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Annual survey of ruthenium and osmium for the year 1993

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Contents

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Abbreviations

acac	acetylacetonate
AES	Auger electron spectroscopy
ampy	2-amino-6-methylpyridine
apt	4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
bim	2,2′-biimidazole
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
biq	2,2′-biquinoline
bp	4,4′,5,5′-tetramethyl-2,2′-biphosphine
bpbzim	2,2′-bis(2-pyridyl)bibenzimidazole
bpm	2,2′-bipyrimidine
bpt	3,5-bis(pyridin-2-yl)-1,2,4-triazole
bpy	bipyridine
bpz	bipyrazine
BSD	2,1,3-benzoselenadiazole
bta	benzotriazol-1-yl
CD	circular dichroism
chp	6-chloro-2-hydroxypyridine
1,5-COD	1,5-cyclooctadiene
COSY	correlated spectroscopy
COT	cyclooctatriene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CP	cross polarization
cyclam	1,4,8,11-tetraazacyclotetradecane
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
DAB	1,4-diaza-1,3-butadiene
DAD	diazadiene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dcpe	$Cy_2PCH_2CH_2PCy_2$
DFT	density functional theory
2,5-DHT	2,5-dihydrothiophene
diop	2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dippe	1,2-bis(diisopropylphosphino)ethane
DMABN	4-*N*,*N*-dimethylaminobenzonitrile
DMAD	dimethyl acetylenedicarboxylate
DMF	dimethyl formamide
dmgh	dimethylglyoxime

dmp	4,4′-dimethyl-2,2′-dipyridine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,1-bis(dimethylphosphino)methane
dmpt	5,6-dimethyl-3-(pyridin-2-yl)-1,2,4-triazine
DMSO	dimethylsulfoxide
DNA	dioxyribonucleic acid
dpb	2,3-di-(2′-pyridyl)(benzo[g]quinoline)
dpp	2,3-bis(2-pyridyl)pyrazine
dppa	1,2-bis(diphenylphosphino)acetylene
dppb	1,2-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppee	1,1-bis(diphenylphosphino)ethene
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	1,1-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
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
DRS	difference reflectance spectroscopy
ECL	electrogenerated chemiluminescence
edta	ethylenediamine tetraacetate
ENDOR	electron–nuclear double resonance
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
FAB	fast atom bombardment
FTIR	Fourier transform IR
Hampy	2-amino-6-methylpyridine
Hbpt	3,5-bis(pyridin-2-yl)-1,2,4-triazole
Hbta	benzotriazole
Hedta	*N*-(hydroxyethyl)ethylenediaminetriacetate
Hfac	hexafluoroacetylacetonate
HMO	Hückel molecular orbital
hp	hydroxypyridinate anion
HPhenoxSQ	1-hydroxy-2,4,6,8-tetra-tert-butylphenoxazinyl
HPLC	high performance liquid chromatography
Im	imidazole
In	indenyl
LDA	lithium diisopropylamide
LITD	laser-induced thermal desorption
MAD	monoazadiene
MAS	magic angle spinning
$\mathrm{Me_4[14]aneS_4}$	1,4,8,11-tetrathiocyclotetradecane
$\mathrm{Me_2Hpz}$	dimethylpyrazole
1,3-$\mathrm{Me_2lum}$	1,3-dimethyllumazine
Mes	mesityl

MLCT	metal-to-ligand charge transfer
nbd	norbornadiene
NAD	nicotinamide-adenine nucleotide, oxidized
N-NeIm	*N*-methylimidazole
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
OEP	octaethylporphyrin
PES	photoelectron spectroscopy
phi	9,10-phenanthrenequinone
PPN	bis(triphenylphosphine)iminium
PP_3	$P(CH_2CH_2PPh_2)_3$
ppq	4-phenyl-2-(2′-pyridyl)quinoline
ppy	2-phenylpyridine
ppz	4,7-phenanthrolino[6,5-b]-pyrazine
py	pyridine
pz	pyrazol-1-yl
(*R*)-prophos	(*R*)-(+)-1,2-bis(diphenylphosphino)propane
saloph	bis(salicylaldehyde)-*o*-phenylenediamine
SCE	saturated calomel electrode
SCF	self-consistent field
SEM	scanning electron microscopy
SIMS	secondary-ion mass spectrometry
tap	1,4,5,8-tetraazaphenanthrene
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
tdpep	$P(CH_2CH_2PPh_2)_3$
TEMPO	2,2,6,6-tetramethylpiperidene-1-oxyl
terpy	2,2:6′,2″-terpyridine
tfpb	4,4,4-trifluoro-1-phenyl-1,3-butanedionate
THF	tetrahydrofuran
TMEDA	*N,N,N′,N″*-tetramethylethylenediamine
TMP	tetramesitylporphyrin
TMphen	3,4,7,8-tetramethyl-1,10-phenanthroline
tmpm	tris(dimethylphosphino)methane
TMSO	tetramethylene sulfoxide
TMT	2,3,4,5-tetramethylthiophene
tpm	tris(1-pyrazolyl)methane
TPP	tetraphenylporphyrin
TPPTS	*meta*-trisulfonated triphenylphosphine
tppz	tetra-2-pyridyl-1,4-pyrazine
tpt	tris(pyridin-2-yl)-1,3,5-triazine
tpterpy	4,4′,4″-triphenyl-2,2′:6′,2″-terpyridine
triphos	$PhP(CH_2CH_2PPh_2)_2$
TTP	$PhP(CH_2CH_2CH_2PPh_2)_2$
vbpy	4-vinyl-4′-methyl-2,2′-bpy

vpy	vinylpyridine
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1. Dissertations

A dissertation that explores the Raman data of osmium porphyrins and diosmium complexes has been published. Resonance Raman spectroscopy reveals the existence of an $^2A_{2u}$ ground electronic state for the osmium octaethylporphine π cations $[\mathrm{Os(OEP^{*-})(CO)}]^+$ and $[\mathrm{Os(OEP^{*-})(CO)(PPh_3)}]^+$. The Os–Os and Os–ligand stretching frequencies for the osmium(III) dimers $\mathrm{Os_2(\mu\text{-}hp)_4Cl_2}$ and $\mathrm{Os_2(\mu\text{-}hp)_4Br_2}$ have been identified by resonance Raman spectroscopy [1]. The oxidation-state-dependent stability of several alkyl-substituted Ru(OEP) systems are described. Electrochemical and chemical techniques have been employed in these studies. The presence of a rapid Ru-to-N aryl migration has been demonstrated upon oxidation of $\mathrm{Ru(OEP)(Ar)_2}$. The bond strength of the Ru–Me bond in Ru(OEP)(Ph)(Me) has been experimentally determined [2]. The effect of axial ligation on the electrochemical and spectroelectrochemical properties of Ru(OEP)(CO)(L) (where L ≡ THF, MeOH or H_2O) has been discussed [3].

The synthesis and reactivity investigation of bis(arylimido)osmium complexes have appeared. The imido complexes of interest are prepared in quantitative yield by an imido transfer sequence involving $\mathrm{OsO_4}$ and $\mathrm{Mo(NAr)_2(OCMe_3)_2}$ [4]. The ruthenium(II) imido complexes $[\mathrm{(cymene)Ru(NAr)}]_2$ have been prepared and their reactivity in intramolecular C–H bond activation and arene displacement explored. Several monomeric osmium(II) imido complexes have also been synthesized. The mechanism associated with the formation of these osmium imido complexes has been presented [5]. Anionic nitridoruthenium(VI) alkyl complexes have been synthesized and examined for their reactivity toward amine and phosphine ligands. The new complexes were also employed in the modeling of isopenicillin *N*-synthetase [6]. The synthesis and NMR characterization of new dihydrogen complexes of osmium(II) tetraamines are discussed. The use of these complexes as recognition probes for biomolecules is described [7]. The electron-transfer properties of ruthenium(III) Schiff base complexes have been studied [8]. New ruthenium(VI) complexes bearing cysteine, alkyl and siloxide ligands have been synthesized and characterized by X-ray crystallography [9]. The chiral ruthenium imine complexes $[\mathrm{CpRu(CO)(PPh_3)(HN{=}CHR)}]^+$ have been prepared from the requisite aldehyde and examined for their ligand substitution chemistry [10].

Ruthenium polypyridyl complexes have been examined in photoexcited electron transfer reactions. Polypyridyl ligands with an attached quencher moiety lower the reducing power of the photoexcited state [11]. Ruthenium(II) polypyridyl complexes containing α-diimine ligands are shown to function as spectroscopic probes of nucleic acid structure. The optical isomers of $[\mathrm{Ru(bpy)_2(ppz)}]^{2+}$ have been examined in differential binding studies employing DNA as a substrate [12]. Charge transfer behavior has been studied in several ruthenium polypyridyl complexes, which are ligated by a spacer to an acceptor molecule [13]. Transient intermolecular electron transfer in $[Ru(bpy)_3]^{2+*}$ has been investigated using resonance Raman spectroscopy [14]. Homoleptic and heteroleptic ruthenium(II) complexes with ancillary diazene ligands have been investigated in quenching studies. The behavior of the lowest luminescent excited state has been examined in acid–base reactions and energy transfer processes. A use of $[Ru(bpy)_3]^{2+}$ as a reliable actinometer for laser lines in the UV–visible spectral region is presented [15]. The X-ray crystal structures of polypyridyl-substituted ruthenium complexes are presented, together with a discussion on bond length changes that serve as indicators on intramolecular hydrogen bonding in Ru–diglyoxime complexes [16]. The mechanism associated with proton-coupled electron transfer in ruthenium and osmium polypyridyl complexes has been studied. The X-ray structure of *trans*-$[Ru^{VI}(terpy)(O)_2(H_2O)][ClO_4]_2$ has been determined, and the spectral characterization of this and related complexes are included. The water oxidation properties of selected ruthenium complexes are outlined [17]. The photophysical and photochemical properties of $[Ru(bpy)_3]^{2+}$ adsorbed onto Vycor glasses over the temperature range 5–50 °C have been investigated. The data obtained from the Vycor-supported system are contrasted with the data obtained from fluid solution work [18]. A two-part dissertation dealing with the determination of the reaction entropy for $[Os(bpy)_3]^{3+/2+}$ in a Nafion film and the synthesis and characterization of monometallic and bimetallic ruthenium(II) complexes with ancillary 4,4′-bipyrimidine and pyridyl viologen ligands has appeared [19]. Zeolite-Y-entrapped homoleptic and heteroleptic ruthenium(II) polypyridyl complexes have been explored as models for solar energy conversion devices [20]. The synthesis, solution characterization and electrochemical properties of a variety of polypyridyl-, nitrosyl- and azide-substituted ruthenium complexes are described [21]. The use of $[Ru(bpy)_3]^{3+}$ as a chemiluminescent detector for underivatized amino acids is discussed. The pH dependence on the chemiluminescence reaction has been investigated [22]. The synthesis and redox behavior of dinuclear pentaamineruthenium complexes joined by dicyanamidobenzene ligands have been described. The results of extended Hückel molecular orbital calculations are discussed relative to the observed antiferromagnetic behavior exhibited by these complexes [23].

The mechanism of the osmium-catalyzed asymmetric dihydroxylation of alkenes using potassium ferricyanide as a reoxidant has been examined. Included in this dissertation are the equilibrium constants for the binding of amine ligands to osmium tetroxide [24]. The osmium-mediated transfer of oxygen, nitrogen, and sulfur to alkenes and acetylenes is presented [25]. The participation of isonicotinamide complexes of ruthenium(III) in the intramolecular oxidation of horse heart and *Candida* derivatives is described [26]. The reactivity of (oxo)(phosphine)ruthenium(IV) and (aqua)(phosphine)ruthenium(II) complexes in the oxidation of organic substrates is reported [27]. High levels of enantioselectivity have been achieved in the osmium-catalyzed asymmetric dihydroxylation of olefins. The results from heterogeneous asymmetric dihydroxylation work are presented [28]. The use of erythro-2-hydroxybenzyl-1-azaadamantane as a ligand in osmium-catalyzed asymmetric dihydroxylation reactions has been assessed. Related ligand syntheses and mechanistic studies on the asymmetric dihydroxylation reaction are presented [29].

Polyhydride and dihydrogen ruthenium compounds have been prepared and spectroscopically examined [30]. The structural chemistry of ruthenium complexes with agostic and ruthenium–hydrogen interactions has been investigated [31]. Hydrogen activation by diphosphine ruthenium complexes has been examined. The diphosphine ligands employed in these studies were dppb and chiraphos. The solid state ^{31}P NMR spectrum of $RuCl_2(dppb)(PPh_3)$ has been found to be similar to that of $RuCl_2(PPh_3)_3$ [32]. A mechanistic study on the C—H bond activation of alkanes using the low valence osmium complex *cis*-$(PMe_3)_4Os(H)$ (neopentyl) has been completed. The activation of N—H and O—H bonds in the reaction between $(PMe_3)_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ and a variety of HX compounds has been reported [33]. The synthesis and fluxionality studies of cyclic allenylruthenium complexes have appeared [34]. The synthesis and thermal decomposition of alkyl–olefin chelate complexes of ruthenium have been studied [35]. The thermally and photochemically promoted arene displacement from ruthenium and osmium arene complexes has been presented [36]. The synthesis of non-classical osmium and ruthenium hydride complexes has been described, and the catalytic hydrogenation properties of these complexes discussed [37]. The heats of protonation of several cyclopentadienyl ruthenium and osmium complexes have been determined by using titration calorimetry. The effects of changing the ancillary ligands on the heat of protonation are described, and the observed linear increase in the basicity, which is dependent on the nature of the attached phosphine ligand, has been discussed [38]. Protonation of *cis,mer*-$RuH_2(CO)(Cyttp)$ by excess HX (where $X \equiv BF_4$ or O_3SCF_3) gives *cis,mer*-$RuX_2(CO)(Cyttp)$, which in the case of $X \equiv O_3SCF_3$ has been characterized by XRD analysis. The X-ray data revealed the existence of two *cis*-oriented O_3SCF_3 ligands [39]. The activation of amide N—H bonds by ruthenium complexes and the hydroamination reactivity of these complexes have been presented [40]. Ruthenium thiophene complexes have been synthesized and examined in desulfurization reactions [41].

The heterobimetallic complex $CpRu(CO)\{\mu\text{-}\eta^2,\eta^1\text{-}CH_2{=}C{=}C(Ph)\}Pt(PPh_3)_2$ has been synthesized from the propargyl complex $CpRu(CO)CH_2C{\equiv}CPh$ and $Pt(PPh_3)_4$. The reactivity of this complex with electrophiles at low temperature has been examined [42]. The synthesis and X-ray crystallographic examination of platinum–ruthenium and platinum–osmium clusters have been described [43]. The ligand substitution kinetics of $Ru_3(CO)_{11}\{P(OEt)_3\}$ and $Ru(CO)_4L$ have been measured in alkane solution. The data obtained from these complexes have been compared with the data obtained from $Ru_3(CO)_{12}$ [44].

A large pyroelectric coefficient has been measured in a ruthenium-containing organic thin film [45]. The use of ruthenium alkyls as potential chemical vapor deposition reagents has been described [46]. The use of $M(CO)_4$ (hexafluoro-2-butyne) (where $M \equiv Ru$ or Os) complexes in the preparation of thin films for electronic materials has been presented. The relationship between the structure and decomposition mechanisms of these precursors and the physical properties of the resulting thin film have been investigated [47]. The synthesis and characterization of one-dimensional rutheniumtetramine-pyrazine polymers have been explored for their photochemical properties and intervalence charge transfer behavior [48]. The hydrodesulfurization mechanism of thiophene by several ruthenium complexes has been discussed [49]. Clay-modified electrodes containing polypyridyl osmium and ruthenium complexes have been prepared and examined for their charge-hopping behavior by cyclic voltammetry [50]. Scanning probe microscopy studies have been conducted on ruthenium complexes in order to understand the electronic coupling in systems that contain two redox active ruthenium centers. The redox active ruthenium centers were separated by variable-length aromatic spacer molecules [51]. New ruthenium complexes derived from Keggin and α-Dawson heteropolytungstates have been prepared and spectroscopically characterized. Redox studies have revealed that the ruthenium center is reducible–oxidizable, and the nature of the resulting ruthenium products has been discussed [52]. The growth of ruthenium-containing carbon fibers has been explored [53]. LITD techniques have been employed in the study of surface diffusion on a potassium-promoted Ru(001) surface. Some of the coadsorbates examined include CO and H_2 [54].

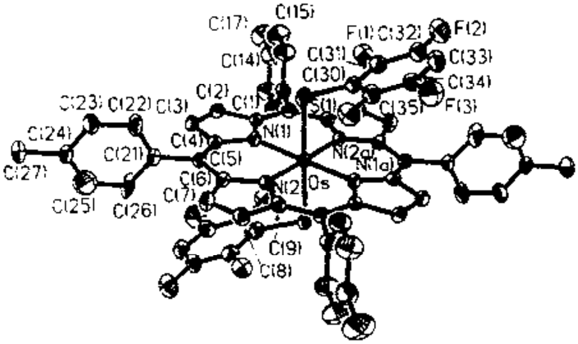
2. Mononuclear complexes

2.1. Organometallic porphyrins

The ethoxycarbonylcarbene complex [Ru(TMP)(=$CHCO_2Et$)] has been obtained from the reaction between Ru(TMP) and ethyl diazoacetate. This same porphyrin carbene catalyzed the formation of diethyl maleate in the presence of excess ethyldiazoacetate at a rate of about one turn-over per second [55]. New heterometallic and homometallic ruthenium and osmium multiply bonded octaethyltetraazaporphyrin dimers have been synthesized and spectroscopically characterized. The redox properties of these dimers have been explored, and the data used in ground-state electronic studies [56]. The first metalloporphyrins to contain an axial bound PF_3 ligand are described. The complexes synthesized are based on [Ru(por)PF_3] (where por ≡ TPP, OEP, or *p*-substituted TPP derivatives), and this report includes detailed spectroscopic and redox studies of these porphyrins. Reactivity comparisons are made relative to the corresponding [Ru(por)(CO)] complexes [57]. The preparation and spectroscopic characterization (IR, UV–visible and ^1H NMR) of ruthenium phthalocyanine complexes containing ancillary phosphine ligands have been presented [58]. Kinetic data are reported for the reaction of cyanide with ruthenium phthalocyanine complexes [59]. New 1-alkynyl(phthalocyaninato)ruthenium(II) compounds have been synthesized with a high yield. The IR frequency of the $\nu(C{\equiv}C)$ band in each compound has been assigned [60]. The synthesis of sterically protected ruthenium porphyrin complexes has appeared. XRD data on the two new porphyrins provide insights into the steric constraints associated with these porphyrins [61]. The oxidation of $Ru^{VI}(TMP)(O)_2$ and $Ru^{VI}(OEP)(O)_2$ using phenoxathiin hexachloroantimonate affords the corresponding porphyrin cations, which have been examined by ESR and UV–visible spectroscopies. The paramagnetic shift observed in the ^1H NMR data of each porphyrin cation has been used in the determination of the nature of the radical orbitals [62]. Electron transfer studies of oligomeric ruthenium porphyrins bridged by 4,4′-azopyridine ligands are reported. An observed intervalence transition that is switched "on" or "off" by a protonation–deprotonation sequence is discussed [63]. The dioxoosmium(VI) porphyrin complexes Os(TTP)(O)$_2$ and Os(OEP)(O)$_2$ react with aryl mercaptans to afford the corresponding diamagnetic osmium(IV) thiols Os(TTP)(SAr)$_2$ and Os(OEP)(SAr)$_2$ respectively. ^{1}H NMR and redox data are presented. The X-ray diffraction structure of Os(TTP)(SC$_6$F$_4$H)$_2$ is given in Fig. 1 [64].

2.2. *Halides*

The synthesis and spectroscopic characterization of two classes of ruthenium chlorides having the formula [*trans*-RuCl$_4$(R$_2$SO)(L)]$^-$ and *mer,cis*-RuCl$_3$(R$_2$SO)(R$_2$SO)(L) have been described. Cyclic voltammetric measurements support the existence of a rapid Ru(III)–Ru(II) redox couple, with formal potentials more positive than other Ru(III) complexes. The X-ray crystal structures of [*trans*-RuCl$_4$(DMSO) (NH$_3$)][Na]·2DMSO, [*trans*-RuCl$_4$(DMSO)(Im)][Na]·H$_2$O·acetone and *mer,cis*-RuCl$_3$(DMSO)(NH$_3$) (S and O bound) have been discussed, and the antitumor properties of selected complexes presented [65]. RuCl$_3$·nH$_2$O reacts with SbPh$_3$ to give *trans*-RuCl$_2$(SbPh$_3$)$_4$, which has been structurally characterized by X-ray diffraction analysis [66]. The synthesis and X-ray diffraction structure of bis(9-β-D-ribofuranosyl-6-mercaptopurine)bis(triphenylphosphine)ruthenium(II) chloride have been published. This is the first structural report of a ruthenium nucleoside compound [67]. The effect of the X group on the reactivity of RuHX(CO)(P^{t}Bu$_2$Me)$_2$ (where X≡I, Cl or F) towards D_2, 2-butyne, and phenylacetylene has been investigated. The results are discussed in the context of X group's ability to function as an "operationally unsaturated" ligand [68]. The reaction between HRu(CO)Cl(PPh$_3$)$_3$ and terminal alkynes in refluxing 1,2-dichloroethane yields the coordinatively unsaturated butenynyl complexes Ru{C(C≡CR)=CHR}(CO)Cl(PPh$_3$)$_2$ with a good yield. These complexes are



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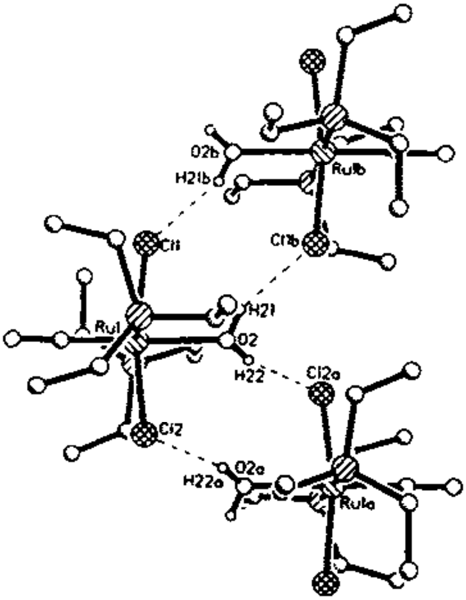

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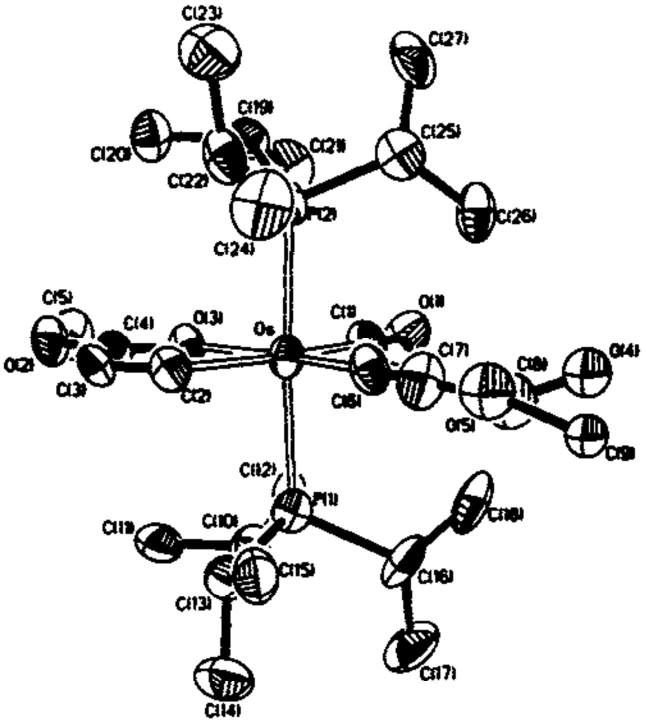
suggested to arise from the C—H bond activation of an acetylene, followed by insertion into a σ-alkynyl bond of the requisite ruthenium complex [69]. Dehydrohalogenation from $HRuCl(CO)(P^tBu_2Me)_2$ gives the unsaturated ruthenium(0) complex $Ru(CO)(P^tBu_2Me)_2$ at low temperatures. Variable-temperature ^{31}P NMR measurements reveal that propylene is activated by the unsaturated ruthenium complex, and the structure is best represented as the oxidative addition product $HRu(CO)(P^tBu_2Me)(\eta^3\text{-allyl})$(*trans*-phosphines) [70]. The electronic spectra and photochemistry of $[Ru(II)\{Sn(II)Cl_3\}_6]^{4-}$ have been studied. Photolysis of this complex gives $[Ru(SnCl_3)_5Cl]^{4-}$ via reactive states that possess intraligand character [71]. The aquo carbonyl complex *trans*-$RuCl_2(PEt_3)_2(CO)(H_2O)$ has been prepared and examined by NMR spectroscopy. X-ray crystallographic data, obtained at low temperatures, reveal the presence of intermolecular O—H···Cl hydrogen bonding, which provides lattice stabilization of the aquo complex [72] (Fig. 2).

