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Annual Survey of Ruthenium and Osmium for the Year 1989*

Michael G. Richmond

Center for Organometallic Research and Education,
Department of Chemistry, University of North Texas,
Denton, TX 76203

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I. Dissertations

The synthesis, electrochemical properties, and fluorescence and phosphorescence spectroscopy of a porphyrin-based microheterogeneous photoreactor, which consists of surfactant-like porphyrins ligated through bipyridines to ruthenium oxide microcolloids, have been described.[1] The catalytic activity of several ruthenium porphyrins in epoxidation, epoxide isomerization, olefin formation, and alkane hydroxylation has been presented.[2] A detailed investigation of the photophysics of $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2'-bipyridine) and related ruthenium complexes possessing high energy metal-ligand charge transfer (MLCT) states that display interactions with higher lying $\pi\pi^*$ states has appeared.[3] High valent ruthenium and osmium complexes have been prepared and their solid-state and solution magnetism examined. The results of olefin epoxidation using cis-$[Ru^{IV}(bpy)_2(py)(O)]^{+2}$ (where py = pyridine) and the redox properties of $[M^{II}(bpy)_2(OH_2)_2]^{+2}$ (where M = Ru or Os) are also included.[4] The ruthenium (IV) oxo compounds $[Ru(bpy)_2(py)(O)]^{2+}$ and $[Ru(trpy)(bpy)(O)]^{2+}$ (where trpy = 2,2':6'2'-terpyridine) have been examined for their oxidative chemistry with a variety of organic compounds.[5] The X-ray crystal structure of $[Ru(trpy)(bpy)(OH_2)]^{2+}$ is also presented.[5] Spectroelectrochemical studies of the mixed ligand Ru(II) complexes $[Ru(trpy)(bpy)(py)]^{2+}$ and $[Ru(trpy)(Ph_2\text{-}bpy)(py)]^{2+}$, have also been reported; a linear correlation between the difference of the first oxidation and reduction potentials versus the emission energies reveals that the redox and spectroscopic orbitals are the same. Spectroelectrochemical and EPR results demonstrate that the trpy ligand is the site of the first reduction.[6] The prevention of back electron transfer in water-splitting reactions has been studied using polypyridine ruthenium(II) complex $[Ru(bpy)_3]^{2+}$, methyl viologen and the triethanolamine.[7] The photochemistry and photophysics of several ruthenium(II) complexes have been investigated. The observed photochemistry originates from either a ligand centered (LC) state or a metal centered state that is thermally populated from a lower lying LC state.[8] Electrochemical and spectroscopic studies of bipyridine ruthenium alkyl oxime complexes have appeared. The complexes display a reversible Ru^{II}/Ru^{III} redox couple. Complete spectral characterization, which includes fast atom bombardment mass spectrometry and NMR spectroscopy, is also presented.[9] Long-range electron transfer in ruthenium-labelled myoglobin has been investigated. The driving force dependence and the dependence of the electron-transfer rates on the reaction free energy are discussed within the context of Marcus theory.[10] The design and applications of a chiral ruthenium probe for A-form nucleic acids have been presented. The chiral complex $[Ru(tmp)_3]^{2+}$ (where tmp = 3,4,7,8-tetramethyl-1,10-phenanthroline) binds cooperatively to A-form helices of various base sequences with little or no binding to B- or Z-form DNAs.[11] Two reports dealing with ruthenium(II) complexes of bpy and 1,10-phen (where 1,10-phen = 1,10-

phenanthroline) have appeared.[12] The studies, which originate from the same research group, discuss the advantages of $[Ru(1,10\text{-phen})_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ as mobile phase additives in reverse phase chromatography.[13] Other reports of nitrogen-substituted ruthenium complexes include the synthesis and reactions of new indole ruthenium complexes,[14] the synthesis, characterization, and aerobic oxidation studies of alkenes catalyzed by 1,2-naphthaquinone mono-oximato ruthenium complexes,[15] and the X-ray adsorption spectroelectrochemisty of $Ru(NH_3)_6{}^{3+/2+}$.[16] Finally, the asymmetric hydroxylation of alkenes to vicinal diols has been stoichiometrically achieved using chiral diamines and OsO_4.[17]

The C-H bond activation properties of $Ru(dmpe)_2(H)(naphthyl)$ (where dmpe = 1,2-dimethylphosphinoethane) are described. Reaction of $Ru(dmpe)_2(H)(naphthyl)$ with o-tolylisocyanides yields the corresponding indole-hydride complexes by a benzylic C-H bond activation sequence, which is followed by an isocyanide/indole isomerization.[18] Several molecular hydrogen complexes derived from $CpRu(P)_2H$ have been reported. The η^2-H_2 hydrogen complexes were prepared by the protonation reaction of the monohydride precursor compounds.[19] The substitutional reactivity of the η^2-H_2 moiety is also discussed. Two reports dealing with ruthenium complexes containing chelating triphosphine ligands have appeared. The new complexes have been fully characterized by IR and NMR spectroscopy and examined for their activation of acetylenes and other unsaturated substrates.[20,21] The syntheses of cis- and trans-$[Ru(trpy)(PEt_3)Cl]_2$, trans-$[Ru(trpy)(PEt_3)_2Cl][Cl]$, and $[Ru(trpy)(PEt_3)_2L]^{x+}$ (where L = NO_2, NO, OH_2, O, MeCH; x = 1-3) are reported. Full spectroscopic characterization is included along with the X-ray diffraction results for $[Ru(trpy)(PEt_3)_2(OH_2)][ClO_4]\cdot 3H_2O$, which is the first aquo trans-diphosphine complex of ruthenium reported.[22] The reaction between $RCpRu(PPh_3)_2Cl$ (where R = H or Me) and the tetra-thiometallates ME_4^{-2} (where M = Mo or W; E = S or Se) is described. The redox properties and the substitutional reactivity of the resulting $[RCpRu(PPh_3)_2]_2MS_4$ are also presented.[23] Ruthenium(II) and ruthenium(IV) aryl thiolates and selenolates have been synthesized and investigated as potential models for heterogeneous metal sulfide hydrodesulfurization catalysts.[24] A luminescence study of Cp_2Ru revealed well resolved vibronic structure that could not be interpreted by a standard Franck-Condon analysis.[25] Oxalate anation in $[Ru(OH_2)_6]^{2+}$ and $[Ru(OH_2)_6]^{3+}$ has been studied as a function of pH and temperature.[26]

Four dissertations dealing with polynuclear complexes were abstracted. The synthesis and preparation of several ruthenium imido clusters have been reported. The relevance of imido ligands to nitroaromatic carbonylation catalysis and reactivity of $Ru_3(CO)_{12}$ with halides and pseudo halide salts are included.[27] The conversion of metal-dioxy carbene complexes into useful organic compounds has been probed using the osmium clusters $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ and $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$. The X-ray diffraction structure of the latter cluster is presented.[28] Heterometallic gold hydride clusters of ruthenium and osmium have been prepared and characterized. The use of Orpen's potential energy modeling technique to indirectly calculate hydride locations is also discussed.[29] Several ruthenium metallacarborane clusters have been synthesized and examined for their catalytic activity in olefin isomerization and hydrogenation reactions.[30]

Other dissertations abstracted include the effect of silica support on monometallic ruthenium and ruthenium-copper bimetallic catalysts,[31] and the surface and catalytic chemistry of osmium carbonyls on basic MgO. Extended X-ray absorption fine structure (EXAFS) spectroscopy is used to chart the course of surface-mediated organometallic reactions.[32] Carbon-supported $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been investigated by Diffuse Reflectance Infrared Spectroscopy. The decomposition of these clusters has been followed under He or H_2.[33] Ruthenium dispersed in Y-zeolites has been examined by NMR spectroscopy. Xenon gas sorbed in the zeolite and CO adsorption have been studied using ^{129}Xe and high resolution magic-angle spinning (^{13}C) NMR methods, respectively.[34] Three reports on the surface chemistry of small molecule adsorption on Ru(001) have appeared.[35,36,37] Finally, the pressure dependence of the normal state properties of the heavy-electron superconductor URu_2Si_2 is described.[38]

II. Mononuclear Complexes

(a) Organometallic Porphyrins

The ruthenium(II) porphyrin complex Ru(TPP)(CO)(EtOH) (where TPP = tetraphenylporphyrin) has been prepared and studied for its reactivity with NOCl, NOBr, $AsPh_3$, and phosphites ligands.[39] Reaction of cyanide with the monocarbonyl complex of ruthenium(II)-uroporphyrin is reported. The applications of *in vivo* cyanide scavenging by ruthenium porphyrins are discussed.[40] The Langmuir-Blodgett (LB) technique has been employed in molecular thin film preparation of ruthenium porphyrins based on mesoporphyrin-9-dimethyl ester. UV irradiation affords porphyrin dimers containing Ru=Ru bonds.[41] The resonance Raman (RR) scattering and infrared (IR) spectra of $[Ru(OEP)_2]^{n+}$ (where OEP = octaethylporphyrin; n = 0, 1, 2; Ru-Ru bond order = 2.0, 2.5, 3.0) are presented. The porphyrin-centered RR and IR active vibrational modes of all the complexes examined are independent of oxidation state and similar to those observed for the monomeric complex Ru(OEP)(CO)(L).[42] The vibrational characterization of multiply bonded $[Os(OEP)]^{n+}$ porphyrins (where n = 0, 1, 2) has also been reported. No vibrational evidence for ground-state intradimer coupling between the π orbitals of the porphyrin rings could be discerned.[43] High-valent ruthenium(IV) and osmium(VI) have been prepared and examined in olefin epoxidation reactions. The reaction of $[Ru^{II}(OEP)(CO)]$ with m-chloroperoxybenzoic acid gives $[Ru^{VI}(OEP)(O)_2]$, which has been isolated and shown to possess one intense IR band attributable to a ν_{as} (O=Ru=O) stretch.[44]

The synthesis and redox chemistry of $Ru(OEP)(Ph)_2$ and Ru(OEP)(Ph) have appeared.[45] Pulse radiolytic studies involving the oxidation of Ru(OEP)(CO) and Ru(TPP)(CO) to

Ru^{III} and Ru^{IV} states are described. The rate constant for chloride ion abstraction from CH_2Cl_2 by the Ru(III) radical cation has been calculated. Reaction in acetonitrile leads to cyanide ion abstraction and formation of Ru^{III}(OEP or TPP)(CO)(CN^-).[46] The nature of the photoexcited state and the photoproduct derived from Ru^{II}(OEP)(CO) in various solvents is reported.[47] Extended X-ray absorption fine structure (EXAFS) spectroscopy results for $[Ru(OEP)]_2^{n+}$ (where n = 0, 1, 2) show that all three oxidation states have two similar transitions. The molecular orbital (MO) ordering scheme of $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*(2-n)}$ is supported.[48] An article dealing with ruthenium-octaethylporphyrin dimers has appeared. The metal-metal distance has been examined by using EXAFS spectroscopy.[49]

(b) Halides

The reaction between $[OsBr_4][Et_4N]_2$ and DMSO gives dibromotetrakis(dimethylsulfoxide)osmium(II). X-Ray diffraction analysis reveals S-bound DMSO ligands; the two bromide ligands are observed to adopt a trans orientation.[50] The ruthenium halide complexes $K_2Ru_2OCl_{10}$ have been examined for their reactivity with NO and NO_2. The reactions were followed by UV-visible spectroscopy and the products were characterized by IR spectroscopy.[51] Far-IR spectra of $[OsCl_5I]^-$, cis-$[OsCl_4I_2]^{2-}$, fac-$[OsCl_3I_3]^{2-}$, $[OsCl_5Br]^-$, and cis-$[OsCl_4Br]^{2-}$ (all as their Cs^+ salts) have been recorded. The results of normal coordinate analysis are presented.[52] The ruthenium fluoride complex $RuOF_4$ has been synthesized from

RuO_4 and KrF_2. Characterization by X-ray powder diffraction, IR spectroscopy, and elemental analysis is included.[53]

The effect of halide and sulfoxide (R_2SO) substitution in ruthenium(II) nitroimidazole complexes is reported. Full solution characterization and radiosensitizing activity is presented.[54] $OsCl(NO)(PPh_3)_2(L)$ (where L = ethylene or PPh_3) reacts with nitrosobenzene by replacement of the labile L ligand. The resulting $OsCl(NO)(PPh_3)_2(ONPh)$ is coordinated to the osmium center through both nitrogen and oxygen as determined by IR spectroscopy.[55] The reaction between $RuCl_3(AsPh_3)_2(MeOH)$ and $RCSNHCO_2Et$ (where R = 2-pyrrolyl, 2-thiophene-yl, or 4-C_6H_4Me) gives diamagnetic complexes of the form $[\{RuCl_2(AsPh_3)(RCSNHCO_2Et)\}_2]$. Solution characterization, magnetic and conductance measurements are presented.[56] A review dealing with substituted osmium carbonyl halides has appeared. Most of the complexes reviewed are divalent octahedral complexes.[57]

(c) Hydrides

Protonation of the dihydride complexes $MH_2[P(OEt)_2Ph]_4$ (where M = Ru or Os) yields the molecular hydrogen complexes $MH(\eta^2\text{-}H)_2[POEt)_2Ph]_4^+$. ^1H NMR T_1 values are less than 100 ms for the coordinated hydrogen moiety.[58] The hydrido dihydrogen complex $RuH(\eta^2\text{-}H_2)(O_2CCF_3)(PCy_3)_2$ (where Cy = cyclohexyl) has been prepared by protonation of $RuH_2(\eta^2\text{-}H)_2(PCy_3)_2$ with CF_3CO_2H. The reactivity of the hydrido dihydrogen complex is discussed and variable-temperature ^1H and $^{31}P\{^1H\}$ spectra are presented.[59] Protonation of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$ gives the corresponding dihydrogen complex $[(\eta^5\text{-}$

$C_5Me_5)Ru(CO)_2(\eta^2-H_2]^+$, which is the first dihydrogen complex not containing ancillary phosphine ligands. The coordinated dihydrogen ligand is activated toward heterolytic cleavage using weak bases.[60] Reaction of $RuCl_2$(Cyttp) (where Cyttp = $PhP[CH_2CH_2CH_2P(Cy_2)]_2$) with NaH and H_2 yields RuH_4(Cyttp), which is best formulated as a dihydride/dihydrogen complex on the basis of ^1H NMR T_1 measurements and $^{31}P\{^1H\}$ NMR evidence. The hydrido dihydrogen complex readily inserts CO_2 into the Ru-H bond to give the formate complex. Complexation of CO, PR_3, and N_2 is described.[61] The known compounds $MH_2(depe)_2$ (where M = Ru, Os; depe = $Et_2PCH_2CH_2PEt_2$) have been synthesized from the cis-dichloride compounds. A mechanism involving two successive η^2-dihydrogen complexes as reaction intermediates is presented.[62] The X-ray crystal structure of $[OsH(\eta^2-H_2)(depe)_2][Ph_4B]$ has appeared.[63]

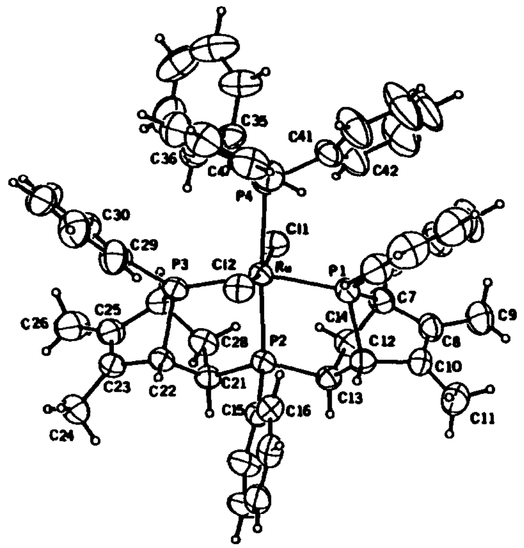
The acid-catalyzed hydrogenolysis of the osmium-carbon bond in fac-$OsH(\eta^2-CH_2PMe_2)(PMe_3)_3$ and cis-$Os(H)(Me)(PMe_3)_4$ has been shown to yield cis-$OsH_2(PMe_3)_4$. These reactions occur under H_2 and involve catalysis by $[OsH_3(PMe_3)_4][TfO]$. A detailed catalytic cycle is presented.[64] Selective H/D exchange in alkylsilanes has been catalyzed by the osmium phosphine complexes $Os(SiMe_2R)H(PMe_3)_4$. The results presented provide the first evidence for a β-hydrogen elimination from a metal silyl ligand. The involvement of a transient osmium silene is invoked in the proposed H/D exchange mechanism.[65] Ortho-Vinylation and alkylation of coordinated triarylphosphines has been observed when either OsH_4L_3 or $[OsH_5L_3]^+$ (where L = triarylphosphine) is treated with acid and ethylene. Rate constants and plausible mechanisms are presented.[66] Facile olefin hydrogenation is reported using $[OsH_5(PMe_2Ph)_3]^+$. Reversible dissociation of H_2 in the presence of ethylene and 1,5-COD (where COD = cyclooctadiene) gives the corresponding olefin complex $[OsH(ethylene)_2(PMe_2Ph)_3]^+$ and $[OsH(1,5\text{-}COD)(PMePh)_3]^+$, respectively. Included in this article are the extended Hückel results of the ethylene complex.[67] A kinetic and mechanistic study of the sequential hydrogenation of phenylacetylene catalyzed by $OsH(Cl)(CO)(PR_3)_2$ (where R = PMe-t-Bu_2 or P-i-Pr_3) has appeared. Evidence is presented that the formation of styryl derivatives determines the observed selectivity in these hydrogenation reactions.[68] The selective hydrocracking of monosaccharide carbon-carbon bonds has been demonstrated by using $H_2Ru(PPh_3)_4$ as a catalyst. Several ruthenium carbonyls are observed by IR spectroscopy during the reactions as a result of the decarbonylation of the aldose sugars.[69]

The reaction between acrylonitrile and $RuH(CO)(O_2CR)(PPh_3)_2$ has been shown to give $Ru(CO)(O_2CR)(PPh_3)_2(CH_3CHCN)$. The σ-bonded insertion complex has been characterized spectroscopically and ^{31}P NMR analysis reveals that the two PPh_3 groups are oriented trans to each other.[70] Insertion of alkyne into the Ru-H bond of $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$ yields alkenyl derivatives. Alkyne insertion proceeds in cis-fashion. The crystal structure of $[Ru(CO)(MeO_2CC{=}CHCO_2Me)(MeCN)_2(PPh_3)_2]^+$ has been determined. Trans phosphine ligands are suggested by ^1H NMR data for every alkyne examined.[71] The reaction of $RuH(CO)Cl(PPh_3)_3$ with methyl propiolate gives two bis-insertion derivatives, which result from a head-to-tail dimerization. An extruded PPh_3 ligand deprotonates the alkyne to give $[Ph_3PH][C\equiv CCO_2Me]$, which subsequently displaces chloride in the σ-bonded complex $Ru(CO)Cl(CH=CHCO_2Me)(PPh_3)_2$.[72]

(d) Phosphines

The conformationally rigid tridentate phosphine ligand phenylbis(7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl)phosphine (L^*) has been prepared from divinylphenylphosphine and 1-phenyl-3,4-dimethylphosphole. Reaction of L^* with $RuCl_2(PPh_3)_3$ yields the new complexes mer-$RuCl_2(PPh_3)L^*$ and trans-$RuCl_2L^*_2$. Full solution characterization by IR and NMR spectroscopies is presented. X-Ray diffraction analysis of the former complex is included. Both of the complexes display reversible Ru(II)/Ru(III) and irreversible Ru(III)/Ru(IV) redox couples. The new polydentate phosphines do not enhance the stability of the oxidized ruthenium center in comparison with other analogous phosphine complexes.[73]

The complex trans,trans,trans-dicarbonylbis(1-phenyl-3,4-dimethylphosphole)ruthenium(II) undergoes intramolecular Diels-Alder [4 + 2] cycloadditions with a wide variety of dieneophiles. Using this route, several novel polydentate ligand systems have been prepared and used in the synthesis of new ruthenium complexes.[74] Ruthenium(II) complexes possessing the phosphine ligands 1-phenyldibenzophosphole (DBP) and 1-phenyl-3,4-dimethylphosphole (DMPP) have been



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reported. The new complexes based on DBP and DMPP are active in hydrogenation and isomerization reactions. A discussion on the procatalyst geometry, nature of the ancillary P-ligand, and the effect of CO on the catalytic turnover numbers is included.[75] Treatment of $RuCl_2(PPh_3)_3$ with triphos ($PhPCH_2CH_2P\{Ph\}CH_2CH_2PPh_2$) yields $RuCl_2(triphos)_2$. Single-crystal X-ray diffraction analysis reveals an octahedral ruthenium center with trans chlorides, one mer-triphos ligand, and one monodentate triphos ligand which is bound through the central phosphorus. $^{31}P\{^1H\}$ NMR data indicate that the monodentate triphos experiences hindered rotation about the Ru-P bond.[76] New ruthenium complexes based on 1,2-bis(dicyclohexylphosphino)ethane (dcpe) have been reported. The octahedral complexes $RuX_2(dcpe)_2$ and trans-$RuH(Cl)(dcpe)_2$ are shown to dissociate halide in solution to give the unsaturated complexes $[RuX(dcpe)_2]^+$ and $[RuH(dcpe)_2]^+$, respectively. These cations are stereochemically nonrigid at room temperature, possessing a trigonal-bipyramidal geometry; the non-phosphine ligand occupies an equatorial site. The X-ray crystal structure of $[RuCl(dcpe)_2][PF_6]$ is included.[77] New octahedral ruthenium complexes based on 1,2-bis(di-p-tolylphosphino)ethane have also been reported.[78] The synthesis and reactivity of $Os(PMe_3)_5$ have appeared. The homoleptic phosphine is nonrigid at room temperature on the NMR time scale. Protonation with triflic acid yields $[OsH(PMe_3)_5][OTf]$. Thermolysis of $Os(PMe_3)_5$ in the presence of various solvents leads to metalation of the PMe_3 ligands.[79] The hydride complexes RuH_2P_4 {where P = $P(OEt)_3$ or $PhP(OEt)_2$} have been prepared and examined in reactions with arenediazonium salts. Insertion of the diazo group into the Ru-H bond affords bis(aryldiazene)and mono(aryldiazenido) products. Full solution characterization is included.[80] The new tridentate ligand $Ph_2P(CH_2CH_2O)_2Me$ (POO) has been reported along with the new complexes cis,cis,trans- and cis,trans,cis-$Ru(CO)_2Cl_2(POO)_2$.[81]

Fluoroalkylation of olefins has been reported using CF_3SO_2Cl and ruthenium(II) phosphine catalysts. A radical-chain mechanism is presented that is initiated by a single-electron-transfer (SET) from the Ru(II) catalyst to CF_3SO_2Cl.[82] Three reports dealing with the catalytic properties of ruthenium-BINAP {where BINAP = 2,2'-bis(dimethylphosphino)-1,1'-binaphthyl} have appeared. Prochiral olefins and ketones have been enantioselectively hydrogenated using $[RuX(arene)\{(S)\text{-BINAP}\}]^+$ (where X = halide;

arene = C_6H_6 or p-$MeC_6H_4CHMe_2$),[83] while buta-1,3-diene-2,3-dicarboxylic acid undergoes a double asymmetric hydrogenation to (S,S)-2,3-dimethylsuccinic acid in extremely high diastereoisomeric and enantiomeric excess using $Ru_2Cl_4\{(R)\text{-BINAP}\}_2NEt_3$.[84] Finally, stereoselective hydrogenation via dynamic kinetic resolution with Ru(II)-BINAP has been presented.[85]

Dipolar [3 + 2] cycloadditions of activated alkynes with the diphosphene complex $(\eta^5\text{-}C_5Me_5)Ru(CO)_2P{=}P\text{-Aryl}$ (where aryl = 2,4,6-t-$Bu_3C_6H_2$) are described. The five-membered metallaheterocycle $(\eta^5\text{-}C_5Me_5)(CO)\overline{Ru[CO(R)C{=}C(R)P}{=}P\text{-Aryl}]$, which is obtained at -70 °C, rapidly experiences a σ/π rearrangement to furnish an η^2-coordinated P=P moiety.[86] The reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2RuP{=}P\text{-Aryl}$ with α,β-unsaturated Michael acceptors yields the transition-metal-functionalized dihydro-1,2-λ^5-oxaphospholes $(\eta^5\text{-}C_5Me_5)(CO)_2Ru\overline{P[OC(R){=}C}(R)CH_2]({=}P\text{-Aryl})$. All new heterocycles were characterized by combustion analyses and solution spectroscopic methods.[87]

(e) Carbonyls

fac-$[Os(CF_3CO_2)_2(pySH)(CO)_3]$ (where pySH = pyridine-2-thione) has been synthesized from $Os(CF_3CO_2)(CO)_4$ and pySH. The initial product contains monodentate trifluoroacetate groups and a S-bound pySH ligand. Elimination of CF_3CO_2H yields fac-$[Os(CF_3CO_2)(pyS)(CO)_3]$, which is shown to possess a bidentate pyS ligand. X-Ray diffraction results of $Os(pyS)_2(CO)_3$ and $Os(pyS)_2(CO)_2$ are also presented.[88] The coordination chemistry of iminooxosulphuranes has been explored using $Ru(CO)(PPh_3)_3L$ (where L = CO, t-BuNC, or 2,6-$Me_2C_6H_3NC$). Replacement of one PPh_3 ligand by R-N=S=O leads to $Ru(CO)(PPh_3)_2L(OSNR)$. Spectroscopic analyses indicate that the heterocumulene ligand is bound to the metal through both the nitrogen and sulfur atoms.[89] The photochemistry of $Ru(CO)_3(i\text{-}Pr_2CH\text{-}DAB)$ (where DAB = 1,4-diaza-1,3-butadiene) has been examined. Optical excitation results in CO loss from the ^3LF state; no reaction is observed from the ^3ML state of the metal R-DAB metallocycle at lower energy.[90].

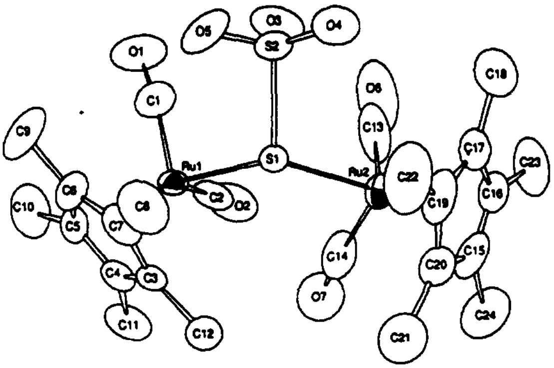
The reaction between $[Ru(CO)_4]^{2-}$ and various heteroallenes is reported. $Ru(CO)_5$ is the major product from the reaction with COS.[91] The synthesis and reactivity of olefin and four- to six-membered metallacycloalkanes based on $M(CO)_4$ (where M = Ru, Os) are reported. Reaction of $[M(CO)_4]^{2-}$ with alkanediyl bis(trifluoromethanesulfonates) provides the corresponding metallacycloalkanes which display varying degrees of stability. X-Ray diffraction results of $(OC)_4\overline{OsCH_2(CH_2)_3CH_2}$ are included.[92] The carbonyl metalates $[M(CO)_4]^{2-}$ (where M = Ru, Os) and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-$ have been allowed to react with $L{\bullet}BH_3$ (where L = THF, Me_2O) to give the metalladiborane complexes $[M(CO)_4(\eta^2\text{-}B_2H_5)]^-$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2(\eta^2\text{-}B_5H_5)$. The structure of the latter compound is best described as a diborane(6) molecule with a $(\eta^5\text{-}C_5H_5)Ru(CO)_2$ unit replacing a bridging hydrogen. Mössbauer data also support the three-center, two-electron bonding scheme between the metal center and the B_2H_5 fragment.[93] Transient IR spectroscopy has been used to study coordinatively unsaturated $Ru(CO)_x$ products formed by excimer laser photolysis of gas-phase $Ru(CO)_5$. $Ru(CO)_4$ and $Ru(CO)_3$ are observed and rate constants for their reaction with CO have been obtained.[94] Substitution of CO by PPh_3 in $Ru(CO)_5$ and $Os(CO)_5$ has been kinetically examined in the presence of Me_3NO. The reactions follow second-order kinetics, showing a first-order dependence on the pentacarbonyl and Me_3NO concentrations. As in previous studies from Basolo's lab, the reaction is zero-order in PPh_3 concentration. $Os(CO)_5$ reacts slightly faster than $Ru(CO)_5$. An explanation is given for the relative reaction rates of $M(CO)_5$ compounds and a comparison is made with the corresponding $M_3(CO)_{12}$ complexes.[95] The kinetics and mechanism of CO substitution derive by a dissociative mechanism. The activation parameters and a discussion of the ligand substitution lability for the triad of $M(CO)_5$ metal carbonyls are discussed.[96] The rates for CO substitution in $Ru(CO_4)L$ (where L = P-, As-, Sb-ligands) have been calculated and resolved into electronic and steric contributions. The steric profile reveals that steric effects are minimal for small cone angle ligands, increasing steadily and substantially as the ligand's cone angle increases. A discussion on the importance of CO loss and methyl migration reactions is presented.[97] A theoretical study on the electronic and molecular structures of $M(CO)_4$ (where M = Ru, Os) has been reported. The ability of these unsaturated tetracarbonyls to activate methane is also discussed.[98]

(f) Sulfur and Oxygen Ligands

The reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with ArSH (where Ar = Ph, p-MeC_6H_4, p-ClC_6H_4) gives the diruthenium complex $[(\eta^5$-

$C_5Me_5)Ru(\mu_2\text{-}SAr)_3Ru(\eta^5\text{-}C_5Me_5)][Cl]$. X-Ray diffraction analysis indicates that a Ru-Ru bond is present in this μ_2-sulfido bridged dimer. When the reaction is run using $PhCH_2SH$ only the doubly bridged complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}SCH_2Ph)Cl]_2$ is isolated. The spectroscopic and redox properties and the ligand substitution reactivity of these complexes are reported.[99] Treatment of $RuCl_2(PPh_3)_3$ and $RuCl_3(PR_3)_3$ (where R = alkyl or aryl) with $Pb(SR)_2$ yields the diamagnetic complex $Ru(SR)_2(PPh_3)_2$ and the paramagnetic complexes $Ru(SR)_3(PR_3)_2$. An X-ray diffraction investigation of $\overline{Ru(SC_6F_5)_2\{PC_6H_4(H}\text{-}2)(Ph_2)_2\}_2$ reveals a pseudo-octahedral geometry with two definite C-H-Ru interactions. A similar C-F-Ru interaction has also been observed in the X-ray structure of $\overline{Ru\{SC_6F_4(F}\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2$. Magnetic data and ESR spectra for the paramagnetic complexes are presented.[100] The synthesis and characterization of $Os(SC_6F_5)_3(PR_3)_2$ and $Os(SC_6F_5)_2(CO)_2(PR_3)_2$ (where R = phosphine) have appeared. Included in this report is the X-ray structure of trans,trans,trans-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$.[101] The ruthenium complexes $[\mu\text{-}S_2\{Ru(PPh_3)({}^1S_4{}^1)\}_2]$ and $[\mu\text{-}S_2\{Ru(PPh_3)({}^{1bu}S_4{}^1)\}_2]$ (where ${}^1S^{1\ 2-}$ = 1,2-bis(2-mercaptophenylthio)ethane; ${}^{1bu}S_4{}^{1\ 2-}$ = 1,2-bis{3,5-di(tert-butylthio)}ethane) have been prepared from $Ru(X)(PPh_3)({}^1S_4{}^1$ or ${}^{1bu}S_4{}^1)$ (where X = PPh_3, N_2H_4) and elemental sulfur. An intense visible absorption band, which is attributed to the Ru_2S_2 core, is observed for each complex in the presence of oxygen. Moreover, a near-IR band is also observed for each complex ~1100 nm, which has been assigned to an intervalence charge transfer (ICT) transition. The ICT in these diamagnetic complexes supports a scheme involving Ru^{II}/Ru^{III} and S^0/S^{2-} transitions. On the basis of band width and solvent dependence, the ICT was classified as a class II charge transfer complex.[102] In a separate report by the same group, the photochemistry of similar ruthenium complexes has appeared.[103] The substitution reactions of 4,6-dimethylpyrimidine-2-thiol (Me_2-pymSH) and bis(4,6-dimethylpyrimidine-2-yl)disulphide ($Me_2pymSSpymMe_2$) with several ruthenium and osmium complexes are described.[104] The radiochemical separation of Ru(III) with 2-mercaptobenzothiazole using solvent extraction techniques has been presented.[105]

SO_2 reacts with $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$ to give $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2(\mu\text{-}S_2O_3)$ in good yields. Single-crystal X-ray examination of the latter complex reveals a dimeric structure with a bridging thiosulfate ligand and terminal carbonyl groups. $S^{18}O_2$ labeling studies indicate that the extra oxygen in the thiosulfate group originates from SO_2.[106]



