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Annual survey of ruthenium and osmium for the year 1991 *

Michael G. Richmond

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

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Contents

1. Dissertations

Singly labeled ruthenium(II) polypyridine cytochrome c complexes have been synthesized and examined in electron transfer reactions involving the ruthenium(II) center and heme center [1]. The photophysics and photochemistry of the ruthenium(II) polypyridyl complex $[Ru(terpy)(bpy)(MeCN)]^{2+}$ have been explored. The observed chemistry is similar to that of $[Ru(terpy)_2]^{2+}$ [2]. The synthesis of ruthenium(II) and osmium(II) polyaza cavity-shaped molecules has been reported. All of the compounds have been fully characterized by spectroscopic and voltammetric techniques [3]. Intervalence electron transfer in binuclear ruthenium complexes has been investigated as a possible model for long-range biological electron transfer. Included in this dissertation are spectroscopic data (IR, NMR, FAB-MS) and cyclic voltammetric data for the new compounds [4]. Solvent effects in D_3 ruthenium(II) polypyridine compounds have been studied by using picosecond resonance Raman spectroscopy. The extent of electron localization in the MLCT as a function of solvent viscosity is reported [5]. Outer-sphere ruthenium(III)–titanium(III) electron transfer reactivity was probed by examining the reaction between $[Ru(NH_3)_5(py)]^{3+}$ and $[Ti(acac)]^{2+}$ and $[Ti(acac)_2]^+$. The

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rates associated with the electron-transfer reactions are discussed with respect to symmetry and electron-donor/electron-acceptor energy mismatch [6]. Ion-pairing interactions on charge propagation within a Nafion film containing $[Os(bpy)_3]^{3+/2+}$ have been studied [7]. Spectroelectrochemical results are presented for $Ru(bpy)_2(CN)_2$, $[Ru(bpy)_2CN]_2CN^+$, $[Ru(bpy)_2]_2dpp^{4+}$, and $[Ru(bpy)_2]_2dpq^{4+}$ [8]. Olefin oxidation has been explored by using the oxo complex $[Ru(bpy)_2(py)(O)]^{2+}$. The oxidation reaction exhibits a first-order dependence on both the oxo complex and olefin. A large primary isotope effect ($k_H/k_D = 18$) is reported for cyclohexene oxidation. The kinetics for ethylbenzene and cumene oxidation by *trans*-$[Ru(terpy)(O)_2(H_2O)]^{2+}$ are included [9].

Ruthenium-edta complexes were synthesized and examined for their optical and electrochemical properties. The reduction of $(edta)_2Ru_2^{III,IV}$ to $(edta)_2Ru_2^{IV}$ is insensitive to added acid, suggesting that H_2O is not coordinated to either dimer [10]. The complexes $[Ru^{II}(hedta)]^-$, Ru^{II}(N,N′-dimethyledda), and $[Ru_2^{II}(ttha)]^{2-}$ have been synthesized and examined in redox reactions with O_2, H_2O_2, and TBHP; these same complexes were also studied for their coordination chemistry with ligands related to uridine and cytidine nucleosides [11].

An artificial nuclease containing ruthenium has been synthesized and examined for its properties in double-stranded cleavage of DNA, site-specificity of the cleavage reaction, and strand scission sequences [12]. Probes for nucleic acid structure have been prepared from ruthenium(II) and 9,10-phenanthrenequinone (phi). The physical and photophysical properties of the phi complex are included in this report [13].

The synthesis and spectroscopic characterization of a ruthenium porphyrin are described from the reaction between $Cp^*Ru(MeCN)_3(OSO_2CF_3)$ and Zn(II) porphyrins. It has been established that the Cp*Ru moiety is situated above the porphyrin plane via nitrogen coordination [14]. The X-ray crystal structure of $(OEP)Ru(CO)(H_2O)$ has been presented [15]. Several new osmium(VI) oxo, imido, and nitrido compounds have been synthesized and examined for their reactivity toward CO. The X-ray crystal structure of $Os(O)(CH_2SiMe_3)_4$ is reported [16]. The tridentate oxygen donor ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ has been used as an ancillary ligand in the preparation of new ruthenium carbonyl complexes, which have been further functionalized to solvent and alkoxide derivatives. The high stability of these derivatives is described [17]. The synthesis and characterization of new ruthenium and osmium catecholate and semiquinonate complexes have appeared. X-Ray diffraction, voltammetric, and spectroscopic data are presented, and the extent of charge distribution in several of the analogues is discussed [18].

The synthesis of new ruthenium complexes possessing sterically hindered thiolate ligands has been published. Data obtained from ^1H NMR spectroscopy, X-ray crystallographic, and FAB-MS analyses are presented along with a discussion of the potential relevance of these systems as model systems for coordinatively unsaturated metal sulfide surface species [19]. Ruthenium and osmium complexes possessing the macrocycle ligand $[9]aneS_3$ have been prepared and examined by spectroelectrochemical methods. Several X-ray crystal structures are included in this dissertation [20].

The reactivity of ruthenium(II) hydrides with alkenes and/or alkynes and in hydrogenation reactions is reported. Dissociative hydrogen loss from $Ru(CO)_2(H)_2(PMe_2Ph)_2$, followed by alkene capture, gives the corresponding alkene complex. Three different geometries have been observed for the alkene complexes, the specific geometry being dependent on the initial hydride complex and alkene used [21]. Several ruthenium phosphine complexes containing Ru–C, Ru–N, and Ru–O bonds have been examined in thermolysis studies [22]. NMR and IR characterization of $RuH_4(PPh_3)_3$ is discussed. Facile dimerization of $RuH_4(PPh_3)_3$ has been shown to give $(Ph_3P)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ [23].

Infrared spectroelectrochemical data on the photoinduced disproportionation of $[Cp^*Ru(CO)_2]_2(PF_6)$ are presented [24]. The use of ultrasound in the synthesis of arene-ruthenium(II) and arene-ruthenium(0) complexes is described. Reactivity studies of the new complexes are included [25]. A study describing the reaction between the thioalkyne $MeSC{\equiv}CSMe$ and $CpRu(PMe_3)_2Cl$ to give initially $[CpRu(PMe_3)_2(MeSC{\equiv}CSMe)]^+$, followed by rearrangement to the vinylidene complex $[CpRu(PMe_3)_2{=}C{=}(SMe)_2]^+$, has appeared. The reactivity of the latter complex toward electrophiles has been thoroughly examined [26]. The synthesis and cycloaddition reactions of the proparagyl ruthenium complex $CpRu(CO)_2CH_2C{\equiv}CPh$ and the allenyl ruthenium complex $CpRu(CO)_2CH{=}C{=}CH_2$ are reported. The utility of these complexes in the stepwise construction of higher nuclearity cluster compounds is stressed [27].

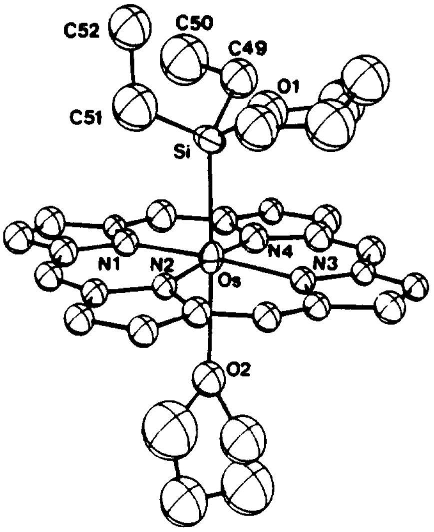
The reaction between $Ru_3(CO)_{12}$ and $[CpFe(CO)_2]^-$ or $[Re(CO)_5]^-$ proceeds with the formation of the cluster adduct $[MRu_3(CO)_{11}]^-$ as determined by infrared stopped-flow spectroscopic measurements. The kinetics and mechanistic schemes for these reactions are discussed [28]. Several di- and trinuclear ruthenium cluster compounds with variable oxidation states have been synthesized and structurally characterized. The structure and bonding of the new compounds are discussed with respect to theoretical MO calculations [29]. Functionalization studies of $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$ using $MPPh_3Cl$ (where M = Cu, Ag, Au) are presented along with phosphine ligand substitution data for the resulting mixed-metal clusters [30]. The synergistic effects for the carbonylation and reduction of nitrobenzene using $Fe_3(CO)_{12}/Ru_3(CO)_{12}$ mixtures are reported [31]. Di- and trinuclear ruthenium complexes possessing a substituted 1,2-bis(phosphine)benzene ligand have been prepared. The thermolysis reactions of many of the isolated complexes have been explored and the catalytic hydrogenation reactivity investigated [32]. Homo- and heterobinuclear ruthenium phosphido-bridged complexes have been synthesized and spectroscopically characterized. The site selectivity of hydride and alkyllithium attack in these complexes and the redox chemistry have been explored [33]. The synthesis and reactivity of ruthenium and osmium clusters containing amine and ynamine ligands are reported [34]. $H_2Ru_6(CO)_{18}$ is reported to decarbonylate spontaneously to $H_2Ru_6(CO)_{17}$. The reactivity of both clusters toward H_2, CO, and KH is outlined. The reaction between $H_2Ru_4(CO)_{12}$ and $BH_3 \cdot THF$ is reported to give the dihedral butterfly cluster $HRu_4(CO)_{12}BH_2$, which has been fully characterized by IR and NMR analyses in addition to X-ray diffraction analysis. In depth reactivity studies of other ruthenium cluster compounds are included [35]. Supported metal clusters have been examined by DRIFTS and EXAFS spectroscopies [36].

A report dealing with solid-state ruthenium oxide chemistry has appeared [37]. Ruthenium ion-exchanged zeolites have been probed for catalytic activity in ammonia synthesis. Ruthenium metal on a zeolite support gave ammonia using H_2 and N_2 at high temperature [38]. The interaction of water and perfluorodiethyl ether with Ru(001) is reported. These materials were studied in order to address the importance of humidity on the surface–lubricant bonding properties displayed by perfluoropolyether lubricants [39]. The preparation and use of a mixed-valence ruthenium cyanide electrode are described [40]. A report on Re/Os isotope geochemistry has appeared [41].

2. Mononuclear complexes

2.1. *Organometallic porphyrins*

Molecular recognition of racemic phosphines has been demonstrated by using ruthenium picket-fence porphyrins bearing optically active α-methoxy-α-(trifluoromethyl)phenylacetyl groups. The studies reveal that a chiral ruthenium porphyrin can function as a haemoprotein model capable of chiral recognition [42]. Electron-transfer sites in (OEP)Ru(CO)L (where L = axial ligand) have been examined by electrochemical techniques. The observed oxidations are ring centered while the site of the two observed reductions is shown to be dependent on the nature of the solvent and the sixth axial ligand [43]. The reaction between $[(TPP)Ru(CO)]^{-\cdot}$ and MeI has been shown to give a methylated ruthenium(II) carbonyl chlorin. Characterization of this product by *in situ* UV-visible and FTIR spectroscopy, spectroelectrochemistry, FAB-MS, and voltammetric techniques is described [44]. Reaction of $[Ru(TPP)]_2$ with HX or I_2 gives the paramagnetic complex $Ru(TPP)X_2$ (where X = halide). The bromo analog was structurally characterized by X-ray diffraction analysis. The diphenyl derivative, $Ru(TPP)(Ph)_2$, is shown to thermally decompose to Ru(TPP)Ph [45]. The synthesis, reactivity, and characterization of the donor-stabilized silylene complexes $(TPP)Os{=}SiR_2 \cdot THF$ are presented. Included in this study is the X-ray structure of the diethyl derivative [46].



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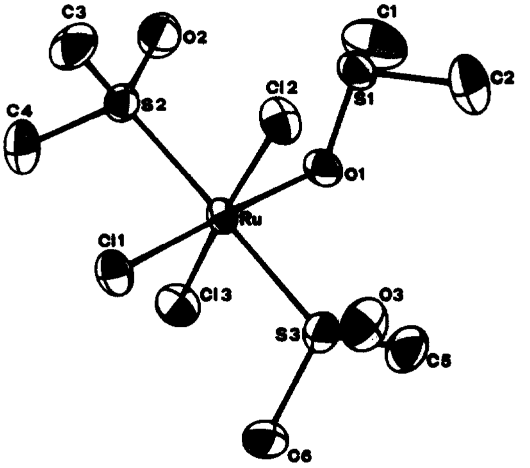
The kinetics and mechanism of C–H bond and alkene oxidation by $[Ru^{VI}LO_2]$ (where L = *para*-substituted TPP) are presented. Tertiary C–H bonds of alkanes are found to react, whereas secondary C–H bonds were essentially inert. A large kinetic isotope effect (k_H/k_D) of *ca.* 12 was found for the allylic oxidation of cyclohexene when $Ru(TPP)(O)_2$ was used [47]. The infrared spectral data for the base-free dioxygen adducts of ruthenium(II) and osmium(II) porphyrins are reported [48]. The isolation and solution characterization of 4-fluorophenylimido osmium(VI) porphyrins are discussed [49]. The synthesis and characterization of a nitrogen-bridged, cofacial metallodiporphyrin complex has been described. The chemical oxidation/reduction behavior of this unique complex has been explored with respect to its potential to function as a model system for dinitrogen reduction [50]. The porphyrin complex $[CoP\{pyRu(NH_3)_5\}_4]^{8+}$ has been obtained at a graphite electrode. Multiple intramolecular electron transfer-reactions involving dioxygen reduction have been demonstrated [51]. Electron transfer from a surfactant-like zinc porphyrin to covalently attached RuO_2 is described [52]. Several covalently linked *meso*-tris(octyloxyphenyl)porphyrin–RuO_2 composite clusters have been examined in photoinduced intramolecular electron-transfer reactions [53].

2.2. Halides

The reactions of $RuCl_2(DMSO)_4$ and $RuCl_2(PPh_3)_3$ with the ligands α,α'-bis[bis{2-(diphenylphosphino)-ethyl}amino]ethane, α,α'-[bis{2-(diphenylphosphino)-ethyl}amino]ethane, and α,α'-bis{2-(diphenylphosphino)}-*m*-xylene have been examined. The resulting products have been separated by column chromatography and spectroscopically characterized [54]. The use of $RuBr_2(DMSO)_3$ as a precursor for the synthesis of ruthenium(II) complexes is described. This same starting material is also reported to function as a catalyst for PPh_3 oxidation by molecular oxygen [55]. *cis*- and *trans*-$RuCl_2(DMSO)_4$ have been allowed to react with monodentate nitrogen donor ligands; the resulting complexes have been characterized by solution and electrochemical methods. This report includes the X-ray crystal structures of *cis,fac*-$RuCl_2(DMSO)_3(NH_3)$ and *trans,cis,cis*-$RuCl_2(DMSO)_2(NH_3)_2 \cdot H_2O$ [56]. The ruthenium(III) complexes $[(DMSO)_2H]$[*trans*-$Ru(DMSO)_2Cl_4$] and *mer*-$Ru(DMSO)_3Cl_3$ have been prepared and characterized by X-ray crystallography. Cyclic voltammetric measurements indicate that the latter complex exists as a mixture of S- and O-bound (DMSO) isomers. Digital CV simulation allowed for the extraction of the isomerization rate constants [57].

$[RuX_6]^{2-}$ has been used as a starting material in the preparation of benzonitrile- and acetonitrile-substituted complexes, for which the cyclic voltammetric data and optical charge-transfer spectra have been measured [58]. Ligand-additivity effects on electrode potentials and charge-transfer spectra have been published [59]. The synthesis and redox chemistry of the ruthenium(III) isonitrile/halide complexes $[RuX_4(CN^tBu)_2]^-$ (where X = Cl, Br) are reported [60].

Hydride complexes are observed in the reaction between $Ru_2Cl(\mu\text{-}O_2CR)_4$ and PPh_3 in boiling 2-methoxyethanol [61]. The reaction between $RuCl_3$ and H_4edta in HCl yields the antitumor complex $[Ru(H_3edta)Cl_2] \cdot 4H_2O$, which has been structurally characterized by X-ray crystallography and shown to possess a stable Ru–O=COHR (glycine) bond [62]. Additive and non-additive ligand effects in the series $[OsBr_6]^{3-}$, $[OsBr_5(CO)]^{2-}$, and *trans*-$[OsBr_4(CO)_4]^-$ and in the series *trans*-$[OsBr_4(MeCN)_2]^-$, *trans*-$[OsBr_4(MeCN)(CO)]^-$, and *trans*-$[OsBr_4(CO)_2]^-$ are described [63]. The vibronic structure of mixed-ligand osmium(IV) complexes is reported [64]. PMe_3 reacts with $[Os(PPh_3)_3X_2]$ and *trans*-$[OsL_4X_2]$ (where L = PMe_2Ph, $AsMe_3$, $SbPh_3$, py; X = Cl, Br) to give *trans*-$[Os(PMe_3)_4X_2]$ [65]. *cis*-$[Ru(IIV)LCl_2]^+$ (where L = N,N′-dimethyl-N,N′-bis{2-pyridylmethyl}ethylenediamine) has been obtained from $[RuCl_5(H_2O)][K]_2$ and L. Ag^+ ions oxidize the cation to the dication in aqueous solution. The X-ray crystal structure of this dication is included in this report along with redox chemistry of both products [66]. The X-ray crystal structure of chloro[(1–3-η : 6–8-η)-2,7-dimethyloctadienediyl](semicarbazide)ruthenium(IV) has appeared [67].



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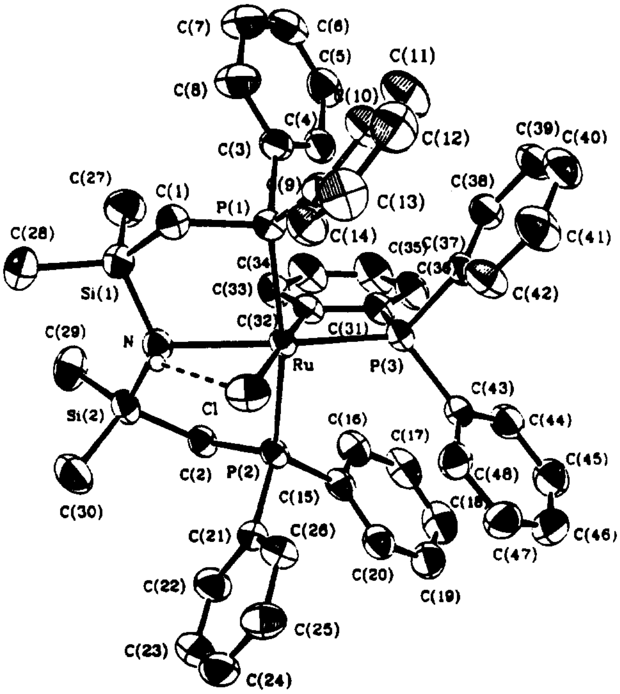
1,3-Dioxolanes and 1,3-dioxanes react with alcohols in the presence of $RuCl_2(PPh_3)_3$ to yield 2-R,R′-1,3-dioxolanes and 2-R,R′-1,3-dioxanes, respectively [68]. The reaction between $RuCl_3 \cdot H_2O$ and 4-methylbuten-2-ones gives stereoisomeric bis(1-oxapentadienyl)ruthenium(II) complexes [69]. The use of $RuCl_2(PPh_3)_3$ in the rearrangement of the natural cyclic peroxide G to ene pentadione and to a bicyclic hemiacetal butenolide is reported [70]. *cis*-Hydroruthenation of alkynes has been observed in the reaction between $RuCl(H)(CO)(BSD)(PPh_3)_2$ and alkynes [71]. The carbene complex $Ru(=CH_2)Cl(NO)(PPh_3)_2$ has been obtained from the reaction of $RuCl(NO)(PPh_3)_2$ with diazomethane. The reactivity of the carbene complex with electrophiles, alkynes, and alkenes has been investigated. The X-ray crystal structure of $Ru(CH_2PPh_3)(\eta^2-C_2F_4)(Cl)(NO)(PPh_3)$, which was obtained from $Ru(=CH_2)Cl(NO)(PPh_3)_2$ and tetrafluoroethylene, is included [72]. Cyclopentadiene desilylation and formation of Cp_2Ru is observed when $RuCl_3 \cdot 3H_2O$ and silylated cyclopentadienes are allowed to react under reflux in alcohol solvent [73]. The ruthenium amide complex $RuCl(PPh_3)[N(SiMe_2CH_2PPh_2)_2]$ has been prepared from $RuCl_2(PPh_3)_3$ and $LiN(SiMe_2CH_2PPh_2)_2$. Reaction of the amide complex with H_2 affords two isomeric amine-hydride complexes possessing the formula $RuCl(PPh_3)H[NH(SiMe_2CH_2PPh_2)_2]$. *ortho* metallation reactions are observed when the amide complex is treated with RLi and RMgX reagents. The X-ray crystal structure of $RuCl(C_6H_4PPh_2)[NH(SiMe_2CH_2PPh_2)_2]$, which exhibits an *ortho*-metalated phenyl group, is reported [74].

2.3. Hydrides

Evidence is presented that supports the insertion of acetone into the Os–H bond of $OsH(Cl)(CO)(P^iPr_3)_2$ along with a working mechanism for the hydrogen transfer from alcohols to ketones. Kinetic data for the hydrogen transfer from 2-propanol to cyclohexanone are reported with the catalyst complex $OsH_2(CO)(P^iPr_3)_2$ [75]. $OsCl_3 \cdot xH_2O$ gives the six-coordinate complex $OsH_2(Cl)_2(PR_3)_2$ (where R = ^{i}Pr, ^{t}Bu$_2$Me) in the presence of refluxing 2-propanol and PR_3. Characterization by solution measurements and X-ray diffraction data for the P^iPr_3 complex are discussed. CO reacts with $OsH_2(Cl)_2(^tBu_2PMe)$ while reaction of the same dihydride with excess PMe_3 affords *cis*-$Os(Cl)_2(PMe_3)_4$. The reactivity of these halide complexes toward hydridic reducing agents is discussed. The catalytic hydrogenation of olefins and dienes using the P^iPr_3 complex is described [76].



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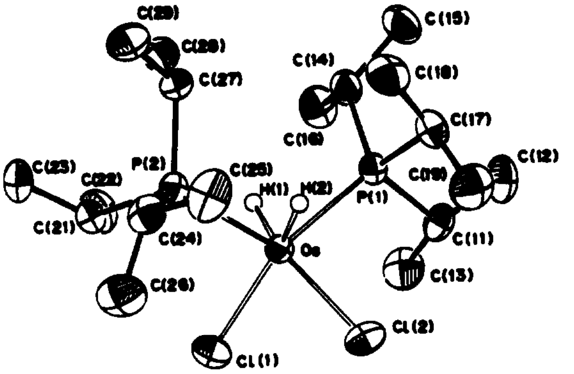

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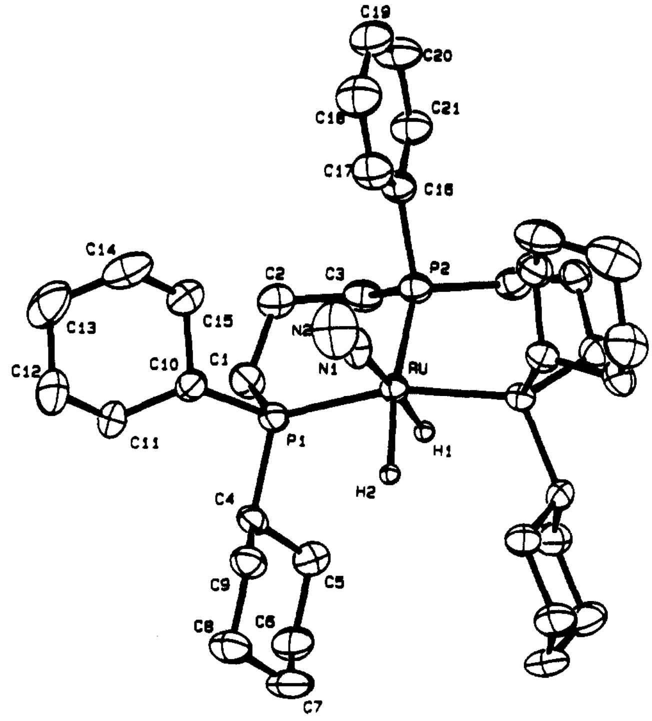
Alkyne insertion into the Ru–H bond of the ruthenium(II) carboxylate complexes $RuH(CO)(O_2CR)(PPh_3)_2$ (where R = Me, Et, Pr, *p*-tolyl, *p*-anisole) is observed at reflux in benzene solvent. The resulting vinylic complex is reported to arise by *cis*-addition of the Ru–H bond to the triple bond [77]. The regioselectivity of conjugated enyne insertion into the Ru–H bond of $RuH(Cl)(CO)(PPh_3)_3$ has been explored [78]. Ligand substitution by acetonitrile in $RuH(Cl)(CO)(PPh_3)_3$ gives the solvent complexes $RuH(Cl)(CO)(MeCN)(PPh_3)_2$ and $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$, as demonstrated by *in situ* NMR studies. The latter complex is isolated in high yields when the starting complex is treated with $NaBF_4$ in acetonitrile. The labile acetonitrile groups react with two-electron donor ligands to ultimately give $[RuH(CO)L_2(PPh_3)_2]^+$. Reaction of the bis(acetonitrile) complex with $[Co(CO)_4]^-$ yields the heterobimetallic complex $Ru(CO)_3(PPh_3)(\mu_2-PPh_2)Co(CO)_3$. Hydroformylation catalysis of 1-hexene is also reported when the bis(acetonitrile) complex was employed as a catalyst precursor [79]. The formation of σ-alkynylruthenium complexes has been observed when $[RuH(CO)(py)_2(PPh_3)_2]^+$ and alkynes have been allowed to react at room temperature. The X-ray crystal structure of $[Ru(CO)(C\equiv CC_6H_{13})(py)_2(PPh_3)_2]^+$ is included in this report [80].

Reaction of the hydride complex $RuH_2(\eta^2-H_2)(Cyttp)$ with CO_2 affords the formate complex $RuH(O_2CH)(Cyttp)$. The reaction is believed to proceed via the unsaturated intermediate $RuH_2(Cyttp)$.



