and ß elimination reactions occur in the molecule, but the α-elimination process was found to be kinetically more favorable. Relationships were suggested between the chemistry occurring on discrete molecular clusters and metal surfaces.[213]
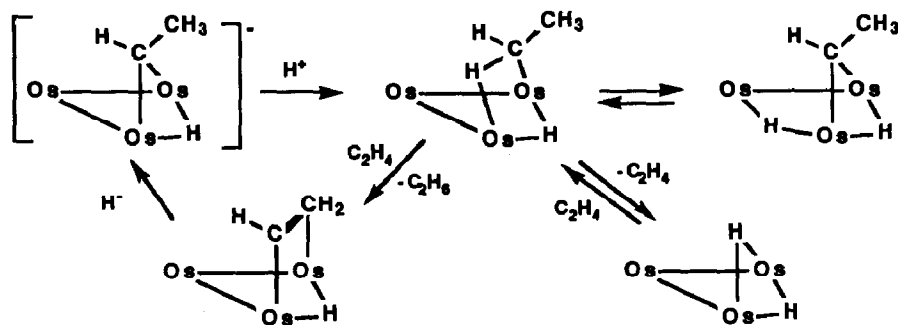
Protonation of $[Os_3(CO)_{10}(\mu-CH_2)(\mu-I)]^-$ with $HBF_4 \cdot Et_2O$ produced a triosmium cluster with a terminal methyl group. The NMR spectra of this complex and partially deuterated analogs are consistent with η¹-coordination of the methyl ligand, rather than the bridging C-H-Os interaction observed in the unsaturated cluster, $Os_3(CO)_{10}(CH_3)(\mu-H)$. The methyl cluster, $Os_3(CO)_{10}(CH_3)(\mu-I)$, reacted with carbon monoxide to form an η¹-acetyl derivative, $Os_3(CO)_{10}(\eta^1-C\{O\}CH_3)(\mu-I)$, and smaller amounts of a bridging acetyl complex, $Os_3(CO)_{10}(\mu-C\{O\}CH_3)(\mu-I)$.[214]

Protonation of $(\mu\text{-H})_3M_3(\mu_3\text{-CR})(CO)_9$ (M= Ru, R= Et; M= Os, R= Me) yielded $[H_3M_3(HCR)(CO)_9]^+$. NMR spectroscopy indicated that the added proton bridges the alkylidyne and metal.[215]

The reductive elimination of hydrocarbon, MeX, from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ was studied. Isotopic labelling of the hydrides showed that at least two of the three reductive elimination steps are intramolecular. The kinetics of the reaction are consistent with the proposed mechanism shown below, involving a sequential formation of the three C-H bonds.[216]

$\cdot = Ru(CO)_3$
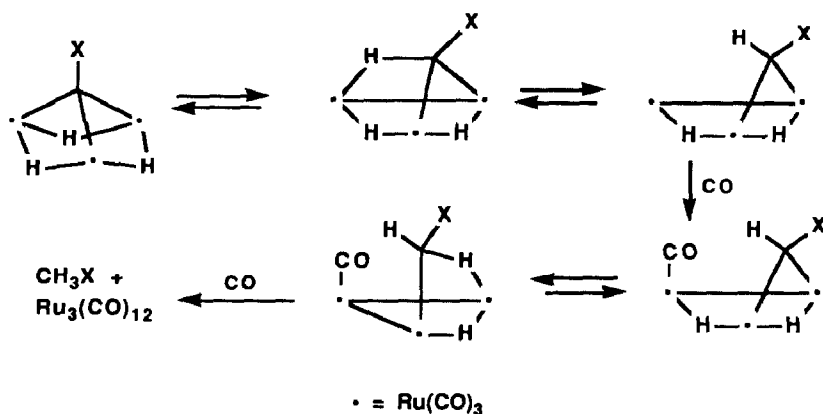
The interaction of alkynes with triosmium and triruthenium clusters has been studied by a variety of spectroscopic techniques, an X-ray crystal structure, and by theoretical calculations. Variable temperature NMR studies on $H_2Os_3(CO)_9(MeC_2Me)$ show a fluxional process in the molecule involving hyride migration and changes in the bonding of the asymmetric alkyne.[217]
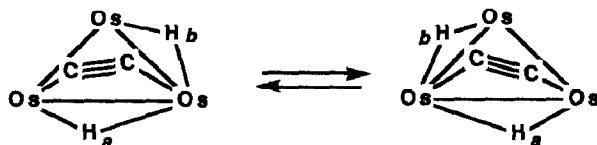
A number of nucleophiles add to the bridging ethyne ligand in $[Os_3H(\mu_3\text{-}C{\equiv}CH)(CO)_9]$. Reactions with ethanol, diethylamine, ammonia, pyridine, and dimethylphenylphosphine gave products resulting from addition to the acetylene ligand. The addition of water to the α- carbon of the acetylene leads to the cleavage of the C≡C, loss of carbon monoxide, and formation of $[Os_3H_3(\mu_3\text{-CH})(CO)_9]$. Another hydrolysis product, formed by addition of water to the β-carbon of the acetylene, is $[Os_3H_3\{\mu_3\text{-CC(O)H}\}(CO)_9]$.[218]

● = Os(CO)₃ → **● = Os(CO)$_3$**

Nu = PMe$_2$Ph, pyridine
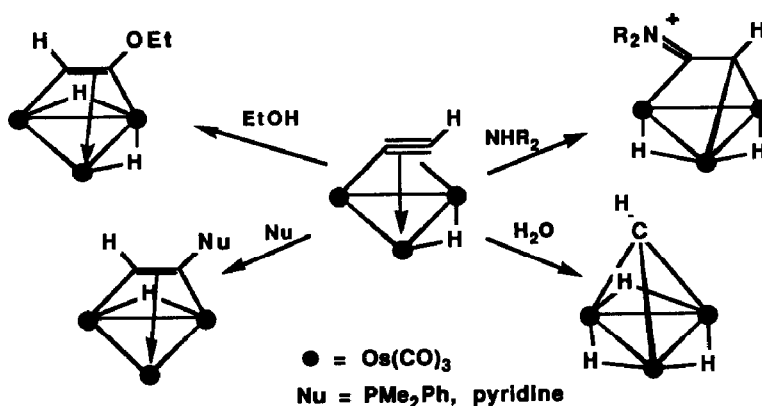
A phosphaalkyne complex of ruthenium, $[Ru_3H(CO)_9(\mu_3\text{-}Me_3C\equiv P)]^-$,was prepared from $[Ru_3H(CO)_{11}]^-$ and $Me_3C\equiv P$.[219]

Vinyl acetate reacts with either $Os_3H_2(CO)_{10}$ or $Os_3(MeCN)_2(CO)_{10}$ to form $Os_3(CO)_{10}(CH_2=CHOCOMe)$, in which the vinyl acetate acts as a chelate.[220]

Two isomers of $Ru_3(\mu\text{-}H)(\mu_3\text{-}Me_2NC_4H_4)(CO)_9$ were formed in the reaction of triruthenium dodecacarbonyl with 1-dimethylamino-2-butyne.[221]

● = Ru(CO)$_3$
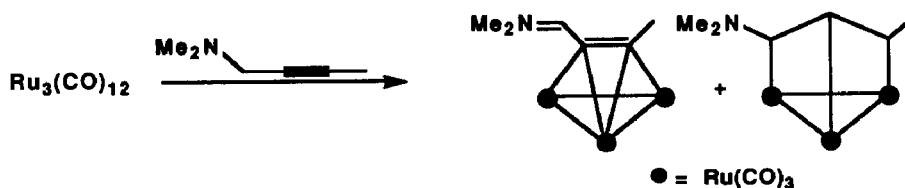
Photolysis of the ruthenium cluster $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$, results in a migration of the methyl group from oxygen to carbon. The product, $HRu_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C(O)CH_3)$, was identified by NMR. Continued photolysis results in fragmentation of the cluster, producing $Ru(CO)_5$ and acetaldehyde.[222]
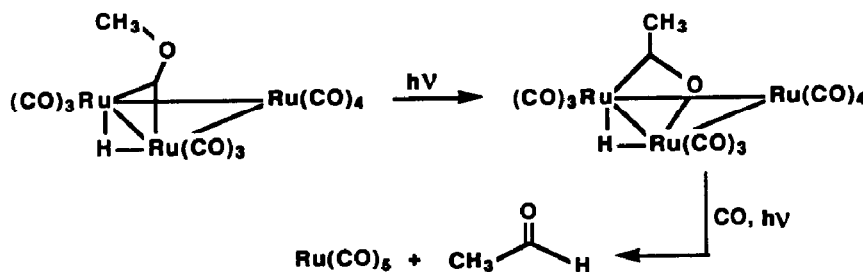
Thermal reaction of a mono-hapto diphenylpyridylphosphine complex, $Ru_3(CO)_{11}(PPh_2py)$, produced a new triruthenium cluster containing a bridging acyl group. An X-ray crystal structure of the product, $Ru_3(CO)_{11}(PPh_2py)$, was obtained.[223]
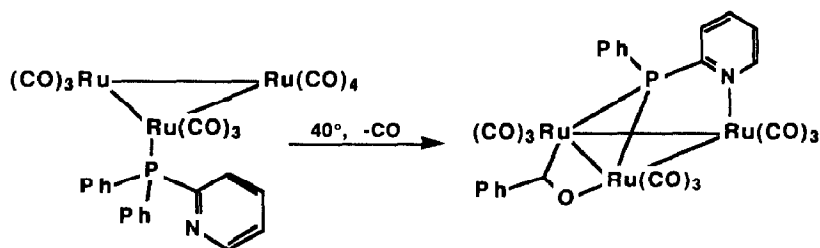
The μ-ketene ligand in $[PPN][Os_3(CO)_{10}(\mu-I)(\mu-CH_2CO)]$ can be converted into η^1-enolate ligands by reaction with nucleophiles, and to acyl and vinyl ligands by reaction with electrophiles. The product of the reaction of $[PPN][Os_3(CO)_{10}(\mu-I)(\mu-CH_2CO)]$ with methanol, $[PPN][Os_3(CO)_{11}-(CH_2C\{O\}OCH_3)]$, has been structurally characterized.[224]

The oxidative addition, with cleavage of the aldehydic C-H bonds, of the 2-formyl derivatives of pyrrole, furan, or thiophene to $Os_3(CO)_{10}(MeCN)_2$ gave bridging acyl complexes, $Os_3H(CO)_{10}(\mu-COC_4H_3X)$ (X= NH, O, S). Thermal decarbonylation of these clusters gave $Os_3H_2(CO)_9(\mu_3-C_4H_2X)$.[225]