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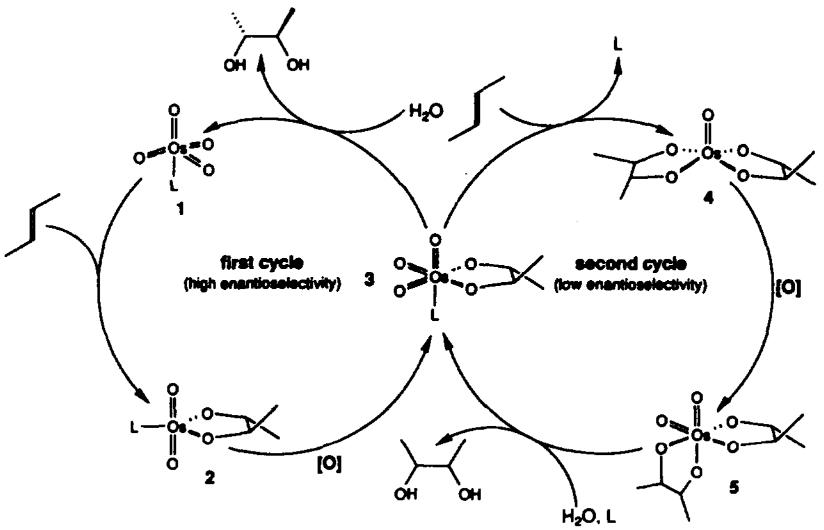
The ruthenium oxo complexes trans-$[Ru^{IV}L(O)(NCO)]^+$ and trans-$[Ru^{IV}L(O)_2]^{2+}$ (where L = meso-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene) have been prepared and examined electrochemically. The X-ray diffraction results of the former cation are presented. The oxidation of alcohols, styrene, and toluene using the latter dioxo complex is discussed.[107] Oxidation of para-substituted N,N-dimethylanilines using $[Ru^{IV}(bpy)_2(O)(PPh_3)]^{2+}$ and $[Ru^{IV}(bpy)_2(O)(PEt_3)]^{2+}$ is reported. Cytochrome P-450-like oxidation reactivity is observed. Tertiary amines are oxidatively dealkylated, yielding the corresponding N-methylaniline and formaldehyde. The rate constants, activation parameters, and Hammett correlations are presented.[108] OsO_4 reacts with pyrogallol (H_2PG) in the presence of pyridine to yield trans-$[OsO_2(PG)_2]^{2-}$ or $OsO_2py_2(PG)$ depending upon the reaction conditions.[109] A report on the osmium-catalyzed asymmetric dihydroxylation of olefins has appeared. More than one catalytic cycle was found to be operative in the olefin dihydroxylation reaction. The branching point in this bimodal reaction involves an osmium(VIII) trioxoglycolate species. The proposed reaction mechanism is shown below.[110]

The new oxo complexes trans-$[RuO_2(py)_4]^{2+}$, trans-$[OsO_2(py)_3(H_2O)]^{2+}$, trans-$[MO_2(py)_2X_2]$ (where M = Ru, Os; X = Cl, Br) and trans-$[Ru_2O_6(py)_4]$ have been reported. The latter two ruthenium oxo complexes function as stoichiometric oxidants for the conversion of primary and secondary alcohols to aldehydes and ketones, respectively. Catalytic oxidation



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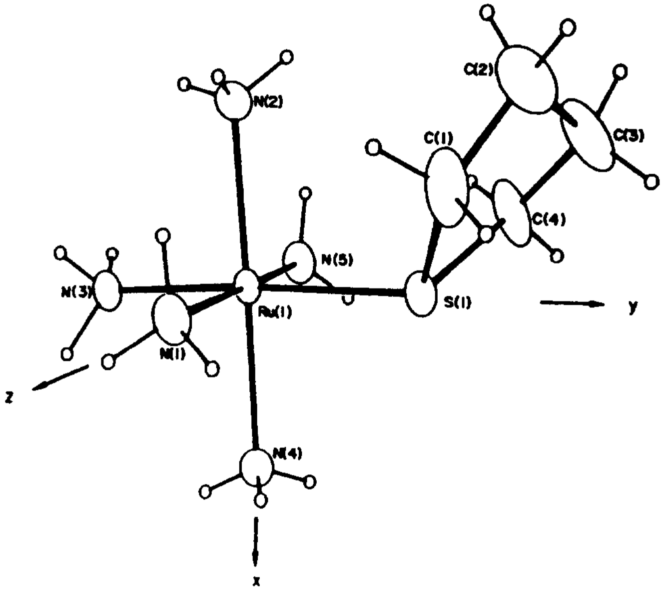
is achieved using N-methylmorpholine N-oxide and $[Bu_4N][ClO_4]$ as co-oxidants.[111] Fourier Transform ion cyclotron resonance spectrometry has been employed in the gas-phase ion-molecule study of OsO_n^+ (n = 0-4) with hydrocarbons and small molecules. Thermochemical data for several pertinent species are presented.[112] Acidification of aqueous solutions containing $[OsO_2(DH)_4]^{2-}$ in the presence of cyanide/$H_2C_2O_4$ and cyanide/AcOH yields $[OsO_2(CN)_2(C_2O_4)]^{2-}$ and $[OsO_2(CN)_2(OH)_2]^{2-}$ respectively.[113] A time-of-flight neutron powder diffraction study of $SrRuO_3$ has been published.[114]

A least-squares method for computing rate constants of reversible, first-order, triangular network reactions has been developed and employed in the study of the isomeric rearrangements of acetylacetonatobis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)ruthenium(III).[115] The electrochemistry of tris(β-diketonato)ruthenium(III) has been examined at platinum electrodes.[116] The oxidation of $Ru^{II}\{CF_3C(O)CHC(O)CF_3\}$ by $Cu(dmp)_2^{2+}$ (where dmp = 2,9-dimethyl-1,10-phenanthroline) has been investigated and the rate of oxidation may be explained by using the Marcus cross reaction.[117] The synthesis of $[Ru(C_2O_4)_3][K]_3$, free of chloride ions, is described along with the single-crystal X-ray structure. The reduction potential, which was obtained by cyclic voltammetry, was recorded and is different from the value previously reported.[118] The synthesis, spectral characterization, and kinetic studies of the ruthenium(II) and ruthenium(III) benzoquinone oxime (BQDH) complexes $Ru(BQDH)_2L_2$ (where L = N, P, and S donor ligands) are reported. Ligand substitution studies reveal a dissociative reaction mechanism and formation of a 5-coordinate intermediate that shows little discrimination toward incoming nucleophiles.[119] Reaction of $RuCl_3$ with 1,2-naphthoquinone 1-oxime (1-NQOH) and 1,2-naphthoquinone 2-oxime (2-NQOH) yields $Ru(1\text{-}NQO)_2$ and $Ru(2\text{-}NQO)_2$, respectively.[120] $[Ru(diene)Cl_2]$ reacts with α-amino acids (aa) in refluxing methanol to produce $[Ru(diene)(aa)]_n$. An X-ray structure of the ruthenium complex $[Ru(1,5\text{-}COD)(D,L\text{-}phe)]_4$ reveals tridentate amino acids with symmetrical carboxyl bridges.[121] The redox potentials, reaction entropies, and thermodynamic parameters for ruthenium(III/II) ethylenediaminetetraacetate (EDTA) and its derivatives are described.[122] A kinetic study of the reaction between thiourea and $Ru^{III}(H\text{-}EDTA)(H_2O)$ has been conducted in aqueous solution as a function of pH, temperature, and ruthenium(III) concentration at constant ionic strength using stopped-flow techniques. The activation parameters support an associative mechanism.[123]

(g) Nitrogen Ligands

The reduction kinetics of $[Ru(NH_3)_5(py)]^{3+}$ and $[Ru_2(AcO)_4]^+$ by [N-(2-hydroxyethyl)ethylenediaminetriacetato] aquotitanium(III) were studied and shown to exhibit second-order kinetics.[124] The general synthesis of pentaammineruthenium(II) complexes of phenylcyanamide ligands is reported along with the autodimerization results of the phenylcyanamide ligands. The phenylcyanamide ligand coordinates in an "end-on" fashion through the nitrile nitrogen. Electrochemical studies reveal a pH dependent Ru(III)/(II) redox couple which is consistent with a one electron/one proton equilibrium over a wide pH range.[125] The same group has also published a paper dealing with the general synthesis for anionic phenylcyanamide ligands based on $Ru(NH_3)_5$. A spectroscopic examination of the new complexes has led to the assignment of the metal charge-transfer bands.[126] The reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and $P(OEt)_2OH$ has been explored. The second-order specific rate constants and the activation parameters are reported.[127] $[M(NH_3)_5(DMU)]^{2+}$ (where M = Ru, Os; DMU = 1,3-dimethyluracil) has been prepared by Zn/Hg reduction of $[Ru(NH_3)_5Cl][Cl]_2$ and $[Os(NH_3)_5(OTf)][OTf]_2$. The new compounds have been characterized by NMR spectroscopy (^1H, ^{13}C), cyclic voltammetry and differential pulse polarography. Labilization of the trans-NH_3 ligand in $[Ru(NH_3)_5(DMU)]^{2+}$ catalyzes the formation of $[Ru(NH_3)_4(H_2O)_2]^{2+}$ and $[Ru(NH_3)_4(H_2O)(DMU)]^{2+}$.[128]

The autoxidation of the pentaammineruthenium(III)-nucleoside complexes 7-[(Ino)Ru$(NH_3)_5]^{3+}$ and 7-[(1-MeIno)Ru$(NH_3)_5]^{3+}$ (where Ino = inosine; MeIno = 1-methylinosine) gives the corresponding 8-keto complexes at high pH. A mechanism involving proton ionization at the C8 position followed by autoxidation as the rate-limiting step is discussed.[129] The synthesis of cis-$[Ru(NH_3)_4(NH_2CH_2CO_2R)_2]^{2+}$ (where R = Me, CH_2Ph, CO_2Et) has been described.[130] Ruthenium(III)-thioether bonding has been examined using structural, spectroscopic, and molecular orbital techniques. X-Ray diffraction structures of $[Ru(NH_3)_5(SC_4H_8)]^{3+}$, $[Ru(NH_3)_5\{S(Me)(Et)\}]^{3+}$ and $[Ru(NH_3)_5(SMe_2)]^{3+}$ display distorted octahedral geometries. The interactions between high-lying thioether donor orbitals and the Ru(III) 4d orbitals and the unusual thioether coordination geometry are discussed.[131]



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The synthesis and characterization of π-vinyl ether complexes based on pentaamineosmium(II) have been described. $[Os(NH_3)_5(\eta^2\text{-butyne})][OTf]_2$ reacts with methanol to yield the π-vinyl ether complex $[Os(NH_3)_5\{\eta^2\text{-cis-MeCH=C(OMe)Me}\}][OTf]_2$. When the same reaction is conducted with H_2O, the π-enol complex $[Os(NH_3)_5\{\eta^2\text{-cis-MeCH=C(OH)Me}\}]^{2+}$ is produced.[132] π-Heterocyclic complexes and a report of metal-induced cycloaddition of pyrrole and maleic anhydride using $[Os(NH_3)_5(OTf)][OTf]_2$ have appeared. Reduction of the above triflate in the presence of the desired heterocycle yields $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-L})]^{2+}$(where L = pyrrole, furan, thiophene). ^1H NMR data rule out the coordination of the heterocycle in a η^1-mode via the heteroatom. The π-coordinated pyrrole complex undergoes a rapid 1,3-dipolar cycloaddition reaction with added maleic anhydride.[133] Arene-to-alkyne linkage isomerizations of diphenylacetylene on pentaamineosmium(II) have been investigated. $[Os(NH_3)_5(OTf)]^{2+}$ reacts with phenylacetylene to yield four complexes, all of which possess an intact alkyne ligand. The kinetically favored mononuclear complex features an η^2-bound aryl group. Linkage isomerization involving an η^2-π aryl to η^2-π alkyne migration has been demonstrated and shown to be accelerated by oxidation of the osmium center.[134] Oxidation of the nitrogen complex $[Os(NH_3)_5(N_2)][Cl]_2$ in neat TfOH using either Br_2 or O_2 gives $[Os(NH_3)_5(OTf)][OTf]_2$ in essentially quantitative yield. The same product may also be obtained from the substitution reaction of $[Os(NH_3)_5Cl][Cl]_2$ in neat TfOH. The measured solvation rate constants are rapid in comparison to other

Os(III) complexes. The redox and spectroscopic properties are reported.[135] Addition of $[OsCl_6][NH_4]_2$ to hydrazine hydrate affords $[Os(NH_3)_5(N_2)][Cl]_2$ and cis-$[Os(NH_3)_4(N_2)_2][Cl]_2$. Continued reaction with hydrazine hydrate gives the former complex in ~90% yield. If the reverse addition is carried out, the heretofore unknown nitrido-bridged complex $[(NH_3)_5OsNOs(NH_3)_5][Cl]_5$ is obtained in ~90 % yield. The electronic absorption spectrum of this latter dimer has been assigned by using a MO diagram along with a spectral comparison with other μ_2-nitrido bridged Ru and Os complexes.[136] UV-visible irradiation of $[Os^{IV}(NH_3)_4N][OTf]_3$ gives the μ-dinitrogen complex $[(NH_3)_4(MeCN)Os(\mu\text{-}N_2)Os(NH_3)_4(MeCN)]^{5+}$. The structure of the dimer was unequivocally established by X-ray diffraction analysis.[137]

The possibility of molecular switching in the mixed-valence compound $[(NH_3)_5Ru\text{-}4,4'\text{-bpy-}Ru(NH_3)_5]^{5+}$ has been theoretically studied. The pathways for electronic coupling have been analyzed and computed as a function of the dihedral angle between the pyridine rings. The dominant electronic coupling interaction involves a π-π coupling. Perpendicular pyridine rings display a σ-π electronic coupling pathway.[138] Three reports have appeared dealing with the Creutz-Taube ion, $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{5+}$ (where pyz = pyrazine). A near- and mid-infrared examination of the Creutz-Taube ion has led to the characterization of a low wavenumber electronic transition at 2000 cm^{-1}. Infrared spectra of $[(NH_3)_5Ru\text{-pyz-}Ru(NH_3)_5]^{n+}$ (where n = 4, 5, 6) are reported and the mixed-valence complex (n = 5) is shown to be intermediate between those of the oxidized and reduced forms of the mixed-valence complex. On the basis of the infrared data, the odd electron in the Creutz-Taube ion is fully delocalized between the two ruthenium centers on the vibrational time scale.[139] The extent of electron delocalization in the Creutz-Taube ion and other mixed-valence complexes has been explored by nonadiabatic quantum treatment of the absorption (IR) line shape. Expressions for calculating the optical spectrum (IR) are described for bridged mixed-valence dimers.[140] A discussion of the electronic structure of $[(NH_3)_5Ru\text{-}pyz\text{-}Ru(NH_3)_5]^{n+}$ (where n = 4, 5, 6) and $[(NH_3)_5Ru\text{-}bqd\text{-}Ru(NH_3)_5]^{n+}$ (where bqd = benzoquinone diimine; n = 4, 5), which utilizes the self-consistent extended Hückel (SCCEHMO) approach, has been presented. The resulting wave functions were used in the calculation of isomer shifts and quadrupole splittings for the ^{99}Ru Mössbauer spectra of the dimer complexes.[141]

The unsymmetrical dimer $[(NC)_5Ru^{II}\text{-}CN\text{-}Ru^{III}(NH_3)_5]^-$ has been examined for optical intervalence enhanced Raman scattering. Raman assignments and the vibrational reorganization energy are discussed.[142] The reactions of e^-aq and $CO_2^\bullet$ radicals with $[(NH_3)_5RuNCRu(bpy)_2CNRu(NH_3)_5]^{6+}$ [3,2,3], $[py(NH_3)_4RuNCRu(bpy)_2CNRu(NH_3)_5]^{6+}$ [3',2,3], and $[py(NH_3)_4RuNCRu(bpy)_2CNRu(NH_3)_4py]^{6+}$ [3',2,3'] are shown to yield the reduced complexes [2,2,3], [2',2,3], and [2',2,3'], respectively. The corresponding [2,2,2], [2',2,2], and [2',2,2] species are formed upon exhaustive irradiation. The reduction rate constants are reported along with the results of the intramolecular electron-transfer reaction involving

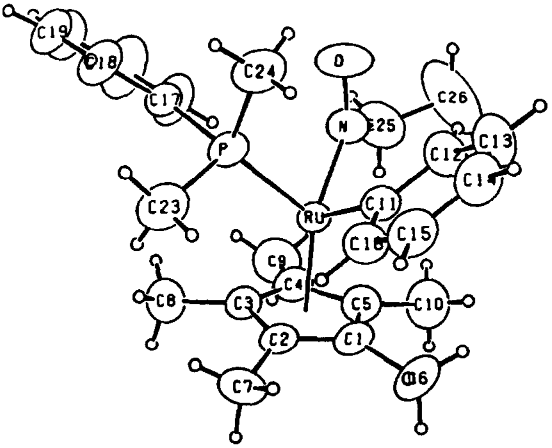
[3',2,2] → [2$^-$,2,3].[143] The intervalence charge-transfer chemistry associated with binuclear ruthenium complexes linked by α,ω-dipyridyl polyenes has been explored. The redox and spectroscopic properties are described. Oxidation affords a near-IR transition which has been attributed to an intervalence transition. The intensity of the intervalence band is discussed in connection with the length of ligating dipyridyl polyene.[144] The first example of intramolecular electron-transfer assistance in a bimolecular redox is reported. Reaction between $[(NH_3)_5Ru^{III}\{\mu$-1,2-bis(4-pyridyl)ethane$\}Fe^{II}(CN)_5]$ and peroxydisulfate does not proceed by direct oxidation of the Fe(II) center, but rather through the electronic isomer $[(NH_3)_5Ru^{II}\{\mu$-1,2-bis(4-pyridyl)ethane$\}Fe^{III}(CN)_5]$. The rate data for oxidation of the Ru(II) center and the importance of biological electron-transfer implications are described.[145] A report dealing with the solvatochromism and piezochromism of mixed-valence Ru(II)/Ru(III) has appeared.[146] The solvent dependent intervalence transition in [2,8-dithiadispiro-[3.1.3.1]decane)decaaminediruthenium(II,III)]$^{5+}$ has been examined. Despite the absence of any correlation between the intervalence transition with any solvent parameter, a dependence on the ionic strength of the medium was observed. The inner-sphere reorganization energy has been calculated using the extrapolated ionic strength data.[147] The effect of pressure on the intervalence transfer band of the weakly coupled mixed valence complex [(μ-2,6-dithiaspiro[3.3]heptane)decaaminediruthenium

(II,III)]$^{5+}$ and the rate of thermal electron-transfer between the ruthenium centers have been presented.[148] The same complex also displays oxidant-dependent nonadiabatic intervalvence transitions.[149]

The intraligand photochemistry of [Ru(CNMe)$_5$(4-styrylpyridine)]$^{2+}$ has been studied. Isomerization of the styrylpyridine is observed upon optical excitation.[150] Treatment of $RuCl_3 \cdot 3H_2O$ with aromatic hydrazides and hydrazones derived from 2,6-diacetylpyridine is reported. Structural assignment of all of the hydrazones are based on spectroscopic, conductance, and magnetic moment data.[151] Various 2-hydroxypyridines (pyOH) react with RuHCl(CO)(PPh$_3$)$_3$, [Ru(CO)$_2$Cl$_2$], and RuCl$_2$(PPh$_3$)$_3$ to give Ru(pyO)$_2$(PPh$_3$)$_2$, Ru(CO)$_2$(pyO)$_2$, and Ru(pyO)(PPh$_3$)$_2$, respectively. The oxypyridines are bound in a bidentate fashion through the N,O atoms.[152] The reaction between 3- and 4-cyanopyridines and benzonitrile with [Ru(CN)$_5$(H$_2$O)]$^{3-}$ has been investigated kinetically. Dissociation and isomerization reactions are also presented.[153]

The synthesis, chemical reactivity and applications in solar energy conversion have been described for ruthenium pyridine complexes.[154] An electrochemical review article that concentrates on the electronic configuration, redox properties, and ligand oxidation levels has appeared.[155]

A paper describing the synthesis of alkylruthenium nitrosyl complexes, migrating insertion of the nitrosyl ligand into the alkylruthenium bond, and conversion of nitrosoalkyl moiety into oximates, carboxamides, and cyanide complexes has been published. Treatment of (η^5-C_5Me_5)Ru(NO)Cl_2 with Grignard or R_3Al reagents leads to the corresponding dialkyl or diaryl complex in good yield. Thermolysis of (η^5-C_5Me_5)Ru(NO)Me_2 with PMe_3 yields (η^5-C_5Me_5)Ru(PMe_3)CN, H_2O, and methane. All of the new products were fully characterized and the X-ray structure of (η^5-C_5Me_5)Ru{N(O)Et}Ph(PPhMe_2) has been presented. Kinetic isotope results and tracer experiments have been carried out. On the basis of these data, plausible mechanisms are presented for the reactivity observed with the nitrosyl ligand.[156]



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The nitrosyl complex Ru(NO)Cl_3(PPh_3)$_2$ has been obtained from nitrosyl chloride, PPh_3, and $RuCl_3 \cdot 3H_2O$ under mild conditions. The use of MeONO and EtONO in place of nitrosyl chloride also affords ruthenium nitrosyl complexes.[157] RuH(CO)Cl(PPh_3)$_3$ reacts with trityl thionitrite in the presence of $HgCl_2$ or HCl to give both Ru(NO)Cl_3(PPh_3)$_2$ and Ru(CO)$_2$$Cl_2$($PPh_3$)$_2$. The reactions of trityl thionitrite with other ruthenium complexes are described.[158]

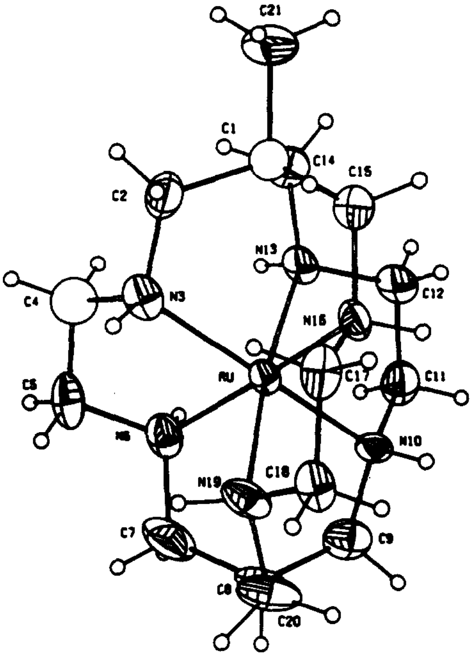
The synthesis of the ligand-bridged complexes $[(tpm)Ru^{III}(\mu\text{-}O)(\mu\text{-}L)_2Ru^{III}(tpm)]^{n+}$ {where L = $O_2P(O)(OH)$, n = 0; L = O_2CO, n = 0; L = O_2CMe, n = 2; tpm = tris(1-pyrazolyl)methane} has appeared. The redox reactivity of these new complexes has been studied using cyclic voltammetric and coulometric techniques. Upon reduction, the ligand-bridged dimer is cleaved to the monomer $[(tpm)Ru(H_2O)_3]^{3+}$. An X-ray structure of the bis(μ-hydrogen phosphate)-bridged complex is also presented. The diamagnetism of these low-spin d^5 Ru(III) centers is attributed to strong electronic coupling through the μ-oxo bridge and the small Ru-O-Ru angle.[159] Reaction of piperidine (R''_2NH) with $[Ru(cycloheptatriene)Cl]_2$ leads to the reactive piperidido complex $[(R''_2N)Ru(cycloheptatriene)(R''_2NH)_2\ Cl]$. This new complex reacts with diazadienes (DAD = RN=CR'-CR'=NR) to give $[(R''_2N)Ru(cycloheptatriene)(DAD)Cl]$. Variable-temperature ^1H NMR analysis of the DAD complex reveals an unexpected conformation and bonding type of the cycloheptatriene ligand.[160] Several mono- and binuclear Ru(II) and Ru(III) Schiff base complexes have been synthesized. The Schiff base complexes are based on N,N'-bis(benzoylacetylacetone)ethylenediamine and N,N'-bis(pyvolylacetylacetone)ethylenediamine.[161] The coordination chemistry of 2,1,3-benzothiadiazole (BTD) and 2,1,3-benzoselenadiazole (BSD) has been studied through the reaction with $MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_3$ (where M = Ru, Os). One PPh_3 is readily displaced by the heterocycle to give $MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2$(BTD or BSD) in quantitative yield. $OsCl_2(CS)(PPh_3)_3$ reacts similarly with BTD and BSD to give

$OsCl_2(CS)(PPh_3)_2$(BTD or BSD). All of the new complexes have been characterized by IR and NMR measurements.[162] The X-ray diffraction results on hexakis(acetonitrile)ruthenium(II) have appeared.[163]

The synthesis and characterization of $[M(NH_3)_5(styrene)]^{2+}$ and $[M(NH_3)_5(olefin)]^{2+}$ (where M = Ru, Os) and the related $[Ru(HEDTA)(olefin)]^-$ are reported. The redox properties of these new complexes have been probed by using cyclic voltammetric and differential-pulse polarographic techniques.[164] A report discussing the kinetics and mechanism of ligand substitution reactions of $Ru(HEDTA)(H_2O)$ with thiocyanide, azide, thiourea, and substituted thioureas has appeared. The kinetics were examined as a function of pH and pressure. An associative mechanism is suggested and the labilization effect of the chelate ligand is discussed and compared with respect to other chelate ligand complexes.[165] The formation of $[Ru^{II}(HEDTA)N_2]^-$ and its reduction to NH_3 by visible light photolysis have been published.[166]

The sexidentate ligand sarcophagine (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) undergoes an oxidative dehydrogenation to give an imine group at the cap portion of the sar ligand when coordinated to ruthenium(III). Intermediate di- and triimine complexes are observed en route to the hexaimine complex. The redox properties of the intermediate species and final hexaimine complex are presented along with the kinetic results. The mechanism for the dehydrogenation sequence is discussed.[167] Encapsulated $[Ru(sar)]^{n+}$ has been examined by X-ray diffraction analysis.

Single-crystal X-ray structure determination of $[Ru^{II}(Mesar)][OTf]_2$ (where Mesar = 1-methyl derivative of sar) and $[Ru^{III}(sar)][OTf]_3$ reveal virtually identical geometries. On the basis of the X-ray structural data, the activation free energy for structural reorganization ($\Delta G^{\ddagger}$ inner sphere) of $[Ru(sar)]^{n+}$ in the electron-electron reaction is predicted to be negligible.[168] The electrochemical oxidation of $[Ru(sar)]^{2+}$ and its relationship to the disproportionation to



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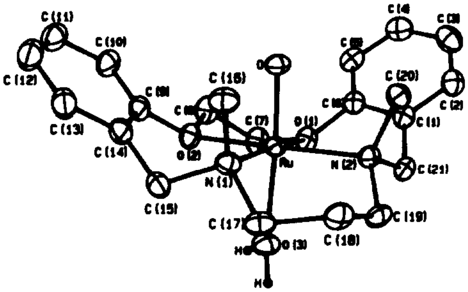
$[Ru(sar)]^{3+}$ in aqueous solution have been investigated. A Pourbaix plot for the ($Ru^{IV/II/II}sar$) system and data comparison with other related complexes are presented.[169] A report dealing with the synthesis and characterization of ruthenium(II) clathrochelate compounds based on boron capping agents has been published. The redox properties have been examined and the stability of these new complexes shown to be dependent on the nature of the substituent attached to the boron cap.[170]

The complex μ-nitrido-bis[(phthalocyaninato)ruthenium] has been prepared. Infrared and esr data suggest that this complex exists as a mixed-valence Ru^{III}-Ru^{IV} dimer, and represents the first example of a ruthenium phthalocyanine complex in oxidation states higher than II.[171] Intense fluid solution photoluminescence has been observed in nitrido- and imido-osmium(VI) complexes. Included in this report is the X-ray structure of $[Os^{VI}(CN)_5N][Ph_4As]_2$.[172] 4-(2-Quinolylazo)phenol reacts with Os(VIII) complexes to give 1:1 violet complexes.[173] The dimethylglyoxime (H_2DMG) complexes $[Ru^{VI}(HDMG)_2(OH)(O)]^{4+}$ have been prepared by electrochemical oxidation of $[Ru^{III}(HDMG)_2(ClO_4)_2]^-$ at pH 1-2 and $[Ru^{VI}(HDMG)_2(H_2O)(O)]^{2+}$ and $[Ru^{VII}(HDMG)_2(O)_2]^+$ at pH 2-3.5. The trans dioxo complex functions as the active catalyst in the electrocatalytic epoxidation of cyclic olefins to epoxides.[174] Schiff bases derived from aromatic aldehydes/ketones and S-benzyldithiocarbazate react with $RuHCl(CO)(PPh_3)_3$ and $RuH_2(CO)(PPh_3)_3$ to give new ruthenium Schiff base complexes. The new complexes have been characterized by convential solution measurements.[175] 2-Formylpyridine(4-phenyl) thiosemicarbazone (L,H) and 2-formylpyridine thiosemicarbazone (LH) have been synthesized and used in the preparation of new Ru(II) and Ru(III) complexes.[176] New ruthenium-oxo complexes have been published. Reaction of $[RuCl_5(H_2O)]^{2-}$ with 1,2-dimethyl-

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane (L_2) affords trans-$[Ru^{III}(L)Cl_2]^{2+}$. Treatment of the dichloro complex in water with Ag^+ yields trans-$[Ru^{III}(L)(OH)(H_2O)]^{2+}$, which is readily oxidized to give trans-$[Ru^{IV}(L)(O)(H_2O)]^{2+}$ (electrochemical oxidation) and trans$[Ru^{VI}(O)(O)_2]^{2+}$ (Ce^{IV} oxidation). The X-ray structure of trans-$[Ru^{IV}(L)(O)(H_2O)][ClO_4]_2 \cdot 2H_2O$ has been determined. The redox chemistry and electrocatalytic oxidation of organic substrates with PhIO are described.[177]



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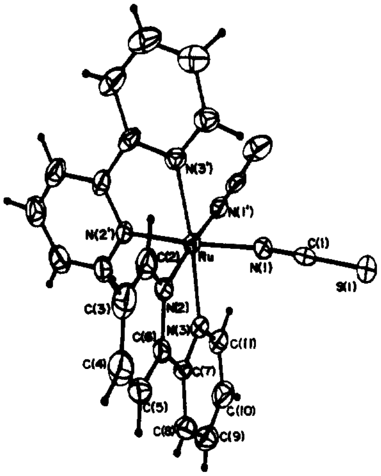
A report describing the driving-force effects on the rate of long-range electronic transfer of two new Ru-modified, Zn-substituted derivatives of horse heart cytochrome c has appeared. Rates of photoinduced charge separation and recombination are reported along with the reorganization energy and the electronic coupling matrix element (H_{AB}).[178] The antimetastatic agent trans-$RuCl_2(DMSO)_4$ reacts with 5'-dGMP to form a diastereomeric pair of isomers through coordination of the guanine N7 and the α-phosphate group. This chelation mode of binding has been characterized by NMR spectroscopy and subsequently separated by HPLC. The complexes are isomers that differ only in their chirality at the ruthenium center.[179] Cross-linked poly(styrene)-co-(polyvinylpyridine) composite electrodes incorporating Ru^{III}(EDTA) have been prepared and examined electrochemically.[180] The semicarbazone ligands $RC(Ph)=NNHC(O)NH_2$ (where R = Et, Pr) have been used in the preparation of $Ru(semicarbazone)_3Cl_3$. The ligand field parameters for these new octahedral complexes have been calculated.[181]

Six review articles describing the chemistry associated with $[Ru(bpy)_3]^{n+}$ have appeared in the literature. The spectroscopy of $[Ru(bpy)_3]^{2+}$ and related systems have been presented in a critical review[182] and a report dealing with homoleptic ruthenium and osmium complexes has appeared.[183] The photochemistry and photophysics of $[Ru(bpy)_3]^{2+}$ have been reported. The existence of localized ligand orbitals and multiple π-π^* emission from mixed-ligand (bpy/phen) complexes is reviewed.[184] Chemical approaches to artificial photosynthesis using $[Ru(bpy)_3]^{2+}$ and mixed-ligand systems are described. This review includes in-depth discussions on energy conversion by electron-transfer quenching, intramolecular control of light-induced electron transfer, and redox catalysis involving water oxidation.[185] The remaining reviews deal with the synthesis and reactivity of polypyridine and related complexes.[186,187]

Solid-state magnetic measurements have been carried out on cis-$[Ru^{IV}(bpy)_2(py)(O)][ClO_4]_2$ using ^1H NMR spectroscopy.