2.3. Hydrides

The conversion of the acetate complex $Ru(OAc)_2(CO)_2(P^nBu_3)_2$ into the dihydrogen complex $Ru(H)_2(CO)_2(P^nBu_3)_2$ has been explored and shown to proceed by way of the monohydrido acetate species $RuH(OAc)(CO)_2(P^nBu_3)_2$ [73]. Terminal alkynes react with the monohydride complex $[RuH(dippe)_2]^+$ to give dihydrogen complexes of the form $[Ru(H_2)(C{\equiv}CR)(dippe)_2]^+$ (where R ≡ Ph or CO_2Me). The X-ray structure of the phenyl complex clearly establishes the coordination geometry about the ruthenium center in this first example of an alkynyl-dihydrogen complex [74]. The observation of reversible H_2 coordination to the d^4 osmium complex $OsH_2Cl_2(P^iPr_3)_2$ is described. The resulting non-classical $OsH_4Cl_2(P^iPr_3)_2$ readily eliminates HCl upon further reaction with H_2 to afford the d^4 dihydrogen complex $Os(H_2)(H)_3Cl(P^iPr_3)_2$; reaction under basic conditions is shown to give $OsH_6(P^iPr_3)_2$ and $[OsH_5(P^iPr_3)_2]^-$. T_1 NMR data support the presence of an η^2-H_2 ligand in the non-classical complex. The X-ray diffraction structure of this same complex is presented [75]. The reversible binding of H_2 and N_2 to $RuCl_2$(*o*-diphenylphosphino-*N*,*N*-dimethylaniline)$\{P(p\text{-tolyl})_3\}$ yields the corresponding η^2-H_2 and σ-N_2 complexes [76]. The results of a variable-temperature ^1H NMR study on agostic interaction and hydrogen exchange in $[Ru(H)(dppb)_2]^+$ and $[RuH(diop)_2]^+$ are presented. Hydrogen exchange between the agostic hydrogen in the phosphine ligand and the terminal hydride has been observed [77]. The pK_a value for the dihydrogen complex $[Os(\eta^2\text{-}H_2)(CO)(pyS)(PPh_3)_2]^+$ has been determined to be about -1. X-ray diffraction analysis reveals a distorted square pyramidal arrangement of non-hydrogen atoms about the osmium center. An H—H distance of 1.08 Å has been determined through the use of a T_1 NMR study [78]. The catalytic hydrogen transfer properties of the non-classical trihydrides $[(PP_3)M(H)(\eta^2\text{-}H_2)]^+$ (where M ≡ Ru or Os) have been studied in α,β-unsaturated ketone reduction reactions. The osmium complex catalyzes these reactions via isomerization of the initially produced allylic alcohols [79]. A report outlining the synthesis and T_1 measurements on the first osmium (η^2-H_2) complexes containing ancillary S-donor ligands has been published [80]. The alkynyl–dihydrogen complex $OsH(C{\equiv}CPh)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ has been isolated from the reaction between $OsH_4(CO)(P^iPr_3)_2$ and phenylacetylene. Under a hydrogen atmosphere the alkynyl–dihydrogen complex is transformed into $OsH_2(\eta^2\text{-styrene})(CO)(P^iPr_3)_2$, after which styrene is liberated and the tetrahydride is regenerated. The reaction of $OsH_4(CO)(P^iPr_3)_2$ with methylpropiolate gives the metallocycle $\overline{Os(C_2CO_2Me)\{CH{=}CHC(OMe){=}O}\}(CO)(P^iPr_3)_2$, the structure of which has been determined by X-ray crystallography [81]. (Fig. 3).

The stereochemistry of alkyne insertion into the Ru—H bond of $RuHCl(CO)_2L_2$ and $RuH_2(CO)_2L_2$ (where L ≡ PMe_2Ph or $AsMe_2Ph$) has been investigated. These complexes are shown to undergo a trans addition of Ru—H to the alkyne, whereas a cis addition is observed for $Ru(CO)H(Cl)(PMe_2Ph)_3$ [82]. The hydrido(phenolate)ruthenium, hydrido(thiophenolate)ruthenium, hydrido(phenolate)osmium and hydrido(thiophenolate)osmium complexes $MH(CO)(EC_6X_5)(P^iPr_3)_2$ have been prepared and characterized. The reactivity of these complexes toward O_2 and CS_2 is discussed [83]. The C—H bond reactivity of alkene carboxylates with $\overline{RuH(ethylene)(PPh_3)_2(PPh_2C}{}_6H_4)$ or $RuH_2(PPh_3)_4$ has been reported to give hydrido(1-alkoxycarbonyl-η^3-allyl-C^1,C^3) ruthenium(II) complexes [84]. The complexes $OsH(\eta^3\text{-}C_3H_5)(CO)(PR_3)_2$ have been obtained from $OsHCl(CO)(PR_3)_2$ and C_3H_5Mg. NMR studies reveal that the ancillary ligands are stereochemically rigid on the NMR time scale. The reactivity of these complexes with various acids has been examined and shown to lead to loss of propene and formation of $OsH(\eta^2\text{-}OAc)(CO)(P^iPr_3)_2$, $OsH_2Cl_2(CO)(P^iPr_3)_2$, and $[OsH(MeCN)_2(CO)(P^iPr_3)_2]^+$ for



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AcOH, HCl and HBF_4–MeCN respectively [85]. The reaction of Cy_3PCS_2 with the hydrido complexes $RuClH(CX)(PPh_3)_3$ (where X≡O or S), $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$ and $RuH(OClO_3)(CO)(CN^tBu)(PPh_3)_2$ has been investigated and the resulting products characterized by ^{31}P NMR spectroscopy [86]. The addition of triethylsilane to phenylacetylene to give *cis*-PhCH=CH($SiEt_3$) is shown to be catalyzed by $RuHCl(CO)(P^iPr_3)_2$. The selectivity observed in this reaction is 100%. A mechanism that proceeds by an initial Si—H bond activation has been presented [87]. New hydride–carbyne and hydride–vinylcarbyne complexes of osmium have been synthesized by allowing $OsH_2Cl_2(P^iPr_3)_2$ to react with terminal alkynes and terminal diynes. The solid state structure of $OsHCl(\equiv CCH_2Ph)(P^iPr_3)_2$ has been solved by XRD analysis, which exhibits a distorted octahedron with the two P^iPr_3 ligands occupying apical positions [88] (Fig. 4).

2.4. Phosphines

The heats (ΔH_{HM}) of protonation of the osmium center in $Os(H)_2(PR_3)_4$ (where $PR_3 \equiv PPhMe_2$, PPh_2Me, $PPh(OEt)_2$ or $P(OEt)_3$) and $Os(H)_4(PR_3)_3$ (where $PR_3 \equiv PPhMe_2$ or PPh_2Me) have been measured by titration calorimetry using CF_3SO_3H. The basicity increases by about 15 kcal mol^{-1} when two hydrides are

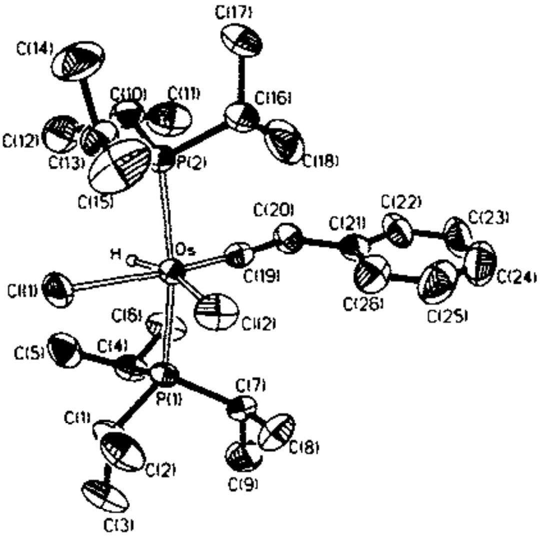
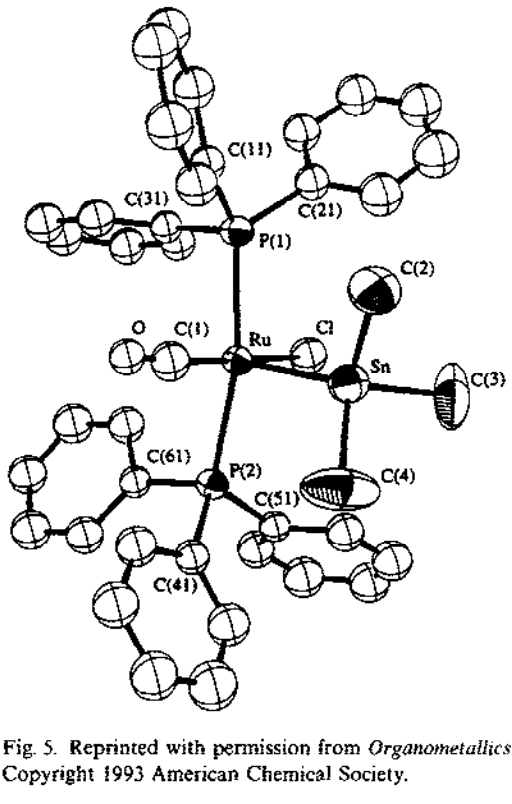


Fig. 4. Reprinted with permission from *Journal of the American Chemical Society*. Copyright 1993 American Chemical Society.

replaced by a PR_3 ligand in $Os(H)_4(PR_3)_3$ [89]. Cleavage of one of the stannylmethyl groups in $Ru(SnMe_3)Cl(CO)(CN$-*p*-tolyl$)(PPh_3)_2$ by iodine furnishes $Ru(SnMe_2Cl)I(CO)(CN$-*p*-tolyl$)(PPh_3)_2$, which reveals that a chloride ligand has migrated from the ruthenium center to the tin center. The displacement of chloride from this product by hydroxide and H_2S has been demonstrated. An X-ray crystal structure of the (thiohydroxyl)stannyl complex has been given in [90]. The problem of the structural characterization of $[Os(PR_3)_3H_5]^+$ has been addressed through the use of ab-initio molecular orbital calculations. The most stable isomer of $[Os(PR_3)_3H_5]^+$ is an eight-coordinated complex, whose polyhedron is derived from a dodecahedron containing the phosphine ligands in B sites [91]. An ab-initio molecular orbital study has been presented for $Os(PR_3)_3H_4$, and the peculiarities of seven-coordinated complexes are discussed [92]. Reaction of the cyclometalated hydride $RuH(PMe_3)_3(MePCH_2)$ with H_2O gives $RuH(OH)(PMe_3)_4$ with an 80% yield by NMR spectroscopy. An analogous hydration reaction was studied with $Ru(ethylene)(dmpe)_2$; however, the major product observed in this reaction was the ruthenium hydroxo dimer $[$*trans*-$RuH(OH)(dmpe)_2{\cdot}H_2O]_2$, which has been characterized by X-ray crystallography [93]. The oxidative addition of a wide variety of group 14 hydrides to osmium(0), osmium(II) and ruthenium(0) phosphine complexes has been thoroughly investigated. Included in this report are T_1 NMR data and the X-ray diffraction structures of $Os(SiEt_3)H(CO)_2(PPh_3)_2$ and $Os\{Ge(p\text{-tolyl})_3\}H(CO)_2(PPh_3)_2$ [94]. Treatment of *cis*-$RuCl_2(PPhMe_2)_4$ with $\{(TMEDA)Li\}_2\{(2\text{-}CH_2C_6H_4)_2\}$ gives the thermally unstable ruthenocycloheptadiene complex $Ru\{(2\text{-}CH_2C_6H_4)_2\}(PPhMe_2)_3$, whose solid structure has been solved by XRD analysis [95]. ^{31}P CP–MAS NMR data have been reported for solid samples of ruthenium complexes [96]. The coordinatively unsaturated complexes $Ru(SnR_3)Cl(CO)(PPh_3)_2$ (where $R \equiv p$-tolyl or Me) are obtained from $RuHCl(CO)(PPh_3)_2$ and $(CH_2{=}CH)SnR_3$. The product is postulated to arise by insertion of the vinylstannane into the Ru—H bond, followed by a β-stannyl elimination from the transient β-stannylethyl derivative. The X-ray crystal structure of $Ru(SnMe_3)Cl(CO)(PPh_3)_2$ exhibits a distorted square pyramid, with the $SnMe_3$ group occupying the apical position [97] (Fig. 5).

The Ru—H mean bond dissociation energy in $RuH_2(dmpe)_2$ has been determined to be about 63.5 kcal mol^{-1} by photoacoustic calorimetry. Also reported was the quantum yield for loss of H_2 ($\phi = 0.85$), which has been measured by transient actinometry. The intermediate $Ru(dmpe)_2$ reacts with CO and N_2 to give the corresponding $Ru(dmpe)_2L$ complex. The measured Ru—H mean bond dissociation and the measured reaction enthalpies have allowed the Ru—CO and Ru—N_2 bond energies to be determined [98]. A report dealing with the in-situ generation of ruthenium-chiral phosphine complexes and their catalytic hydrogenation activity has been published [99]. The new BINAP complexes RCpRU{S—(—)—BINAP}Cl (where R≡H or Me) have been synthesized from $RCpRu(PPh_3)_2Cl$ and S—(—)—BINAP in refluxing toluene. The X-ray structure of the methylcyclopentadienyl complex has been solved. These new BINAP complexes are effective catalysts



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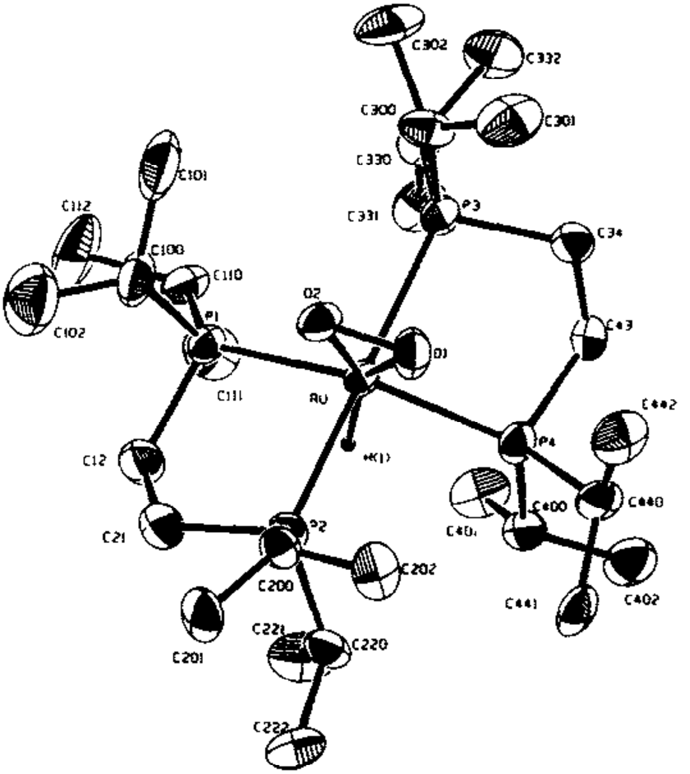
for the enantioselective hydrogenation of β-ketoesters [100]. The synthesis and spectroscopic characterization of rigid rod σ-acetylide complexes of ruthenium and osmium have been described. The complex *trans*-Ru(dppe)$_2$(C≡C−Ph)$_2$ exhibits a linear arrangement of the acetylenic units about the ruthenium center, as determined by X-ray crystallography [101]. Novel secondary allenylidene ruthenium complexes have been obtained from the reaction between *cis*-Ru(dppm)$_2$Cl$_2$ and HC≡CCH(OH)R. The product allenylidene complexes possess a *trans* geometry at the ruthenium center [102]. Terminal alkynes react with *cis*-RuCl$_2$(dppm)$_2$ to give vinylidene complexes of the form *trans*-[RuCl(dppm)$_2$(=C=CHR)]$^+$ [103]. The reaction between *cis*-RuCl$_2$(dppm)$_2$ and acetylene affords the ruthenium vinylidene complex *trans*-[RuCl(dppm)$_2$(=C=CH$_2$)]$^+$, the structure of which has been solved by X-ray crystallography. The resulting vinylidene complexes isolated from the reaction using terminal alkynes have also been described [104]. The redox properties and X-ray crystal structure of [RuCl(dppp)$_2$]$^+$ have been presented [105]. The iodosobenzene and persulfate oxygenation of saturated alkanes using ruthenium(III) diphosphine complexes has been presented [106]. The X-ray crystal structure and reactivity of Ru{C$_6$H$_4$(NH)$_2$-1,2}(PPh$_3$)$_3$ with π-acid ligands have been published [107]. The synthesis and solution characterization of ether–phosphine ruthenium(II) complexes of the form Cl$_2$Ru(P−O)$_2$ and *trans*-RuCl$_2$(P∼O)(P−O) have been described. The variable-temperature ^{31}P NMR spectra have led to the elucidation of rearrangement pathways and evaluation of the thermodynamic parameters associated with each P−O ligand [108]. The new tetradentate ligand P(CH$_2$CH$_2$PCy$_2$)$_3$ has been synthesized and studied for its reactivity with RuCl$_2$(PPh$_3$)$_3$. The initial species from this reaction is the five-coordinated square-pyramidal complex [RuCl{P(CH$_2$CH$_2$PCy$_2$)$_3$}]$^+$, which has been isolated as its tetraphenylborate salt. Reaction of this product with NaBH$_4$ gives *mer*-RuH(η^2-BH$_4$){η^3-P(CH$_2$CH$_2$PCy$_2$)$_3$·BH$_3$}, where the BH$_3$ ligand is attached to one of the dangling PCy$_2$ groups of the tetradentate phosphine [109]. Oxygen coordination at the dihydrogen-binding site in [RuH(η^2-H$_2$) (dippe)$_2$]$^+$ has been demonstrated. The XRD structure of [RuH(O$_2$)(dippe)$_2$]$^+$ reveals that the dioxygen ligand is bound in an η^2 fashion [110] (Fig. 6).

2.5. *Carbonyls*

The carbonyl complexes M(CO)$_4$(hexafluoro-2-butyne) (where M = Ru or Os) afford thin films of metal when treated with H$_2$ at elevated temperatures. The resulting ruthenium film was found to be highly reflective. All thin films were characterized by AES, XPS and XRD analyses. In the absence of an H$_2$ carrier gas, the dinuclear complexes M$_2${μ-η^1,η^1,η^4-C$_4$(CF$_3$)$_4$}(CO)$_6$ are formed, as a result of alkyne coupling [111]. The reaction between benzylamine and Ru(CO)$_4$(SiPhMe$_2$)I leads to the production of the ruthenium(II) complex Ru(CO)$_2$(PhCH$_2$NH$_2$)$_2$(SiPhMe$_2$)I, the molecular structure of which has been determined by X-ray crystallography [112]. Water-soluble ruthenium complexes have been obtained from the reaction between Ru(CO)$_3$(PPh$_3$)$_2$ and dicarboxylic acids. The use of oxalic acid gives Ru(CO)$_2$(PPh$_3$)$_2$(O$_2$CCO$_2$H)$_2$, which, when



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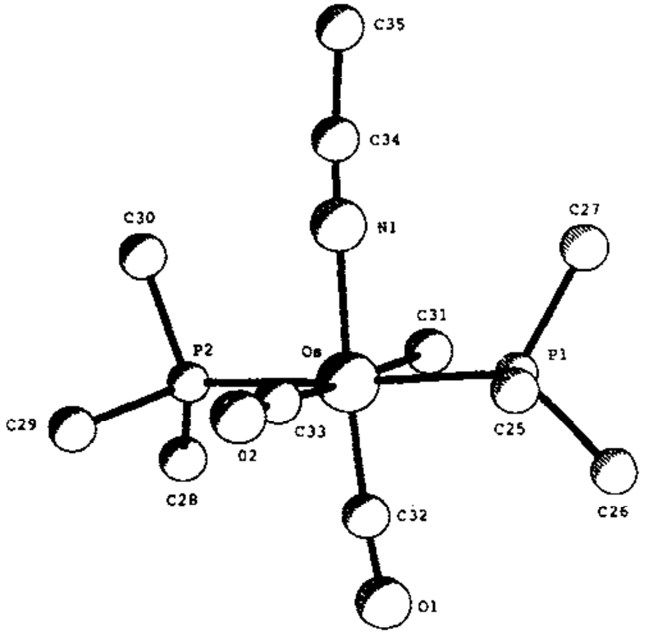
allowed to react with Et_3N followed by $Pt(PPh_3)_3$, gives the RuPt dimer $Ru(CO)_2(PPh_3)_2(\mu\text{-}O_2CCO_2)_2Pt(PPh_3)_2$ [113]. Coordination of the tetrafluoroborate anion has been observed when $Ru(CO)_2(PPh_3)_2Cl_2$ is treated with $AgBF_4$. The use of the resulting $Ru(CO)_2(PPh_3)_2(BF_4)_2$ as a 14 e^- cation precursor ($Ru^{II}(CO)_2(PPh_3)_2^{2+}$) has been described [114]. Diyne coordination has been shown in the reaction between $Ru(CO)_2(PPh_3)_2$ and diphenylbutadiyne. Protonation of $Ru(CO)_2(PPh_3)_2(\eta^2\text{-}PhC{\equiv}C{-}C{\equiv}Ph)$ by HPF_6 and HCl furnishes the new complexes $[Ru(CO)_2(PPh_3)_2(\eta^3\text{-}PhC{\equiv}C{-}C{=}CHPh]^+$ and $Ru(CO)_2(PPh_3)_2(\eta^1\text{-}PhC{\equiv}C{-}C{=}CHPh)Cl$ respectively. The X-ray crystal structure of the former complex has been determined, and the reactivity of these new complexes towards two-electron donor ligands described [115]. The oxidative addition of methyl iodide to substituted ruthenium carbonyls has been explored. $Ru(CO)_4PMe_3$ reacts with MeI to give $Ru(CO)_3(PMe_3)(Me)I$. The stereochemistry associated with the oxidative addition has been outlined [116]. The oxidative addition of MeI to $Os(CO)_4PMe_3$ and $Os(CO)_3(PMe_3)_2$ gives the osmium complexes $[Os(CO)_4(PMe_3)Me][I]$ and $[Os(CO)_3(PMe_3)_2Me][I]$ respectively. Thermolysis of the ionic products leads to CO loss in each case. Included in this report is the X-ray structure of



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$[Os(CO)_3(PMe_3)(MeCN)Me]^+$ (Fig. 7), which was isolated during the HPLC purification of $Os(CO)_2(PMe_3)_2(Me)I$ [117].