The electronic structure of a series of triosmium clusters was investigated by photoelectron spectroscopy and molecular orbital calculations. Data were reported for the series of osmium clusters: $(\mu-H)_3Os_3(CO)_9BL$ (L=CO, PMe$_3$), $(\mu-H)_2Os_3(CO)_9CCO$, and $(\mu-H)_3Os_3(CO)_9CX$ (X= Ph, Cl, Br). The boron in the osmium borylidyne cluster was shown to be similar to a pseudo metal with in the cluster framework.[226]

A triosmium cluster with two capping alkylidyne ligands was synthesized and structurally characterized. Treatment of $(\mu-H)Os_3(CO)_{10}(\mu-COMe)$ with PhLi and $MeOSO_2CF_3$ produced $Os_3(CO)_9(\mu_3-CPh)(\mu_3-COMe)$. The product can be reversibly protonated. Substitution of triphenylphosphine for CO gives $Os_3(CO)_8(PPh_3)(\mu_3-CPh)(\mu_3-COMe)$ and $Os_3(CO)_7(PPh_3)_2(\mu_3-CPh)(\mu_3-COMe)$.[227] The hydrogenation of $Os_3(CO)_9(\mu_3-CPh)(\mu_3-COMe)$ results in alkylidyne-alkylidyne coupling to form an alkyne complex, $(\mu-H)_2Os_3(CO)_9(\mu_3,\eta^2-C_2(OMe)Ph)$. Sequential reduction and protonation generates the phenylacetylide complex, $(\mu-H)Os_3(CO)_9(\mu_3,\eta^2-C_2Ph)$. The phenylacetylide complex can also be prepared by reduction followed by protonation of $(\mu-H)Os_3(CO)_{10}(\mu_3-CPh)$.[228]

A triruthenium complex containing both a methylene unit and an oxygen-bound ketene was formed by the reaction of $Ru_3(CO)_{10}(dppm)$ with diazomethane. The product, $Ru_3(CO)_7(\mu_3,\eta^3-C(O)CH_2)(\mu-CH_2)(dppm)$, was obtained in 30% yield. This

reacts with carbon monoxide to produce a bimetallic complex, $Ru_2(CO)_5(\mu,\eta^4\text{-}CH_2C(O)CH_2)(dppm)$, containing an η^4–oxaallyl unit derived from the CO induced coupling of the methylene and ketene ligands. $Ru_3(CO)_{12}$ is also produced in the reaction. Both new complexes were structurally characterized.[229]

● = $Ru(CO)_3$
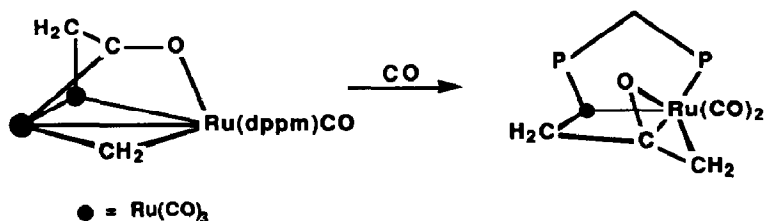
The synthesis and reactions of a triosmium cluster containing a cyclopentadienyl ligand were reported. Cyclopentadiene displaces the coordinated acetonitrile in $Os_3(CO)_{10}(MeCN)_2$ to form a labile cyclopentadiene complex, $Os_3(CO)_{10}(\eta^4\text{-}C_5H_6)$. Hydride abstraction with triphenylcarbenium tetrafluororoborate gave $Os_3(CO)_{10}(\eta^5\text{-}C_5H_5)$. Reaction of this species with BH_4^- or Cl^- gave hydride and chloride addition products in which a metal-metal bond has been cleaved. The linear complex, $Os_3(CO)_{10}(\eta^5\text{-}C_5H_5)Cl$ was structurally characterized. Thermolysis with loss of CO produced the triangulo cluster $Os_3(CO)_8(\eta^4\text{-}C_5H_6)(\mu\text{-}Cl)$.[230] Treatment of $Os_3(CO)_{12}$ with pentamethylcyclopentadiene produced only mononuclear pentamethylcyclopentadienyl-osmium derivatives.[231]

Thermolysis of a triruthenium cluster complex with bis(diphenylphosphino)methane ligands, $Ru_3(CO)_8(\mu\text{-}dppm)_2$, gave products resulting from C-H and C-P cleavage of the dppm ligand. The complex $Ru_3(\mu\text{-}H)(CO)_7\{\mu_4\text{-}\eta^4\text{-}PhPCHP(C_6H_4)Ph\}(\mu\text{-}dppm)$ was isolated in low yield from the reaction and structurally characterized. It was shown that this complex is an intermediate in the formation of the major reaction product, $Ru_3(\mu\text{-}H)(CO)_7(\mu_3\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}CHPPh_2)(\mu\text{-}dppm)$.[232]
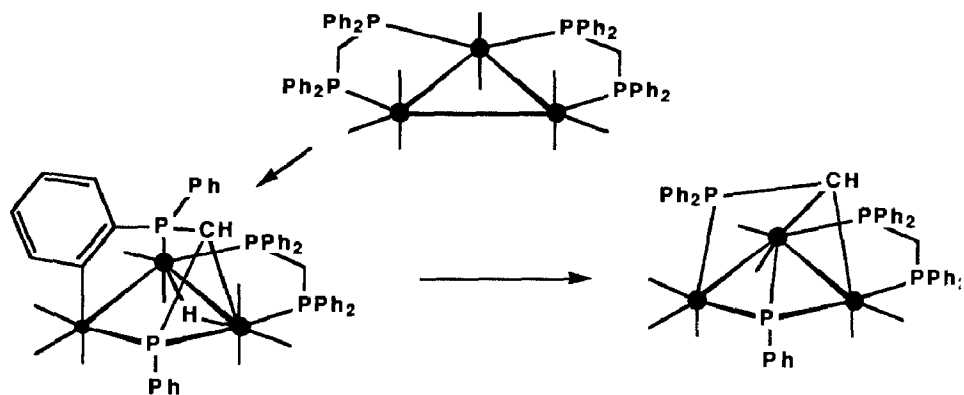
Reactions of $Ru_3(CO)_{12}$ with polynuclear heteroaromatic nitrogen compounds including quinoline, 1,2,3,4-tetrahydroquimoline, phenanthridine, and 9,10-dihydrophenanthridine, resulted in the oxidative addition of a C-H bond of the nitrogen compound to the ruthenium cluster. The crystal structure of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ was obtained.[233]

(b) Ru_4 and Os_4 Complexes

The syntheses of tetraruthenium carbido clusters $Ru_4C(CO)_{13}$, $Ru_4H_2C(CO)_{12}$, and $[HRu_4C(CO)_{12}]^-$ were reported and the X-ray crystal structure of $Ru_4C(CO)_{13}$ was obtained.[234]

Several new sulfido clusters were prepared. Diethylamine and carbon monoxide add to $Os_4(CO)_{12}(\mu_3\text{-}S)$ under mild conditions to form $Os_4(CO)_{12}(NHMe_2)(\mu_3\text{-}S)$ and $Os_4(CO)_{13}(\mu_3\text{-}S)$. An X-ray crystal structure of the diethylamine adduct showed the cluster to consist of a nearly planar array of the four osmium atoms with the amine bonded to the osmium atom not bonded to the sulfur. Hydrogen adds to $Os_4(CO)_{12}(\mu_3\text{-}S)$ to give a dihydride, $Os_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}S)$. This molecule is a closo cluster as shown by X-ray diffraction.[235] An unsaturated osmium cluster, $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC\equiv CCO_2Me)$, was prepared by thermolysis of $Os_4(CO)_{12}[\mu_4\text{-}SC(CO_2Me)CH]$. Reactions with hydrogen and carbon monoxide were reported.[236] Reactions with phenylacetylene and allene opened the closo clusters and produced $Os_4(CO)_{11}[\mu_4\text{-}\eta^3\text{-}SC(Ph)=CHC\equiv CCO_2Me]$ or $Os_4(CO)_{11}[\mu\text{-}CMe_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C=CHCMe_2](\mu_3\text{-}S)$.[237]
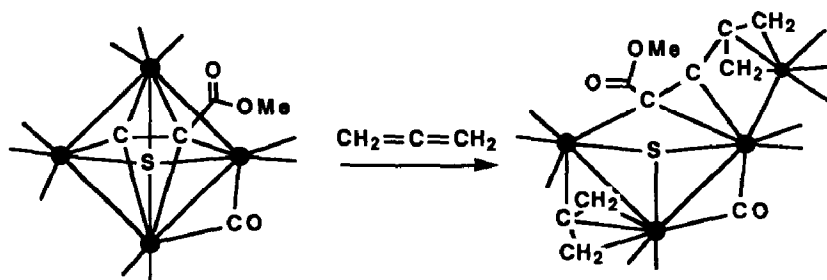
The triruthenium cluster, $Ru_3(CO)_9(\mu_3\text{-}S)_2$ reacts with $Ru(CO)_5$ to form $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$, which was structurally characterized.[238]

The vibrational spectra of $[Os_4O_4(CO)_{12}]$ was analyzed. The molecule is a non-centrosymmetric molecule showing a centrosymmetric infrared and Raman mutually exclusive spectral pattern.[239]

The protonation of three tetranuclear nitrido clusters produced imido clusters and hydrido-nitrido clusters. Protonation of $[FeRu_3N(CO)_{12}]^{1-}$ in a CO atmosphere gave $FeRu_2(NH)(CO)_{10}$, $[FeRu_4N(CO)_{14}]^{1-}$, $HFeRu_3N(CO)_{12}$ and $Ru_3(CO)_{12}$. Protonation of $[FeRu_3N\{P(OMe)_3\}_2(CO)_{10}]^{1-}$ gave $FeRu_2(NH)\{P(OMe)_3\}_2(CO)_9$. While protonation of $[Ru_4N(CO)_{12}]^{1-}$ produced $Ru_3(NH)(CO)_{10}$, $[Ru_5N(CO)_{14}]^{1-}$, $HRu_4N(CO)_{12}$, and $Ru_3(CO)_{12}$.[240]

The metal-nitride stretching vibrations in the IR spectrum of a series of tetranuclear clusters were assigned. The vibrations in the 900-590 cm^{-1} region were analyzed for the clusters $[M_4(\mu_4\text{-}N)(CO)_{12}(\mu\text{-}L)]$ (M= Ru, L= H, NCO, NO; M= Os, L= H) and $[Ru_4(\mu_4\text{-}N)(CO)_{11}(\mu\text{-}H)_3]$.[241]