The oxo complex possesses a nonmagnetic ground state; the first excited state lies 79 cm^{-1} higher in energy in the solid state and 56 cm^{-1} in solution. The involvement of spin character in $2e^-$ oxo transfer chemistry is described.[188] The oxidation properties of cis- and trans-$[Os^{VI}(bpy)(O)_2]^{2+}$ have been examined. Both dioxo complexes react with mono- and bidentate phosphines to yield the corresponding coordinated phosphine oxide complexes. A mechanism based on kinetic data, reagent stoichiometry, cyclic voltammetric and UV-visible data is presented.[189] Controlled potential electrolysis of cis-$[Ru(bpy\text{-}4,4'\text{-}dicarboxylate)_2(H_2O)_2]^{2+}$ in acidic solution affords the oxo-bridged dimer $[(bpy\text{-}4,4'\text{-}dicarboxylate)_2(H_2O)Ru^{III}\text{-}O\text{-}Ru^{III}(H_2O)(bpy\text{-}4,4'\text{-}dicarboxylate)]^{4+}$. The catalytic activity of the oxo dimer has been examined in water oxidation reactions.[190] Chiral osmium oxo complexes have been prepared and used as oxidants in asymmetric dihydroxylation reactions. The chirality derives from the ancillary N,N'-dialkyl-2,2'-bipyrrolidine ligand. The observed enantioselectivity depends on both the N-alkyl group and the reaction solvent.[191]

The nature of the redox orbital in cis-$[Ru(bpy)_2(CN)_2]^n$ (where n = 0, 1, 2) has been probed by using FT-IR, UV-visible, and resonance Raman (RR) spectroscopy. The latter two spectroscopic methods reveal that the redox orbital is localized on a single bpy ligand. No vibronic coupling is observed between the two bpy ligands. The RR data indicate that the average frequency shift of bpy modes upon reduction is much smaller than suggested by earlier studies, being on the order of ~10 cm^{-1}.[192] Excited-state proton-transfer processes of cis-$Ru(bpy)_2(CN)_2$ have been investigated in acetonitrile and actonitrile/water solvent systems.[193] The redox quenching of excited cis-$Ru(1,10\text{-phen})_2(CN)_2$ is reported. Reductive quenching by aromatic amines and oxidative quenching using nitroaromatics reveal an anomalous temperature dependence, which has been explained by the standard and/or electrostatic enthalpy and entropy changes associated with the electron-transfer step.[194] The relative proton affinity of $[Ru(bpy)_2X_2]$ complexes (where X = Cl, Br, I, NCS, CN, NO_2) has been determined by using liquid Secondary-Ion Mass Spectometry. Differences in the π-acceptor properties of the ligands correlate with the proton affinities of the ligands.[195] The X-ray structures of cis-$[Ru(bpy)_2(NCS)_2]$, solvated with MeCN and DMSO, have been determined. The variable-temperature FT-IR and NMR spectra are presented and discussed.[196]



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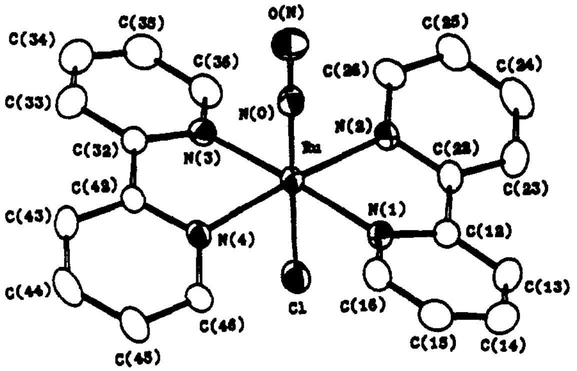
Osmium(II) bipyridine complexes with an ancillary N-methyl-4,4'-bipyridinium (MQ^+) ligand have been studied by UV-visible spectroscopy and cyclic voltammetry. The effect of the pyridine ring conformation in the MQ^+ ligand has been examined with respect to intramolecular electron-transfer reactivity. The excited-state energetics of these chromophore-quencher complexes are thoroughly discussed.[197] Reactivity modulation of the MLCT excited states by the hydrido ligand in $[M(bpy)_2(CO)X][PF_6]$ (where M = Ru, Os; X = H, D) has been explored. The reported data suggest that the ν(Os-H) mode does not significantly affect the emission spectrum nor the nonradiative decay process. In comparison, the analogous ruthenium complex exhibits a significant k_H/k_D kinetic isotope effect for nonradiative decay.[198] The intense MLCT transition observed has been examined by using resonance and preresonance Raman spectroscopy.[199] Picosecond Raman studies reveal that rapid intermolecular proton transfer occurs in the excited state of $[Ru(bpy)(NH_3)_5]^{2+}$. The role of solvent dynamics and the lifetimes of pertinent species are presented.[200]

The surfactant-active osmium complexes cis-$[OsL_2(CO)NC(CH_2)_nMe]^{2+}$ (where L_2 = bpy, 1,10-phen; n = 0-19) have been prepared and examined for intramolecular excited-state reactivity. The nitrile ligand is activated to thermal nucleophilic attack, and luminescent adducts are observed with various alcohols and amines. Photodecomposition is observed through nitrile labilization.[201] The high-energy MLCT states for $[Ru(bpy)_2(dppe)]^{2+}$ (where dppe = $Ph_2PCH_2CH_2PPh_2$)

have been reexamined and compared with other Ru(bpy)$_2$ complexes. An interaction between the singlet MLCT states and the π-π^* states has been identified.[202]

A kinetic study on the ligand substitution of L by Cl$^-$ or MeCN in cis-[Ru(bpy)$_2$(L)(X)]$^+$ (where X = NO$_3$; L = pyridine, MeCN) has been carried out. Rate enhancements observed with the nitrate are discussed in terms of the nitrate's ability to function as a bidentate ligand.[203] Coordination of the Ru(bpy)$_2$$^{2+}$ fragment to the O(4), N(5) atoms of 1,3-dimethyllumazine has been achieved. Absorption spectroscopic and cyclic voltammetric data are presented and the reduced species are discussed in terms of thermodynamically and kinetically stabilized coenzyme models.[204] Facile perdeuteration of bpy is reported. Reaction of bpy-d$_8$ with RuCl$_3$•3H$_2$O affords Ru(bpy-d$_8$)$_2$Cl$_2$·2H$_2$O, which was subsequently allowed to react with 5,6,10,11-tetrahydro-16,18-diazadipyrido[2,3-a:3'2'-n]pentacene (L) to give [Ru(bpy-d$_8$)L]$^{2+}$. Use of the deuterated bpy ligands greatly assisted in the ^{1}H NMR assignment of this complex.[205] The new alkylruthenium complexes cis-Ru(t-Bu-bpy)$_2$R$_2$ (where R = Me, Et, CH$_2$-cyclo-C$_6$H$_{11}$, CH$_2$SiMe$_2$CH=CH$_2$, CH$_2$SiMe$_3$, CH$_2$SiMe$_2$Ph; t-Bu bpy = 4,4'-di-t-butyl-2,2'-bpy) and trans-Ru(t-Bu-bpy)$_2$R'$_2$ (where R' = CH$_2$CMe$_2$Ph) have been synthesized and fully characterized. The X-ray structure of the diethyl derivative is presented and the stereochemical rigidity and electron-transfer properties are briefly described.[206] The redox properties of cis- and trans-[Ru(bpy)$_2$Cl(NO)]$^{2+}$ have been examined and their differences discussed. The X-ray structure of trans-$[Ru(bpy)_2Cl(NO)]^{2+}$ has been determined.[207]



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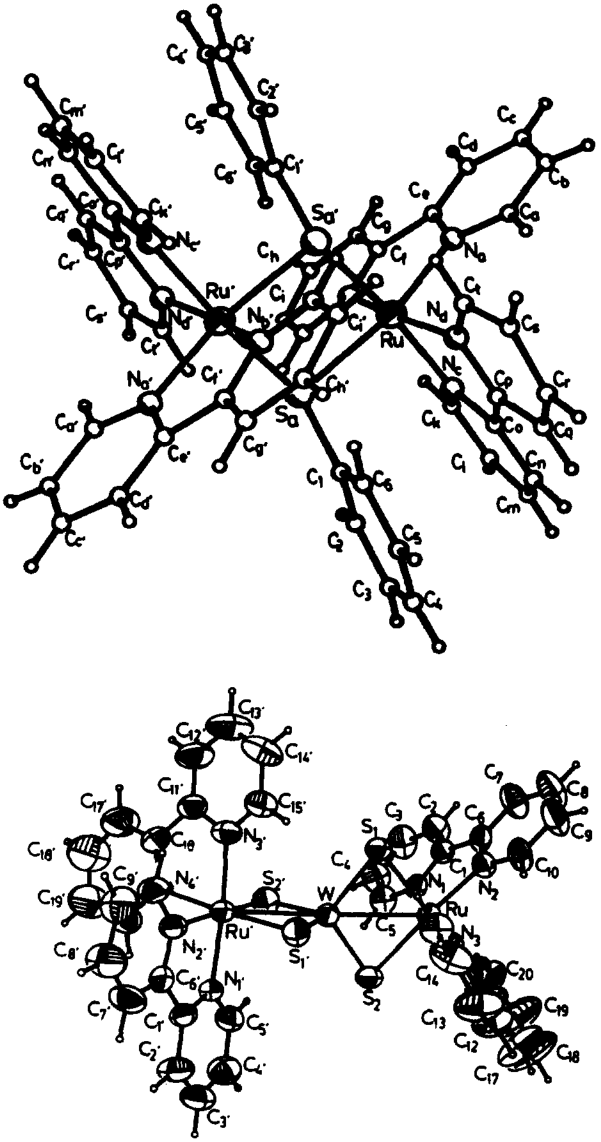
The binuclear and trinuclear heterometallic complexes $[(NC)Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5]^{2-}$ and $[(NC)_5Cr\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Cr(CN)_5]^{4-}$ have been prepared and their photophysical reactivity investigated. Visible light absorption by the $Ru(bpy)_2{}^{2+}$ chromophore allows for the observation of phosphorescence from the $Cr(CN)_5{}^{3-}$ luminophore. The rate of intramolecular intervalence energy transfer, which originates from the MLCT triplet of the Ru(II) fragment and ends at the doublet state of the $Cr(CN)_5{}^{3-}$ fragment, is estimated to possess a lifetime $\tau < 10$ ns. The excited-state absorption spectra are presented and the occurrence of electron-transfer doublet-doublet annihilation is discussed.[208]

The redox thermodynamics of $[(bpy)_2(Cl)Ru\text{-}L\text{-}Ru(NH_3)_4(py)]^{5+/4+/3+}$ {where L = pyrazine, bpy, bis(pyridyl)ethane} have been evaluated. Unusual entropy and electronic coupling effects in mixed-solvents systems are discussed.[209] The polychromophoric complexes $[(NC)(bpy)_2Ru^{II}\text{-}CN\text{-}Ru^{II}(bpy)_2(CN)]^+$ (2,2), $[(NC)(bpy)_2Ru^{II}\text{-}CN\text{-}Ru^{II}(1,10\text{-phen})_2(CN)]^+$ (2,2'), and $[(NC)(bpy)_2Ru^{II}\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}NC\text{-}Ru^{II}(bpy)_2(CN)]^{2+}$ (2,2,2) have been prepared and investigated by spectroscopic and photochemical methods. The redox properties and emission spectra have also been examined. Intense metal-to-metal ($Ru^{II} \rightarrow Ru^{II}$) intervalence transitions, typical of class II complexes, are observed for the mixed-valence complexes in the near-IR region. No emission data for the (2,3), (2,3'), and (2,3,2) complexes were observed due to a highly efficient intramolecular electron-transfer quenching process.[210] Ruthenium(II) bipyridine complexes containing ancillary sulfur ligands have been synthesized. The following sulfur ligands were used: WS_4^{2-}, $Mo_2S_4(\text{ethanedithiolate})_2^{2+}$, S_5^{2-}, thiolates, and dithiolene. All of the new complexes were fully characterized by the usual solution spectroscopies and the redox properties, as determined by cyclic voltammetric measurements, are reported. Several of the complexes displayed a reasonably stable $Ru^{2+/3+}$ redox couple, which allowed for the ESR examination of the resulting ruthenium(III) complex; the isotropic ruthenium hyperfine splitting was on the order of 16 Gauss. The X-ray crystal structures of $\{[Ru(bpy)_2]_2WS_4\}[PF_6]_2$ and $\{[Ru(bpy)_2(SC_6H_5)_2]_2\}[OTf]_2$ have been determined.[211]



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Excited-state resonance Raman and luminescence spectra of $Ru(bpy)_3^{2+}$ in anionic micelles have been published. The data suggest that the negative micellar surface repels the optically excited electron.[212] The resonance Raman spectra and excited-state lifetimes for several 3,3'-polymethylene-

2,2'-bipyridine complexes of Ru(II) have been presented. The monomethylene-bridged complex shows different resonance Raman and emission data in comparison to its longer polymethylene chain homologues. The observed spectral trends correlate with the degree of planarity distortion experienced by the bipyridine ligands.[213] A report describing the near-infrared surface-enhanced Raman spectra of $[Ru(bpy)_3]^{2+}$ using Cu and Ag electrodes has appeared.[214] The energetics of electron transfer between ligands in the MLCT states of $[Ru(bpy)_3]^{2+}$ have been investigated by using picosecond Raman spectroscopy. It is shown that interligand coupling is not strong enough to overcome the vibrational reorganization energy required for electron delocalization.[215] Resonance Raman scattering spectroscopy has been used in the examination of excited-state electron transfer between $[Ru(bpy)_3]^{2+}$ and MV^{2+}. Stern-Volmer quenching data, which is based on the luminescence quantum yield vs. $[MV^{2+}]$, reveal that the quenching process is diffusion controlled.[216] Several substituted bipyridines and their $[Ru(bpy)_3]^{2+}$ complexes have been examined by Raman spectroscopy. The same complexes were then immobilized on TiO_2 and the metal-oxygen vibrational modes assigned by using resonance Raman spectroscopy.[217] Two color picosecond Raman spectroscopy has been employed in a study of interligand electron transfer in the excited MLCT states of mixed ligand ruthenium(II) bipyridine complexes. The results are discussed within the context of electron transfer theory.[218] Heteroleptic ruthenium(II) complexes with 2,2'-bipyridine and 1,4,5,8,9,12-hexaazatriphenylene adsorbed on silver sols have been investigated via surface-enhanced resonance Raman scattering spectroscopy.[219]

The electron-transport dynamics of polymer immobilized $[Ru(bpy)_2Cl]^{2+/1+}$ moieties have been studied. The ruthenium fragment was incorporated into a partially quaternized polyvinylpyridine polymer and then examined for its luminescence and redox properties.[220] Ruthenium and osmium complexes containing the ligand 5-chlorophenanthroline have been used as starting materials in the electrochemical assembly of metallopolymeric electrode coatings and examined by electrochemical techniques. Auger electron spectroscopy confirms the proposed thin film mechanism which involves carbon-chlorine bond cleavage as the initial step.[221] Cyclic voltammetry studies of zeolite-incorporated $[Os(bpy)_3]^{2+}$ reveal that the $[Os(bpy)_3]^{2+}$ complexes occupy the outer surface of the zeolite. The surface species are shown to mediate electron transfer to and from the smaller redox active cations imbedded within the zeolite structure.[222] The permeability of $Os(bpy)_2Cl_2$ through platinum electrode polymerized cobalt tetrakis(o-aminophenyl)porphyrin has been evaluated by using rotating-disk voltammetry.[223] Chemiluminescence detection of the Belouzov-Zhabotinski reaction using $[Ru(bpy)_3]^{2+}$ as a catalyst is reported.[224] $[Os(bpy)_3]^{2+}$ has been used as a large cation in order to evaluate the electrochemical behavior of $[Fe(CN)_6]^{4-}$-polycation complexes.[225]

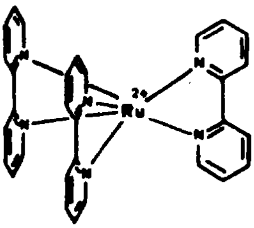
The redox response of the resolved forms of $[Ru(bpy)_3]^{2+}$ at a cholesteric liquid crystal modified electrode is reported.[226] Hydrogel-immobilized $[Ru(bpy)_3]^{2+}$ has been examined electrochemically and kinetic parameters in different supporting electrolytes are reported.[227] Electrochemiluminescence (ECL) of $[Ru(bpy)_3]^{2+}$ has been observed in a mixed solvent system. Both the presence of water and oxygen are required for ECL.[228] $Ru(bpy)_2Cl_2$ has been condensed with poly(4-vinylpyridine) and methylolacrylamide copolymers to yield chemically modified electrodes; the redox properties of these electrodes are presented.[229] Multicomponent, redox-conductive metallopolymeric films containing ruthenium and osmium have been prepared. The polymeric microstructures are discussed and potential applications as electrochemical sensors are suggested.[230] A report describing the electrocatalytic reduction of carbon dioxide using a ruthenium/rhenium chemically modified electrode has been presented.[231] The rate of charge transport through $[Os(bpy)_2(poly\text{-}4\text{-}vinylpyridine)Cl]^+$ has been established by electrochemical techniques; the results are discussed in relation to sensor application technology.[232] Photochemical electron transfer at liquid•liquid interfaces has been studied. The photoredox couple consists of $[Ru(bpy)_3]^{2+}$ dissolved in an organic phase and MV^{2+} dissolved in the aqueous phase. The measured photocurrent results from an electron transfer between the excited $[Ru(bpy)_3]^{2+}$ complex and MV^{2+}.[233]

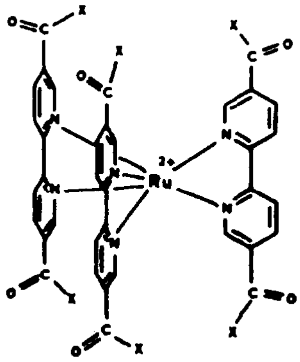
A paper describing the solid-state voltammetry of $[Ru(bpy)_3]^{2+}$ dissolved in poly(ethylene oxide) films has appeared.[234] Langmuir-Blodgett (L-B) monolayers of surfactant-derivatized $[Ru(bpy)_3]^{2+}$ have been synthesized at an indium-tin electrode and fully investigated by using cyclic voltammetry. Information concerning electron transfer in the organized monolayer and mass transfer across the L-B monolayer is presented.[235]

The synthesis of $[Ru\{4,4'-bis(1R,2S,5R)-(-)-menthylcarboxy)-2,2'-bpy\}]^{2+}$ has been described. This chiral complex has been employed as a photosensitizer in photoinduced enantioselective electron-transfer reactions.[236] $[Ru(bpy)_3]^{2+}$ and mixed-ligand ruthenium(II) complexes have been examined spectroscopically. The results of photoselection and luminescence spectra are reported along with a discussion on the perturbations in the π^* energy levels.[237] The two lowest excited states in $[Ru(bpy)_3]^{2+}$, which are assigned to Ru 4d→bpy π^* charge-transfer transitions, have been observed by using zero-magnetic field optically detected magnetic resonance. The degenerate classification of these states is in agreement with a sublevel splitting which is calculated to be on the order of 0.1 cm^{-1}.[238] The rate constants for the scavenging of $[Ru(bpy)_3]^{2+}$ by EDTA in aqueous solution are reported.[239] Reductive quenching of $[Ru(bpy)_3]^{2+}$ by cyanometalate electron donors has been studied by using laser flash photolysis/transient absorbance and emission spectroscopy.[240] The effect of solvent polarizability on the energy of the intraligand, long-axis-polarized $\pi\rightarrow\pi^*$ bpy transition in $[Ru(bpy)_3]^{2+}$, $Ru(bpy)_2Cl_2$, and $Ru(bpy)_2(CN)_2$ has been investigated.[241] The synthesis of the novel hemicage ruthenium(II) polypyridine $[Ru\{(Mebpy)_3C_6H_3\}]^{2+}$ has been reported. Reaction of the carbanion of 5,5-dimethyl-2,2'-bpy with 1,3,5-tris(bromomethyl)benzene gives $(Mebpy)_3C_6H_3$, which was then allowed to react with $Ru(DMSO)_4Cl_2$. The redox and spectroscopic properties of this new complex have been explored.[242]

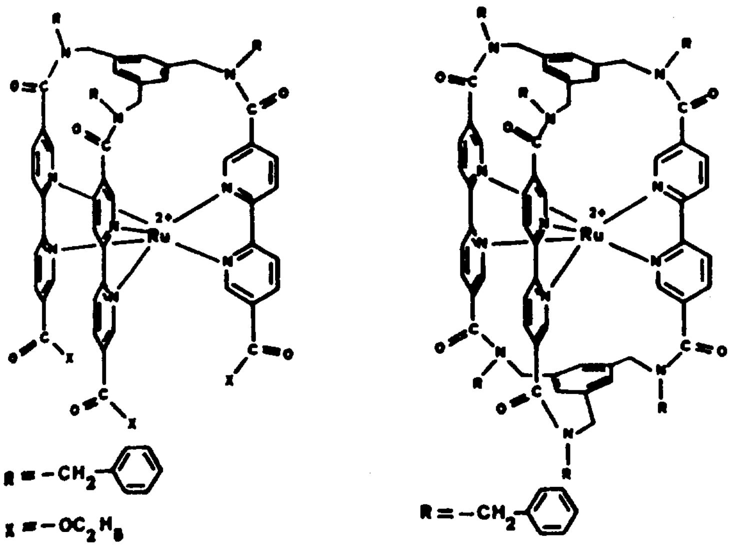
The pressure and temperature dependence of the emission and lifetime of $[Ru(bpy)_3]^{2+}$ has been examined by using nanosecond time-resolved emission spectroscopy. The role of viscosity-dependent solvent relaxation in the MLCT excited state is discussed.[243] $[Ru(bpy)_3]^{2+}$ and related tris(α-diimine) complexes have been studied as photosensitizers with surfactant media. Complex emission intensity and lifetime curves result with added surfactants. It is shown that lifetime curves are dependent on the charges and hydrophobicities of the ruthenium(II) complexes and surfactant.[244] A study of photoinduced electron-transfer reactivity of surfactant-modified ruthenium(II) bpy complexes has been published. The surfactant ruthenium(II) bpy derivatives contain either one or two long alkyl chains on a single bpy ligand. Photophysical studies are reported and the quantum yields for MV^{2+} photoreduction were calculated and compared with values obtained using $[Ru(bpy)_3]^{2+}$.[245] Intramicellar quenching rate constants of photoexcited $[Ru(bpy)_3]^{2+}$ have allowed for the evaluation of several viologen surface diffusion coefficients. The viologens examined possessed alkyl groups ranging from methyl to hexyl. The calculated diffusion coefficients are correlated with the hydrophobicity of the alkyl groups associated with MV^{2+}.[246] ESR spectroscopy has been used to assess the efficiency of photoinduced electron transfer from $[Ru(bpy)_3]^{2+}$ bound to sodium dodecyl sulfate micelles to MV^{2+}. The micelle and viologen alkyl chain lengths are shown to play a crucial role in determining the electron-transfer efficiency.[247] Counterion effects have been explored through luminescence quenching studies using $[Ru(4,4'\text{-dicarboxy-}2,2'\text{-bpy})_3]^{2+}$ as an extramicellar probe.[248] The luminescence decay of $[Ru(bpy)_3]^{2+}$ in the presence of $Fe(CN)_6^{3-}$ has been studied in reverse micelles and water-in-oil microemulsions.[249]

Oxidative quenching of excited $[Ru(bpy)_3]^{2+}$ by neutral aromatic electron acceptors has been reported. The quenching exhibited an anomalous negative temperature dependence for the electron-transfer step, which has been ascribed to a large contribution from the back electron-transfer step. The quenching mechanism is explained on the basis of the rate constant and the relevant activation parameters.[250] The rate constants (k_q) and activation parameters for reductive quenching of excited $[Ru(bpy)_3]^{2+}$ by aromatic amines have appeared. The quenching by tertiary amines is faster than that by primary and secondary amines when k_q are compared at the same free energy change. A discussion on the importance of the outer-sphere reorganization energy and the nature of the quenching agent is presented.[251] The rate of optically induced electron transfer from the $[Ru(bpy)_3]^{2+}$-like center in N-ethylated copolymers of 4-vinylpyridine and $[Ru(bpy)_2(4\text{-methyl-}4\text{-vinyl-}2,2'\text{-bpy})]^{2+}$ to MV^{2+}, propylviologensulfonate, and ferric ion has been determined as a function of ionic strength. Laser flash photolysis studies have allowed the yields of Ru(III) centers and reduced quencher to be determined.[252] The possible participation of a non-emitting excited state in $[Ru(bpy)_3]^{2+}$ has been suggested. The basis for a non-emitting state derives from the observation that the luminescence of $[Ru(bpy)_3]^{2+}$ is not quenched at all by added Et_3N.[253] Luminescence quenching of excited $[Ru(bpy)_3]^{2+}$ by aromatic amines has been investigated. The bimolecular rate constants for the electron-transfer process have been measured and activation enthalpies and entropies determined for each quencher. The results are discussed within the framework of Marcus theory.[254] The photochemistry and photophysics of caged and uncaged ruthenium(II)-polypyridine complexes are reported and compared with the appropriate parent complex. The caged complexes are shown to possess a longer excited-state lifetime in fluid solution and are observed to be more stable toward ligand photodissociation than the corresponding uncaged complex.[255]





$X = -OC_2H_5$



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MLCT excitation in $[Ru(bpyCH_2OCH_2An)_3]^{2+}$ [where $bpyCH_2OCH_2An$ = {4-(9-anthrylmethoxy)methyl}-4'-methyl-2,2'-bpy] undergoes efficient intramolecular energy transfer (< 5 ns) to one of the pendant anthryl ligands to yield the anthryl triplet. The triplet lifetime has been measured and oxidative quenching occurs at the triplet, which is followed by rapid intramolecular electron transfer to give $[(bpyCH_2OCH_2An)_2Ru^{III}(bpyCH_2OCH_2An)]^{3+}$.[256] Long-range energy transfer in a soluble polymer has been demonstrated. The polymer system is based on a 1:1 copolymer of styrene:m,p-(chloromethyl)stryene that contains Ru^{II}(bpy) and Os^{II}(bpy) chromophores and derivatized 9-anthracenemethanol moieties that function as excited-state quenchers. The polymer system has been examined in energy-transfer "cascade" processes. Photoexcitation of the Ru(II) chromophore affords a high-energy MLCT excited state that is quenched by an anthryl moiety. Energy transfer from the anthryl triplet to the Os(II) chromophore completes the energy-transfer "cascade" pathway. Direct energy transfer from excited Ru(II) to Os(II) was not observed, despite the fact that the energy transfer is thermodynamically favored. Lifetime and emission spectral results are also presented.[257]

A paper describing the deconvolution of the luminescence and magnetic circularly polarized luminescence spectra of the lowest excited states of $[Ru(bpy)_3]^{2+}$ has appeared.[258] $[Ru(bpy)_3]^{2+}$ has been examined for luminescence activity using the time-correlated single photon counting (SPC) method. The strengths and limitations of SCP technique in the analysis of $[Ru(bpy)_3]^{2+}$ are discussed.[259] The Stark effect spectra have been recorded for $[Ru(bpy)_3]^{2+}$ and other related α-diimine complexes.[260] A report dealing with the chiroptical absorption and luminescence properties of $[Tb(dipicolinate)_3]^{3-}$ with resolved $[Ru(1,10\text{-}phen)_3]^{2+}$ is presented.[261] Spontaneous racemic and "pseudoracemic" interactions involving optically active $[Ru(bpy)_3]^{2+}$ adsorbed on smectite clays have been studied. The factors responsible for chiral recognition within the clay are discussed.[262] $[Ru(bpy)_3]^{2+}$ has been used as an adsorption probe in Al_2O_3/sodium dodecyl sulfate hemimicelles. Steady-state luminescence emission results are used to explain surface aggregation processes.[263] Highly resolved emission excitation, and absorption spectra of $[Os(bpy)_3]^{2+}$ doped into a single-crystal $[Ru(bpy)_3]^{2+}$ matrix have been observed from 2-16 K.[264] Intermolecular electron transfer on colloidal alumina-coated silica has been studied using $[Ru(bpy)_3]^{2+}$ and [Ru(bathophenanthroline disulfate)]$^{4-}$ sensitizers. The kinetics and quantum yields of electron transfer quenching of the ruthenium complexes are compared.[265] The temperature dependent photophysics and photochemistry of $[Ru(bpy)_3]^{2+}$ adsorbed onto porous Vycor glass have been investigated.[266] A study dealing with the spin-orbit coupling and magnetic field effects on the efficiency of photoinduced induced electron transfer in $[Ru(bpy)_3]^{2+}$ has appeared. Nanosecond laser spectroscopy has been used to determine the rates of reductive and oxidative quenching. The magnetokinetic behavior of the radical pairs is discussed in terms of a strongly spin-orbit mixed Kramers doublet.[267]

DNA oligomers and duplexes containing a covalently attached $[Ru(bpy)_3]^{2+}$ group have been synthesized and examined as starting materials in the construction of macromolecules possessing redox active subunits.[268] The spectroscopic and binding properties of ruthenium(II) α-diimine complexes attached to DNA have been reported. DNA binding affinity has been evaluated through the systematic variation of the ancillary α-diimine ligands.[269]

The photoinduced enzyme-catalyzed reduction of nitrate and nitrite to ammonia is described. The artificial photosystem consists of the photosensitizer $[Ru(bpy)_3]^{2+}$, the electron relay MV^{2+}, the sacrificial electron donor EDTA, and the enzymes nitrate and nitrite reductase.[270] An X-ray diffraction determination of $[Os(bpy)_3][PF_6]_2$ has appeared.[271] Stable binuclear o- and p-semiquinone complexes based on $Ru(bpy)_2$ are reported. Reaction of 4,7-phenanthroline-5,6-semiquinone (phdo) and 2,5-bis(diphenylphosphino)-p-benzosemiquinone (bppq) with $Ru(bpy)_2Cl_2$ affords the paramagnetic dimers $[\{Ru(bpy)_2\}_2(\mu\text{-phdo})]^{3+}$ and $[\{Ru(bpy)_2\}_2(\mu\text{-bppq})]^{3+}$, respectively. The redox activity of these N,O:N',O'-coordinated and P,O:P',O'-coordinated complexes has been explored by using electrochemical techniques in addition to further characterization by UV-visible/near-IR spectroscopy. The (3+) complexes have also been examined by esr analysis which reveals that these dimers are borderline between radical anion complexes and metal-centered mixed-valent dimers.[272] $[Ru(bpy)_3]^{2+}$ has been used as a standard for NMR comparison with $[Rh(bpy)_3]^{3+}$.[273] A kinetic study on the associative photosubstitution of $[Ru(bpy)_3]^{2+}$ in aqueous acidic solution has appeared. The quantum yield for the breaking of the Ru-N(bpy) bond is reported. A reactivity order was established as a function of the incoming X^- ligand.[274] Oxidation of aqueous $[Ru(bpy)_3]^{2+}$ by the fluoroxysulfate ion has been investigated through the use of stopped-flow spectrophotometry. The reported activation parameters are consistent with a bimolecular reaction that shows no dependence on either the counter cation or solution acidity.[275] $[Os(bpy)_3]^{2+}$ has been used as cross-reactant in the study of electron-transfer reactions involving Mn(II) and Mn(III) complexes. The cross-reactant kinetic data are discussed within the context of Marcus theory.[276] The reaction between $[Ru^{III}(NH_3)_5(1\text{-methyl-}4,4'\text{-bpy})]^{4+}$ and $^{\bullet}CO_2^-$

has been examined and an intermediate assigned to $[Ru^{II}(NH_3)_5(1\text{-methyl-}4,4'\text{-bpy})]^{3+}$ has been proposed.[277] The emission spectrum of $[Ru(bpy)_3]^{2+}$ has been recorded in a mixed-crystal of $[Zn(bpy)_3]^{2+}$. The energy differences between states, decay rate constants and spectra of the mixed crystal are found to be similar to those in the neat crystal of $[Ru(bpy)_3]^{2+}$.[278]