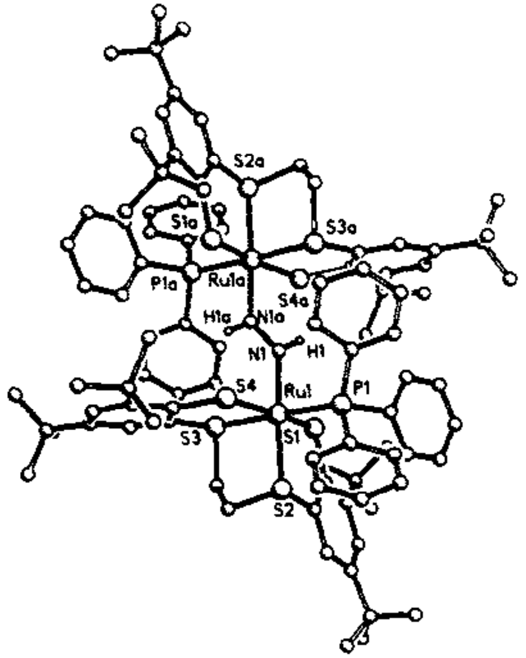
2.6. Sulfur and Oxygen Ligands

The reaction between $[OsO_2Cl_4]^{2-}$ and excess dineopentylzinc proceeds to give water- and air-stable $OsO_2(CH_2{-}{}^tBu)_2$. The reactivity of this dioxo complex with $Ta(CH{=}{}^tBu)(CH_2{-}{}^tBu)_3$ gives the monomeric pseudotetrahedral complex $Os(CH{-}{}^tBu)_2(CH_2{-}{}^tBu)_2$, which contains neopentyl and neopentylidene groups [118]. The tetrakis(2-methylpropyl)oxoosmium complex $OsO_2(Me_2CHCH_2)_4$ has been synthesized from $OsO_2(py)_2(O_2C_2H_4)$ and Me_2CHCH_2MgCl. X-ray crystallographic analysis reveals that the product possesses a square-pyramidal geometry of unusual C_4 molecular symmetry. No β-elimination reactivity is observed up to 100 °C [119]. A report dealing with the asymmetric bisosmylation of buckminsterfullerene yields enantiomerically enriched chiral isomers, which have been characterized by CD spectroscopy [120]. An approach designed to tether buckminsterfullerene to silicon surfaces by a $(pyridyl)_n{-}Os{-}O_4{-}C_{60}$ linkage has been presented [121]. The osmylation of C_{70} with OsO_4 in pyridine furnishes two isomers of $C_{70}\{OsO_4(py)_2\}$, which have been separated by HPLC and characterized by NMR spectroscopy [122].

Evidence for semicore effects in the valence photoelectron spectrum of OsO_4 has been presented. The experimentally obtained PES data are compared with data obtained from molecular orbital calculations [123]. The osmium(VIII) oxofluoride *cis*-OsO_2F_4 is synthesized from the reaction between KrF_2 and OsO_4 in anhydrous HF. An electron diffraction study and a DFT calculation revealed that the molecule possesses C_{2v} symmetry [124]. The equilibrium geometries of OsO_4, OsO_3F_2, OsO_2F_4 and OsF_8 have been calculated using ab-initio molecular orbital calculations at the Hartree–Fock and MP2 levels. A comparison between the calculated geometries and vibrational frequencies with available experimental data shows good agreement [125]. The synthesis and X-ray crystal structure of OsO_3F_2 and OsO_2F_4 have been published [126]. Thin films of ruthenium dioxide have been produced at low temperature from the chemical vapor deposition of ruthenium tetraoxide. The film's morphology, adhesion properties and purity were thoroughly characterized by the normal surface science techniques (XRD, SEM and XPS) [127].

The kinetic data for the reduction of *trans*-[Ru(1,4,8,11-tetramethyl-1,4,8,11-tetraazocyclotetradecane) $(O)_2]^{2+}$ in aqueous acidic solution have been reported. The activation parameters for the conversion of the dioxo complex to the monooxo–H_2O complex suggest that this reaction proceeds by an inner sphere mechanism [128]. The reaction of $[Ru(H_2O)_6]^{2+}$ with a series of monodentate ligands has been studied using UV–visible or NMR spectroscopy. For the ligand DMSO, the spectroscopic data reveal that the DMSO binds to the ruthenium center by the sulfur atom [129]. The synthesis of the $[RuO_4]^-$ ion from an alkaline solution of $RuCl_3$ containing excess bromate is discussed. Perruthenate anion oxidation of primary alcohols, activated alkyl halides, aldehydes, 1,2-diols and nitroalkanes to carboxylic acids is demonstrated, and the advantages of the synthesis of $[RuO_4]^-$ from sources other than RuO_4 have been discussed [130]. A study presenting the electronic, spectroscopic and redox data for $Ru\{P(C_{18}H_{37})_3\}_2$(3,5-di-*tert*-butyl-*o*-benzosemiquinonate) has been published. The construction of Langmuir–Blodgett films were facilitated by the long alkyl chains of the phosphine ligand [131]. The results of a mechanistic study on the enantioselectivity in the Sharpless catalytic system using OsO_4-modified cinchona alkaloids have been presented [132]. Kinetic data for the dihydroxylation of olefins using osmium tetraoxide and cinchona alkaloids have been discussed, and mechanistic schemes presented [133].

The complex $RuCl_2(PPh_3)$(1,4,7-trithiacyclononane) has been isolated from the reaction between $RuCl_2(PPh_3)_3$ and 1,4,7-trithiacyclononane. Use of the large crown ether 1,4,8,11-tetrathiacyclotetradecane yields the ionic complex *cis*-[RuCl(1,4,8,11-tetrathiacyclotetradecane)]$^+$. The molecular structures of both crown ether products have been determined by X-ray crystallography [134]. The syntheses, molecular structure and variable-temperature isomerization rates for the isomers of $[Os(S_2CNEt_2)_2(PPh_3)_2]^{0,+}$ have been published. The X-ray crystal structures of three complexes have been given in [135]. The one-pot synthesis of Ru(ClH)(PPh_3)[1,2-bis{(2-mercapto-3,5-di-*tert*-butylphenyl)thio}ethane] from $RuCl_2(PPh_3)_3$, HCl gas and the corresponding thiol complex has been published. The addition of bases results in the elimination of HCl and generation of the coordinatively unsaturated complex Ru(PPh_3)[1,2-bis{(2-mercapto-3,5-di-*tert*-butyl(phenyl)thio}ethane], which reacts readily with such Lewis bases as azide,



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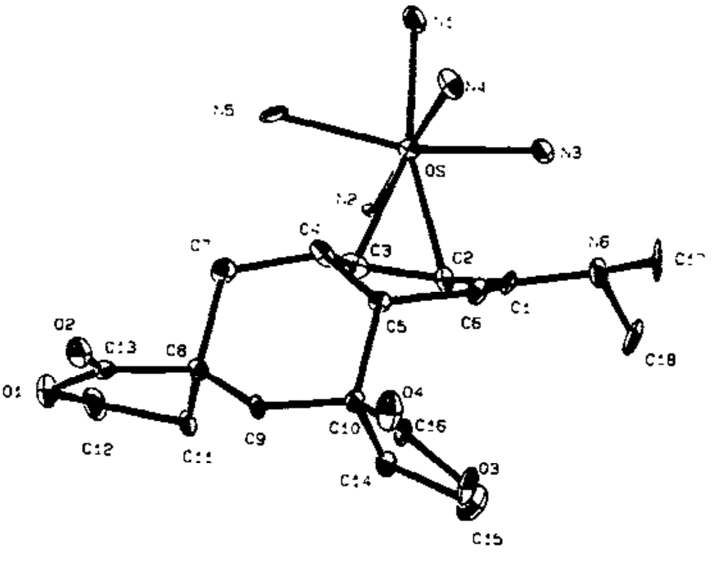
ammonia and hydrazine. The X-ray crystal structure of the hydrazine-bridged ruthenium dimer is reported [136] (Fig. 8).

2.7. *Nitrogen ligands*

The magnetic properties and the X-ray crystal structure of $[Ru(NH_3)_6][SCN]_3$ have been examined, and a crystal field model with no assumptions about symmetry has been discussed [137]. Pentaamineosmium(III) coordination to both the N(7) and C(8) positions of purine rings has been demonstrated in the X-ray structures of 7-[(9-methylhypoxanthine)$Os(NH_3)_5][Cl]_3$ and 8-[1,3,7-(trimethylxanthine)-$Os(NH_3)_5][Cl]_3$ [138]. The synthesis and reactivity of monohydrido complexes of osmium(IV) amines of coordination number 7 have been presented [139]. The synthesis and spectroscopic characterization of the ethene–ethyne complex $[Os(en)_2(CH{\equiv}CH)(CH_2{=}CH_2)]^{2+}$ from the molecular hydrogen complex $[Os(en)_2(H_2O)(\eta^2-H_2)]^{2+}$ have been published. X-ray crystallography confirms the structure of the product and supports the presence of trans ethene and ethyne groups. The competition for πd electron density by the two π acids results in the orthogonal arrangement of the ethene and ethyne ligands [140]. The standard reaction rate constant for $[Ru(NH_3)_6]^{3+/2+}$ has been measured by fast-scan voltammetry at a carbon fiber [141]. Electrochemical quartz crystal microbalance measurements have been carried out on $[Ru(NH_3)_5]^{3+}$. The frequency response has been discussed with respect to changes in density and viscosity of the depletion layer during cyclic voltammetry experiemtns [142]. Kinetic studies have been conducted on the stability of pentaamineosmium(II) adducts. The examined π-ligand adducts were generated from $Os(NH_3)_5(OTf)_3$ by zinc amalgam reduction [143]. Clay-modified electrodes bearing the redox-active cations $[Ru(NH_3)_6]^{3+}$ and $[Os(bpy)(py)Cl]^+$ have been prepared and examined in conjunction with rectifying electrodes based on redox polymer bilayers and related molecular electronic devices [144]. The results of a theoretical study on the molecular hydrogen complex $[Os(NH_3)_4(OAc)(\eta^2-H_2)]^+$ have been presented, with emphasis on the near doubling of the H—H bond length and the inability of the SCF method to predict an accurate geometry for the title complex [145]. Redox-induced linkage isomerizations in pentaamineruthenium(II) and pentaamineruthenium(III) complexes containing an ambidentate acrylamide ligand are reported. The ruthenium(II) center is shown to have an affinity for the π-acceptor alkene ligand, while the ruthenium(III) center prefers the strong π-donor amide ligand [146]. The use of $[Ru(NH_3)_5py]^{3+/2+}$ as an oxidant in the reduction and oxidation cross-reaction kinetics of a copper macrocyclic has appeared. [147]. The synthesis and use of *cis*-$[Ru(NH_3)_4(acetone)_2]^{2+}$ as a precursor for *cis*-tetraamineruthenium(II) complexes have been described [148]. Dearomatization of anilines has been observed during the complexation to pentaamineosmium(II). This has led to the production of functionalized 3-aminocyclohexanes under the appropriate reaction conditions. The X-ray structure of one of the "$Os(NH_3)_5^{2+}$" activated anilines has been given [149] (Fig. 9).

Treatment of the nitrido complex $[Os^{VI}(N)Cl_4]^-$ with bis(diphenylarsino)-ethane proceeds by displacement of one chloride ligand to give



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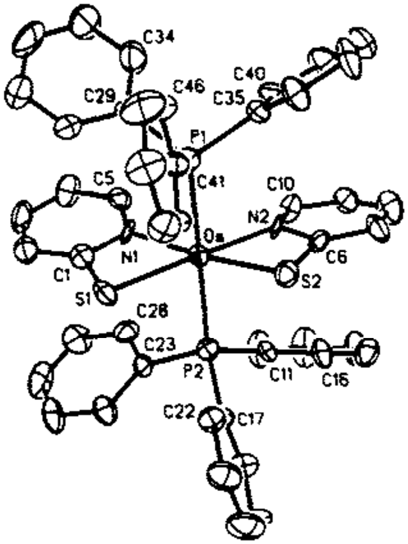
$Os^{IV}(N)Cl_3(Ph_2AsCH_2CH_2AsPh_2)$, which has been characterized by XRD analysis. The chlorine atoms adopt meridional positions in this distorted octahedron. Included in [150] are the photoluminescent properties of this new complex. The reaction between $[Os(N)Cl_4]^-$ and 2,3-diamino-2,3-dimethylbutane(H_2L) gives $[Os(N)Cl(H_2L)_2]^{2+}$, which may be converted to $[Os(N)(H_2L)_2]^{3+}$ by treatment with CF_3SO_3H. The X-ray structure of the former product and the redox properties of these complexes have been discussed [151]. The synthesis of $Os(NAr)_2O_2$ and $Os(NAr)_3O$ by an oxo–imido exchange between OsO_4 and $Mo(NAr)_2(O{-}^tBu)_2$ has been outlined. Phosphine substitution in the dioxo–diimido complex affords the corresponding diphosphine complexes $Os(NAr)_2L_2$ (where $L \equiv PMe_3$, PMe_2Ph or $PMePh_2$) [152].

Hydrated nitrosylruthenium(III) chloride has been allowed to react with 2-methyl-8-quinolinol in acetic acid solution. The product isolated from this reaction is *cis*-Ru(OAc)(2-methyl-8-quinolinol)(NO), which is shown to contain cis-(O,O) and trans-(N,N) quinolate ligands. The photoisomerization of the cis form to the trans form has been demonstrated, and the quantum yields for the cis→trans and reverse reactions measured. Conditions that lead to Ru—NO bond rupture have been discussed [153]. The Schiff bases formed from 4-substituted benzaldehydes and 2-aminophenol have been investigated for their reactivity with $Ru(PPh_3)_3X_2$ (where $X \equiv Cl$ or Br). *O*-Metallation of the phenolic Schiff base has been observed, and the ligand-field spectra have been analyzed [154]. The substitution reactivity of *N,N'*-diphenylamidines PhN=C(R)—NHPh (where R ≡ H, Me, Et or Ph) with the ruthenium and osmium complexes $MH_2(CO)(PPh_3)_3$, $MH(Cl)(CO)(PPh_3)_3$ and $M(O_2CCF_3)_2(CO)(PPh_3)_2$ has been reported. The product amidinato complexes have been characterized in solution by NMR spectroscopy [155]. Mononuclear and binuclear complexes have been isolated from the reaction between $RuX_2(DMSO)_4$ (where $X \equiv Cl$ or Br) and 1-diphenylphosphino-2-(2-pyridyl)ethane. An X-ray structure of the dimer $[Ru_2Cl_2(P{-}N)_4]^{2+}$ has been given in Ref. [156]. The synthesis and solution spectroscopic properties of $Os(2\text{-aminophenol})_3$ have appeared. Also included in [157] are the 4-methyl- and 4-*tert*-butyl-substituted derivatives. Treatment of $RuCl_3 \cdot 3H_2O$ and the 2-quinaldinate anion with dppm and PPh_3 furnishes the phosphine-substituted complexes trans-Ru(2-quinaldinate)$_2$(dppm)$_2$ and *cis*- and *trans*-Ru(2-quinaldinate)$_2$(PPh_3)$_2$ respectively. The dppm-substituted complex exhibits two bidentate *N,O*-quinaldinate and two monodentate dppm ligands, as confirmed by X-ray crystallography. All compounds were characterized in solution by IR and NMR (^1H and ^{31}P) spectroscopies [158]. Data relating to the reversible pH-dependent Os^{IV}(amide)—Os^{III}(amine) redox couple in aqueous solution in *trans*-$[Os^{III}(2,3\text{-diamino-2,3-dimethylbutane})Cl_2]^+$ have appeared. This proton-coupled electron transfer reaction is the first of its kind reported for an osmium complex [159]. Kinetic data for the reduction of the cyano complex $[Os(CN)_6]^{3-}$ by 1,2- and 1,4-dihydroxybenzene compounds are presented. Mechanistic schemes and application of the Marcus theory to these reactions have been discussed [160]. Reductive quenching of the red emission of *trans*-$Os(O)_2$(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been investigated. It is found that the excited state is a strong oxidant that is effectively quenched by the reducing anions nitride, azide and iodide [161]. The reaction between [Ru(acac)(1,4,7-trimethyl-1,4,7-triazacyclononane)(HO)]$^+$ and sodium sulfide under aqueous alkaline conditions affords the corresponding μ-disulfido complex [{Ru(acac)(thiocrownether)}$_2$($\mu-S_2$)]$^{2+}$, whose X-ray structure has been solved. On the basis of the observed magnetic and redox properties, this complex is described as an exchange-coupled dinuclear ruthenium(III) species with a μ-disulfido (S_2^{2-}) bridge [162]. Treatment of Ru(1,4,7-trimethyl-1,4,7-triazacyclononane)$Cl_3 \cdot H_2O$ with [acac][Na] in aqueous solution at pH > 8 gives the hydroxy complex [Ru(1,4,7-trimethyl-1,4,7-triazacyclononane)(acac)(OH)]$^+$. When the same reaction is conducted in methanol solvent, the corresponding methoxide complex is produced. Heating the hydroxy complex at high temperature leads to the elimination of H_2O and formation of the oxo-bridged complex [{Ru(1,4,7-trimethyl-1,4,7-triazacyclononane)(acac)}$_2$($\mu-O$]$^{2+}$, whose molecular structure has been established by X-ray crystallography [163]. New pyridinecarbaldimine ligands have been synthesized from pyridinecarboxaldehyde and amines and allowed to react with polymeric [$RuCl_2(CO)_2$]$_n$. The solution characterization of the new nitrogen-substituted complexes is presented along with the X-ray structure of one of the products [164]. MAD (RCH=CHCH=NR′) complexes of the form $Ru(CO)_2(PPh_3)(\eta^4-RCH=CHCH=NR')$ have been synthesized and spectroscopically characterized by IR and NMR spectroscopies. The X-ray crystal structure of the complex derived from PhCH=CHCH=NPh exhibits a distorted square pyramidal geometry, where the MAD ligand occupies three facial sites [165]. Cerium(IV) oxidation of $Os(PPh_3)_2$(pyridine-2-thiol)$_2$ leads to the production of [$Os(PPh_3)_2$(pyridine-2-thiol)$_2$]$^+$, which exists in two geometric isomers. The solid state structure of the cis,cis,trans osmium(III) complex has been determined by XRD analysis [166] (Fig. 10).

The oxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$ by thallic ions has been shown to be catalyzed by a dispersion of $RuO_2 \cdot xH_2O$. An electrochemical model involving redox catalysis supports the proposed reaction mechanism [167]. The kinetics of the oxidation of $[Ru(bpy)_3]^{2+/3+}$ by Tl^{3+} ions have been examined as a function of $[Ru(bpy)_3^{2+}]$, $[Tl^{3+}]$, $[Tl^+]$, $[RuO_2 \cdot xH_2O]$ and temperature. This work has been discussed in terms of reversible heterogeneous redox catalysis [168]. Cyclic voltammetry data for a $[Ru(bpy)_3]^{2+}$-coated film of poly(ethylene oxide) in CO_2 have been reported [169]. The luminescence properties of tris(α,α'-diimine)ruthenium(II) complexes and their emission quenching by oxygen, methylviologen and Cu^{2+} ions have been investigated in the presence of a variety of polyelectrolytes. The data reveal that the polyelectrolytes influence the photophysical and photochemical properties of the diimine complexes [170]. The luminescence intensities and lifetimes of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(py)_2]^{2+}$ have been examined as a function of pressure in a variety of media. The observed absorption is assigned to a ^{3}MLCT transition that terminates on an orbital localized primarily on the bpy ligand [171]. Use of the sol–gel method to prepare silica gel films containing $[Ru(bpy)_3]^{2+}$ has been discussed. The ruthenium complex retains its electrochemical and photoelectrochemical properties in the silica gel matrix [172]. Ion diffusion in solid films and heterogeneous kinetics at the film–solution interface have been explored by using



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$[Ru(NH_3)_6]^{2+}$ and $[Os(bpy)_3]^{2+}$ as the solution components [173]. $[Ru(bpy)_3]^{2+}$ has been examined in photoinduced electron transfer and energy transfer reactions using methylviologen and $[Os(bpy)_3]^{2+}$, both of which have been exchanged into zeolite Y. A reaction mechanism that involves intrazeolite electron transfer is favored [174]. The complexes $[Ru(bpy)_3]^{2+}$, $[Ru(bpz)_3]^{2+}$ and $[Ru(bpz)_2(bpm)]^{2+}$ were the subject of a photophysical study in neat and mixed MeCN–H_2O solutions. The temperature-dependent lifetimes, emission spectra and quantum yields have been reported, and the radiationless transitions discussed with respect to the energy gap law [175]. Highly resolved emission spectra have been recorded for $[Os(bpy\text{-}h_8)_n(bpy-d_8)_{3-n}]^{2-}$ (where $n=0$–3) doped into a single-crystal host of $[Zn(bpy)_3][ClO_4]_2$ at 1.3 K. It has been shown that the lowest excited electronic state is delocalized over all three of the bpy ligands [176]. The kinetics of thermodynamically disfavored electron transfer cross-reactions at the interface between redox polymers and solutions have been examined by using $[Os(bpy)_3]^{3+}$ incorporated in a Nafion film [177]. A Langmuir monolayer containing $[Ru(bpy)_3]^{2+}$ exhibits oscillation luminescence in a Belousov–Zhabotinskii reactor. The use of fluorescence microscopy in the study of this reaction is described [178]. Photoinduced electron transfer in $[Ru(bpy)_3]^{2+}$ has been observed using the technique of optical second-harmonic generation [179]. An ultrathin polymer film containing $[Ru(bpy)_3]^{2+}$ has been explored in the photocatalytic reduction of viologen, and the resulting asymmetric property exhibited by the film has been discussed [180]. The redox properties of $[Ru(bpy)_3]^{2+}$ have been examined as a function of the dielectric constant of the solvent. The potential separation between the $+1/0$ and $0/-1$ redox couples increases with decreasing solvent polarity. The stability of these redox couples has been discussed, and data have been presented for the observed E_rC_i reaction in

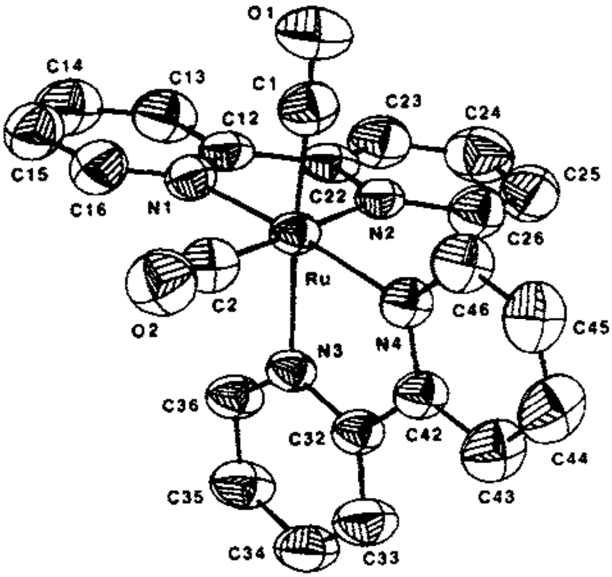
N-methylacetamide solvent [181]. The synthesis and solution characterization of mono- and bis-*meso*-substituted porphyrins containing an orthogonal $[Ru(bpy)_3]^{2+}$ group(s) have been published. The cyclic voltammetry data for these complexes show a mixing of the ruthenium and porphyrin redox couples [182]. Attachment of $[Ru(bpy)_3]^{2+}$ to a polyelectrolyte has been discussed, and the luminescence quenching of the excited ruthenium chromophore by several multivalent anions examined [183]. The attachment of a protoheme to a bpy ring in $[Ru(bpy)_3]^{2+}$ has been demonstrated, and the resulting complex studied in light-driven reactions as a model for dioxygen storage proteins [184]. The synthesis and characterization of a soluble pendent polymer complex containing a ruthenium(II) polypyridyl chromophore have appeared. The polymer consists of a poly(5,5′-diyl-2,2′-bipyridine), with attached $Ru(bpy)_2$ moieties. The redox chemistry and ESR data have been compared with analogous data obtained from monomeric ruthenium polypyridyl complexes [185].

The development and evaluation of an enzyme-based reactor–sensor system derived from the oxidation–reduction polymer poly{$[Os(bpy)_2(\text{vinylpyridine})Cl]^{2+/3-}$} have been described. This biosensor was used in the amperometric detection of glucose [186]. The chemical cross-linking of *p*-dibromobenzene, 1,5-dibromopentane and 1,10-dibromodecane with the redox polymer $[Os(bpy)_2(\text{polyvpy})_{10}Cl][Cl]$ has been achieved, and the isolated polymer-modified electrodes examined for their electrochemical properties [187]. The determination of mercury using a chemically modified electrode containing amino acids and electropolymerized $[Ru(vbpy)_3]^{2+}$ has been described [188]. The electron transfer cross-reaction rate constants for the oxidation of $[Fe(4,7\text{-}Me_2-1,10\text{-phen})_3]^{2+}$ at a redox polymer based on poly$[Os(bpy)_2(vpy)_2]^{3+}$ have been measured as a function of the polyether solution. These rate constants have been discussed with respect to the polymer chain segment and subsegment motions [189]. Chemically modified electrodes containing ($\frac{1}{3}$poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ —co-$\frac{2}{3}$poly-$[Ru(vbpy)_3]^{2+}$ and poly-*cis*-$[Ru\{4\text{-(2-pyrrol-1-yl-ethyl)-4'-methyl-2,2'-bpy}\}_2(H_2O)_2]^{2+}$ have been prepared and evaluated for their electron transport properties. The electrocatalytic oxidation of benzyl alcohol has also been explored [190]. Electric dichroism data that support the intercalation of optically active $[Ru(bpy)_2(phi)]^{2+}$ into DNA have appeared. The nature of the intercalation structure has been presented [191]. The synthesis and luminescence behavior of mixed-ligand complexes of $Ru(bpy)_2$ and $Os(bpy)_2$ have been reported. The mixed ligand used in this study was bis(picolyl) amine, which affords complexes with a "dangling" pyridine ligand [192]. A photocatalytic asymmetric synthesis of (R)-(+)-1,1′-bi-2-naphthol derivatives using Δ-$[Ru(4,4\text{-di(1R,2S,5R)-(−)-menthoxycarbonyl-2,2'-bpy})_3]^{2+}$ has appeared [193]. The enantioselective photoreduction of *rac*-$[Co(acac)_3]$ and *rac*-$[Co(edta)]^-$ using the same ruthenium catalyst has also been published [194]. The synthesis and spectral and electrochemical properties of polypyridylruthenium(II) complexes containing either an ancillary hydroquinone- and quinone-substituted diimine ligand have been presented [195].