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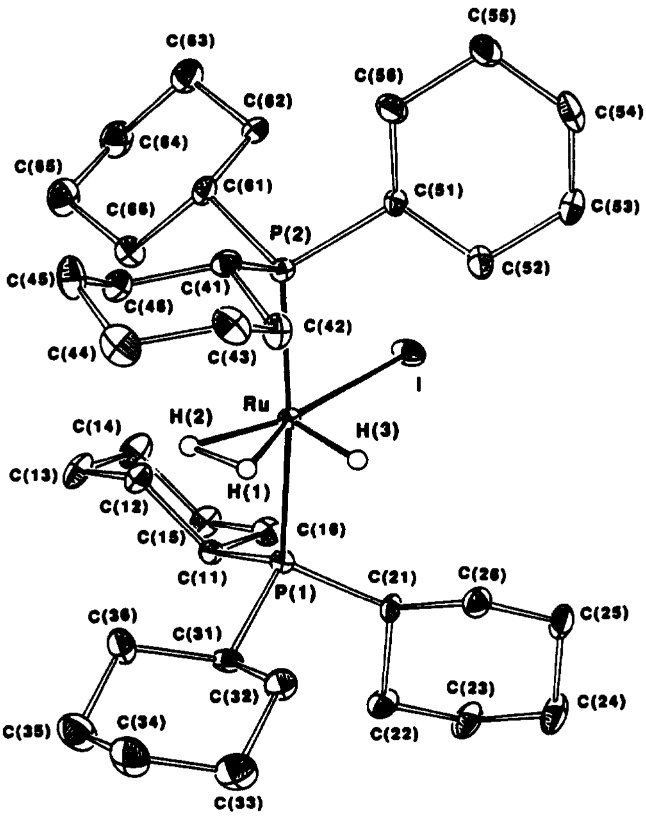
Product characterization by IR, ^1H and ^{31}P NMR spectroscopies suggests that the formate moiety is bound to the ruthenium in a bidentate fashion. The reactivity of other CO_2-like molecules with $RuH_2(\eta^2\text{-}H_2)$(Cyttp) is reported [81]. RuH(Cl)(Cyttp) reacts with PhC≡C–C≡CPh to yield initially *syn,mer*-$RuCl(\eta^3\text{-}PhC_3CHPh)$(Cyttp), followed by isomerization to the *anti,mer* isomer. The reactivity of other alkynes with RuH(Cl)(Cyttp) and RuH_4(Cyttp) is described and mechanisms for the observed alkyne coupling products are presented [82]. The hydride complex $RuH(BH_4)$(Cyttp) has been isolated from the reaction of $RuCl_2$(Cyttp) and $NaBH_4$. Use of $LiAlH_4$ gives the corresponding monohydride complex RuHCl(Cyttp), while the molecular hydrogen complex $RuH_2(\eta^2\text{-}H_2)$(Cyttp) may be obtained when NaH is used as the source of hydride and the reaction is carried out under H_2(g). Ligand substitution of H_2 from this latter complex to give RuH_2L(Cyttp) is described. The X-ray crystal structure of $RuH_2(N_2)$(Cyttp) is reported [83].

The chemoselective reduction of α,β-unsaturated alcohols to allylic alcohols has been demonstrated when the nonclassical trihydride $[RuH(\eta^2\text{-}H_2)(tdpep)]^+$ is used as the reducing agent. Also reported is the reaction between $[RuH(\eta^2\text{-}H_2)(tdpep)]^+$ and acyclic ketones (aldehydes), which yields the carboxylate complexes $[Ru(O_2CR)(tdpep)]^+$ [84]. The reaction between $RuCl_2$(tdpep) and various hydridic reducing agents is described. The role played by the tdpep ligand in the stabilization, solution fluxionality, and structure of the new ruthenium complexes is discussed [85]. The molecular hydrogen complexes $[RuH(\eta^2\text{-}H_2)P_4]^+$ {where P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$} have been examined for their reactivity in selective alkyne hydrogenation reactions. The X-ray crystal structure of $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]^+$ is also included in this report [86]. ^1H and ^{31}P NMR studies of $RuH_4(PPh_3)_3$ and its isotopomers have been conducted in order to address the nature of the ancillary Ru–H bonds [87]. $RuH_2(PPh_3)_3$, formed by H_2 loss from $RuH_4(PPh_3)_3$, is shown to dimerize and give $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$. The same dihydride reacts with ethanol to yield $RuH_2(PPh_3)_3(CO)$ as a result of ethanol decarbonylation [88]. Kinetic data for H_2 loss from the polyhydride complexes $[RuH_3(PPh_3)_3]^-$, $RuH_4(PPh_3)_3$, $[RuH_5(PPh_3)_3]^+$, $OsH_4(p\text{-tol}_3P)_3$, and $[OsH_5(p\text{-tol}_3P)]^+$ are reported. H_2 dissociation is facilitated by protonation and is diminished in going from a given ruthenium complex to the analogous osmium complex [89]. Several new cyclopentadienylruthenium complexes containing a dihydrogen ligand have been synthesized and their pKa values measured [90]. The synthesis, X-ray structure, and extended Hückel MO calculations of the 16-electron dihydrogen complex $RuH_2(\eta^2\text{-}H_2)(PCy_3)_2$ have appeared. Reaction of this latter complex with either PhI or MeI yields the iodo complex $RuH(\eta^2\text{-}H_2)I(PCy_3)_2$. An analogous reaction between the dihydride and CH_2Cl_2 gives the chloro complex [91].

A rapidly spinning $\eta^2\text{-}H_2$ ligand with a long H-H distance (*ca.* 0.99 A) has been reported for *trans*-$[OsH(\eta^2\text{-}H_2)(dppe)_2]^+$. Other supporting evidence includes a short T_1 value for the $\eta^2\text{-}H_2$ ligand in the complex *trans*-$[OsH(\eta^2\text{-}H_2)(dppe\text{-}d_{20})_2]^+$ and a large $^1J_{HD}$ value in the isotopomer *trans*-$[OsH(\eta^2\text{-}HD)(dppe)_2]^+$ [92]. $OsH_4(p\text{-tolyl}_3P)$ and related isotopomers have been investigated by T_1 measurements as a function of temperature. The contributions to the relaxation rates of the hydride ligands are influenced by the neighboring hydrides (62%) and the *ortho* protons of the PR_3 ligand (33%) [93]. The synthesis and ^1H NMR relaxation data for $[MH(\eta^2\text{-}H_2)(R_2PCH_2CH_2PR_2)_2]^+$ (where M = Ru, Os; R = Et, Ph) have been reported. The formation of the dihydrogen complexes and the metal dihydrogen interaction are thoroughly discussed [94].

2.4. Phosphines

The homogeneous carbonylation of nitroaromatics has been modeled by using $Ru(dppe)(CO)_3$. Two relevant intermediates have been characterized and data are presented on the carbamate-forming step. The



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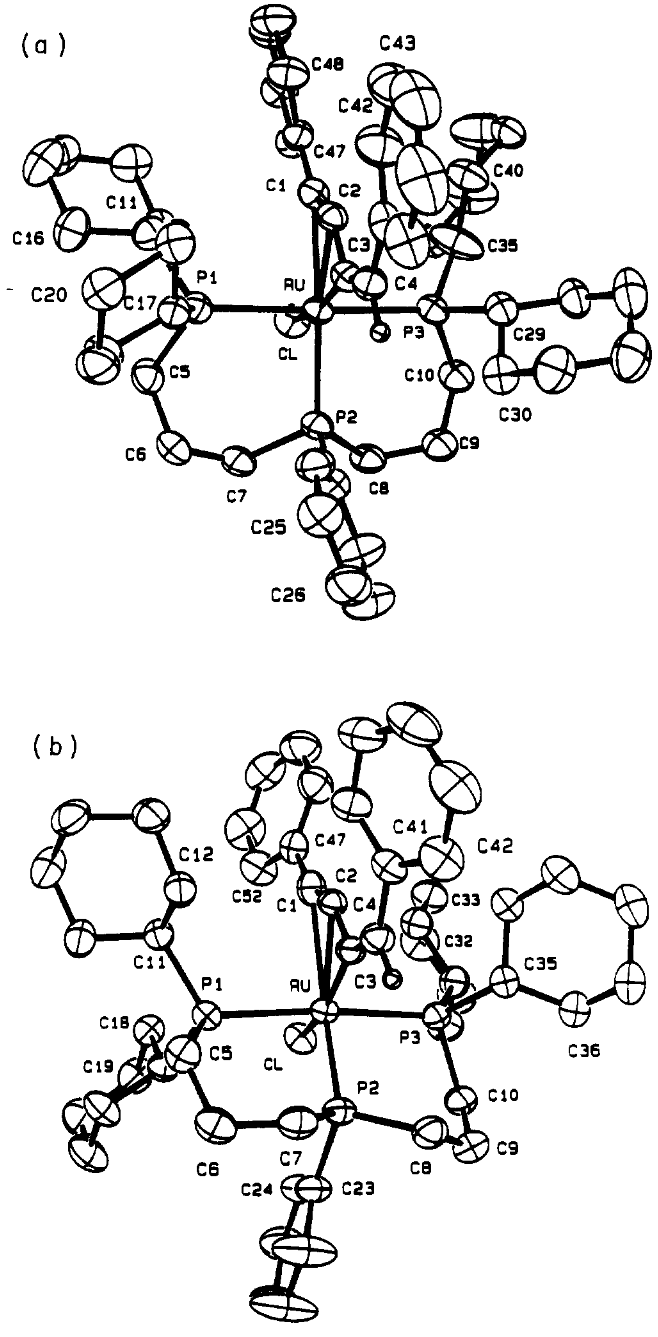
molecular structure of Ru[C(O)N(p-ClC$_6$H$_4$)O](dppe)(CO)$_2$ accompanies the report [95]. Cyclic voltammetric data are reported for a series of Ru(PR$_3$)$_2$(CO)$_3$ complexes. A reversible oxidation (0/+1), whose potential is dependent on the basicity of the ancillary phosphine, is observed for each complex. The radical cations were also characterized by IR and ESR spectroscopy [96]. *cis*-RuCl$_2$(dppm)$_2$ reacts with HC≡CCR$_2$OH and HC≡CC(Me)=CH$_2$ to give the allenylidene complexes *trans*-[RuCl(dppm)$_2$(=C=C=CR$_2$)]$^+$, while the same reaction with HC≡C–C≡CC(Ph)$_2$OSiMe$_3$ yields a new allenylidene complex that has experienced C–H bond activation [97]. A structural study of [Os(EtSCS$_2$)$_2$(PPh$_3$)$_2$]$^{0/1+}$ that deals with isomeric coordination geometries by valence state has appeared [98]. The results of diastereoselective hydrogenation of methyl 2-benzamidomethyl-3-oxobutanoate using [RuI{(R)-binap}(p-cymene)][I] are reported [99]. The synthesis and catalytic hydrogenation activity of Ru(Cl)$_2$(PPh$_3$){(S)-biphemp} and RuH(η^2-BH$_4$)(PPh$_3$){(S)-biphemp} have been described [100]. The X-ray structure of bis(tiglato){(R)-binap}ruthenium(II) has been solved and its involvement in asymmetric hydrogenation discussed [101].

Thiol and disulfide oxidation addition reactions have been explored with the ruthenium complex Ru(CO)$_2$(PPh$_3$)$_3$. *cis,cis,trans*-RuH(SR)(CO)$_2$(PPh$_3$)$_2$ and *cis, cis,trans*-Ru(SR)$_2$(CO)$_2$(PPh$_3$)$_2$ have been isolated and spectroscopically characterized. The X-ray crystal structures of three of the products are reported [102]. RuCl$_2$(PPh$_3$)$_4$ reacts with one equiv. of Ph$_2$PO$_2$CCH=CR′R″ (where R′, R″ = H, Me) by phosphine displacement to give RuCl$_2$(PPh$_3$)$_2$(Ph$_2$PO$_2$CCH=CR′R″); coordination of the mixed anhydride ligand is demonstrated to occur by both P and O groups [103]. The substitution of PPh$_3$ in OsH(Cl)(CO)(PPh$_3$)$_3$ by a range of phosphorus ligands has been reported [104]. The synthesis and NMR data for the dihydrogen complexes [MX(η^2-H$_2$)(dcpe)$_2$]$^+$ (where M = Ru, X = H, Cl; M = Os, X = Cl) have been published. Variable-temperature and T_1 NMR studies confirm the existence of a coordinated hydrogen ligand [105]. The reaction between [Ru(CO)$_2$(PPh$_3$)$_2$(THF)$_2$]$^{2+}$ and [TCNQ][Li] affords the N-bond TCNQ complex Ru(PPh$_3$)$_2$(TCNQ), which has been structurally characterized by X-ray diffraction analysis. It is shown that the ruthenium is tetrahedrally disposed in stacked dimeric units [106]. *trans*-Ru(PMe$_3$)$_4$Cl$_2$ has been used as a starting material for the preparation of *trans*-Ru(PMe$_3$)$_4$(C≡CPh)$_2$ and *trans*-Ru(PMe$_3$)$_4$(C≡CC$_6$H$_4$C≡CSnMe$_3$)$_2$ [107]. Catalytic dimerization of terminal alkynes is reported when the complexes L$_4$RuH(Ph) {where L$_4$ = P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$, N(CH$_2$CH$_2$PPh$_2$)$_3$, MeSi(CH$_2$PMe$_2$)$_3$/PMe$_3$} are employed as catalyst precursors [108]. Inter- and intramolecular C–H bond activation chemistry is reported for (pp$_3$)RuCl$_2$ {where pp$_3$ = P(o-C$_6$H$_4$PMe$_2$)$_3$} and related polydentate ligand systems [109]. Oligomeric carbosilanes are the products in the dehydrogenative coupling of trialkylsilanes when Ru(H)$_3$(SiMe$_3$)(PMe$_3$)$_3$ is employed as a catalyst. Turnover numbers and rate data for H$_2$ evolution are presented [110]. The X-ray crystallographic data for *syn,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp), *anti,mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp), and *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) have been published [111].

Migratory insertion, reductive elimination, β-hydrogen elimination, and cyclometalation reactions have been investigated with the ruthenium complexes Ru(PMe$_3$)$_4$(R)(enolate). Variable-temperature NMR data establish the existence of a dynamic equilibrium between the O- and C-bound enolates. The X-ray crystal structures of Ru(PMe$_3$)$_4${η^2-OC(CH$_2$)C$_6$H$_4$} and Ru(PMe$_3$)$_4$(Ph){O(CCHCMe$_2$)CH$_2$CMe$_2$CH$_2$} are presented [112]. The reductive elimination and oxidative addition of C–H bonds to complexes derived from Ru(dmpm)$_2$ are reported [113]. The structure and reactivity of several ruthenium oxametallacyclobutane and oxametallacyclobutene complexes are discussed. A



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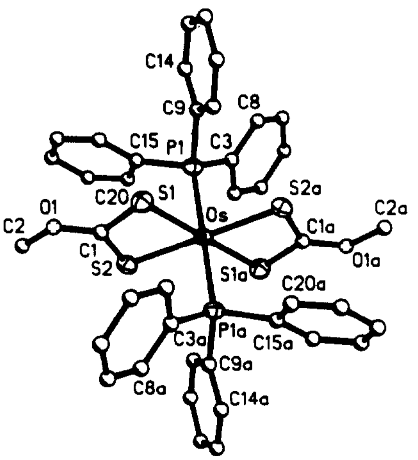
C–C bond cleavage is observed to occur by a β-methyl elimination scheme for $Ru(PMe_3)_4\{OC(Me)(Ph)CH_2\}$, whereas the analogous dmpe-substituted complex is inert. Included in this report is the X-ray crystal structure of $Ru(PMe_3)_4\{(CH_2)_2CO\}$ [114]. A report dealing with the synthesis and reactivity of ruthenium hydrido aryloxides and arylamides has appeared. N–H and O–H elimination processes, proton-catalyzed exchange reactions, and ruthenium–X bond strengths have been explored and pertinent mechanisms outlined [115]. The ruthenium benzyne complex $Ru(PMe_3)_4(\eta^2\text{-}C_6H_4)$ has been obtained from $Ru(PMe_3)_4(Ph)(Me)$ and $Ru(PMe_3)_4(Ph)_2$ during thermolysis reactions. It is demonstrated that the reaction involves an initial reversible dissociation of PMe_3. σ-Bond metathesis chemistry is described for the benzyne complex with the C–H bonds of benzene and toluene, the N–H bond of aniline, and O–H bonds of *p*-cresol, isopropanol, and H_2O [116]. Inter- and intramolecular C–H bond activation and formation and the mechanisms associated with these reactions are reported for the complexes $Ru(PMe_3)_4(X)(H)$ (where X = aryl, benzyl) [117]. CO and CO_2 insertion chemistry in the ruthenium benzyl, arylamido, and aryloxide complexes has been explored with a series of $Ru(PMe_3)_4$-substituted complexes. The X-ray crystal structure of $Ru(PMe_3)_4\{\eta^4\text{-}OC(O)C_6H_4CH_2\}$ is presented [118]. The reactivity of $RuH_2(PMe_3)_4$ with various phenols to give *cis*-$Ru(PMe_3)_4(H)(OR')$ (where R' = phenoxide) is discussed and the X-ray crystal of *cis*-$Ru(PMe_3)_4(H)(OC_6H_4\text{-}p\text{-}Me)$ presented. The protonation chemistry of $RuH_2(PMe_3)_4$ with added phenol indicates the presence of the ionic complex $[RuH_3(PMe_3)_4][OPh]$ at low temperature by NMR spectroscopy; this ionic complex is converted to the observed ruthenium hydrido aryloxide upon warming [119].

2.5. *Carbonyls*

The synthesis and characterization of the η^4-silitrimethylenemethane complex $Mes^t_2BuC_3H_3Ru(CO)_3$ have appeared [120]. The reactivity of aldehydes with bis(dimethylgermyl)alkaneruthenium tetracarbonyls has been shown to proceed by an insertion–elimination sequence. Germylated heterocycles were the major organic products [121]. $Ru(CO)_2(PPh_3)_3$ reacts with diphenylbutadiyne, HPF_6, and isonitrile to give $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)_2(RNC)(PPh_3)_2]^+$ [122]. *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CR)_2$ and *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}C\text{–}C{\equiv}CR)_2$ have been synthesized and characterized spectroscopically in solution. Two X-ray structures also accompany the communication [123].

2.6. *Sulfur and oxygen ligands*

π-Electron delocalization and ruthenium sulfur multiple bonding in ruthenium bis-1,2-benzenedithiolate complexes have been examined by using electrochemical methods and X-ray crystallography [124]. Reaction of $Os(SR)_3(PMe_2Ph)_2$ (where R = C_6F_5, C_6HF_4) with benzoic acid or HCl yields the corresponding osmium(III) complex $Os(SR)_2(O_2CPh)(PMe_2Ph)_2$ and the osmium(IV) chloride complex $OsCl(SR)_3(PMe_2Ph)_2$, respectively. The X-ray crystal structure of Os



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$(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2$ is shown to possess *trans* thiolate groups [125]. The electrochemical behavior of a series of ruthenium sulfides has been reported. The complexes, which have the stoichiometry $RuX_2(R_2SO)_n(R_2S)_{4-n}$ (where $n = 1$–4), have been studied for ligand-additivity relationships and for their catalytic properties in oxygen oxidations of alcohols [126]. The first example of a reaction involving sulfur atom transfer has been reported. The (μ-persulfido)ruthenium(IV) complex $[\{(edta\text{-}H)Ru^{IV}\}S_2]^{2-}$ is shown to be the active species responsible for sulfur atom transfer to cyclohexene [127]. The synthesis and characterization of ruthenium(II) complexes with ancillary 1,5-dithiacyclooctane ligands are described. Several X-ray crystal structures are presented [128]. A study on the isomer preference of $[Os(xanthate)_2(PPh_3)_2]^n$ (where $n = 0, 1$) has appeared. *Cis* isomers are observed when $n = 0$, and *trans* isomers are observed after oxidation to the osmium(III) complex. The formal redox potentials and equilibrium constants are reported for the redox and isomerization cycles. The X-ray crystal structures of *cis*- and *trans*-$Os(Mex)_2(PPh_3)_2$ and *trans*-$[Os(Mex)_2(PPh_3)_2]^+$ (where Mex = methyl xanthate) are given [129].

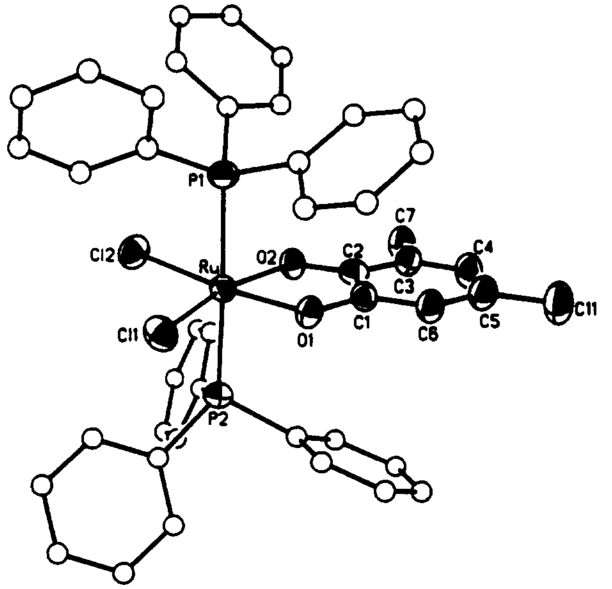
Kinetic data are reported for the complexation of oxalate to $[Ru(H_2O)_6]^{2+}$. In acid solution, the rate-determining step involves the monoanion of oxalic acid and the hexaaquo ruthenium complex. A comparison of the kinetic and activation data for $[HC_2O_4]^-$ with other substitution data reveals that an interchange mechanism is operative [130]. C–H Bond cleavage reactions have been observed when the oxo complex $[RuL(O)]^{2+}$ (where HL = {2-hydroxy-2-(2-pyridyl)-ethyl}bis{2-(2-pyridyl)ethyl}amine) was employed as the oxidant. Kinetic isotope data are reported for alcohol oxidation reactions. The mechanism of C–H bond oxidation is included [131]. The kinetics and mechanism of the oxidation of hypophosphite with chloramine T using osmium tetraoxide have been published [132]. The involvement of an autocatalytic component in the osmium-catalyzed reaction of chlorate and the hydrazinium cation has been explored [133]. The synthesis and spectroscopic characterization of stable ruthenium(V) and osmium(V) oxo complexes containing α-hydroxy carboxylate and α-amino carboxylate ligands are described [134]. A report dealing with the kinetics and mechanism of electron transfer from L-ascorbic acid to $[Ru(edta)(O)]^-$ has appeared. Activation parameters are reported and a mechanism that involves a rate-determining outer-sphere electron transfer from L-ascorbic acid to the ruthenium oxo complex is discussed [135]. The X-ray crystal structure of an osmium oxo complex containing a chiral tetradentate binaphthyl bis-amide ligand has been presented [136]. The reaction between osmium tetroxide and hydroxylamine hydrochloride in the presence of oxalate ions has been examined. The product of this reaction is $[Os(NO)(C_2O_4)_2]^-$, which can be further functionalized with added HX (where X = halide). The X-ray crystal structure of $[Os(NO)(Br)_5][Hphen]_2$ accompanies this report [137]. Treatment of osmium tetraoxide with neat $^tBuNH(SiMe_3)$ gives the first homoleptic osmium(VIII) imido complex, $Os(N^tBu)_4$, and the tetranuclear osmium(VI)-oxo complex $[(^tBu)_2Os(\mu\text{-}N^tBu)_2(\mu\text{-}O)Os(^tBu)]_2$. The reactivity of both complexes has been studied [138]. ESR data for $[RuO_4]^-$ in frozen glasses of CH_2Cl_2 are reported. The preparation of the new salt $[RuO_4][PPh_4]$ is also described [139]. The synthesis of new *trans*-dioxoosmium(VI) complexes derived from dibasic tetradentate Schiff ligands has appeared. The redox properties of these complexes have been investigated by using cyclic voltammetry. X-Ray crystallography has been used to determine the molecular structure of two of the new compounds [140].

Oxoruthenium(VI) complexes containing an ancillary cysteine ligand have been synthesized and spectroscopically characterized. The cysteine ligand is shown to coordinate to the ruthenium center in a bidentate fashions via the sulfur and oxygen atoms [141]. Reaction of osmium tetraoxide with Me_2Zn or $MeTi(O^iPr)_3$ yields methylosmium oxides of the form $(Me)_xOs_yO_z$ in low to moderated yields. Methylation of the glycolate osmium(VI) complex $\overline{Os(O)(OCH_2CH_2O)_2}$ gives $Me_4Os{=}O$ in quantitative yield. The synthesis and electron diffraction structure of $Et_4Os{=}O$ are discussed. Cyclic voltammetric studies indicate that $Me_4Os{=}O$ undergoes a quasi-reversible one-electron reduction ($E_{1/2} = -1.58$ V *vs.* Ag/AgCl) and an irreversible oxidation ($E_p^a = 2.2$ V) [142]. The first perfluorophenyl compound of osmium has been obtained from the reaction between $Os(O)_2(OCH_2CH_2O)$ and $(C_6F_5)_2Zn \cdot (py)_2$. X-Ray diffraction analysis of $(\eta^1\text{-}C_6F_5)_2Os(O)_2(py)_2$ has established the molecular structure of the title compound [143]. Glycolate osmium(VI) complexes have been used as starting materials for the synthesis of alkylosmium(VI) complexes. The X-ray crystal structures of several $R_2Os(O)_2L_x$ (where $x = 1, 2$) complexes are reported [144].

The X-ray crystal structure and 2D NMR analysis of (buckminsterfullerene)(OsO_4)(4-tert-pyridine)$_2$ have been presented [145]. In another report, osmylated buckminsterfullerene has been examined for statistical ^{13}C distribution using buckminsterfullerene that had been prepared from ^{13}C powder [146].

The X-ray crystal structure of the heterocumulene complex *trans*-$Os(NO)Cl(PPh_3)_2(OSNC_6H_4Me\text{-}4)$ has been determined in order to verify the existence of a pseudo-olefinic coordination of the η^2-NS moiety [147]. Diastereoisomerization in bis-β-diketonoto-1,5-cyclooctadiene ruthenium(II) complexes has been investigated by variable-temperature NMR measurements [148]. The carboxylate complex $Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(H_2O)_2$ has been synthesized from the chloro-bridged dimer $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(Cl)_2]_2$ [149]. Asymmetric hydrogenation of α,β-unsaturated carboxylic acids has been studied with the catalysts bis(carboxylato){(*R*)- and (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl}ruthenium(II). On the basis of the observed rate law and isotope labeling studies, the rate-determining step is suggested to involve a substrate-containing bis(carboxylato)ruthenium complex that heterolytically splits H_2 to give a metal hydride. The hydrogenation mechanism with tiglic acid is presented [150]. Reaction of $RuCl_3 \cdot H_2O$ with acetylacetone in KCl yields $[Ru(acac)_2(Cl)_2]^-$, which is shown by X-ray crystallography to possess *trans* chloride ligands. This complex serves as a starting material for the synthesis of a variety of *trans*-(acac)$_2$ complexes of ruthenium(II), -(III), and -(IV) [151]. Zinc reduction of Ru(acac)$_3$ in the presence of 1,3-dienes yields $Ru(\eta^4\text{-diene})(acac)_2$ (where diene = 2,3-dimethyl-1,3-butadiene, 2,4-hexadiene, 1,3-cyclohexadiene, 2,4-dimethyl-1,3-pentadiene). The X-ray crystal structures of the latter two complexes are reported [152].