The first cluster containing a tetrabridging imido ligand, $Ru_4(\mu_4\text{-}NH)(CO)_{11}(Ph_2C_2)$, was formed by treatment of $[PPN][Ru_4N(CO)_{12}]$ with CF_3SO_3H in the presence of diphenylacetylene. An X-ray crystal structure showed the distorted ruthenium square to be capped on one face by the imido group and by the acetylene on the other. A small amount of $Ru_4(\mu_4\text{-}NH)(CO)_{11}(Ph_2C_2)$ was also formed in the reaction.[242]

The nitrile ligand in $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ was converted to an amido ligand by treatment with $[N(PPh_3)_2]NO_2$. The product, $[Os_4H(CO)_{12}(\mu_3\text{-}NCOMe)_2]^-$, reacted with $[MPPh_3]^+$ (M=Au or Cu) to form $[Os_4H(CO)_{12}(\mu_3\text{-}NCOMe)_2(MPPh_3)]$.[243]

Acetylene was found to insert into the skeletal framework of closo-$[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ to form $[Ru_4(\mu_4\text{-}PPh)\{\mu_4\text{-}\eta^3\text{-}P(Ph)CHCH\}(\mu_2\text{-}CO)(CO)_{10}]$.[244] A tetraruthenium cluster containing a bridging η^1,η^2-acetylide ligand, $Ru_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$, was prepared by the carbon monoxide induced phosphorus-carbon bond cleavage in the diphenylphosphinoacetylide cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}$.[245]

The synthesis of $Os_4(CO)_{14}(PMe_3)$ by decarbonylation of $Os_4(CO)_{15}(PMe_3)$ with Me_3NO was reported. Unlike other 62 electron tetranuclear clusters which adopt a butterfly configuration, an X-ray crystal structure showed the product to be an irregular, planar cluster. The ^{13}C NMR spectra showed that the molecule is fluxional. A process involving metal framework rearrangement was proposed.[246]
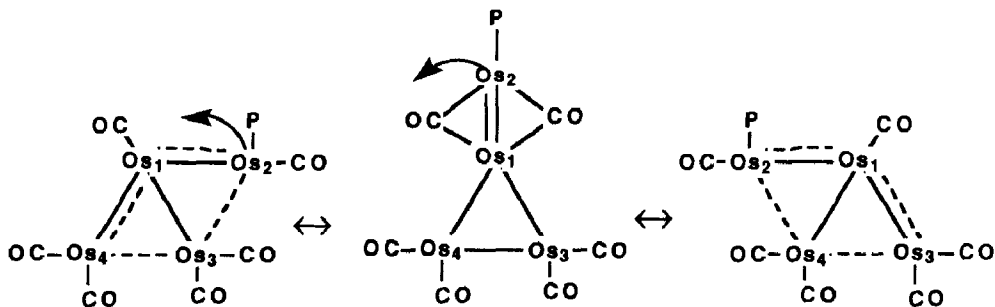
An X-ray crystal structure was reported on the ruthenium cluster decacarbonyl-tetra-μ-hydrido-μ-[methylenebis(diphenylphosphine)-P,P'] tetrahedro-tetraruthenium.[247]

(c) Ru₅ and Os₅ Complexes

Molecular orbital calculations were used to compare the bonding of a carbide and a sulfide in the vertex of an octahedral M_5E cluster.[248]

The synthesis and structure of a pentaosmium cluster containing a phosphinoalkyne ligand, $Os_5(\mu-\eta^2-PC_2PPh_2)(\mu-PPh_2)(CO)_{13}$, was reported.[249]

Reaction chemistry of a pentanuclear ruthenium cluster was reported. Diphenyldiazomethane added to $[Ru_5(CO)_{13}(\mu_4-\eta^2-C_2Ph)(\mu-PPh_2)]$ to form an a product with an intact, μ_4-coordinated diphenyldiazomethane ligand.[250] The addition of diphenylphosphine to without loss of carbon monoxide to $[Ru_5(CO)_{13}(\mu_4-\eta^2-C_2Ph)(\mu-PPh_2)]$ produces a bis-phosphido cluster $[(\mu-H)Ru_5(CO)_{13}(\mu_4-\eta^2-C_2Ph)(\mu-PPh_2)_2]$.[251]
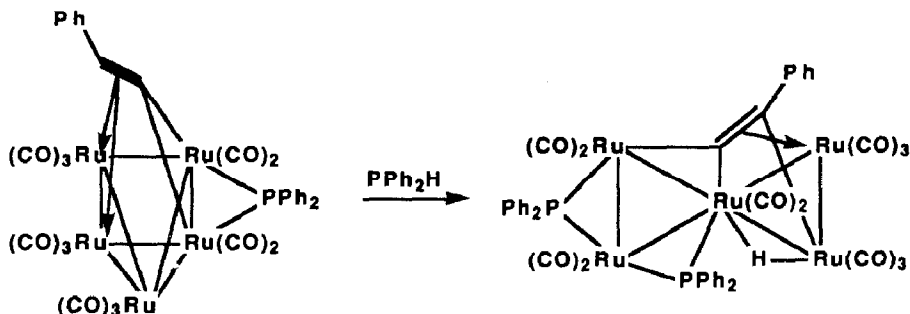
The reaction of $Ru_5C(CO)_{15}$ with bisdiphenylphosphino)ethane produced $Ru_5C(CO)_{15}(dppe)$. An X-ray crystal structure showed that the square pyramidal geometry of the starting cluster complex had been opened up to wing-tip bridged butterfly structure with a unidentate diphosphine ligand.[252] A phosphido-bridged pentaruthenium carbido cluster, $Ru_5C(CO)_{13}(\mu\text{-}PPh_2)$, was prepared by the reaction of $Ru_5C(CO)_{15}$ and diphenylphosphine and was structurally characterized. A similar product, , was obtained in the reaction with $PPh\{CH_2CH_2Si(OEt)_2\}H$. This compound was successfully tethered to silica, but decomposed on an alumina support.[253]

(d) Ru₆ and Os₆ Complexes

The reaction of $Ru_3(CO)_{12}$ with $PPhH_2$ produced $Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}$ and $Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}$. The capping phenylphosphinidene ligand imposes trigonal pyramidal geometry on these cluster. The structures were determined by X-ray.[254]

Decarbonylation of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with $Me_3NO\cdot2H_2O$ produced $Os_3(CO)_8(\mu_3\text{-}S)(NMe_3)(\mu\text{-}OH)(\mu\text{-}H)$ in 44% yield. The product reacted with additional $Os_3(CO)_{10}(\mu_3\text{-}S)$ to form an Os_6 cluster, $Os_6(CO)_{18}(\mu_3\text{-}S)(\mu_4\text{-}S)(\mu\text{-}OH)(\mu\text{-}H)$. X-ray crystal structures were obtained for both new complexes.[255]
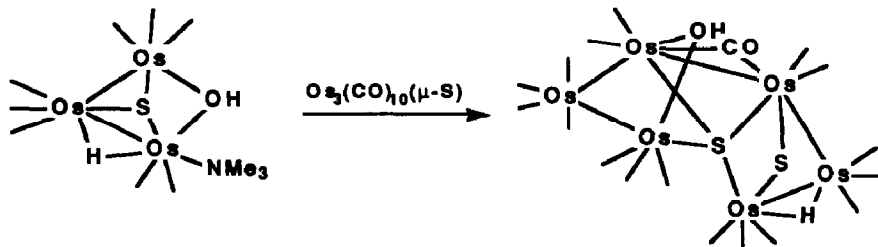
The reaction of $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ with Me_3NO produced two isomers of $Os_3(CO)_8(\mu_3\text{-}SC_6H_4)(NMe_3)(\mu\text{-}H)_2$ in 21% and 10% yield, respectively. Refluxing one of these isomers in heptane produced three isomers of a hexaosmium cluster containing a dimethyl carbene ligand, $Os_3(CO)_{16}[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$. X-ray crystal structures of two of the isomers were obtained.[256]
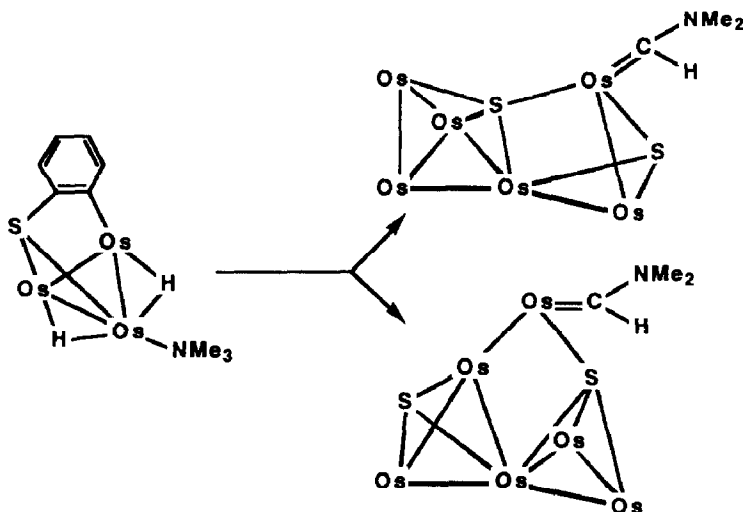
An improved synthesis of was reported for [Os$_6$(CO)$_{20}$(MeCN)] and [Os$_6$(CO)$_{19}$(MeCN)$_2$]. These raft-like clusters were formed by the coupling of [Os$_3$(CO)$_{10}$(MeCN)$_2$] in the presence of PdCl$_2$. Reactions of the Os$_6$ clusters with trimethylphosphite have been shown to give simple substitution products.[257] The reactions of methylacetylene and phenylacetylene with [Os$_6$(CO)$_{20}$(MeCN)] initially gives [Os$_6$(CO)$_{20}${C=C(H)R}]. This represents the first formation of a vinylidene cluster from a non-hydrido precursor. No reaction was observed with disubstituted alkynes. Osmium pentacarbonyl is lost from the cluster under thermal conditions to form a pentanuclear cluster complex [Os$_5$(CO)$_{15}${C=C(H)R}].[258]