Photolysis of $Ru(bpy)(CO)_2Cl_2$ or $[Ru(bpy)(CO)Cl_3]^-$ in MeCN solution leads to CO loss and substitution by MeCN. The redox properties of all new complexes have been examined [196]. The synthesis of pyridyltriazole-substituted $Ru(bpy)_2$

complexes has been discussed, and the effect of the pyridyltriazole ligand on the physical properties of each ruthenium complex examined by spectroscopic and chemical methods [197]. A study on the effect of hydrophobic and hydrophilic interactions on the diastereoisomers of Δ- and Λ-[Ru(amino acid)$(bpy)_2]^+$ has been published [198]. Bipyridylruthenium(II) complexes containing a dipyrido[2,3-a;2′,3′-h]phenazine ligand have been synthesized and examined by electronic absorption and emission spectroscopy. The observed MLCT transition has been discussed relative to other bipyridylruthenium(II) systems [199]. An investigation on the photoinduced electron transfer in amino acid assemblies containing a ruthenium bipyridyl chromophore is described. The assembly systems consist of a donor–chromophore–acceptor triad [200]. The reaction between *cis*-Ru(bpy)(biq)Cl_2 with imidazoles has been studied. Substitution of one chloride ligand has been observed to occur exclusively trans to the biq ligand, yielding *cis*-$[Ru(bpy)(biq)(imidazole)Cl]^+$. These data support a stronger trans influence for the biq ligand relative to the bpy ligand. The ^1H NMR and electrochemical data have been discussed [201]. The synthesis and variable-temperature ^1H NMR data for bipyridylruthenium(II) complexes bearing a dihydrazone ligand have appeared. These new complexes were prepared from the reaction between $Ru(bpy)_2Cl_2$ and the requisite dihydrazone derivative. The X-ray structure of $[Ru(bpy)_2\{$biacetyl di(phenylhydrazone)$\}]^{2+}$ has been given in [202]. The synthesis and solution characterization of alkynyl- and vinyl-linked crown ether–bipyridyl ruthenium(II) complexes have been presented. The alkali and alkaline earth metal recognition exhibited by these crown ethers has been outlined [203]. A report on ruthenium mediation in protein cross-linking and stabilization has been published. The model complex employed in this study was derived from $Ru(bpy)_2(CO_3)$ and cytochrome C [204]. σ-Tunneling pathways through aromatic residues have been observed in ruthenium-modified cytochromes C. The rates of intramolecular electron transfer reactions in these systems have been measured by using a laser flash-quench process [205]. Rate constants for photoinduced electron transfer in ruthenium(II) polypyridyl complexes, which are linked to an iron heme, have been reported. The kinetic data and the inverse dependence on driving force are discussed in the context of the Marcus theory [206]. Synthetic conditions for the synthesis of enantiometrically pure Δ-$[Ru(polypyridyl)_3]^{2+}$ using the new ligand chiragen[6], which is derived from a pinene-linked bpy ligand, have been reported [207]. Thin films of poly-$Ru(CO)_2\{$4-(2-pyrrol-1-ylethyl)-4,4′-methyl(-2,2′-bpy)$\}Cl_2$ and poly-$Ru(CO)_2\{$4,4′-bis(3-pyrrol-1-ylpropyloxy)carbonyl-2,2′-bpy$\}Cl_2$ have been prepared on platinum and indium - tin oxide electrodes by anodic electropolymerization methods. The electrochemical and spectroelectrochemical properties of these films have been explored, and the creation of photoimages has been investigated [208]. Intense MLCT activity in the red near-IR region has been recorded for ruthenium(III) and osmium(III) complexes possessing a bpy ligand which carries electron-donor substituents [209]. Molecular level photovoltaics have been examined by use of the complexes *cis*-M$\{4,4'$-$(CO_2H)_2$bpy$\}_2CN_2$ (where M ≡ Ru or Os), which have been attached to sol–gel-processed TiO_2 electrodes. Incident-photo-to-current efficiencies exceeding 90% are reported for the ruthenium complex [210]. The electron diffusion coefficient for the redox polymer derived from poly(vpy) and $[Os(bpy)_2Cl]^{+/2+}$ has been measured by steady state voltammetry. The effects of hydration on the cross-linked redox polymer have been discussed [211]. A spectroscopic investigation on the binding of enantiomerically pure $[Ru(bpy)_2(ppz)]^{2+}$ to calf thymus DNA has been published. The binding modes were elucidated using absorption, fluorescence and resonance-enhanced Raman spectroscopies [212]. Ultrafast photoinduced switching of second-harmonic intensity from a Langmuir–Blodgett polypyridylruthenium-containing film has been demonstrated by laser techniques [213]. The protonation of the excited states of ruthenium(II) complexes bearing bpy, bpz and bpm ligands has been studied in aqueous solution. Also included in this study are the rate constants for protonation [214]. The resonance Raman and time-resolved resonance Raman spectra of ruthenium(II) polypyridyl complexes have been measured [215]. Treatment of $Ru(bpy)_2Cl_2$ with large polyaza cavity-shaped ligands gives new ruthenium(II) complexes that can incorporate a second ruthenium(II) or osmium(II) polypyridyl moiety into a distal ligand site. An X-ray crystal structure of one of the diruthenium complexes has been presented [216]. The X-ray crystal structures of $[Ru(bpy)_2(CO)_2][PF_6]_2$, $[Ru(bpy)_2(CO)\{C(O))Me\}][Ph_4B]\cdot MeCN$ and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]\cdot 3H_2O$ have been crystallographically determined as part of a comparative study on CO_2 reduction products [217] (Fig. 11).

New ruthenium-based chromophore-quencher complexes have been synthesized and examined in electron transfer reactions. The electron donor moiety is a 4-methyl-4′-(*N*-phenothiazylmethyl)-2,2′-bpy ligand and the electron acceptor is an *N*-methyl-4,4′-bipyridinium cation, both of which are attached to a ruthenium(II)-tpm



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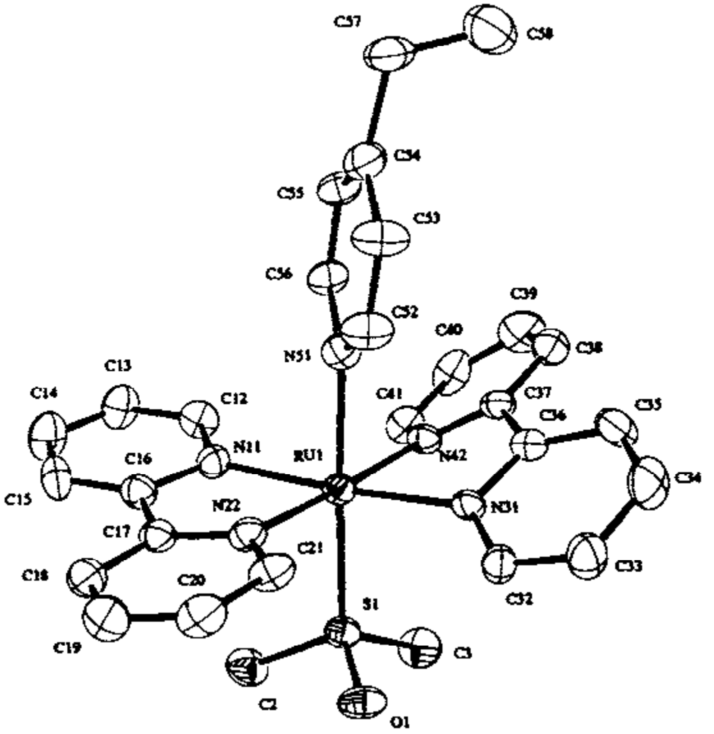
group. Intramolecular electron transfer has been shown to take place following laser flash excitation [218]. The results on the ground- and excited-state properties of *cis*-$Ru(bpy)_2(NO_2)(X)$ (where $X \equiv NO_2$ or CN) and *cis*-$[Ru(bpy)_2(NO_2)(py)]^+$ have been presented. The effect of the ancillary ligands on the MLCT and dd states has been discussed [219]. The complex $Ru(bpy)_2(N_3)_2$ has been shown to undergo photosubstitution by a free-radical mechanism in chloroform solvent [220]. The use of the oxo(phosphine)ruthenium(IV) complexes $[Ru(bpy)_2(O)PR_3]^+$ (where $PR_3 \equiv$ various phosphines) as oxidation catalysts has been published. The substrates chosen for study were sulfides and sulfoxides. Included in Ref. [221] are kinetic data, Hammett correlations and a working mechanism that has been found to be substrate dependent. The synthesis and characterization of ruthenium complexes containing a pyridine ligand with an appended metallocyclam moiety have been reported [222]. Substituent effects and bonding characteristics have been examined in $[Ru(bpy)_2(L{-}L)]^+$ complexes (where $L{-}L \equiv$ *o*-benzoquinone diimines, *o*-semiquinone diimines, *o*-benzenediamides or *o*-phenylenediamines). Use of the electronic and electrochemical data has allowed the construction of a map of the orbital energies as a function of the Hammett parameter of the substituents [223]. The synthesis and characterization of diimine ruthenium(II) complexes of the form $[Ru(H_2O)(diimine)(terpy)]^{2+}$ have been reported. The rate constants for H_2O replacement by MeCN have been measured in HNO_3-$NaNO_3$. On the basis of linear regression analyses, the cone angle of each ancillary diimine ligand has been calculated for the first time [224]. The kinetics and mechanism of diasteromeric isomerization of $[Ru(bpy)_2(1,1'\text{-biq})]$ have been published [225]. The complex $[Ru(4\text{-methyl-}2,2'\text{-bpy})_3]^{2+}$ and its methyl-deuteriated analogue have been studied by resonance Raman and time-resolved resonance Raman spectroscopy. Evidence is presented that supports a polarization of the radical fragment of the ^{3}MLCT states [226]. Cyclic voltammetry data on the dehydrogenation of α-amino acids coordinated to an $Ru(bpy)_2$ moiety have been published [227]. The low temperature electrochemical reduction of $[Ru(2,3\text{-dpp})_n(bpy)_{3-n}]^{2+}$ (where $n = 1$-3) has been investigated in DMF solution up to a limit of −3.1 V vs. SCE. Overlapping cyclic voltammetric waves have been resolved by using convolutive analysis, and the simulation techniques and the redox potentials reported [228]. Polypyridylruthenium complexes with a 2,2′-azobis(pyridine) ligand have been prepared. The structural requirements for intramolecular electron transfer in the $[Ru^{II}(azopyridine^-)(azopyridine)(bpy)]^{2+}$ complex have been discussed [229]. The effect of donors and acceptors on the twist angle of $[Ru(bpy)_2(3,4\text{-diamino-}3',4'\text{-diiminodihydrobiphenyl})]^{2+}$ has been investigated for its solvatochromic behavior in a visible-region electronic transition. The potential use of this complex as a molecular switch device has been described [230]. The "molecular light switch" complex $[Ru(bpy)_2(dppz)]^{2+}$ has been the subject of a cyclic voltammetry, UV–visible and ESR-ENDOR study. Interpretation of the radical anion using HMO–McLachlan calculations has allowed the π spin populations and orbital energies to be addressed [231]. New polypyridylruthenium(II) complexes containing a fused phenanthroline–pteridinedione ligand have been synthesized and their electrochemical properties examined [232]. Treatment of *trans*-$[Ru(bpy)_2(H_2O)_2]^{2+}$

with DMSO furnishes the corresponding bis-DMSO complex *trans*-$[Ru(bpy)_2(DMSO)_2]^{2+}$, which has been allowed to react with pyridine to give a mono-substituted pyridine complex. The molecular structure of *trans*-$[Ru(bpy)_2(DMSO)(4\text{-}Etpy)][PF_6]_2$ has been established by XRD analysis [233] (Fig. 12).

The electrochemical and spectroscopic properties of monomeric and oligomeric ruthenium and osmium complexes possessing a tppz ligand have been investigated. All monomeric complexes exhibited luminescence behavior at both room temperature and liquid-nitrogen temperature [234]. Enantioselective quenching of the luminescence of Dy(III) and Tb(III) complexes by resolved $[Ru(1,10\text{-}phen)_3]^{2+}$ is presented. The quenching has been discussed by using a model involving encounter pair formation, reorientation and energy transfer [235]. The binding of calf thymus DNA to ruthenium-substituted dpb complexes has been examined [236]. The DNA binding of Δ- and Λ-$[Ru(1,10\text{-}phen)_2(dppz)]^{2+}$ has been probed by linear dichroism and steady state and time-resolved luminescence spectroscopies. Differences in the luminescence quantum yields in the presence of DNA are attributed to different intercalation geometries of the dppz ligand [237]. The synthesis and redox examination of ruthenium(II) complexes possessing tridentate 2,6-bis(benzimidazol-2-yl)pyridine



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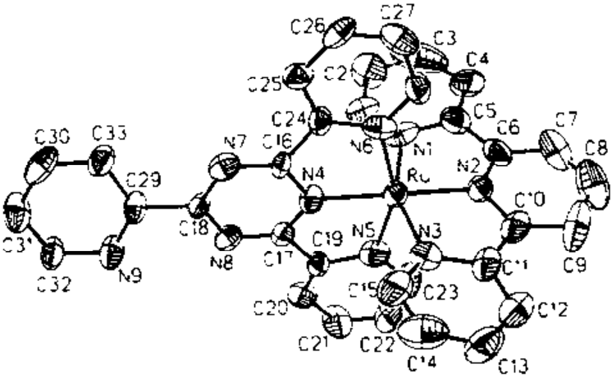
ligands have been presented. The new complexes were characterized by ^1H and ^{13}C NMR spectroscopy [238]. Binary and ternary ruthenium(III) complexes have been prepared with ancillary 2-(2-hydroxyphenyl)pyridine and 6-(2-hydroxyphenyl)pyridine ligands. The cyclic voltammetry data and ESR spectra of these complexes are included in [239]. The reaction between $[RuCl_2(1,5\text{-}COD)]_n$ and poly(pyrazol-1-yl)methane ligands yields neutral six-coordinated ruthenium(II) complexes, for which the X-ray structure of $[RuCl(1,5\text{-}COD)\{bis(5\text{-}trimethylsilylpyrazol\text{-}1\text{-}yl)methane\}]^+$ has been solved [240]. New ruthenium complexes with 2,6-bis(pyrazol-1-yl)pyridine ligands have been prepared and characterized in solution by NMR (^1H and ^{13}C), IR and UV–visible spectroscopies [241]. 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole, which is a polydentate and ambidentate ligand, reacts with $[Ru(CO)_2Cl_2]_n$ to give two bidentate coordination isomers of $Ru(CO)_2Cl_2(apt)$. Both of these isomers have been characterized by XRD analysis [242]. The regeneration of NAD^+ in enzymatic synthesis has been modeled with the ruthenium(II) complex $[Ru(1,10\text{-}phen\text{-}5,6\text{-}dione)_3]^{2+}$ [243]. A two-dimensional COSY NMR study on the *mer* and *fac* isomers of $[Ru(dpp)_3]^{2+}$ has appeared. The isomer assignment was also supported by ^{99}Ru NMR data [244].

Reductive coupling of the radical anion of 2,2′-bpy with LDA gives the ligand 2,2′:4′,2″:6″,2‴-quaterpyridine by a 2,4-coupling. This asymmetric ligand has been allowed to react with $Ru(bpy)_2Cl_2$ and $Ru(terpy)Cl_3$ to give $[Ru(bpy)_2(L)]^{2+}$ and $[Ru(terpy)Cl(L)]^+$ respectively. The redox chemistry and luminescence properties of these complexes have been reported [245]. The photosensitizing moiety Ru(terpy)(bpy) has been used in the synthesis of new mononuclear and dinuclear complexes as well as mixed-valence complexes [246]. Treatment of the cyclometallating ligand 6-phenyl-2,2′-bpy with $Ru(terpy)Cl_3$ in acetic acid leads to the *N,N′*-bonded complex $[Ru(terpy)(N,N)Cl]^+$. When the same reaction is conducted in water, the corresponding cyclometallated cation $[Ru(terpy)(N,N)]^+$ is isolated. Both complexes were characterized by ^1H NMR, FAB mass spectrometry and cyclic voltammetry techniques. [247] New ditopic ligands having two 2,2′:6′,2″-terpy or two 4′-phenyl-2,2′:6′,2″-terpy subunits and an alkynyl bridge have been synthesized and employed in the construction of rigid rod-like ruthenium(II) complexes [248]. A cyclometallated diruthenium complex has been isolated from the coupling of a mononuclear ruthenium(II) complex bearing a 4′-chloro-substituted 2,2′:6′,2″-terpy ligand [249]. The use of ruthenium(II)-2,2′:6′,2″-terpy triads in the synthesis of cascade polymers has appeared [250]. The luminescence properties of rigid rod-like terpy complexes formed from the coupling of two $[M(terpy)_2]^{2+}$ units (where M ≡ Ru or Os; terpy ≡ 4′-(*p*-tolyl)-2,2′:6′,2″-terpy) have been studied. It is shown that electronic energy transfer proceeds through the phenyl spacers [251]. Long-range coupling in mixed-valence diruthenium complexes ligated by bis-terpy ligands with variable-length bridges has been observed in fluid solution [252]. The synthesis and redox properties of new oxoruthenium(IV) complexes have been published. The complexes are based on $[Ru(terpy)(L)(H_2O)]^{2+}$ (where L ≡ diimine ligands), and the X-ray structure of $[Ru(terpy)(\eta^3\text{-}tpt)]^{2+}$ has been given in Ref. 253 (Fig. 13). The oxidation of the aquo complex to the corresponding oxo complex may function as a component DNA cleavage agent [253].



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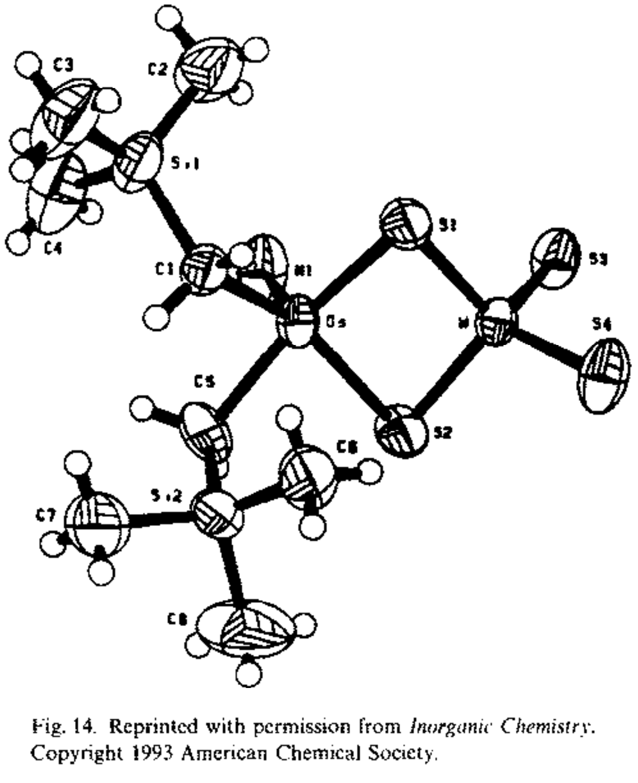
The mixed-metal complex [(terpy)Ru{tetrakis(2-pyridyl)pyrazine}$IrCl_3$]$^+$ has been synthesized and examined for its electrochemical and spectroelectrochemical properties. Intramolecular photosensitization schemes were mentioned given the presence of the light-absorbing ruthenium center and the catalytically active iridium center. Fluid solution emission was observed, and the energy and lifetime of the luminescence have been determined [254]. The mixed-ligand complexes [Ru(bpy)$_2$(bpt)Ru(1,10-phen)$_2$]$_3$ and [Ru(1,10-phen)(bpt)Ru(bpy)$_2$]$^{3+}$ have been examined for their excited-state properties and the data used in a reactivity comparison with the appropriate monomeric diimine complexes. It is shown that the N(1) site of the triazole ring is oxidized [255]. The observation of a weak intervalence transition in [$(NH_3)_4$Ru{μ-3,6-bis(2-pyridyl)-1,2,4,5-tetrazine}Ru$(NH_3)_4$]^n (where $n=3$–5) has been reported. The similarity of this complex with the Creutz–Taube ion has been discussed [256]. The cyano-bridged ruthenium(III)–iron(II) complex [Ru(edta)(NC)Fe$(CN)_5$]$^{5-}$ has been prepared from the reaction between ferrocyanide and [Ru(Hedta)Cl]$^-$. A temperature-dependent intervalence transition has been observed in aqueous solution. The rate and activation data for the formation of this dimer have been measured by using stopped-flow methods, and a proposed mechanism has been presented [257]. Data related to the spectroscopic and electrochemical characterization of the asymmetric diruthenium(II) complex [(bpy)$_2$Ru(bpm)Ru$(NH_3)_4$]$^{4+}$ have been published [258]. Electronic coupling in several mixed-valence diruthenium complexes has been examined within the context of the Mulliken theory on donor–acceptor interactions. The complexes investigated in this study have the form [L$(NH_3)_4$Ru$-L_b-$Ru$(NH_3)_5$]$^{4+/5+/6+}$ (where $L\equiv NH_3$ or substituted pyridine; $L_b\equiv$pyrazine or 4-cyanopyridine) [259]. Ruthenium ammine–crown ether interactions have been explored by charge transfer absorption, electrochemical, and NMR measurements [260]. Slow intramolecular electron transfer in Ru(III)–Ti(III) complexes bridged by the dianion of dihydroxyquinones has been observed [261]. Treatment of the nitrido complexes [Os(N)R_2Cl_2]$^-$ (where $R\equiv$Me or CH_2SiMe_3) with either [MoS_4]$^{2-}$ or [WS_4]$^{2-}$ affords the corresponding sulfur-bridged complexes $[Os(N)R_2(\mu\text{-}S)_2MS_2]^-$. When an excess of $[WS_4]^{2-}$ is used, the isolated product is shown to be a trimetallic complex in which two $Os(N)R_2$ units are bridged by a tetrathiotungstate moiety. XRD analyses have established the structures of $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}S)_2WS_2]^-$ and $[(Me_3SiCH_2)_2(N)Os]_2(\mu\text{-}WS_4)$ [262] (Fig. 14).