4,4′-Bipyridyl reacts with $[Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)]_2$ to afford the bipyridyl-bridged complex $[Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]_2(\mu\text{-}4,4'\text{-bipyridyl})$. A single two-electron oxidation is observed by bulk electrolysis and cyclic voltammetry. A ligand-localized oxidation is observed in the latter complex after treatment with $[NO][PF_6]$ [153]. New semiquinone complexes derived from $Os(PPh_3)_2(Cl)_3(MeOH)$ have been prepared and characterized by spectroscopic and electrochemical methods. The complex $Os(PPh_3)_2(Cl)_2(o\text{-}O_2C_6H_4)$ serves as a catalyst for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones in the presence of the co-oxidant N-methylmorpholine-N-oxide [154]. The synthesis and characterization of $Os(PPh_3)_2(Cl)_2(Q)$ and $Os(PPh_3)_2(Q)_2$ (where Q = 3,5-di-tert-butyl-1,2-quinone, tetrachloro-1,2-quinone) are reported and their redox chemistry explored and compared with the analogous ruthenium analogues. The X-ray crystal structure of $Os(PPh_3)_2(Cl)_2\{o\text{-}O_2C_6H_2\text{-}(3,5\text{-}^tBu)_2\}$ reveals that quinone ligand is best described as a hybrid of semiquinone and catechol [155]. The structure and bonding in bis(quinone) complexes of ruthenium have been reported. $Ru(PPh_3)_2(Cl)_2\{o\text{-}O_2C_6H_2\text{-}(3,5\text{-}^tBu)_2\}$ has been crystallographically characterized and is described as exhibiting a semiquinone ligand and a Ru(III) center. The observed diamagnetism arises from strong antiferromagnetic coupling between the Ru(III) center and the coordinated radical. Displacement of the chlorides with a second catecholate ligand yields the corresponding bis(quinone) complex [156].



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2.7. *Nitrogen ligands*

The trigonal planar imido complex $Os(NR)_3$ (where $R = 2,6\text{-}C_6H_3\text{-}^iPr_2$) has been prepared in moderate yield from osmium tetraoxide and 2,6-diisopropylphenyl isocyanate. Reaction of the imido complex with P-ligands yields the square-planar complexes *trans*-$Os(NR)_2L_2$. The oxo complex $Os(NR)_3(O)$, prepared from $Os(NR)_3$ and trimethylamine oxide, reacts with alkenes to give metallaimidazolidene complexes, Os[N(R)CHR′CHR′N(R)](NR)(O). X-Ray crystal structures and SCF-Xα-SW calculations are included [157]. The nitrido complex $[OsN(Cl)_4]^-$ has been used as a starting material in the synthesis of mono- and polypyridyl osmium nitrido complexes. The nitrido complexes are reduced in protic media to give the corresponding monoamine complexes [158]. N–N bond coupling is observed when $OsN(Cl)_3(py)_2$ is heated at 100°C. N_2 and *mer*-$Os(Cl)_3(py)_3$ are the observed products in the thermolysis reactions [159]. $Os(NR)_4$ (where R = ^{t}Bu) has been allowed to react with carboxylic acids and halogens. Reported are the X-ray crystal structures of $(RN)Os(O)(O_2CR)_2(NH_2R)_2 \cdot RCO_2H$, $(RN)_2Os(\mu\text{-}NR)X_2$ (where X = Cl, I) and $[Os_2(NR)_4(\mu\text{-}NR)_2][I_3]$ [160]. The nitrido complexes $[MN\{RN(O)NR\}(Cl)_2]^-$ (where M = Ru, Os; R = ^{t}Bu) have been synthesized from $[Ru(O)_2(Cl)_3]^-$ and $[M(O)_2(Cl)_4]^-$ in the presence of excess ^{t}BuNCO. X-Ray crystallography reveals that the nitrido complexes adopt a distorted square-pyramidal geometry with axial nitrido groups [161]. Nitridoruthenium(VI) and nitridoosmium(VI) compounds containing ancillary N-acetyl-L-cysteinato, 3-sulfidopropionato, and 3-sulfidopropionamidato ligands are presented. X-Ray diffraction analysis and spectroscopic methods (IR and NMR) have been used in the characterization of these new compounds [162].

The X-ray crystal structures of $[M(CN)_6][Na]_4 \cdot H_2O$ (where M = Ru, Os) have been solved [163]. ^{13}C NMR line-broadening measurements have been conducted in order to study the electron self-exchange in the $[Os(CN)_6]^{4-/3-}$ couple. The effect of acidity on the electron-exchange rate constants is described. The exchange rate constants are discussed with respect to the inner-sphere and solvent reorganization barriers [164].

The synthesis and spectroscopic characterization of $Ru(CO)_2(CH_3C{=}CHCH{=}N^iPr)_2$, which contains a 3e-donating σ-N, σ-C coordinated 1-aza-1,3-dien-4-yl ligand, are discussed [165]. Dibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradecane has been used in the synthesis of a new macrocyclic ruthenium complex [166]. Ruthenium(III) Schiff base compounds have been synthesized and investigated for reversible carbon monoxide binding [167]. The synthesis and structural characterization of ruthenium(II) complexes containing ancillary diglycine and triglycine ligands are reported [168]. N_2 binding to $[Ru(H_2O)_6]^{2+}$ has been examined by ^{17}O NMR spectroscopy as a function of N_2 pressure [169].

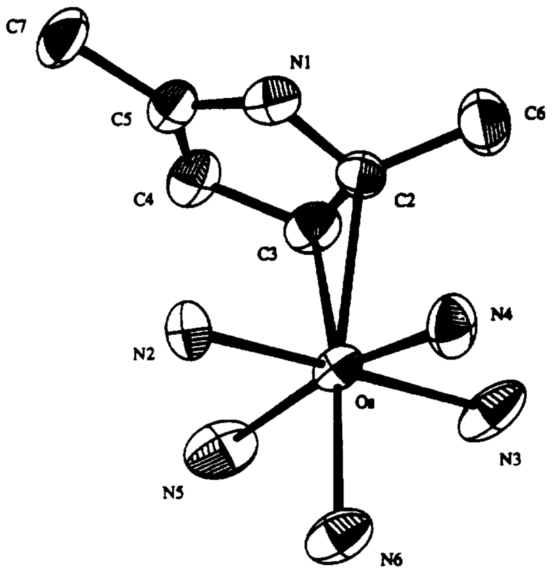
The affinity of N-methylpyrazinium cations for edta complexes of ruthenium(II) and ruthenium(III) has been explored by using cyclic and rotating ring-disk voltammetry. Rate constants, equilibrium constants, and the formal electrode potentials are reported and a square scheme discussed [170]. The redox behavior of the electroactive anion $[Ru(edta)(H_2O)]^{3-}$ with a soluble polyelectrolyte has been described and analyzed [171].

The redox properties and X-ray crystal structure of {bis(2-pyridyl)phosphinato}{tris(2-pyridyl)phosphine oxide}ruthenium(II), $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$, are reported. This particular complex was isolated from the synthesis of $[Ru(py_3P{=}O)_2]^{2+}$ [172]. The redox behavior of *trans*-$[Ru(Cl)(O)(py)_4]^+$ in various solvents has been studied. The oxo complex is oxidized to the ruthenium(V) complex, $[Ru(Cl)(O)(py)_4]^{2+}$, which is capable of oxidizing organic compounds [173]. The octahedral complex $Ru(nbd)L_2$ (where HL = 2(1*H*)-pyridinethione) is shown to possess *trans* sulfur atoms by X-ray crystallography [174]. New ruthenium complexes containing ancillary 1,2-dioxolene ligands are reported. The complexes, *trans*-$[Ru(Rpy)_2(dioxolene)_2]^n$ (where $n = -1, 0, +1$), have been examined by cyclic voltammetry and their electronic structures are discussed by using simple molecular orbital models [175].

Nitrosyl–nitrite interconversion in pentacyanoruthenate(II) complexes has been investigated by studying the nucleophilic addition of HO^- to $[Ru(CN)_5(NO)]^{2-}$ [176]. The isolation and X-ray crystallographic analyses of the osmium nitrosyl complexes $Os(NO)Br_3(Et_2S)(Et_2SO)$ and $Os(NO)Cl_2(Et_2PPh)_2(MeOCH_2CH_2O)$ are reported [177]. Trichloronitrosylruthenium reacts with tetraphenylphosphonium polysulfide in ammoniacal acetonitrile to give $[Ru(NO)(NH_3)(S_4)_2][PPh_4]$, which has been fully characterized by X-ray diffraction analysis [178]. A study describing the electrocatalytic reduction of nitrite ions by $[Ru^{II}(Hedta)(NO^+)]^0$ has appeared. Nitrite is reduced to N_2O, N_2, $[NH_3OH]^+$, or $[NH_4]^+$ with the selectivity being dependent on the pH and applied potential [179].

The allyl complex $[Os(NH_3)_5(\eta^3\text{-}C_3H_5)]^{3+}$ has been obtained from the allyl ether complex $[Os(NH_3)_5(C_3H_5)_2O]^{2+}$ upon treatment with triflic acid. The title complex is redox silent over the potential range + 1.5 to − 1.5 V *vs.* NHE. Nucleophiles add readily to a terminal allyl carbon. The affinity of the $[Os(NH_3)_5]^{2+}$ fragment for diene coordination is demonstrated [180]. The synthesis and characterization of a bis(pentaammine osmium(II)) pyrene complex are discussed. The complex $[\{Os(NH_3)_5\}_2(\mu\text{-pyrene})][OTf]_4 \cdot 4(acetone)$ is shown by cyclic voltammetry to exhibit weak communication between the osmium centers [181]. The enamine character of a 2,3-η^2-coordinated pyrrole has been reported with the isolation and characterization of $[Os(NH_3)_5\{(2,3\text{-}\eta^2\text{-})\text{-}2,5\text{-dimethylpyrrole}\}]^{2+}$. The X-ray crystal structure and enamine reactivity are discussed [182].

Photoaquation studies have been conducted with



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cis-$Ru^{II}(NH_3)_4L_2$ and *cis*-$Ru^{II}(NH_3)_4(isn)L$ (where L = nitrogen ligand) in ammonia solution. Both complexes possess ligand field and MLCT states as the lowest energy excited states. An excited-state “tuning“ model is presented to explain the relative quantum yields in the photoreactions. For a given coordinate axis, labilization of the weaker π-acceptor ligand is observed [183]. Intramolecular entropy changes in $[Ru(NH_3)_6]^{3+/2+}$ have been examined through far-IR spectroscopy [184]. Electrochemical investigations of the band energies of irradiated FeS_2 with the mediator $[Ru(NH_3)_6]^{3+}$ are described [185]. The reduction behavior of $[Ru(NH_3)_6]^{3+}$ at rotating disk electrodes in aqueous solutions containing poly(styrenesulfonate) has been explored. The effect of the association of $[Ru(NH_3)_6]^{3+}$ with the polyanion on the formal potential and the diffusion coefficient is reported [186]. Cyclic and rotating disk voltammetry data for $[Ru(NH_3)_6]^{3+}$ at bare and polymer-coated electrodes have been presented [187]. A report on the use of scanning electrochemical microscopy in generation/collection experiments with $[Ru(NH_3)_6]^{3+}$ as the electroactive species has been reported [188]. *trans*-$[Ru(NH_3)_4\{P(OEt_3)_3\}(H_2O)]^{2+}$ is oxidized to the corresponding ruthenium(III) complex. The product, which was examined by cyclic voltammetry and ESR spectroscopy, is observed to decompose in aqueous solution according to $4Ru(III) \rightleftharpoons 3Ru(II) + Ru(VI)$ [189]. Molecular hysteresis behavior is observed in the cyclic voltammograms of (1,5-dithiacyclooctane 1-oxide)bis{pentaamineruthenium(II)} [190]. Cyclic voltammetric data for $[Ru(NH_3)_6]^{3+}$ at a bare gold electrode and Langmuir–Blodgett functionalized electrodes have appeared [191]. Electroabsorption (Stark Effect) spectroscopic data on mono- and biruthenium charge-transfer compounds are presented [192].

Highly resolved MLCT spectra have been recorded for small amounts of $[Os(bpy)_3]^{2+}$ doped into $[Ru(bpy)_3]^{2+}$. The nature of the lowest emitting excited states is discussed [193]. Diffusion-limited reactions at solid–liquid interfaces have been studied with excited $[Ru(bpy)_3]^{2+}$ adsorbed on porous silica and anthracene [194]. New benzo- and aza-crown ether-bipyridyl ruthenium(II) complexes have been examined for their molecular recognition of alkali and alkaline earth metal cations. The syntheses and emission data for the studied complexes are presented and discussed [195]. Lysine-modified polypyridylruthenium(II) complexes have been synthesized and examined for intramolecular electron-transfer reactions. The unique chromophore-quencher assemblies are proposed as possible systems for the conversion of stored energy into chemical redox energy [196]. Competitive energy and electron-transfer quenching studies of excited $[Ru(bpy)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ by ferrocene and methylated ferrocenes have been published [197]. Energy transfer in the “inverted region“ has been investigated by studying the quenching of the MLCT excited states of bipyridine-substituted osmium(II) complexes by anthracene and 2,3-benzanthracene. The energy transfer in the “inverted region“ is easily observed because the rate constants are below the diffusion-controlled limit [198]. Photoinduced electron transfer mediated by $[Ru(bpy)_3]^{2+}$ trapped in sol–gel glasses has been described [199].

Size-selective electrochemistry has been demonstrated with a poly$[Ru(vbpy)_3]^{2+}$-modified platinum electrode. The origin of this phenomenon arises from a size-selective transport barrier for diffusion to the underlying electrode [200]. A study on the electrochemistry and photocurrents of $[Ru(bpy)_3]^{2+}$ and methyl viologen immobilized in carrageenan hydrogel has appeared [201]. Polypyridylruthenium(II) complexes have been examined in films at the air/water interface by on-trough voltammetry [202]. Polypyridylruthenium(II) complexes containing a bromomethyl-substituted bipyridyl ligand have been synthesized and used to prepare thin polymeric films on electrode surfaces [203]. Tin(IV) oxide electrodes have been modified with $[Ru(bpy)_2(bpdc)]^{2+}$ and examined by XPS and SEM. The chemical stability of these electrodes was examined under a variety of conditions [204]. The electron-transfer cross-reaction rate constant of $[Fe(4,7\text{-}Me_2\text{-}Phen)_3]^{2+}$ by poly$[Os(bpy)_2(vpy)_2]^{3+}$ has been measured by employing microelectrode voltammetry [205]. $[Ru(bpy)_3]^{2+}$ has been used as a luminescence probe in ion-transport processes [206]. Ion association and electric field effects on electron hopping in the $[Os(bpy)_3]^{3+/2+}$ redox couple incorporated in Nafion films are presented [207]. The photocatalytic properties of $[Ru(bpdc)_3]^{2+}$-derivatized semiconductor particles have been investigated [208].

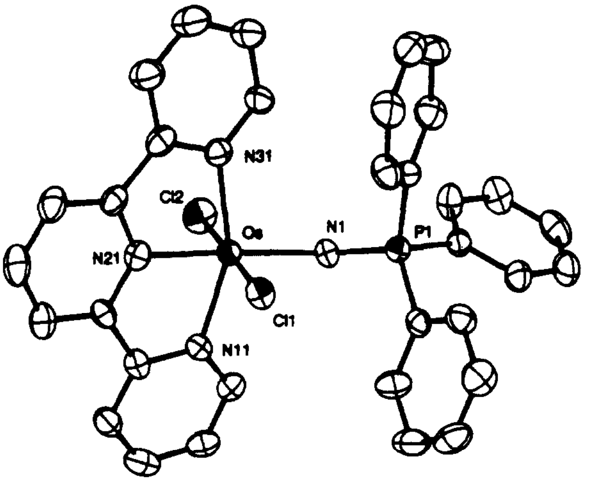
X-Ray diffraction and electric dichroism measurements are reported for the binding structures of enantiomeric and racemic $[Ru(phen)_3]^{2+}$ with sodium montmorillonite [209]. Thiosulfate oxidation by $[Os(phen)_3]^{3+}$ in aqueous media has been studied by stopped-flow spectrophotometry. Rate constant data and the reaction stoichiometry are reported and discussed [210].

Edta and $[S_2O_8]^{2-}$ function as reductive and oxidative quenchers, respectively, for excited $[Ru(bpz)_3]^{2+}$. The observed photocurrents associated with the quenching reaction are presented and discussed with respect to a working theoretical model related to the photocurrent dependence on the applied potential [211]. ECL behavior has been studied in the oxidative quenching of $[Ru(bpz)_3]^{2+}$ with peroxydisulfate in aqueous solution [212].

cis-$[Ru(bpy)_2(CO)H]^+$ is reported to function as a catalyst for the electrochemical reduction of CO_2 in $MeCN/H_2O$. A plausible mechanism for the production of formate is presented [213]. The complexes Ru $(bpy)_2LL$ and $Ru(py)_4LL$ (where LL = 1,2-dihydroxybenzene, 2-aminophenol, 1,2-diaminobenzene) have been examined for orbital mixing and electronic structure by electrochemical and spectroscopic methods [214]. A spectroelectrochemical study on the oxidized and reduced forms of $[\{Ru(bpy)_2(CN)\}_2CN]^+$ has been carried out. The one-electron product is shown to be a valence delocalized species on the basis of the reported data [215]. Kinetic data for the oxidation of aromatic hydrocarbons and THF by *trans*-$[Ru^{VI}L(O)_2]^{2+}$ (where L = chelating nitrogen ligand) are reported. The kinetic isotope data and activation parameters are presented and a hydrogen-atom abstraction mechanism is discussed [216]. A report describing the isolation and characterization of the intermediate produced during photolysis of $[Ru(bpy)_2(L–L)]^{2+}$ (where L–L = 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole} in MeCN has been published. The intermediate is shown to possess a monodentate L–L ligand that is coordinated by the nitrogen atom of the triazole ring. Upon heating, MeCN is displaced and the original complex is regenerated [217]. Methane hydroxylation has been observed by using the oxidant *cis*-$[Ru(2,9\text{-}Me_2Phen)_2S_2]^{2+}$ (where S = MeCN or H_2O) and H_2O_2. The reaction between the latter two reagents has been studied spectrophotometrically by UV-vis and NMR spectroscopies. A ruthenium(VI) oxo complex, *cis*-$[Ru^{VI}(2,9\text{-}Me_2Phen)(O)_2]^{2+}$, is suggested as the active oxidation catalyst on the basis of the spectroscopic data [218]. Resonance Raman spectra for several nitrogen-substituted ruthenium complexes have been published [219]. The complex $[Ru(bpy)_2(1,3\text{-}Me_2lum)]^{2+}$ has been prepared and examined by cyclic voltammetry [220]. Resonance Raman data are reported for a diruthenium complex that contains a 1,4,5,8-tetraoxonaphthalene ligand [221]. The synthesis, redox properties, and reactivity of $[Ru^{VI}(5,5'\text{-}Me_2bpy)_2(O)_2]^{2+}$ have been published. The oxidation of alcohols to ketones/aldehydes, THF to γ-butyrolactone, alkenes to epoxides, and hydrocarbons to alcohols/ketones is discussed [222].

A new bis(terpyridine)ruthenium(II) catenate complex has been synthesized. Like other bis(terpyridine) complexes, the catenate complex is nonluminescent at room temperature in MeCN solvent [223]. (Polypyridyl)ruthenium(II) complexes have been investigated by using fast atom bombardment tandem mass spectrometry. Confirmation of structure and details about complex fragmentation are provided by low-energy collision-induced dissociation (CID) spectra [224]. Acetonitrile substitution in $[Ru(terpy)(bpy)(MeCN)]^{2+}$ by added ligand is observed upon irradiation into the metal-to-ligand absorption band. The quantum yields for MeCN displacement have been measured. The analogous osmium complex is substitutionally inert, a phenomenon explained by a dissociative reaction mechanism involving a reactive ^{3}d–d state. The X-ray crystal structure of $[Ru(terpy)(bpy)(py)](PF_6)_2 \cdot$(acetone) accompanies this report [225]. The synthesis and electron-transfer reactivity of a ruthenium(II)-bis(terpyridine) photosensitizer covalently linked to electron donor and acceptor groups are described. Emission and transient absorption spectra are presented [226]. The effect of phenyl groups on the excited-state lifetimes of ruthenium(II) terpyridyl complexes is published [227]. The synthesis and redox properties of a tris(2,2′-bpy)ruthenium(II) dimer coupled at the C4 carbon have been reported [228]. Oxidative quenching of ruthenium(II)-diimine complexes by $[MV]^{2+}$ has been studied by pulsed laser photolysis. A weak dependence of the rate constant of back electron transfer (k_{bet}) on ΔG^0 is discussed [229]. Photoelectrodes of electropolymerized molecular ruthenium(II) and osmium(II) diads have been prepared and characterized [230]. The synthesis of a mixed-valence ruthenium complex containing a 3,3′,5,5′-tetrapyridyl/biphenyl ligand is described. The comproportionation constant for the reaction $Ru_2^{III,III} + Ru_2^{II,II} \rightleftarrows 2Ru_2^{III,II}$ is reported [231].

A study on the photophysical and photochemical properties of ruthenium and osmium complexes possessing substituted terpyridines has appeared. MLCT excited-state quenching data reveal that [Ru(tpter-



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py)$_2$]$^{2+}$ is an effective electron-transfer agent under light irradiation [232]. The synthesis and characterization of [Ru(terpy)(6,6′-Cl$_2$bpy)(H$_2$O)]$^{2+}$ are reported. This ruthenium(II) complex is oxidized by ceric ions to the corresponding oxo complex, which is an active oxidant for hydrocarbons. The mechanism of alkene oxidation by Ru^{IV}=O is discussed [233]. A luminescent study of cyclometallated [Ru(4′-tolyl-terpy)(6-Phpy)]$^+$ has been published. The redox properties and spectroscopic characterization of this complex are included [234]. The synthesis and characterization of mono- and dinuclear ruthenium polypyridyl complexes have been published [235]. *trans*-[Os^{VI}(terpy)(Cl)$_2$(N)]$^+$ reacts with PPh$_3$ to yield the complex *trans*-[Os(terpy)(Cl)$_2$(NPPh$_3$)]$^+$, which is shown by X-ray crystallography to contain a phosphoraminato ligand. The reaction was found to be first order in both PPh$_3$ and Os(VI) [236].

The synthesis of RuL$_2$(Cl)$_2$ and [RuL$_3$]$^{2+}$ {where L = 2-(arylazo)pyridine} from RuCl$_3 \cdot x$H$_2$O and [AgL$_2$][ClO$_4$] is described [237]. The acid–base properties of [Ru(bpy)$_2${3-(pyrazin-2-yl)-1,2,4-triazole}]$^{2+}$ have been investigated [238]. Several ruthenium(II) complexes bearing a dbtd ligand have been synthesized and examined by resonance Raman spectroscopy and electrochemical methods. The X-ray crystal structure of [Ru(bpy)$_2$(dbtd)][PF$_6$]$_2 \cdot$ acetone is presented [239]. Tetraammineruthenium(II) complexes with the heterocyclic bridging ligand bptz have been synthesized and spectroscopically characterized [240]. The synthesis of [Ru(dpb)$_3$]$^{2+}$ is reported. The complex exhibits a low energy emission spectrum that is explained by using the energy gap law. A comparison of the redox properties of [Ru(dpb)$_3$]$^{2+}$ with other homologous complexes is presented [241]. Polypyridyl-bridged osmium(II) complexes have been synthesized and characterized by electrochemical and spectroscopic methods. It is shown that the polypyridyl bridging ligand is responsible for controlling the potential of the first reduction step and the energy of the lowest energy MLCT state. The LUMO is assigned to a π^* orbital associated with the bridging polypyridyl ligand [242]. Two ruthenium complexes possessing the ligand σ-(2-thienyl)-2,2′-bipyridine (HL) have been prepared. The X-ray crystal structures of *mer*-Ru(HL)(py)(Cl)$_3$ and [Ru(HL)$_2$(Cl)][BF$_4$]$\cdot$CH$_2$Cl$_2$ are reported and discussed with respect to the coordination mode adopted by the ancillary HL ligand [243]. The synthesis and luminescence properties of [Ru(bpy)$_2$(ppq)]$^{2+}$ and [Ru(bpqpy)$_2$]$^{2+}$ have been published. On the basis of the luminescence and redox properties, it is suggested that the former complex would function as an ideal copolymer agent [244].

New ruthenium(II) complexes containing σ-(N-pyrazolyl)- and σ-(N-pyrazolylmethyl)-2,2′-bipyridine ligands have been reported. The redox properties and electronic absorption data have been recorded and are discussed with respect to other ruthenium(II) systems [245]. A report on the pH control of the photophysical properties of ruthenium(II) complexes possessing 3-(pyrazin-2-yl)-1,2,4-triazole ligands has appeared [246]. The ligand qpy has been used in the synthesis of new ruthenium(II) complexes. Data from luminescence and electrochemical studies are presented [247]. Zeolite-entrapped bis-heteroleptic ruthenium(II) polypyridyl complexes have been synthesized and examined by absorption and resonance Raman spectroscopies [248]. Reduced ruthenium(II)-diimine complexes have been explored in aqueous solution by using radiation chemical and electrochemical techniques. The use of these complexes as electron-transfer photosensitizers is discussed [249]. Nonradiative decay rate constants for polypyridyl ruthenium(II) complexes have been calculated from emission spectral profiles [250]. The photophysics and photochemistry of polymer-immobilized polypyridyl ruthenium(II) complexes have been examined in connection as an oxygen sensor device [251]. The synthesis and characterization of *trans*-[RuL(Cl)(PMe$_3$)$_2$]$^+$ {where L = 2,6-bis(3-phenylpyrazol-1-yl) pyridine} are reported. The X-ray crystal structure reveals that nitrogen atoms occupy three meridional sites [252].