Time-dependent photoselection data are presented for $[Ru(bpy)_2(1,10\text{-phen})]^{2+}$, $[Ru(bpy)(1,10\text{-phen})_2]^{2+}$, $[Ru(1,10\text{-phen})_3]^{2+}$, $[Ru(bpz)_3]^{2+}$, and $[Ru(pq)_3]^{2+}$ (where bpz = 2,2'-bipyrazine; pq = 2,2'-pyridylquinoline). The correct mechanism for localization of the emitting triplet in $[Ru(bpy)_3]^{2+}$ is discussed.[279] The photochemistry of mixed-ligand ruthenium(II) complexes has been reported. Luminescence lifetime and quantum yield data reveal that a localized MLCT excited state is intimately involved in the decay of the excited state. HPLC analyses of the organic photoproducts have been used to determine which ancillary ligand is photolabilized.[280] The photoelectrochemistry of thin-film molecular-level chromophore-quencher assemblies has been studied. The chromophore unit was $[Ru(bpy)_2(5\text{-}NH_2\text{-}1,10\text{-phen})]^{2+}$, which was chemically attached to chlorosulfonated polystyrene through a sulfonamide linkage. Oxidative quenching of the MLCT excited state(s) by MV^{2+} in the presence of the reductive scavenger triethanolamine (TEDA) is the working model responsible for the observed photocurrents. A laser flash photolysis study was carried out and the results indicate that only a fraction of the chromophores contribute to the photocurrent.[281] Several ruthenium(II) complexes have been examined in photosubstitution reactions. Emission and electrochemical data for the newly synthesized compounds are also presented. Adherence to the energy gap law is demonstrated for several homologous compounds under a set of limiting conditions.[282] The acid-base behavior in the ground and MLCT excited states of polypyridyl ruthenium(II) complexes with protonatable ligands has been evaluated. A localized electron model for the MLCT excited state is presented for complexes containing several protonatable ligands on the basis of the difference in the pka between the ground and excited state (Δpka).[283] A study dealing with the effects of experimental and calculated ligand properties on the electronic structure of several ruthenium(II) polyazines has appeared. Ground-state basicities, π^* orbital energies, and electron densities at the coordinating nitrogen atoms are shown to be important factors that determine the redox potentials and MLCT absorption energies.[284]

Extended Hückel MO calculations have been performed on $[Ru(bpy)_2(2,2'\text{-bi-}1,8\text{-naphthyridine})]^{2+}$. The results are discussed as a function of the dihedral angle between the two naphthyridine rings.[285] Mono- and bimetallic complexes based on Ru^{II}(1,10-phen) are described. The MLCT absorption spectra indicate that the ancillary diimine ligands 2,3-(2'-pyridyl)pyrazine (dpp) and 2,3-bis(2'-pyridyl)quinoxaline (dpq) exhibit localized MLCT bands. The redox properties and correlations between the excited-state donor energies and the excited-state redox couples are presented.[286] Excited-state lifetime measurements are reported for $[Ru(bpy)_2(bpz)]^{2+}$ and its protonated form, $[Ru(bpy)_2(bpzH)]^{3+}$. The latter complex exhibits no phosphorescence.[287] The tetrametallic complexes $Ru[(dpp)Ru(bpy)_2]_3{}^{8+}$, $Ru[(dpp)Ru(1,10\text{-phen})_2]_3{}^{8+}$, and $Ru[(dpp)Ru(tpy)(Cl)]_3{}^{5+}$ have been prepared from $[Ru(dpp)_3]^{2+}$ and examined by emission spectroscopy and cyclic voltammetry.[288] The photochemical, photophysical, and redox properties of twelve tris chelate ruthenium(II) complexes are described. Correlations between the redox potentials of the $RuL_3{}^{2+}$ complexes and the redox potentials/pKa of L are presented. Photosensitization results using MV^{2+} are compared to $[Ru(bpy)_3]^{2+}$.[289] Photochemical, radiation chemical, and electrochemical techniques have been employed in the reduction of $[Ru(bpm)_3]^{2+}$ (where bpm = 2,2'-bipyrimidine). For reductive quenching by TEOA, evidence is presented that indicates that the back electron transfer between the geminate pair $[Ru(bpm)_3]^+$ and $TEOA^{+\bullet}$ occurs within the solvent cage and in the "inverted Marcus" region.[290] The resonance Raman spectra and spectroelectrochemical properties of ruthenium(II) HAT (1,4,5,8,9,12-hexaazatriphenylene) complexes are described.[291]

$[Ru(bpz)_3]^{2+}$ has been examined by using time-resolved spectrofluorimetry and pulsed laser flash photolysis as a function of pH, reductive quencher, and MV^{2+}. The photodynamics are discussed and kinetic data are presented.[292] A kinetic study on the reductive quenching of photoexcited $[Ru(bpz)_3]^{2+}$ by oxalate ion has appeared.[293] The phosphorescence from $[Ru(bpy)_2(bpz)]^{2+}$ is shown to originate from the lowest Ru→bpz charge-transfer excited triplet state. Coordination of Ag^+ ions to the peripheral bipyrazine nitrogens was observed and Stern-Volmer quenching studies are reported for the excited-state formation constant with Ag^+. An increase in the excited-state basicity of the coordinated bipyrazine ligand leads to a larger formation constant as compared to the ground-state complex.[294] The luminescence and redox chemistry of $[(bpy)_2Ru(dpp)Ru(bpy)(dpp)Ru(bpy)_2]^{6+}$ and its dpp-bridged biquinoline derivative are reported.[295] New triammineruthenium(II) complexes with a 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) bridging ligand are described. Redox studies indicate that effective communication between the ruthenium(II) is facilitated by the tppz ligand.[296] A report describing the enhanced excited-state basicity in $[Ru(bpy)_2(dpp)]^{2+}$ and $[Ru(bpy)_2(ppz)]^{2+}$ (where ppz = [4,7]-phenanthrolino[5,6-b]pyrazine) has been published.[297] The new carbonyl complexes $Ru(CO)_2(2,3\text{-dpp})Cl_2$, $Ru(CO)_2(2,5\text{-dpp})Cl_2$, $Ru(CO)_2Cl_2(\mu\text{-}2,3\text{-dpp})Ru(CO)_2Cl_2$, and $[Ru(CO)_2Cl_2]_2(\mu\text{-}2,5\text{-dpp})$ are described. Complete solution characterization as well as luminescence and redox data are included. All of the complexes are photosensitive, exhibiting CO loss from the lowest ^3LC excited state.[298] The photophysical and redox properties of mono- and binuclear complexes containing the 2,3-dpp bridging ligand are discussed. A strong through-ligand communication between the two metal centers in $[(bpy)_2Os^{II}(\mu\text{-}2,3\text{-dpp})M^{II}(bpy)_2]^{4+}$ (where M = Ru, Os) is observed.[299]

Ruthenium complexes with the 3,5-bis(pyridin-2-yl)-1,2,4-triazolate (bpt) ligand have been synthesized and spectroscopically investigated.[300] The effect of nonchromophoric ligands on the photochemical and photophysical properties of ruthenium(II) complexes containing the ligand 3,6-bis(2-pyridyl)pyridazine (dppi) is reported. The complexes studied include $Ru(dppi)(CO)_2Cl_2$, $[Ru(dppi)(CO)_3Cl]^+$, $[Ru(dppi)(CO)_2(CO_2Et)Cl]^+$, and $[Ru(dppi)(\eta^6-C_6H_6)Cl]^+$. The carbonyl complexes lose a CO ligand upon optical excitation and reveal quantum yields that are related to the energy gap between the lowest excited state(s) and the reactive metal-centered level.[301] The spectrophotometric and redox investigations are reported for ruthenium(II) complexes bearing the ligand bis(2,2'-bpy){2-(2'-pyridyl)benzimidazole}. The reported complexes have the ability to function as spectrophotometric and electrochemical probes in the examination of microstructure in biopolymers.[302] The Λ and Δ diastereomers of $[Ru(Hpa)_3]^{2+}$ and $[Ru(bpy)_2(Hpa)]^{2+}$ (where Hpa = di-2-pyridylamine) have been separated by ion exchange chromatography and absolute configurations assigned by using CD spectroscopy.[303]

The quantum yields of triplet MLCT excited state formation and triplet-triplet absorption spectra of $[Ru(NN)_3]^{2+}$ {where NN = bpy, 2-(2'-pyridyl)thiazole, 2-(2'-pyrazinyl)thiazole, 2-(2'-pyridyl)selenazole, 2-(2'-pyridyl)benzothiazole, 5-(2'-pyridyl)-1,2,4-thiadiazole, and 2,2'-bithiazole} have been measured.[304] The MLCT bands of bpt-ligated ruthenium complexes have been assigned through the use of resonance Raman spectroscopy and differential-pulse polarographic measurements.[305] The preparation and characterization of new binuclear ruthenium complexes containing rigid aromatic spacers are described. The species allow for the metal-metal separation to be varied between 8 Å and 20 Å. Broad intervalence transitions are observed for the mixed-valence species, which together with the cyclic voltammetric data, suggest that the ruthenium centers interact weakly.[306] The structure of cis-bis(4-allyl-4H-1,2,4-triazole)bis(2,2'-bpy)ruthenium(II) has been determined.[307] Multiple binding modes for the ligand 6-(thienyl)-2,2'-bpy (tbpy) have been observed. Reaction of tbpy with $RuCl_3 \cdot 3H_2O$ affords ruthenium complexes containing N,N,S- and N,N-donor tbpy ligands. The X-ray diffraction structure of $[RuCl(tbpy)_2]^{2+}$ accompanies the report.[308] Reversible oxidation half-wave potentials are shown to be additive according to the number of ancillary polypyridine or β-diketone ligands (L) in $[Ru(bpy)_{3-x}L_x]^{2+}$. The magnitude of the π-donor/π-acceptor ability of the L ligands has been measured.[309]

The effect of remote substituents on the redox and spectroscopic properties of $[Ru(trpy)_2]^{2+}$ has been examined.[310] The synthesis and photosubstitution reactions of trans-$Ru(trpy)LCl_2$, cis-$[Ru(trpy)L_2Cl]^+$, and $[Ru(trpy)L_3]^{2+}$ (where L = py, MeCN, 4-methylpy, PrCN) are described. The latter two complexes undergo efficient photosubstitution of L by solvent or chloride. Quantum yields, absorption spectroscopy, and cyclic voltammetric data are presented and a working photosubstitution mechanism based on the angular overlap model is discussed.[311] A report describing pH-induced intramolecular quenching of ligand-bridged ruthenium and osmium complexes has appeared. The complex $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)Ru^{II}(bpy)_2(H_2O)]^{4+}$ exhibits a Ru(II)→bpy MLCT excitation, which is followed by a rapid energy transfer to the lower $Os(III)(trpy^{\bullet -})$ MLCT state. Increasing the solution pH gives $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)Ru^{II}(bpy)_2(OH)]^{3+}$, which displays Ru(II)(OH) site quenching of the $Os(III)(trpy^{\bullet -})$ MLCT state.[312] Ruthenium and osmium trpy complexes that are covalently linked to the electron acceptor MV^{2+} and the electron donor phenothiazine have been prepared. Efficient intramolecular vectorial electron transfer is observed in the osmium complex.[313] The synthesis and redox properties of a new class of ruthenium(II) complexes containing planar tridentate ligands based on 2,6-bis(N-pyrazoyl)pyridine have been published.[314]

Mixed-metal complexes containing ruthenium, rhenium, and the bridging HAT ligand are reported. UV-visible transitions are dominated by the ruthenium chromophore. The redox and luminescence properties of these mixed-metal complexes are discussed and correlations made with the number of $Re(CO)_3Cl$ units present.[315] The reaction between $[Os(2,3\text{-}dpp)_3]^{2+}$ and $Ru(bpy)_2Cl_2$ gives the new heterometallic complex $Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3{}^{8+}$. Luminescence is shown to occur from the central osmium atom, which functions to collect the energy absorbed by the peripheral ruthenium chromophores.[316]

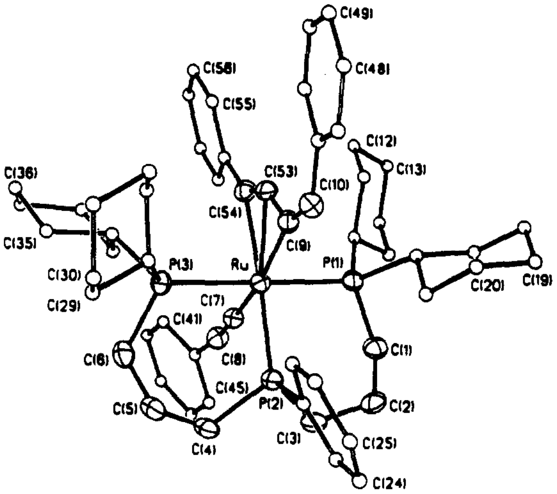
(h) Alkenyl and Alkylidene Complexes

Insertion of alkynes into the metal-hydride bond of $MHCl(CO)[PMe(t\text{-}Bu)_2]_2$ (where M = Ru, Os) gives the corresponding five-coordinate vinyl complex $M(E\text{-}CH{=}CHR)Cl(CO)[PMe(t\text{-}Bu)_2]_2$. Use of methyl propionate affords two different vinyl-metal complexes as a result of α and β vinyl carbonyl coordination; in both of these isomers, the carbomethoxy group is coordinated to the metal center. Included in this report are the X-ray diffraction results of $\overline{Os[C(=CH_2)-C(OMe)=O}]Cl(CO)[PMe(t\text{-}Bu)_2]_2$. The rearrangement of $Os(E\text{-}CH{=}CHR)Cl(CO)[PMe(t\text{-}Bu)_2]_2$ to form the Z-isomer, which possesses a chelating vinyl group, is demonstrated.[317] The reaction of $RuHCl(CO)_2(PMe_2Ph)_2$ with alkynes has been reported. Alkyne insertion into the Ru-H bond is shown to occur in a cis fashion for $PhC\equiv CH$ and $t\text{-}BuC\equiv CH$; however, it is suggested that the addition of $MeO_2CC\equiv CCO_2Me$ may proceed in a trans manner. Alkyne hydrogenation is observed with $RuH_2(CO)_2(PMe_2Ph)_2$. The reaction is believed to proceed by the rate-determining formation of the vinyl-hydride complex, which is followed by the reductive elimination of alkene and additional alkyne uptake.[318] The selectivity of alkyne insertion into the Ru-carbon and Ru-chlorine bonds has been explored. Reaction of $MeO_2CC\equiv CCO_2Me$ with $Ru(CO)_2(C_6H_4X)(PMe_2Ph)_2$ (where X = H, Cl, Me, OMe) involves CO displacement by the alkyne, followed by alkyne insertion into the Ru-aryl bond. The reactivity and full solution characterization of all final products are described.[319] The synthesis and reactivity of bis-alkynyl and hydrido-alkynyl ruthenium(II) and osmium(II) complexes have been published. Reaction of PhC≡CH with $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ or $MH(\eta^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ gives $M(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$. The bis-alkynyl complexes undergo ready substitution with CO, P-ligands, or alkynes to afford the six-coordinate complexes $M(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2L$. The selective reduction of phenylacetylene to styrene is described and shown to be catalyzed by $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2L$.[320]

The arene complex $(\eta^6\text{-}C_6Me_6)RuCl_2(PMe_3)$ reacts with $HC{\equiv}CCR_2OH$ and $NaPF_6$ in MeOH to give $[(\eta^6\text{-}C_6Me_6)Ru\{=C(OMe)CH_2CR_2OMe\}Cl(PMe_3)]^+$ or $[(\eta^6\text{-}C_6Me_6)Ru\{=C(OMe)CH{=}CR_2\}]^+$. An allenylidene-ruthenium intermediate is invoked in the proposed mechanistic scheme. Cyclic voltammetric analysis reveals a reversible ruthenium oxidation and an irreversible alkene oxidation.[321]

A kinetic examination for η^2-alkyne rearrangement in $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(\eta^2\text{-}HC{\equiv}CMe)]^+$ to the vinylidene complex $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2\{=C{=}C(H)(Me)\}]^+$ has been reported. The vinylidene complex releases $HC{\equiv}CMe$ at elevated temperatures in the presence of MeCN with formation of $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(MeCN)]^+$. The activation parameters and a working mechanism are presented.[322] Several ruthenium benzylidyne complexes have been synthesized and examined in benzylidyne transfer reactions. Methylation of $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)\{C(O)Ph\}$ using Meerwein's reagent, followed by hydride reduction, gives the α-ether complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)\{CH(OMe)Ph\}$. Treatment of the α-ether complex with trimethylsilyl triflate affords the benzylidene complex $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(=CHPh)]^+$. 4-Substituted benzylidene complexes were prepared through the identical sequence. The barrier to aryl ring rotation was measured for each complex and the results were correlated.[323]

Phenyl acetylene reacts with RuH_4(cyttp) to give Ru(CCPh)(η^3-PhC_3CHPh)(cyttp) which possesses an acetylide and the carbon-carbon coupling product η^3-PhC_3CHPh. This new complex has been fully characterized by using solution NMR techniques and X-ray diffraction analysis.[324]



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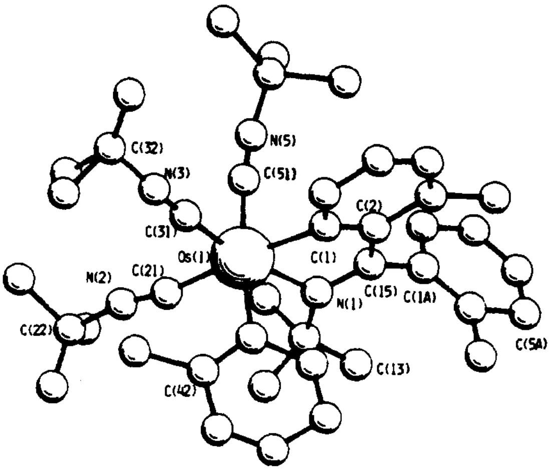
(i) π-Complexes

The homoleptic o-tolyl complexes $M(2\text{-}MeC_6H_4)_4$ (where M = Ru, Os) have been examined electrochemically. One-electron oxidation yields the corresponding cations, which have been fully characterized. The X-ray crystal structure of $[Os(2\text{-}MeC_6H_4)_4]^+$ is reported.[325] In a separate report, the reactivity of $Os(2\text{-}MeC_6H_4)_4$ toward Lewis bases has been presented. Reductive coupling to the osmium(II) η^6-biaryl derivative is observed when $Os(2\text{-}MeC_6H_4)_4$ is treated with PMe_3 or CO. The formation of the biaryl derivative proceeds through a $\sigma \rightarrow \pi$ rearrangement sequence. Reaction of $Os(2\text{-}MeC_6H_4)_4$ with isocyanides yields two products: cis-$Os(2\text{-}MeC_6H_4)_2(CNR)_4$ and fac-$Os[C,N\text{-}3\text{-}Me\{2\text{-}C(2\text{-}MeC_6H_4)NC\text{-}t\text{-}Bu\}C_6H_3](2\text{-}MeC_6H_4)(CNR)_3$. This latter complex derives from an ortho-hydrogen activation/isocyanide insertion reaction. Reaction pathways and the X-ray structures of the above two complexes are presented.[326]



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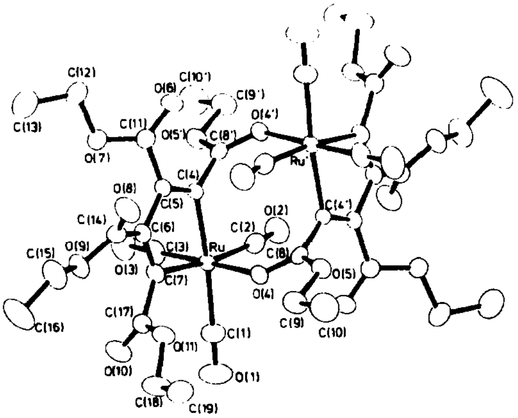
A report describing the regioselective and diastereoselective addition of MeLi to chiral (pentadienyl)ruthenium complexes has appeared. The electron-rich (pentadienyl)ruthenium complexes react with MeLi exclusively at the internal C2 position of the polyene ligand. Solution NMR results and the X-ray structure of (2-methyl-1,3,4,5-pentenediyl)$Ru(PMe_3)(PPh_3)(CO)$ are included.[327] The product from the reaction between Ru(CO)(CN-p-tolyl)(PPh_3)$_3$ and maleic anhydride has been isolated and structurally characterized. A trigonal bipyramidal geometry about the ruthenium center is observed with a π-coordinated maleic anhydride ligand residing in the equatorial plane.[328] The ethylene complex OsCl(NO)(CH_2=CH_2)(PPh_3)$_2$ reacts with {(p-tolylsulfonyl)imino}oxo-λ^4-sulfane (O=S=$NSO_2C_6H_4$Me-4) by either substitution or by electrophilic attack at the ethylene ligand to give OsCl(NO)(η^2-$OSNSO_2C_6H_4$Me-4)(PPh_3)$_2$ or Os{CH_2CH_2S(=$NSO_2C_6H_4$Me-4)O}Cl(NO)(PPh_3)$_2$, respectively. The latter osmacycle complex is made up of a five-membered ring with carbon- and oxygen-osmium bonds. The X-ray structure of the osmacycle is presented.[329] The reaction of (η^2-ethylene)Ru(CO)$_4$ with activated olefins and alkynes has been reported. The electron-poor alkynes react to form tricyclic complexes containing two tricarbonylruthenacyclopentadiene rings. The X-ray crystal structure of the ruthenacyclopentadiene complex derived from $EtO_2CC{\equiv}CCO_2Et$ is included.[330]



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An easy preparation of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2][K]$ has been reported. Ultrasound irradiation (20 KHz) of clean potassium metal and $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ affords the corresponding potassium metalate in high yield. The ruthenium anion was alkylated with MeI and $MeOCH_2Cl$.[331] The synthesis and reactivity of tetrakis(trifluoromethyl)cyclopentadienide $[C_5(CF_3)_4(OSiEt_3)]^-$ have been described. Reaction of $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)_3]^+$ with $[C_5(CF_3)_4(OSiEt_3)]^-$ yields the mixed-polyene complex $(\eta^5\text{-}C_5Me_5)\{C_5(CF_3)_4(OSiEt_3)\}Ru$.[332] The synthesis and redox properties of $(\eta^5\text{-}C_5Ph_5)Ru(CO)_2Br$ have been reported. Reaction of $Ru_3(CO)_{12}$ with C_5Ph_5Br yields the pentaphenylcyclopentadienyl complex, which reacts with P-ligands in the presence of Me_3NO to give $(\eta^5\text{-}C_5Ph_5)Ru(CO)(P\text{-}ligand)Br$. Halide abstraction reactions to yield $[(\eta^5\text{-}C_5Ph_5)Ru(CO)(L)(L')]^+$ are also presented. The esr data are discussed for several of the 17-electron species.[333] Metathetical replacement of the chloride ligands in $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with NaBr or KI affords the corresponding tetrabromide and tetraiodide, respectively. Reaction of these dimers with cobaltocene furnishes the paramagnetic mixed-valence $Ru^{II/III}$ complexes $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}X)_3Ru(\eta^5\text{-}C_5Me_5)]$, which are susceptible to further reduction to $[(\eta^5\text{-}C_5Me_5)RuX]_n$. Alkoxo complexes are produced when $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ is allowed to react with alcohols in the presence of K_2CO_3.[334] The redox chemistry of $(\eta^5\text{-}C_5Me_5)Ru(P)Cl_2$ (where P = tertiary phosphine) has been published. All of the 17-electron complexes examined exhibit electrochemically reversible $Ru^{III/IV}$ and irreversible $Ru^{III/II}$ redox couples. The effect of the solvent on the redox behavior and mechanisms dealing with chloride addition to electrooxidized (η^5-C_5Me_5)Ru(P)Cl are discussed.[335] A paper describing the electrochemistry of [(η^5-C_5Me_5)RuX_2]$_2$ and (η^5-C_5Me_5)RuL_2X (where L = phosphine, diene, bpy) was published. The redox behavior of the dimer is shown to be dependent on the solvent and the supporting electrolyte.[336]

Indirect 2D NMR measurements have allowed for the determination of $\delta(^{187}Os)$, J{Os,(H,P)}, and $T_1(^{187}Os)$ in (η^5-C_5H_5)OsP_2R complexes. The advantage in obtaining ^{187}Os T_1 values with the described NMR technique is stressed.[337] The kinetics and mechanism of phosphine exchange in (η^5-C_5Me_5)Ru$(PMe_3)_2$X have been investigated by NMR spectroscopy. The activation parameters for phosphine dissociation are reported along with the steric and electronic contributions associated with each system. The large variation in activation enthalpies as a function of the ancillary X ligand suggests that the functional group additivity approach to organometallic thermochemistry should be used with caution.[338] The synthesis and reactivity of (η^5-C_5Me_5)$RuCl_2PR_3$ (where R = Me, Ph, Cy, $CHMe_2$) are presented. Reaction of these dichlorides with [Et_3BH][Li] affords the trihydride complexes (η^5-C_5Me_5)RuH_3PR_3. The anomalous NMR behavior of these trihydrides is discussed in terms of an equilibrium that involves a classical trihydride and a complex that is described as a hydride/molecular hydrogen complex or a trihydrogen complex.[339]

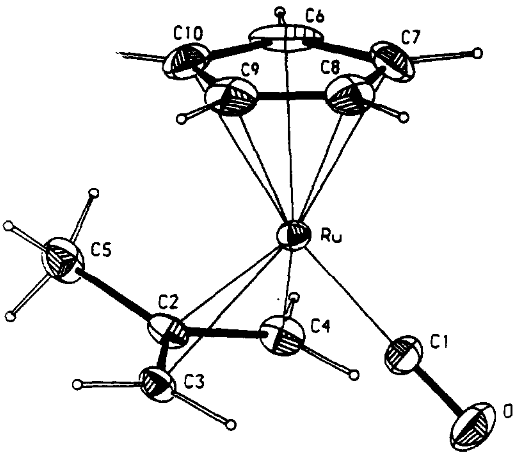
The reactivity of the carbene complex [(η^5-

$C_5H_5)Ru(CO)_2\{=C(SMe)_2\}]^+$ has been examined in reduction and addition reactions. Irradiation of this complex in MeCN affords the solvent complex $[(\eta^5-C_5H_5)Ru(CO)(MeCN)\{=C(SMe)_2\}]^+$.[340] A report on the synthesis of ruthenium and osmium η^5-borole complexes has appeared. Reaction of $(\eta^5-C_4H_4BPh)M(CO)_3$ with cyclopentadiene under photochemical conditions gives the mixed-polyene complex $(\eta^5-C_4H_4BPh)MH(\eta^5-C_5H_5)$.[341] The complex $(\eta^5-C_5H_5)Ru(\eta^6-C_6H_6)BPh_3$ has been resubjected to a field desorption mass spectrometry study. Thermolysis reactions were also carried out and the results discussed.[342] Several new cyclopentadienylruthenium(II) complexes have been prepared with ancillary amino acid ligands. Facile acetonitrile displacement in $[(\eta^5-C_5H_5)Ru(MeCN)_3]^+$ by the aromatic ring of the amino acid furnishes the mixed $(\eta^5-C_5H_5)/(\eta^6$-aromatic amino acid) complex in good yield. All of the new complexes were characterized by combustion analyses and NMR spectroscopy.[343] Nitrogen heterocycles react with $[(\eta^5-C_5H_5)Ru(MeCN)_3]^+$ to yield N-bonded complexes or η^6-heterocyclic complexes. The N-bonded complexes $[(\eta^5-C_5H_5)RuN_3]^+$ were formed by using pyridine, 2-methylpyridine, 2,4-dimethylpyridine, and quinoline, while the complexes $[(\eta^5-C_5H_5)Ru(\eta^6\text{-heterocycle})]^+$ were obtained when 2,4,6-trimethylpyridine, 2-methylquinoline, and 1,2,3,4-tetrahydroquinoline were employed. A $N(\eta^1)\rightarrow\pi(\eta^6)$ rearrangement was observed for several of the N-bonded complexes.[344]

The results of a single-crystal X-ray diffraction study of $(\eta^5-C_5H_4C_2CO_2Me)Ru(PPh_3)_2Cl$ have appeared. The product was obtained from the reaction between $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(C_2Ph)$ and $MeO_2CC{\equiv}CCO_2Me$.[345] P-Ligand exchange reactions in $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ are reported. The X-ray structures of $(\eta^5\text{-}C_5H_5)Ru\{P(OMe)_3\}_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru\{P(OMe)_3\}_2[C\{=C(CN)_2\}CPh=C(CN)_2]$ are included.[346] The reaction of MeI and Me_3SiCH_2I with the molecular hydrogen complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(\eta^2\text{-}H_2)]^+$ is shown to occur by H_2 loss and coordination of the alkyl iodide. The complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(IR)]^+$ (where R = Me, CH_2SiMe_3) have been isolated and fully characterized by solution techniques. The X-ray structure of the MeI complex has been solved. An independent synthesis of the cationic methyl iodide complex has been achieved from the reaction between $MeSO_3CF_3$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)I$.[347]

New coumarin laser dye complexes based on cyclopentadienylruthenium(II) are reported. The synthesis and photochemistry of these new complexes are presented and discussed.[348] A structural study on exo- and endo-$(\eta^5\text{-}C_5H_5)(\eta^3\text{-}2\text{-methylallyl})Ru(CO)$ has appeared. Differences in interligand crowding are shown to be responsible for the relative thermodynamic stability of the two isomers.[349]

The reaction between $[(Cl)P=N\{2,4,6\text{-}(t\text{-}Bu)_3C_6H_2\}]$ and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2][K]$ furnishes $(\eta^5\text{-}C_5H_5)Ru(CO)_2[P=N\{2,4,6\text{-}(t\text{-}Bu)_3C_6H_2\}]$. This new metalloiminophosphane has been characterized by solution techniques.[350] Thermolysis of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ with elemental sulfur affords the binuclear S_5-bridged complex $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2(\mu\text{-}S_5)$, which reacts readily with acid chlorides to give S-bond monothiocarboxylate



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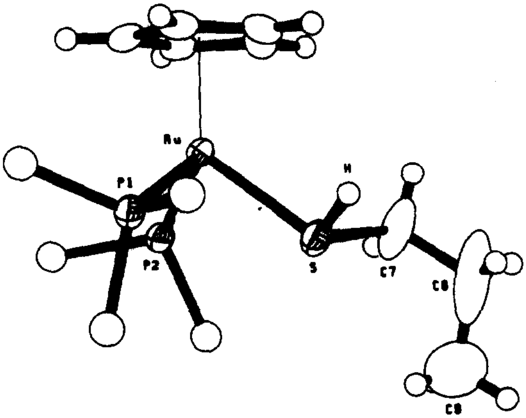
complexes (η^5-C_5H_5)Ru(CO)$_2$SC(O)R. The crystal structure of (η^5-C_5H_5)Ru(CO)$_2$SC(O)(2-nitrobenzene) has been solved.[351]

Thiophene displacement in [(η^5-C_5H_5)Ru(η^5-thiophene)]$^+$ by methyl-substituted thiophenes has been reported. The equilibrium constants for thiophene displacement and the rates of deuterium exchange are discussed in relation to hydrodesulfurization reactions.[352] The synthesis and reactivity of (η^5-C_5H_5)Ru(PPh$_3$)$_2$SH have been examined. The metallothiol complex was prepared from the reaction of (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl with NaSH and (η^5-C_5H_5)Ru(PPh$_3$)$_2$H with elemental sulfur. Carbonylation of the metallothiol affords (η^5-C_5H_5)Ru(PPh$_3$)(CO)SH. Protonation and alkylation of the metallothiol furnishes the hydrogen sulfide complex [(η^5-C_5H_5)Ru(PPh$_3$)$_2$(SH$_2$)]$^+$ and the thiol complex [(η^5-C_5H_5)Ru(PPh$_3$)$_2$(RSH)]$^+$, respectively. The structure of [(η^5-C_5H_5)Ru(PPh$_3$)$_2$(PrSH)]$^+$ was determined by X-ray diffraction analysis. The redox behavior and spectroscopic data for these new complexes are discussed.[353]



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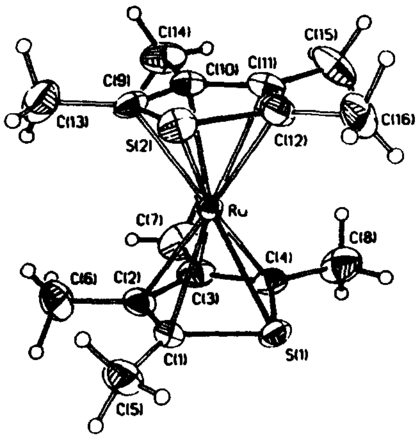
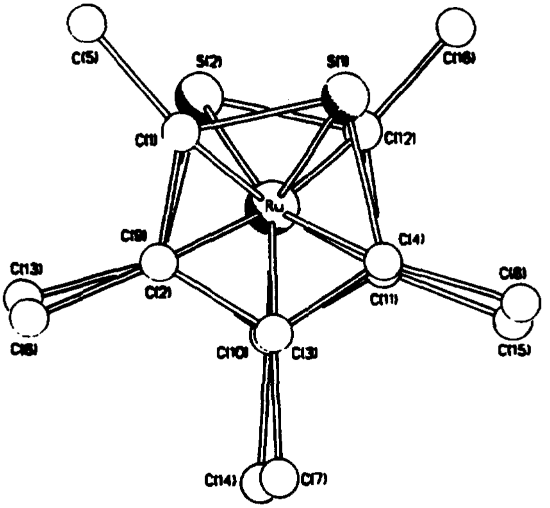
Reaction between $[(cymene)RuCl_2]_2$ and tetramethylthiophene (TMT) yields $[(\eta^5\text{-TMT})RuCl_2]_2$, which undergoes ready reaction with added L (H_2O or MeCN) to give $[(\eta^5\text{-TMT})RuL_3]^+$. The X-ray diffraction structure and redox behavior of $[(\eta^5\text{-TMT})_2Ru]^{2+}$, which is prepared by the Ag^+ oxidation of $[(\eta^5\text{-TMT})RuCl_2]_2$ in the presence of TMT, are described. The bis-TMT complex undergoes two reversible one-electron reductions. Phosphine and amine complexes are also presented along with the X-ray structure of $[(\eta^5\text{-TMT})Ru(Cl)]S^+$.[354]





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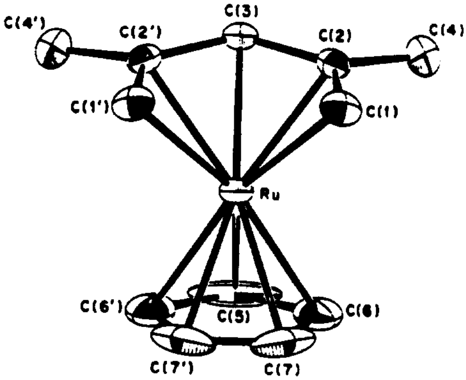
Substituted cyclopentadienyl and indenyl ruthenium complexes have been synthesized and trends in the ^1H NMR spectra described. The reaction between $(\eta^5\text{-}C_5H_4Me)Ru(CO)_2I$ and $(\eta^5\text{-}C_9H_7)Ru(CO)_2I$ with added ligand (phosphines, phosphites, and isonitriles) in the presence of the catalyst $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ gives the corresponding monosubstituted products $(\eta^5\text{-}C_5H_4Me)Ru(CO)(L)I$ and $(\eta^5\text{-}C_9H_7)Ru(CO)(L)I$, respectively. The X-ray structure of $(\eta^5\text{-}C_9H_7)Ru(CO)\{P(CH_2Ph)_3\}I$ and proton NOE measurements, which have been used to determine preferential conformations of the cyclopentadienyl ligand, are included in this report.[355] Two optically active indenylruthenium(II) complexes have been prepared from the reaction between $(\eta^5\text{-}C_9H_7)Ru$(1,5-cyclooctadiene)Cl and the chiral diphosphines (S,S)-1,2-dimethyl-1,2-ethanediylbis(diphenylphosphine) (chiraphos) and (R,R)-1,2-cyclopentanediylbis(diphenylphosphine)(cypenphos).