Several mixed-metal Os(II)–Ru(II) trimetallic complexes that are bridged by polypyridyl ligands have been prepared and examined by IR, near-IR and UV–visible spectroscopies, and by electrochemical methods. The investigated complexes have the form $[\{(bpy)_2Ru(b_L)\}_2OsCl_2]^{4+}$ (where $b_L \equiv$ dpp, dpq or dpb) [263]. Tris(bipyridine) complexes of Ru(II)–Os(II), Ru(II)–Ru(III), Os(II)–Os(III) and Ru(II)–Os(III) that are separated by the rigid spacer 1,4-bis[2-(2,2′-bipyridin-5-yl)ethenyl]bicyclo[2.2.2]octane have been prepared and examined as models for electron transfer processes in supramolecular complexes. Rate constants for photoinduced energy and electron transfer processes have been given in Ref. [264]. FAB mass spectrometry data have been reported for the polynuclear rhenium(I)–ruthenium(II) complexes $[Re(CO)_3(1,10\text{-}phen)CN-\{Ru(bpy)_2(CN)\}_n\ Ru(bpy)_2(CN)]^{(n+1)+}$ (where $n = 0$–2). The fragmentation patterns exhibit decomposition pathways involving CO and bpy ligand loss, bpy ligand oxidative addition and cleavage of the CN—Ru bond [265]. The synthesis and redox investigation of Os—Os and Os—Ru mixed-valence complexes ligated by



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polyazine bridging ligands have been discussed. Spectroelectrochemical data indicate that the mixed-valence Os(II)–Os(III) and Os(III)–Ru(II) complexes are best considered as Robin and Day class II complexes [266]. Diruthenium(II) and diosmium(II) complexes possessing a 3,5-bis(2-pyridyl)-1,2,4-triazole cyclohexyl-bridged spacer ligand have been prepared and examined for their absorption and luminescence properties, in addition to their and redox behavior. Data are presented that support the existence of a weak electronic communication between the metals [267]. Oxidative coupling of [M(4′-p-tolyl-2,2′:6′,2′q-terpy)(1,3-di-*o*-pyridylbenzene)]$^+$ (where M ≡ Ru or Os) affords the corresponding dimers with the bis-cyclometallating bridging ligand 3,3′,5,5′-tetrapyridylbiphenyl. The comproportionation constant K_c for each mixed-valence M(II)–M(III) dimer has been evaluated by cyclic voltammetry [268]. Excited-state charge recombination in $Ru(CN)_4[Cr(cyclam)(CN)_2]_2$ has been studied and discussed in terms of photochemical molecular devices [269]. A report dealing with photoinduced electron transfer processes in covalently linked ruthenium and cobalt complexes bearing polypyridyl ligands has appeared [270]. The intervalence charge transfer energetics in $[(NH_3)_5Ru^{III}$-4,4′-bpy-$Ru^{II}(NH_3)_5]^{5+}$ have been investigated as a function of solvent. The absorption energies are discussed with respect to the Marcus–Hush theory [271]. The L-proline-bridged complexes $[(bpy)_2Ru^{II})$4-carboxy-4′-methyl-2,2′-bpy)-$(L\text{-}pro)_n$-$Co^{III}(NH_3)_5]^{4+}$ (where $n = 1 \cdot 6$) have been synthesized from $[(bpy)_2Ru$(4-carboxy-4′-methyl-2,2′-bpy)] and $[(NH_3)_5Co(L\text{-}pro)_n]$ monomers. The intramolecular electron transfer rates and activation parameters have been reported [272]. The complexes $[(bpy)_2RuCl$-pyrazine-$Ru(NH_3)_5]^{4+}$ and [(4,4′-methyl-2,2′-bpy)RuCl-pyrazine-$Ru(NH_3)_4$(4-methylpyridine)]$^{4+}$ have been examined for their optical intervalence charge transfer behavior as a function of temperature [273]. Intrastrand electron and energy transfer between polypridyl ruthenium and osmium units on a copolymer of styrene and *p*-(chloromethyl)styrene have been investigated by laser flash photolysis. The polymer synthesis and rate constants for intramolecular electron transfer have been discussed [274]. The synthesis and energetics for electron transfer in $[(bpy)_2Ru(L{-}L)Co(bpy)_2]^{5+}$ (where L−L ≡ 2,6-bis(2′-pyridyl)-benzodiimidazole, bpbzim or 1,5-bis{2′-(2″-pyridyl)-benzimidazoyl} pentene) have been reported [275]. Transient IR spectroscopy data on [(1,10-phen)$(CO)_3Re^I(NC)Ru^{II}(CN)(bpy)_2]^+$ reveal that optical excitation leads to the oxidized rhenium species [(1,10-phen$^{\bullet -}$)$(CO)_3Re^{II}(NC)Ru^{II}(CN)(bpy)_2]^+$, which is followed by a rapid Re^{II}(1,10-phen$^{\bullet -}$) → Ru^{II}(bpy) energy transfer. The use of suitable monomeric models that support the transient IR assignments have been discussed [276].

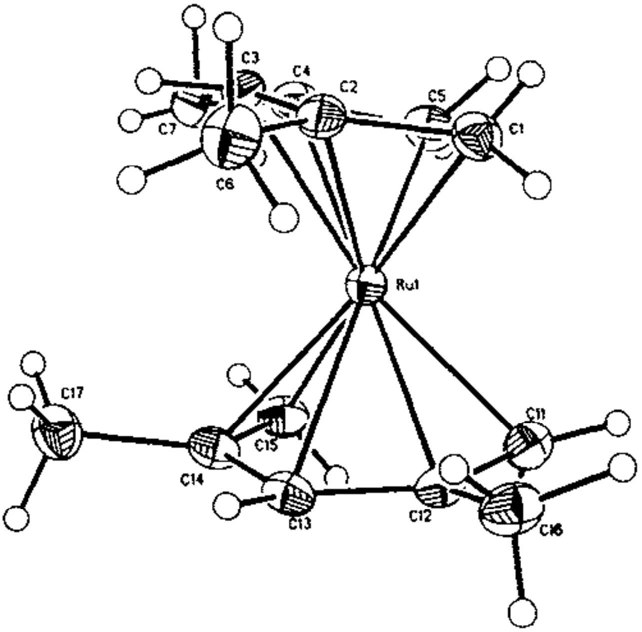
The effects of macrocyclic ether encapsulation of the Creutz–Taube ion have been explored by near-IR absorption spectroscopy [277]. A report dealing with the kinetics and mechanism of H_2O substitution by thiourea in $[(NH_3)_5Ru^{II}(edta)Ru^{III}(H_2O)]^{2+}$ has appeared. The rate data and activation parameters are consistent with an associative interchange mechanism [278]. Dinuclear ruthenium(II) and trinuclear ruthenium(II)–copper(I) complexes with ditopic ligands have been prepared and spectroscopically characterized [279]. The synthesis and intramolecular rate constants for electron transfer in ruthenium iron protein models are reported. The protein modeled in this study is based on this photosynthetic bacterium *Chromatium vinosum* [280]. Resonance Raman spectral data on the polypyridyl complexes $[(bpy)_2Ru(dpp)Ru(biq)_2]^{4+}$ and $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$ have been published. The lowest excited states in these complexes are assigned to an Ru→biq charge transfer [281]. A spectroelectrochemical study on the mixed-metal ruthenium(II)–iridium(II) complexes $[\{(bpy)_2Ru(b_L)\}_2IrCl_2]^{5+}$ (where $b_L \equiv$ dpp, dpq or dpb) has been presented [282]. A ruthenium(II)-to-central-cobalt(III) metal-to-metal charge transfer in the trinuclear complex $[(NH_3)_5Co^{III}(\mu\text{-NC})Co^{III}(CN)_4(\mu\text{-CN})Ru^{II}(CN)_5]^{3-}$ has been observed and shown to lead to a redox decomposition of the complex [283]. Solvent-dependent energy transfer in the mixed-metal ruthenium(II)–rhenium(I) complex $[Ru(bpy)_2\{$1,2-bis(4-methyl-2,2′-bipyridyl-4′-yl)ethane$\}Re(CO)_3(py)]^{3+}$ has been demonstrated. Assignments for the observed UV–visible absorptions have been made and a discussion on the energy transfer process has been presented [284]. The chromatographic separation and spectroscopic characterization of the diastereoisomeric pairs of dinuclear ruthenium(II)–osmium(II) complexes ligated by polypyridyl ligands have been discussed [285]. The redox properties of the bimetallic ruthenium complexes $[\{(bpy)_2Ru\}_2(L_b)]^{4+}$ (where $L_b \equiv$ 6,7-dichloro-dpq or 6,7-dimethyl-dpq) have been examined. Included in Ref. [286] are the syntheses for these new dpq-substituted ligands. The synthesis and use of the spacer ligand 1,4-bis[2-(2,2′-bipyridine-5-yl)ethynyl]bicyclo[2.2.2]octane in the construction of ruthenium(II)–ruthenium(II), ruthenium(II)–osmium(II) and osmium(II)–osmium(II) complexes have been published. The absorption and luminescence data for all new complexes have been presented [287].

2.8. *π complexes*

Acetate metathesis of the chloride ion in $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)]_2$ using AgOAc affords the monomeric complex $Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(OAc)$, which exhibits a chelating acetate group. The reactivity of this bis(allyl)ruthenium complex with halogenated acetic acids and thioacetic acid has been discussed [288]. Treatment of the ruthenium(IV) chloro-bridged dimer $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)]_2$ with EtSH leads to bridge cleavage and production of $Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(EtSH)$. Continued reaction has been shown to give $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl]_2(\mu\text{-}Cl)(\mu\text{-}SEt)$ and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SEt)]_2$. All three products have been examined by cyclic voltammetry methods, with the observed electrochemical data discussed [289]. The use of Ru(1,5-COD)(COT) for the preparation of small particles of ruthenium has been presented. The colloidal ruthenium particles have been characterized by electron microscopy and IR spectroscopy [290].

IR spectroscopic data on the ionic hydrogen bond in $[Cp^*_2OsH]^+$ and the equilibrium between CF_3CO_2H and Cp^*_2Os have been presented. The structures of the ion pairs $[Cp^*_2OsH][X]$ (where $X \equiv BF_4$, PF_6 or CF_3SO_3) in solution and the solid state have been discussed [291]. The interaction between $[Cp^*_2OsH][PF_6]$ and N and O bases has been investigated by IR spectroscopy. No evidence is obtained for the deprotonation of $[Cp^*_2OsH]^+$ by either Et_3N or pyridine [292]. The reaction between ferrocenylruthenocenylmethane and chlororuthenocenium(IV) or bromoruthenocenium(IV) salts gives the corresponding α,α-ferrocenylruthenocenylmethylium salts, whose structures have been assigned on the basis of ^{57}Fe Mössbauer and NMR (^{1}H and ^{13}C) spectroscopy studies. The temperature-dependent NMR data on the rotation about the exocyclic $-CH^+$ moiety has been discussed and the energy barrier calculated by using ^{1}H NMR line simulation data [293]. ^{1}H and ^{13}C NMR spectroscopy studies on iodoferrocenylruthenocenium salts have been conducted. Variable-temperature NMR data indicate the presence of a strong interaction between the ruthenium and iron centers in the mixed metallocene system. At low temperatures the cation is formulated as $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+$, while at room temperature the structure is best represented as $[Fe^{III}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+$ [294]. Treatment of 1,1″-biruthenocene with iodoruthenocenium salts leads to an oxidation of the former metallocene, giving [iodo-1,1″-biruthenocenium(II,IV)]$^+$. Electron exchange between the Ru(II) and Ru(IV) centers has been evaluated by variable-temperature NMR measurements. The activation energy for electron exchange increases as a function of the solvent's dielectric constant [295]. Stacking reactions of $Cp^*Ru(C_5H_5BMe)$ with metallo-electrophiles give triple-decker complexes with a bridging boratabenzene ligand [296]. The synthesis and characterization of phenylazoruthenocene have been published [297]. Electrochemical studies in solution on $Cp^*(\eta^5\text{-}C_5F_5)Ru$ have been carried out and the data compared with gas-phase oxidation data obtained using the electron transfer equilibrium method. The electronic effect exhibited by the C_5F_5 ligand has been compared with other cyclopentadienyl ligands [298]. Cp*CpRu reacts with $[Cp^*Ru(OMe)]_2$ to furnish the triple-decker complex $[Cp^*Ru(\mu\text{-}Cp)RuCp^*]^+$, where the unsubstituted cyclopentadienyl ring functions as the ligating bridge. The X-ray structure of the $CF_3SO_3 \cdot THF$ salt has been solved [299]. A report describing the synthesis, characterization and XRD structure of hydroxyruthenocene has appeared [300]. Multiple desilylation of (trimethylsilyl)cyclopentadiene, bis(trimethylsilyl)cyclopentadiene and tris(trimethylsilyl)cyclopentadiene by $RuCl_3 \cdot xH_2O$ has been reported to give ruthenocene with high yields [301]. The decamercuration of ruthenocene using mercuric acetate proceeds with an 88% yield. The (acetoxymercurio)ruthenocene complex was characterized by NMR spectroscopy and X-ray crystallography. Halogenation reactions give good yields of the decahaloruthenocenes (X ≡ Cl, Br or I) [302]. Lithioruthenocene and 1,1′-dilithioruthenocene react with DMF to give the respective aldehydes. Lithiation selectivity studies have been reported [303]. Zinc reduction of $RuCl_3 \cdot 3H_2O$ in the presence of 5,5-dimethylcyclohexadiene yields bis(6,6-dimethylcyclohexadienyl)ruthenium. Similar reactions were conducted with polymeric $[Cp^*RuCl_2]_n$ and related dienes. The X-ray crystal structure of bis(η^5-2,4-dimethylpentadienyl)ruthenium has been determined [304] (Fig. 15).

The oxidative electrochemistry of the hydride complexes $CpRu(PR_3)_2H$ (where $(PR_3)_2 \equiv 2PPh_3$, dppm, dppe or dppp) has been explored. Each complex undergoes a one-electron oxidation, the reversibility of which has been discussed. Chemical oxidation in MeCN gives both $[CpRu(PR_3)_2(MeCN)]^+$ and $[CpRu(PR_3)_2H_2]^+$, which is indicative of proton transfer from $[CpRu(PR_3)_2H]^{\cdot +}$ to $CpRu(PR_3)_2H$.



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The mechanism for this reaction has been established by derivative cyclic voltammetry. Included in Ref. [305] is the X-ray structure of $\mathrm{CpRu(PPh_3)_2H}$. ^{1}H NMR data from the reaction of Cp*RuLX (where $\mathrm{L \equiv P^iPr_2Ph}$; $\mathrm{X \equiv Br}$, I, $\mathrm{OSiPh_3}$, NHPh or $\mathrm{OCH_2CF_3}$) with H_2 and silanes have been presented and mechanistic schemes for the oxidation reactions discussed [306]. The oxidation chemistry of the trihydride complex $\mathrm{Cp^*Ru(PPh_3)H_3}$ has been explored as part of an effort to generate a molecular hydrogen complex [307].

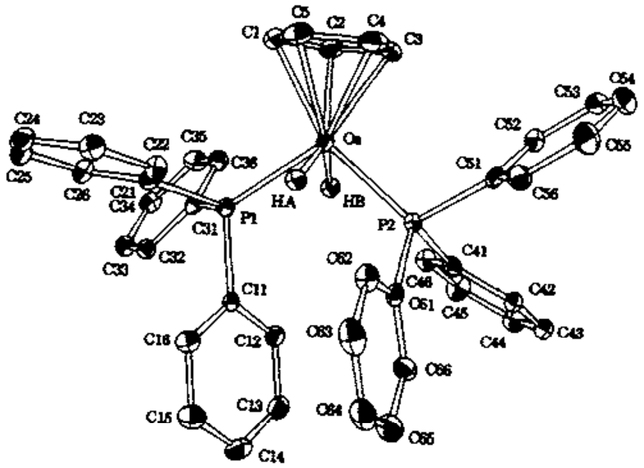
The trimethylsilylmethyl complex $\mathrm{CpRu(CO)_2CH_2SiMe_3}$ has been prepared from $\mathrm{CpRu(CO)_2Cl}$ and $\mathrm{ClMgCH_2SiMe_3}$, and an XRD study has confirmed the molecular structure of this complex [308]. The construction of cyclopentadienylruthenium-containing dendrimers has been described [309]. The reactivity of the Lewis acid complex "$\mathrm{CpRu(CO)(PPh_3)^+}$" towards a wide variety of donors has been investigated. The X-ray structure of $\mathrm{[CpRu(CO)(PPh_3)(EtOH)]^+}$ has been presented [310]. The cyclopentadienyl complexes $\mathrm{CpRu(CO)_2\{(CH_2)_nX\}}$ (where $n=3$, $\mathrm{X \equiv Cl}$, Br or I; $n=4$, 5, $X \equiv \mathrm{Br}$ or I) have been synthesized and characterized in solution by IR and NMR spectroscopies, and by mass spectrometry [311]. Irradiation of $\mathrm{[Cp^*Ru(CO)_2]_2}$ or $\mathrm{Cp^*Ru(CO)_2Me}$ in the presence of azobenzene or 4,4′-dimethylazobenzene yields the orthometallated complexes Cp*Ru(CO){(phenylazo)phenyl} and Cp*Ru(CO){(4,4′-dimethyl)(phenylazo)phenyl} respectively [312].

The MeCN-substituted complex $\mathrm{[CpRu(dppf)(MeCN)]^+}$, which was prepared from CpRu(dppf)Cl, MeCN and $\mathrm{NH_4PF_6}$, exhibits no bonding interaction between the ruthenium and iron centers. The use of CpRu(dppf)Cl in the synthesis of vinylidene and acetylide complexes has been reported [313]. Treatment of $[Cp^*Ru(MeCN)_3]^+$ with indene and fluorene yields the corresponding mixed-polyene complexes $[Cp^*Ru(indene)]^+$ and $[Cp^*Ru(fluorene)]^+$ respectively. Both of these products react with NaH to give stable zwitterionic complexes [314]. Photodimerization of $[CpRu(\eta^6$-dibenzo-*p*-quinodimethane$]^+$ has been reported to furnish the ruthenium adduct of the intramolecular photoisomer of [2.2](9,10)anthracenophene [315]. The reaction of $Cp^*RuCl(\eta^4$-butadiene) with excess 1,5-hexadiene and AgOTf gives a 2-(3′-butenyl)-1,5-hexadiene complex of ruthenium, as a result of regiospecific C(4) homologation at the internal carbon atom of the 1,5-hexadiene. The observed C—C bond coupling has been discussed with respect to codimerization and oligomerization reactions exhibited by this complex [316]. The X-ray structure of the 2:1 inclusion complex formed from $[CpRu(\eta^6\text{-}C_6H_6)][PF_6]$ and α-cyclodextrin has been solved [317]. The coordination of "Cp^*Ru^+" to dibenzo-*p*-quinodimethane ligand systems has been studied [318]. The electrophilic fragment "Cp^*Ru^+" has been allowed to react with unsaturated acyclic hydrocarbons. Examples of catalytic carbon–carbon bond activation have been discussed [319]. A paper describing the ion-pairing effects in the photochemistry of $[CpOs(\eta^6\text{-}C_6H_6)]^+$ has appeared. These studies have allowed for the isolation of the solvated complex $[CpOs(MeCN)_3]^+$ with a high yield [320]. Model hydrodesulfurization studies using cyclopentadienylruthenium complexes have been discussed. Treatment of $CpRu(PMe_3)_2Cl$ with 2-benzothienyllithium gives the corresponding σ-bonded aryl complex $CpRu(PMe_3)_2$(2-benzo[*b*]thiophene), which when treated with acid rearranges to the S-bound $[CpRu(PMe_3)_2$(2-benzo[*b*]thiophene)$]^+$ [321]. Equilibrium and kinetic studies on S-coordinated thiophenes in $[CpRu(CO)_2(\eta^1$-S-thiophenes$)]^+$ and $[CpRu(CO)(PPh_3)(\eta^1$-S-thiophenes$)]^+$ have been reported [322]. The thermolysis of $(MeCp)Ru(PPh_3)_2(EH)$ (where $E \equiv S$ or Se) affords the cubane clusters $(MeCp)_4Ru_4S_4$. When $E \equiv S$, the coproducts have been shown to be PPh_3 and H_2. An alternative synthesis for the tellurium cluster $(MeCp)_4Ru_4Te_4$ has been presented. The cyclic voltammetry studies on these cubane clusters are described, and a discussion on the mobility of the Ru—Ru bonds in the mixed-valence Ru^{IV}–Ru^{III} clusters has been given in Ref. [323]. The mercaptan complexes $[CpRu(PPh_3)_2(RSH)]^+$ (where R ≡ benzyl or phenethyl) have been prepared and characterized as model substrate–catalyst systems for hydrodesulfurization processes. The solid state structure of $[CpRu(PPh_3)_2(PhCH_2CH_2SH)]^+$ has been determined crystallographically [324].

The complexes [CpRu(MeCN)(2,4-cyclopentadien-1-one)$]^+$ and [CpRu(2,4-cyclopentadien-1-one)$]_2^{2+}$ have been synthesized and shown to function as precursors to derivatives of ring-attacked polyenes. The X-ray structure of both complexes have been solved [325] η^1-Iodoalkane complexes of the form $[CpRu(CO)(PPh_3)(\eta^1\text{-IR})]^+$ have been prepared and examined for their reactivity with fluoride ion sources. Fluoride ion reacts with the η^1-iodoalkanes to afford the iodo complex $CpRu(CO)(PPh_3)I$ as the major product [326]. The enthalpies of reaction of Cp^*Ru(1,5-COD)Cl with monodentate phosphine and arsine ligands have been measured by anaerobic solution calorimetry. The stability ordering of the resulting Cp^*RuL_2Cl products is $AsEt_3 < PPh_3 < PEt_3 < PPh_2Me <$

$P(OPh)_3 < PPhMe_2 < PMe_3 < P(OMe)_3$. The factors influencing the Ru−L bond disruption enthalpies have been discussed [327]. Ruthenium butatrienylidene complexes have been synthesized from $CpRu(PPh_3)_2(C{\equiv}CCOCHMe_2)$ and trifluoroacetic anhydride. The X-ray crystal structures of $CpRu(PPh_3)_2\{{=}CC(OCOCF_3)CMe_2\}$ and $[CpRu(PPh_3)_2\{{=}C(COCF_3)C(OCOCF_3)\}][H(CF_3CO_2)_2]$ confirm the identity of the products. Included in Ref. [328] are NMR data and a working mechanism related to product formation. Treatment of the methylallyl complex $CpRu(PPh_3)(\eta^3\text{-}2\text{-}MeC_3H_4)$ with acetic acid gives the η^2-acetate $CpRu(PPh_3)(\eta^2\text{-}OAc)$, which upon exposure to CO gives $CpRu(PPh_3)(CO)(\eta^1\text{-}OAc)$. Methyl propiolate reacts with the η^2-acetate complex to give the cyclic vinyl ester $Cp\overline{Ru(PPh_3)C\{{=}CHCO_2MeOC(Me)O}\}$ instead of the expected vinylidene complex. Variable-temperature NMR measurements reveal that rapid *E*–*Z* isomerization at the exocyclic alkene occurs in solution. An X-ray structure confirms the nature of the metallocycle product [329]. A mechanistic study on cyclopentadienylruthenium-mediated cycloadditions between conjugated dienes and acetylene is reported. This study employs complexes of the form (Cp or Cp*)$RuCl(\eta^4$-diene), which were activated toward acetylene by treatment with AgOTf [330]. The reaction of the electrophilic "Cp^*Ru^+" fragment, which is generated by protonation of $[Cp^*Ru(OMe)]_2$, with oestradiol and oestrone gives the corresponding mixed-sandwich complexes $[Cp^*Ru(\eta^6\text{-arylsteroid})]^+$. Selective aromatization of the A ring of steroid substrates by C−O, C−H and C−C bond activation has been described [331]. The enthalpies of protonation of (Cp or Cp*)$M(PR'_3)X$ (where M ≡ Ru, Os; PR_3,PR'_3 ≡ various phosphines; X ≡ H, Cl, Br or I) have been measured by titration calorimetry. The ligand and metal effects on the ΔH_{HM} values are discussed, and the linear correlation between the basicities (ΔH_{HM}) of the $CpOs(PR_3)_2Br$ complexes and the basicities (ΔH_{HP}) of the ancillary PR_3 ligands presented. The molecular structure of trans-$[CpOs(PPh_3)_2H_2]^+$ has been determined by XRD analysis [332] (Fig. 16).