The hexanuclear osmium clusters [Os$_6$H$_2$(CO)$_{20}$L(μ_3-PH)] (L= CO, MeCN) were synthesized by mild heating of [Os$_3$H(CO)$_{10}$(μ_2-PH$_2$)] with [Os$_3$(CO)$_{12-n}$(MeCN)$_n$] (n=1,2). The X-ray crystal structure of [Os$_6$H$_2$(CO)$_{20}$(MeCN)(μ_3-PH)] was determined. Weak bases readily deprotonate [Os$_6$H$_2$(CO)$_{21}$(μ_3-PH)]. The crystal structure of the product of this hexanuclear cluster with sodium carbonate and methanol, [Os$_6$H$_2$(CO)$_{20}$L(μ_3-PH)], was determined by X-ray diffraction.[259]
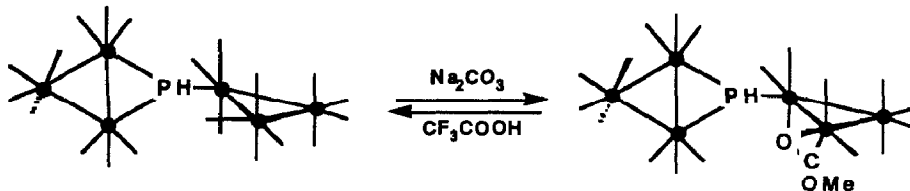
Hexaosmium clusters with interstitial phosphorus, [Os$_6$H(CO)$_{18}$(μ_6-P)] and [Os$_6$(CO)$_{18}$(μ_6-P)]$^-$, were prepared by the thermolysis of [Os$_6$H$_2$(CO)$_{21}$(μ_3-PH)] and [Os$_6$H(CO)$_{21}$(μ_3-PH)]$^-$, respectively. Each of these reacted with [AuPPh$_3$]$^+$ to give [Os$_6$(AuPPh$_3$)(CO)$_{18}$(μ_6-P)] which was structurally characterized.[260]

(e) Higher Nuclearity Complexes

Decarbonylation of osmium clusters with trimethylamine oxide has been used as a method for the synthesis of clusters of higher nuclearity. The reaction of $[Os_5(CO)_{16}]$ with $ONMe_3$ followed by treatment with $[OsH_2(CO)_4]$ produced $[Os_6H_2(CO)_{19}]$. This new hexanuclear cluster was found to rearrange to the known cluster $[Os_6H_2(CO)_{18}]$.[261] The new heptanuclear cluster complexes $[Os_7H_2(CO)_{22}]$ and $[Os_7H_2(CO)_{21}]$ and previously prepared $[Os_7H_2(CO)_{20}]$ were prepared in 13, 41, and 26% yield respectively by reaction of $[Os_6(CO)_{18}]$ with trimethylamine oxide. All were structurally characterized.[262]

$[Os_7H_2(CO)_{22}]$ $[Os_7H_2(CO)_{21}]$ $[Os_7H_2(CO)_{20}]$
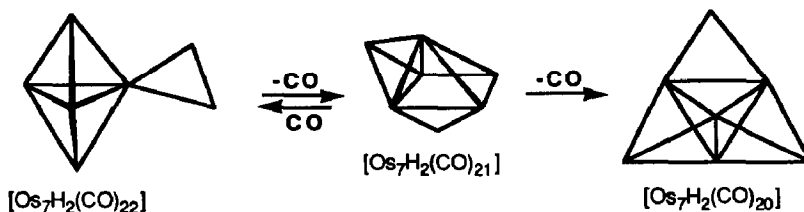
A high nuclearity ruthenium cluster, $Ru_8(CO)_{15}(\mu\text{-}CO)(\eta\text{-tol})(\mu_4\text{-}S)_2$ was prepared from $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Ru_3(CO)_{12}$ in refluxing toluene. The structure of the product as determined by an X-ray crystal structure shows the metal atoms arranged in the form of two fused square pyramids in which the square bases are bridged by sulfido ligands.[263]

The reaction between $Ru_3(CO)_{12}$ and PPh_2H produced a number of ruthenium clusters including $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)(\mu_2\text{-}CO)_2(CO)_{17}]$. The octaruthenium complex was shown by an X-ray crystal structure to have an encapsulated phosphide surrounded by a square antiprism of ruthenium atoms.[264]

(f) Mixed Metal Cluster Complexes
1. Clusters Containing Main Group Metals

Silicon and tin derivatives of triosmium clusters were structurally characterized. The diphenylsilane ligand in $HOs_3(\mu\text{-}H)_2(CO)_{10}(SiHPh_2)$ is bonded in an equatorial position on the triosmium triangle while the dimethyltin group in $Os_3(\mu\text{-}H)_2(CO)_{10}(SnMe_2)$ is axially coordinated.[265] Addition of stannous chloride to $Os_3(\mu\text{-}CH_2)(CO)_{11}$ gives a tin-osmium cluster complex, $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$. The product was obtained in 91% yield and was characterized spectroscopically and by an X-ray crystal structure. The molecule has a nearly planar, butterfly arrangement of the metal atoms.[266]

188

$Os_3(\mu\text{-}CH_2)(CO)_{11}$ + $SnCl_2$ $\longrightarrow$

$$(CO)_4Os \underset{H_2C-\!-Os(CO)_3}{\overset{Cl,\ Cl}{\diagdown Sn \diagup}} Os(CO)_4$$

Phenylethynylgold compounds were found to oxidatively add to $Os_3(CO)_{10}(MeCN)_2$ to form double and triple-bridged phenethynyl triosmium clusters.[267]

$Os_3(CO)_{10}(MeCN)_2$ + $Ph\text{—}\!\equiv\!\text{—}AuL$ $\longrightarrow$ [OC—cluster—AuL with Ph] $\xrightarrow{-CO}$ [cluster with Ph, AuL]
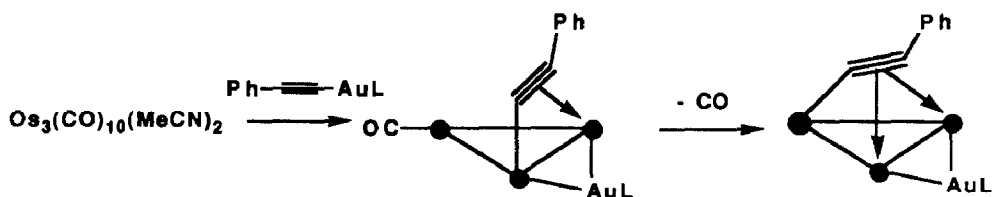
Proton decoupled ^{109}Ag NMR studies on the ruthenium-silver cluster $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (n= 1, 2, 4) have been reported. Using the INEPT pulse sequence, resonances for the silver atoms were observed. Variable temperature studies showed a fluxional process involving rearrangement of the metal skeletons.[268]

X-ray crystal structures of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2PCH_2PPh_2\}(CO)_{12}]$ and $[Ag_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2PCH_2PPh_2\}(CO)_{12}]$ were obtained. The structure of the former complex consists of a capped square-based pyramidal metal core with an apical ruthenium atom. The latter complex has a trigonal bipyramidal metal core. The silver-ruthenium cluster is fluxional in solution at room temperature and a Berry pseudo-rotation of the metal core is proposed to account for this.[269]

Mössbauer spectroscopy data on ruthenium-gold cluster complexes detected structurally non-equivalent gold atoms bearing the same exo atoms. The ^{197}Au mössbauer spectra of $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$, $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ were obtained.[270] The reaction of $AuPPh_3NO_3$ with $RuH_2(dppm)_2$ produced a new

ruthenium-gold complex, $[Au_2Ru(H)_2(dppm)_2(PPh_3)_2][NO_3]_2$ which was characterized by an X-ray crystal structure. The hydride ligands were located in the structure and found to bridge the ruthenium and gold atoms.[271]

$$RuH_2(dppm)_2 + 2AuPPh_3NO_3 \longrightarrow$$
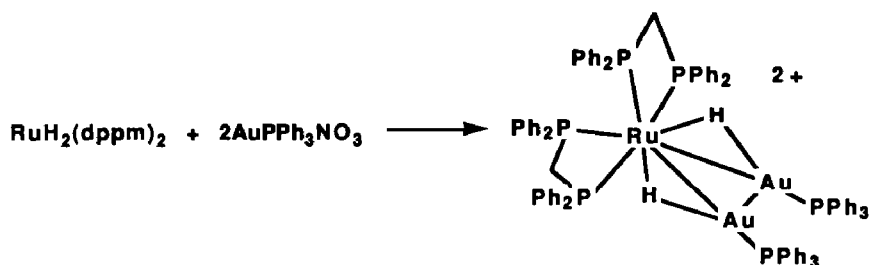
The osmium gold cluster complex, 1,1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-μ-methoxymethylidyne-2,3-μ-triphenylphosphineaurio-triangulo-triosmium, was structurally characterized.[272]

Mixed metal clusters containing the asymmetric bidentate ligands $Ph_2As(CH_2)_nPPh_2$ (n= 1, 2) were prepared by treatment of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with $[M(NCMe)_4][PF_6]$ (M= Cu, Ag) and the bidentate ligand. The products, $[N(PPh_3)_2]_2[M_2\{Ph_2As(CH_2)_nPPh_2\}Ru_4(\mu\text{-}H)_2(CO)_{12}]$, were isolated in 65-70% yield.[273]

The reactions were studied of the ruthenium-mercury cluster, $IHgRu_3(CO)_9(\mu_3\text{-}C_2\text{-}t\text{-}Bu)$ with $Ru_3(CO)_{12}$, $HRu_3(CO)_{11}^-$ and $Ru(CO)_4^{-2}$. Each reaction produced the new cluster complex $cis\text{-}Ru(CO)_4[HgRu_3(CO)_9(\mu_3\text{-}C_2\text{-}t\text{-}Bu)]_2$. This species was characterized by IR NMR and X-ray crystallography. Each mercury atom bridges an edge of a triruthenium cluster and is terminally bonded to a ruthenium tetracarbonyl moiety.[274]

The heterometallic clusters, $MRu_4(\mu\text{-}H)_3(CO)_{12}(PR_3)$ and $MRu_3(CO)_9(C_2Bu^t)(PR_3)$ (M= Cu, Ag), were prepared from $[N(PPh_3)_2][Ru_4(\mu\text{-}H)_3(CO)_{12}]$ or $[N(PPh_3)_2][Ru_3(CO)_9(C_2Bu^t)]$, tertiary phosphines, and $[M(MeCN)_4]PF_6$. X-ray crystal structures of two copper complexes were obtained and the structural similarities and differences among mixed-metal cluster compounds containing copper, silver, or gold atoms ligated by phosphines was discussed.[275]

Crystallographic data appeared for octadecacarbonyl-1,2,3:4,5,6-bis-μ_3-[(η-toluene)cuprio]-octahedro-hexaruthenium.[276]