X-Ray crystal structures and the formation of cationic complexes are also described.[356]

Chlorocarbon solvents are shown to form electron donor-acceptor (EDA) complexes with $(\eta^5\text{-}C_5H_5)_2Ru$ and $(\eta^5\text{-}C_5H_5)_2Os$. Optical excitation into the charge-transfer absorption band of the EDA complex gives chlorocarbon radicals that have been trapped by nitroxide spin traps and characterized by ESR spectroscopy.[357] Ruthenocene has been detected at the picogram level using gas chromatography-flame photometry.[358] The electron distribution and bonding in osmocene have been investigated by using He(I) and He(II) valence photoelectron spectroscopy. The data indicate that covalent bonding is more pronounced in osmocene than in ferrocene.[359] He(I) and He(II) photoelectron spectra and the results of extended Hückel MO calculations on $(\eta^5\text{-}C_9H_7)_2Ru$ and $(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_5)Ru$ are reported. The indenyl complexes exhibit lower first ionization energies than ruthenocene, indicating that the indenyl ring is more electron releasing in comparison to the cyclopentadienyl ring.[360] Half-open ruthenocene and osmocene complexes have been synthesized and examined by photoelectron spectroscopy and INDO MO calculations. Reaction of $RuCl_3\cdot 3H_2O$ and $[OsCl_6][Na]_2$ with cyclopentadiene (1 equiv) and 2,4-dimethyl-1,3-pentadiene gives $(\eta^5\text{-}C_5H_5)M(\eta^5\text{-}2,4\text{-}C_7H_{11})$.

The X-ray structure of the ruthenium complex is presented. Proton exchange with the four terminal hydrogens of the pentadienyl ligand has been confirmed by variable-temperature ^1H NMR spectroscopy.[361]



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Agostic interactions have been documented in the polyene complexes $[(\eta^5-C_7H_{11})_2RuH]^+$, $[(\eta^5-C_5H_5)(\eta^5-C_7H_{11})RuH]^+$, and $[(\eta^5-C_5Me_5)(\eta^5-C_7H_{11})RuH]^+$. Variable-temperature ^1H NMR measurements indicate that three distinct fluxional processes are present with the lowest energy process being attributed to an agostic Ru-H-C interaction involving a terminal carbon atom of the open polyene ligand.[362] Substituted ruthenocenes have been synthesized from the reaction between $(\eta^5-C_5H_5)Ru(1,5\text{-cyclooctadiene})X$ (where X = Cl, Br), $(\eta^5-C_9H_7)Ru(1,5\text{-cyclooctadiene})Cl$, and $[(\eta^5-C_5Me_5)RuCl]_4$ with substituted 3-vinyl-1-cyclopropenes. All of the complexes were fully characterized by solution methods.[363] Rates and activation parameters have been obtained for the ruthenocene-bromoruthenocene electron self-exchange in MeCN.[364]

The α-metallocenylcarbocation complex $[(\eta^5\text{-}C_5Me_5)\overline{Os(\eta^5\text{-}C_5Me_4CH_2})]^+$ has been prepared from $(\eta^5\text{-}C_5Me_5)Os(\eta^5\text{-}C_5Me_4CH_2OH)$ with $NaBPh_4$ in acid. The solid-state structure has been determined by X-ray diffraction analysis.[365] The crystal structure of $[(\eta^5\text{-}C_5Me_5)\overline{Ru(\eta^5\text{-}C_5Me_4C}H_2)]^+$ has appeared in a separate report. A discussion on the stability of α-metallocenylcarbocations and X-ray data comparisons within the family are presented.[366]

The reaction of $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)_3]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ with a variety of aromatic hydrocarbons is advocated as a route to novel solid-state organometallic building blocks.[367] New low-dimensional solids have been prepared from polycyanoanions and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6Me_6)]^+$, $[(\eta^5\text{-}C_5Me_5)Ru]_2[\eta^6,\eta^6\text{-}\{2_2\}\text{(paracyclophane)}]$, and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_5)]_4X$ (where X = C,Si). The redox behavior and conductivity data are given and magnetic susceptibility and ESR data have been used to establish the presence of energetically accessible triplet species.[368]

The reactive methanol solvate complex $[(\eta^5\text{-}C_5H_5)Ru(MeOH)_3]^+$, prepared from $[(\eta^5\text{-}C_5H_5)Ru(OMe)]_2$ and CF_3SO_3H, has been allowed to react with diphenylacetylene, benzoic acid, and phenol to furnish the corresponding η^6-aromatic complexes. Reaction of phenol and benzoic acid with the μ_2-methoxy bridged complex affords the neutral complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^5\text{-}C_6H_5O)]$ and the zwitterionic complex $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5CO_2^-)]^+$, respectively. The reactivity and characterization of these new complexes are discussed.[369] A mild procedure for the selective formation of aryl ethers and triaryl diethers using $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]^+$ has appeared. The $(\eta^5\text{-}C_5H_5)Ru^+$ fragment activates halo-substituted arenes to nucleophilic addition-elimination reactions.[370] $[(\eta^5\text{-}C_5H_5)RuH_2(PPh_3)_2]^+$ has been prepared from organic sulphonic acids and the corresponding monohydride complex. Metathesis with $[Na][BPh_4]$ gives the ion-pair complex $[(\eta^5\text{-}C_5H_5)RuH_2(PPh_3)_2][BPh_4]$, which has been characterized by ^{31}P NMR spectroscopy and field desorption mass spectrometry.[371]

A report documenting the two one-electron components of a two-electron electrochemical redox couple has appeared. The redox behavior of $[(\eta^6\text{-}C_6Me_6)_2Ru]^{2+}$ has been examined by using cyclic voltammetry and digital simulation. Included in this report are the redox potentials for the $Ru^{2+/1+}$ and $Ru^{1+/0}$ couples, electron-transfer parameters, and pertinent discusions on electron-transfer criteria as related to Marcus theory.[372]

The organometallic chemistry of arene ruthenium and osmium complexes has been reviewed.[373] The synthesis and reactivity of the benzyne complex $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ have been described. This benzyne complex udergoes a variety of C-C, C-H, N-H, and O-H bond activation reactions. X-Ray crystallographic data on the benzyne complex are included.[374] Neutral and cationic arene(carbonyl)metal complexes of ruthenium and osmium have been synthesized. Reaction of $(\eta^6\text{-}C_6H_6)Os(CO)L$ (where L = phosphine or phosphite) with acid gives the hydridoosmium(I) complexes $[(\eta^6\text{-}C_6H_6)Os(CO)L(H)]^+$, which regenerates the starting material upon treatment with NaH. The hydrido(ethylene) complex $[(\eta^6\text{-}$

C_6H_6)Os(CO)(ethylene)(H)]$^+$ has been prepared from (η^6-C_6H_6)Os(CO)(Me)$_2$ by hydride abstraction using [Ph_3C][BF_4]. The use of (η^6-C_6Me_6)$RuCl_2$(CO) as a starting material for the synthesis of arene ruthenium complexes is discussed.[375] Sodium naphthalide reduction of (η^6-C_6Me_6)$RuCl_2$(CO) and (η^6-C_6H_6)OsI_2L (where L = PMe_3 or CO) under ethylene or propylene is shown to give the corresponding alkene complexes.[376] Zinc reduction of (η^6-C_6H_6)OsI_2(PR_3) in methanol furnishes the corresponding hydrido(iodo)osmium complexes in good yields. The synthesis and spectroscopic properties of related hydrido(methyl) and Os/Cu dimers are presented.[377][(η^6-o-$MeC_6H_4CO_2Me$)$RuCl_2$]$_2$ has been allowed to react with (+)-neomenthyldiphenylphosphine (NMDPP) to give the monomeric diastereomers (η^6-o-$MeC_6H_4CO_2Me$)$RuCl_2$(NMDPP), which have been separated and spectroscopically characterized. An X-ray structure of one of the diastereomers is presented and its absolute configuration at the chiral planar center established.[378]

The kinetics for MeCN substitution in [(η^6-HMB)Ru(η^6-anth)]$^{2+}$ (where HMB = hexamethylbenzene; anth = anthracene) have been reported. Preferential solvation of the dication by MeCN is indicated on the basis of kinetic measurements in mixed-solvent systems and a nonlinear shift of the ^{1}H NMR resonance of the HMB ligand with CD_3CN in CD_2Cl_2.[379] The electrochemistry of the ruthenium carborane complex (η^6-C_6H_6)Ru($Et_2C_2B_4H_4$) has been explored. Cyclic voltammetric data reveal a reversible one-electron oxidation at scan rates greater than 0.5 V/s. The stabilizing effect of the carboranyl ligand in the reported complex is contrasted with the analogous cyclopentadienyl complex.[380] Benzylideneaniline and Ag^+ ions have been allowed to react with $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)Cl_2$ to give the cationic ortho metalated imine complex $[(\eta^6\text{-}C_6Me_6)RuN(Ph){=}CH(C_6H_4)]^+$. The addition of nucleophiles to the imine complex is shown to proceed diastereoselectively and in a kinetically controlled manner to yield the corresponding amide complex $(\eta^6\text{-}C_6Me_6)RuN(Ph)CH(Nu)(C_6H_4)$.[381] α-Diphenylphosphinoketones react with areneruthenium complexes to give $(\eta^6\text{-arene})RuCl\{\eta^2\text{-}Ph_2PCR{=}C(R')O\}$. X-Ray diffraction and NMR spectroscopic data are presented.[382] Donor-acceptor solids of $[(\eta^6\text{-}C_6Me_6)_2Ru][iso\text{-}C_4(CN)_6]$ and $[(\eta^6\text{-}C_6Me_3H_3)_2Ru][iso\text{-}C_4(CN)_6]$ have been synthesized. Both complexes exhibit "zigzag" linear chains of alternating cations and anions in the solid state as shown by X-ray diffraction analysis. The observed solution charge-transfer absorbances and the redox properties are discussed within the context of Mulliken theory.[383]

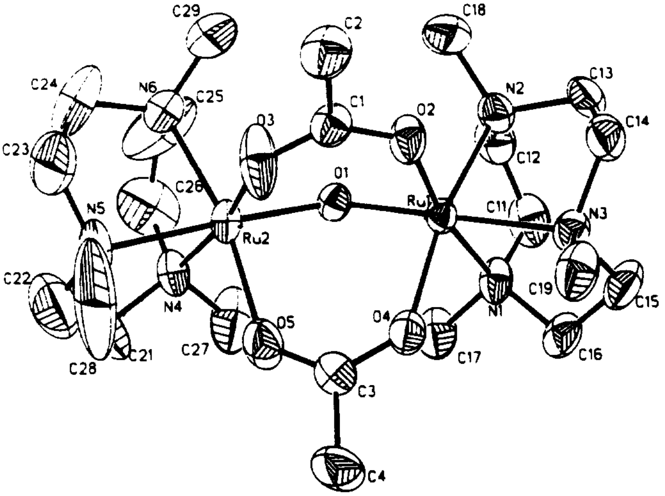
III. Dinuclear Complexes

(a) Homodinuclear Complexes

The reaction between $Ru(OAc)_4Cl$ and L-mandelic acid (Hmand) affords $Ru_2(mand)_4(H_2O)_2$ and $[Ru_3O(mand)_6(H_2O)_3]^+$ as a result of substitution and disproportionation, respectively. The former Ru_2(II,II) mandelate complex has been structurally characterized.[384] Zinc amalgam reduction of $[Ru_2L_2(\mu_2\text{-}O)(\mu_2\text{-}OAc)]^{2+}$ (where L = N,N',N''-trimethyl-1,4,7-triazacyclononane) yields $[Ru_2L_2(\mu_2\text{-}OH)_3]^{2+}$. Oxidation of this hydroxy complex with sodium persulfate yields $[Ru_2L_2(\mu_2\text{-}OH)_3]^{3+}$, which is shown to undergo autoxidation to $[Ru_2L_2(\mu_2\text{-}O)_3]^{2+}$.[385] The complexes $Os_2(OAc)_2(CO)_4(PPh_3)(\eta^1\text{-}L)$ and $Os_2(OAc)_2(CO)_4(\eta^1\text{-}L)_2$ {where L = dppm, dppe, 1,2-$C_6H_4(AsMe_2)_2$} have been prepared and are shown to contain a pendent phosphine (or arsine) ligand(s).[386] Phosphine- and arsinophosphine-substituted dinuclear osmium complexes are reported. $Os_2(OAc)_2(CO)_4(MeCN)_2$ reacts with several different bidentate ligands (one equiv.) to give binuclear units that are ligated by the bidentate ligand. Use of dppm (two equiv.) yields $Os_2(OAc)_2(CO)_4(\eta\text{-}dppm)_2$, which is shown by X-ray diffraction analysis to have axially substituted dppm groups.[387] Two reports describing the vapor-phase He(I) and He(II) photoelectron spectra of $Ru_2(O_2CCF_3)_4$ and $Ru_2(O_2CCF_3)_2(NO)_2$ have appeared. MO calculations have been carried out and the results are discussed with respect to the ground-state assignments of these dimers.[388,389]

$Ru_2(O_2CR)_4$ (where R = alkyl group) complexes have been synthesized and subjected to a magnetic susceptibility study. The data reveal a low-temperature M_s=0 state with a thermally accessible triplet excited state. The liquid crystal behavior is also reported.[390] The diruthenium(II,III) dimer $[Ru_2(O_2Ac)_4(H_2O)_2]^+$ undergoes rapid axial anation with Cl^- to give $Ru_2(O_2Ac)_4(H_2O)Cl$ and $[Ru_2(O_2Ac)_4Cl_2]^-$. The formation constants and the redox behavior are reported. Outer-sphere electron-transfer reactions using $[Ti(H_2O)_6]^{3+}$ and $[Ti(H_2O)_5(OH)]^{2+}$ as reducing agents have been studied.[391] Diamagnetic (μ-oxo)bis(μ-carboxylato)diruthenium(III) dications with a capping 1,4,7-trimethylazacyclononane ligand

(N_3) have been obtained from the hydrolysis of $N_3RuCl_3 \cdot H_2O$ in aqueous solution containing carboxylic acids. The structures of $[(N_3)_2Ru_2^{III}(\mu\text{-}O)(\mu\text{-}OAc)_2]^{2+}$ and $[(N_3)_2Ru^{III}Ru^{IV}(\mu\text{-}O)(\mu\text{-}OAc)_2]^{3+}$, the products of persulfate oxidation, have been solved. The two Ru^{III} centers in the dication exhibit strong intramolecular antiferromagnetic coupling.[392]



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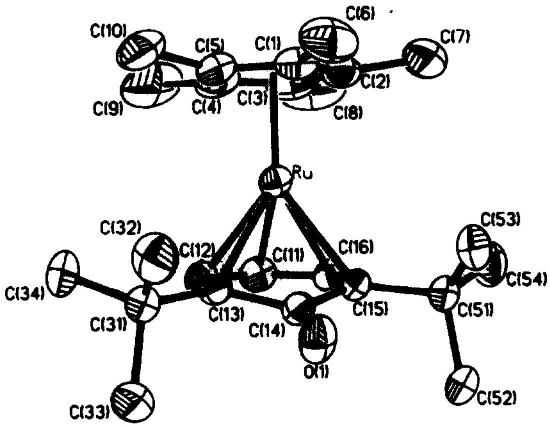
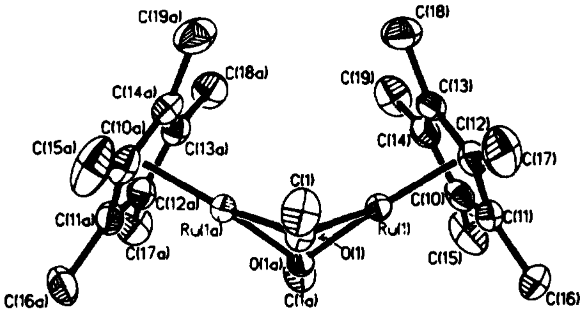
Treatment of $[Ru_2(O_2CR)_4Cl]$ (where R = Me, Ph) with aspirinate (2-acetoxybenzoate) affords $[Ru_2(\mu\text{-}asp)_4Cl]$, which upon reaction with AgO_2CCF_3 or $PhCO_2H$ gives $[Ru_2(\mu\text{-}asp)_4(O_2CCF_3)]$ and $[Ru_2(\mu\text{-}asp)_2(\mu\text{-}O_2CPh)_2)Cl]$, respectively. IR spectra, conductivity, cyclic voltammetry, and magnetic susceptibility data are presented.[393] The reaction between $RuCl_3 \cdot H_2O$ and PBu_3 gives one or more products depending on the reaction conditions. The new complexes $Ru_2Cl_6(PBu_3)_4$, $Ru_2Cl_5(PBu_3)_4$, $Ru_2Cl_6(PBu_3)_3$, and $Ru_3Cl_8(PBu_3)_4$ have been isolated and three of the four structures determined by X-ray diffraction analysis.[394] Reaction of $[Os_2Cl_8][PPh_3Me]$ with HI gas furnishes $[Os_4I_{14}]^{2-}$, which is shown by X-ray diffraction analysis to contain two $Os_2I_8{}^{2-}$ units fused together on a common edge.[395]

Chloro-bridged ruthenium dimers have been obtained from the reaction between $Ru(MeCN)_2Cl_2(PPh_3)_2$ and COS.[396] Alkoxy- and aryloxy-bridged ruthenium dimers are reported. The methoxy-bridged dimer $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OMe)]_2$ has been prepared by several methods and its X-ray structure solved. Reaction of ethoxide with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ gives the corresponding ethoxide-bridged dimer, whose X-ray structure is presented. CO reacts with these alkoxy dimers to give $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OR)CO]_2$. The η^5-oxocyclohexadienyl complex $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3O)$ has been isolated from the reaction between $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ and $[Li][O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3]$ and fully characterized by NMR and X-ray analyses.[397]





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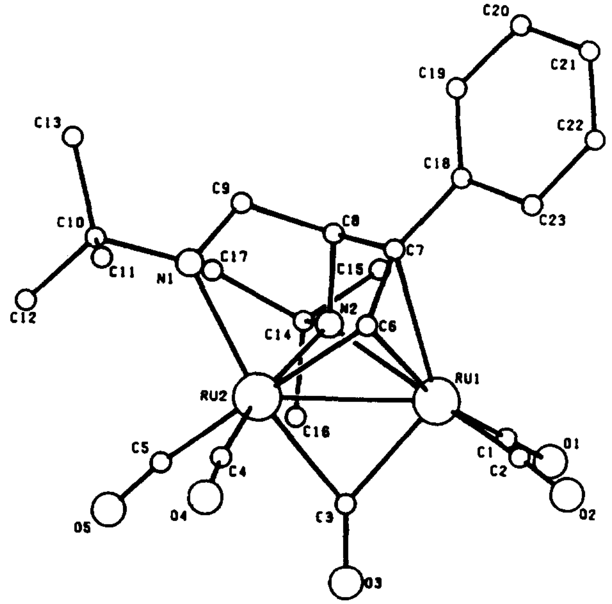
The pyrazolate-bridged dimers $Ru_2(CO)_6(\mu_2\text{-pz})_2$ (where pz = pyrazole, 3,5-dimethylpyrazole) have been prepared from $Ru_3(CO)_{12}$ and examined in ligand substitution reactions with PPh_3 and 1,1'-bis(diphenylphosphino)ferrocene (dppf). Reaction with carboxylic acids gives $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}O_2CR)_2(\mu_1\text{-}\eta^1\text{-Hpz})_2$, which possesses bridging carboxylates and a monodentate pyrazole ligand.[398] In a separate report by the same group, $Ru_2(CO)_6(\mu_2\text{-pz})_2$ dimers have been allowed to react with several bidentate phosphines to yield diphosphine-bridged mono-substituted products $Ru_2(CO)_6(\mu_2\text{-pz})_2(\mu_2\text{-}\eta^2\text{-P-P})$. The hydrido-bridged dimers $Ru_2(\mu_2\text{-H})(CO)_3(\mu_2\text{-}\eta^2\text{-3,5-Me}_2\text{pz})_2[\mu_1\text{-}\eta^1\text{-PPh}_2\text{XPPh}(C_6H_4)]$ (where X = CH_2CH_2, $CH_2\{C_6H_{10}\}CH_2$) have been obtained from an ortho-metalation sequence; the X-ray crystal structure of the dppe metalated dimer has been solved.[399] Reaction of $RuCl_3$ with CO and pyrazole, followed by zinc reduction, gives $Ru_2(CO)_6(\mu_2\text{-pz})_2$. Oxidative addition reactions with I_2 are shown to give the iodo-bridged complex $[Ru_2(CO)_6(\mu_2\text{-I})(\mu_2\text{-pz})_2]^+$ or $Ru_2(CO)_6I_2(\mu_2\text{-pz})_2$ depending on the ruthenium : iodine ratio used. NMR data and the X-ray structures of $Ru_2(CO)_6(\mu_2\text{-}3,5\text{-}Me_2pz)_2$ and $[Ru_2(CO)_6(\mu_2\text{-}I)(\mu_2\text{-}3,5\text{-}Me_2pz)_2]^+$ are presented.[400]

The reactivity of $Ru_2(CO)_6$(t-Bu-DAB) (where t-Bu-DAB = t-BuN=CHCH=N-t-Bu) towards alkynes has been found to give $Ru_2(CO)_6$[t-BuN=CHCN(t-Bu)CR=CR'] as a result of direct electrophilic attack of the alkyne on the η^2-C=N imine moiety. The X-ray structure of this complex (R = R' = CF_3) consists of two nonbonding $Ru(CO)_3$ units which are bridged by imine and alkyne linkages. The X-ray structures of other pertinent complexes are presented and the factors responsible for the C-C bond coupling observed during alkyne activation are discussed.[401]



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N,N-Diethylamino-1-propyne (DEAP) has been allowed to react with $Ru_2(CO)_6$(i-Pr-DAB). The complex $Ru_2(CO)_5$(i-Pr-DAB)(DEAP) has been isolated and characterized by IR and NMR spectroscopies. The reactivity of the mixed-metal dimer

$FeRu(CO)_6$(i-Pr-DAB) toward DEAP is also described.[402] The results from the reaction between $Ru_2(CO)_6$(i-Pr-DAB) and phenylacetylene have been published. Two isomeric complexes $Ru_2(CO)_4$(i-Pr-DAB)(μ_2-PhC≡CH), which could not be separated, were obtained and characterized by solution techniques. A mechanism involving dissociative CO loss and a concomitant coordination change in the i-Pr-DAB ligand from 6e → 8e, followed by alkyne coordination, is proposed.[403]

Reversible C-C coupling and flyover bridge formation have been documented in the reactions of $Ru_2(CO)_6$(i-Pr-Pyca) (where i-Pr-Pyca = pyridine-2-carbaldimine) with alkynes. X-Ray crystallographic characterization of several of the products and NMR data are given.[404]

The Xα-SW MO results on the electronic structure of $Ru_2(RNNNR)_4$ (where R = C_6H_4-4-Me) have been reported. The calculated electronic configuration, $\sigma^2\pi^4\delta^2\pi^{*4}$, is in agreement with the known structural features and the diamagnetism exhibited by the dimer.[405] Oxidation of $Ru_2(PhNNNPh)_4$ by $AgPF_6$ in CH_2Cl_2/Et_2O gives the Ru_2^{5+} complex $Ru_2(PhNNNPh)_4(OPF_4)$. Axial coordination of the OPF_4 ligand has been confirmed by a single-crystal X-ray diffraction analysis.[406] The diazadiene-chelated dimer $[RuMe(CO)_2(DAD)]_2$ (where DAD = MeN=CHCH=NMe) has been prepared and its structure determined by X-ray crystallography.[407] Cyclic voltammetric data for $Ru_2(MeC_5NH_3NH)_3(OAc)Cl$ have been obtained in DMSO. The redox chemistry and the effect of added chloride and Ag^+ ions are discussed.[408]

The new dinuclear ruthenium complexes $Ru_2(CO)_4$(μ_2-2-

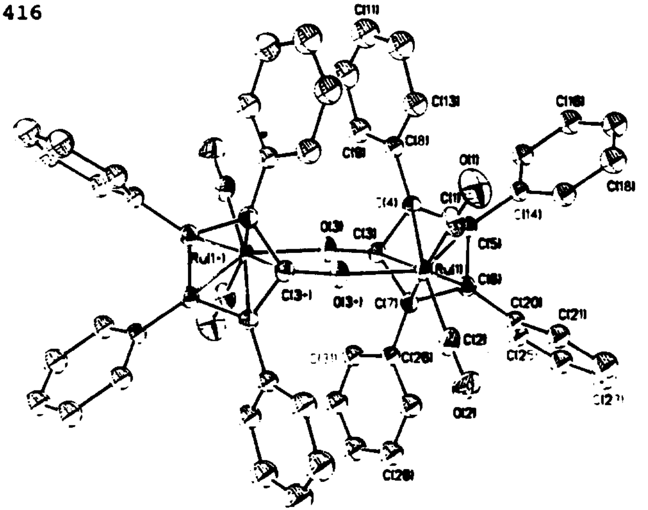
oxypyridine)$_2$(PPh$_3$)$_2$ and Ru$_2$(CO)$_4$(μ_2-2-mercaptothiazole)$_2$(PPh$_3$)$_2$ were synthesized from Ru$_2$(CO)$_4$(OAc)$_2$(PPh$_3$)$_2$ and the appropriate heterocycle. The X-ray structure of the latter complex has been determined.[409] Amino acids react with [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ to yield (η^6-C$_6$H$_6$)Ru(amino acid)Cl. The synthesis and X-ray crystal structures of three amino acid complexes are described.[410] Polymeric clusters of [Ru$_2$(CO)$_4$(μ_2-η^2-HNOCR$_2$)]$_n$ (where R = Me, Et, Pr, Ph) have been obtained from the reaction of Ru$_3$(CO)$_{12}$ with amides. Depolymerization is observed in coordinating solvents or suitable donor ligands. X-Ray structures of Ru$_2$(CO)$_4$(μ_2-η^1-HNOCMe)$_2$(PPh$_3$)$_2$ and Ru$_2$(CO)$_4$(μ_2-η^1-HNOCPh)$_2$(MeCN)$_2$ reveal that the CO groups are trans to the bridging amide ligands.[411]

The synthesis and properties of the nitrido-bridged complexes [Os$_2$N(NH$_3$)$_8$Cl$_2$][Cl]$_3$ and [Os$_2$N(NH$_3$)$_7$Cl$_3$][Cl]$_2$, products of the ammonolysis of [OsCl$_6$][Na]$_2$, are reported. The use of these dimers as materials for DNA-selective, electron-dense stains for electron microscopy is described.[412]

Diosmacyclobutane has been prepared from Os(CO)$_5$ and acetylene through the intermediate alkyne complex Os(CO)$_4$(HC≡CH). Reaction of Os(CO)$_4$(HC≡CH) with Ru(CO)$_5$ proceeds readily at -20 °C and without any ligand loss to give OsRu(CO)$_9$(HC≡CH), which is shown by ^{13}C NMR spectroscopy to contain a dimetallacyclopentenone core. Reactions of Os(CO)$_4$(HC≡CH) with (η^5-C$_5$H$_5$)M(CO)$_2$ (where M = Co, Rh, Ir) are also described.[413]

ESR spectroscopy (single crystal) has been used to examine triplet excitons in $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\eta^6,\eta^6\text{-}[2_2]\text{-}paracyclophane)][TCNQ]_2$. An anisotropic spectrum characteristic of an excitonic species was observed over the temperature range 77-150 K and is attributed to electronic interactions between different TCNQ acceptor stacks.[414] The synthesis of the ethoxy-bridged paracyclophane complex $[(\eta^6\text{-}C_6H_{16})Ru(\mu_2\text{-}OEt)Ru(\eta^6\text{-}C_6H_{16})]^+$ has been presented. The cation has a confacial-bioctahedral geometry, as determined by X-ray crystallography.[415]

The synthesis, X-ray structure, and catalytic properties of $[(\eta^5\text{-}C_4Ph_4CO)Ru(CO)_2]_2$ have appeared. X-Ray diffraction analysis indicates that the cyclopentadienone carbonyl is bent back from the plane of the diene. Crossover experiments reveal that dimer dissociation is a low-energy process. Mononuclear complexes $(\eta^4\text{-}C_4Ph_4CO)Ru(CO)_2L$ (where L = CO, PPh_3, amines) are readily obtained by dimer cleavage. The reaction of the dimer with hydrogen gives $(\eta^4\text{-}C_4Ph_4CO)Ru(CO)_2H$ and the role of this hydride in hydrogenation reactions is discussed.[416]



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A corrigendum on the correct space group for $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ has appeared.[417] The divinyl complex $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)(CH{=}CH_2)Ru(\eta^5\text{-}C_5Me_5)$ reacts to give the dinuclear complex $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)(\mu\text{-}\eta^4\text{-}C_4H_4)Ru(\eta^5\text{-}C_5Me_5)$ upon thermolysis. The structure has been established by X-ray diffraction analysis.[418]

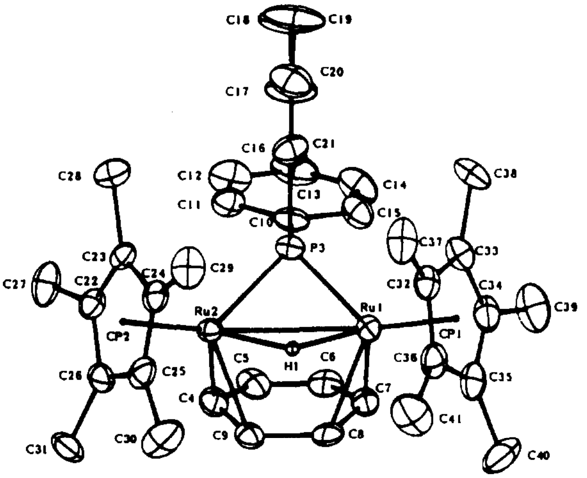
The μ_2-methylene group in $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2(MeCN)(\mu_2\text{-}CH_2)$ couples with allene to give $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2\{\mu\text{-}\eta^1,\eta^3\text{-}CH_2C(CH_2)_2\}$. The trimethylenemethane complex has been isolated and characterized by NMR spectroscopy and X-ray crystallography. The reactivity of this new complex toward H^+ and CO is described.[419] Reaction of the μ-alkylidene complex $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu_2\text{-}CMe_2)$ with MeLi, followed by treatment with HBF_4, gives the di-μ-alkylidene complex $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2(\mu_2\text{-}CMe)(\mu_2\text{-}CMe_2)]^+$. Deprotonation to the μ_2-vinylidene complex is described along with the results of hydride addition, which occurs at the μ_2-CMe moiety.[420] The disproportionation of the μ_2-ethylidyne complex $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu_2\text{-}CMe)]^+$ to $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu_2\text{-}CCH_2)$ and $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu_2\text{-}CHMe)$ occurs readily upon either chemical or electrochemical single-electron reduction. The two products arise from the decomposition of the transient radical $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu_2\text{-}CMe)^\bullet$. Derivative cyclic voltammetry results and a working mechanism are discussed.[421]