Kinetic data on intramolecular photoinduced metal–metal charge transfer in [(NH$_3$)$_5$Ru^{III}NCFe^{II}(CN)$_5$]$^-$ have been reported [253]. Optical electron-transfer energetics in a symmetrical mixed-valence system have been investigated as a function of added crown ether [254]. The complexes [(CN)$_5$Fe(pyCN)Ru(NH$_3$)$_5$]$^-$ (*meta* and *para* isomers) have been synthesized and examined electrochemically. The *para* isomer exhibits an intravalence transition that is discussed in terms of Hush theory [255]. The oxidation of pyrazine-bridged ruthenium dimers by peroxydisulfate has been examined. A mixed-valence Ru^{II}, Ru^{III} complex has been fully characterized [256]. Long-range antiferromagnetic coupling between the ruthenium centers in $[\mu\text{-L}\{(NH_3)_5Ru\}_2]^{4+}$ (where L = 1,4-dicyanamido-2,3,5,6-tetramethylbenzene dianion) has been observed. Cyclic voltammetric data and the temperature-dependent magnetic properties are included in this report [257]. Dinuclear bis(pentammineruthenium) complexes containing a bridging 4,4'-azopyridine ligand have been prepared and investigated for metal–metal electronic coupling. An intervalence absorption is detected upon oxidation [258]. A report describing the synthesis of ruthenium complexes containing a σ- and μ-pyrazine and σ- and μ-dppm ligands has appeared [259]. The use of 1,10-phenanthroline-5,6-dione as a bridging ligand in the synthesis of a ruthenium/platinum complex is described [260]. Solvent-induced and polyether-ligand-induced redox isomerizations in the mixed-valence ion *trans*-$[(py)(NH_3)_4Ru(4\text{-NCpy})Ru(bpy)_2Cl]^{4+}$ have been explored by electrochemical reaction entropy and resonance Raman spectroscopic experiments [261]. A report on directional energy transfer in luminescent tetranuclear ruthenium(II) polypyridyl complexes has been published [262].

The electronic structure of a heterodinuclear complex containing a bis(bipyridyl)ruthenium(II) fragment has been studied. The metal centers are connected by a bridging bpm ligand. Cyclic voltammetric measurements and esr data reveal that only a weak interaction exists between the metal centers [263]. The ground- and excited-state properties of polypyridylruthenium(II) complexes bridged by dpp, biq, and bpy ligands are reported [264]. The decanuclear ruthenium(II)-polypyridyl complex $Ru[(\mu\text{-2,3-dpp})Ru\{(\mu\text{-2,3-dpp})Ru(bpy)_2\}_2]_3^{20+}$ has been prepared from $[Ru(2,3\text{-dpp})_3]^{2+}$. The redox properties, absorption spectrum, and luminescence behavior are discussed [265]. Polynuclear ruthenium(II) polypyridyl complexes containing 2,5-dpp bridging ligands have been synthesized. The hexanuclear derivatives exhibit intense UV absorptions that are assigned to MLCT bands. Luminescence occurs from the lowest ^{3}MLCT excited state. Electrochemical studies indicate that the peripheral Ru^{2+} ions are easier to oxidize than the interior Ru^{2+} ion(s) [266]. Mono- and dinuclear ruthenium(II) complexes with either a 2,3-dpp or 2,5-dpp bridging ligand are reported. The photochemical behavior has been examined and the quantum yields for reactant disappearance are reported [267].

The redox properties of symmetrical and asymmetrical dinuclear ruthenium and osmium complexes connected by a 2,2'-bzim ligand have been published. The reduction potentials are discussed with respect to the π^* orbital energy level of the ancillary bpy ligands [268]. The acid/base properties of $[M(L)_2(bpbzimH_2)M(L)_2]^{4+}$ (where M = Ru, Os; L = bpy, 1,10-phen) have been explored. The pKa values are shown to reflect the oxidation state of both metals. The effect of protonation on the intervalence absorption band of the mixed-valence complexes is described [269].

The synthesis, electrochemistry, absorption spectra, and luminescence behavior of mono- and dinuclear osmium(II) complexes containing bipyridine and 3,5-bis(pyridin-2-yl)-1,2,4-triazole ligands are reported [270]. The first stereospecific preparation of polynuclear ruthenium(II) complexes with the chiral ligand Λ-$Ru^{III}(1,10\text{-phen})_2$ has appeared [271].

Unsymmetrical dinuclear ruthenium(II) complexes with a tpt ligand have been synthesized and characterized by ^{1}H NMR spectroscopy [272]. Mono- and dinuclear ruthenium(II) complexes containing ancillary triazole ligands have been prepared and investigated for intervalence-transition absorptions [273].

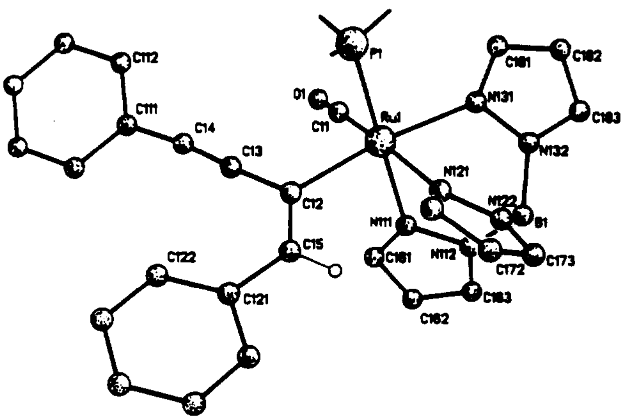
2.8. Alkenyl and alkylidene complexes

$Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2$ (where R = ^{t}Bu, Ph) reacts with PhLi to yield the corresponding phenyl-substituted complex, $Ru(CO)_2(CH{=}CHR)Ph(PMe_2Ph)_2$, at low temperature [274]. Treatment of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ with sodium formate gives the formate complex $Ru(O_2CH)(CO)(RC{=}CHR')(PPh_3)_2$, which is shown by X-ray crystallography to possess an η^2-formate ligand [275]. CS_2 and CO_2 insertion into the Ru–alkenyl bond of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ is shown to afford $Ru(CO)Cl(S_2CRC{=}CHR')(PPh_3)_2$ and $Ru(CO)Cl(O_2CRC{=}CHR')(PPh_3)_2$, respectively. The identity and coordination mode of the alkenedithiocarboxylate and alkenecarboxylate ligands have been established by NMR and IR spectroscopies [276]. The alkenyl complex $Ru(CO)(CH{=}CHPh)Cl(py)(PPh_3)_2$ gives (E,E)-1,4-diphenylbuta-1,3-diene and the ruthenium(II) hydride $Ru(CO)(H)Cl(py)(PPh_3)_3$ in alcohol solvent. The mechanism for this reaction and deuterium-labeling studies are presented [277]. $\{N(CH_2CH_2PPh_2)_3\}RuCl_2$ reacts with diphenyl propargyl alcohol to yield a ruthenium-allenylidene complex. The molecular structure of the product has been established by X-ray diffraction analysis [278]. The coordinatively unsaturated alkenyl complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ (where R, R' = various alkyls, Ph, CO_2Me, CO_2Et) react with CO to yield the η^2-acyl complexes $Ru(CO)Cl(\eta^2\text{-O=C-CR=CHR'})(PPh_3)_2$. The new complexes were characterized by IR and NMR spectroscopies [279]. Reaction of $[HB(pz)_3]^-$ with the coordinatively unsaturated σ-

vinyl complexes Ru(CO)Cl(CR=CHR)$(PPh_3)_2$ (where R = H, Me, Ph) yields Ru(CO)(CR=CHR)(PPh_3){HB-$(pz)_3$} by way of halide and PPh_3 loss. The molecular structure of Ru(CO){C(C≡CPh)=CHPh}(PPh_3){HB-$(pz)_3$} has been determined by X-ray diffraction analysis [280].

2.9. π-Complexes

$(\eta^2\text{-}C_2H_4)Ru(CO)_4$ reacts with activated alkynes RC≡CR (R = various alkyl esters) to give tricyclic complexes possessing two tricarbonylruthenacyclopentadiene rings [281]. Catalytic dehydrohalogenation coupling of vinyl halides with alkenes is observed when Ru(COD)(COT) is used as the catalyst precursor [282]. Cycloaddition reactions are reported when $(\eta^4$-cycloheptatriene)$Ru(CO)_3$ is allowed to react with electron-deficient dieneophiles. The X-ray crystal structure of the [3 + 2] TCNE adduct has been solved [283]. The ruthenium complex $[Ru(COT)(Cl)_2]_x$ has been prepared from $RuCl_3 \cdot xH_2O$ and 1,3,5,7-cyclooctatetraene in boiling ethanol. The reactivity of this new complex has been explored and the synthesis of polyolefinic products discussed [284]. The ruthenium(IV) bis-allyl dimer $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(Cl)(\mu\text{-}Cl)]_2$ reacts with pyrazine to give the pyrazine-bridged complex $[\{\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}C_4H_4N_2)$. ^1H NMR spectroscopy and single-crystal X-ray diffraction analysis were used to characterize the product [285]. The X-ray crystal structure of $Ru(H_2O)_2\{\eta^1\text{-}(O){:}\eta^2\text{-}(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ is reported. This particular complex was isolated from the reaction between $[Ru(H_2O)_6]^{2+}$ and 3-pentenoic acid [286]. The air- and water-stable complex $[(\eta^3:\eta^2{:}\eta^3\text{-}C_{12}H_{18})Ru(Cl)(H_2O)]^+$ has been prepared from the corresponding dichloride and $[Ag][BF_4]$. The new complex was characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography [287]. The reaction between $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(Cl)(\mu\text{-}Cl)]_2$ (where $C_{10}H_{16}$ = 2,7-dimethyloctadienediyl) and benzothiazole-2-thiol and pyridine-2-thiol is described [288]. Ligand substitution reactions with the above complex have been examined and the X-ray crystal structure of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(Cl)(MeCN)_2]^+$ is reported [289]. The hydride complex $[RuH(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]^+$, which is obtained upon the low-temperature protonation of $Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{16})$, isomerizes to $[RuH(\eta^5\text{-}C_8H_{11})_2]^+$ during warm-up. The mechanism is discussed and the X-ray structure of the latter complex is presented [290]. Regio- and stereocontrolled dimerization of t-butylacetylene to (*Z*)-1,4-di-t-butylbutatriene is catalyzed by Ru(COD)(COT) and $Ru(CO)(PPh_3)_3(H)_2$. The X-ray crystal structure of $RuCl(CO)(PPh_3)_2\{C(C{\equiv}C^tBu){=}CH^tBu\}$ is reported [291].



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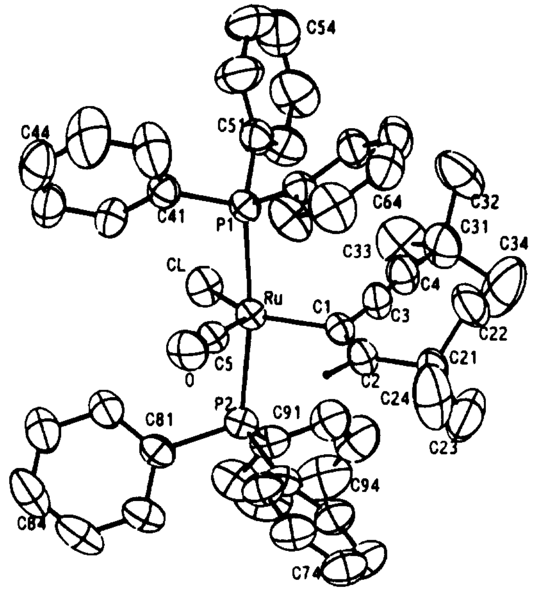

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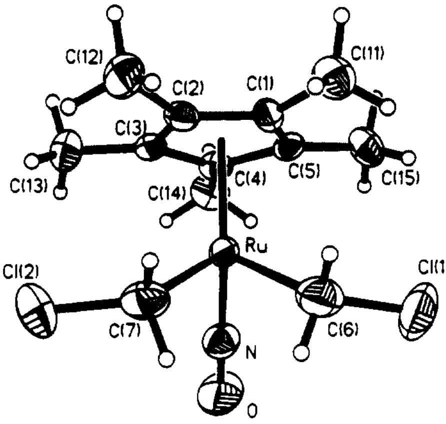
Hydrogen loss from one of the methyl groups of a pentamethylcyclopentadiene ligand has been demonstrated. Treatment of $[Cp^*Ru(Cl)_2]_2$ with dimethyl sulfoxide yields $(C_5Me_4CH_2)Ru(Cl)_2(DMSO)$, which reacts with HCl to give $(C_5Me_4CH_2)Ru(Cl)_3(Me_2S)$. Both of these new complexes were characterized by NMR and IR spectroscopies and by X-ray diffraction analysis in the case of the former complex [292]. The synthesis of the reactive ruthenium complexes $[(ring)Ru(OTf)_2]_x$ (where ring = *p*-cymene, TMT) has been described. Facile ligand substitution to give $[(ring)RuL_3]^{2+}$ is observed. Reaction of $(TMT)Ru(OTf)_2$ with D_2O yields $[(TMT)Ru(D_2O)_3]^{2+}$; the sandwich complex $[(TMT)_2Ru]^{2+}$ has been isolated when the tris-aquo complex is heated at 150°C [293].

^tBuSH reacts with $CpRu(PPh_3)(CN^tBu)Cl$ and $CpRu(dppm)Cl$ in MeOH to give the corresponding thiol complexes $[CpRu(PPh_3)(CN^tBu)(HS^tBu)]^+$ and $[CpRu(dppm)(HS^tBu)]^+$. The latter complex has been structurally characterized by X-ray diffraction analysis [294]. The first example of a side-on coordination of sulfene is reported. Treatment of $[CpRu(dppm)(SO_2)]^+$ with diazomethane gives $[CpRu(dppm)(CH_2{=}SO_2)]^+$. The reactivity of the sulfene complex towards anionic and neutral nucleophiles is described [295]. Air-sensitive thiol complexes have been obtained from the reaction between $CpRu(L)(L')Cl$ {where $L = L' = PPh(OMe)_2$, PPh_2OMe, $P(OMe)_3$; $L = PPh_3$, $L' = CO$, $P(OMe_3)_3$} and ^tBuSH. Air oxidation yields the paramagnetic complexes $[CpRu(L)(L')(S^tBu)]^+$; the X-ray diffraction structure of the PPh_2OMe derivative ($L = L'$) is presented [296]. The synthesis of thiosulfinato complexes $CpRu(PPh_3)(CO)\{SS(O)R\}$ (where $R = {}^nPr$, ^iPr, $4\text{-}C_6H_4Me$) and the X-ray structure of $CpRu(PPh_3)(CO)\{SS(O)_2\text{-}4\text{-}C_6H_4Me\}$ have been published [297]. The reactivity of the cationic vinylidene complex $[CpRu(PMe_3)_2\{{=}C{=}(SMe_2)\}]^+$ has been explored with a wide variety of electrophiles. Anionic nucleophiles displace the dimethylsulfide ligand. The X-ray crystal structure of $[CpRu(PMe_3)_2\{S(Me)C{=}C\text{-}(H)(SMe)\}]^+$ accompanies this report [298]. A study on the displacement of chloride in $CpRu(PMe_3)_2Cl$ by $MeSC{\equiv}CSMe$ has appeared. The chemistry of the resulting sulfur-bound alkyne complex, $[CpRu(PMe_3)_2\{S(Me)C{\equiv}SMe\}]^+$, and the structural data for the first sulfoniovinylidene dicationic complex $[CpRu(PMe_3)_2\{{=}C{=}C(H)(SMe_2)\}]^{2+}$ are discussed [299]. The reaction between $MeCpRu(dppe)Cl$ and $[ReS_4][Bu_4N]$ yields the unidentate thiometalate complex $MeCpRu\text{-}(dppe)(SReS_3)$. The X-ray crystal structure is presented and the spectroscopic and redox data are discussed [300]. The synthesis and X-ray crystal structure of $[CpRu(PMe_3)_2(2,5\text{-DHT})]^+$ have been published [301]. The synthesis of new cyclopentadienylruthenium thiol complexes has been published. Treatment of $CpRu(L)(L')Cl$ (L, L' = CO, phosphines) with $^nBu_3SnSR$ (where R = Ph, tolyl) yields the corresponding thiol derivative $CpRu(L)(L')SR$ [302].

$Cp^*RuH_3(PPh_3)$ reacts with $P(OMe)_3$ to give $Cp^*RuH(PPh_3)\{P(OMe_3)\}$ while reaction with HBF_4 produces $[Cp^*RuH_2(PPh_3)_2]^+$. The complex $Cp^*RuH_3(PCy_3)$ is shown to react with HBF_4 by H_2 evolution and formation of $[Cp^*Ru\{C_6H_9P(Cy)_2\}]^+$, which is shown by X-ray crystallography to possess a coordinated C=C double bond and an agostic Ru–H interaction [303]. A study on dinitrogen coordination to $[CpRu(diphosphine)(\eta^2\text{-}H_2)]^+$ has been reported [304]. Catalysts for H/D exchange between ROH and D_2 have been screened. The dihydrogen complexes $[CpRu(CO)(PR_3)(\eta^2\text{-}H_2)]^+$ (where R = Ph, Cy) are inactive, but the complex $[Ru(dppe)_2H(\eta^2\text{-}H_2)]^+$ is moderately active in the isotope exchange [305].

The synthesis, NMR spectra, and extended Hückel molecular orbital calculations of $[(C_5Me_5)M\{C_5Me_3(CH_2)\}]^{2+}$ (where M = Ru, Os) have been presented. The dications exist primarily as 1,2-isomers and exhibit substantial bending of the CH_2^+ groups out of the plane of the Cp ring [306]. The design and evaluation of a high-pressure cyclic voltammetry cell have been discussed. The electrochemistry of osmocene as a function of CO pressure was studied [307]. Variable-temperature ^1H and ^{13}C NMR studies on 1,1',3,3'-tetra(alkyl)ruthenocenes (where alkyl = t-pentyl, t-butyl) have been reported and the energy barriers for restricted rotations of the Cp rings have been calculated [308]. Bis(methylthio)ruthenocene has been allowed to react with $PtCl_2$. The NMR behavior of the resulting complex has been analyzed by variable-temperature bandshape analyses [309]. NMR data for magnesium coordination to a ruthenocene-containing cryptand have been collected and analyzed. The nature of the host–guest complex is described [310]. The synthesis and study of α-metallocenylcarbinols (where M = Ru, Os) have been published [311]. An IR solution study dealing with hydrogen bonding and conformations of permethylated α-metallocenylcarbinols (where M = Ru, Os) has appeared [312]. The same research group has also published their solid-state IR data on the same complexes in a separate report [313]. The energy barriers to bridge reversal in trisulfur- and triselenium-bridged [3] metallocenephanes (where M = Ru, Os) have been calculated by using NMR spectroscopy [314]. The electronic absorption data for Cp_2M, Cp_2^*M, and $CpRuCp^*$ (where M = Ru, Os) in the gaseous state have been recorded and compared with solution data obtained in pentane [315]. The synthesis and nonlinear optical properties of ruthenium polyene complexes are described [316]. A report describing the X-ray structure of a ruthenocene-containing crytand complex has appeared [317]. Treatment of $[(p\text{-cymene})RuCl_2]_2$ with $[C_5HPh_4]^-$ gives the sandwich complex $(\eta^5\text{-}C_5HPh_4)_2Ru$, whose molecular structure has been established by X-ray crystallography. The ruthenocene complex is reported to be stable towards oxidation and reduction [318].

The oxidative electrochemistry of $CpRu(CO)(PPh_3)H$ has been explored. The dihydrogen complex $[CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)]^+$ is obtained when the monohydride is oxidized by ferrocenium hexafluorophosphate in CD_2Cl_2 while $[CpRu(CO)(PPh_3)(MeCN\text{-}d_3)]^+$, $HRu(CO)(PPh_3)(MeCN\text{-}d_3)_3$, and cyclopentadiene were observed when the reaction was carried out in $MeCN\text{-}d_3$ [319]. The reaction between



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$CpRu(PPh_3)_2H$ and the trityl reagent $[tol_3C][PF_6]$ affords *trans*-$[\{\eta^5\text{-}C_5H_4(tol_3C)\}Ru(PPh_3)_2H_2]^+$ as a result of trityl cation attachment to the Cp ring. Mechanisms are presented and evidence discussed that supports an initial electrophilic attack by the trityl cation at the Cp ring coupled with an electron transfer process [320]. A detailed electrochemical study of $CpRu(CO)(PMe_3)H$ has been published [321].

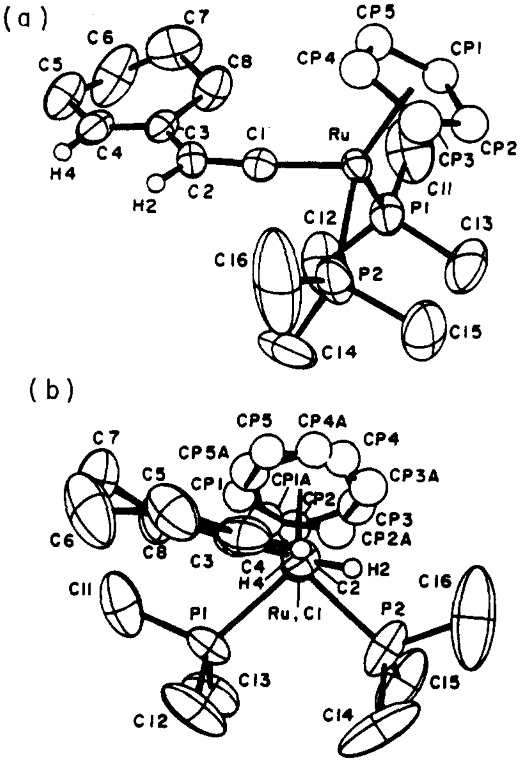
The synthesis of $[Cp^*Ru(\mu\text{-}NO)]_2$ has been reported. X-Ray diffraction analysis reveals that the dimer possesses a Ru=Ru double bond. Starting with $Cp^*Ru(NO)Cl_2$, it is shown that the intermediate complex $[Cp^*Ru(\mu\text{-}NO)Cl]_2$, which contains a Ru–Ru single bond, serves as a precursor complex to $[Cp^*Ru(NO)]_2$. The reactivity of $Cp^*Ru(NO)(aryl)_2$ in reductive elimination reactions is discussed [322]. Treatment of $Cp^*Ru(NO)Cl_2$ with diazomethane in the presence of Cu powder affords $Cp^*Ru(NO)(CH_2Cl)(Cl)$ and $Cp^*Ru(NO)(CH_2Cl)_2$. Upon photolysis or thermolysis, the bis(chloromethyl)complex yields ethylene and $Cp^*Ru(NO)Cl_2$. The mechanism for the extrusion of ethylene and the X-ray crystal structure of $Cp^*Ru(NO)(CH_2Cl)_2$ are presented [323].

The synthesis and photophysics of cyclopentadienylruthenium(II) complexes that possess a fluorescent arene ligand have been published. The requirements for emission are outlined [324]. A report describing fluorescent intermediates observed in the reaction between $[CpRu(MeCN)_3]^+$ and 7-aminocoumarin laser dyes is presented. Spectroscopic measurements reveal that the fluorescent intermediates contain a laser dye that is bound to the ruthenium via substituent groups present in the dyes [325]. $[Cp^*Ru(MeCN)_3]^+$ has been allowed to react with heteroaromatic nitrogen ligands to give η^1-nitrogen bound and η^6-nitrogen bound complexes. Ligand-exchange reactions of $[Cp^*Ru(\eta^6\text{-pyridine})]^+$ with MeCN-d_3 and pyridine-d_5 indicate that the η^6-pyridine undergoes facile exchange with the solvent [326]. The bonding mode of nitrogen heterocyclic ligands to “$CpRu^+$“ has been investigated. $N(\eta^1)$ to $\pi(\eta^6)$ rearrangements and ligand-exchange reactions are discussed [327]. [2.2]anthracenophane reacts with $[Cp^*Ru(MeCN)_3]^+$ to give *trans*-$[(Cp^*Ru)_2(\eta^6:\eta^6\text{-dibenzo-}p\text{-quinodimethane}]^{2+}$ and $[Cp^*Ru(\eta^6\text{-dibenzo-}p\text{-quinodimethane})]^+$. The X-ray crystal structure of the latter complex is presented [328].

The photochemical reactivity of $CpRu(CO)_2(NO_2)$ in a matrix at 13 K has been explored. Irradiation at $\lambda > 350$ nm leads to exo-$CpRu(CO)_2(ONO)$ and endo-$CpRu(CO)_2(ONO)$. Both of these linkage isomerization products are formed reversibly from $CpRu(CO)_2(NO_2)$. Photolysis at $\lambda < 254$ nm gives the nitrosyl complex $CpRu(CO)(NO)$ and CO_2. The mechanism associated with this last reaction is discussed [329]. The reactivity of the σ,η^3(5e)-butadienylruthenium complexes $CpRu\{=C(Ph)\text{-}\eta^3\text{-}C(Ph)C(Ph)CHO\}$ and $CpRu\{=C(Ph)\text{-}\eta^3\text{-}C(Ph)C(Ph)CH(Ph)\}$ with $P(OMe)_3$, diphenylacetylene, hydronium ions, and aryldiazonium cations is described [330]. The synthesis and reactivity of cationic vinylvinylidene and neutral enynyl complexes starting from $CpRu(PMe_3)_2Cl$ have been published. All new complexes were characterized by IR and NMR spectroscopies and by X-ray diffraction analysis in the case of $[CpRu(C{=}CHR)(PMe_3)_2]^+$ (where R = cyclohexenyl) [331].

New ruthenium(II) complexes containing the tridentate oxygen ligands $\eta^3\text{-}[RPO(C_6H_4O)_2]^{2-}$, $\eta^3\text{-}[CpCo\{PO(OEt)_2\}_3]^-$, and $\eta^3\text{-}HC(POPh_2)_3$ have been prepared and their reactivity explored. The report includes the X-ray crystal structure of $(\eta^6\text{-}C_6H_6)Ru\{\eta^3\text{-}PhPO(C_6H_4O)_2\}$ [332]. $[Os(N)Cl_2(CH_2SiMe_3)_2]^-$ reacts with [Cp][Na] and [Cp*][Li] to give the first cyclopentadienyl nitrido complexes $CpOs(N)(CH_2SiMe_3)_2$ and $Cp^*Os(N)(CH_2SiMe_3)_2$, respectively. The X-ray crystal structure of the silver-bridged complex $[\{CpOs(CH_2SiMe_3)_2\}_2(\mu\text{-}NAgN)]^+$ is presented. The reactivity of the nitrido ligand towards electrophiles has been examined [333]. Treatment of $CpRu(PPh_3)_2Cl$ with $P(OMe)_3$ gives $CpRu(PPh_3)\{P(OMe)_3\}Cl$, which has been structurally characterized by X-ray crystallography. The cyclometalated complex $CpRu(PPh_3)\{P(OPh)_2(OC_6H_4)\}$ has been obtained from the reaction between $CpRu(PPh_3)\{P(OPh)_3\}Cl$ and silver triflate [334]. The synthesis and reactivity of cyclopentadienylruthenium(II) amine and amide complexes have appeared. Each CpRu(II) complex possesses an ancillary dcpe ligand. Several X-ray crystal structures are included in this report [335]. The reaction between CpRu(dcpe)Cl and silver triflate and NH_3 yields $[CpRu(dcpe)(NH_3)]^+$, which upon treatment with hydride yields the amide complex $CpRu(NH_2)(dcpe)$. Both of these complexes have been characterized by X-ray crystallography. Other dcpe-substituted complexes are presented [336]. Estradiol and estradienyl complexes with a "Cp*Ru(II)" moiety have been synthesized and characterized by solution measurements [337]. New ruthenium sandwich complexes have been prepared and characterized [338]. 1,1-difluoroethylene reacts with $CpRu(CO)_2Me$ to give $CpRu(CO)_2CH_2CF_3$. The ease of HF elimination is discussed in the context of the observed reactivity [339]. A review article on the chemistry and utility of ruthenium-complexed indoles has been published [340]. The reaction of the cationic vinylidene complexes $[CpRuL_2\{=C=C(Me)Ph\}]^+$ (where $L_2 = PMe_3$, dppe) with sodium cyanide proceeds by a stereoselective addition sequence that yields the corresponding η^1-vinyl complexes in high yield [341]. New *para*-benzoquinonyl/ hydroquinonyl-substituted cyclopentadienylruthenium complexes have been prepared [342]. Naturally occurring ring-C aromatic diterpenoids have been allowed to react with the "$CpRu^+$" fragment. The products, which exist as epimeric pairs, have been characterized by NMR spectroscopy [343].