Large, heterometallic clusters containing osmium and either gold or mercury have been prepared from $[Os_{10}C(CO)_{24}]^{2-}$. Treatment of this Os_{10} cluster with PPh_3AuBr and $AgClO_4$ produced $[Os_{10}C(CO)_{24}AuBr]^-$. Upon standing, an additional decaosmium cluster adds to the product to form $[Os_{20}Au(C)_2(CO)_{24}]^{2-}$. Similar mercury-containing compounds were prepared from $[Os_{10}C(CO)_{24}]^{2-}$ and RHgX.[277] The reaction between $[Os_{10}C(CO)_{24}]^{2-}$ and $[Cu(MeCN)_4][BF_4]$ or PPh_3AuCl produced $[Os_{10}C(CO)_{24}ML]^-$ (ML= Cu(MeCN), AuPPh_3). The X-ray crystal structures of $[Os_{10}C(CO)_{24}ML]^-$ were obtained.[278]

2. Clusters with Other Transition Metals

The reactions of [CpMo(CO)$_2$]$_2$ and CpMo(CO)$_3$ with H$_2$Os$_3$(CO)$_{10}$ in the presence of hydrogen produced the heterometallic clusters Cp$_2$Mo$_2$(μ-H)$_2$Os$_3$(CO)$_{12}$ and CpMo(μ-H)$_3$Os$_3$(CO)$_{11}$. Yields of products are related to the concentration of hydrogen. Both products were structurally characterized.[279]

The crystal structure of (η^5-C$_5$H$_5$)WOs$_3$(CO)$_{12}$(μ_3-CC$_6$H$_4$Me)(μ-H)$_2$ was obtained. The triangular triosmium core is capped by an asymmetrically bridging tolyl carbyne ligand. The reaction of this complex with hydrogen and carbon monoxide releases CpW(CO)$_3$H and forms (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CTol) and (μ-H)Os$_3$(CO)$_{10}$(μ_3-CTol). Labelling studies suggest that CpWOs$_3$(CO)$_{12}$(μ_3-CTol)(μ-H)$_2$ is an intermediate in the formation of CpWOs$_3$(CO)$_{11}$[μ_3-η^2-C(O)CH$_2$Tol]. The latter complex is the major product in the reaction of CpW(CO)$_2$(CC$_6$H$_4$Me) with H$_2$Os$_3$(CO)$_{10}$.[280]

The bridging sulfur atom in Os$_5$(CO)$_{15}$(μ_4-S) donates a total of four electrons to the osmium cluster and retains an electron pair. Treatment with W(CO)$_5$(PPh$_3$), produces a hexanuclear complex in which the sulfur acts as a two electron donor to the tungsten atom. The product was characterized by a X-ray crystal structure.[281]
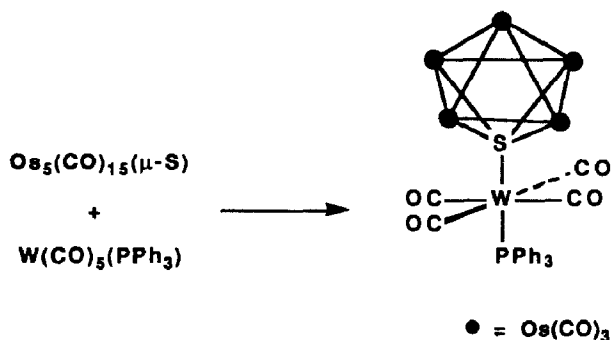
Osmium clusters with manganese or rhenium were prepared. An allenyl-substituted μ-alkylidyne triosmium complex was formed by the reaction of dimethylphenylphosphine with HOs$_3$(CO)$_9${μ_3-η^2-C=C(Ph)(CO)-C=C(Ph)Re(CO)$_4$}. The X-ray crystal structure of HOs$_3$(CO)$_{10}${μ-CC(Ph)=C=C(Ph)Re(PMe$_2$Ph)(CO)$_4$} was obtained.[282] The preparation and crystal structure of hydro[(carboxycyclopentadienyl)tricarbonylmanganese]-decacarbonyl-triangulo-triosmium was reported.[283]

Cluster complexes with iron and ruthenium or osmium were reported. The reaction of [Fe$_3$(CO)$_{11}$]$^{2-}$ with Fe$_2$Ru(CO)$_{12}$ produces a hexanuclear cluster, [Fe$_4$Ru$_2$(CO)$_{22}$]$^{2-}$. The geometry of this cluster unusual, with two Fe$_2$Ru triangles linked by an Ru-Ru bond.[284] The reaction of [Ru(CO)$_3$Cl$_2$]$_2$ with [FeCO)$_4$]$^{2-}$ in water produced the mixed metal clusters Fe$_2$Ru(CO)$_{12}$, H$_2$Fe$_2$Ru$_2$(CO)$_{13}$, and variable

amounts of $H_2FeRu_3(CO)_{13}$.[285] Thermal decomposition of heterometallic clusters on a magnesia support produced small, bimetallic particles. The complexes $H_2FeOs_3(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$ gave 10-15 Å bimetallic particles, while mixtures of $Fe_3(CO)_{12}$ and $M_3(CO)_{12}$ produced particles containing no iron.[286]

The coupling of a phosphinidene-bridged osmium cluster, $[H_2Os_3(CO)_9PR]$ (R= Ph, C_6H_{11}), with the metal carbonyl clusters $[M_3(CO)_{12}]$ (M= Os, Ru) produced hexanuclear clusters, $[M_3Os_3(CO)_{17}(PR)]$, pentanuclear clusters, $[M_2Os_3(CO)_{15}(PR)]$, and tetranuclear clusters, $[H_2MOs_3(CO)_{12}(PR)]$. The ^{31}P-^{187}Os coupling constants from the ^{31}P NMR were used to assign structures in $[Ru_2Os_3(CO)_{15}(PR)]$.[287]

Clusters containing cobalt as well as ruthenium or osmium, $[M_3Co(CO)_{13}]^-$, were prepared by the reaction of $Co(CO)_4^-$ with $M_3(CO)_{10}(MeCN)_2$. A similar reaction between $M'(CO)_4^{2-}$ and $M_3(CO)_{10}(MeCN)_2$ (M', M = Ru, Os) provided a route to osmium-ruthenium tetranuclear clusters.[288] Selectivity in carbonyl substitution reactions was observed in the ruthenium-cobalt heterometallic cluster complex, $HRuCo_3(CO)_{12}$. Substitution of CO for amine ligands occurs preferentially at the ruthenium center while triphenylphosphine substitution occurs at cobalt.[289] Substitution of carbon monoxide for 1,2-bis(diphenylphosphino)ethane in $H_3Ru_3Co(CO)_{12}$ produced $H_3Ru_3Co(CO)_{10}(dppe)$ in which the bidentate phosphine ligand chelates to one ruthenium center. A similar substitution reaction on $HRuCo_3(CO)_{12}$ gave $HRuCo_3(CO)_{10}(dppe)$ in which the phosphine bridges two cobalt centers.[290]

Addition of $\{Cu(PPh_3)Cl\}_4$ or $Au(PPh_3)Cl$ to $HRuCo_3(CO)_{12}$ results in the addition of the $M(PPh_3)$ moiety to the cobalt-ruthenium cluster. Triphenylphosphine addition to $RuCo_3(CO)_{12}(\mu$-$Cu\{PPh_3\})$ produces the salt $[Cu(PPh_3)_3][RuCo_3(CO)_{12}]$.[291]

The synthesis of $H_2Ru_2Rh_2(CO)_{12}$ was reported. Variable temperature NMR studies showed that the structure is related to that of $Rh_4(CO)_{12}$. Both the hydrides and carbonyls were fluxional.[292] X-ray crystallography and NMR spectroscopy were used to study the structure of $H_2Ru_2Rh_2(CO)_{11}(PPh_3)$. The structure was found to be similar to $H_2Ru_2Rh_2(CO)_{12}$ with phosphine substitution at the basal rhodium atom.[293]

The reaction between $Os_3(CO)_{11}(\mu$-$CH_2)$ and $(Ph_3P)_2Pt(C_2H_2)$ produced a new tetranuclear cluster $Os_3Pt(\mu$-$CH_2)(CO)_{11}(PPh_3)_2$. The X-ray crystal structure shows the the platinum bonded to only one osmium of the osmium triangle and the methylene ligand bridging the platinum-osmium bond. Carbon monoxide readily substitutes for the phosphine ligands in this molecule, while diphenyl acetylene displaces only one of the phosphine groups.[294]

Five osmium-platinum cluster complexes were isolated in the reaction of $Pt(PPh_3)_2C_2H_4$ with $Os_5(CO)_{15}(\mu^4\text{-S})$. The square pyramidal complex $PtOs_4(CO)_{13}(PPh_3)(\mu^4\text{-S})$ was isolated in 6% yield and characterized spectroscopically and by X-ray diffraction. Another complex isolated in 7% yield contains an edge-bridged $Os(CO)_3PPh_3$ unit on the square pyramidal cluster framework. Carbon monoxide converts $PtOs_5(CO)_{15}(PPh_3)_2(\mu^4\text{-S})$ to $PtOs_4(CO)_{13}(PPh_3)(\mu^4\text{-S})$ and is probably the precursor to this compound in the substitution reaction.[295] The complex $PtOs_5(CO)_{15}(PPh_3)(\mu^4\text{-S})$ was isolated in 5% yield and structurally characterized.[296]

Pt(PPh₃)₂C₂H₄ ... PPh₃ ... Ph₃P ... S ... CO ... Ph₃P ... S
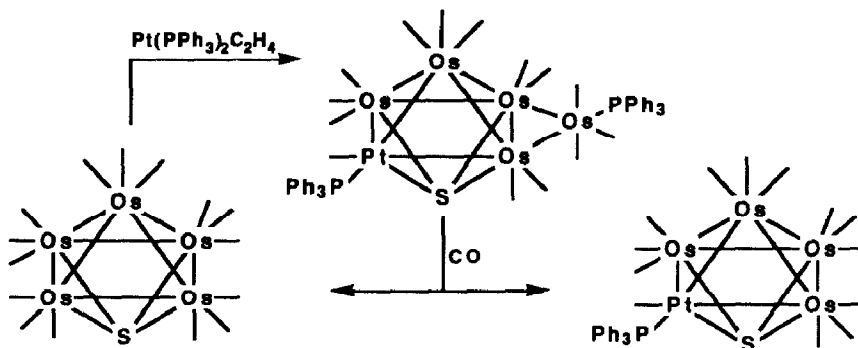
A similar reaction between $Pt(PPhMe_2)_4$ and $Os_4(CO)_{12}(\mu_3\text{-S})_2$ produced $PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-S})_2$ and $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-S})_2$. Both were characterized by X-ray crystal structures.[297]