Allylic C−H bond activation in $CpRu(\eta^3\text{-}C_3H_5)Br_2$ has been reported to give new cationic bis(η^3-allyl)ruthenium(IV) complexes. Treatment of $CpRu(\eta^3\text{-}C_3H_5)Br_2$ with AgOTf in the presence of propene gives an isomeric mixture of $[CpRu(\eta^3\text{-}C_3H_5)_2]^+$, where the allyl ligands exhibit exo–endo and endo–endo configurations [333]. Carbene addition to the coordinated sulfur dioxide in $[Cp^*RuL_2(\eta^1\text{-}SO_2)]^+$ (where L_2 ≡ dppm or $2PMe_3$) yields the η^2(C,S)-sulfene complexes $[CpRuL_2(\eta^2\text{-}CHR{=}SO_2)]^+$ (where R ≡ H or Me). The coordination of the sulfene ligand has been confirmed by an XRD study on the $CH_2{-}SO_2$-substituted complex. The reactivity of the sulfene ligand has been examined [334]. The reaction of 1-alkyne-1-thiolates $R{-}C{\equiv}CSLi$ (where R ≡ $SiMe_3$ or ferrocene) with $CpRu(PPh_3)_2Cl$ has been shown to give $CpRu(PPh_3)_2(S{-}C{\equiv}CR)$. Product characterization by IR and NMR spectroscopies is included [335]. The synthesis of ethynyl-substituted ruthenium complexes and their use as precursors in the synthesis of allenylidene and cumulenylidene complexes are reported. The initial ethynyl complexes are prepared from $[CpRu(PPh_3)_2(THF)]^+$ and lithium acetylides. X-ray structures of the two forms of $[CpRu(PPh_3)_2]_2(\mu\text{-}C_4)$ and $CpRu(PPh_3)_2\{C{\equiv}(O)Me\}$ are included in Ref. [336]. The complexes



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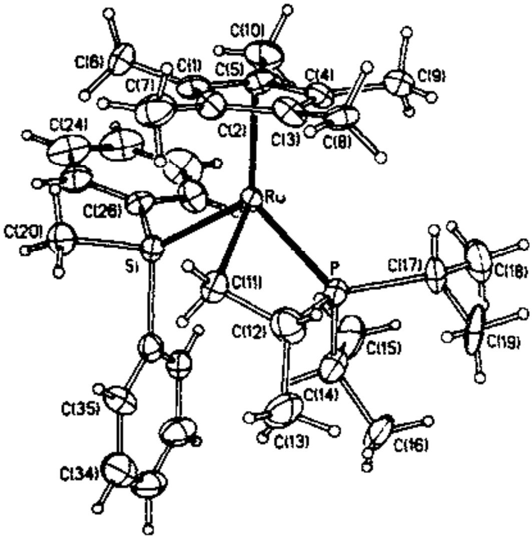
$Cp^*Ru(DMSO)_2Cl$, $Cp^*Ru(TMEDA)Cl$, and $Cp^*Ru(TMEDA)Br$ have been prepared from $[Cp^*RuCl]_4$. The X-ray structures of the two chloro-substituted complexes have been presented. NMR studies reveal that halide loss is facile in the TMEDA complexes, and a process involving the 16-electron species $[Cp^*Ru(TMEDA)]^+$ has been discussed [337]. Ruthenium complexes containing diphosphacyclopentadienyl and triphosphacyclopentadienyl rings have been synthesized and characterized in solution by IR and NMR spectroscopies [338]. The synthesis of several ruthenium and osmium cyclopentadienyl complexes containing ancillary nitrosyl and nitrile ligands from (Cp, MeCp, Cp*)$M(PPh_3)_2CN$ have been presented. Cyclic voltammetry data indicate the presence of an accessible $M^{+/2+}$ redox couple in all the new complexes [339]. Irreversible binding of dioxygen to $[Cp^*Ru(dppe)]^+$ yields the side-on bonded peroxide $[Cp^*Ru(dppe)(\eta^2\text{-}O_2]^+$, as shown by XRD analysis. The coordination of H_2, Cl_2, and NO has also been discussed [340]. The synthesis and XRD structure of the stable η^5-germacyclopentadienyl complex $Cp^*Ru\{\eta^5\text{-}C_4Me_4GeSi(SiMe_3)_3\}$ have been presented [341]. A reinterpretation of the bonding in the X-ray structure of Cp*Ru(acac) has been published [342]. New ruthenium–silene complexes of the form $Cp^*Ru(PR_3)H(\eta^2\text{-}CH_2{=}SiR'_2)$ (where $R \equiv {}^iPr$, $R' \equiv Me$; $R \equiv$ cyclohexyl, $R' \equiv Me$; $R \equiv {}^iPr$, $R' \equiv Ph$; $R \equiv$ cyclohexyl, $R' \equiv Ph$) have been prepared from $Cp^*Ru(PR_3)Cl$ and $ClMgCh_2SiHR'_2$. $Cp^*Ru(P^iPr_3)H(\eta^2\text{-}CH_2{=}SiPh_2)$, whose X-ray structure has been determined, has been shown to decompose thermally in solution to give the cyclometallated complex $Cp^*\overline{Ru\{^iPr_2P(CMeH)CH_2}\}(H)(SiMePh_2)$ (Fig. 17), which exists as a diastereomeric mixture. Kinetic data on the metallocycle reaction indicate that the rate-determining step involves silene rotation, whereby the silene carbon is placed near the migrating hydride ligand [343].

The synthesis of the water-soluble half-sandwich complex $[Ru(\eta^6\text{-}MeC_6H_4{}^iPr\text{-}p)(H_2O)\{(S)\text{-}(\alpha\text{-methylbenzyl})\text{salicylaldimine}\}]^+$ is reported. XRD analysis has con-



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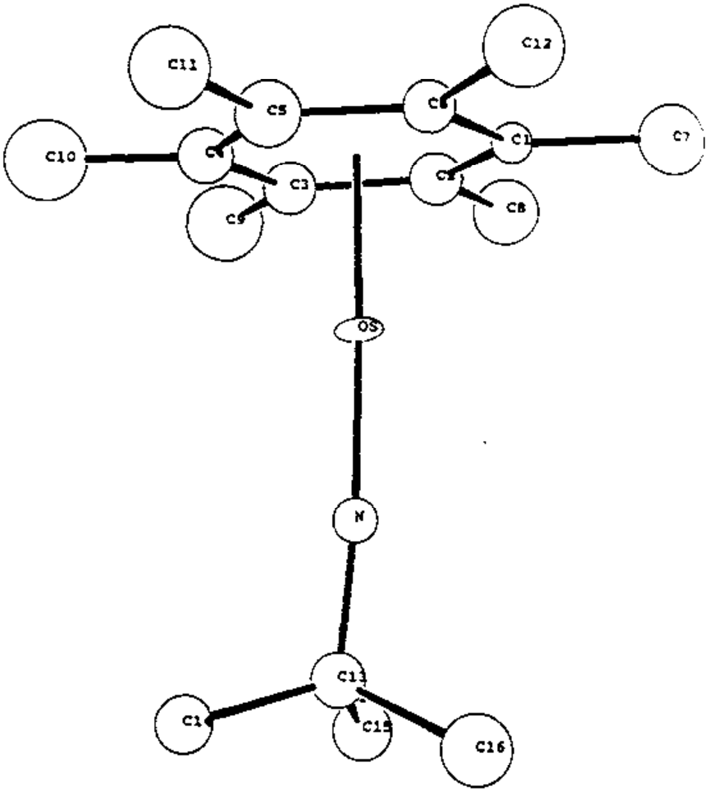
firmed the molecular structure of this complex, which exists as a 1:1 mixture of diastereomers in the unit cell. Replacement of the H_2O ligand by a variety of ligands has been discussed [344]. A study on the reactivity of β-keto phosphines with $[Ru(\eta^6\text{-arene})Cl_2]_2$ has been published. Included in Ref. [345] are the X-ray crystal structures of $[(p\text{-cymene})\,Ru\{\alpha^3\text{-}CH{=}C(Ph)CH(COBPPh_2)C(^tBu){=}O\}]^+$, $[(\text{mesitylene})\,Ru\{\alpha^3\text{-}CH{=}C(Ph)C(Me)(PPh_2)C(Et){=}O\}]^+$ and $[(\text{mesitylene})Ru\{\eta^3\text{-}CH(PPh_2)CPh{=}C(H)C(^tBu){=}O]^+$. Treatment of ruthenium(III) chloride with the non-conjugated tetraene 1,4,5,8,9,10-hexahydroanthracene affords the η^6-arene complex $Ru(\eta^6\text{-1,4,9,10-tetrahydroanthracene})\,Cl_2(DMSO)$, which results from the aromatization of one of the terminal arene rings. The X-ray structure has been presented, and reactions involving DMSO displacement have been described. The ^1H and ^{13}C NMR spectral data have been discussed with respect to the observed ring current effects [346]. Carbene-type amidoosmium complexes have been prepared and characterized. Primary amines react with $(Mes)Os(P^iPr_3)Cl_2$ to give ultimately the amidoosmium(II) complexes $[(Mes)Os(-NHR)(P^iPr_3)]^+$. The thermolysis reactivity and conversion to aldimino(hydrido)osmium complexes have been presented [347]. Chiral half-sandwich compounds of (arene)ruthenium(III) with ancillary α-amino acids have been synthesized and spectroscopically characterized. The molecular structure of one of the products has been solved by X-ray crystallography [348]. Half-sandwich osmium complexes with oxime, imines and azavinylidene ligands have been synthesized by using either $(\eta^6\text{-}C_6H_6)OsHI(PMe^tBu_2)$ or $(\eta^6\text{-arene})Os(PR_3)X_2$ as a starting material. The reactivity of the ancillary nitrogen ligands has been explored, and the X-ray crystal structure of $[(\eta^6\text{-}C_6H_6)Os({=}N{=}CPh_2)(PMe^tBu_2)]^+$, which reveals an allene-like arrangement of ligands about the

Os=N=C moiety, determined [349]. Nucleophilic additions to [(η^6-arene)(η^6-[2.2]paracyclophane)ruthenium]$^{2+}$ (where arene=benzene, *p*-cymene, 1,2,4,5-Me$_4$benzene, pentamethylbenzene or hexamethylbenzene) have been reported to yield highly fluxional agostic cyclohexenyl derivatives. Hydride attack does not occur at the paracyclophane ring, suggesting that these reactions are not charge controlled. Mechanistic studies, including deuterium label studies, have been carried out. The behavior of the agostic complexes has been examined by using variable-temperature ^{1}H NMR spectroscopy [350]. The reaction between [M(arene)Cl$_2$]$_2$ (where M=Ru or Os) and CH$_2$=C(CH$_2$SnMe$_3$)$_2$ gives the allylmetal complexes MCl{CH$_2$C(CH$_2$SnMe$_3$)CH$_2$}(arene) and the sandwich complexes M(trimethylenemethane)(arene) as the major products. The identity of these compounds has been established by NMR measurements and XRD analyses in the case of (η^6-benzene)RuCl{CH$_2$C(CH$_2$SnMe$_3$)CH$_2$}, (η^6-benzene)Ru(trimethylene-methane) and Ru(CO)$_3$(trimethylenemethane). This latter product was isolated from the reaction employing [Ru(CO)$_3$Cl$_2$]$_2$ as a starting material [351]. Olefin–ruthenium complexes of the form (η^6-C$_6$Me$_6$)Ru(CO)(CH$_2$=CHR) (where R=H, Me or Et) have been isolated from the reaction between (η^6-C$_6$Me$_6$)Ru(CO)Cl$_2$ and RCH$_2$CH$_2$MgI [352]. (η^6-Arene) (η^4-diene)ruthenium complexes have been synthesized from (η^6-arene)RuCl$_2$(py) and butenediylmagnesium compounds. The XRD structure of (η^6-C$_6$H$_6$)Ru(η^4-butadiene) has been solved [353]. The synthesis, X-ray structure and redox properties of the bis(arene) complex [(*p*-cymene)$_2$Ru]$^{2+}$ have been described [354]. The low oxidation state osmium–imido complexes (η^6-*p*-cymene)OsN–^{t}Bu and (η^6-C$_6$Me$_6$)OsN-^{t}Bu (Fig. 18) have been prepared from (η^6-arene)OsCl$_2$ and four equivalents of LiNH-^{t}Bu. X-ray crystallographic analysis of the hexamethylbenzene complex and ^{15}N NMR data support the presence of a nearly linear imido moiety. Imide–amine exchange studies reveal a large primary isotope effect ($k_H/k_D=5.7$) when D$_2$N(2,6-Me$_2$C$_6$H$_3$) is used as the entering amine. A mechanism involving a bis(amide) intermediate has been presented, and imido cycloaddition reactivity with ^{t}BuNCO and RN$_3$ has been described [355].

Oximatoruthenium(II) complexes [(η^6-C$_6$H$_6$)Ru(η^2-ON=CRR′)(P^{i}Pr$_3$)]$^+$ have been prepared and examined as substrates in nucleophilic addition reactions. Ligand exchange of the oximato moiety with the imine HN=CPh$_2$ yields the corresponding azavinylidene complex [(η^6-C$_6$H$_6$)Ru(=N=CPh$_2$) (P^{i}Pr$_3$)]$^+$ [356]. The synthesis of chiral arene-substituted ruthenium(II) complexes with an ancillary chiraphos, diop or BINAP ligand has been reported [357]. Adenine reacts with [(η^6-C$_6$H$_6$)RuCl$_2$]$_2$ to give [[{(η^6-C$_6$H$_6$)RuCl(μ-adenine)}$_4$]$^{4+}$. The same reaction with 3-aminopyrazole has been examined [358]. The hydride reduction reactivity of [Ru(η^6-C$_6$Me$_6$)(η^6-paracyclophane)]$^{2+}$ has been explored and the resulting ring-attacked diene products characterized by NMR spectroscopy. The presence of a highly fluxional complex with a single endo agostic hydrogen atom is shown to be rapidly exchanging with the terminal olefin carbon of the cyclohexadiene moiety [359]. α-Aminocarboxylates react with (η^6-C$_6$H$_6$)Os(PR$_3$)I$_2$ to furnish the chelate complexes of the form $[(\eta^6\text{-C}_6\text{H}_6)\overline{\text{Os}\{\text{OC(O)CH(R')N}}\text{H}_2\}(\text{PR}_3)]^+$. All products were spectroscopically characterized by NMR and in certain cases by X-ray crystallography [360]. NMR (^{13}C and ^{31}P) data on RuCl$_2$(*p*-cymene){CH$_2$(PPh$_2$)P(S)Ph$_2$}



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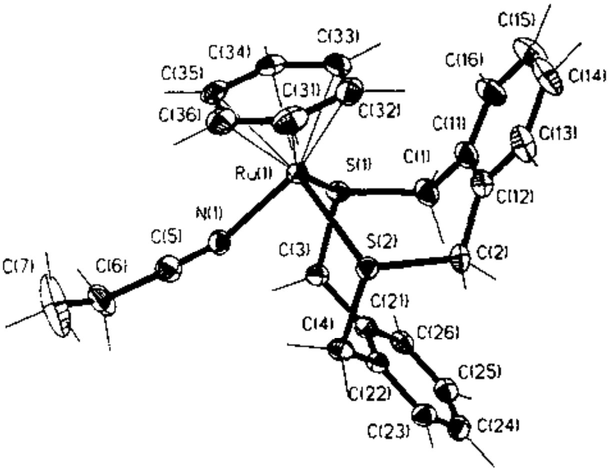
have been discussed and the solid state structure determined by X-ray crystallography, which revealed the presence of a monodentate P-bonded ligand [361]. Polyene ring reactivity has been investigated in the reactions of hydroxide with $[(\eta^6\text{-arene})Ru(\eta^5\text{-}C_4R_4S)]^{2+}$. It has been shown that hydroxide attacks the sulfur atom to give $[(\eta^6\text{-arene})Ru(\eta^4\text{-}C_4R_4S\text{-}1\text{-}OH)]^+$, which has been characterized by ^1H NMR spectroscopy. This complex rearranges to the corresponding 2-hydroxythiophene-yl derivatives $[(\eta^6\text{-arene})Ru(\eta^4\text{-}C_4R_4S\text{-}2\text{-}OH)]^+$. Related NMR reactivity studies and the synthesis of vinyl–thiolate complexes have been presented [362]. The mechanism for proton-induced C—S bond cleavage in $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S)$ has been established by NMR spectroscopy measurements in both fluid solution and the solid state [363]. Chloride ion abstraction from $[(\eta^6\text{-benzene})RuCl_2]_2$ in MeCN solution by $TlPF_6$, NH_4PF_6, $LiBF_4$, or $KAsF_6$ yields the bis-solvent complex $[(\eta^6\text{-benzene})Ru(MeCN)_2Cl]^+$. Both MeCN ligands may be displaced by monodentate and bidentate ligands. Disproportionation of $[(\eta^6\text{-benzene})Ru(MeCN)_2Cl]^+$ occurs in $MeNO_2$ to give $[\{(\eta^6\text{-benzene})Ru\}_2(\eta\text{-}Cl)_3]^+$ [364]. The preparation of new carbyne and carbene osmium complexes has been reported from η^6-arene $Os(NH_3)_5$



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and $Os(NH_3)_4$ derivatives. The X-ray structure of $[Os(NH_3)_5(\equiv CPh)]^{3+}$, which was prepared from $[Os(NH_3)_5]^{3+}$ and benzaldehyde dimethyl acetal under acidic conditions, exhibits a linear carbyne–osmium linkage [365]. Several (phosphinoalkyl)silanol complexes derived from $[(\eta^6\text{-arene})RuCl_2]_2$ and $CpRu(PPh_3)_2Cl$ have been described [366]. A report on the synthesis and NMR characterization of (π-benzene)ruthenium complexes of 2,11-dithia-[3.3]orthocyclophane and 2,11-diselena[3.3]orthocyclophane has appeared. The title cyclophanes were prepared by using the tris(acetone) complex $[(\eta^6\text{-benzene})Ru(acetone)_3]^{2+}$, and the X-ray structure of the 2,11-dithia[3.3]orthocyclophane complex (Fig. 19) has been discussed [367].

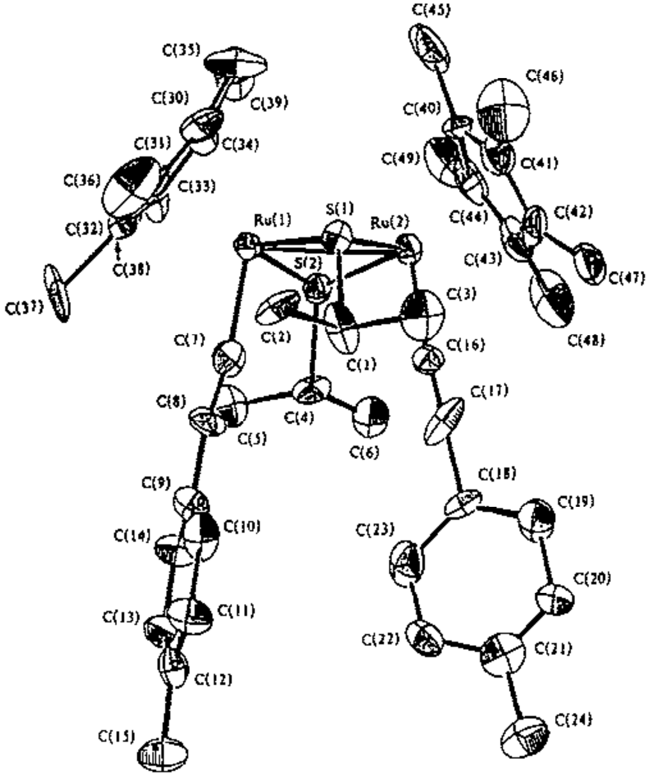
3. Dinuclear complexes

3.1. Homodinuclear complexes

The thermolysis reactivity of the diphosphazane-bridged complexes $Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$, $Ru_2H_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ and $Ru_2\{\mu\text{-}OC(O)\}(CO)_4\}\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ (where $R \equiv Me$ or ^iPr) has been explored. All of these dimers afford the unsaturated complexes $Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ as the major reaction product, which have been established by XRD analyses. Treatment of these unsaturated dimers with a variety of nucleophiles and electrophiles gives coordinatively saturated complexes, all of which are described [368]. The $AgSbF_6$ oxidation of $Ru_2\{(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ in ROH gives the corresponding solvent complexes $[Ru_2(CO)_5(R'OH)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2][SbF_6]_2$, whereas the aquo complexes are stable, the alcohol complexes decompose to give the alkoxycarbonyl-bridged species $[\mathrm{Ru_2(\mu\text{-}\eta^2\text{-}OC(OR')\}(CO)_4\{\mu\text{-}(RO)_2PN(Et)R(OR)_2\}_2]^+}$. The mechanisms associated with these reactions and pertinent X-ray crystal structures have been presented [369]. Ethyne reacts with $\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}$ in toluene at 80°C and with $\mathrm{Ru_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}$ in toluene at room temperature to give the ethenediyl-bridged dimer $\mathrm{Ru_2(\mu\text{-}\sigma^2\text{-}HC{=}CH)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}$ when $\mathrm{R \equiv Me}$ and the vinylidene-bridged complex $\mathrm{Ru_2(\mu\text{-}\sigma^2\text{-}C{=}CH_2)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2}$ when $\mathrm{R \equiv {}^iPr}$. When terminal alkynes were examined, product mixtures of these isomers were observed [370]. Optical excitation in $\mathrm{Ru_2(CO)_4\{\mu\text{-}({}^iPrO)_2PN(Et)P(O^iPr)_2\}_2}$ leads to dealkylation of one of the bridging phosphite-type ligands and formation of $\mathrm{Ru_2H(CO)_5\{\mu\text{-}({}^iPrO)_2PN\text{-}(Et)P(O^iPr)_2\}\{\mu\text{-}({}^iPrO)P(O)N(Et)P(O^iPr)_2\}}$. The X-ray crystal structure of this product has been solved, and a mechanism involving photolabilization of an isopropyl radical as the first step in this Arbuzov-type reaction presented [371].

The synthesis of the thiolate-bridged complexes $\mathrm{[Ru(\mu\text{-}SR)(S_2CNMe_2)\text{-}(CO)(PPh_3]_2}$ (where $\mathrm{R \equiv Ph}$ or Et) from $\mathrm{RuH(S_2CNMe_2)(CO)(PPh_3]_2}$ and excess thiol has been discussed. Electrochemical data reveal that these dithiocarbamate complexes undergo multiple electron oxidation. The X-ray crystal structures of $\mathrm{[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2^{0,2+}}$ have been presented, and the formation of an Ru—Ru bond in the oxidized dimer with respect to other reactions that exhibit one-step two-electron reactions has been discussed [372]. The preparation and oxidative addition of alkyl halides at the diruthenium center in the thiolate-bridged complexes $\mathrm{[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]}$ (where $\mathrm{R \equiv {}^iPr}$, $\mathrm{{}^tBu}$ or $\mathrm{2,6\text{-}Me_2C_6H_3}$) have been described [373]. The insertion of diphenylacetylene into the carbon–sulfur bond of PhNCS at a diruthenium center has been documented. Treatment of $\mathrm{Cp_2Ru_2(CO)(\mu\text{-}CO)(\{\mu\text{-}C(O)C(Ph){-}C(PH)\}}$ with PhNCS yields $\mathrm{Cp_2Ru_2(CO)(\mu\text{-}CO)\{\text{-}SC(Ph){=}C(Ph)C({=}NPh)\}}$, whose molecular structure was established by X-ray crystallography [374]. Reaction of the coordinatively unsaturated complex $\mathrm{[Cp^*Ru(\mu_2\text{-}S^iPr)_2RuCp^*]}$ with (p-tolyl)C≡CH yields novel ruthenacyclopentadienyl complexes, as confirmed by NMR and XRD analyses [375]. The heterocyclic thioamides 2-mercapto-1-methylimidazole and 4,5-diphenyl-2-mercaptoimidazole have been allowed to react with $[(p\text{-cymene})\mathrm{RuCl_2}]_2$. The resulting heterocyclic-bridged ruthenium dimers have been crystallographically characterized [376]. The thiolate-bridged dimers $\mathrm{[Cp^*Ru(\mu\text{-}SR)]_2}$ have been isolated from the reaction between RSH and $\mathrm{[Cp^*Ru(\mu\text{-}OMe)]_2}$. Carbonylation reactivity and oxidation migration of a $\mathrm{C_6F_6}$ group from sulfur to ruthenium have been reported [377]. Terminal alkynes react with the paramagnetic complex $\mathrm{Cp^*Ru(\mu_2\text{-}S^iPr)_3RuCp^*}$ to give the diamagnetic diacetylide complexes $\mathrm{Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}S^iPr)_2Ru(C{\equiv}CR)Cp^*}$. Mixed diacetylide complexes have been described by using the monoacetylide complex $\mathrm{Cp^*Ru(C{\equiv}C^tBu)(\mu_2\text{-}S^iPr)_2Ru(S^iPr)Cp^*}$ as a starting material. Acetylide coupling reactions, which are accompanied by aromatic C—H bond activation, and the protonation chemistry of various complexes have been outlined. The solid state structures have been solved by XRD analysis [378] (Fig. 20).