New alkanediyl complexes have been synthesized from $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-$ and $I(CH_2)_2I$. Full solution characterization is reported and the X-ray structure of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2[\mu\text{-}(CH_2)_5]$ has been determined.[422] NMR data and X-ray diffraction analysis reveal the presence of intramolecular H•••F bonding between the μ_2-CH_2 and alkene ligand in $(\eta^5$-$C_5H_5)_2Ru_2(CO)_2(CF_2{=}CFR)(\mu_2$-$CH_2)$ (where R = F, CF_3). HF elimination and methylene-alkene coupling to give $(\eta^5$-$C_5H_5)_2Ru_2(CO)_2(\mu$-CHCFCFR) has been observed.[423] A report describing the reactivity of $(\eta^5$-$C_5H_5)_2Ru_2(CO)_2(CH_2{=}CH_2)(\mu_2$-$CH_2)$ has been published. Thermolysis gives propene as a result of methylene-ethylene coupling, while Ag^+ oxidation affords the μ-vinyl cation $[(\eta^5$-$C_5H_5)_2Ru_2(CO)_2(CH_2{=}CH_2)(\mu_2$-$CH_2)]^+$. Reaction of hydride with this latter dimer gives $(\eta^5$-$C_5H_5)_2Ru_2(CO)_2(\mu$-$CHCH_3)(\mu_2$-$CH_2)$, which is shown to release propene more efficiently than the original methylene-bridged dimer.[424]

The synthesis and X-ray structure of $(\eta^5,\eta^5$-$C_5H_5CH_2C_5H_5)Ru_2(CO)_4$ has been described. The bis(cyclopentadienyl)methane-bridged complex is obtained in good yield from $Ru_3(CO)_{12}$ and bis(cyclopentadienyl)methane. The reactivity of $(\eta^5,\eta^5$-$C_5H_5CH_2C_5H_5)Ru_2(CO)_4$ toward I_2, hydride, and diphenylacetylene is also described.[425]

The 1,2-di-σ bonding mode for the ethylene ligand in $Os_2(CO)_8(\mu_2,\eta^2$-$C_2H_4)$ has been confirmed through vibrational measurements. The results may be considered as a vibrational model for molecular ethylene chemisorption.[426]

^{31}P spin-lattice relaxation times (T_1) have been measured for dinuclear and trinuclear phosphido-bridged complexes. The chemical shift anisotropy (CSA) contribution to spin-lattice relaxation is shown to dominate over other possible contributions. The correlation time, λ_c, is also reported.[427] Phosphorus-carbon coupling constants in three phosphido-bridged ruthenium dimers have been determined by using 2D NMR techniques. The values obtained for $^{2}J_{PRuC}$ show a correlation with the crystallographically determined μ_2-P-Ru-C angle.[428] Reaction of $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ with PPh_3 gives $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu\text{-}\eta^2,\eta^2,\text{-}C_6H_4)Ru(\eta^5\text{-}C_5Me_5)$ as a result of P-C(aryl) bond cleavage. Variable-temperature NMR studies and the X-ray diffraction structure are discussed.[429]



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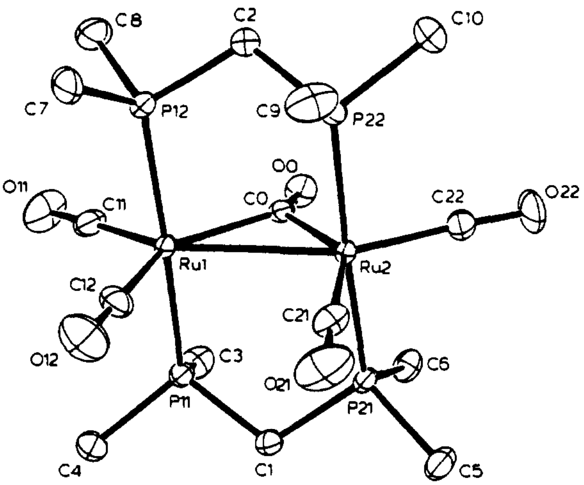
The dichloro-bridged complex Ru_2Cl_4(dbbp) {where dbbp = 1,4-bis(diphenylphosphino)butane} reacts with hydrogen to give the molecular hydrogen complex $(\eta^2\text{-}H_2)(dbbp)Ru(\mu_2\text{-}Cl)_3Ru(dbbp)Cl$. The H-H distance in this complex has been determined by ^1H NMR spin-lattice measurements. The substitution of H_2 by N_2 and the transfer hydrogenation reactivity are discussed.[430]

The reactivity of the diphosphazane-bridged dimer $Ru_2(CO)_5\{\mu-(RO)_2PN(Et)P(OR)_2\}_2$ (where R = Me, i-Pr) toward $AuCl(PPh_3)$, $[Cu(MeCN)_4]^+$, and $HgCl_2$ has been explored. Cationic products have been obtained which show either terminal or bridging coordination of the heterometallic species.[431] $Ru_2(CO)_4(O_2CR)_2(MeCN)_2$ (where R = Me,Et) reacts with the chiral diphosphines R,R-DIOP and S,S-DIOP {where DIOP = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane} to yield the substitution products $Ru_2(CO)_4(O_2CR)_2(DIOP)$. Solution NMR measurements reveal that the DIOP ligand bridges adjacent ruthenium centers. These enantiomerically pure dimers catalyze the hydrogenation of hydroxyacetone to 1,2-propanediol in low enantiomeric excess.[432] The synthesis and reactivity of $Ru_2(CO)_7(dppm)$ have been reported. The solution dynamics of the ancillary CO ligands have been investigated through the use of variable-temperature ^{13}C NMR spectroscopy.[433] The dimer $Ru_2(CO)_5(dmpm)_2$ {where dmpm = bis(dimethylphosphino)methane} has been prepared from dmpm and $Ru_3(CO)_{12}$. Protonation occurs at the Ru-Ru bond to give $[Ru_2(\mu_2-H)(CO)_5(dmpm)_2]^+$, while diphenylacetylene reacts to give $Ru_2(CO)_4(dmpm)_2(PhC{\equiv}CH)$. This latter product, which contains a σ_2-bridging acetylene ligand, has been determined by X-ray diffraction analysis. The structure of the parent dimer was also established by X-ray crystallography.[434]



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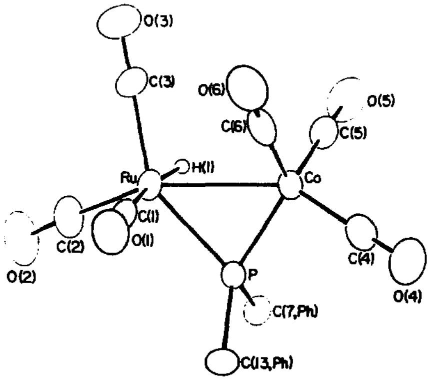
(b) Heterodinuclear Complexes

The triple decker complexes $(\eta^5\text{-}N_5C_4H_2R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Ru(\eta^6\text{-}1,4\text{-}Me_2C_6H_4)$ (where R = H, Me) have been synthesized and spectroscopically characterized.[435] A full paper describing the synthesis and properties of mixed-metal carborane complexes has appeared. The "pseudo-triple-decker" complex $(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}\eta^5\text{-}Et_2C_2B_3H_3)Ru(CO)_3$ has been synthesized from $[(\eta^5\text{-}C_5Me_5)Co(\eta^5\text{-}Et_2C_2B_3H_3)]^{2-}$ and $Ru(CO)_3Cl_2$. The X-ray structures of $(cymene)Ru(\mu\text{-}\eta^5\text{-}Et_2C_2B_3H_3)Ru(cymene)$ and $(cymene)Ru(\mu\text{-}\eta^5\text{-}Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5H_5)$ have been determined.[436] Synthetic and mechanistic studies on triple decker complexes possessing a bridging 1H-borole ligand are described. Reaction of $(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_4H_4BPh)$ with $[(\eta^6\text{-}C_6Me_6)Ru(acetone)_3]^+$ gives $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}\eta^5\text{-}C_4H_4BPh)Co(\eta^5\text{-}C_5H_5)]^{2+}$ as an air-sensitive powder, which upon treatment with KI degrades to the known sandwich compound $(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}\eta^5\text{-}C_4H_4BPh)$.[437,438]

The stereoselective trans addition of deuterium to the coordinated DAB ligand in $FeRu(CO)_6(DAB)$ complexes has been reported. The kinetics for the reaction and the X-ray crystal structure determinations of $FeRu(CO)_6\{\mu,\eta^1\text{-}N(R)CH_2CR'HN(R)\}$ (where R = i-Pr; R' = H, Me) are included.[439] The dimer $FeRu(CO)_6$(i-Pr-DAB) has been allowed to react with a variety of alkynes. Alkyne coordination at the $Fe(CO)_3$ center and alkyne coupling with the η^2-C≡N moiety of the DAB ligand have been demonstrated.[440]

The synthesis and reactivity of $[(X)(CO)_3Ru(\mu_2\text{-}PPh_2)Co(CO)_3]^-$ (where X = H, Br, I) have been published. All of the products result from the site-selective substitution of a CO group on the ruthenium atom of $(CO)_4Ru(\mu_2\text{-}PPh_2)Co(CO)_3$. ^{31}P NMR spectroscopy and X-ray diffraction analysis have been used to establish the location of the hydride ligand in $[H(CO)_3Ru(\mu_2\text{-}PPh_2)Co(CO)_3]^-$.[441]



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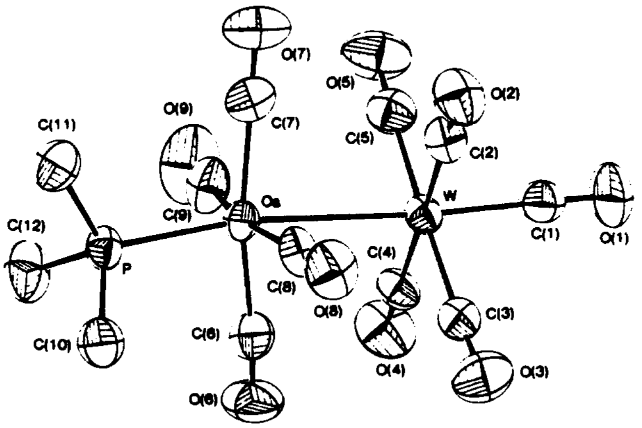
The interaction of $HgCl_2$ with ruthenocenophanes has been examined. Structural studies reveal that the formation of a

Ru-Hg bond occurs when $HgCl_2$ is treated with 1,4,7,10,13-pentaoxa-, 1,13-dioxa-4,7,10-trithia[13]-, and 1,4,7,10,13,16-hexaoxa[16](1,1')ruthenocenophanes.[442] The mixed-metal complexes $(\eta^5-C_5Me_5)RuH_3(PCy_3)CuCl$ and $[\{(\eta^5-C_5Me_5)RuH_3(PCy_3)\}_2Cu]^+$ have been prepared and examined by variable-temperature ^1H NMR spectroscopy. The former complex exhibits a high-field hydride AB_2 spectrum that shows a large temperature dependent AB coupling constant.[443] Bimetallic hydrocarbon-bridged complexes containing $Ru(CO)_3$ moieties have been described.[444]

The reaction between $Os(CO)_4(PR_3)$ (where R = Me, OMe, Ph) and $M(CO)_5(THF)$ (M = Cr, Mo, W) gives the unbridged, dative metal-metal bonded dimers $(R_3P)(OC)_4OsM(CO)_5$. X-Ray structural results of $(Me_3P)(OC)_4OsCr(CO)_5$ and $(Me_3P)(OC)_4OsW(CO)_5$ are presented and unequivocally establish the presence of a dative Os-M bond. The results of a variable-temperature ^{13}C NMR analysis reveal that the solid-state structure is maintained in solution.[445]



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The early-late heterometallic dimers $(\eta^5\text{-}C_5H_5)(OC)_2RuTi(NMe_2)_2(2,6\text{-}Me_2\text{-}C_6H_3O)$ and $(\eta^5\text{-}C_5H_5)(OC)_2RuTi(NMe_2)(2,6\text{-}Me_2\text{-}C_6H_3O)_2$, prepared from $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ and $Ti(NMe_2)_3(2,6\text{-}Me_2\text{-}C_6H_3O)$ and $Ti(NMe_2)_2(2,6\text{-}Me_2\text{-}C_6H_3O)_2$, respectively, have been structurally characterized.[446] $[RuH_3(PPh_3)_3]^-$ reacts with $[Rh(1,5\text{-}COD)Cl]_2$ to initially give $(1,5\text{-}COD)Rh(\mu_2\text{-}H)_3Ru(PPh_3)_3$ as the kinetic product. Rearrangement to the thermodynamically more stable isomer $(1,5\text{-}COD)RhH(\mu_2\text{-}H)RuH(PPh_3)_3$ occurs at room temperature as determined by ^1H and ^{31}P NMR spectroscopy.[447] A radioactive bimetallic complex has been prepared from ruthenocenecarboxylic acid (^{103}Ru) and a platinum(II) phosphine complex. Both metals were attached via a peptide linkage. The results of organ distribution studies indicate that the $^{103}RuPt$ complex accumulates mainly in the liver and spleen.[448]

IV. Polynuclear Complexes

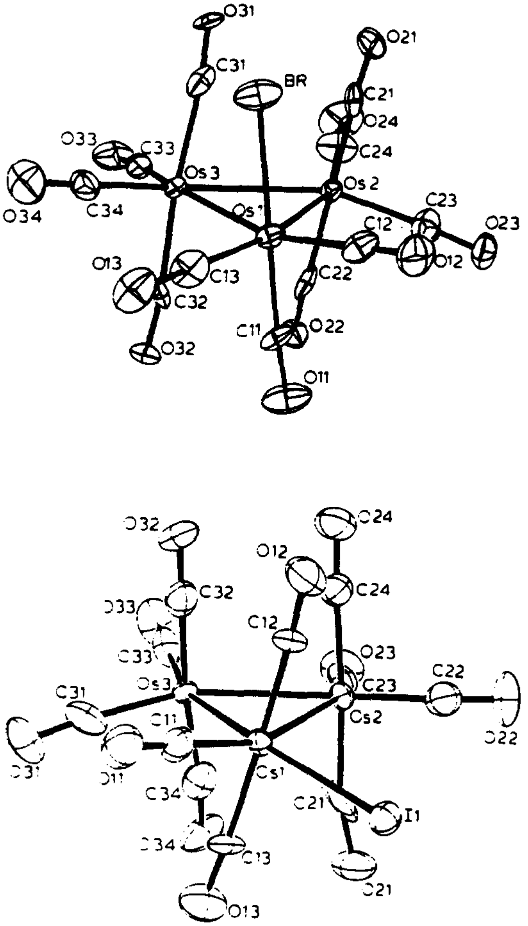
(a) Trinuclear Clusters

1. Simple and Hydrocarbon Ligands

Catalytic dehydro alkyne insertion reactions between 2-butyne and nido-2,3-$Et_2C_2B_4H_4$ to give nido-4,5-Me_2-7,8-$Et_2C_2B_4H_4$ using $Ru_3(CO)_{12}$ and $Ru_3(CO)_9(PPh_3)_3$ have been reported.[449] $Ru_3(CO)_{12}$ mediated cycloaddition reactions of 3-t-Bu-1,1,2,2-tetrafluoro-1,2-disilacyclobutene and several 1,3-butadienes have been explored. The involvement of ruthenium silametallocycles in the cycloaddition reactions is discussed.[450] The reaction between $(RO)_2PN(Et)P(OR)_2$ (where R = Me, i-Pr) and $Ru_3(CO)_{12}$ is reported to give a large number of trinuclear and tetranuclear phosphine-substituted clusters.[451]

The reaction dynamics of photosubstitution intermediates derived from $Ru_3(CO)_{12}$ have been presented. Dissociative CO loss occurs upon optical excitation and the $Ru_3(CO)_{11}$ formed is rapidly trapped in a second-order reaction by CO or added nucleophile. The rate constants for the reaction between $Ru_3(CO)_{11}(THF)$ and CO have been measured. The flash-photolysis system employs a XeCl excimer-laser excitation source and an IR detection system.[452] The photoinduced fragmentation of $Ru_3(CO)_{12}$ in the presence of added ligand (phosphines, phosphites, CO, alkenes) proceeds by a non-radical isomer of $Ru_3(CO)_{12}$. This reactive isomer may revert back to $Ru_3(CO)_{12}$ or react with L to form $[Ru_3(CO)_{12}L]$. Quantum yields, kinetic data, and a plausible mechanism based on the experimental data are discussed.[453]

The anionic chloride cluster $[Ru_3(CO)_{11}Cl]^-$ has been isolated from the reaction between $Ru_3(CO)_{12}$ and [PPN][Cl] {where $PPN^+ = (PPh_3)_2N^+$}. X-Ray diffraction analysis reveals that the cluster possesses three μ_2-bridging CO groups and that the chloride ligand occupies an axial substitution site.[454] Axial and equatorial substitution by halides has been observed in $Os_3(CO)_{12}$. $Os_3(CO)_{12}$ reacts with [PPN][X] (where X = halide) in the presence of Me_3NO to yield $[Os_3(CO)_{11}X][PPN]$. Single-crystal X-ray diffraction analysis reveals that the bromide occupies an axial site while the iodide ligand is coordinated in the equatorial plane. Variable-temperature ^{13}C NMR studies indicate that the solid-state structures of $[Os_3(CO)_{11}Br]^-$ and $[Os_3(CO)_{11}I]^-$ are maintained in solution. ^{13}C NMR results on $[Os_3(CO)_{11}Cl]^-$ and $[Os_3(CO)_{11}(NCO)]^-$, prepared by using $[PPN][N_3]$, suggest that the unique ligand resides in an axial position. The solution dynamics for these clusters are also discussed.[455]



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A report on the halide-promoted reactions of alkynes with $Ru_3(CO)_{12}$ has appeared. Reaction of $[Ru_3(CO)_{11}Cl]^-$, formed from $Ru_3(CO)_{12}$ and $[PPN][Cl]$, with alkynes gives

$[Ru_3(CO)_9(\mu,\eta^2\text{-alkyne})(\mu_2\text{-Cl})]^-$; the X-ray structure of the diphenylacetylene derived cluster has been solved. The reactivity of these alkyne clusters is also presented.[456] $SnCl_4$ reacts with $M_3(CO)_{12}$ (where M = Ru, Os) at room temperature to give $M_3(CO)_{12}(Cl)(SnCl_3)$ in quantitative yield. ^{13}C NMR spectral data indicate that a $ClOs_3(SnCl_3)$ arrangement exists with the chloride ligand cis and the $SnCl_3$ ligand trans to the linear Os_3 chain.[457] The energetics for the carbonyl merry-go-round process in $M_3(CO)_{12}$ have been examined by extended Hückel MO calculations. The potential barrier for CO migration is higher for $Os_3(CO)_{12}$ than for $Ru_3(CO)_{12}$ but is found to be nearly equal when the $M_3(CO)_6$ fragments are compared.[458]

Efficient HPLC separations of $Os_3(CO)_{12}$, $Os_3(CO)_{11}(MeCN)$, and $Os_3(CO)_{10}(MeCN)_2$ have been achieved by using normal and reverse-phase chromatographic techniques. The relative retention times are shown to correlate with molecular structures.[459] The kinetics for the reaction of $Os_3(CO)_{11}(MeCN)$ with H_2 and CO, and of $Os_3(CO)_{10}(MeCN)_2$ with H_2, have been investigated in the presence of MeCN. The rate-limiting step involves the dissociative loss of MeCN. Rate constants for nucleophilic attack on $[Os_3(CO)_{11}]$ follow the order MeCN $>$ PPh_3 $\approx$ CO $>$ H_2.[460] $Os_3(CO)_{10}(MeCN)_2$ reacts with $Me_3SiC{\equiv}CH$ to yield $Os_3(CO)_{10}(Me_3SiC{\equiv}CH)$. The coordinated acetylene exists in a $\mu_3\text{-}\eta^2(\parallel)$ mode relative to the triosmium plane. This cluster is transformed into $HOs_3(CO)_9(C{\equiv}CSiMe_3)$ either on standing for a prolonged period of time or by thermolysis in hexane. The structure of this cluster has been determined and spectroscopically characterized.[461] The allyl cluster $[Os_3(CO)_{11}(\eta^3-C_3H_5)]^+$ has been prepared from $Os_3(CO)_{11}(MeCN)$ and allyl alcohol in the presence of HBF_4. IR and NMR data are presented along with the single-crystal X-ray results.[462] Ethynylferrocene has been allowed to react with $Os_3(CO)_{10}(MeCN)_2$ to give the alkyne cluster $Os_3(\mu_3-CHCFc)(\mu_2-CO)(CO)_9$ (where Fc = ferrocene), which upon photolysis or thermolysis loses CO to furnish $Os_3(\mu_2-H)(\mu_3-C_2Fc)(CO)_9$. If the decarbonylation is carried out with added sulfur, the sulfido-bridged cluster $Os_3(\mu_3-S)(\mu_3-CHCFc)(CO)_9$ is obtained. X-Ray diffraction studies have established the structures of all three of these clusters. The results of a variable-temperature ^1H NMR study of $Os_3(\mu_3-CHCFc)(\mu_2-CO)(CO)_9$ are presented and the fluxional pathways related to alkyne scrambling discussed.[463] Carbon-arsine bond cleavage has been observed in the thermolysis reaction between $Os_3(CO)_{11}(MeCN)$ and $As(p-tol)_3$. The isolated product, $Os_3(CO)_9(\mu_3-AsC_6H_4Me)(\mu_3-C_6H_3Me)$, has been fully characterized and its molecular structure determined.[464]

Carbon-carbon σ-bond and carbon-hydrogen bond activation have been observed in the reaction between $Os_3(\mu_2-H)_2(CO)_{10}$ and 3,3-dimethylcyclopropene. The products $Os_3(\mu_2-H)(\mu_2-CCH_2CHMe_2)(CO)_{10}$ and $Os_3(\mu_2-H)(\mu_3-CCH=CMe_2)(CO)_{10}$ were isolated and characterized by ^1H and ^{13}C NMR measurements. X-Ray diffraction analysis has established the structure of the former cluster. Deuterium labeling studies using $Os_3(\mu_2-D)_2(CO)_{10}$ are discussed.[465] The X-ray structure of the methyl(phenyl)vinylidene complex $Ru_3(\mu_2-H)_2(CO)_9\{\mu_3-\eta^2-$

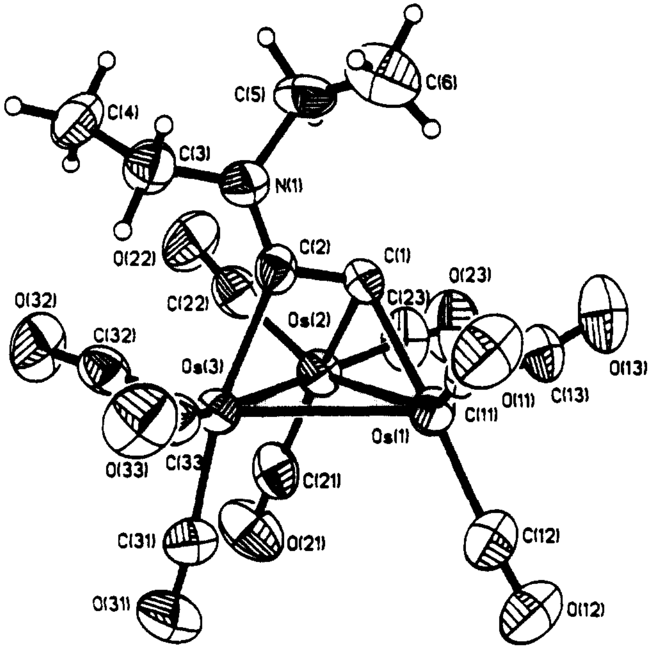
C=C(Me)Ph} has been solved. The structure consists of a triangular array of rutheniums that is capped by the alkenylidene ligand.[466] The trinuclear cluster $Ru_3(CO)_7(Cl)_2(OC_6H_{11})_2$ has been isolated from transfer hydrogenation reactions. Single-crystal X-ray diffraction results are presented.[467]

The ortho-metallation product $[Ru_3(\mu_2\text{-}H)(CO)_8(PPh_3)(PPhC_6H_4)]^-$ has been obtained from the reaction between $[Ru_3(\mu_2\text{-}H)(CO)_{11}]^-$ and PPh_3. X-Ray diffraction analysis has confirmed the structure of this cluster. Protonation affords the dihydride cluster $Ru_3(\mu_2\text{-}H)_2(CO)_8(PPh_3)(PPhC_6H_4)$, which upon deprotonation yields an isomer of the original anionic hydride cluster.[468] Catalytic isomerization of allylic alcohol to propionaldehyde has been reported with the cluster catalyst $[Ru_3(\mu_2\text{-}H)(CO)_{11}]^-$. The mechanism involving intact Ru_3 clusters is discussed on the basis of the kinetic data and isotope labelling studies.[469]

The results of high-pressure kinetic studies on the carbonylation of $Ru_3(\mu_2\text{-}H)_2(CO)_9\{\mu_3\text{-}C(O)Me\}$ and on the hydrogenation of $Ru_3(\mu_2\text{-}H)(CO)_{10}\{\mu_3\text{-}C(O)Me\}$ have appeared. Activation volumes are reported and partial molar volumes are used to construct a volume profile for these reactions.[470] The photochemistry of $Ru_3(\mu_2\text{-}H)(CO)_{10}\{\mu_3\text{-}C(O)Me\}$ has been examined. Optical excitation under CO leads to the formation of $Ru_3(\mu_2\text{-}H)(CO)_{10}\{\mu,\sigma^1\text{-}C(O)Me\}$. Quantum yields and the results of ^{13}C labelling studies are reported for this photoisomerization reaction.[471] The carbene cluster

$Os_3(CO)_9\{\sigma^1\text{-}C(OMe)Ph\}(\mu_3\text{-}CPh)\{\mu_3\text{-}C(O)Me\}$ has been synthesized from $Os_3(CO)_9(\mu_3\text{-}CPh)\{\mu_3\text{-}C(O)Me\}$. A structural determination and NMR spectroscopic data are included.[472]

Treatment of $Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ with $Ph_2PC{\equiv}CPh$ and Me_3NO gives the phosphine-substituted cluster $Ru_3(\mu_2\text{-}H)(CO)_8(Ph_2PC{\equiv}CPh)(\mu_3,\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$, which has been characterized by NMR measurements. Thermolysis furnishes the new cluster $Ru_3(CO)_8\{\mu_3,\eta^4\text{-}C(t\text{-}Bu)CC(H)C(Ph)(PPh_2)\}$, whose structure has been solved by X-ray diffraction analysis. A mechanism for the formation of this latter cluster is presented.[473] The isomeric clusters $Os_3(\mu_2\text{-}H)_2(CO)_9(CCHOEt)$ and $Os_3(\mu_2\text{-}H)_2(CO)_9(CHCOEt)$ have been obtained from the reaction between EtOH and $Os_3(\mu_2\text{-}H)_2(CO)_9(C{\equiv}CH)$. The molecular structures of these two clusters are reported and variable-temperature ^1H NMR data, which reveal a rapid enantiomerization process for each cluster, are discussed. Alternative synthetic routes and the reactivity of these cluster are presented.[474] A report describing alkyne and carbonyl dynamics in $Os_3(CO)_9(alkyne)L$ {where $L = PPh_3$, PMe_3, $P(OMe)_3$} has appeared.[475] The reactivity of $Os_3(\mu_2\text{-}H)(CO)_9(C{\equiv}CH)$ toward nitrogen nucleophiles has been explored. Pyridine, ammonia, and diethylamine all attack the α-carbon of the triply bridging ethynyl ligand. While pyridine addition is reversible, ammonia and diethylamine additions are irreversible. The molecular structure of $Os_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}Et_2NC{\equiv}CH)$ has been solved and the dynamic solution behavior examined by ^1H NMR spectroscopy.[476]



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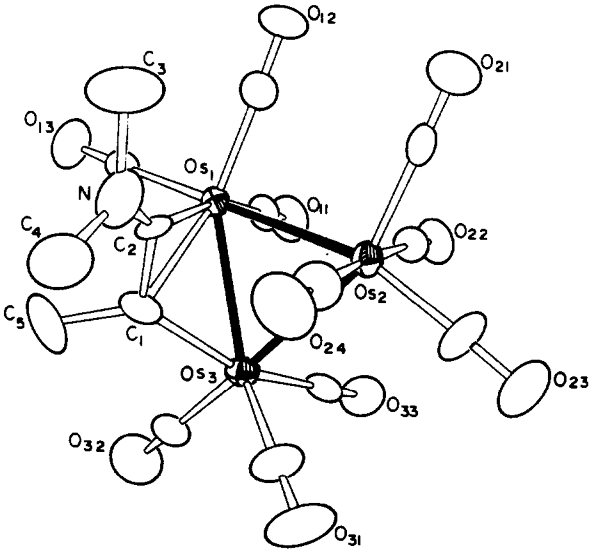
Triruthenium metallacyclopentadienyl clusters $Ru_3(CO)_8(RC{\equiv}CR)_2$ have been examined by electrochemical techniques and MO calculations. Linear correlations between the $E_{1/2}$ values and UV-visible absorbance data are observed and are discussed within the context of the MO calculation results.[477] X-Ray structures have been reported for $[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-}OMe)_2]^+$ and $[(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}OMe)]_2$.[478]

The face-capping arene ligand in $Os_3(CO)_9(\mu_3,\eta^2,\eta^2,\eta^2\text{-}C_6H_5R)$ undergoes reaction with hydride and carbanions by exo attack. The exo-addition products $[Os_3(CO)_9(\mu_3,\eta^2,\sigma,\eta^2\text{-}C_6H_5RR')]^-$ have been allowed to react with electrophiles to yield $Os_3(\mu_2\text{-}E)(CO)_9(\mu_3,\eta^2,\sigma,\eta^2\text{-}C_6H_5RR')$ {where E = H, $Au(PEt_3)$}. The X-ray structure of the hydride-addition product $[Os_3(CO)_9(\mu_3,\eta^2,\sigma,\eta^2\text{-}C_6H_5H)]^-$ has been determined.[479]

Electrophilic acetylation and alkylation reactions of (benzyne)triosmium clusters are reported. IR and NMR data are included for most of the new products.[480] The benzyne-substituted cluster $Os_3(\mu_2\text{-}H)_2(CO)_9(C_6H_4)$ reacts with diphenylacetylene to give $Os_3(CO)_7(C_6H_4)\{PhCC(H)Ph\}_2$, whose structure has been crystallographically determined.[481]

Ynamine insertion into the C-N bond of the (dimethylamino)carbene cluster of $Os_3(CO)_8\{C(H)NMe_2\}(\mu_3\text{-}S)(\mu_2\text{-}H)_2$ yields $Os_3(CO)_8\{C(H)=C(Me)C(NMe_2)_2\}$. Full solution characterization and the X-ray diffraction results are described.[482] The ynamine cluster $Os_3(CO)_{10}(\mu\text{-}MeCCNMe_2)$ has been synthesized from MeC_2NMe_2 and $Os_3(CO)_{10}(MeCN)_2$. The unusual edge-bridging coordination mode of the ynamine has been explained by the existence of a strong N-C π bond formed between the alkyne and amino group. Structural determinations of $Os_3(CO)_{10}(\mu\text{-}MeCCNMe_2)$ and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}CH_2CCNMe_2)(\mu_2\text{-}H)$, the product of decarbonylation and C-H bond activation, are included.[483]



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A report on proline and cystine modified triruthenium clusters has appeared. The enantioselective isomerization of nerol to citrinellal is described.[484] The vinyl triosmium cluster $Os_3(CO)_{10}(\mu_2\text{-}Br)(CH{=}CHPh)$ has been synthesized from $Os_3(\mu_2\text{-}H)_2(CO)_{10}$ and $PhC{\equiv}CBr$. Thermolysis reactions to give $Os_3(CO)_9(\mu_2\text{-}H)(\mu_2\text{-}Br)(C{=}CHPh)$ are reported along with the X-ray structures of these two clusters.[485]

A report on the spectroelectrochemical properties of $Ru_3(O)(OAc)_6(isonicotinamide)_3$ has been presented.[486]