The addition of $Pt(COD)_2$ to $Os_6(CO)_{18-n}(MeCN)_n$ (n= 1,2) produced $Os_6Pt_2(CO)_{17}(COD)_2$ and $Os_6Pt_2(CO)_{16}(COD)_2$.[298]

Substitution of carbon monoxide for tertiary phosphine ligands on $CpNiOs_3(\mu\text{-H})_3(CO)_9$ was facilitated by trimethylamine oxide.[299] The osmium-nickel clusters catalyzed the isomerization and selective hydrogenation of one double bond of dienes. An μ_3,η^3-allyl triosmium complex, $CpNiOs_3(\mu\text{-H})(MeCCHCMe)(CO)_9$, was isolated from the reaction mixture containing 1,3-pentadiene.[300] The reaction of $Ru_3(\mu\text{-H})(CO)_9(\mu\text{-PPh}_2)$ with $Cp_2Ni_2(CO)_2$ gave $Ni_2Ru_3Cp_2(CO)_9(\mu_5\text{-PPh})$. The X-ray crystal structure of this complex showed it to have an open square pyramid geometry.[301]

Heterotrimetallic alkyne clusters containing ruthenium or osmium, $CpNiCoM(CO)_6(C_2RR')$, were prepared from $CpNiCo(CO)_3(C_2RR')$ and $M(CO)_5$. The alkyne ligand was found to be parallel to the Ni-M edge of the cluster. An X-ray crystal structure was obtained of the ruthenium containing cluster.[302]

The osmium-nickel cluster, $CpNiOs_3(\mu\text{-H})_3(CO)_8(PPh_2H)$, was prepared from $CpNiOs_3(\mu\text{-H})_3(CO)_8(PPh_2H)$ and diphenylphosphine in the presence of

trimethylamine-N-oxide. Treatment with sodium hydride followed by mercury dibromide produced $CpNiOs_3(\mu-H)_2(CO)_8(PPh_2H)(\mu-HgBr)$, which was characterized by ^1H and ^{31}P NMR.[303]

(g) Supported Os and Ru Clusters

EXAFS was used to determine the structure of alumina supported osmium carbonyl clusters derived from $Os_3(CO)_{12}$. Two types of osmium species are present, a mononuclear Os(II) species on the support, and a triosmium cluster.The data indicate that two of the three osmium atoms in the cluster are bonded to surface oxygen atoms. The mononuclear osmium species is bonded through three surface oxygens.[304] Another EXAFS study of the osmium carbonyl on alumina, silica, and titania showed the initial absorbate, $Os_3H(CO)_{10}(\mu-O-oxide)$ or $Os_3(OH)(CO)_{10}(\mu-O-oxide)$. Pyrolysis gave a mixture of surface bound osmium tricarbonyl, and osmium dicarbonyl fragments.[305]

The reactivity of the osmium carbonyl clusters $H_4Os_4(CO)_{12}$ and $H_3Os_4(CO)_{12}I$ with the surface of partially hydroxylated magnesia, lanthanum oxides, and zinc oxides was investigated. The basic surfaces were found to deprotonate the osmium clusters to form surface-bound species, rather than acting as nucleophiles on the coordinated CO of the clusters. The authors also suggest that the supports abstract I^+ from the iodo cluster complex.[306] The mixed metal clusters $H_2FeM_3(CO)_{13}$ (M= Os, Ru) were deprotonated by a hydroxylated magnesia surface. The surface absorbed $[HFeM_3(CO)_{13}]^-$ were identified by IR spectroscopy.[307]

Solid state 31P NMR spectroscopy was used to study surface attached triosmium clusters. The silylated phosphine clusters $Os_3(CO)_{11}L$, $H_2Os_3(CO)_{10}L$ and $H_2Os_3(CO)_9L$ (L= $PPh_2CH_2CH_2Si(OEt)_3$) were prepared and anchored to a silica support. The results indicate that $Os_3(CO)_{11}L$-silica and $H_2Os_3(CO)_{10}L$-silica maintain their integrity on the support while $H_2Os_3(CO)_9L$-silica has a very different structure on the support than $H_2Os_3(CO)_9L$ has in solution.[308]

The catalytic activity of mono and polynuclear compounds supported on zeolites was the subject of a report.[309]

IV. Catalytic and Synthetic Reactions
Reactions Of Carbon Monoxide and Related Molecules

New metal complexes were used as water gas shift catalysts. A high activity, low temperature catalyst for the water gas shift reaction was prepared from $Ru_3(CO)_{12}$ and 2,2'-bipyridine in a 3:1 ratio.[310] Catalysis of the water gas shift reaction by $(\eta^4-C_5Ph_4O)Ru(CO)_3$ was observed. The complex also catalyzed the reduction of ketones with CO and water. Sodium carbonate was found to accelerate the rate of the reaction.[311]

There was continued activity on carbon monoxide reduction catalyzed by osmium and ruthenium complexes. Imidazoles were found to enhance the reactivity of $Ru_3(CO)_{12}$ on the homogeneous hydrogenation of carbon monoxide. The imidazole increased the selectivity for ethylene glycol formation although methanol was still the major product under the reaction conditions.[312] A report is available on metallocarboranes structurally engineered for the reduction of carbon monoxide.[313] Hydrocarbon synthesis by a photo-Fischer-Tropsch reaction used water and carbon monoxide as substrates.[314]

High molecularity osmium and ruthenium clusters have been observed on carbon monoxide hydrogenation catalysts prepared by impregnation of H_2OsCl_6 or $RuCl_3$ on magnesia. The carbonyl clusters $[Os_{10}C(CO)_{24}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ are formed under reaction conditions.[315]

Several ruthenium(0) complexes, including $Ru(CO)_4(PPh_3)$, were found to catalyze the hydroformylation of ethylene and propylene under photochemical conditions. UV irradiation is proposed to cause the dissociation of carbon monoxide from the ruthenium center to generate the active catalyst.[316] Fourier transform infrared spectroscopy studies on a ruthenium/potassium/alumina catalyst indicated that ruthenium formyl intermediates may be involved in the catalytic carbonylation of alkenes.[317]

Homogeneous ruthenium-cobalt catalysts with iodide promoters were found to be effective for the homologation of the alkoxy moiety of carboxylic esters. Ethyl esters are homologated more readily than esters of higher alkyl groups.[318] Methanol homologation was catalyzed in solution by a mixture of rhodium complexes, ruthenium complexes and methyl iodine. Various monomeric complexes of these metals and mixed metal clusters were examined for activity in this reaction.[319]

Hydrogenations and Isomerizations

Several catalysts were effective for the reduction of organic oxygenates. The influence of the phosphine ligand and solvent was examined in the catalytic hydrogenation of dimethyl oxalate to methyl glycolate by $Ru(CO)_2(CH_3COO)_2(PR_3)_2$. Although complexes with either PPh_3 or PBu_3 showed 100% selectivity in reduction of the diester, the tributylphosphine derivative was far more active. Aromatic solvents favor additional reduction of the methyl glycolate to ethylene glycol.[320]

A series of osmium and ruthenium complexes containing hydride, phosphine and carboxylate ligands, $MHX(CO)(PR_3)_3$, were found to be active catalysts for the homogeneous hydrogenation of aldehydes and ketones to the corresponding alcohols. A study of the rate of propionaldehyde conversion to propanol under varying reaction conditions and with catalyts containing different carboxylate ligands led to the formulation of led to the formulation of the proposed mechanism shown below.[321]
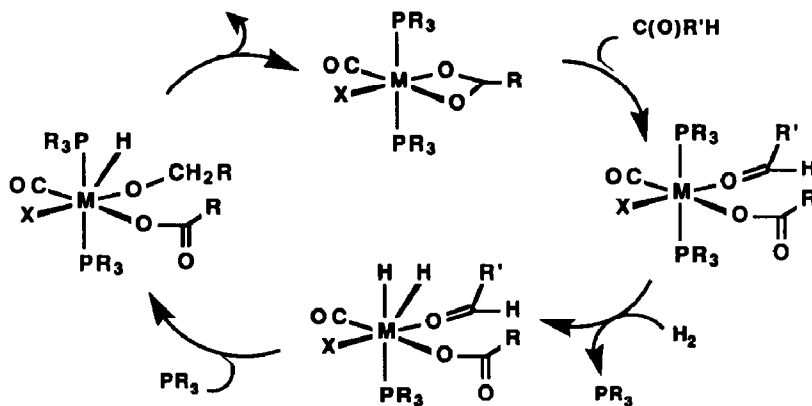
Catalysts were developed for arene hydrogenation. Small ruthenium particles on silica, active for the hydrogenation of cyclohexene or benzene, were prepared by the hydrogenolysis of supported ruthenium(η^4-cyclooctadiene)(η^6-cyclooctatriene).[322] The partial hydrogenation of benzene was catalyzed by ruthenium complexes prepared by a chemical mixing procedure.[323] Pyrene and fluoranthene were selectively hydrogenated with various noble metal catalysts.[324]

The ruthenium clusters $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ are less active catalysts for reductions employing N-benzyl 1,4-dihydronicotinamide than other metal carbonyls because of the stability of intermediate hydrido carbonyls.[325]

Several orthometallated complexes were found to have enhanced catalytic activity towards the hydrogenation of olefins than relative to non-orthometallated species. A new ruthenium complex, $RuCl\{P(OPh)_3\}_3\{P(OPh)_2(OC_6H_5)\}$, was prepared from $P(o\text{-}OC_6H_4)_3$ and $HClRu(PPh_3)_3$ and was found to be more active than $RhCl(PPh_3)_3$ for the hydrogenation of internal and terminal olefins.[326] The ruthenium complexes $RuCl\{P(OPh)_3\}_3\{P(OPh)_2(OC_6H_5)\}$ and $Ru\{P(OPh)_3\}_2\{P(OPh)_2(OC_6H_5)\}_2$ are also catalysts for the polymerization of styrene and the ortho ethylation of phenol with ethylene.[327]