The alkylation of $CpRu(PPh_3)(^tBuNC)H$ with $[Ph_3C][BF_4]$, $[Et_3O][BF_4]$, or $[Me_3O][BF_4]$ gives $[\{CpRu(PPh_3)(^tBuNC)\}_2(\mu\text{-}H)]^+$ with low diastereoselectivity. High diastereoselectivity to the same dimer is observed when the molecular hydrogen complex $[CpRu(PPh_3)(^tBuNC)(\eta^2\text{-}H_2)]^+$ is treated with hydrogen [344]. $BrMg(CH_2)_4MgBr$ reacts with $Cp^*RuBr_2\{\eta^3\text{-}CH_2C(R)CH_2\}$ (where R = H, Me) to give the ruthenium(II) alkyl-butadiene complexes $Cp^*Ru(\eta^4\text{-}C_4H_6)\{\eta^1\text{-}CH_2CH(R)CH_3\}$. A double β-hydrogen elimination from ruthenacyclopentane species has been observed and is discussed in the proposed mechanism [345]. The synthesis and crystallographic study of the diastereomers of CpRu{(−)-Norphos}I are presented [346]. The long-chain alkyl halides $CpRu(CO)_2R$ (where $R = n\text{-}C_6H_{13}$ to $n\text{-}C_{12}H_{25}$) have been synthesized and characterized by IR and NMR measurements [347]. Cationic cyclopentadienylruthenium complexes, $[CpRuL_2(NCR)]^+$ (where L_2 = P-ligand; R = aryl), have been synthesized and used in the preparation of Langmuir–Blodgett films [348]. $[(\eta^5\text{-}C_5Me_4Et)RuCl]_4$ reacts with either pyridine or ethylene by *trans* addition to afford the dimers $[(\eta^5\text{-}C_5Me_4Et)RuL(Cl)]_2$. Oxidation of the pyridine complex yields the mixed-valence complex $[\{(\eta^5\text{-}(C_5Me_4Et)Ru(py)\}_2(\mu\text{-}Cl)_2]^+$ [349]. The reactivity of the organometallic Lewis acids $[CpRuL_1L_2]^+$ (where L_1 = CO, PPh_3; $L_2 = PPh_3$) with aldehydes, ketones, and amines is reported. All Lewis acid–base complexes have been characterized and the effects of conformational isomerism discussed when applicable [350]. The reaction between $CpRu(PPh_3)_2Cl$ and AgC≡CPh has been investigated and the isolated products characterized by X-ray crystallography [351]. Three products have been isolated when $CpRu(PPh_3)_2X$ (where X = Cl, I) was allowed to react with $C_2(CO_2Me)_2$. The X-ray crystal structures of the new complexes are included in this study along with plausible mechanisms for product formation [352].



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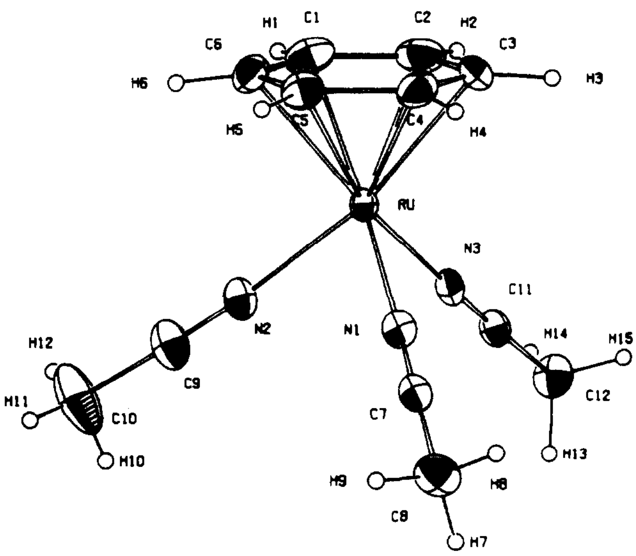
The mixed-carborane sandwich complexes $(\eta^6\text{-arene})Ru(\eta^5\text{-}Et_2C_2B_4H_4)$ have been examined by electrochemical methods [353]. A report describing the synthesis, characterization, and redox investigestion of pyrrolyl- and phospholyl-containing ruthenium sandwich complexes has appeared [354].

The π-arene complex $[Cp^*Ru(\eta^6\text{-}PhC{\equiv}CPh]^+$ has been obtained from the reaction between PhC≡CPh and $[Cp^*Ru(OMe)]_2$ in the presence of acid. The complexation of other arenes proceeds in an analogous fashion. Several X-ray crystal structures are included with this report [355]. The activation of carbon–hydrogen, carbon–oxygen, and carbon–carbon bonds has been observed with the "Cp^*Ru^+" fragment, which is generated from $[Cp^*Ru(OMe)]_2$ and triflic acid [356]. Treatment of $[Cp^*Ru(OMe)]_2$ with triflic acid, followed by reaction with various steroids, leads to selective aromatization of the A ring of steroids via a "Cp^*Ru^+" assisted demethylation sequence [357].

The reaction between $[(\eta^6\text{-}C_6H_6)Ru(acetone)_3]^{2+}$ and 2,11-dithia[3.3]orthocyclophane affords the cyclometalated complex $[(\eta^6\text{-}C_6H_6)Ru(o\text{-}C_6H_4\text{-}CHSCH_2\text{-}o\text{-}C_6H_4CH_2SCH_2)]^+$ as a result of sulfur coordination and deprotonation of one of the methylene groups. This new complex has been characterized by NMR spectroscopy and X-ray crystallography [358]. Nucleophile addition to the less sterically hindered ring in $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}[2.2]paracyclophane)]^{2+}$ has been investigated. The exo course of nucleophile attack is demonstrated by an isotopic labelling study [359]. Pyrazole reacts with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in H_2O/MeOH to give $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}pz)_2Ru(\eta^6\text{-}C_6H_6)]^+$ and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}pz)Ru(\eta^6\text{-}C_6H_6)]^+$, both of which have been structurally characterized by X-ray crystallography. These complexes serve as starting materials for hydroxo-bridged complexes [360]. C–H bond activation and formation of the arene complex $(\eta^6\text{-}C_6H_5R)RuP_2$ {where $P_2 = (C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$} have been observed when $Ru(P_2)_2H_2$ is thermolyzed with alkanes and arenes [361]. Electrophilic aromatic substitutions on arenes coordinated to the $Os(NH_3)_5$ moiety are reported [362]. The synthesis and X-ray crystal structure of the trimethylenemethane complex $Ru\{\eta^4\text{-}C(CH_2)_3\}(\eta^6\text{-}C_6H_6)$ have appeared. This complex is readily obtained from the reaction between $[(\eta^6\text{-}arene)RuCl_2]_2$ and $[C(CH_2)_3]^{2-}$ or $CH_2{=}C(CH_2SnMe_3)_2$ [363]. The synthesis and fluxional behavior of ruthenium(0) and osmium(0) containing the 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane ligand are discussed. This report includes a crystal structure of $[Ru(C_{18}H_{15})(\eta^6\text{-}C_6H_3Me_3)]^+$ which displays an agostic Ru–H interaction [364]. The X-ray crystal structure of $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3][PF_6]_2$ has been determined. The acetonitrile exchange rates have been measured as a function of temperature and pressure by using ^1H NMR spectroscopy. An interchange mechanism (I) has been established for the arene complex, whereas a dissociative pathway (B) involving $[Cp]^-$ loss was observed when the complex $[CpRu(MeCN)_3]^+$ was examined [365].

Treatment of $Ru(acac)_2(\eta^4\text{-}C_8H_{12})$ with sodium naphthalide furnishes the naphthalene complex $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ in moderate yield. The rate of naphthalene replacement by various arenes has been measured by ^1H NMR spectroscopy. The hydrogenation activity of the naphthalene complex is reported [366]. The ruthenium imido complexes $[(\eta^6\text{-}C_6H_6)Ru(N\text{-}2,6\text{-}R_2C_6H_3)]_2$ (where $R = {}^iPr$, Me) have been synthesized from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $NH(2,6\text{-}R_2C_6H_3)]^-$. X-Ray crystallographic analysis reveals the existence of a bent Ru_2N_2 bridge [367]. Monomeric imido osmium complexes have been prepared and investigated for their reactivity in exchange reactions with amines, alcohols, and thiols. The imido complexes, $(\eta^6\text{-}arene)Os(N^tBu)$ (where arene = C_6Me_6, *p*-cymene), are obtained in high yield from the reaction between $[(\eta^6\text{-}arene)OsCl_2]_2$ and excess $[NH^tBu]^-$. The X-ray crystal structure of the C_6Me_6 complex is reported [368].



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Starting with either $[(\eta^6\text{-}arene)OsX_2]$ or $[(\eta^6\text{-}arene)OsLX_2]$ (where L = P-ligand), new synthetic routes to azavinylidene half-sandwich complexes $[(\eta^6\text{-}arene)OsL({=}N{=}CR_2)]^+$ are presented [369]. The synthesis and reactivity of $(\eta^6\text{-}mes)Os(CNR)Cl_2$ (where R = Me, Ph, ^tBu) have been described. MeLi and PhLi react with the dihalide complexes by halide displacement to give $(\eta^6\text{-}mes)Os(CNR)_2R_2$. The carbene complex $(\eta^6\text{-}mes)Os\{{=}C(NHMe)Ph\}Ph_2$ has been isolated from the reaction between PhMeBr and $(\eta^6\text{-}mes)Os(CNMe)Cl_2$. The molecular structure of this carbene complex has been determined by X-ray diffraction analysis [370]. The reaction of $(\eta^6\text{-}C_6H_6)OsLI_2$ (where L = P-ligand) with terminal alkynes has been explored. Complexes containing alkynyl, vinyl, vinylidene, thio- and selenoketene ligands are described [371]. A study on the controlled fragmentation of EtOH into H_2 and the ligands CH_3, H, and CO has appeared. It is shown that $[(\eta^6\text{-}mes)OsCl_2]_x$ reacts with EtOH in the presence of propene and Na_2CO_3 to give $(\eta^6\text{-}mes)OsH(CH_3)CO$ and H_2. Isotopic labeling studies and the mechanism for this reaction are discussed [372]. The synthesis and reactivity of neutral alkenyl and cationic vinylidene complexes, $(\eta^6\text{-}C_6H_6)Os(C{\equiv}CR')(PR_3)I$ and $[(\eta^6\text{-}C_6H_6)Os({=}C{=}CHR')(PR_3)I]^+$ (where R′ = H, Me, ^nBu, ^tBu) respectively, have been published [373]. A high-yield synthesis of $(\eta^6\text{-}mes)Os(L)Cl_2$ (where L = P-ligands) from $[(\eta^6\text{-mes})OsCl_2]_x$ is presented. The corresponding bis(carboxylato)osmium complexes $(\eta^6\text{-mes})OsL(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)$ (where R = Me, CF_3) are obtained when the dihalide complexes are treated with excess AgO_2CR [374].

Cationic osmium trihydride complexes, $[(\eta^6\text{-}C_6H_6)Os(L)H_3]^+$ (where L = P-ligands), have been prepared and examined by ^1H NMR spectroscopy. In particular, the temperature-dependent proton–proton coupling constants are discussed within the frame of a quantum mechanical exchange phenomenon [375]. The activation of alkenylacetylenes by areneruthenium(II) complexes has been published [376]. The reaction between terminal alkynes and $(\eta^6\text{-}C_6Me_6)Ru(L)Cl_2$ (where L = P-ligands) in alcohol solvent is reported to give the alkoxyalkylcarbene complexes $[(\eta^6\text{-}C_6Me_6)Ru(L)(Cl)(=C(OR')(CH_2R)]^+$ [377].

Cyclometalation of phenylphosphine and neopentyl ligands in ruthenium(II) complexes has been observed [378]. The synthesis of ruthenium amide complexes containing *ortho*-metalated imine ligands is described [379]. The crystallographic results of diastereoisomeric $(\eta^6\text{-cymene})$ruthenium(II) chiral Schiff base complexes have been published [380].

3. Dinuclear complexes

3.1. Homodinuclear complexes

Treatment of $Ru_2(Cl)(\mu\text{-}O_2CMe)_4$ with pyridine-2-carboxylic acid affords the diruthenium(II) complex $Ru_2(pyca)_4$ and the ruthenium(III) complex $[Ru(pyca)_3]\cdot H_2O$. Both of these complexes react with PPh_3 to give PPh_3-substituted derivatives [381]. Four dfm anions add to $Os_2(O_2CMe)_4Cl_2$ to give the complex $Os_2(dfm)_4Cl_2$, which is shown to possess an Os_2^{6+} core. X-Ray diffraction and magnetic susceptibility data are presented. A ground-state configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2$ is reported for this new complex [382]. The synthesis, structure, and redox properties of the ruthenium(III) dimers $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6]^{2+}$ and $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ have been published. The solution ^1H NMR data are consistent with the solid-state structures [383]. 1,2-Diaminoethane reacts with the diruthenium(III) complex $[Ru_2(O)(O_2CAr)_2(PPh_3)_2(MeCN)_4]^{2+}$ (where Ar = various arenes) by addition to the two facial MeCN ligands to yield $[Ru_2(O)(O_2CAr)_2\{NH_2CH_2CH_2NHC(Me)NH\}_2(PPh_3)_2]^{2+}$. The products contain two seven-membered amino-amidine chelating ligands as confirmed by spectroscopic data and an X-ray diffraction study of the $C_6H_4\text{-}p\text{-}OMe$ derivative [384].

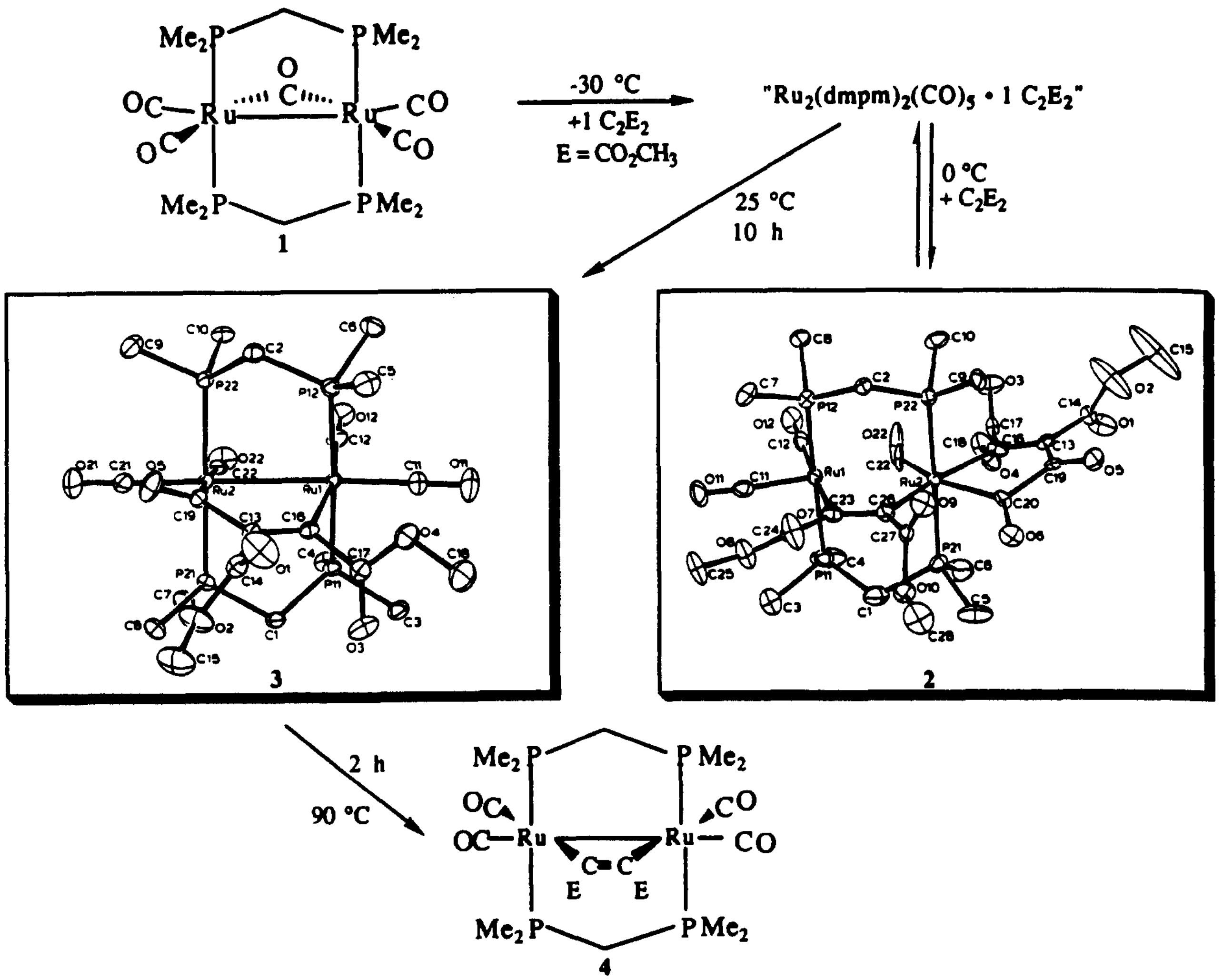
$Ru_2(\sigma$-fluoro-2-hydroxypyridine$)_4$(THF) has been synthesized and characterized by X-ray crystallography and magnetic susceptibility measurements. The ground-state configuration has been determined through the aid of SCF-Xα molecular orbital calculations [385]. A report describing the structures, magnetism, and redox properties of di- and trinuclear ruthenium complexes containing face-shared bioctahedra has appeared [386]. The synthesis and X-ray crystal structure of $Ru_2[(p\text{-tol})NC(H)N(p\text{-tol})]_4$ is reported. SCF-Xα calculations were performed [387]. The edge-shared bioctahedral complexes $Ru_2Cl_6(PR_3)_4$ (where R = Et, Bu) have been examined by epr spectroscopy. The g values are reported and are used in a discussion on the molecular structure of $Ru_2Cl_6P_4$ complexes [388]. The triply bonded osmium(III) dimers $[Os_2X_8]^{2-}$ (where X = Cl, Br) react with isocyanide ligands and CO by dimer cleavage. The 17-electron, paramagnetic complexes $[OsX_4(CNR)_2]^-$ have been obtained in high yield in the reaction with isocyanides. X-Ray diffraction data for $[OsCl_4(CNxyl)_2]^-$ and $OsCl_{4-x}Br_x(CO)(DMSO)$ (where $x \approx 1.32$) are presented [389].Carboxylic acids react with the tetrahydride-bridged dimer $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ to yield $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}O_2CR)_2RuCp^*$ (where R = H, Me, CF_3, adamantyl). Spin–lattice relaxation data reveal that the CF_3 derivative contains classical hydride ligands. The molecular structure of this same complex has been determined by X-ray crystallography [390]. Treatment of the paramagnetic dimers $Cp^*Ru(\mu\text{-}S^iPr)_xRuCp^*$ (where $x = 2, 3$) with $HC{\equiv}CSiMe_3$ yields $Cp^*Ru(\mu\text{-}H)(\mu\text{-}S^iPr)\{\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC(=CHSiMe_3)C{\equiv}CSiMe_3\}RuCp^*$, which upon air oxidation releases $(Me_3SiC{\equiv}C)_2C{=}CHSiMe_3$. An analogous reaction using $HC{\equiv}CTol$ is discussed [391]. The X-ray crystal structure of the bis(phenol) adduct of $Cp^*Ru(\eta^5\text{-oxocyclohexadienyl})$ has been published [392]. The dimer complex $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}CO)RuCp^*$ has been obtained from nucleophilic and electrophilic degradation reactions involving $[Cp^*RuOMe]_2$. Isotopic labeling studies have allowed the mechanism to be elucidated. A ruthenium–ruthenium triple bond is assigned to the bridging hydride complex on the basis of the X-ray data [393].

Data from a single-crystal neutron diffraction study of $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ have been published. A discussion of this complex and its relationship to chemisorbed ethylene is presented [394]. A detailed cryoelectrochemical study of the cleavage of the radical anion of $[CpRu(CO)_2]_2$ is described. Double potential step chronoamperometric data have been recorded and used to evaluate the rate constant for ruthenium–ruthenium bond cleavage in $[CpRu(CO)_2]_2^{-\cdot}$ at 77°C. The cathodic scan cyclic voltammogram of $[CpRu(CO)_2]_2$ was observed to be irreversible under all conditions [395]. *cis*- and *trans*-Diester-substituted alkenes are shown to react with $Ru_2(dmpm)_2(CO)_5$ to give *trans*-

substituted diruthenacyclobutanes. The reaction proceeds in a stepwise and reversible fashion with the proposed involvement of a zwitterionic intermediate. The X-ray crystal structure of $Ru_2(dmpm)_2(CO)_4\{\mu$-η^1:η^1-$C_2(H)_2(CO_2Me)_2\}$ is presented and discussed [396]. The reaction between $Ru_2(dmpm)_2(CO)_5$ and DMAD is accompanied by an unusual double insertion of CO into the transient ruthenium–alkyne bond. The X-ray crystal structures of two key intermediates are reported [397].

Halogenation of $Ru_2(\mu$-$CO)(CO)_4\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$ gives $[Ru_2X(CO)_5\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2]^+$ (where R = Me, ^iPr; X = Cl, Br, I), which possesses a terminally bound halogen atom. These products react with $Me_3NO \cdot 2H_2O$ in the presence of halide ions to yield $Ru_2(\mu$-$X)(X)(CO)_3\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$ [398]. Thermolysis of $Ru_2(\mu$-$CO)(CO)_4\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$ or $Ru_2H_2(CO)_4\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$ affords the unsaturated complex $Ru_2(CO)_4\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$. The reactivity of the tetracarbonyl and the X-ray structures of the two starting materials are reported [399]. Cyclic voltammetry studies have been carried out on $Ru_2(\mu$-$CO)(CO)_4\{\mu$-$(RO)_2PN(Et)P(OR)_2\}_2$. ECE and ECEC mechanisms have been observed during the electrochemical oxidation, the exact pathway being dependent on the nature of the solvent [400].

The dimeric complex $Ru_2(CO)_6(\mu$-$C_{10}H_8N_2)$ (where $C_{10}H_8N_2$ = 1,8-diaminonaphthalene) has been obtained from $Ru_3(CO)_{12}$ and $C_{10}H_{10}N_2$ at 110°C. The reactivity of the ruthenium–ruthenium bond in the dimer is demonstrated by reaction with halogens, HBF_4, and DMAD. P-Ligand substitution chemistry yields mono-, bis-, and trisubstituted dimers [401]. The complex $Ru_2(CO)_4(PPh_3)_2\{\mu$-$1,2$-$(NH)_2C_6H_4\}$ has been examined with various diphosphines. The products have



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been characterized by IR and NMR spectroscopy in addition to X-ray diffraction analysis in the case of the complex $Ru_2(CO)_2(PPh_3)_2(dppm)\{\mu\text{-}1,2\text{-}(NH)_2C_6H_4\}\cdot$ toluene [402]. The complexes $Ru_2(CO)_6(\mu\text{-}SePh)_2$ and $\{Ru(\mu\text{-}SePh)_2(CO)_2\}_x$ have been isolated from the reaction between $Ru_3(CO)_{12}$ and Ph_2Se_2. X-Ray crystallography reveals that the phenyl groups adopt an anti configuration. The anti phenyl groups are maintained in solution as indicated by IR and NMR measurements [403]. The addition reactions of protons and metal electrophiles to the ruthenium–ruthenium bond in $Ru_2(CO)_4(^iPr_3P)_2(\mu\text{-}C_{10}H_8N_2)$ are reported. The X-ray crystal structure of $[Ru_2(CO)_4(^iPr_3P)_2(\mu\text{-}AgPPh_3)(\mu\text{-}C_{10}H_8N_2)]^+$ is included in this report [404]. The reaction between $Ru_2(CO)_4(^iPr_3P)_2(\mu\text{-}C_{10}H_8N_2)$ and HgX_2 (where X = Cl, Br, I) has been found to yield trinuclear Ru_2Hg clusters [405].

The bimetallic allenyl complex $Ru_2(CO)_6(\mu\text{-}\eta^1:\eta^2\text{-}PhC{=}C{=}CH_2)(\mu\text{-}PPh_2)$ reacts with H_2NR or ^tBuNC at the β-carbon to form zwitterionic dimetallacyclopentane and dimetallacyclopentene complexes. The X-ray crystal structures of three complexes and extended Hückel molecular orbital data are presented [406]. The bis(pentadienyl)dianion $[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2][K]_2$ has been allowed to react with $(Cp^*RuCl)_4$ to give $\{4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2\}\{Cp^*Ru\}_2$. The X-ray crystal structure and solution NMR data are presented [407]. The catalytic disproportionation of aldehydes with $[(C_4Ph_4COHOCC_4Ph_4)(\mu\text{-}H)][(CO)_4Ru]_2$ in the presence of formic acid is reported. Kinetic studies have been carried out and turnover numbers and the rate expression are presented. The proposed mechanism includes a detailed cycle for the bimolecular transformation of RCHO to esters [408]. Cyclometallated (N,C) benzamido mono- and bisruthenium(II) complexes have been synthesized and structurally characterized from the reaction between NH_2COR (where R = CF_3, Ph) and $RuH_2(CO)(PPh_3)_3$ [409]. The thiolate-bridged complex $[(CO)_4(PPh_3)_2Ru_2(\mu_2\text{-}SEt)_4(\mu_3SEt)_2Na_2(THF)_2]$ has been isolated from the reaction between *cis,cis,trans*-$RuCl_2(CO)_2(PPh_3)_2$ and [EtS][Na] and characterized by X-ray crystallography [410]. An electrochemical and X-ray crystallographic study on $Ru_2(\mu\text{-}2\text{-pyridine})(CO)_4(2\text{-pyridine})$ has appeared [411]. The electronic structure of $Ru_2(CO)_6\{\mu,\mu'\text{-}N(R)CH_2CH_2N(R)\}$ and the mixed-metal iron-ruthenium analog has been investigated by using UV-photoelectron spectroscopy and SCF first-principle discrete variational (DV) $X\alpha$ calculations [412].