2. Phosphine Ligands

The kinetics for phosphine and arsine ligand substitution reactions in $Ru_3(CO)_{11}\{P(OEt)_3\}$ have been reported. A two term rate law, which is composed of ligand-dependent and a ligand-independent pathways, is observed. The activation parameters reported here have been used with previously reported data obtained for $Ru_3(CO)_{12}$ and other $Ru_3(CO)_{11}L$ clusters to construct an isokinetic plot. The steric and electronic contributions to the second-order rate constant (k_2) have been evaluated.[487]

$Ru_3(CO)_9(PPh_3)_3$ reacts with a variety of binucleating amines to give the ruthenium(I) dimers $Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2$ (where L = 2-pyridone, N-methyl-2-mercaptoimidazole, pyrazole, 1,8-diaminonaphthalene). The X-ray diffraction structure of the complex formed in the reaction using the last ligand is included.[488] The synthesis and reactivity of $Os_3(CO)_{10}(PEt_3)(MeCN)$ have been published. Treatment of $Os_3(CO)_{11}(PEt_3)$ in MeCN with the decarbonylating agent Me_3NO yields the monoacetonitrile cluster, which reacts readily with

H^+ ion to give $[Os_3(\mu_2\text{-}H)(CO)_{10}(PEt_3)(MeCN)]^+$.[489] Substituent effects on the Ru-Ru and Ru-P bond lengths and a discussion on the effects of the chosen refinement model on Ru-C and C≡O bond lengths in the clusters $Ru_3(CO)_{11}(PEt_3)$ and $Ru_3(CO)_{11}\{P(OMe)_3\}$ have been published.[490]

Two reports on phosphine-substituted and phosphido-bridged ruthenium clusters have been published. t-Butylacetylene is selectively hydrogenated to 3,3-dimethyl-1-butene using $Ru_3(CO)_{12-x}(PPh_2H)_x$ (where x = 1-3), $Ru_3(\mu_2\text{-}H)(CO)_{10-x}(\mu\text{-}PPh_2)$ (where x = 0,1), $Ru_3(\mu_2\text{-}H)(CO)_8(\mu\text{-}PPh_2)_2$, and $Ru_3(\mu_2\text{-}H)(CO)_7(\mu\text{-}PPh_2)_3$ as catalyst precursors. The involvement of cluster catalysts and alkyne-substituted cluster intermediates are discussed.[491] Many of these same clusters have also been examined in diphenylacetylene hydrogenation and stilbene isomerization reactions. The nature of the alkyne and its influence on the rate of the hydrogenation reaction are described.[492]

Chelating and bridging modes of bidentate P,P and P,As ligands in $Ru_3(\mu_2\text{-}H)(CO)_7(C\equiv C\text{-}t\text{-}Bu)(L\text{-}L)$ have been observed by NMR spectroscopy. Use of the rigid diphosphine cis-$Ph_2PCH{=}CHPPh_2$ yields only the chelated phosphine complex $Ru_3(\mu_2\text{-}H)(CO)_7(C\equiv C\text{-}t\text{-}Bu)(cis\text{-}Ph_2PCH{=}CHPPh_2)$. Variable-temperature NMR results indicate that bridging ligands readily interconvert between axial and equatorial positions.[493] The molecular structure of $Ru_3(CO)_{10}(DIOP)$ has been determined. The DIOP ligand exhibits equatorial substitution.[494] The stereochemical disposition of the ancillary P-ligands in several tetra-substituted clusters $Ru_3(CO)_8(P)_4$ has been established by X-ray crystallography. The synthesis and isolation of many other P-ligand and As-ligand clusters derived from $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are also described.[495]

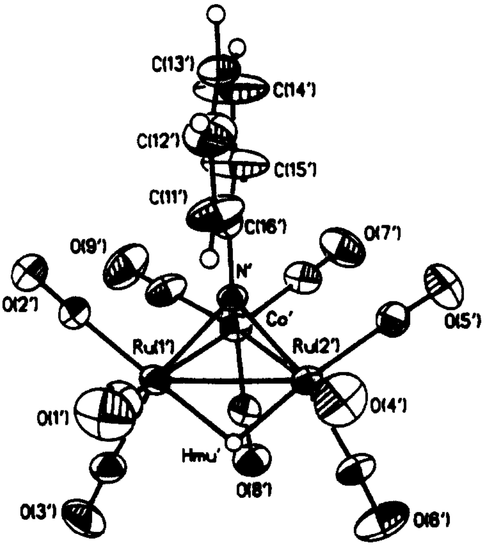
Halogen-induced fragmentation of $[Ru_3(\mu_2\text{-}H)(CO)_8(PPh_3)(PPhC_6H_4)]^-$ to the neutral dimer complexes $Ru_2(CO)_5(PPh_3)(\mu_2\text{-}PPh_2)(\mu_2\text{-}X)$ (where X = Br, I) has been reported. The observed products have been characterized by solution measurements and X-ray diffraction analysis in the case of the μ_2-bridged iodo dimer.[496]

Cyclometallation of $Os_3(\mu_2\text{-}H)(CO)_{10}(PPh_2)$ proceeds under thermolysis conditions to give $Os_3(\mu_2\text{-}H)_2(CO)_9\{P(C_6H_4)Ph\}$ in good yield. The molecular structure was established by X-ray crystallography. Ligand substitution reactions have also been examined and the products $Os_3(\mu_2\text{-}H)(CO)_9L(PPh_2)$, formed by the reversal of cyclometallation, have been fully characterized. These same phosphine-substituted clusters were observed to give the cyclometallated products $Os_3(\mu_2\text{-}H)_2(CO)_8L\{P(C_6H_4)Ph\}$ upon thermal decarbonylation.[497] In a follow-up article, the reactivity of $Os_3(\mu_2\text{-}H)_2(CO)_9\{P(C_6H_4)Ph\}$ toward Brønsted acids (HX) has been explored. These reactions proceed initially by protonation, followed by anion coordination, to furnish the clusters $Os_3(\mu_2\text{-}H)_2(\eta^1\text{-}X)(CO)_9(PPh_2)$ (where X = Cl, Br, OAc, CF_3CO_2). The X-ray structure of the trifluoromethylacetate cluster confirms the η^1-binding nature of the trifluoromethylacetate ligand. Reaction of H_2 with $Os_3(\mu_2\text{-}H)_2(CO)_9\{P(C_6H_4)Ph\}$ proceeds with C-P bond cleavage and affords the phosphinidene-capped cluster $Os_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)$.[498]

3. Nitrogen Ligands

$Ru_3(CO)_{12}$ reacts with 1,2-arenediamines to yield μ-amido complexes. 1,2-Phenylene and 4,5-dimethyl-1,2-phenylene react with $Ru_3(CO)_{12}$ to give the trinuclear clusters $Ru_3(\mu_2\text{-}H)(\mu\text{-}H_3N_2arene)(CO)_9$, which possesses μ_2-amido and σ-bonded amino functionalities. The reaction with 1,8-diaminonaphthalene leads to cluster fragmentation and formation of the dinuclear complex $Ru_2(CO)_6(\mu_2\text{-}H_2N_2naph)$.[499] The diazene ligand 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene (dtn) reacts with $Ru_3(CO)_{12}$ to furnish $Ru_3(CO)_9(dtn)$. The identity of this new cluster has been assigned on the basis of solution characterization, which includes variable-temperature ^{13}C NMR measurements.[500] Binuclear metallapyrrolidone complexes $Ru_2(\mu\text{-dppm})(CO)_4\{\mu_2\text{-}\eta^3\text{-}RC{=}CPhC(O)NPh\}$ (where R = H, Ph) have been isolated from the reaction between $Ru_3(CO)_8(\mu\text{-dppm})(\mu_3\text{-NPh})$ and $PhC{\equiv}CR$. The molecular structure of the complex derived from phenylacetylene has been determined.[501]

μ_3-Imido clusters $[Ru_3(CO)_9(X)(\mu_3\text{-NPh})]^-$ (where X = Cl, Br, I, CN) have been synthesized from $Ru_3(CO)_{12}$ and nitrosobenzene in the presence of [PPN][X], or from the reaction between $Ru_3(CO)_9(\mu_3\text{-NPh})$ and [PPN][X]. The hydride analogue $[Ru_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-NPh})]^-$ has been obtained from the reaction between $[Ru_3(CO)_{11}(\mu_2\text{-}H)]^-$ and nitrosobenzene. Similar methodology is reported for the synthesis of the triosmium and mixed-metal analogues. Treatment of $Ru_3(CO)_{10}(\mu_3\text{-NPh})$, prepared from $Ru_3(CO)_{11}(MeCN)$ and nitrosobenzene, with RLi reagents (where R = Me, Ph) yields the anionic acyl clusters $[Ru_3(CO)_9\{C(O)R\}(\mu_3\text{-NPh})]^-$, which when placed under CO and protonated undergo imido-acyl coupling to produce $Ru_3(CO)_{10}(\mu_2\text{-}H)\{\mu_2\text{-}N(Ph)C(O)R\}$. The possible involvement of these imido complexes in reduction reactions of nitroaromatics is discussed and the X-ray crystal structures of $[Ru_3(CO)_9(I)(\mu_3\text{-}NPh)]^-$ and $CoRu_2(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}NPh)$ are presented.[502]



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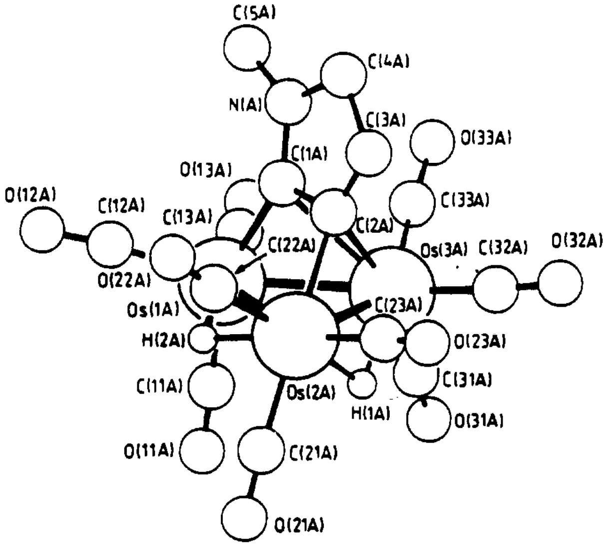
The reaction between $Os_3(CO)_{12}$ and indole has led to the cluster $Os_3(CO)_8(\mu_2\text{-}H)_2(\mu\text{-}\overline{C_6H_4CH_2C}{=}N)_2$ in moderate yield. An X-ray structure determination indicates that the indolyl ligands each bridge two osmium atoms via the nitrogen and the ortho-metallated C-2 atom. The observed structure is discussed with respect to the trapping of an unstable tautomer of indole. A reactivity comparison with the reaction between

$Os_3(CO)_{12}$ and pyrrole (and N-methylpyrrole) is also included.[503] The crystal structures of $Os_3(CO)_9(\mu_2\text{-}H)(\overline{XCH{=}CHC{=}C})$ (where X = NMe, S) have been presented and compared with the benzyne cluster $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3,\eta^2\text{-}C_6H_4)$. The benzyne-substituted cluster adopts a parallel ligand geometry, while in $Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3,\eta^2\text{-}Et_2NC_2H)$ the (diethylamino)ethyne ligand is distorted toward a perpendicular geometry. This parallel → perpendicular geometry distortion is discussed in terms of the heteroatom.[504]



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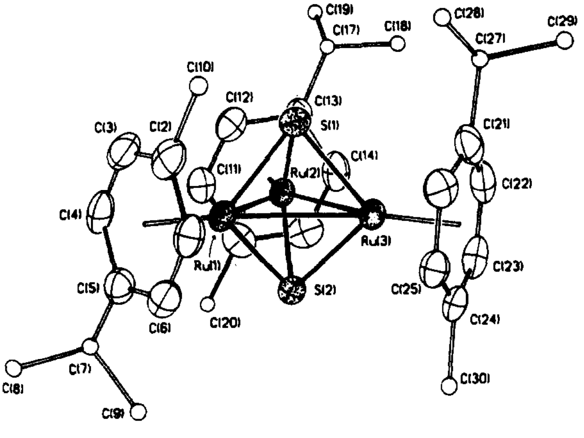
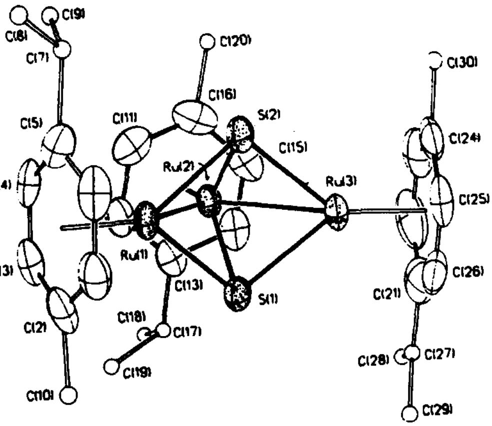
4. Sulfur Ligands

The insertion of 2,3-dihydrothiophene (2,3-DHT) into the osmium-hydride bond of $Os_3(\mu_2\text{-}H)_2(CO)_9(PPh_3)$ has been examined as a model reaction for thiophene hydrodesulfurization processes. The isolated product $Os_3(\mu_2\text{-}H)(CO)_9(DHT{\bullet}H)(PPh_3)$ has been fully characterized by spectroscopic and X-ray diffraction methods. The low-temperature ^{1}H NMR spectrum reveals the presence of two high-field doublets which are attributed to μ_2-hydrides that flank the PPh_3 ligand.[505] A report has appeared that describes the first (arene)Ru and (arene)Os sulfido clusters. The reaction between $[(p\text{-cymene})MCl_2]_2$ (where M = Ru, Os) and $(Me_3Si)_2S$, methanolic NaSH, or aqueous Na_2S as the sulfide sources yields the dicationic clusters $[(p\text{-cymene})_3M_3(\mu_3\text{-}S)_2]^{2+}$. The molecular structures of $[(p\text{-cymene})_3Ru_3(\mu_3\text{-}S)_2]^{2+}$ and neutral $(p\text{-cymene})_3Ru_3(\mu_3\text{-}S)_2$, prepared by cobaltocene reduction, have been established by X-ray diffraction analyses. The dicationic clusters adopt a closo M_3S_2 core, whereas the neutral clusters exhibit a nido M_3S_2 core in agreement with theoretical predictions. Cyclic voltammetric data are reported for these new cluster complexes and it is shown that the closo triruthenium cluster undergoes two distinct one-electron reductions during the closo → nido transformation. The comproportionation constant K_c has been evaluated for the triruthenium system.[506]





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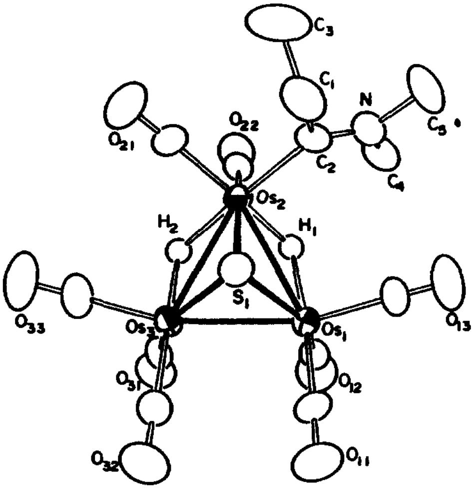
Alkylidyne-alkyne coupling on triruthenium clusters has been demonstrated. The reaction of $Ru_3(\mu_2\text{-H})_3(CO)_9(\mu_3\text{-CSEt})$ with alkynes yields $Ru_3(\mu_2\text{-H})(CO)_9(\mu_3,\eta^3\text{-EtSCCRCR})$ and $Ru_3(CO)_9(\mu_2\text{-SEt})(\mu_3,\eta^3\text{-CCRCHR})$ (where R = Me, Ph). These isomeric clusters contain a 1,3-dimetalloallyl and a 1,1-dimetalloallyl ligand, respectively. Full solution characterization accompanies this report along with the structural determination of the latter cluster. Isomerization reactions and cluster-centered hydrocarbon chain growth processes are discussed.[507] The 1,1-hydrogenation of ynamine ligands has been shown to give alkyl(dialkylamino)carbene complexes. The reaction between $Os_3(CO)_9(\mu_3\text{-Me}_2C_2NMe_2)(\mu_3\text{-S})$ and H_2 gives $Os_3(CO)_8\{C(Et)NMe_2\}(\mu_3\text{-S})(\mu_2\text{-H})_2$ as a result of ynamine hydrogenation. Both clusters were examined by X-ray diffraction analysis.[508]



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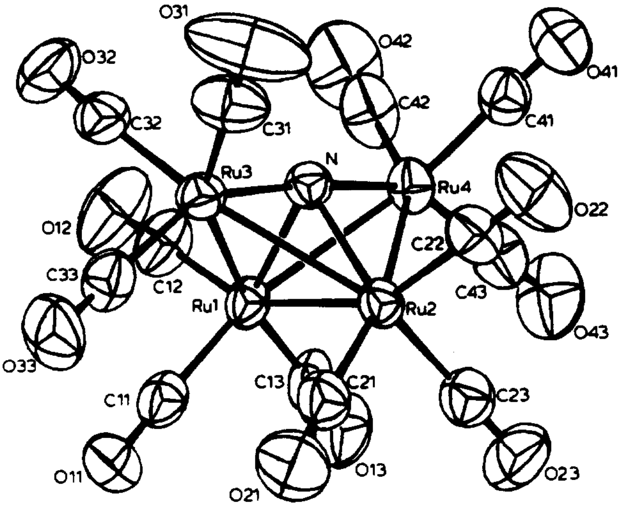
(b) Tetranuclear Clusters

The X-ray structure of a third modification of $[Ru_4(\mu_2\text{-}H)_3(CO)_{12}][PPN]$ has appeared.[509] A report on the synthesis and structure of $Ru_4(CO)_{12}(\mu_4\text{-}Et_2N_2)$ has been presented. The tetraruthenium core exhibits a folded bicyclobutane-type structure.[510] The synthesis and reactivity of $Ru_4(CO)_8L_2[(-)\text{-DIOP}]_3$ (where H_2L = glutaric acid) have been described. The molecular structure was assigned on the basis of solution NMR and IR spectra. The hydrogenation of prochiral substrates is also reported.[511]

$Os_4(CO)_{14}$ reacts with EHR_3 (where E = Si, Ge, Sn; R = Me, Ph) to furnish the air-sensitive clusters $Os_4(\mu_2\text{-}H)(CO)_{14}(ER_3)$. The molecular structure of the trimethyltin cluster has been determined by X-ray diffraction analysis. ^{13}C NMR data reveal that the ancillary CO groups are static in contrast to other Os_4 cluster complexes.[512]

The electronic structures of the butterfly clusters $[Ru_4(CO)_{12}(\mu_4\text{-}N)]^-$ and $[FeRu_3(CO)_{12}(\mu_4\text{-}N)]^-$ have been investigated by using Fenske-Hall MO calculations. Included in this report is the X-ray structure of the former tetraruthenium cluster, the coordinates of which were used in the MO calculations.[513]



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(c) Pentanuclear Clusters

The chemistry associated with the phosphido-bridged cluster $Ru_5(CO)_{13}(\mu_2\text{-}PPh_2)(\mu_5\text{-}C_2PPh_2)$ has been investigated. Treatment with CO gives $Ru_5(CO)_{15}(\mu_2\text{-}PPh_2)(\mu_5\text{-}C_2PPh_2)$, which upon further reaction with CO yields isomeric clusters containing Ru_2-spiked and Ru_3 cores. The reactivity of these clusters has been studied under H_2 and the molecular structures of $Ru_5(CO)_{13}(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(\mu_5\text{-}CCHPPh_2)$, $Ru_5(CO)_{12}(\mu_2\text{-}H)_2(\mu_2\text{-}PPh_2)(\mu_5\text{-}CCH_2PPh_2)$, and $Ru_5(CO)_{11}C(\mu_2\text{-}H)_3(\mu_2\text{-}PPh_2)(PMePPh_2)$ have been established by X-ray crystallography.[514]

Excess pyridine reacts with $Ru_5(CO)_{15}(\mu_5\text{-}C)$ to give an equimolar mixture of two isomers of $Ru_5(CO)_{14}(\mu_5\text{-}C)(\mu_2\text{-}H)(C_5H_4N)$, which differ only in the orientation of the cyclometallated pyridine ligand. X-Ray crystallography has confirmed the nature of the isomeric products. Both of these clusters undergo thermal decarbonylation to give the same product $Ru_5(CO)_{13}(\mu_5\text{-}C)(\mu_2\text{-}H)(C_5H_4N)$.[515] The clusters $Os_5(CO)_{15}(\mu_2\text{-}H)(\mu_2\text{-}MPPh_3)$ (where M = Cu, Ag, Au) and $Os_5(CO)_{15}(\mu_2\text{-}H)(\mu_2\text{-}AuPMe_3)$ have been obtained from the reaction between $[Os_5(CO)_{15}(\mu_2\text{-}H)]^-$ and $MCl(PPh_3)$ or $AuCl(PMe_3)$ in the presence of $TlPF_6$. The cluster $Os_5(CO)_{15}(\mu_2\text{-}H)(\mu_2\text{-}AuPPh_3)$ has been crystallographically analyzed. The copper and silver clusters are noticeably less stable than the gold clusters, reverting back to the starting cluster on standing in solution. The reaction between $[Os_5(CO)_{15}]^{2-}$ and the above electrophiles is also described.[516]

An article on the application of Stone's tensor surface harmonic (TSH) theory has appeared. The results from the TSH theory for $[Ru_5(CO)_{15}]^{2-}$ show that all of the frontier orbitals are clearly identifiable. TSH results for $[Os_4(CO)_{13}]^{2-}$, ruthenium metalloborane clusters, $Ru_6(CO)_{17}(\mu_6\text{-}C)$, and $[Os_{10}(CO)_{12}(\mu_2\text{-}CO)_{12}(\mu_6\text{-}C)$ are also described.[517]

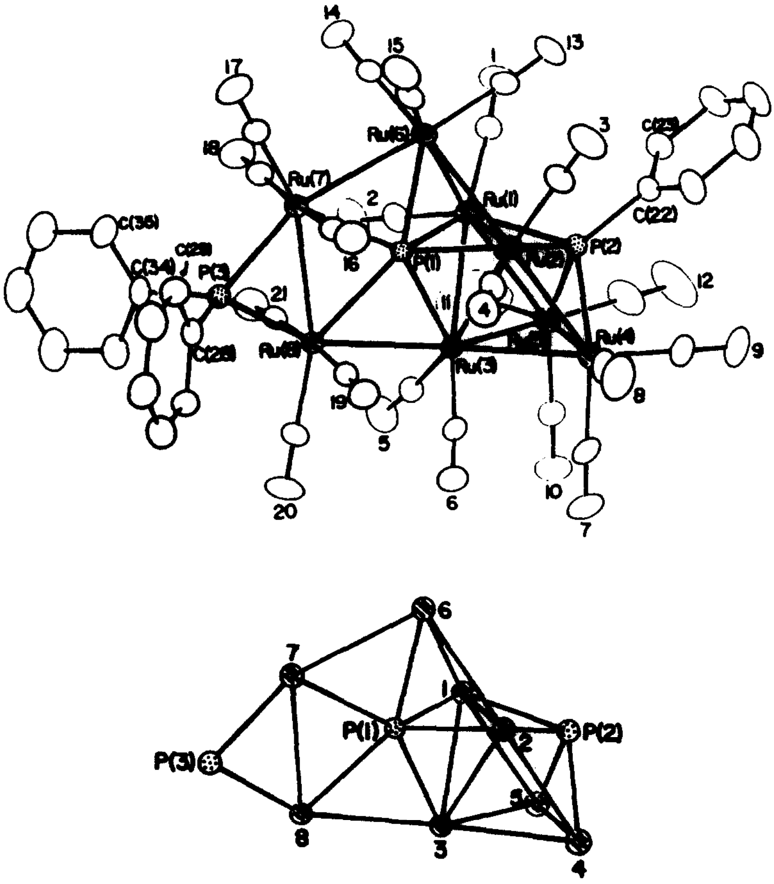
(d) Hexanuclear Clusters

Chemical or electrochemical oxidation of $[Ru_6(CO)_{16}(\mu_6\text{-}C)]^{2-}$ in the presence of added ligand affords the monosubstituted clusters $Ru_6(CO)_{16}L(\mu_6\text{-}C)$ {where L = CO, $P(OMe)_3$, PPh_3, $PMePh_2$}. When the same reaction is carried out with disubstituted alkynes, the products are the alkyne-substituted clusters $Ru_6(CO)_{16}(alkyne)(\mu_6\text{-}C)$ (where alkyne = PhC_2Et, EtC_2Me). Oxidation in the presence of C_5Me_5H or C_6H_5Me gives $Ru_6(CO)_{16}(\mu_2\text{-}H)(\eta^5\text{-}C_5Me_5)(\mu_6\text{-}C)$ and $Ru_6(CO)_{16}(\mu_2\text{-}H)(\eta^6\text{-}C_6Me_5Me)(\mu_6\text{-}C)$, respectively.[518]

The hexaosmium cluster $Os_6(CO)_{20}(\mu_3\text{-}S)(\mu_4\text{-}S)$ has been prepared in low yield from the photolysis reaction of $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ under CO. The structure of the product cluster was determined crystallographically. Photolysis of the hexaosmium cluster under nitrogen gives $Os_6(CO)_{17}(\mu_4\text{-}S)_2$.[519] The activated "raft" cluster $Os_6(CO)_{20}(MeCN)$ reacts with Ph_2PH or $PhPH_2$ to give $Os_6(CO)_{20}(Ph_2PH)$ and $Os_6(CO)_{20}(PhPH_2)$, respectively. Thermolysis of the former cluster gives the phosphido-capped cluster $Os_6(CO)_{16}(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)$ as the sole product. Two phosphinidene-capped clusters have been isolated from the thermolysis reaction of the phenylphosphine-substituted cluster; $Os_6(CO)_{18}(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)$, whose X-ray structure has been determined, and the known cluster $Os_5(CO)_{15}(\mu_4\text{-}PPh)$ have been isolated and characterized.[520]

(e) Higher Nuclearity Clusters

The octaruthenium cluster $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$ has been isolated in low yield from the thermolysis reaction of $Ru_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)$. An X-ray structure confirms the presence of the three different coordination environments for the phosphorus atoms.[521]



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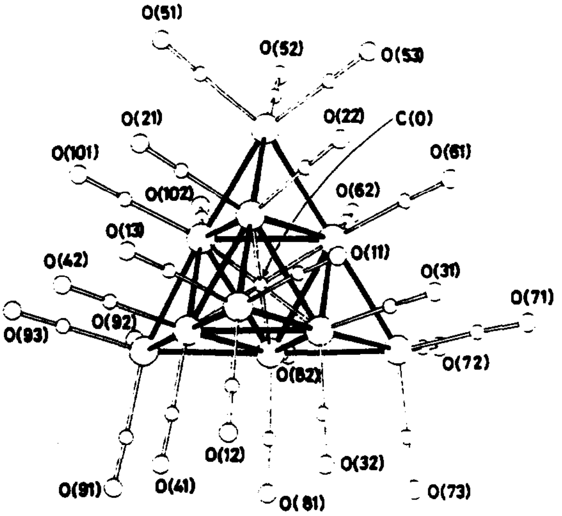
Two reports describing separate syntheses and X-ray structure determination of the decaruthenium cluster $[Ru_{10}(CO)_{24}(\mu_6\text{-}C)]^{2-}$ have been published. Treatment of

$Ru_3(CO)_{12}$ in heptane in the presence of mesitylene gives the anionic carbide cluster and the corresponding mono-hydride cluster $[Ru_{10}(CO)_{24}(H)(\mu_6\text{-}C)]^-$. Both of these clusters display fluxional CO ligands as determined by variable-temperature ^{13}C NMR spectroscopy. On the basis of NMR measurements, the hydride ligand in the latter cluster is assigned to a site within one of the Ru_4 cavities.[522] The thermolysis reaction between $[Ru_6(CO)_{16}(\mu_6\text{-}C)]^-$ and $Ru_3(CO)_{12}$ also yields $[Ru_{10}(CO)_{24}(\mu_6\text{-}C)]^{2-}$ in 81% yield. The X-ray structure is shown below.[523]



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An overview on the electronic structure of large organometallic clusters has been published. Emphasis on "metametallic" properties is presented.[524]

The new cluster $[Os_{11}(CO)_{27}(\mu_6\text{-}C)]^{2-}$ has been synthesized from the pyrolysis of $Os_3(CO)_{12}$. Reaction with $[Cu(MeCN)_4]^+$

yields both $[Os_{11}(CO)_{27}(\mu_6\text{-}C)\{Cu(MeCN)\}]^-$ and $Os_{11}(CO)_{27}(\mu_6\text{-}C)\{Cu(MeCN)\}_2$. The parent undecaosmium cluster was allowed to react with I_2/I^- to yield $[Os_{11}(CO)_{27}(\mu_6\text{-}C)I]^-$ and $Os_{11}(CO)_{27}(\mu_6\text{-}C)I_2$, while reaction with $[Au(PMe_2Ph)]^+$ or $[Cu(PMe_2Ph)]^+$ yields $[Os_{11}(CO)_{27}(\mu_6\text{-}C)\{Au(PMe_2Ph)\}]^+$ and $[Os_{11}(CO)_{27}(\mu_6\text{-}C)\{Cu(PMe_2Ph)\}]^+$, respectively. The molecular structures of several of these clusters have been determined.[525]

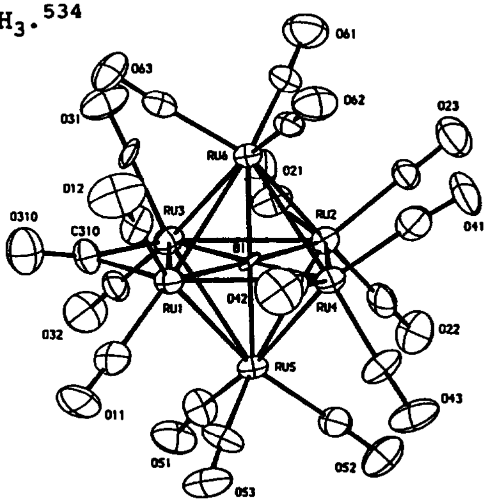
(f) Mixed-Metal Clusters

1. Clusters Containing Main Group Atoms

An article dealing with the framework chirality and optical activity of ruthenium-containing tetrahedrane clusters has appeared.[526]

Synthetic routes to $M_3(CO)_9(\mu_3\text{-}Te)_2$ (where M = Ru, Os) and $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$ have been published. The reaction between $M_3(CO)_{10}(MeCN)_2$ and $Fe_2(CO)_6(\mu_2\text{-}Te)_2$ occurs readily at room temperature to yield the clusters $M_3(CO)_9(\mu_3\text{-}Te)_2$. Treatment of $Os_3(CO)_{11}(MeCN)$ with $Fe_2(CO)_6(\mu_2\text{-}Te)_2$ yields $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$, which has been characterized by IR spectroscopy and mass spectrometry. Irradiation or thermolysis of the cluster furnishes $Os_3(CO)_9(\mu_3\text{-}Te)_2$.[527] $Ru_4(CO)_{12}(\mu_4\text{-}Te)_2$ has been synthesized from $Ru_3(CO)_{12}$ and $Fe_3(CO)_9(\mu_3\text{-}Te)_2$. This new cluster has been characterized by IR spectroscopy and mass spectrometry and its structure is compared to the known pentaruthenium cluster $Ru_5(CO)_{15}(\mu_4\text{-}S)$.[528] The room temperature reaction between $Ru_3(CO)_{12}$ and $Fe_2(CO)_6(\mu_2\text{-}Te)_2$ affords $Fe_2Ru_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$. X-Ray structural analysis indicates that the cluster consists of an $Fe_2(CO)_6$ fragment and a $Ru_3(CO)_{11}$ fragment connected by the bridging telluride ligands.[529] A low-yield synthesis of $Os_3(CO)_{10}(\mu_2\text{-H})(\mu_2\text{-TeC}_6H_4OMe)$ starting from $[Os_3(CO)_{11}(\mu_2\text{-H})]^-$ and its thermal conversion to $Os_3(CO)_9(\mu_3\text{-Te})_2$ are reported.[530] The tellurium-bridged cluster $Os_3(CO)_9(\mu_2\text{-H})_2(\mu_3\text{-Te})$ has been prepared from $Os_3(CO)_{10}(MeCN)_2$ and H_2Te. Solution characterization, including the observation of $^2J_{Te-H}$ coupling, and the X-ray crystallographic results are presented.[531]