The interpretation of the IR spectra of diosmium oxo(esters) has been published. Isotopic labeling studies (^{18}O) have allowed for the assignment of the Os=O and



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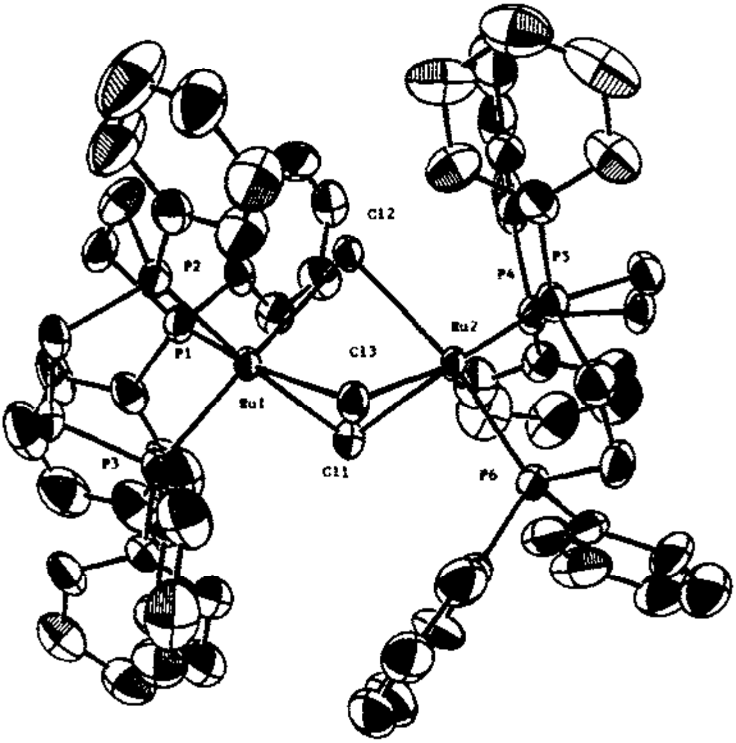
Os—O (terminal and bridge) stretches [379]. The synthesis and X-ray structure of $Os_2(2\text{-phenylbenzoate})_4Cl_2$ have been published. Magnetic susceptibility data support the existence of strong spin–orbit coupling which prevents an unequivocal assignment of the ground state [380]. An electrochemical study of the oxo-bridged complex $[Ru_2(\mu\text{-O})(\mu\text{-OAc})_2(N\text{-MeIm})_6]^{2+}$ provides evidence for a one-step two-electron-transfer for the $Ru_2^{III} \rightleftarrows Ru_2^{II}$ couple [381]. Electrochemical and aquation kinetic data on $[(\mu\text{-O})Ru(NH_3)_4(HCO_2)]_2^{3+}$, a component of "ruthenium red", have been reported. The structure of the oxo-bridged dimer has been determined by X-ray crystallography [382]. The dimeric complexes $[Ru(RCO_2)(CO)_2L]_2$ have been employed as catalysts for RCO_2H addition reactions to alkynes [383]. An X-ray study on the carboxylate-bridged complexes $Ru_2(O_2CR)_2(CO)_4L_2$ has appeared [384]. The hydrolysis products derived from $[Cp^*Ru(OMe)]_2$ and $[(\eta^5\text{-}C_5Me_4Et)Ru(OMe)]_2$ have been isolated and characterized. Both reagents give the corresponding tetrameric hydroxide as the major product [385]. The ruthenium(II) dimer $[Br_6(TMSO)_2Ru_2(\mu_2\text{-TMSO})_2(\mu_3\text{-TMSO})_2Li_2(TMSO)_2]$ has been isolated from the reaction between $RuCl_3{\cdot}3H_2O$, LiBr and TMSO. An X-ray structure of this molecule shows both O- and S-bonded TMSO ligands [386]. The use of sulfate and phosphate ligands for the stabilization of the Ru_2^{6+} core is discussed. An improved synthesis of the sulfate complex $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ has been reported together with the first synthesis of $[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]^{4-}$. The ground state of the sulfate complex has been determined to have the unusual $\sigma^2\pi^4\delta\pi^{*2}\delta^*$ configuration [387].

The synthesis and molecular structure of Ru_2(*N*,*N*′-diphenylformamidinate)$_4$($C{\equiv}CPh$)$_2$ have been presented. The cyclic voltammetry and ESR data on the radical anion have been discussed [388]. A report on the synthesis, molecular structure, and electrochemical properties of Ru_2(2,3,4,5,6-pentafluoro-2-anilinopyridinate)$_4$($C{\equiv}CPh$)$_2$ has been published [389]. Reversible CO insertion into the ruthenium-amido bond of $Ru_2(CO)_6\{MeC{=}C(H)CH_2N{-}^iPr\}$ and $Ru_2(CO)_6\{RCC(H)N{-}^tBu\}$ (where $R \equiv {}^iPr$, or benzyl) is promoted by irradiation with UV–visible light under CO. Data have been presented that support a scheme where CO is coordinated to a ruthenium center prior to insertion. The X-ray crystal structures of two of the insertion products have been presented [390]. New ruthenium carbonyls with bridging carboxylates and bipyridine or 1,10-phen ligands have been synthesized and characterized by NMR and XRD analyses [391]. Hydrogenation of the central C—C bond of coordinated α-diimine ligand has been observed in diruthenium complexes. Isotopic labeling results using D_2 have been presented and the intervention of an HD_2 containing diruthenium complex has been discussed [392]. The synthesis and electrochemical properties of the alkoxide-bridged ruthenium(II) dimers $[Ru(bpy)_2(\mu\text{-}OR)_2]^{2+}$ (where $R \equiv Me$ or Et) have appeared. A strong intervalence charge transfer is observed in each complex [393]. Benzamidato and toluamidato complexes of ruthenium and osmium have been prepared [394].

Five new ruthenium(I)–ruthenium(I) carbonyl complexes, two of which contain polyoxoanion ligands, have been synthesized and fully characterized [395]. Oligomerization of alkynes has been examined with the diruthenium complexes $Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$ (where $R \equiv Ph$ or CF_3). This report includes the X-ray structures of $Cp_2Ru_2(CO)\{\mu\text{-}C_4(CF_3)_4\}$ (two isomers) and $Cp_2Ru_2\{\mu\text{-}C_8(CF_3)_2(CO_2Me)_6\}$; the latter structure possesses a C_6 ring with a C_2 tail [396]. Succinimide reacts with $RuHCl(PPh_3)_3$ in refluxing toluene to give the succinimido-bridged complex $Ru_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-succinimide})(PPh_3)_4$, which has been characterized in solution by IR and NMR (^1H and ^{31}P) analyses and in the solid state by XRD analysis [397]. β- and γ-Dehydrogenation of N^iPr_2 is observed in the reaction between LiN^iPr_2 and $[Cp^*Ru(\mu_3\text{-}Cl)]_4$. The product isolated from this reaction is the azaallyl complex $Cp^*_2Ru_2(H)(^iPrNC_3H_5)$ [398]. Reversible C—Si bond cleavage is reported for the methylene–silyl complex $Cp^*_2Ru_2(\mu\text{-}CH_2(\mu\text{-}Cl)(SiMe_3)$. The reactivity and X-ray structure of this complex have been discussed. This is the first example of rapid and reversible C—Si cleavage in a transition metal complex [399]. The use of $^{13}C\{^1H\}$ NOE and $^{187}Os{-}^{13}C$ coupling NMR data to study the fluxional behavior of the σ,π-vinyl complexes $Os_2\{\mu\text{-}CH{=}C(H)Ph\}(\mu\text{-}Br)(CO)_{6-n}(PPh_3)_n$ (where $n = 1,2$) is presented. The X-ray structure of the bis(triphenylphosphine) complex has been given in Ref. [400]. Tetrafluoroethylene reacts with $[Cp^*RuCl]_4$ to produce the dimer complex $[Cp^*RuCl(CF_2{=}CF_2)]_2$, which has been the subject of an XRD study. Dimer-tomonomer cleavage has been observed upon treatment with neutral donor ligands. The observation of low barriers to propeller rotation of the C_2F_4 ligand in these complexes has been discussed with respect to the metallocyclopropane structure [401]. Treatment of $Cp_2Ru_2(CO)_4$ with the isonitrile ligand $CNCH_2Ph$ in the presence of Me_3NO gives $Cp_2Ru_2(CO)_3(CNCH_2Ph)$, which has been alkylated at the nitrogen center using methyl triflate. The alkylation product, $[Cp_2Ru_2(CO)_3\{\mu\text{-}CN(Me)CH_2Ph\}]^+$, has been examined in hydride addition reactions [402]. Reduction of the μ-methylene complex $Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(CO)_2$ with hydrosilanes yields alkanes. Intermediate dinuclear hydrido-methylene and methyl intermediates have been observed, and a plausible Fischer–Tropsch methanation scheme has been presented [403]. Acetylene reacts with the silyl-methylene complex $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)Cl$ to give the first unsubstituted metallabenzene complex $Cp^*_2Ru_2(\eta^2,\eta^5\text{-}C_5H_5)(SiMe_3)$. This novel product has been characterized in solution by NMR spectroscopy and by X-ray crystallography [404]. Spin trapping of the radicals derived from $Cp_2Ru_2(CO)_4$ has been reported [405]. The dinuclear complex $Ru_2(CO)_7\{\mu_2\text{-}C(H)C(Ph)C(H)C(O)Ph\}$ has been isolated from the reaction between $Ru_3(CO)_{12}$ and the phosphorus ylide $Me_3P{=}CHC(O)Ph$. The alkyne insertion chemistry exhibited by this dimer has been outlined [406]. The polydentate phosphine ligands bis{2-(diphenylphosphino)ethyl}phenylphosphine and bis{3-(diphenylphosphino)propyl}phenylphosphine have been studied in reactions with ruthenium complexes. Several dinuclear and mononuclear X-ray crystal structures have been reported [407]. (Fig. 21).

3.2. *Heterodinuclear complexes*

The mixed-metal silylene complex $(CO)_4OsSi(STol\text{-}p)RuCp^*(PMe_3)_2$ has been synthesized from $[Os(CO)_4]^{2-}$ and $[Cp^*Ru(PMe_3)_2(STol\text{-}p)]^{2+}$ with a low yield. XRD analysis reveals the presence of a planar silicon atom, indicative of π bonding to one or more of the substituent groups [408]. Bis(acyl)-bridged rhenium–ruthenium complexes have been synthesized [409]. The heterodinuclear α-diimine complexes $FeRu(CO)_6(C_5H_4N\text{-}2\text{-}CH{=}NR)$ (where $R \equiv {}^iPr$, cyclohexyl or ${}^tBu$) may be obtained from $Ru_2(CO)_4(C_5H_4N\text{-}2\text{-}CH{=}NR)$ and $Fe_2(CO)_9$ [410]. Reaction of $FeRu(CO)_6(C_5H_4N\text{-}2\text{-}CH{=}N{-}{}^iPr)$ with activated alkynes proceeds with C—C bond coupling and C—H bond activation [411]. Heterodinuclear monoazadienyl complexes have been prepared from $Ru(CO)_3Cl\{RC{=}C(H)C(H){=}N{-}{}^iPr\}$ (where $R \equiv Ph$ or Me) and carbonyl metallates. The carbonyl metallates examined include $[Co(CO)_4]^-$, $[CpFe(CO)_2]^-$ and $[Mn(CO)_5]^-$, which give the ruthenaazadienyls $RuCo(CO)_6\{RC{=}C(H)C(H){=}N{-}{}^iPr\}$, $CpFeRu(CO)_4\{RCH{=}C(H)C(H){=}N{-}{}^iPr\}$, and $RuMn(CO)_8\{RC{=}C(H)C(H){=}N{-}{}^iPr\}$ respectively. Solution IR and NMR data and X-ray crystal structures have been presented [412]. Photolysis of $Ru_2(CO)_6\{RC{=}C(H)CH_2N{-}{}^iPr\}$ (where $R \equiv Ph$ or Me) with $Fe_2(CO)_9$ gives the heterodinuclear hydride complex $HFeRu(CO)_5\{RC{=}C(H)C(H){=}N{-}{}^iPr\}$ with a 35% yield. The mechanism associated with this reaction has been examined [413]. The formation of heterotetranuclear chain complexes from $HFeRu(CO)_5\{RC{=}C(H)C(H){=}N{-}{}^iPr\}$ (where $R \equiv Ph$ or Me) has been reported.



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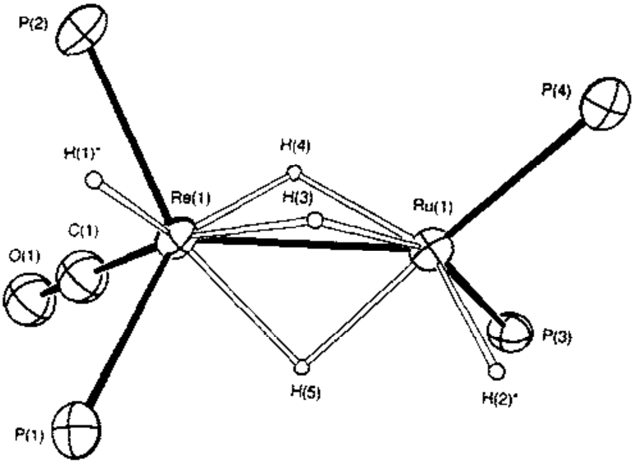
The hydrogenation of styrene and α-methylstyrene using these complexes has been described [414]. The 30-electron complex (CO)$(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ was prepared from $[ReH_6(PPh_3)_2]^-$ and RuHCl(CO)$(PPh_3)_3$ and the solid state structure determined by X-ray crystallography. The position of the terminal hydrides has been established by using the program HYDEX. Ethylene reacts with this unsaturated dimer to give (CO)$(PPh_3)_2Re(\mu\text{-}H)_3Ru$(ethylene)$(PPh_3)_2$ [415] (Fig. 22).

4. Polynuclear complexes

4.1. Trinuclear clusters

4.1.1. Simple and hydrocarbon ligands

The oxo-bridged clusters $[Ru_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^-$ and $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ undergo H_2O substitution by CD_3OD, the kinetics of which have been measured by ^1H NMR spectroscopy. A dissociative mechanism has been proposed and the influence of (metal dπ)–(oxygen pπ) interactions in controlling the rate of H_2O substitution has been discussed [416]. Reaction of ruthenium trichloride



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with carboxylic acids yields the carboxylate cluster $[Ru_3O(O_2CR)_6(H_2O)_3]^{n+}$. The X-ray structures of the acetate and formate complexes ($n=1$) and the acetate complex ($n=2$) have been solved [417]. Water exchange by isonicotinamide in $[Ru_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ has been studied using ^{17}O NMR and UV–visible spectroscopies. The kinetic data support an I_d mechanism for the substitution reaction [418]. The redox reactions of the ruthenium(III, III, III) and ruthenium(III, III, II) clusters $[Ru_3\ (\mu_3\text{-}O)(\mu\text{-}OAc)_6(py)_3]^n$ (where $n=1$ and 0 respectively) have been explored by pulse radiolysis methods [419].

The IR and Raman carbonyl bands in $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ have been assigned by a normal coordinate calculation. The use of an accurate force field from the related cluster $Ru_3(CO)_{12}$ in the above calculation has been described [420]. Reaction of $Os_3H_2(CO)_{10}$ or $M_3(CO)_{10}(MeCN)_2$ (where $M \equiv Ru$ or Os) with cyclohexa-1,3-diene affords the dienyl clusters $M_3H(CO)_9(\mu_3\text{-}\sigma\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_7)$. The molecular structure of the ruthenium cluster has been crystallographically determined [421]. A report describing a more convenient synthesis of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ directly from $Ru_3(CO)_{12}$ has appeared. The same reaction using $Os_3(CO)_{12}$ proceeds to give $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$, whose molecular structure was solved by XRD analysis [422]. The hydrogenation of acenaphthylene by $Ru_3(CO)_{12}$ has been shown to give $(\mu_2\text{:}\eta^1\text{:}\eta^5\text{-}C_{12}H_{10})Ru_3H_2(CO)_7$ from $(\mu_3\text{:}\eta^2\text{:}\eta^3\text{:}\eta^5\text{-}C_{12}H_8)Ru_3(CO)_7$. The isolation and full characterization (solution and X-ray) of these two clusters have been discussed [423]. The results of an ab-initio molecular orbital study on the electronic structure and the rotational barrier of benzene in $Os_3(CO)_9(C_6H_6)$ have been described. Comparisons have been made with other polynuclear benzene and ethylene complexes, as well as mononuclear benzene and ethylene complexes [424].

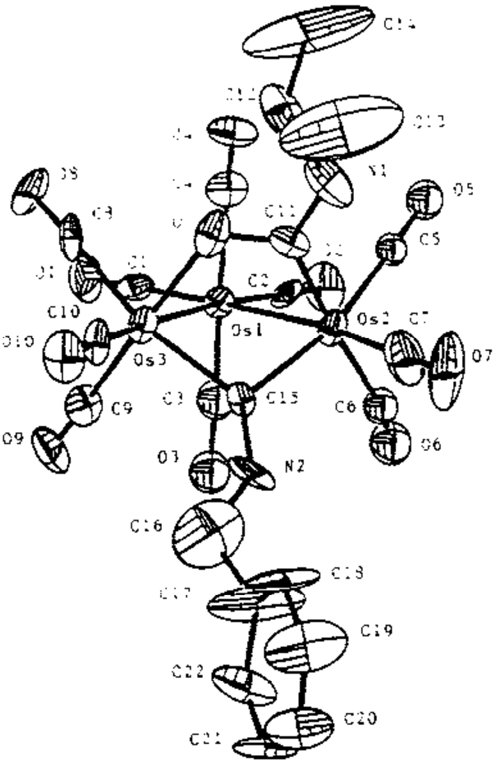
The reversible addition of CO to the electronically unsaturated cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$ has been studied and the kinetic data reported. An energy profile has been constructed and the kinetic data have been contrasted with analogous reactions. H_2 loss from $Os_3(\mu\text{-}H)_2(CO)_{10}$ has also been observed and the kinetic parameters have been presented [425]. Kinetic studies on the reaction of chloride ion on $Ru_3(CO)_{12}$ are presented. The source of the chloride ion is from [PPN] [Cl], and the data indicate that the chloride ion may attack both the carbonyl and the ruthenium centers. No intermediates were observed in these studies [426]. The isolation and X-ray crystallographic characterization of $Ru_3(\mu\text{-}Cl)_2(THF)_2(CO)_8$ have been published [427]. The molecular structures of gaseous RuF_5 and OsF_5 have been examined by gas-phase electron diffraction methods. At 120 °C, the major constituents are trimeric molecules with small amounts of dimeric molecules [428].

The synthesis of large osmium clusters using $Os_3(CO)_{10}(MeCN)_2$ have been described [429]. Reaction of oxygen with $[Os_3(\mu\text{-}H)(CO)_{11}]^-$, followed by treatment with $Os_6(CO)_{18}$, ultimately gives the osmium cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}O_2C)Os_6(CO)_{17}]^-$ [430]. Reaction of $Ru_3(CO)_{12}$ with the thiourea PhNHC(S)-$NEt(CH_2)_2$NHC(S)NHPh to yield $[Ru_3(\mu\text{-}H)(CO)_9]_2\{SC(NPh)N(Et)(CH_2)_2\text{-}NH(PhN)CS\}$ has been presented [431]. The high yield synthesis of $Os_3(CO)_{11}(CNR)$ (where R ≡ Pr, ^{i}Pr, benzyl or Ph) from $Os_3(CO)_{12}$ has been published. The reaction employs phosphine imides as deoxygenation reagents. It is shown that the geometrical and electronic properties of the imide control the rate of the reaction [432]. The synthesis and reactivity of $[Os_3(CO)_{11}]^{2-}$ have been reported. Protonation of the dianion gives the corresponding monohydride $[Os_3H(CO)_{11}]^-$. Cluster expansion reactions using $[Os_3(CO)_{11}]^{2-}$ with $Os_3(CO)_{12}$ have been examined and shown to produce a variety of Os_4, Os_5, and Os_7 clusters. The X-ray structures of $[Os_3H(CO)_{11}]^-$ and $H_2Os_4(CO)_{13}$ have been solved [433]. The reaction between $Ru_3(CO)_{12}$ and $Et_2NC(S)SSC(S)NEt_2$ has been studied [434]. The alkyne-bridged cluster $Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)$ reacts with PhLi to give $[Os_3(CO)_9\{C(O)Ph\}(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)]^-$, which upon methylation with methyl triflate yields the corresponding carbene cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)\{\mu\text{-}C(OMe)Ph\}$. Protonation of this cluster affords $[Os_3(CO)_9(\mu\text{-}\eta^3\text{-}C_3Ph_3)]^+$, whose reactivity has been examined. The X-ray structure of the neutral carbene cluster has been solved [435]. The reactivity of $Ru_3(CO)_{12}$ with the phosphorous ylide $Ph_3P{=}C(CH)_4$ has been investigated, and the resulting triruthenium clusters, which contain $\mu_2\text{-}\eta^5{:}\eta^1\text{-}C_5H_4$ units, fully characterized by XRD analysis and IR and NMR spectroscopies [436]. Asymmetrical thioalkynes have been allowed to react with $Ru_3(CO)_{12}$ [437]. The symmetrical 1,3-diynes RC_2C_2R (where R ≡ Me, Et, Ph, ^{t}Bu or $SiMe_3$) displace the MeCN ligands in $Os_3(CO)_{10}(MeCN)_2$ to give $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}RC_2C_2R)$. The thermal decarbonylation behavior of these clusters has been studied and found to undergo diyne C−C bond cleavage, giving clusters of the form $Os_3(CO)_9(\mu\text{-}\eta\text{-}C_2R)(\mu_3\eta^2\text{-}C_2R)$ [438]. An examination of the isolobal relationship between $Ru(CO)_3$ and BH in the clusters $Ru_3(CO)_9(CH)_2$ and $(BH)_3(CH)_2$ has been reported [439]. An electrochemical study on the reduction of $Ru_3(CO)_{12}$ has appeared. The details of the electrochemical reaction have been discussed, and the electrochemical behavior of the cluster $[Ru_3(CO)_{11}]_2(\mu\text{-}dppa)$ presented. This latter cluster does not show any electrochemically detectable redox communication between the $Ru_3(CO)_{11}$ moieties [440]. The thermolysis reactivity of $M_3(CO)_{11}(MeCN)$ (where M ≡ Ru or Os) and $Ru_4(CO)_{11}(\mu\text{-}H)_4(MeCN)$ with the phosphine ligand 1,4-bis(diphenylphosphino)buta-1,3-diyne has been published. The pyrolysis products have been isolated and characterized by solution and solid state techniques [441].

Protonation of the Os$-$Os bond in $Os_3(CO)_{10}(CNPr)(MeCN)$ by Brønsted acids yields $[Os_3(\mu\text{-H})(CO)_{10}(CNPr)(MeCN)]^+$, which reacts with acetate ion by MeCN substitution to give $Os_3(\mu\text{-H})(CO)_{10}(CNPr)(\eta^1\text{-OAc})$. The mechanistic details of these reactions and the X-ray crystal structures of $Os_3(\mu\text{-H})(CO)_{10}(CNPr)(\eta^1\text{-}O_2CCF_3)$ and $Os_3(\mu\text{-H})(CO)_{10}(CNPr)(\eta^1\text{-}O_2CC{\equiv}CH)$ have been discussed [442]. Data on the electrochemical and chemical oxidation of the clusters $HRu_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^3\text{-XCCRCR}')$ have been published. The radical cations are stabilized by π donors ($X \equiv OR$ or NEt_2) [443]. The interaction of primary amines with the osmium isocyanide clusters $Os_3(CO)_{11}(CNR)$ has been explored and found to yield initially the carboxamido clusters $Os_3(CO)_{10}(\mu_2\text{-CONHR}')(\mu_2\text{-C{=}NHR})$. Further reaction with excess amine gives $Os_3(CO)_9(NH_2R')(\mu_2\text{-CONHR}')(\mu_2\text{-C{=}NHR})$, as a result of CO loss. These last two clusters have been shown to exist in equilibrium. Column chromatography of the amine-substituted cluster over silica gel furnishes $Os_3(CO)_9(\mu\text{-H})(\mu_2\text{-CONHR}')(CNR)$. Isocyanide ligand transformations and reversible Os$-$Os bond cleavage and formation schemes have been presented with respect to the observed cluster reactivity. The X-ray structures of $Os_3(CO)_{10}(\mu_2\text{-CONH}^i\text{Pr})(\mu_2\text{-C{=}NHCN}_2\text{Ph})$, $Os_3(CO)_9(NH_2{}^i\text{Pr})(\mu_2\text{-CONH}^i\text{Pr})(\mu_2\text{-C{=}NHPh})$ and $Os_3(CO)_9(\mu\text{-H})(\mu_2\text{-CONH}^i\text{Pr})(\mu_2\text{-CNCH}_2\text{Ph})$ (Fig. 23) have been determined and their structural features discussed [444].