3.2. Heterodinuclear complexes

$CpRu(CO)_2I$ has been allowed to react with $[Mn(CO)_5][Na]$ to yield $CpRuMn(CO)_7$. Treatment of this heptacarbonyl complex with Ph_2PH gives the new phosphido-bridged ruthenium-manganese complexes $CpRuMn(CO)_5(\mu\text{-}H)(\mu\text{-}PPh_2)$, *trans*- and *cis*-$Cp_2Ru_2(CO)_2(\mu\text{-}H)(\mu\text{-}PPh_2)$, $CpRuMn_2(CO)_9(\mu\text{-}H)(\mu\text{-}PPh_2)_2$, and $CpRuMn(CO)_8(Ph_2PH)(\mu\text{-}H)(\mu\text{-}PPh_2)_2$. The X-ray crystal structures of several of these products have been solved [413]. The synthesis and X-ray crystal structure of $CpRu(CO)_2Mo(\eta^7\text{-}C_7H_7)(CO)_2$ have been published. Solution IR studies reveal that a solvent-dependent conformation involving *cis/trans* polyene rings is present [414]. Long-chain $Cp(CO)_2Fe(CH_2)_xRuCp(CO)_2$ (where $x = 4$–6) complexes have been synthesized and characterized by IR and NMR spectroscopy and mass spectrometry. The X-ray crystal structure of the complex with $x = 6$ indicates that the methylene chain adopts a zigzag conformation. The thermal stability of these complexes have been investigated by using differential scanning calorimetry [415]. The reduction chemistry associated with the $\mu\text{-}\eta^1(C):\eta^2(O,O')\text{-}CO_2$ complex $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ is reported. The formaldehyde complex $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$ is obtained from the former complex upon treatment with 2 equiv. of $Cp_2Zr(H)Cl$. The results of an isotopic labeling study and a mechanism showing ^{13}C exchange between the terminal carbonyls and the carboxylate group are presented [416]. The synthesis and fluxional NMR behavior of the ruthenium-rhenium η^2-dihydrogen complex $[(PPh_3)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)Ru(\eta^2\text{-}H_2)(PPh_3)_2]^+$ have appeared. Included in this report is the reactivity of related complexes with $CHCl_3$ and acid [417]. A report on the redox chemistry of $WRu(fulvalene)(CO)_5$ has been presented. The W–Ru bond is shown to undergo a two-electron reduction to the dianion via an ECE process [418]. The stable anion $[(\eta^5:\eta^{5'}\text{-}C_{10}H_8)_2RuCo]^-$ has been obtained from the electrochemical reduction of the corresponding monocationic complex [419].

The synthesis and reactivity of heterobimetallic ruthenium-rhodium and ruthenium-iridium complexes containing bridging pyrazolate ligands are described [420]. Synergism in heterobimetallic ruthenium-iridium catalysts has been observed. The complexes $Ru(H)(CO)(PPh_3)_2(\mu\text{-}bzim)Ir(1,5\text{-}COD)$ and $Ru(H)(CO)(PPh_3)_2(\mu\text{-}pz)Ir(tetraflurobenzobarrelene)$ are reported to be more active in the hydrogenation of cyclohexene than all suitable mononuclear complexes examined [421].

The X-ray structure and redox properties of the cyano-bridged complex *cis*-$[(dppe)(Et_3P)(CO)_2Mn(\mu\text{-}CN)Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]\cdot CH_2Cl_2$ have been reported [422]. The reaction of CpRu(dppen)Cl and CpRu(dppm)Cl with $[Rh(CO)_2Cl]_2$ gives the heterobimetallic complexes $CpRu(\mu\text{-}CO)_2(\mu\text{-}L_2)RhCl_2$ in excellent yield. X-Ray crystallographic data on CpRu-

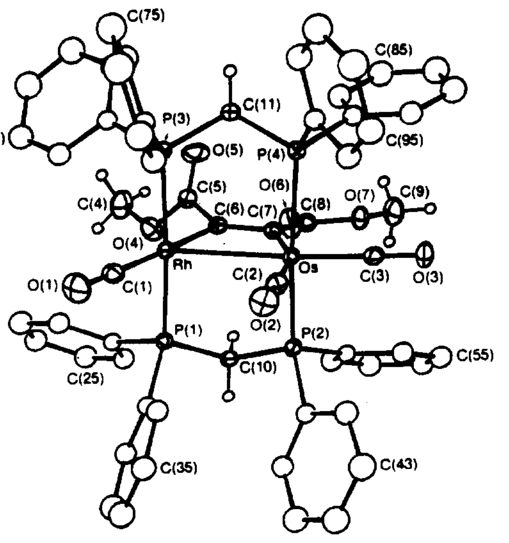
(dppen)Cl and $CpRu(\mu\text{-}CO)_2(\mu\text{-dppm})RhCl_2$ are presented [423]. $[HOs(CO)_4]^-$ reacts with $Ir(Cl)(\eta^2\text{-dppm})_2$ to yield the heterobimetallic complex $IrOs(H)_2(CO)_3\{\mu_2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2)(dppm)\}$, which exhibits an *ortho*-metalated phenyl group at the iridium center. The *ortho* metalation is reversed upon treatment with electrophiles, which gives the hydride-bridged complexes $[IrOs(CO)_3(\mu\text{-}H)(\mu\text{-}X)(dppm)_2]^+$ (where X = H, $AuPPh_3$). Several crystal structures are presented and the X-ray data are discussed [424]. Treatment of $RhOs(H)(CO)_3(dppm)_2$ with CCl_4 yields $RhOs(Cl)(CO)_3(dppm)_2$, while protonation yields $[RhOs(\mu\text{-}H)_2(CO)_3(dppm)_2]^+$. This latter complex loses H_2 in the presence of CO to afford $[RhOs(CO)_4(dppm)_2]^+$, which is shown to react with DMAD to give the alkyne-bridged complex $[RhOs(CO)_2(\mu\text{-}CO)(\mu\text{-dmad})(dppm)_2]^+$. The complex $[RhOs(CO)_3(\mu\text{-dmad})(dppm)_2]^+$ has been isolated and characterized by X-ray diffraction analysis [425].

4. Polynuclear complexes

4.1. Trinuclear clusters

4.1.1. Simple and hydrocarbon ligands

An electrochemical study of $Ru_3(CO)_{12}$ in acetone and CH_2Cl_2 solvents has been conducted. Polarographic and cyclic voltammetric data indicate that the observed two-electron reduction process occurs via an EE mechanism with ruthenium–ruthenium bond cleavage accompanying the first electron-transfer step [426]. High-pressure IR spectroscopy has been used to study the $Ru_3(CO)_{12}/Ru(CO)_5$ equilibrium. Thermodynamic data for the equilibrium are presented [427]. $Ru_3(CO)_{12}$ crystallization has been studied by using potential energy calculations and computer graphic analysis. The crystal building process was examined by using interlocking tetra-, tri-, and dicarbonyl units of independent molecules [428]. Electron transfer between $[M_3(CO)_{11}]^{2-}$ and $M'_3(CO)_{12}$ (where M = Os, M′ = Ru, Fe; M′ = Fe, M = Ru) has been observed to give $[M'_3(CO)_{11}]^{2-}$ and $M_3(CO)_{12}$. Isotopic labeling data indicate that an outer-sphere electron-transfer mechanism is operative and does not involve a CO^{2+} transfer process [429]. The thermolysis reaction involving $Ru_3(CO)_{12}$ and $PhPH_2$ affords a complex mixture of high nuclearity phosphinidene-capped ruthenium clusters [430]. (*R*)-Campherhydrazone reacts with $Ru_3(CO)_{12}$ to give $Ru_3(CO)_9(\mu_2\text{-}H)\{\mu_3\text{-}\eta^2\text{-}(R)\text{-}NHN{=}C\text{-}CH_2CH(CMe_2)CH_2CH_2CMe\}$, which has been structurally characterized by X-ray diffraction analysis [431]. Thermolysis of $Ru_3(CO)_{12}$ with 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives gives the corresponding $Ru_3(CO)_9(\mu_2\text{-}H)_2$(7-oxabicyclo[2.2.1]hept-5-yn-yl) clusters [432]. Cyclometalation has been observed in the reaction between $Ru_3(CO)_{12}$ and 1-aza 1,3-diene ligands. The primary products are four- and five-membered azaruthenacycles [433]. The synthesis and crystallographic characterization of the two diastereomers of $Ru_3(CO)_6\{MeC{=}C(H)C(H){=}N^iPr\}_2$ are published. The complex contains two β-metalated monoazadien-4-yl ligands [434].



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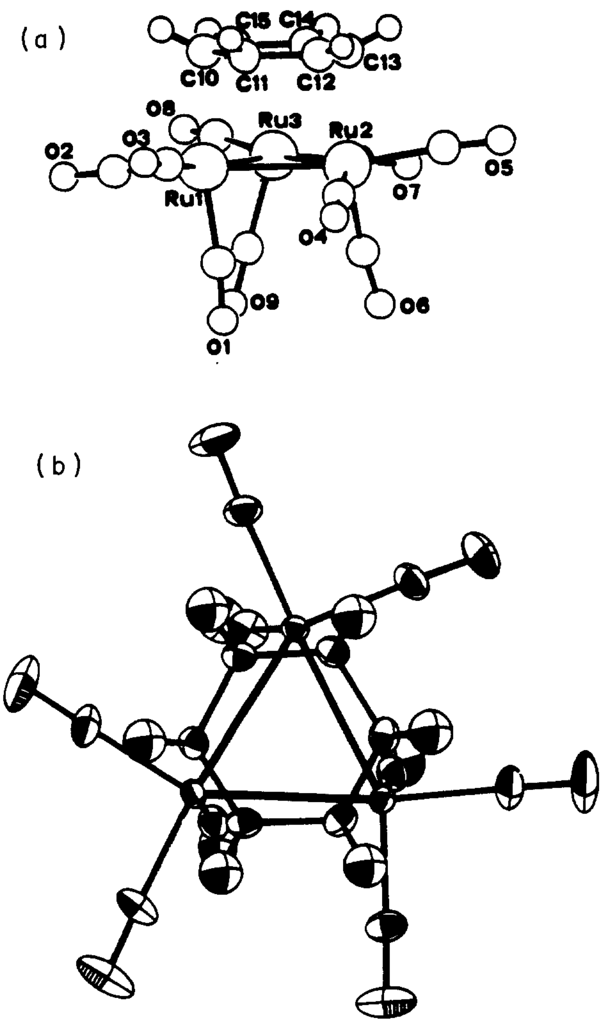
An example of a $\mu_3\text{-}\eta^3$-siloxyl ligand has been documented. The reaction between $Os_3(CO)_{10}(MeCN)_2$ and $HSi(OEt)_3$ proceeds readily at room temperature to afford $Os_3(CO)_{10}(MeCN)\{Si(OEt)_3\}(\mu\text{-}H)$ as the initial product. This cluster is transformed to $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Si(OEt)_3)(\mu\text{-}H)$ upon thermolysis in heptane. Both clusters have been characterized by IR and NMR spectroscopy in addition to X-ray diffraction analysis. The latter cluster adds 2 moles of CO at elevated temperature to give $Os_3(CO)_{11}\{Si(OEt)_3\}(\mu\text{-}H)$ [435]. $Os_3(CO)_{10}(MeCN)_2$ has been allowed to react with $Fe(\eta^5\text{-}C_4H_4N)Cp$ to give the *ortho*-metalated cluster $Os_3(CO)_{10}(\mu\text{-}H)\{(C_4H_3N)FeCp\}$. X-Ray diffraction analysis reveals that the osmium cluster is ligated to the Fe atom by the pyrrolyl moiety. IR spectroelectrochemical data for the corresponding radical cation have been recorded at −25°C and are discussed in terms of the extent of interaction between the cluster and the azaferrocene ligand. Analogous data for $Os_3(CO)_{10}(\mu\text{-}H)\{(C_4H_3N)Mn(CO)_3\}$ are presented [436]. The reactions of methoxyallene and isomeric methyl proparagyl ether with $Os_3(CO)_{11}(MeCN)$ and $Ru_3(CO)_{10}(MeCN)_2$ are described. Included in this report is the X-ray crystal structure of $Os_3(CO)_{11}$

(μ,η^1,η^3-$CH_2CCHOMe$) [437]. $Os_3(CO)_{10}(MeCN)_2$ reacts with oxalic acid to afford $\{Os_3(CO)_{10}(\mu\text{-}H)\}_2$-$(C_2O_4)$. The molecular structure of the product has been determined by X-ray crystallography [438]. A triple oxidative addition has been observed in the reaction between $Os_3(CO)_{10}(MeCN)_2$ and PhSeSePh. The first cluster observed is $Os_3(CO)_{10}(\mu\text{-}SePh)_2$, which is unstable in solution, transforming ultimately to $Os_3(CO)_8(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3Se)_2$. The identity of this latter cluster was unequivocally determined by X-ray diffraction analysis [439].

The reactivity of $[Ru_3(CO)_9(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)]^-$ with dppm has been investigated. Depending upon the reaction conditions, both $Ru_3(CO)_7$(dppm) (μ_3-η^2-PhC≡CPh) and $Ru_3(CO)_8$(dppm)(μ_3-η^2-PhC≡CPh) are observed. The former cluster reacts readily with added dppm and H_2, and the products of these reactions have been fully characterized by IR and NMR spectroscopy [440]. The activation volumes for intramolecular exchange of the hydride ligands in $Os_3(CO)_{10}(PPh_3)(H)(\mu\text{-}H)$ and $Ru_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}CHCO_2Me)$ have been measured by ^1H NMR spectroscopy [441]. Halide-promoted CO labilization of alkyne-substituted $Ru_3(CO)_{12}$ clusters has been examined as a way to produce new ruthenium clusters [442]. Variable-temperature ^{13}C NMR data are presented for a 1:1 mixture of $[HRu_3(CO)_{11}]^-$ and $[DRu_3(CO)_{11}]^-$. The NMR data are discussed in terms of intramolecular CO exchange pathways [443]. A study on the kinetics of ^{13}CO exchange with $[HM_3(CO)_{11}]^-$ and $[DM_3(CO)_{11}]^-$ (where M = Ru, Os) has appeared. ^{13}CO–^{12}CO exchange occurs by two parallel pathways and the ion-pairing ability of the gegencation is shown to influence the rate of the exchange reactions [444].

The triosmium cluster $Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)$-$(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ was the subject of a kinetic analysis dealing with stereochemical nonrigidty of the μ_3-benzene and ethylene ligands. Four intramolecular dynamical processes have been observed in the solid state by ^{13}C CP/MAS NMR measurements [445]. The solid-state structure of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ has been established by X-ray crystallography. Fenske–Hall calculations have been carried out and the bonding of the benzene ring to the metal frame is discussed [446].

Triosmium and triruthenium carbon radicals have been examined for their reactivity toward fluorobenzene and hexafluorobenzene [447]. The cluster $H_3Os_3(CO)_9(\mu_3\text{-}CCO_2Me)$ has been prepared from $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$. Thermolysis of the latter cluster proceeds by way of a rearrangement to the alkylidene tautomer $H_2Os_3(CO)_9\{\mu_3,\eta^2\text{-}CHC(O)OMe\}$. The synthesis of other cluster complexes from $[H_3Os_3(CO)_9$-$(CCO)]^+$ is described [448]. Treatment of $Os_3(CO)_9(\mu$-H$)_3(\mu_3$-CH) with neat trifluoromethanesulfonic acid affords the triflate cluster $Os_3(CO)_9(H)_2(O_3SCF_3)_2$. The reactivity of the bis(triflate) cluster with protonic acids is reported. The X-ray crystal structure of $Os_3(CO)_9(\mu\text{-}H)_2(\mu,\eta^2\text{-}O_2CMe)(\eta^1\text{-}O_3SCF_3)$, which was isolated from the reaction of AcOH with the bis(triflate) cluster, is included in this report [449].



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Benzyl isonitrile reacts with $Os_3(CO)_{10}(\mu\text{-}Br)$-(CH=CHPh) to give $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-}Br)$-(CH=CHPh), whereas the same reaction with PPh_3 affords the diosmium complex $Os_2(CO)_5(PPh_3)(\mu\text{-}Br)$-(CH=CHPh). Variable-temperature NMR data reveal that the ethenyl group in $Os_3(CO)_9(CNCH_2Ph)(\mu\text{-}Br)$-(CH=CHPh) is static. The X-ray structures of both products are presented [450]. The reactivity of the triosmium clusters $Os_3(CO)_9(\mu\text{-}H)_2Ar$ (Ar = C_6H_4, C_9H_6, C_4H_3N, C_4H_2NMe) toward P-ligands has been investigated. Facile CO substitution to give Os_3-

$(CO)_{9-n}(PR_3)_n(\mu\text{-}H)_2Ar$ (where $n = 1, 2$) is observed when the cluster is chemically activated by trimethylamine oxide. The report includes the X-ray crystal structure of $Os_3(CO)_7[P(OMe)_3]_2(\mu\text{-}H)_2(C_4H_3N)$ [451]. The bis(trifluoromethyl)nitroxyl radical, $(CF_3)_2NO$, reacts with $Os_3(CO)_{11}(\mu\text{-}H)(H)$ to afford $Os_3(CO)_{11}(\mu\text{-}H)[(CF_3)_2NO]$ via abstraction of the terminal hydride. The IR and X-ray diffraction data for this product are presented and the radical substitution mechanism outlined [452]. The reactivity of the bridging aminocarbene ligand in $Os_3(CO)_9(\mu\text{-}H)_2[\mu_3\text{-}C(Et)NMe(CH)]$ has been explored [453]. Mechanistic studies on intramolecular metal-to-ligand hydrogen transfer reactions in the the cluster complexes $Os_3(CO)_{10}(X)(\mu\text{-}X)(CNR)$ (where R = Me, Ph, *p*-tolyl, *o*-tolyl, 2,4-$C_6H_3Me_2$; X = H, D) have been published [454]. A redox study of the triosmium clusters $Os_3(CO)_9L(\mu\text{-}H)_2$ and $Os_3(CO)_{10}L(\mu\text{-}H)(H)$ (where L = CO, PPh_3, $ArPh_3$) has appeared. The unsaturated clusters exhibit complicated redox behavior which involves an adsorption process [455].

4.1.2. Phosphine ligands

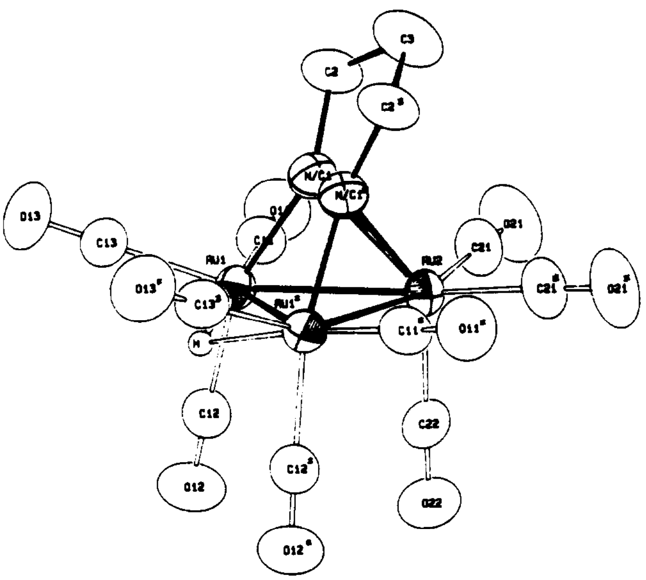
The synthesis, redox properties, and X-ray crystal structures of $Ru_3Cl_8(PR_3)_4$ (where R = Me, Et) have been reported. SCF-Xα-SW molecular orbital calculations have been carried out and the data compared with previous results for $[Ru_3Cl_{12}]^{4-}$ [456]. Trinuclear ruthenium clusters of the form $[Ru_3Cl_6(PR_3)_6]^+$ (where R = Et, Bu) have been isolated and structurally characterized by X-ray crystallography [457].

$Ru_3(CO)_{10}(PMe_2Ph)_2$ reacts with DMAD to yield $Ru_3(\mu_3\text{-}DMAD)(\mu\text{-}CO)(CO)_7(PMe_2Ph)_2$. It is shown that the alkyne is attached to the closed Ru_3 triangle in a $\mu_3\text{-}\eta^2\text{-}\|$ mode [458]. The use of tris(alkynyl)phosphines, $(RC{\equiv}C)_3P$, in the synthesis of phosphido and phosphinidene clusters is reported. The clusters that have been isolated and structurally characterized include $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)\{\mu_2\text{-}P(C{\equiv}C^tBu)_2\}$ (where M = Ru, Os) and $Ru_4(CO)_{10}(\mu_4\text{-}\eta^4\text{-}t\text{-}C{\equiv}C\text{-}C{\equiv}C^tBu)\{\mu_4\text{-}P(C{\equiv}C^tBu\}$ [459]. The carbonylation of benzyne has been observed in $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$ and $Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_4\text{-}C_6H_4)$. The former cluster reacts with CO to give $Ru_3(CO)_8(\mu\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4CO)$ while the latter gives $Ru_3(CO)_{10}(\mu_3\text{-}PPh)\{\mu\text{-}C_6H_4(CO)_2\}$ and/or $Ru_2(CO)_7\{\mu\text{-}P(Ph)C(O)C_6H_4\}$. The identity of all products has been confirmed by X-ray diffraction analysis [460]. Phosphine-ligand substitution on $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}COMe)$ has afforded the new clusters $Ru_3(CO)_6(\mu\text{-}H)_3(\mu_3\text{-}COMe)\{\mu_3\text{-}(PPh_2CH_2)_3CMe\}$ and $Ru_3(CO)_7(\mu\text{-}H)_3(\mu_3\text{-}COMe)\{\mu_2\text{-}(PPh_2)_3CH\}$, which have been structurally characterized by X-ray diffraction analysis. Both clusters may be oxidized to the corresponding 47-electron radical cations, which have been characterized by EPR spectroscopy [461]. Phosphine addition and substitution reactions on $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2)$ and $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeCH_2C{=}NCH_2CH_2Me)$ are reported [462].

$Os_3(CO)_{10}(MeCN)_2$ reacts with $(CF_3)_2PN{=}PPh_3$ to yield $Os_3(CO)_{10}\{(CF_3)_2PN{=}PPh_3\}_2$. X-Ray crystallography indicates that the diphosphazene ligands occupy equatorial sites [463]. Decarbonylation of the phenylphosphole cluster $Os_3(CO)_{11}(PhPC_4H_4)$ gives the oxidative addition product $Os_3(CO)_9(\mu_3\text{-}PhPC_4H_4)$ as a result of triosmium and phosphole ring opening. Thermolysis of this product is accompanied by CO loss, triosmium ring closure and reorganization of the phosphole ligand [464]. Cyclopentadienylidenetriphenylphosphorane, $Ph_3PC_5H_4$, reacts with $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Ph_3PC_5H_3)$. X-Ray diffraction analysis shows that the C_5 ring is bonded through a single carbon atom to two osmium centers. The cluster is considered to be zwitterionic with an uncoordinated phosphonium substituent and an osmium center that carries a formal negative charge [465]. Ring opening *vs.* phenyl–phosphorus bond cleavage in the reaction between 3,4-dimethyl-1-phenylphosphole and $Os_3(CO)_{12-x}(MeCN)_x$ (where $x = 1, 2$) has been investigated [466]. The cluster $Os_3(CO)_{10}(H)(\mu\text{-}PhPH)$ is deprotonated to give $[Os_3(CO)_{10}(H)(\mu\text{-}PPh)]^-$. Treatment of this anion with acid regenerates the starting material with the phenyl group oriented exo to the $Os(CO)_4$ group. The reactivity of the anionic cluster with MeI is reported, and the spectroscopic data and X-ray diffraction structure of the product cluster $Os_3(CO)_{10}(H)(\mu\text{-}PMePh)$ are presented [467].

4.1.3. Nitrogen ligands

The coordination of carbamates, hydrazides, guanidines and ureas to $Ru_3(CO)_{12}$ has been studied. The isolation and X-ray structure of $Ru_3(CO)_9(\mu_2\text{-}H)\{\mu_3\text{-}\eta^2\text{-}(1R,2S,5R)\text{-}8\text{-phenylmenthyl carbamate}\}$ are described [468]. Reductive carbonylation of 2-nitrobiphenyl in MeCN gives carbazole and 2-aminobiphenyl when $Ru_3(CO)_{12}$ is used as the catalyst. Included in this report is the X-ray crystal structure of $Ru_3(CO)_9(\mu_3\text{-}NC_6H_4\text{-}o\text{-}C_6H_5)_2$, which was isolated from the reaction between $Ru_3(CO)_{12}$ and 2-nitrosobiphenyl [469]. Irradiation of $Ru_3(CO)_{12}$ with Et_2N_2 affords the triruthenium cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2Et_2)$. This cluster rearranges to $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN{=}CHMe)$ upon heating. Both isomeric clusters are hydrogenated to give $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtNNHEt)$. The X-ray crystal structure of the latter cluster is presented and the ancillary nitrogen ligand is described as a hydrazine-like group [470]. The reaction of N-methylpyrrolidine with $Ru_3(CO)_{12}$ and $Os_3(CO)_{10}$-



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$(MeCN)_2$ has been explored. The major product from $Ru_3(CO)_{12}$ is dependent on the method used to activate the cluster. Full solution characterization and several X-ray structures are included. The X-ray structure of $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CH\text{-}N{=}CCH_2CH_2CH_2)$, which was obtained when the promoter $Fe_2(CO)_4(\mu\text{-}SCH_2Me)_2(PPh_3)_2$ was employed in the reaction, is shown below [471].

Treatment of $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-ampy})$ with Ph_2Hg affords the hexaruthenium cluster $Ru_6(CO)_{18}(\mu_4\text{-}Hg)(\mu_3\text{-ampy})_2$. X-Ray diffraction analysis of the THF solvate reveals that the mercury atom bridges two $Ru_3(CO)_9(\mu_3\text{-ampy})$ fragments via the NH-bridged ruthenium atoms [472]. The synthesis and reactivity of Ph_2PH-substituted clusters derived from $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-ampy})$ and $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-ampy})]^+$ have been published [473]. PPh_3 substitution chemistry, protonation studies, and methoxycarbonyl cluster synthesis in $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-ampy})$ are described [474].