Rapid catalytic hydrogenation of 3,3-dimethylbutene in THF under mild conditions was reported. The anion-promoted ruthenium clusters, $[Ru_3(\mu^2\text{-}NCO)(CO)_{10}]$ and $[Ru_3X(CO)_{10}]$ (X= Cl, Br) were the catalyst precursor for the hydrogenation. Kinetics of the reaction were investigated.[328] The mechanism of the homogeneous catalytic hydrogenation was studied through the use of the osmium analogs. The hydrogenation reaction was found to be much slower with the osmium complex and intermediates in the reaction could be observed and characterized. The mechanism proposed for the reaction is shown below. The X-ray crystal structure of an intermediate alkyl complex (R = succinoyl) was determined.[329]

196
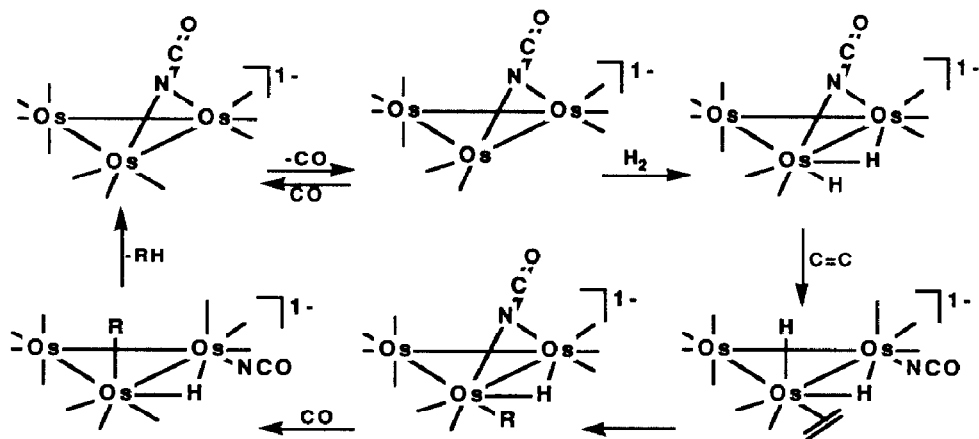
The hydrogenolysis of n-butylamine catalyzed by a graphite supported ruthenium catalyst resulted in the formation of propene and butene.[330]

Hydrogen transfer reactions were catalyzed by heterogenized ruthenium(II) complexes attached to a polycarboxylate matrix.[331]

The heterometallic complex $(\eta^5\text{-}C_5H_5)NiRu_3(\mu\text{-}H)_3(CO)_9$ was found to catalyze the hydrogenation of the terminal double bond of conjugated dienes and certain monoenes. Isomerization as well as hydrogenation reactions proceed with cyclohexenes and cyclohexadienes.[332]

Reductions involving biological molecules were catalyzed by osmium and ruthenium complexes. The asymmetric hydrogenation of amino acids precursors was affected by chiral ruthenium complexes.[333] The hydrogenolysis of glucose solutions occurred over solid catalysts.[334] Chemically modified carbohydrates were highly efficient regio- and stereoselective catalysts for hydrogenation.[335]

Ruthenium catalysts for reductions and other transformations of nitrobenzene were reported. Homogeneous and supported anionic carbonyl clusters were found to be catalysts in hydrogenation and transfer hydrogenation reactions.[336] Homogeneous catalytic hydrogenation, transfer hydrogenation and nitrobenzene carbonylation reactions were studied with dodecacarbonyltriruthenium as the catalyst.[337] It was suggested that arylimidoruthenium clusters are intermediates in the carbonylation of nitrobenzene with dodecacarbonyltriruthenium.[338] An X-ray crystal structure of $Ru_3(CO)_7(NPh)(\eta^6\text{-}C_6H_6)$ was obtained. This complex is isolated in the reaction between nitrobenzene and triruthenium dodecacarbonyl in the the presence of dicobalt octacarbonyl.[339] Selectivity for the reduction of nitroaromatic compounds is achieved with a catalyst system consisting of palladium on carbon,

$RuCl_2(PPh_3)_3$, formic acid and triethylamine. The hydrogen used in the reaction is derived from formic acid and triethylamine.[340]

A ruthenium hydrido phosphine complex, $RuH_2(PPh_3)_4$, has proven to be an effective catalyst for the condensation of nitriles with amides in the presence of two equivalents of water. The acylation is selective for the primary amines in the presence of secondary amines. Aminonitriles undergo polycondensation.[341]

$$R^1CN \ + \ HNR^2R^3 \ + \ H_2O \ \xrightarrow{\ RuH_2(PPh_3)_4\ } \ R^1CONR^2R^3 \ + \ HNH_3$$
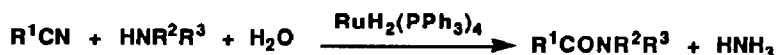
Ruthenium(II) complexes of imines catalyze the hydrosilation of isoprene with high selectivity.[342]

Asymmetric double bond isomerization of 4,7-dihydro- to 4,5-dihydro-1,3-dioxepins was reported.[343]

Oxidations

A frontier molecular orbital study appeared on the oxidation of olefins with osmium tetroxide and other osmium(VIII) derivatives, OsO_2X_2 (X = O and NR). The authors assume a [3+2] cycloaddition mechanism for the reaction of olefins with the metal complex although a [2+2] mechanism can not be ruled out based on orbital symmetry. The [3+2] cycloaddition can be classified as a metal catalyzed forbidden reaction according to this analysis. It is proposed that pyridine and other nitrogen bases cause a distortion from T_d to C_{2v} symmetry in the osmium complex, and that distortion accelerates the rate of the reaction with olefins.[344]

Intermediates in the amination and oxyamination of olefins by $OsO_2(NR)_2$ and $OsO_3(NR)$ were isolated. NMR indicated a dimeric structure for the heterometallocyclic products, analogous to the osmate ester intermediate known for OsO_4 oxidation of olefins.[345]

Hyperconjugative effects of allylic substituents were not found to be important in osmylations. The same stereoselectivity was found for oxidation with OsO_4 of olefins containing bulky σ-donors in the allylic position as for olefins containing bulky acceptors in that position.[346]

Asymmetric oxidation of olefins to diols with osmium tetroxide has been achieved by coordination of chiral diamines to the metal center. Chiral diamines derived from L-tartaric acid were used to prepare a chiral osmium oxide reagent.[347] The osmium complex derived from osmium tetroxide and (-)-(R,R)-N,N,N'N'-tetramethylcyclohexane-1,2-trans-diamine oxidized certain olefins with high selectivity.[348]

Osmium tetroxide was used to produce isobacteriochlorins from zinc oxoclorins.[349]

Osmium and ruthenium complexes have been used to epoxidize olefins. The oxidations of styrene and *cis* and *trans* -stilbene with [(bpy)$_2$(py)RuO]$^{2+}$ were examined. Reactions were found to be first order in both olefin and metal complex. The reactions were catalytic in ruthenium complex when NaOCl was used as the co-oxidant. Solvolysis of product to benzaldehyde occurred under reaction conditions required for the catalytic reaction.[350] An osmium(III) complex was found to catalyze the epoxidation of cyclohexene in the presence of iodosobenzene. The osmium complex, *trans*-[Os(bpb)(PPh$_3$)Cl] (bpbH$_2$= N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene), was prepared by the reaction of N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene with potassium osmate, followed by treatment with triphenylphosphine. In a reaction carried out in the dark with an excess of iodosobenze and cyclohexene, a total of 18 turnovers of cyclohexene oxide were produced in 6.5 hours, but the chemical yield, based on phenyl iodide produced, was only 3.6%.[351] Osmium(III)-porphyrin complexes catalyzed the epoxidation and hydroxylation of alkenes with iodosobenzene. Ocataethylporphyrin and meso-tetraphenylporphyrin complexes of osmium(III), [Os(porphyrin)(PBu$_3$)Br], were prepared by the bromine oxidation of [Os(porphyrin)(PBu$_3$)(CO)]. The catalysts converted cyclohexene to a mixture of cyclohexene oxide, cyclohexene-2-ol, cyclohexanone, and cyclohexenone. Oxidation of styrene was also studied.[352]

Alcohol oxidation was achieved in reactions with osmium and ruthenium complexes. Reactivity toward alcohols of *trans*-[RuCl(O)(py)$_4$]$^+$ was examined.[353] A light-induced electron-transfer reaction converted 2-propanol to acetone. The kinetics of formation of hydrogen peroxide and acetone by irradiation with visible light of aqueous solutions containing tris(2,2'-bipyridine)ruthenium(II) complex, 2-propanol and oxygen were reported.[354] A ruthenium-tin catalyst was found to be an effective photocatalyst for the dehydrogenation of 2-propanol. The mixture of RuCl$_3$ and SnCl$_2$ gave 47.7 turnovers of acetone and hydrogen per hour under UV irradiation.[355] Cerium or ruthenium complexes were found to catalyze the NaBrO$_4$ oxidation of alcohols.[356] An investigation was carried out on the kinetics and mechanism of osmium(VIII) catalyzed oxidation of benzyl alcohol and benzylamine by alkaline hexacyanoferrate(III) ion.[357]

A high valent ruthenium complex, *trans*-[Ru(bpy)$_2$O$_2$]$^{+2}$, was found to be a very powerful oxidant capable of oxidizing water.[358]

Kinetics of the ruthenium(III) catalyzed oxidation of aldoses by N-bromosuccinimide in aqueous acetic acid was studied.[359] Ruthenium(III) and ruthenium(III)-aminopolycarboxylic acid chelate complexes catalyzed the oxidation of ascorbic acid by molecular oxygen.[360] Data on the thermodynamics of this reaction was published.[361]