The ten-vertex isocloso cluster $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-isocloso-1-RuB}_9H_9]$ has been obtained from $[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-nido-6-RuB}_9H_{13}]$ and Me_2S.[532] The stepwise reduction of MeNC to Me_2NH has been observed by using $[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-nido-5-RuB}_9H_{13}]$. Several intermediates have been identified in this reaction and one of them, $[\mu\text{-6,9-(NMe}_2)\text{-10-(PMe}_2Ph)\text{-5-}(\eta^6\text{-}C_6Me_6)\text{-arachno-5-RuB}_9H_{10}]$, has been structurally characterized.[533] The synthesis and structure of $Ru_6(CO)_{17}(\mu_6\text{-B})(\mu_2\text{-H})$ has been described. This new cluster was synthesized in 10% yield from $Ru_3(CO)_{12}$ and BH_3.[534]



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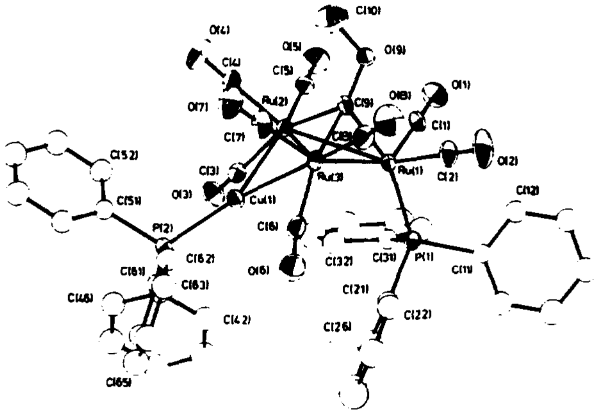
2. Clusters Containing Other Metals

A review article describing the chemistry of metal cluster complexes containing heteroatom-substituted carbene ligands has been published. Mixed-metal and homonuclear clusters are included.[535]

The synthesis and variable-temperature ^{13}C NMR data of the cycloheptatrienyl-bridged dimer $(\mu\text{-}C_7H_7)Ru(CO)_3Ir(CO)_2$ are presented. Dppm reacts with the dimer to give the bridging phosphine complex $(\mu\text{-}C_7H_7)Ru(CO)_2(dppm)Ir(CO)$.[536] A high-yield synthesis of $[HOsRe(CO)_8Br][PPN]$ has been reported from the reaction between $[HOs(CO)_4]^-$ and $BrRe(CO)_5$. X-Ray diffraction analysis confirms the dimeric nature of this complex.[537]

The clusters $(OC)_5M(\mu\text{-}C_5H_4PPh_2)Ru(CO)(\mu\text{-}CO)_2Ru(CO)(\eta^5\text{-}C_5H_5)$ (where M = Mo, W) have been prepared from the reaction between $[M(CO)_5(PPh_2)]^-$ and $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$. The observed products result from the nucleophilic attack of $[M(CO)_5(PPh_2)]^-$ on the cyclopentadienyl ligand of $(\eta^5\text{-}C_5H_5)Ru(CO)_2Cl$. X-Ray diffraction data are presented for the tungsten analogue.[538] $[Ru_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}COMe)]^-$, prepared by the deprotonation of $Ru_3(\mu_2\text{-}H)_3(CO)_9(\mu_3\text{-}COMe)$, has been allowed to react with $M(PPh_3)Cl$ (where M = Cu, Ag, Au) to give the heterometallic clusters $Ru_3(\mu_2\text{-}H)_2(CO)_9(\mu_3\text{-}COMe)(\mu_2\text{-}MPPh_3)$. Treatment with PPh_3 yields the corresponding phosphine-substituted clusters, which in the case of the gold analogue has been structurally characterized.[539]



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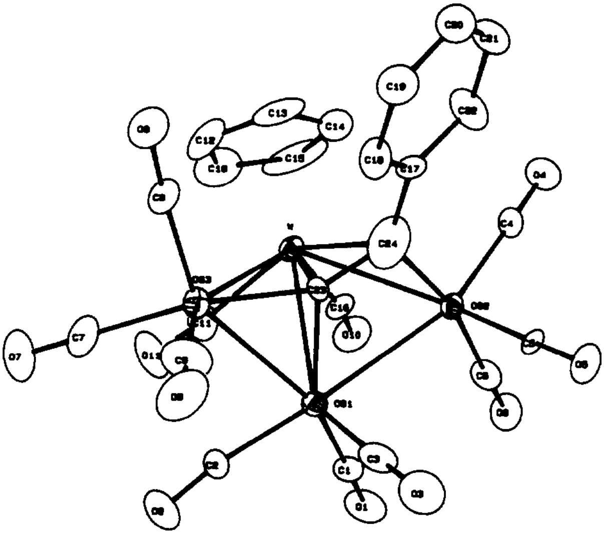
$W(CO)_6$ and $W(CO)_5(PMe_2Ph)$ were allowed to react with $M_3(CO)_{10}(\mu_3\text{-}S)$ (where M = Ru, Os) under photochemical conditions to furnish the clusters $M_2W(CO)_{10}L(\mu_3\text{-}S)$ (where L = CO, PMe_2Ph) and $Os_3W(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)$. Full solution characterization and selected diffraction structures are discussed.[540] ^{199}Hg NMR data for $(\mu_3\text{-}\eta^2\text{-}C_2\text{-t-Bu})(CO)_9Ru_3(\mu\text{-}Hg)X$ (where X = Cl, Br, I) and $(\mu_3\text{-}\eta^2\text{-}C_2\text{-t-Bu})(CO)_9Ru_3(\mu\text{-}Hg)M$ {where M = $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $Mn(CO)_5$, $Re(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $(\eta^5\text{-}C_5H_5)Ru(CO)_2$, $Co(CO)_4$} have been reported. The data are discussed and compared with other reported ^{199}Hg NMR data. No correlation between the ^{199}Hg chemical shifts and the Hg-M bond length was observed. Considerable variation in the linewidth of the ^{199}Hg resonances is observed, which correlates with the efficiency of scalar coupling relaxation of the ancillary quadrupolar nuclei.[541] Photolysis of $Ru_3(CO)_{12}$ in the presence of Ph_3AuN_3 produces $Ru_3(CO)_{10}(\mu\text{-}AuPPh_3)(\mu\text{-}NCO)$.[542] The heteronuclear allenyl cluster $(\eta^5\text{-}$

$C_5H_5)W(CO)_2(\mu\text{-}PhCH{=}C{=}CH_2)Ru_2(CO)_6$ has been synthesized in 21% yield from the photolysis reaction between $Ru_3(CO)_{12}$ and the propargyl complex $(\eta^5\text{-}C_5H_5)W(CO)_2CH_2C{\equiv}CPh$.[543]

The butterfly clusters $(\eta^5\text{-}C_5R_5)WRu_3(CO)_{12}(\mu_2\text{-}H)$ (where R = H, Me) have been structurally characterized and the solution dynamics examined. Facile interconversion of the terminal, μ_2-bridging, and μ_4-bridging CO ligands has been observed.[544] The cluster $(\eta^5\text{-}C_5H_5)WRu_3(CO)_9(\mu\text{-}NPh)(C{\equiv}CPh)$, which is shown by X-ray diffraction analysis to contain a bridging imido group and a μ_4-η^2-acetylide ligand, has been explored for its reactivity toward H_2 and alkynes. H_2 reduction of the acetylide ligand affords the cluster $(\eta^5\text{-}C_5H_5)WRu_3(CO)_8(\mu\text{-}NPh)(\mu\text{-}H)_2(CHCHPh)$, whose structure has been solved and shown to possess a trans vinyl group.[545] Scission of the coordinated acetylide ligand has been reported in $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}(C{\equiv}CPh)$. Excess ditolylacetylene effects the scission of the acetylide bond to give $(\eta^5\text{-}C_5H_5)WOs_3(CO)_8(\mu_3\text{-}CPh)\{\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2\}$. The molecular structures of both of these clusters are given and their reactivity under CO and H_2 discussed.[546]

The site preference for the hydride ligand in $(\eta^5\text{-}C_5Me_5)WOs_3(CO)_{12}(\mu\text{-}H)$ has been determined through the use of X-ray diffraction analysis and solution NMR measurements. The X-ray structure indicates that the hydride ligand bridges a W-Os bond while NMR analysis reveals that the solid-state isomer is in equilibrium with a second isomer that possesses an Os-Os bridging hydride ligand.[547] Hydrogenation of $(\eta^5\text{-}C_5R_5)WM_3(CO)_{12}(\mu\text{-}H)$ (where M = Ru, Os; R = H, Me) proceeds by



CO loss and H_2 uptake to give $(\eta^5\text{-}C_5R_5)WM_3(CO)_{11}(\mu\text{-}H)_3$; the X-ray structure of $(\eta^5\text{-}C_5Me_5)WRu_3(CO)_{11}(\mu\text{-}H)_3$ has been solved. The results of solution NMR measurements are compared with the solid-state structure.[548]

Competitive addition and substitution reactions $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ with phosphines are reported. Reaction with $P(OMe)_3$ yields $(\eta^5\text{-}C_5H_5)WOs_3(CO)_9\{P(OMe)_3\}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ and $(\eta^5\text{-}C_5H_5)WOs_3(CO)_8\{P(OMe)_3\}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$, the result of addition and substitution, respectively. Full solution characterization, including variable-temperature ^{13}C NMR results, and structural determinations are presented. The ligand Ph_2PMe reacts to give only the corresponding substitution product.[549]

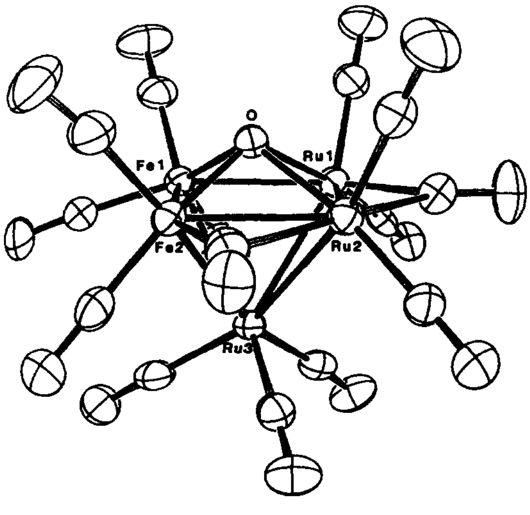
The synthesis and reactivity of $W_2RuPt(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_7(\eta^5\text{-}C_5H_5)_2$ are discussed. Reaction with PMe_2Ph

gives the corresponding mono-phosphine cluster, whose molecular structure has been determined by X-ray crystallography.[550]

A report documenting the coordination change of a methoxymethylidene ligand has appeared. The cluster $Ru_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}COMe)\{Rh(CO)_2PPh_3\}$ rearranges with CO loss to furnish $Ru_3Rh(CO)_{10}(\mu_2\text{-}H)_2(PPh_3)(\mu\text{-}COMe)$, which affords the anionic cluster $[Ru_3Rh(CO)_{11}(PPH_3)(\mu_2\text{-}H)_2]^-$ upon loss of the methyl group. The methyl group is lost, presumably as methane, when the μ-COMe ligated cluster is treated with K-Selectride. Structural determinations for the first two clusters accompany this report.[551] The reaction of $[Rh(CO)_4]^-$ with $Ru_3(CO)_{12}$, followed by acidification using H_3PO_4, yields the hydride cluster $Ru_3Rh(CO)_{12}(\mu_2\text{-}H)_3$, which has been examined by X-ray diffraction analysis and ^1H NMR spectroscopy. On the basis of computer-simulated space filling models and the absence of Rh-H coupling in the NMR spectra, it is proposed that the hydrides bridge adjacent ruthenium centers in a μ_2 fashion.[552] The structural and reactivity trends of $M_4(CO)_{12}H_x$ (where M = mixed Fe, Ru, Co, Rh systems) clusters have been described. In particular, metal-metal bond distances and ^1H NMR parameters are correlated.[553] The clusters $HRuCo_3(CO)_{12}$, $HRuCo_2Rh(CO)_{12}$, $HRuCoRh_2(CO)_{12}$, $HRuRh_3(CO)_{12}$, $H_2Ru_2CoRh(CO)_{12}$, and $H_2Ru_2Rh_2(CO)_{12}$ have been obtained as a mixture from the reaction between $[Rh(CO)_4]^-$ and $RuCo_2(CO)_{11}$. Characterization by ^1H NMR analysis is included.[554] The cluster $Ru_3Rh(\mu_2\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)$ reacts with the tripod ligand $MeC(CH_2PPh_2)_3$

to give $Ru_3(\mu_2\text{-H})\{\mu\text{-PhPCH}_2(Ph_2PCH_2)_2CMe\}(CO)_8$. Formation of the μ_2-phosphido system is accompanied by loss of benzene. The fluxional properties of the μ_2-phosphido system and crystal structure of the product cluster are discussed.[555]

The synthesis and solution structure of $[OsRh_4(CO)_{15}]^{2-}$ are reported. The mixed-metal cluster is reported to be isostructural with $[FeRh_4(CO)_{15}]^{2-}$ and $[RuRh_4(CO)_{15}]^{2-}$ on the basis of variable-temperature ^{13}C NMR measurements.[556] The oxo-bridged cluster $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-O})]^{2-}$ has been obtained from the reaction between $Ru_3(CO)_{10}(MeCN)_2$ and $[Fe_3(CO)_9(\mu_3\text{-O})]^{2-}$. Characterization by ^{17}O NMR spectroscopy and X-ray diffraction analysis is included.[557]



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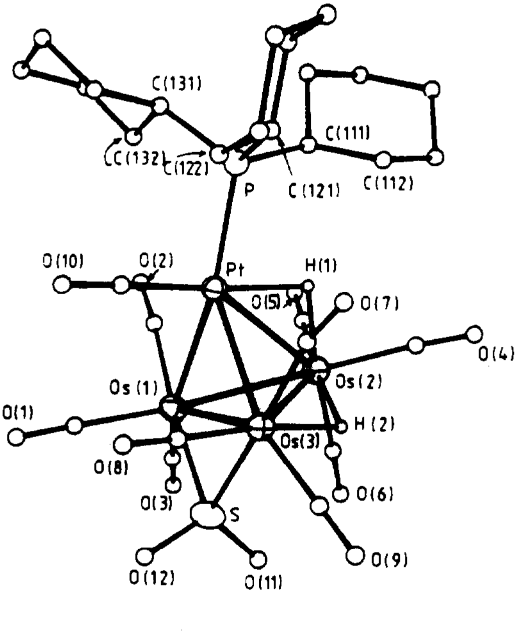
The synthesis and X-ray structure of $NiOs_3(CO)_9(\eta^5\text{-}C_5H_5)(\mu_2\text{-H})_2\{\mu_2\text{-Cu(PPh}_3)\}$ are reported. The cluster is composed of a $NiOs_3$ tetrahedron and displays an Os-Os bond that is bridged by the $Cu(PPh_3)$ fragment. Catalytic dehydrogenation results of this cluster supported on Chromosorb are discussed.[558]

2D ^{13}C EXSY measurements have provided information on CO fluxional pathways in $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ and $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$. Hydride fluxionality is discussed and activation energies for hydride exchange and CO exchange are presented.[559] SO_2 is allowed to react with $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ to furnish the 60-electron cluster $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PCy_3)$, whose structure has been determined by X-ray crystallography and NMR spectroscopy. The $\mu\text{-}SO_2$ ligand bridges an Os-Os bond in this tetrahedral cluster. Low-temperature ^1H NMR analysis indicates that the initially formed product of SO_2 addition is a butterfly cluster with a Pt-bound SO_2 ligand. Solution isomerization of the isolated product is discussed.[560]



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The unsaturated cluster $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ is allowed to react with excess 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane at 90 °C to give $Os_3Pt(\mu_3\text{-}S)_2(CO)_9(PCy_3)(\eta^1\text{-}C{=}C_6H_6Me_4)$ as the major product. The product, whose structure was established by X-ray crystallography, contains a spiked triangular Os_3Pt core with two μ_3-S groups ligating an Os_3 and Os_2Pt face; the terminal η^1-vinylidene ligand, formed by C=S bond cleavage of the thiokektene, is coordinated to an Os center.[561] A report on the facile conversion of a hydrido alkynyl ligand to a vinylidene ligand on a Ru_3Pt cluster has appeared. Included in this report are the synthesis, solution characterization, and X-ray crystal structures of several Ru_3Pt clusters.[562]

The effect of bidentate phosphine ligands on the framework structures of Ru_4Au_2 clusters has been investigated. The clusters $Ru_4Au_2(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_xPPh_2\}(CO)_{12}$ (where $x = 1\text{-}6$) have been synthesized and examined by variable-temperature ^1H and $^{31}P\{^1H\}$ NMR analyses in order to elucidate the dynamic behavior of gold atom site exchange. X-Ray structural results on the dppm- and the dppe-substituted clusters are included.[563] $\Delta G^{\neq}$ values for intramolecular metal core rearrangements in the clusters $Ru_4M_2(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_xPPh_2\}(CO)_{12}$ (where M = Cu, Ag; $x = 1\text{-}6$) have been calculated by using band-shape data obtained from variable-temperature $^{31}P\{^1H\}$ or ^1H NMR spectra. The ligand complexes with cis-$Ph_2CH{=}CHPPh_2$ and $Ph_2P(CH_2)_{1,2}AsPPh_2$ have been synthesized in the case of the Ru_4Cu_2 series and studied spectroscopically.[564]

Two equivalents of $ClCuP(CH_2Ph)_3$ have been allowed to react with $[Ru_4(CO)_{12}(\mu\text{-}H)_2]^{2-}$ in the presence of $TlPF_6$ to yield the known cluster $Ru_4Cu_2(\mu_3\text{-}H)_2(CO)_{12}\{\mu\text{-}P(CH_2Ph)_2(\eta^2\text{-}CH_2Ph)\}$ and $Ru_4Cu_2(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2$. The identity of this latter cluster has been established by X-ray crystallography.[565]

Group IB metal exchange reactions have been explored with the mixed-metal clusters $Ru_4M_2(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}$ (where M = Cu, Ag) by using $[Ag(MeCN)_4]^+$ and $AuCl(SC_4H_8)$. Yields of the corresponding replacement products range from 65 - 75%.[566]

The reactivity and solution dynamics of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2\text{-t-Bu})]_2(\mu_4\text{-}Hg)$ are reported. Phosphine substitution has been achieved under photochemical, thermal, and electron-transfer conditions.[567]

Variable-temperature solid-state ^1H NMR measurements on $[HRu_{10}(CO)_{24}C]^-$ reveal that the hydride ligand occupies an interstitial position within a tetrahedral site of a Ru cap at ambient temperatures. Hydride migration to an externally-bound position on or above one of the uncapped triangular cluster faces is observed as the temperature is lowered.[568] The cluster $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ has been isolated from the reaction between $[Ru_{10}(CO)_{24}C]^{2-}$ and $Hg(O_2CCF_3)_2$. X-Ray structural analysis shows that the cluster is composed of two tricapped octahedral Ru_9 cluster fragments, which are ligated by a Hg_3 triangular unit.[569]

The reactivity and polyhedral fluxionality in $Os_{10}C(CO)_{24}\{M(PR_3)\}_2$ (where M = Au, PR_3 = PMe_2Ph; M = Ag, PR_3

= PPh_3), $Os_{10}C(CO)_{24}\{Au(PEt_3)\}\{Ag(PPh_3)\}$, $[Os_{10}C(CO)_{24}\{Au(PMe_2Ph)\}]^+$, and $[Os_{10}C(CO)_{24}\{M(PR_3)\}]^-$ (where M = Au, PR_3 = PMe_2Ph; M = Ag, PR_3 = PPh_3; M = Cu, PR_3 = PPh_3) have been studied.[570]

The reaction between Y_3Ru and YI_3 at elevated temperatures yields $Y_7I_{12}Ru$ and $Y_6I_{10}Ru$. The latter complex has been structurally characterized and its bonding examined through the aid of charge-iterative extended Hückel MO calculations.[571] A report on the synthesis and magnetic properties of the dysprosium ruthenium phosphide cluster $Dy_5Ru_{19}P_{12}$ has been presented. The molecular structure of this cluster has been crystallographically established. Magnetic studies reveal a spontaneous magnetization occurs at low temperature, which is then followed by adherence to the paramagnetic Curie-Weiss law.[572]

V. Miscellaneous Chemistry

(a) Heterogeneous and Supported Complexes

Extended X-ray absorption fine structure (EXAFS) spectroscopy results are presented for $Ru_3(CO)_{12}$ supported on SiO_2. The first observed species is suggested to be $Ru_3(CO)_{10}(\mu\text{-}H)(OSi\equiv)_n$ {where n = 1, μ-OSi (bridging); n = 2, OSi≡ (terminal)} based on Ru-O(surface) bond length measurements. Air oxidation gives the geminal dicarbonyl species $Ru(CO)_2$(surface).[573] $Ru_3(CO)_{12}$ decomposition on an oxygen-free carbon support has been investigated by using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The hydride cluster $H_4Ru_4(CO)_{12}$ is observed when $Ru_3(CO)_{12}$ is thermolyzed under H_2. Ru/C systems have been obtained and explored as CO hydrogenation catalysts. The measured turnover frequencies suggest that small Ru crystallites function as the active catalysts.[574]

Osmium clusters trapped in the pores of zeolite Y (basic form) are reported to function as CO hydrogenation catalysts. The major organic products are derived from C_2-C_4 containing material. The catalytic activity and selectivity of this system show only minimal activity loss over time.[575]

The thermal decomposition of $Os_3(CO)_{12}$ on an oxygen-free carbon support has been examined by the DRIFTS method. Osmium crystallites have been prepared and explored as CO hydrogenation catalysts. The first-order rate constants of decomposition under He or H_2 have been measured and compared with literature values for nucleophilic substitution reactions in solution.[576] Results from temperature-programmed decomposition studies of $Os_3(CO)_{12}$ supported on SiO_2 and Al_2O_3 are reported. The grafted hydrido cluster $HOs_3(CO)_{10}(OM)$ (where M = Si, Al) was observed prior to the formation of the oxidized surface complex $[Os(CO)_x(OM_2)]_n$.[577]

The surface-bound clusters $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ have been obtained from $H_4Os_4(CO)_{12}$ on MgO. Extraction of these anions from the MgO support has been achieved by cation metathesis.[578] $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ have been synthesized from $Os_3(CO)_{12}$ adsorbed on MgO and H_2OsCl_6 adsorbed on MgO, respectively. Cation metathesis releases these clusters in high yield, making this surface-mediated reaction the method of choice for the synthesis of these clusters.[579]

DRIFTS analyses of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ thermally deposited on a clean carbon surface are presented. Included in this study are calorimetric measurements of the heats of CO adsorption and activation energies for both decarbonylation and methanation.[580] Isomerization reactions of 1,5-COD using SiO_2-supported $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ catalysts have been published.[581]

Ethanol dehydrogenation and ethylene hydration to acetaldehyde are reported for the supported cluster $(\eta^5-C_5H_5)NiOs_3(\mu-H)_2(CO)_9(\mu-CuPPh_3)$. Reaction mechanisms and the effect of different oxide supports are discussed.[582]

The surface chemistry of ruthenium/copper catalysts has been reviewed.[583] The clusters $RuCo_2(CO)_{11}$ and $HRuCo_3(CO)_{12}$ have been adsorbed onto hydroxylated aluminum oxide. The initially adsorbed species is $RuCo_2(CO)_{10}$(ads) in the case of the former cluster, which is converted to $RuCo_3(CO)_{12}^-$(ads, solvent) upon the addition of ether solvents. The latter cluster is adsorbed as the anion $RuCo_3(CO)_{12}^-$(ads). IR spectral data reveal that adsorbed clusters do not possess bridging carbonyl groups.[584] The grafted anionic clusters $[HFeM_3(CO)_{13}]^-$ (where M = Ru, Os) have been observed from the reaction between $H_2FeM_3(CO)_{13}$ and hydroxylated magnesia. The chemical reactivity of these grafted anionic clusters has been investigated *in vacuo* and in the presence of CO and H_2. Methanation and water-gas shift reactions are presented.[585]

The preparation and catalytic behavior of anchored ruthenium/rhodium complexes have been presented. Water-gas shift reactivity was explored through the use of a flow reactor system.[586] Mixed-metal ruthenium/platinum supported catalysts have been studied in hydrogenlysis, isomerization, and cyclization reactions using pentane. The supports used were MgO, SiO_2, and Al_2O_3.[587]

Bimetallic RuSn, RuPb, RuGe/Al_2O_3 catalysts have been prepared from Ru/Al_2O_3 and examined for their reactivity toward 2,2,3,3-tetramethylbutane.[588] Thiophene hydrodesulfurization activity and oxygen chemisorption for RuS_2 supported on γ-Al_2O_3 have been studied.[589] ZrO_2-supported ruthenium has been investigated by EPR spectroscopy. Two different paramagnetic ruthenium centers are observed. The interaction of CO, NO, and O_2 with this system is discussed.[590] An EXAFS study on the structural changes induced in the pretreatment of a TiO_2-supported iron/ruthenium catalyst has appeared.[591] The reaction of CO and NH_3 over Ru/X (where X = Al_2O_3, SiO_2, TiO_2) has been examined. Coordinated isocyanate was observed by IR spectroscopy for all of the supports except TiO_2.[592] The interaction of $Ru(acac)_3$ with γ-Al_2O_3 has been studied. No reaction was observed with coordinatively unsaturated Al^{3+} sites, which makes this system only the second known example where a metal acetylacetonate complex does not form a complex with γ-alumina.[593] X-Ray photoelectron spectroscopy (XPS) has been used to characterize the nature of the interaction between RuO_2 and Teflon. A "ruthenate-like" compound is proposed that involves the anchoring of Ru^{VIII} to the Teflon surface.[594] The results from acetaldehyde polymerization and decomposition experiments on Ru(001) have appeared.[595] A report on the general voltage-step responses and impedances of mixed-conductor films and diodes has been published. The system examined was based on the electron/anion mixed conductor $[Os^{II/III}ClO_4^-]$ and the electron/cation mixed conductor $[Ir^{II/III}$ H^+ or $-M^+$ oxide$]$.[596]

(b) CO and CO_2 Reductions

The role of metal carbonyl complexes as catalysts for CO hydrogenation has been reviewed. Unpromoted and halide-promoted ruthenium systems are discussed and recent developments using ruthenium catalysts are presented.[597]

CO_2 has been reduced to formic acid and formaldehyde with $[Ru^{III}(EDTA\text{-}H)Cl]^-$. The rates of product formation are presented for this stoichiometric CO_2 reduction reaction. A working mechanism is presented.[598]

(c) Oxidation Reactions

The complex formed from $[RuO_4]^-$ and 2-hydroxy-2-ethylbutyric acid has been shown to function as an oxidant toward alcohols. The oxidation can be made catalytic with added N-methylmorpholine N-oxide.[599] Oxidative cleavage of styrene by O_2 has been demonstrated with the catalysts $[RuCl(dpp)_2]^+$ and trans-$[RuCl_2(dpp)]$ {where dpp = 1,3-bis(diphenylphosphino)propane}. Kinetic data for benzaldehyde formation are presented.[600] Ruthenium-salen complexes have been prepared and examined as oxidation catalysts. Norbornene and cyclooctene are epoxidized with the ruthenium-salen complexes and the co-oxidant iodosylbenzene. Oxidative cleavage of the pendent double bond in styrene, which gives benzaldehyde, competes with epoxidation.[601]

Three reports on water oxidation by Ce^{IV} ions mediated by activated $RuO_2{\bullet}xH_2O$ have been published.[602,603,604] Liquid phase oxidation of alkanes and alkenes using the ruthenium heteropolyanion $[SiRu(H_2O)W_{11}O_{39}]^{5-}$ has been explored. The co-oxidants used in the study were potassium persulphate, sodium periodate, t-butyl hydroperoxide, and iodosylbenzene. The selectivity was observed to be dependent on the co-oxidant employed.[605] Efficient water cleavage by visible light has been reported by using a Ru-red/Nafion-coated CdS electrode. The relationship of this system to photosystem II is discussed.[606] The results of the RuO_4 oxidation of tricyclic methanohydroazulenes have been presented.[607] The oxidation of diisopropylidene-D-glucose to ulose has been achieved through an indirect electrooxidation procedure using RuO_4 and chloride as recycling mediators.[608]

The stoichiometric oxidation of benzylic and allylic alcohols to aldehydes and secondary alcohols to ketones has been observed with the oxo complex $[OsO_4]^-$. The vibrational and cyclic voltammetric data of $[OsO_4]^-$ are also presented and compared with that of $[RuO_4]^-$.[609] Two reports describing the osmylation results of substituted-methylenecyclohexanes have appeared.[610,611]

(d) Carbon-Carbon Bond Forming Reactions

The hydroformylation of ethylene using different ruthenium catalyst precursors has been explored by EXAFS. The effect of iodine and alkali metal halides on the reaction is addressed. While kinetic data reveal that mononuclear complexes function as the active catalyst at low metal concentrations, EXAFS data indicate that the ruthenium cluster $[Ru_3(CO)_{11}H]^-$ is the predominant species in active hydroformylation solutions.[612] The hydroformylation and hydroesterification of alkenes has been studied using hydrido carbonyl ruthenium complexes. Cooperative effects between acidic (H^+) and hydridic (H^-) ruthenium species are discussed.[613]

Ruthenium-catalyzed aldol and Michael reactions of activated nitriles are reported. Novel chemo- and stereoselective reactivity has been observed with the catalyst $RuH_2(PPh_3)_4$.[614] Coupling reactions between vinyl ketones and aldehydes have been reported with $RuH_2(PPh_3)_4$ as a catalyst. The role of an intermediate Ru-enolate and cross-coupling selectivity are discussed.[615]

Alkylation of aldehydes with allylic acetates has been obtained with added $Ru_3(CO)_{12}$ and $RuCl_3 \bullet xH_2O$ as catalysts. The homoallylic alcohols are formed in good yields.[616] A simple route to α,β-unsaturated aldehydes starting from prop-2-ynols is reported when $RuCl_2(PPh_3)_3$ is used as a catalyst.[617]

(e) Hydrogen Production and Hydrogenation Reactions

The catalytic production of hydrogen from ethanol has been demonstrated with $RuH_2(N_2)(PPh_3)_3$ in the presence of added base. Irradiation with visible light helps to drive the reaction by promoting the release of CO. The mechanism for hydrogen production is presented.[618] The hydrogenation activity of $RuCl_2(PPh_3)_3$ attached to polysiloxane-phosphine ligands has been reported. Hydrolytic condensation of

$(EtO)_3Si(CH_2)_nPPh_2$ (n = 2,3) with $Si(OEt)_4$ affords the solid polysiloxane ligands used in this study. 1-Hexene is isomerized during the catalytic reaction and the internal alkenes formed are hydrogenated at the same rate as 1-hexene. Catalyst recycling studies are described.[619]

Unsaturated aldehydes have been reduced to the corresponding allylic alcohols using $RuCl_2(m\text{-}SPPh_3)_2$ (where m-$SPPh_3$ = m-sulphophenyldiphenylphosphine) and HCO_2Na/H_2O. The reductions exhibit high product yields and short reaction times.[620] The hydrogenation activity of $RuO_2{\bullet}xH_2O$ has been explored. Hydrogen evolution using water as a feedstock is observed only after $RuO_2{\bullet}xH_2O$ has been substantially reduced.[621]

(f) Other Catalytic Reactions

Trimethylsilylethene reacts with triethylsilane in the presence of the catalyst precursor $Ru_3(CO)_{12}$ to give (E)-1,2-bis(trimethylsilyl)ethene and (E)-1-triethylsilyl-2-trimethylsilylethene. The yield of the former product is greatly increased by using an excess of trimethylsilylethene. Use of other hydrosilanes provides a general synthesis for the formation of (E)-1,2-disilylethenes.[622] In a separate report, the synthesis of 1,2-bis(silyl)ethenes has been presented. The catalysts used in these coupling reactions were $RuCl_3{\bullet}3H_2O$ and $RuCl_2(PPh_3)_3$.[623] A report describing the reduction of nitroarenes to anilines by CO and H_2O has appeared. Pertinent intermediates and a multistep catalytic mechanism are discussed.[624]

N-Substituted aminoalcohols have been cyclized to N-substituted azacycloalkanes in good yields using the catalyst $RuCl_2(PPh_3)_3$.[625] The clusters $Ru_3(CO)_{12}$, $[HRu_3(CO)_{11}]^-$, and $[H_3Ru_3(CO)_{12}]^-$ have been observed to catalyze the carbonylation of cyclic amines. Piperidine, 3-methylpiperidine, pyrrolidine, morpholine, and piperazine all react to give the corresponding formamides in the presence of CO or CO/H_2.[626] Catalytic N-alkylation of amines by alcohols has been documented. The catalysts employed in this study were $RuCl_3 \bullet 3H_2O$ and $Ru_3(CO)_{12}$. A mechanism that involves an alcohol dehydrogenation step and amine attack at a ruthenium coordinated aldehyde is presented.[627] Finally, catalytic N-alkylation of amides, imides, and lactams by alcohols has been investigated. The generality of these reactions make them attractive for the large-scale production of commodity chemicals.[628]

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