The synthesis of 1,1,1-tris(isocyanomethyl)ethane and its use as a ligand in the reaction with $Os_3(CO)_{10}(MeCN)_2$ have appeared. The isolated cluster $Os_3(CO)_9(\text{trisNC})$ is shown to contain a face-capping isocyanide ligand [475]. The cluster $H_2Os_3(CO)_{10}$ reacts with the heterocumulene ligand $PhN{=}C{=}C{=}PPh_3$ to yield $HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PhNCHCPPh_3)$. X-Ray diffraction analysis indicates that the 1,2-dipolar ligand bridges the metallic frame [476]. Terminal alkynes have been allowed to react with the carbene cluster $Os_3(CO)_{11}\{C(Et)NMe_2\}$. When $^tBuC{\equiv}CH$ is used, the new cluster $Os_3(CO)_9\{C(Et)NMe_2\}\{\mu_3\text{-}C(H)C^tBu\}$ and the known cluster $Os_3(CO)_{10}\{\mu\text{-}H_2CNMe(Et)\}(\mu\text{-}H)$ are the major products isolated [477]. The reactivity of $Os_3(CO)_{10}(MeCN)_2$ with secondary mixed amines $NHR'R$ (where $R = Et$; $R' = Me$, Pr) has been examined [478].

4.1.4. Sulfur ligands

The thienyl complexes $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}C_4H_2RS)$ (where $R = H$, Me) have been synthesized from the respective thiophene and $Os_3(CO)_{10}(MeCN)_2$. Solution studies indicate that these clusters exist as a mixture of exo and endo isomers, which interconvert by a transient S-bonded intermediate [479]. Thietane ring opening by nucleophiles has been observed in a triosmium cluster. The cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SCH_2CMe_2CH_2Cl)$, which contains a chloride-opened thietane ring, was obtained from the reaction between $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$ and $[Et_4N][Cl]$ [480]. 3,3-Dimethylthietane reacts with $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$ to afford $Os_3(CO)_{11}(SCH_2CMe_2CH_2)$ and $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$, respectively. The former cluster, which is shown by X-ray crystallography to contain a S-coordinated ancillary ligand, reacts with additional 3,3-dimethylthietane to yield $Os_3(CO)_{10}\{(\mu\text{-}SCH_2CMe_2CH_2)_3\}$. This new cluster possesses an 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand that is formed by the ring-opening oligomerization of three ligands [481].

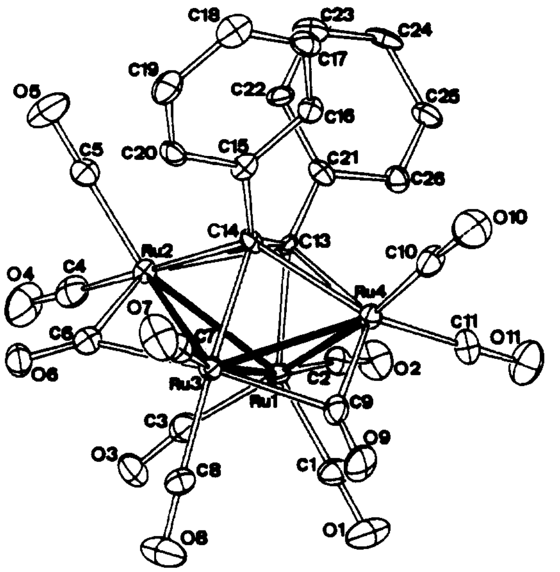
4.2. Tetranuclear clusters

Vibrational spectra of the μ_2-hydride ligands in $M_4(CO)_{12}(\mu\text{-}H)_4$ (where $M = Ru$, Os) have been interpreted in terms of D_{2d} molecular symmetry [482]. ^{17}O NMR measurements have been employed in the characterization of the tetraruthenium aquo clusters $H_n[Ru_4O_6(OH_2)_{12}]^{(4+n)+}$ (where $n = 0$–4) [483]. The linear tetraruthenium cluster $Ru_4(CO)_{10}\{MeC{=}C(H)C(H){=}N^iPr\}_2$ reacts with oxidizing agents at elevated temperatures by fragmentation to give $[Ru(CO)_2X\{MeC{=}C(H)C(H){=}N^iPr\}]_2$ and $[Ru(CO)_3X_2]_2$ (where $X =$ Cl, Br, I). The acceleratory effect of CO on the fragmentation is discussed [484]. The 62-electron butterfly cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ reacts with azobenzene to yield the 64-electron cluster $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhN_2Ph)$. X-Ray crystallography reveals that the polyhedron of this cluster is derived from a capped trigonal prismatic Ru_4PN_2 core [485]. The molecular structure of $Ru_4(CO)_{10}\{(CH_2{=}C(H)C(H){=}N^tBu)_2\}$ has been determined by X-ray crystallography [486]. The relationships between the structure and redox properties of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)$ and $[Ru_4(CO)_{11}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]^{2-}$ are reported. The latter cluster is obtained from the former cluster upon two-electron reduction. The transformations involved between these two clusters are shown to involve six species on the basis of cyclic voltammetry data. Digital simulation of the cyclic voltammetry data have enabled a mechanism to be constructed. Included in this report is the X-ray structure of the anionic cluster [487].

Trimethylamine oxide activation of $Os_4(CO)_{12}(\mu\text{-}H)_4$ in MeCN affords the reactive solvent cluster $Os_4(CO)_{10}(MeCN)_2(\mu\text{-}H)_4$. Cyclohexa-1,3-diene has been allowed to react with this cluster to give $Os_4(CO)_{10}(\mu\text{-}H)_2(\eta^6\text{-}C_6H_6)$ and $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$. The X-ray diffraction structure of each cluster is presented along with the reaction conditions that allow for the interconversion of the former cluster to the latter cluster [488]. Benzene ligand displacement in $Os_4(CO)_{10}(\mu\text{-}H)_2(\eta^6\text{-}C_6H_6)$ is observed when the cluster is treated with diphenylacetylene and Me_3NO. The product $Os_4(CO)_9(\mu\text{-}H)_2(Ph_2C_2)_2$ has been characterized by X-ray crystallography [489]. Molecular organization and dynamic behavior in the arene cluster complexes $Os_4(CO)_{10}(\mu\text{-}H)_2(\eta^6\text{-arene})$, $Ru_6C(CO)_{14}(\eta^6\text{-toluene})$, $Ru_6C(CO)_{10}(\eta^6\text{-mesitylene})$, and $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ have been explored by using packing potential-energy calculations and computer graphics analysis [490].

4.3. Pentanuclear clusters

Site-selective $P(OEt)_3$ substitution in $Ru_5(CO)_{13}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$ is reported. Basal substitution is observed during thermolysis while wing-tip substitution is achieved when the cluster is activated by Me_3NO. The X-ray crystal structures of both mono-substituted isomers and the disubstituted cluster, which contains basal and wing-tip $P(OEt)_3$ ligands, are presented [491]. Isomerization and elimination of phenylphosphinidene from $Ru_5(CO)_{13}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$ during thermolysis afford the new cluster $Ru_5(CO)_{13}(\mu_5\text{-}C_2Ph)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ [492]. The reaction between halides and $Ru_5(CO)_{13}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$ yields the characterized clusters $Ru_4(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$ and $Ru_5(CO)_{11}(\mu\text{-}Br)\{\mu_5\text{-}C{\equiv}CC(O)CH_2CH{=}CH_2\}(\mu\text{-}PPh_2)_2$ [493]. PPh_3 reacts initially with $Ru_5(CO)_{13}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$ to afford the corresponding mono-substituted PPh_3 cluster, followed by the conversion to $Ru_5(CO)_{10}(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2$. The identity of this cluster has been determined by X-ray crystallography [494].



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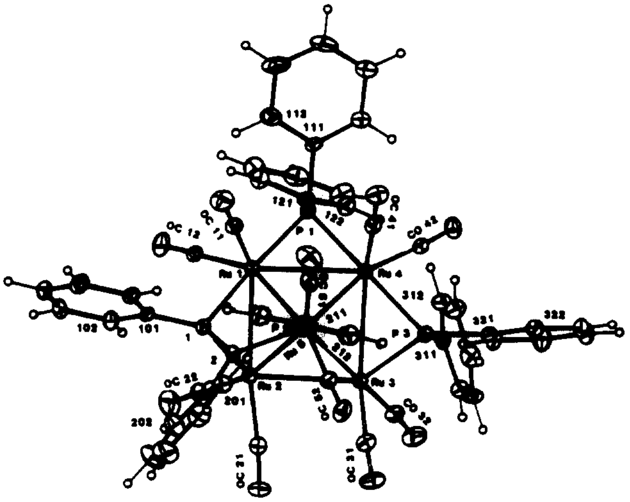

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X-Ray crystallography has been used to determine the molecular structure of $H_2Os_5(CO)_{13}(Ph_2C_2)\{PhC_2(H)C_6H_6\}$, which was isolated from the reaction between $[HOs_3(CO)_{11}]^-$ and Ph_2C_2 [495].

4.4. Hexanuclear clusters

The cleavage of a C–O bond in $[Ru_6(CO)_{18}]^{2-}$ by triflic anhydride gives the carbide cluster $Ru_6C(CO)_{17}$ [496]. The solution and crystal structures of $H_2Ru_6(CO)_{15}L(C_6H_4O)$ {where L = CO, $P(OMe)_3$} have been studied by ^1H NMR spectroscopy and X-ray crystallography [497]. New arenecarbonylcarbide clusters of the form $(arene)Ru_6C(CO)_{14}$ have been synthesized. The new clusters include arene groups with functional substituents [498].

The hexaosmium-arsenic clusters $[(CO)_{11}Os_3As\{Os_3(CO)_9H_3\}]$ and $[(CO)_9H_3Os_3As\{Os_3(CO)_9H_3\}]$ have been obtained from the reaction between AsH_3 and $Os_3(CO)_{11}(MeCN)$ [499]. $Os_6(CO)_{18}$ reacts with 2 equiv of R_3NO (where R = Me, Et) in non-coordinating solvents to give $[HOs_6(CO)_{17}]^-$. The structure of the new cluster was established by variable-temperature ^1H and ^{13}C NMR and ^2D NMR measurements. The mechanism associated with this reaction is presented [500]. Synthetic routes to $Os_6(CO)_{17}L$ (where L = phosphine, arsine, stibine) are reported [501].

4.5. Higher nuclearity clusters

An X-ray diffraction study of $Os_7(CO)_{20}\{P(OMe)_3\}$ has appeared. The polyhedral core consists of a capped octahedron with a capping osmium group that bears the $P(OMe)_3$ group [502]. The cluster $Os_7(CO)_{18}(\mu_3\text{-}CPh)_2$ has been obtained from the reaction between $Os_7(CO)_{20}H_2$ and Ph_2C_2. Continued reaction in refluxing toluene yields $Os_7(CO)_{15}(\mu_3\text{-}CPh)_4$. The X-ray crystal structures of both clusters are presented [503].

The isolation and characterization of $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]^-$ have been published. The anionic product is one of several clusters isolated from the reaction between $[HOs_3(CO)_{11}]^-$ and $Os_3(CO)_{10}(MeCN)_2$ [504].

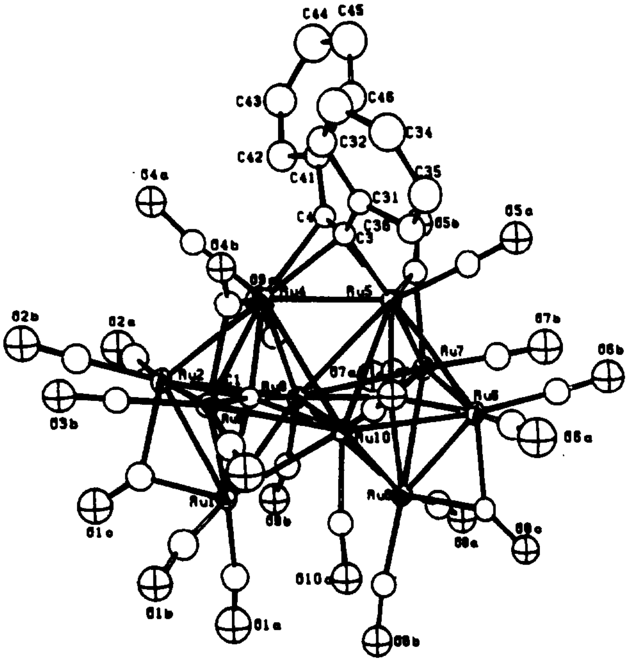
The carbide cluster $[Ru_{10}C(CO)_{24}]^{2-}$ undergoes a facile fragmentation to $Ru_3(CO)_{12}$ and $[Ru_6C(CO)_{16}]^{2-}$ when placed under CO. A similar fragmentation reaction is observed with $[HRu_{10}C(CO)_{24}]^-$ [505]. Reversible coordination of diphenylacetylene to the polyhedral core of $[Ru_{10}C_2(CO)_{24}]^{2-}$ is reported. The X-ray crystal structure of $[Ru_{10}C_2(CO)_{22}(C_2Ph_2)]^{2-}$ reveals that ligand coordination also promotes apical–hinge ruthenium–ruthenium bond formation [506].

4.6. Mixed-metal clusters

4.6.1. Clusters containing Main Group atoms

The tetraruthenaborane butterfly cluster $HRu_4(CO)_{12}BH_2$ reacts with 1-phenyl-1-propyne to afford $HRu_4(CO)_{12}B(H)C(Ph)CMeH$ in addition to 1-phenyl-2,3-dimethylazulene [507].

The cluster $Fe_2Ru(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Te)$ and $Fe_{4-x}Ru_x(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}Te)$ (where $x = 0\text{–}2$) have been synthesized [508]. Selenophene and tellurophene (*cyclo*-C_4H_4X, where X = Se, Te) have been allowed to react with $Ru_3(CO)_{12}$, $Os_3(CO)_{11}(MeCN)$, and $Os_3(CO)_{10}(MeCN)_2$. Facile ring opening of the organic ligand is observed and the X-ray crystal structures of $Os_6(CO)_{20}(\mu\text{-}H)(\mu_3\text{-}Se)(\mu_4\text{-}C_4H_3)$ and $Ru_4(CO)_{11}(\mu_3\text{-}Se)(\mu_4\text{-}C_4H_4)$ are reported [509]. C–H bond activation in cyclohexane and pentane has been observed when $Os_3(CO)_{11}(MeCN)$ reacts with $Te(CF_3)_2$ in the above solvents. Included in this report are the mechanism associated with C–H bond activation and the X-ray crystal structure of $Os_3(CO)_{11}\{Te(C_6H_{11})_2\}$ [510]. Two-electron oxidation of $(MeCp)_4Ru_4S_4$ gives the dicationic cluster $[(MeCp)_4Ru_4S_4]^{2+}$, which has been structurally characterized by X-ray diffraction analysis.



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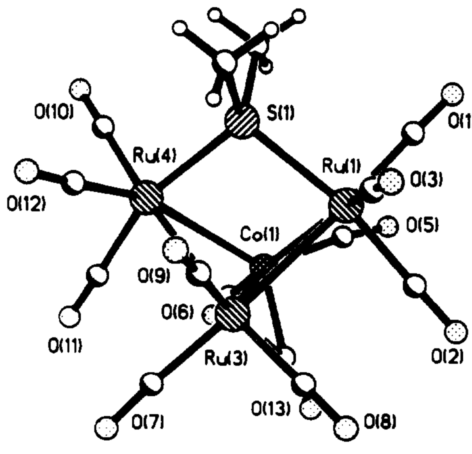
The mobility of the metal–metal bonds has been demonstrated by variable-temperature ^1H NMR spectroscopy [511]. Tetranuclear butterfly clusters bearing a bridging SMe_2 ligand are reported. The X-ray crystal structures of $Ru_4(CO)_{13}(SMe_2)$, $H_2Ru_4(CO)_{12}(SMe_2)$, and $HRu_3Co(CO)_{12}(SMe_2)$ are presented and their structures compared [512].

The cluster $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ has been isolated from the reaction between $Hg(O_2CCF_3)_2$ and $[Os_{10}C(CO)_{24}]^{2-}$. X-Ray diffraction analysis reveals that a central Hg_3 triangle ligates two tricapped-octahedral Os_9 fragments. Demercuration to $[Os_{18}Hg_2$-



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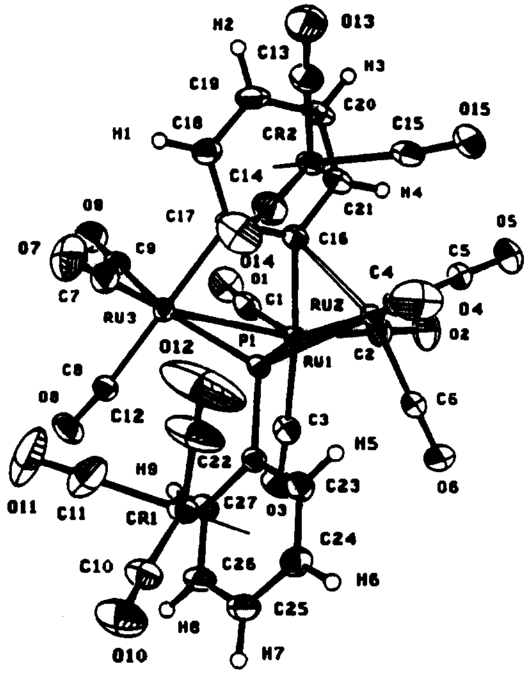
$C_2(CO)_{42}]^{2-}$ is observed upon irradiation with visible light. Quantum yield data for Hg extrusion and CO loss are reported [513]. The synthesis and X-ray structure of the mercury-bridged clusters $[\{Ru_6C(CO)_{16}\}_2Hg]^{2-}$ and $[\{Ru_5C(CO)_{14}(\mu\text{-}Cl)\}_2Hg_2Cl_2]$ have appeared [514].

Stannylene addition to $Os_3(CO)_{10}(\mu\text{-}H)_2$ gives $Os_3(CO)_{10}(\mu\text{-}H)SnR$ {where R = $C(SiMe_3)_2C_5H_4N\text{-}2$}. The molecular structure of this cluster has been determined by X-ray crystallography [515].

4.6.2. *Clusters containing other metals*

The reaction between $Os(CO)_{5-x}(CN^tBu)_x$ (where $x = 1$, 2) and $M(CO)_5(THF)$ (where M = Cr, Mo, W) gives the dimeric complexes $(CO)_{5-x}(^tBuNC)_xOsM(CO)_5$. The metal centers are linked together by an unbridged, dative metal–metal bond, with the 18-electron $Os(CO)_{5-x}(CN^tBu)_x$ moiety acting as a 2-electron donor ligand. The X-ray crystal structures of both chromium derivatives are reported [516]. Reaction of the vinylpropargyl complex $CpW(CO)_2CH_2C{\equiv}C\text{-}CH{=}CH_2$ with either $Ru_3(CO)_{10}(MeCN)_2$ or $Os_3(CO)_{10}(MeCN)_2$ affords the clusters $CpWRu_2(CO)_8(\mu_3\text{-}\eta^1,\eta^1,\eta^1,\eta^2\text{-}CH_2CCCH{=}CH_2)$ and $CpWOs_3(CO)_{13}(\mu_4\text{-}\eta^1,\eta^1,\eta^1,\eta^2\text{-}CH_2CCCH{=}CH_2)$, respectively. The X-ray diffraction data for the former cluster and an unusual tetranuclear cluster derived from the latter cluster are presented [517]. A paper dealing with the synthesis and reactivity of heteronuclear metal-μ-allenyl complexes has appeared. The X-ray crystal structure of $(CO)_6Ru_2(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}RC{=}C{=}CCH_2)WCp(CO)_2$ is included and discussed [518]. The reaction of the acetylide cluster $CpWOs_2(CO)_8(C{\equiv}CPh)$ with $LW(CO)_3H$ (L = Cp, Cp*) has been examined. The tetranuclear clusters $CpLW_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$ and $CpLW_2Os_2(CO)_9(CCHPh)$ have been isolated and structurally characterized. These isomeric clusters readily interconvert in refluxing toluene [519]. $CpW(CO)_3(C{\equiv}CPh)$ and $Os_3(CO)_{10}(Me_2C_2)$ have been allowed to react to give the butterfly cluster $WOs_3Cp(CO)_{10}(CMeCMeCCPh)$. Treatment of this cluster with Me_3NO, followed by thermolysis in toluene, yields the spiked triangular cluster $WOs_3Cp(CO)_9(\mu\text{-}H)\{CMeCMeCC(\mu_2\text{-}\eta^2\text{-}C_6H_4)\}$. The thermolysis products from this cluster are presented and their X-ray crystal structures are discussed [520]. The X-ray structures of the isomeric 60-electron butterfly clusters $WOs_3Cp^*(CO)_7(\mu_3\text{-}CPh)\{CMeCMeCC(tol)C(tol)\}$ are presented [521]. The reactivity of the acetylide clusters $WRu_2(CO)_8(C{\equiv}CR)Cp$ with $CpW(CO)_3(C{\equiv}CR)$ (where R = Ph, $C_6H_4F\text{-}p$) has been explored [522]. The synthesis, characterization, and X-ray diffraction structures of $CpWRu_3(CO)_9(\mu_3\text{-}COMe)(C{=}CHPh)$, $Cp_2W_2Ru_3(CO)_9\{CC(Ph)C(OMe)\}(C{=}CHPh)$, and $Cp_2W_2Ru_3(CO)_9(COMe)(C{\equiv}CPh)$ have been reported [523]. $[Cp^*RuCl_2]_2$ reacts with $[WS_4]^{2-}$ in refluxing THF to afford $[(\mu_2\text{-}S_2)(Cp^*Ru)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2WS]$ while $Cp^*RuCl(\mu\text{-}S^iPr)_2RuCp^*$ reacts with $[MS_4]^{2-}$ (where M = Mo, W) to give the dimer $Cp^*Ru(\mu\text{-}S_2)(\mu\text{-}S^iPr)_2RuCp^*$ [524]. The benzyne cluster $Ru_3(CO)_9[\mu_3\text{-}P\{C_6H_5Cr(CO)_3\}](\mu_3\text{-}C_6H_4Cr(CO)_3)$ has been isolated from the reaction between $Ru_3(CO)_{12}$ and $PhP\{C_6H_5Cr(CO)_3\}$. X-Ray diffraction analysis indicates that the aryne moiety, $C_6H_4Cr(CO)_3$, is η^2-bound to the three ruthenium atoms and that a Cr → Ru bond is present [525].



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$[Ru_3(CO)_9(\mu_3\text{-}O)]^{2-}$ reacts with $[Mn(CO)_3(MeCN)_3]^+$ in acetone to afford the butterfly cluster $[MnRu_3(CO)_{12}\{\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)Me\}]^-$. The presence of the bridging acetamidato ligand has been confirmed by X-ray diffraction analysis [526]. The reaction between $Ru_3(CO)_{12}$ and $Re_2(pyS)_2(CO)_6$ yields a series of $ReRu_3$, Re_2Ru_2, and Re_3Ru complexes. The cleavage of the C–S bond in the pyridine-2-thionate ligand and the X-ray data on $ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}$ and $Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}$ and $Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}$ are discussed [527].

Chemical reduction of $Os_3(CO)_{10}(R^1C_2R^2)$ (where $R^1 = R^2$ = Me, Et, Ph; R^1 = H, Me, R^2 = H, Et, Ph) gives the dianionic cluster $[Os_3(CO)_9(R^1C_2R^2)]^{2-}$, which upon treatment with $HBF_4 \cdot Et_2O$ or $AuPPh_3Cl$ yields $Os_3(CO)_9(R^1C_2R^2)(X)(Y)$ (where X = Y = H,

$AuPPh_3$). The new clusters (η^6-arene)Ru($R^1C_2R^2$)-$Os_3(CO)_9$ (where arene = C_6H_6, C_6Me_6) have been obtained from the reaction between [(η^6-arene)Ru $(MeCN)_3]^+$ and the dianionic cluster. The X-ray crystal structure of the C_6Me_6-substituted cluster confirms the presence of a butterfly polyhedral core with a ruthenium wingtip atom [528]. The synthesis and characterization of the mixed-chalcogen cluster $Fe_2Ru(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ have been published [529]. The tetranuclear clusters $Fe_2Ru_2(CO)_{11}(\mu_4\text{-Se})(\mu_4\text{-Te})$ and $Fe_3Ru(CO)_{11}(\mu_4\text{-Se})(\mu_4\text{-Te})$ have recently been prepared and spectroscopically characterized [530].

The reaction between $CpIr(CO)_2$ (where Cp = Cp, Cp*) and $Os(CO)_4(\eta^2\text{-cyclooctene})$ gives the clusters $CpIr(CO)[Os(CO)_4]_2$. X-Ray diffraction analysis of the Cp* derivative confirms the molecular structure of this triangular cluster. Carbonyl fluxionality has been examined by variable-temperature ^{13}C NMR measurements and the exchange pathways discussed [531]. The synthesis and X-ray diffraction data for the clusters $Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2$ and $Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})$ are presented [532]. Trirutheniumrhodium tetranuclear clusters have been synthesized and spectroscopically characterized. Starting from $Ru_3(CO)_9H_3(\mu_3\text{-COMe})$ and $[Rh(CO)_3(PPh_3)_2]^+$, several clusters have been isolated. This report includes the X-ray crystal structure of $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$ [533]. Treatment of $Ru_3Rh(CO)_{10}(\mu\text{-H})_2Cp$ with PPh_3 and $P(OMe)_3$ and $Ru_3Rh(CO)_{10}(\mu\text{-H})_2Cp^*$ with PPh_3 gives phosphine-substituted clusters. The solution structures and isomerization have been studied by ^1H and ^{31}P NMR spectroscopy. The molecular structure of $Ru_3Rh(CO)_8(\mu\text{-H})_2(PPh_3)_2Cp$ has been determined [534]. The reaction between $Cp_3Rh_3(\mu\text{-CO})_3$ and “$CpRu^+$“ yields the half-sandwich complex $[Cp_4RuRh_3(\mu\text{-CO})_3]^+$ [535]. The same research group has published the results on the reaction between $[CpRu(MeCN)_3]^+$ (where Cp = Cp, Cp*) and $Cp_3Rh_3(\mu\text{-CO})_3$. A crystallographic study on the Cp* derivative confirms the tetrahedral nature of the product cluster [536]. The cluster $Ru_5Co(CO)_{12}(\mu_4\text{-PPh})(\mu_4\text{-C}_2Ph)(\mu\text{-PPh})Cp$ has been isolated from the reaction between $Ru_5(CO)_{13}(\mu_5\text{-C}_2PPh_2)(\mu\text{-PPh}_2)$ and $CpCo(CO)_2$. X-Ray diffraction analysis reveals an irregular envelope conformation [537]. The tetrahedral cluster $HRuCo_3(CO)_{12}$ has been investigated in ligand substitution reactions using ^{59}Co NMR spectroscopy. The ability of ^{59}Co NMR measurements to ascertain the site of ligand substitution is discussed [538].