Potentiometric, spectrophotometric, electrochemical, and kinetic measurements were obtained on the oxidation of triphenylphosphine by molecular oxygen

catalyzed by a ruthenium(III)-EDTA-triphenylphosphine complex. A μ-peroxo ruthenium(IV) complex, $[Ru(EDTA)(PPh_3)]_2O_2$, was proposed to be an intermediate in the reaction.[362]
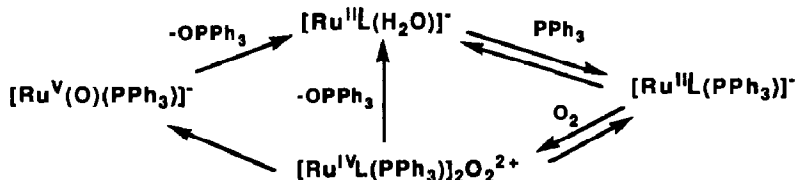
The ruthenium complex trans-$RuX_2(Me_2SO)_4$ (X= Cl, Br) had been previously found to catalyze the oxidation of thioethers with molecular oxygen. A recent study was carried out with the ruthenium complexes and thioethers in the absence of oxygen in order to identify possible reaction intermediates. Complexes of the type trans-$RuX_2(R_2S)_{4-n}(Me_2SO)_n$ were isolated from these reactions. The thioethers studied included dimethyl sulfide (n= 2-4), tetrahydrothiophene (n= 4), di-tert-butyl sulfide (n= 1), and diethyl sulfide (n= 2-3). Complexes of multidentate thioethers were also prepared. A crystal structure of trans-$RuCl_2\{CH_3C(CH_2SCH_2CH_3)_3\}(Me_2SO)$ was obtained.[363] The reactions of trans-$RuX_2(Me_2SO)_4$ with the tridentate sulfur donor ligand 3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane produced $RuCl_2$-$\{EtS(CH_2)_3SO(CH_2)_3SEt\}(Me_2SO)$. Crystal structures of the dichloro and dibromo complexes were obtained which showed meridional coordination of the tridentate ligand and a cis orientation of the halides.[364] The reactions of trans-$RuBr_2(tetrahydrothiophene)_4$ with the tridentate sulfur donor ligand bis(3-(ethylsulfinyl)propyl)sulfide produced $RuBr_2\{EtS(O)(CH_2)_3S(CH_2)_3-S(O)Et\}(SC_4H_8)$. Two isomers of the product with meridonal (major isomer) and equatorial coordination of the tridentate ligand were identified. The major isomer was structurally characterized.[365]
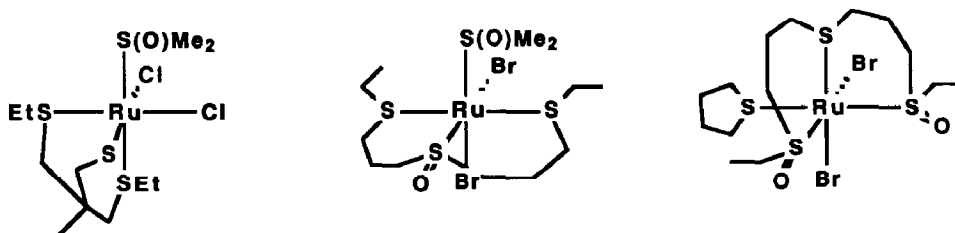
Oxidations of amines have been carried out. The oxidative N-dealkylation of triethylamine by molecular oxygen was catalyzed by a ruthenium(III) ethylenediaminetetraacetic acid complex.[366] Dehydrogenation of amines was reported.[367]

The liquid-phase oxidation of deactivated methylbenzenes by aqueous sodium hypochlorite was catalyzed by ruthenium salts under phase-transfer catalytic conditions.[368]

Carbon-Carbon Bond Formation

Intramolecular cyclometallation of sp^3 hybridized carbon-hydrogen bonds has been used in the catalytic synthesis of indoles by a ruthenium complex. A ruthenium complex which is known to activate certain C-H bonds, $Ru(dmpe)_2(naphthyl)H$, converts 2,6-xylyl isocyanide to 7-methylindole at 140°C. A mechanism was proposed for the process based on NMR studies at lower temperature. The isocyanide reacts with the ruthenium complex to form $Ru(dmpe)_2(CNC_6H_3Me_2)$. Orthometallation of the isocyanide precedes insertion of the isocyanide into the ruthenium-carbon bond. Reductive elimination regenerates $Ru(dmpe)_2$.[369]
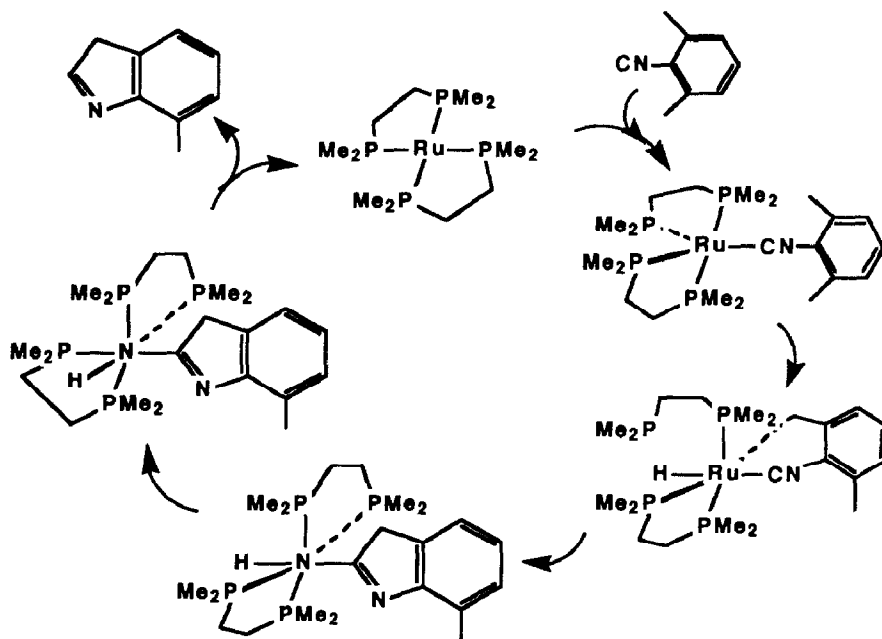
The N-heterocyclisation of 2-aminophenethyl alcohols into indole derivatives was catalyzed by $RuCl_2(PPh_3)_3$.[370]

The ruthenium carbonyl cluster $Ru_3(CO)_{12}$ catalyzed the reaction of carbon dioxide, diethylamine, and hex-1-yne or phenylacetylene to vinylcarbamates $RCH=CHOC(O)NEt_2$ (R= Bu^n, Ph).[371] This cluster is also an effective homogeneous catalyst for the carbonylation of amines and the hydroamidation of olefins. A mechanism involving a ruthenium carbamoyl as a key common intermediate was proposed.[372]

A hydrido ruthenium complex has been shown to be active for the isomerization, oligomerization and polymerization of olefins. The protonation of (η^6-cyclooctatriene)ruthenium(1,5-cyclooctadiene) at low temperature produced $[RuH(\eta^6-C_8H_{10})(\eta^4-C_8H_{12}]^+$. This rearranges to $[RuH(\eta^5-C_8H_{11})_2]^+$. Terminal olefins are isomerized by these complexes and certain other olefins, including isoprene and methyl acrylate, are polymerized in dichloromethane solution.[373]

A homogeneous ruthenium(0) catalyst was found to catalyze the dimerization of methyl acrylate to the hexanedioate. The active catalyst was prepared by the reduction of ruthenium trichloride with zinc in methanol. Various phosphine and phosphite additives were found to moderately activate the system, but also increased the amount of branched dimer produced. An intermediate was isolated and structurally characterized from a reaction mixture containing trimethylphosphite.[374]
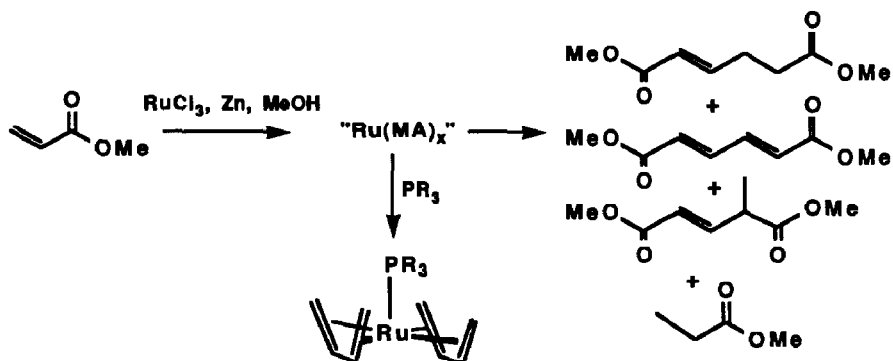
Two equivalents of sodium naphthalenide greatly increase the activity of $(C_6H_6)Ru(CH_2=CHCO_2CH_3)_2$ in the tail to tail dimerization of acrylates. Hexanenedioate is the principle product but some oligomerization of the acrylate also occurs.[375]

The ruthenium complexes $RuCl_3$, $[RuCl_2(C_6H_6)]_2$, $[RuCl_2(NBD)]_n$, $[RuCl_2(py)_2(NBD)]$ have been used as catalyst precursors in the coupling and alkylation of furan and thiophene with alcohols. A mechanism involving C-H activation by ruthenium(II) intermediates was proposed.[376]

Z= O, S;
R= Me, Et, Pr
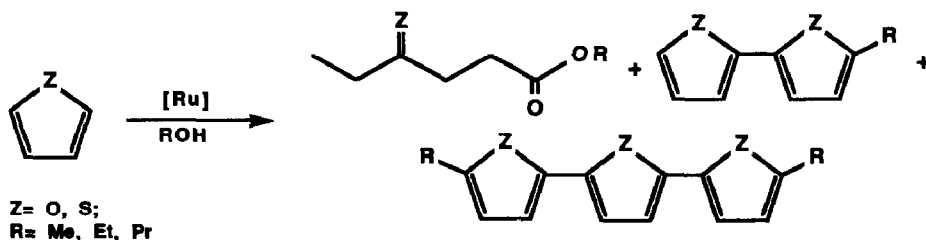
Several ruthenium complexes supported on alumina were investigated as catalysts for the reduction of carbon dioxide with hydrogen to methane. The activity of

the ruthenium complexes for this reaction increased in the order $Ru(CO)_5$, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $Ru_6C(CO)_{17}$. The anionic clusters $[PPN][HCO_2Ru_3(CO)_{10}]$, $KH_3Ru_4(CO)_{12}$, and $[PPN][H_3Ru_4(CO)_{12}]$ were less active than the neutral cluster complexes. Ruthenium trichloride was a poorer catalyst than any of the low valent complexes.[377]

V. Reviews and Theses

The annual surveys of osmium and ruthenium for the years 1983 and 1984 were published.[378,379] A review appeared on catalysis by osmium metal clusters.[380] A review in Russian on organometallic complexes of the platinum metals was published.[381]

Theses on aspects of the organometallic chemistry of ruthenium and osmium were submitted in 1986. A thesis appeared on X-ray structural studies on tungstacyclobutadiene complexes and tungsten-triosmium cluster complexes.[382] A thesis by Li concerned X-ray structural studies on tungsten, triosmium and tungsten-triosmium organometallics derived from alkylidyne or dinitrogen ligands.[383] Rutkowski investigated the kinetics of electron transfer reactions between thallium(III) and a series of mononuclear and binuclear ruthenium complexes.[384] A thesis by Kobs concerned the reactions of osmium tetroxide with tertiary amines, imidazoles and proteins.[385]

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