The synthesis and examination of the fluxional behavior of the 58-electron clusters $Os_3Pt(CO)_9(\mu\text{-H})_2(PtPCy_3)(OsPR_3)$ (where R = various groups) are reported. These clusters are prepared by allowing $Os_3(CO)_9(\mu\text{-H})_2(PR_3)$ to react with $Pt(ethylene)_2PCy_3$. The steric bulk of the PR_3 ligand determines the structure(s) adopted by each cluster. The X-ray molecular structure of the PPh_3 derivative has been determined [539]. $Ru_3Pt(CO)_9L_2(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}{\equiv}C^tBu)$ (where L_2 = dppe) reacts with $Ph_2PC{\equiv}CPPh_2$ to give the butterfly cluster $Ru_3Pt(CO)_7L_2(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^2\text{-C}{\equiv}C^tBu)$. The molecular structure of this cluster and its conversion onto the vinylidene tautomer are discussed [540]. The synthesis and characterization of new osmium/platinum clusters are reported. Treatment of $Os_3(CO)_{11}(MeCN)$ with “PtL_2“ fragments yields the platinum-bridged clusters $Os_3Pt(CO)_{11}L$, which are shown to contain a planar butterfly arrangement of core metal atoms [541]. The seven-vertex osmaplatinaborane clusters $(CO)(PPh_3)_2\overline{HOsL(Cl)Pt}B_5H_7$ (where L = PMe_2Ph, PPh_3) have been prepared from the reaction between PtL_2Cl_2 and the six-vertex *nido* osmaborane complex $(CO)(PPh_3)_2OsB_5H_9$. Thermal reactivity studies and NMR data are presented and discussed [542].

$Pt_2Os_4(CO)_{18}$ reacts with 1,5-COD at 97°C to give the carbonyl cluster $Pt_2Os_4(CO)_{12}(1,5\text{-COD})_2$ and $Pt_2Os_4(CO)_{11}(1,5\text{-COD})_2$. The interconversion between these two clusters and their molecular structures are discussed [543]. Thermolysis of $Pt_2Os_3(CO)_{10}(1,5\text{-COD})_2$ in hexane gives the new clusters $Pt_4Os_6(CO)_{22}(1,5\text{-COD})$ and $Pt_5Os_6(CO)_{21}(1,5\text{-COD})_2$, in addition to an unknown cluster species. X-Ray crystallography has established the identity of these new clusters [544]. The clusters $Pt_2Os_3(CO)_{10}(1,5\text{-COD})_2$ and $PtOs_3(CO)_8(1,5\text{-COD})(\mu\text{-C}_8H_{11})(\mu\text{-H})$ have been isolated from the reaction between $Os_3(CO)_{10}(MeCN)_2$ and $Pt(1,5\text{-COD})_2$. Full solution and solid-state characterization of these clusters is described [545]. $Pt_2Os_4(CO)_{18}$ and 1,5-COD have been allowed to react at 97°C to afford the clusters $Pt_2Os_4(CO)_{12}(1,5\text{-COD})_2$ and $Pt_2Os_4(CO)_{11}(1,5\text{-COD})_2$. The X-ray crystal structures of these clusters and their reactivity toward H_2S are presented [546]. Photolysis of $Pt_2M_4(CO)_{18}$ (where M = Ru, Os) in the presence of 1,5-COD yields a variety of mixed-metal clusters. When M = Ru, the clusters $PtRu_4(CO)_{12}(\mu_4\text{-CO})(1,5\text{-COD})$ and $PtRu_5(CO)_{20}(1,5\text{-COD})$ have been isolated and structurally characterized. Of the several osmium/platinum clusters obtained, the clusters $Pt_2Os_4(CO)_{17}$ and $Pt_2Os_4(CO)_{15}(1,5\text{-COD})$ were investigated by cyclic voltammetry. The X-ray structure of $PtRu_4(CO)_{12}(\mu_4\text{-CO})(1,5\text{-COD})$ is shown below [547].

H_2 and $Pt_2Os_4(CO)_{18}$ have been allowed to react at room temperature to give the new hydrogen-rich clusters $PtOs_5(CO)_{16}(\mu\text{-H})_6$, $Pt_2Os_5(CO)_{17}(\mu\text{-H})_6$, $Pt_2Os_7(CO)_{23}(\mu\text{-H})_8$, and $Pt_2Os_6(CO)_{18}(\mu\text{-H})_8$. X-Ray diffraction analyses of these clusters reveal that these clusters possess vertex-shared polyhedra with platinum

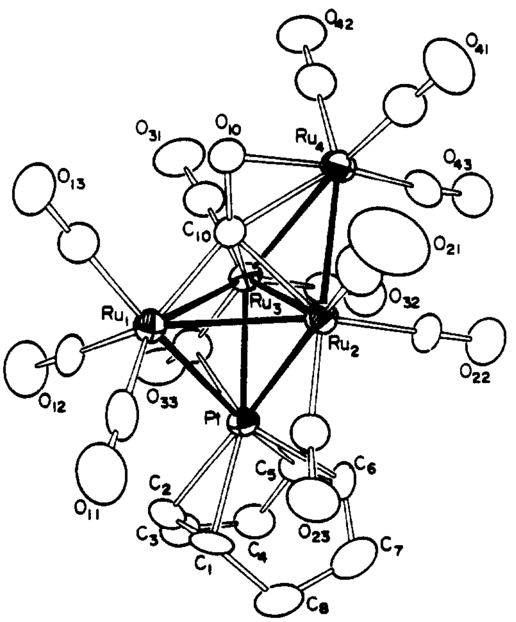
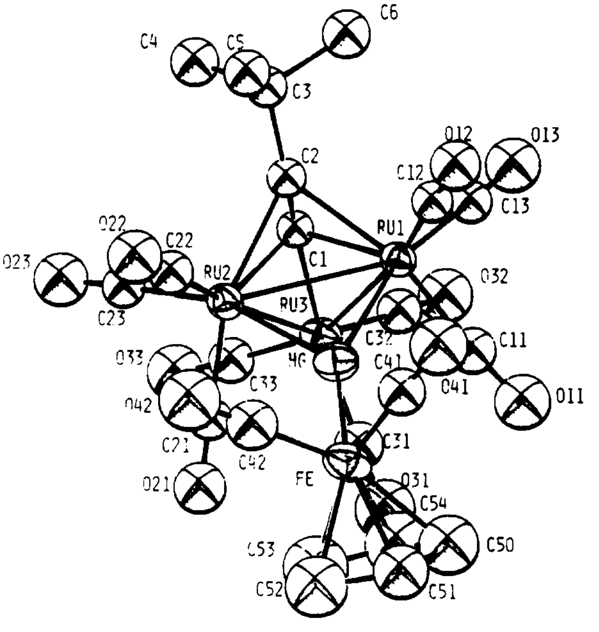


Fig. 26. Reprinted with permission from *Inorganic Chemistry*, Copyright 1991 American Chemical Society.

atoms at the vertex-sharing sites. A scheme showing the interconversion pathways between these clusters is presented [548]. H–S bond activation has been observed in the reaction between $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ and H_2S. The isolated product, $PtOs_5(CO)_{15}(\mu_3\text{-}S)(\mu\text{-}H)_6$, was characterized by IR, NMR (^1H and ^{13}C), and single-crystal X-ray diffraction analyses. The molecular structure is derived from a $PtOs_3$ tetrahedron that is fused to a $PtOs_2$ triangle. Variable-temperature ^1H and ^{13}C NMR measurements indicate the existence of a novel intramolecular rotation of the Os_3 triangular group relative to the Os_2S moiety at the vertex-sharing platinum atom [549]. The reaction between $Os_3(CO)_{10}(\mu\text{-}H)_2$ and Pt(1,5-COD)$_2$ gives $Pt_2Os_3(CO)_9$(1,5-COD)$_2(\mu\text{-}H)_2$ at room temperature. Thermolysis of this cluster in hexane proceeds by way of a condensation sequence to yield $Pt_4Os_6(CO)_{21}$(1,5-COD)$(\mu\text{-}H)_2$. X-Ray diffraction data show that the former cluster contains a triangular Os_3 array that is capped on one face by a Pt(1,5-COD) fragment and bridged on one edge by the remaining Pt(1,5-COD) fragment [550].

Facile heteronuclear decapping in the cluster $Ru_3(CO)_9H_2(\mu_3\text{-}COMe)\{Cu(PPh_3)\}$ by PPh_3 yields $[Ru_3(CO)_9H_2(\mu_3\text{-}COMe)]^-$. A similar reaction is observed with the silver-substituted cluster [551]. $Cp^*Ru(PCy_3)H_3$ reacts with $Au\{N(SiMe_3)_2\}(PPh_3)$ to produce $Cp^*RuPCy_3(\mu\text{-}H)_2Au(PPh_3)$ and $Cp^*RuPCy_3(\mu\text{-}H)\{Au(PPh_3)\}_2$ depending on the reaction conditions [552]. The carbido cluster $Os_6AuC(CO)_{20}(\mu\text{-}OMe)$ has been synthesized from the reaction between $Os_3(CO)_{10}(\mu\text{-}AuPEt_3)(\mu\text{-}COMe)$ and $Os_3(CO)_{10}(MeCN)_2$. X-Ray diffraction analysis indicates that the gold atom ligates an Os_2 fragment and an Os_4 carbido fragment [553]. Deprotonation of $HOs_3(CO)_{10}(HC{=}CHMe)$, followed by treatment of Et_3PAuCl, affords the new cluster $Os_3(CO)_{10}(\mu_2\text{-}\eta^3\text{-}C_3H_5)(AuPEt_3)$. The electronic structure of this cluster has been explored by using Fenske–Hall MO calculations [554]. Metal framework rearrangements in cluster compounds possessing Ru_3Au_2 fragments have been examined [555]. The ruthenium/copper complex $Ru_2(CO)_8(\mu\text{-}CuPCy_3)_2$ has been prepared from $[Ru_2(CO)_8]^{2-}$, PCy_3, and $[Cu(MeCN)_4]^+$. The X-ray structure confirms the butterfly nature of this complex and the asymmetric nature of the bridging $Cu(PCy_3)$ groups; this latter aspect is discussed in terms of a second-order Jahn–Teller effect [556].

The clusters $HOs_5Hg_2(CO)_{15}(O_2CCF_3)_3$ and *cis*-$Os_4(CO)_{12}(O_2CCF_3)_2$ have been isolated from the reaction between $Hg(O_2CCF_3)_2$ and $Os_6(CO)_{18}$. Both clusters have been characterized by X-ray crystallography [557]. Mercury-bridged clusters have been synthesized and studied for polyhedral rearrangements by variable-temperature ^1H and ^{13}C NMR spectroscopies. The clusters discussed by this report include $(\mu_3\text{-}\eta^2\text{-}C_2^tBu)(CO)_9M_3(\mu_3\text{-}Hg)M'$ {where M = Ru, Os; M′ = $CpFe(CO)_2$, $CpRu(CO)_2$, $CpMe(CO)_3$, $Co(CO)_4$} and $\{(\mu\text{-}H)(\mu_3\text{-}S)(CO)_9Os_3\}_2(\mu_4\text{-}Hg)$ [558].



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5. Miscellaneous chemistry

5.1. Heterogeneous and supported complexes

Silica-supported osmium carbonyl clusters have been examined by using ^{13}C MAS NMR measurements. The cluster complexes $HOs_3(CO)_{10}(OR)$ (where R = Me, Ph, $SiEt_3$), $HOs_3(CO)_{10}(O_2CH)$, $Os_3(CO)_{10}(OMe)_2$, and $[Os(CO)_3Cl_2]_2$ have been studied and their spectra assigned by comparison to solution NMR spectra. Reported are the isotropic chemical shift tensors for each carbonyl resonance [559]. The complex $H_2Os(CO)_4$ has been introduced into the pores of zeolite Y and then examined in CO hydrogenation reactions. EXAFS data are presented for the zeolite catalyst before and after catalytic runs. Triosmium clusters are observed to form in the zeolite cages [560]. Infrared data on dinitrogen adsorbed on ruthenium metal supported on Al_2O_3 and MgO have been published [561].

Propane hydrogenation and hydrogenolysis reactions are reported for a Ru/TiO_2 catalyst system [562]. The effect of the oxides of Ca, Sc, and Ti on a Ru/SiO_2 catalyst has been investigated in butane hydrogenolysis reactions [563]. Ru/TiO_2 catalysts derived from $RuCl_3$ have been examined for their activity and selectivity in butane hydrogenolysis reactions [564]. The results from the selective hydrogenation of ethyl acetate to ethanol using a Ru/Sn catalyst are discussed [565]. Hysteresis has been observed during ammonia synthesis using ruthenium catalysts supported on carbon-covered alumina [566]. Ruthenium red, $[Ru_3O_2(NH_3)_{14}][Cl]_6$, intercalated in a smectite clay has been explored for its thermal stability, reactivity with CO and CO/H_2, and hydroformylation activity [567]. A Ru/SiO_2 catalyst, which was prepared by the sol–gel method, was examined by UV-visible diffuse reflectance spectroscopy [568]. Studies on the activation and interaction of $[Ru(NH_3)_6]^{3+}$ with absorbates in H–X zeolites are published. The absorbates examined include CO, NO, O_2, and water [569].

Kinetic data for xylose hydrogenation and glycerol hydrogenolysis are reported for ruthenium and sulfur-modified ruthenium catalysts [570]. Polyol conversions have been studied with copper- and platinum-modified ruthenium/charcoal catalysts [571].

The experimental results of oxygen desorption on gold/ruthenium(001) have been published [572]. XPS data have appeared for a thin film of palladium on ruthenium(001). The electronic perturbations in the bimetallic system and the CO chemisorption activity are discussed [573].

Monophasic compounds of compositions $Mo_{6-x}Ru_xTe_8$ (where $x = 0.5$, 1.0, 1.5) have been prepared and characterized by X-ray powder diffraction measurements [574]. The synthesis, structure, and bonding in the heterometallic condensed complexes Pr_4I_5M (where M = Ru, Os) and La_4I_5Ru are reported [575].

The photocatalytic activity of alkali-metal titanates with ruthenium has been investigated in water splitting reactions [576]. Water electrolysis has been examined with RuO_2 colloid catalysts [577].

5.2. CO and CO_2 reactions

The carbonylation of nitroaromatics in methanol is reported to give N-arylmethylcarbamates when the binuclear complex $Ru_2(dmpm)_2(CO)_5$ is used as a catalyst. Cylindrical Internal Reflectance (CIR) FTIR measurements have been used to help establish the course of the catalysis [578]. $Ru_3(CO)_{12}$ functions as a catalyst precursor in the reduction of nitroaromatics to amines and ureas [579]. Dinuclear μ-carboxylatoruthenium complexes have been studied as catalysts in the hydroformylation of alkenes. Aldehyde selectivity data and the absence of alkene hydrogenation are discussed [580]. Kinetic data have been presented for the oxidative carbonylation of methylamine to methylurethane. The catalyst used in this study was $Ru(saloph)Cl_2$ [581].

5.3. Oxidation reactions

The aerobic oxidation of cyclohexene by several aqua(phosphine)ruthenium(II) complexes has been examined. The mechanism associated with the oxidation reaction and correlations of catalyst turnovers with the rate constants for ligand substitution and Hammett σ_p values are presented [582]. Kinetic data for the oxidation of water to oxygen by cerium(IV) ions and ruthenium(IV) oxide have been published [583]. A triple catalytic system composed of $RuCl(OAc)(PPh_3)$-hydroquinone-Co(salophen)(PPh_3) has been shown to aerobically oxidize primary alcohols to aldehydes by a multi-step electron-transfer mechanism [584]. 2-Methylnaphthalene and naphthalene are oxidized to 2-methylnaphthoquinone-1,4 and naphthoquinone, respectively, when ruthenium compounds are employed as catalysts [585]. The long-chain alcohols octanol, dodecanol, and hexadecanols are oxidized to the corresponding aldehydes and carboxylic acids when $RuCl_2(PPh_3)_3$ is used as a catalyst. The oxidant is based on a mixture of N-methylmorpholine and H_2O_2. Oxygen transfer from N-methylmorpholine to a dihydrido-ruthenium species affords the active oxidation catalyst [586].

The kinetics and mechanism of triphenylphosphine oxidation have been explored with the ruthenium system aqua(propylenediaminetetraacetato)ruthenium (III). The oxidant used was potassium hydrogen persulfate [587]. Cyclohexane and cyclohexanol oxidations with $[Ru(edta)(O)]^-$ have been examined at pH 5.0

using spectrophotometric techniques. Rate and activation data are consistent with a mechanism that involves a high-valent ruthenium(V) oxo species [588]. Diethylamine and triethylamine oxidation is observed when $[Ru(edta)(O)]^-$ is used as a catalyst. The major oxidation products result from N-dealkylation of the amine substrate [589]. The kinetics and mechanism of triphenylphosphine oxidation with iodosylbenzene and the catalyst $Ru(hedta)(H_2O)$ are discussed [590]. Toluene and benzyl alcohol oxidations to benzyl alcohol and benzaldehyde, respectively, are reported with the catalyst $[Ru(edta)(O)]^-$. Saturation kinetics are observed and a plausible mechanism is presented [591].

5.4. H_2 Production and hydrogenation reactions

The selective hydrogenation of α,β-unsaturated aldehydes is catalyzed by a mixture of $RuCl_3$ and the water-soluble phosphine TPPTS. The factors controlling the activity and selectivity are described and a working catalytic mechanism is presented [592]. The 62-electron cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ has been examined as a catalyst precursor in the homogeneous hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene [593]. Chiral ruthenium clusters have been employed as catalysts in the hydrogenation of racemic mixtures of α-pinene and camphene. High diastereoselectivity to the *cis*-hydrogenation products are observed [594]. Transfer hydrogenation of ketones by isopropanol has been studied with the catalyst $RuCl_2(PPh_3)_3$ and co-catalyst NaOH. Turnover numbers per hour up to 900 were observed. No hydrogenation activity was observed in the absence of NaOH [595]. The hydrogenation of 9,10-dimethylanthracene with the catalyst complex $[RuH(PPh_3)_2(\eta^6\text{-}9,10\text{-dimethylanthracene})]^+$ proceeds initially to give 1,2-dihydro-9,10-dimethylanthracene, followed by hydrogenation of the 1,2-dihydro complex to 1,2,3,4-tetrahydro-9,10-dimethylanthracene. The rate law and kinetic data for these reactions are reported [596]. Catalytic hydrogenation of all-*trans*-retinal to all-*trans*-retinol by a variety of ruthenium catalysts has been described [597]. Dimethyl oxalate hydrogenation gives ethylene glycol when the catalyst $Ru_2(CO)_4(OAc)_2(P^iPr_3)_2$ was employed. Substrate decomposition is avoided by carrying out the hydrogenation reaction at 120°C to give methyl glycolate, followed by hydrogenation of methyl glycolate at 180°C, which then yields ethylene glycol [598].

Syn gas production from paraformaldehyde is reported for a ruthenium-phosphine system. The best source of syn gas is from aqueous methyl formate solutions using a catalyst system composed of $Ru_3(CO)_{12}/PCy_3$ [599]. Hydrogen generation from methanolic solutions containing $RuCl_3$ and sodium methoxide has been reported. A correlation between the nature of the ruthenium catalyst and the catalyst activity is discussed [600]. The catalysis of the water–gas shift reaction using a $Ru_3(CO)_{12}/2,2'$-bpy system has been described [601].

5.5. Other catalytic reactions

Hydrosilylation of phenylacetylene with triethylsilane has been studied with the catalyst complex $Os(H)(Cl)(CO)(P^iPr_3)_2$. Intermediates have been isolated and the mechanism is discussed [602]. 2,4-Dienes have been synthesized in high yields with high regioselectivity by the codimerization of acetylenes and alkenes using the catalyst Ru(1,5-COD)(COT) [603]. Terminal alkynes may be selectively coupled to *Z*-1,4-disubstituted butenynes with the catalyst precursors $[\{P(CH_2CH_2PPh_2)_3\}Ru(H)(H_2)]^+$ and $[\{P(CH_2CH_2PPh_2)_3\}Ru(H)(N_2)]^+$ [604]. Ruthenium sulphide has been used as catalyst in the synthesis of quinoline oligomers. The reaction proceeds by way of a catalytic dehydrogenative co-oligomerization scheme involving 1,2,3,4-tetrahydroquinoline and quinoline [605].

The polymer-supported cluster $[H_2Os_3(CO)_9\text{-}(PPh_2)_x\text{-}C_{10}H_{6-x}]_n$ (where $x = 2$, 3; $n \approx 55$) exhibits higher catalytic activity for the isomerization of 1-hexene than either the polystyrene-supported cluster $H_2Os_3(CO)_9$-(polymer) or free $H_2Os_3(CO)_{10}$ [606]. Di-amination products and ethanolamines are obtained when ethylene glycol and primary amines are allowed to react in the presence of $RuCl_2(PPh_3)_3$. The steric effects and selectivity control associated with these reactions are discussed [607]. Isomerization of 1,5-COD and 1-hexene to 1,3-COD and (*E*)-/(*Z*)-2-hexene, respectively, has been investigated by using the catalyst complex $Ru(\eta^6\text{-naphthalene})(\eta^4\text{-}1,5\text{-COD})$ in acetonitrile solvent [608]. C_3–C_5 polyols and C_6 sugars undergo selective dehydroxylation in aqueous solution using the catalyst precursor $[Ru(CO)_3I_3]^-$ [609]. Olefin epoxidation using a ruthenium(III)–edta–ascorbate–H_2O_2 system has been described [610].

The $Ru_3(CO)_{12}$-catalyzed reaction of CO, 1-hexene and diethylmethylsilane is reported to give the corresponding silyl enol ethers [611]. The cross-metathesis of alkenes with vinyltriethoxysilane using both $RuCl_3 \cdot nH_2O$ and $RuCl_2(PPh_3)_3$ has been demonstrated. The stoichiometry and mechanism for this reaction are discussed [612]. The selective cross-disproportionation of vinylsilanes and mono-substituted alkenes is catalyzed by $RuCl(CO)H(PPh_3)_3$ [613].

6. Abbreviations

acac	acetoacetonate
bbpe	*trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)-ethene

binap	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
biq	2,2′-biquinoline
bpbzim	2,2′-bis(2-pyridyl)bibenzimidazole
biphemp	2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl
bpnp	2,7-bis(2-pyridyl)-1,8-naphthyridine
bpqpy	2,6-bis(4′-phenyl-2′-quinolyl)quinoline
bptz	3,6-bis(2-pyridyl)-1,2,4,5-tetrazine
BSD	benzo-2,1,3-selenadiazole
bta	benzotriazol-1-yl
bpy	bipyridine
bpz	bipyrazine
bzim	benzimidazole
1,5-COD	1,5-cyclooctadiene
COT	cyclooctatriene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
DAB	1,4-diaza-1,3-butadiene
DAD	diazadiene
dbtd	5,5′-dimethyl-2,2′-bi-1,3,4-thiadiazole
dcnp	1,8-naphthyridine-2,7-dicarboxylate(−2)
dcpe	$Cy_2PCH_2CH_2PCy_2$
dfm	di-*p*-tolylformamidine
2,5-DHT	2,5-dihydrothiophene
DMAD	dimethyl acetylenedicarboxylate
dmdppe	(1,1-dimethyl-2,2-diphenylphosphino) ethane
dmp	4,4′-dimethyl-2,2′-bipyridine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,1-bis(dimethylphosphino)methane
dmpt	5,6-dimethyl-3-(pyridin-2-yl)-1,2,4-triazine
dpb	2,3-di-(2′-pyridyl)(benzo[g]quinoline)
dpp	2,3-bis(2-pyridyl)pyrazine
dppe	1,2-bis(diphenylphosphino)ethane
dppen	1,1-bis(diphenylphosphino)ethene
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	1,1-bis(diphenylphosphino)methane
dppt	5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine
dppz	dipyrido[3,2-*a*:2′,3′-*c*]phenazine
dpq	2,3-bis(2′-pyridyl)quinoxaline
ECL	electrogenerated chemiluminescence
etp	$PhP(CH_2CH_2PPh_2)_2$
Hampy	2-amino-6-methylpyridine
Hbta	benzotriazole
Hdfm	di-*p*-tolylformamidine
hedta	N-(hydroxyethyl)ethylenediaminetriacetate
Hfac	hexafluoroacetylacetonate
Hpyca	pyridine-2-carboxylic acid

Hpz	pyrazole
In	indenyl
Me_2Hpz	dimethylpyrazole
1,3-Me_2lum	1,3-dimethyllumazine
mes	1,3,5-trimethylbenzene
MLCT	metal-to-ligand charge transfer
NBD	norbornadiene
nmcp	neomenthylcyclopentadienyl
N-MeIm	N-methylimidazole
OEP	octaethylporphyrin
phi	9,10-phenanthrenequinone
PPN	bis(triphenylphosphine)iminium
ppq	4-phenyl-2-(2′-pyridyl)quinoline
py	pyridine
pz	pyrazol-1-yl
(*R*)-prophos	(*R*)-(+)-1,2-bis(diphenylphosphino)-propane
qpy	2,2′:4,4″:4′,4‴-quaterpyridine
saloph	bis(salicylaldehyde)-*o*-phenylenediamine
SIMS	secondary ion mass spectrometry
tap	1,4,5,8-tetraazaphenanthrene
tcne	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
tdpep	$P(CH_2CH_2PPh_2)_3$
tepa	tris(2-{2-pyridyl}ethyl)amine
terpy	2,2:6′,2″-terpyridine
tfpb	4,4,4-trifluoro-1-phenyl-1,3-butanedionate
tmen	N,N,N′,N″-tetramethylethylenediamine
TMP	tetramesitylporphyrin
TMSO	tetramethylene sulfoxide
TMT	2,3,4,5-tetramethylthiophene
tpm	tris(1-pyrazolyl)methane
TPP	tetraphenylporphyrin
TPPTS	*meta*-trisulfonated triphenylphosphine
tpt	tris(pyridin-2-yl)-1,3,5-triazine
tpterpy	4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine
ttp	$PhP(CH_2CH_2CH_2PPh_2)_2$
vpy	vinylpyridine
XPS	X-ray photoelectron spectroscopy

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