4.1.2. *Phosphine ligands*

Kinetic data for CO substitution in $[Os_3(CO)_{10}LX]^-$ (where $L \equiv PPh_3$ or CO; $X \equiv NCO^-, Cl^-, Br^-$ or I^-) by PPh_3 have been reported. The activation parameters are indicative of a mechanism involving CO loss that is assisted by the X ligand. Mechanistic details and the effect of the bridging X ligand on the transition state of the substitution reaction have been discussed [445]. Reaction of the triphosphazene ligand $(CF_3)_2P{=}N{=}P(CF_3)_2{=}N{=}PPh_3$ with $Os_3(CO)_{11}(MeCN)$ gives $Os_3(CO)_{11}\{(CF_3)_2P{=}N{=}P(CF_3)_2{=}N{=}PPh_3\}$, which has been shown by XRD analysis to contain a highly delocalized $P{=}N{=}P{=}N{=}P$ moiety with P(IV), P(V), and P(VI) atoms [446]. 3-Hexyne reacts with the triruthenium cluster $H_2Ru_3(CO)_9(\mu_3\text{-C}{-}PPh_3)$ to give, in sequential formation, the clusters $HRu_3(CO)_8(\mu_3\text{-C}{-}PPh_3)(\mu\text{-EtC{=}CHEt})$, $Ru_3(CO)_7(\mu_3\text{-C}{-}PPh_3)(\mu\text{-EtC{=}CHEt})_2$ and $Ru_3(CO)_8(PPh_3)(\mu_3\text{-}C_5Et_3Ac)$. The X-ray structure of the last cluster reveals the presence of an open $Ru_3(CO)_8(PPh_3)$ triangle that is tethered by a (1-rutheno-2,3,4-triethyl,5-acetyl)cyclopentadienyl ligand. Plausible mechanisms have been presented for the formation of each product cluster [447]. The unsaturated cluster $Os_3(\mu\text{-H})(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}$ has been explored for its reactivity with alkynes. In the case of diphenylacetylene, the cluster $Os_3(CO)_7(PhC{\equiv}CPh)(dppm)$ has been isolated and shown to possess a $\mu_3\text{-}\eta^2$ ($\perp$) alkyne ligand. The structural changes in the alkyne coordination mode during two-electron reduction have been studied [448]. Bis(trifluoromethyl)arsinous azide, $(CF_3)_2As{-}N{=}PPh_3$, has been allowed to react with PPh_3 to give



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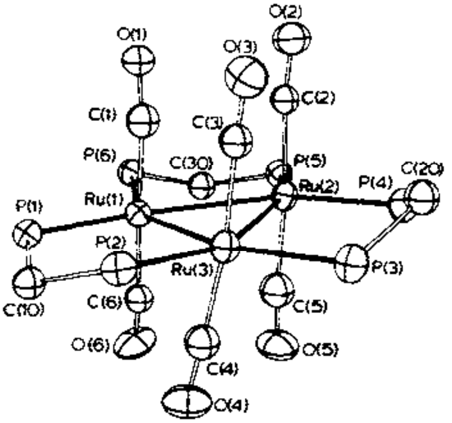
$(CF_3)_2As{-}N{=}PPh_3$, which in turn has been examined for its CO substitution reactivity with $Os_3(CO)_{11}(MeCN)$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$. The isolated clusters from these reactions are $Os_3(CO)_{11}\{(CF_3)_2As{=}N{=}PPh_3\}$ and $Os_3(\mu\text{-}H)_2(CO)_9\{(CF_3)_2As{=}N{=}PPh_3\}$ respectively. The X-ray structures of both clusters have been determined and the results discussed with respect to the highly delocalized As=N=P linkage [449]. P—C bond cleavage has been observed in the reaction between $(CF_3)_2C(OH)PH(CF_3)$ and $Os_3(CO)_{11}(MeCN)$ to give the phosphido-bridged cluster $Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}PH(CF_3)\}$ and the linked cluster $[\{Os_3(\mu\text{-}H)(CO)_{11}\}\{\mu\text{-}PH(CF_3)\}\{Os_3(CO)_{11}\}]$. Reaction with bis(acetonitrile) cluster $Os_3(CO)_{10}(MeCN)_2$ gave only $Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}HN{=}C(Me)P(CF_3)\}$, the structure of which has been established by XRD analysis [450]. The clusters $Os_3(\mu\text{-}H)(CO)_{10}L\{ON(CF_3)_2\}$ (where $L \equiv PPh_3$, $AsPh_3$ or $SbPh_3$) have been synthesized from $Os_3H_2(CO)_{10}L$ and the bis(trifluoromethyl)nitroxyl radical $(CF_3)_2NO$ and characterized by ^{19}F NMR measurements and X-ray crystallography. The temperature-dependent ^{19}F NMR spectra originate from a restricted rotation about the N—O bond [451]. The synthesis and XRD data on the clusters $HRu_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^3\text{-}XCCRCR')$ have been published [452]. The 50-electron cluster $Ru_3(\mu_3\text{-}H)(CO)_6(\mu\text{-}PPh_2)_3\{\mu\text{-}P(Ph)C_6H_4\}$, which contains a triply bridging hydride ligand and an orthometallated phenyl ring, has been isolated from the reaction between $Ru_3(CO)_{12}$ and Ph_2PPPh_2. The molecular structure of this cluster has been crystallographically determined [453]. The reaction of phosphabenzene with $Os_3H_2(CO)_{10}$ gives the clusters $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}C_5H_5P)$ and $Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}C_{10}H_{11}P_2)$. The latter cluster, whose structure has been solved, results from the coupling of phosphabenzene rings [454]. The first example of a cluster that contains phosphino-phosphinidene moieties has appeared. The product $Ru_3(CO)_9(P_5C_5{}^tBu_5)$ has been isolated from the reaction between $Fe(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)$ and $Ru_3(CO)_{12}$ [455]. The reaction of alkynes with the phosphoniomethylidyne-bridged cluster $H_2Ru_3(CO)_9(\mu\text{-}_3\text{-}C{-}PPh_3)$ has been investigated. Alkyne insertion into the $Ru{-}H$ and $Ru{-}\mu_3\text{-}C$ bonds are observed, depending upon the conditions chosen [456]. The oxidative addition of phosphorus ylides to $Ru_3(CO)_{12}$ yields a variety of products. The isolation and characterization of these products have been presented [457]. The X-ray structure of $Ru_3(CO)_{10}$\{*cis*-1,2-bis(diphenylphosphino)ethene\} has been solved and the existence of a chelating diphosphine ligand established [458]. Reaction of $Ru(OAc)_3$ with dppm and CO gives a good yield of $Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2$ and a low yield of $Ru_3(CO)_6(\mu\text{-}dppm)_3$. The X-ray structure of the triruthenium cluster has been determined and the protonation chemistry investigated. The fluxional behavior of the hydride ligand in $[Ru_3(\mu\text{-}H)(CO)_6(\mu\text{-}dppm)_2]^+$ has been studied by ^1H NMR spectroscopy [459] (Fig. 24).

Treatment of functionalized phosphines with $Ru_3(CO)_{10}(\mu\text{-}dppm)$ yields μ_3-acyl- and μ_3-imidoyl-substituted clusters. The isolated clusters include $Ru_3(\mu\text{-}H)(CO)_6(\mu_3\text{-}O{=}CC_6H_4PPh_2)(\mu\text{-}dppm)$ and $Ru_3(\mu\text{-}H)(CO)_6(\mu_3\text{-}CPh{=}NC_6H_4PPh_2)$ [460]. The 2-pyridyldiphenylphosphine-bridged cluster $Os_3(CO)_{10}(\mu\text{-}Ph_2PC_5H_4N)$ exhibits fluxional behavior involving the rapid axial migration of the pyridine unit between two osmium centers. The phosphorus atom is shown to remain coordinated to the



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third osmium center [461]. New triosmium clusters containing 2-pyridylphosphine ligands have been prepared and characterized in solution by IR and NMR spectroscopies and in the solid state by X-ray crystallography. Protonation and thermolysis reactivity studies have been presented [462]. Tri(2-pyridyl)phosphine reacts with $Ru_3(CO)_{12}$ under chloride ion catalysis to give the P−C bond cleavage product $Ru_3(\mu\text{-}2\text{-}C_5H_4N)\{\mu_3\text{-}P(2\text{-}C_5H_4N)_2\}(CO)_9$. No spectroscopic evidence for simple substitution products was obtained, suggesting a spontaneous decarbonylation of $Ru_3(CO)_n\{P(2\text{-}C_5H_4N)_3\}$ (where $n = 11$ and/or 10). Analogous ligand types also exhibit facile P−C bond cleavage reactivity [463]. Framework expansion vs. edge opening has been demonstrated in the reaction of $Ru_3\{\mu\text{-}C(O)(C_6H_5)\}\{\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N)\}(CO)_9$ with Ph_2PH. The isolated 50-electron cluster $Ru_5\{\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N)\}\{\mu\text{-}P(C_6H_5)_2\}_3(CO)_6$ consists of a triangular array of ruthenium atoms capped by a phenylpyridylphosphido moiety, as determined by XRD analysis (Fig. 25). The redox properties of this cluster have been examined by cyclic voltammetry and rotating-disk-electrode voltammetry, and the solid state structure has been discussed with respect to the data obtained from extended Hückel molecular calculations [464].

4.1.3. Nitrogen ligands

The cluster $Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^2\text{-}NC_5H_8)$ and $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}NC_5H_8)$ have been isolated from the reaction of $Ru_3(CO)_{12}$ with piperidine. Under mild thermolysis

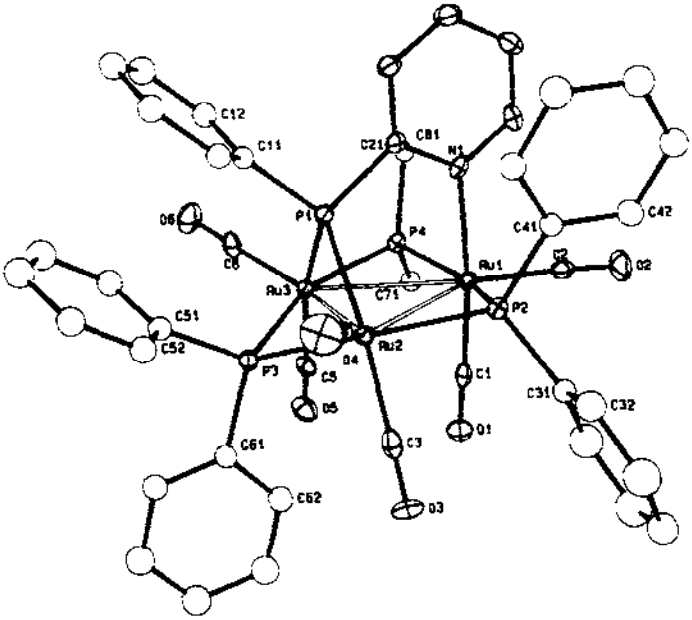
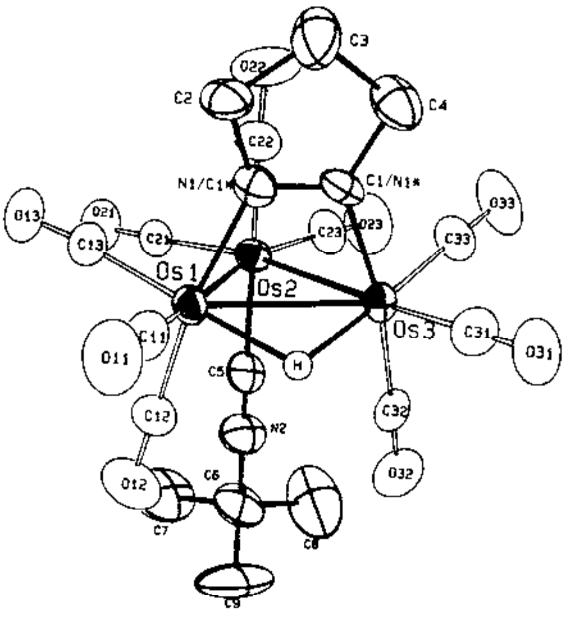


Fig. 25. Reprinted with permission from *Inorganic Chemistry*. Copyright 1993 American Chemical Society.

the former decacarbonyl cluster loses CO and furnishes the nonacarbonyl cluster. Elimination of the μ_3-η^2-piperidyl ligand under hydrogenation conditions has been discussed. The X-ray structures of both clusters have been solved and an analysis of the core structure discussed [465]. Silanes and diphenylacetylene have been allowed to react with the cluster $\mathrm{Ru_3(\mu\text{-}H)(CO)_9(\mu_3,\eta^2\text{-}ampy)}$ and $\mathrm{Ru_3(\mu\text{-}H)(CO)_8(PPh_3)(\mu_3,\eta^2\text{-}ampy)}$. No hydrosilation of diphenylacetylene was observed in these reactions. Several new silyl–alkyne clusters have been isolated from these reactions and structurally characterized by X-ray crystallography [466]. C—P bond cleavage in $\mathrm{Ru_3(\mu\text{-}H)(CO)_7(PPh_3)_2(\mu_3,\eta^2\text{-}ampy)}$ occurs under hydrogen at elevated temperatures to give $\mathrm{Ru_3(CO)_6(\mu\text{-}PPh_2)_2(\mu\text{-}Ph)(\mu_3,\eta^2\text{-}ampy)}$, which has been shown to contain a bridging η^1-phenyl moiety. Replacement of hydrogen with diphenylacetylene also leads to C—P bond cleavage and formation of $\mathrm{Ru_3(CO)_5(PPh_3)(\mu\text{-}PPh_2)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}(Ph)}$. This latter cluster contains a terminal η-phenyl ligand. The X-ray crystal structures of both products are included in Ref. [467]. Evidence for metal cluster catalysis in the hydrogenation of diphenylacetylene to stilbene is presented. The metal cluster $\mathrm{Ru_3(\mu\text{-}H)(CO)_8(PPh_3)(\mu_3\text{-}ampy)}$ has been shown to be a starting material for the production of $\mathrm{Ru_3(CO)_7(PPh_3)(\mu,\eta^1{:}\eta^2\text{-}Ph_2C_2H)(\mu_3\text{-}ampy)}$ and $\mathrm{Ru_3(\mu\text{-}H)_2(CO)_6(PPh_3)(\mu,\eta^1{:}\eta^2\text{-}Ph_2C_2H)(\mu_3\text{-}ampy)}$, which result from diphenylacetylene and $\mathrm{H_2}$ activation. Kinetic data, rate expressions, and a plausible cluster-based mechanism have been presented [468]. The reactivity of the edge-bridged cluster $\mathrm{Ru_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-}pyridazine)}$ with $\mathrm{R_3SiH}$ and $\mathrm{R_3SnH}$ has been investigated. Activation of two equivalents of silane or stannane affords the clusters $\mathrm{Ru_3(\mu\text{-}H)_2(ER_3)_2(CO)_8(\mu\text{-}pyridazine)}$ (where $\mathrm{ER_3 \equiv SiEt_3, SiPh_3, Si(OMe)_3, SnBu_3}$ or $\mathrm{SnPh_3}$), all of which have been characterized by IR and ^{1}H NMR measurements, and in the case of the cluster with $\mathrm{E \equiv SiEt_3}$ by X-ray crystallography [469]. Hydrogenation transfer studies with the azoalkane-bridged cluster $\mathrm{Ru_3(CO)_9(RCH_2N{=}NCH_2R)}$ (where $\mathrm{R \equiv H}$ or Me) have been outlined. Isomerization to the hydrazonide-bridged clusters $\mathrm{HRu_3(CO)_9(RCH_2N{-}N{=}CHR)}$ has been observed in refluxing toluene [470]. The reactivity of alkynes with the hydrazide-bridged clusters $\mathrm{HRu_3(CO)_9(RN{-}NR_2)}$ has been explored and the isolated products characterized by IR and NMR spectroscopy [471]. The synthesis and characterization of *syn*-periplanar bisazo ruthenium clusters have appeared [472]. Azetidine reacts with $\mathrm{Os_3(CO)_{10}(MeCN)_2}$ to give $\mathrm{Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2(\mu\text{-}H)}$ with a moderate yield. The presence of the four-membered ring and the bridging of two osmium centers by nitrogen were confirmed by XRD analysis. Thermolysis of this cluster yields the new clusters $\mathrm{Os_3(CO)_{10}\{\mu\text{-}N{=}C(H)Et\}(\mu\text{-}H)}$ and $\mathrm{Os_3(CO)_9(\mu_3\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)}$ and the known cluster $\mathrm{Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})\ (\mu\text{-}H)_3}$. The X-ray structures of these thermolysis products are included in Ref. [473]. A report dealing with the synthesis and fluxional behavior of imidoyl clusters and their isocyanid-substituted derivatives has been published. The clusters examined include $\mathrm{Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}\overline{C{=}NCH_2CH_2C}H_2)}$, $\mathrm{Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}\overline{NCH_2CH_2CH_2C}H_2)}$ and $\mathrm{Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}MeCH_2C{=}NCH_2CH_2Me)}$. The X-ray crystal structures of five compounds have been reported [474] (Fig. 26).



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4.1.4. *Sulfur ligands*

Osmium clusters containing bridging stannanethione and stannaneselone ligands have been obtained from the reaction of $Os_3(CO)_{12}$ and the requisite ligand [475]. Treatment of $Os_3(CO)_{10}(MeCN)_2$ with tetrahydrothiophene gives the triosmium cluster $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2C}H_2)_2$. Thermolysis of this product at 97 °C furnishes $Os_3(CO)_{10}(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}(\overline{SCH_2CH_2CH_2C}H)\}$ as a result of tetrahydrothiophene ligand loss and C–H bond activation. Further heating at 125 °C leads to ring-opening cleavage of one of the C–S bonds and formation of butenethiolate-substituted cluster $Os_3(CO)_9\{\mu\text{-}\eta^3\text{-}S(CH_2)_2CH{=}CH_2\}(\mu\text{-}H)$. These reactions have been examined using an isotopically substituted tetrahydrothiophene ligand, allowing for the delineation of the pathways associated with each reaction [476]. 1-(Phenylthio)cyclobutene reacts with $Os_3(CO)_{10}(MeCN)_2$ at room temperature to afford the clusters $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)$ (μ-SPh) and $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-}SPh)$. The existence of a μ-η^2-cyclobutenyl ligand in both of these clusters was established by XRD analysis. Treatment of the triosmium product with Me_3NO gives the above diosmium complex and $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C{\equiv}CCH_2C}h_2)(\mu\text{-}SPh)(\mu\text{-}H)$, the latter of which has been shown to contain a triply bridging cyclobutyne ligand. The thermolysis of this cyclobutyne complex and the X-ray crystal structure of other related clusters have been discussed [477]. The clusters $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)$ (μ-SPh), $Os_3(CO)_7\{\mu\text{-}C(Ph)(H)C(Ph)\}\text{-}\{\mu\text{-}\overline{C(Ph)CCH_2C}H_2\}(\mu_3\text{-}S)$ and $Os_3(CO)_7\{\mu\text{-}C(Ph)C(Ph)\overline{CCCH_2C}H_2\}(\mu\text{-}SPh)$ (μ-H) have been isolated from the reaction between $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}H_2)$

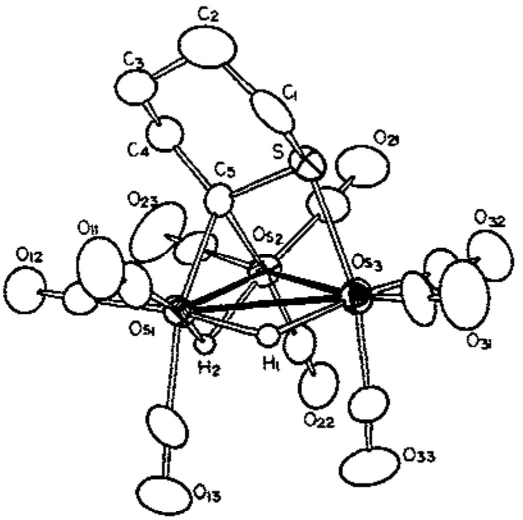


Fig. 27. reprinted with permission from *Organometallics*. Copyright 1993 American Chemical Society.

$(\mu\text{-SPh})(\mu\text{-H})$ and diphenylacetylene in refluxing heptane. Both triosmium cluster products have been structurally characterized by X-ray crystallography [478]. 4-*tert*-Butyl-4-methyl-1-(phenylthio)cyclobutene reacts with $Os_3(CO)_{10}(MeCN)_2$ at room temperature to give $Os_3(CO)_{10}\{\mu\text{-PhS}\overline{C_2CH_2C}(Me)^tBu\}(\mu\text{-H})$, as a result of MeCN displacement and C—H bond activation of the alkene moiety. CO loss from this cluster yields $Os_3(CO)_9\{\mu_3\text{-SPh}\overline{C_2CH_2C}(Me)^tBu\}(\mu\text{-H})$, which contains a metallated cyclobutenyl ligand. Heating this nonacarbonyl cluster at 125 °C leads to C—S bond cleavage and production of the new cluster $Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu\}(\mu_3\text{-S})$. The X-ray structures of the triosmium cluster products have been discussed [479]. The transformations of thiacyclohexane by the triosmium clusters $Os_3(CO)_{12}$, $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$ have been investigated. The clusters isolated include $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2CH_2})_2$, $Os_3(CO)_8(\mu\text{-}\overline{SCH_2CH_2CH_2C})\{S(CH_2)_5\}(\mu\text{-H})_2$, $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2CH_2CH_2})$ and $Os_3(CO)_9(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2CH})(\mu\text{-H})$. The X-ray crystal structures of three of these products are presented [480] (Fig. 27).

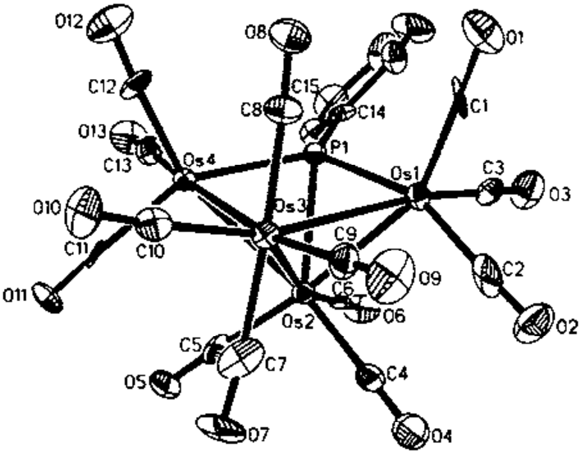
4.2. *Tetranuclear clusters*

The photochemistry of $Ru_4H_2(CO)_{13}$ has been examined by UV–visible and FTIR spectroscopies at 77 K in 3-methylpentane and a polystyrene film. CO dissociation is observed upon optical excitation with 313 nm light. The unsaturated cluster $Ru_4H_2(CO)_{12}$ has been spectroscopically characterized and a discussion on the photochemical process and its relationship to the photochemistry of silica-absorbed $Ru_4H_2(CO)_{13}$ has been presented [481]. Catechol oxidative addition to $Ru_3(CO)_{12}$ gives the tetraruthenium cluster $\{Ru_2(\eta^2,\mu_2,\eta^{\pi}\text{-}O_2C_6H_4)(CO)_4\}_2$. The X-ray crystal structures of two complexes have been described [482]. The reactivity of the diastereomers of the linear tetraruthenium cluster $Ru_4(CO)_{10}\{MeC{=}C(H)C(H){=}N{-}{}^iPr\}_2$ has been examined in thermal isomerizations [483]. The synthesis of $Os_4(CO)_9(\eta^6\text{-benzene})(\text{alkyne})$ from $[Os_3(CO)_9(\text{alkyne})]^{2-}$ and $[Os(\eta^6\text{-benzene})(MeCN)_3]^{2+}$ has been reported. The X-ray structure of butyne-substituted cluster has been determined and the observed butterfly cluster reveals the presence of a benzene ligand at one of the wing-tip osmium atoms [484]. Treatment of the cyclic phosphine ligand $P_4{}^tBu_4$ with $Ru_3(CO)_{12}$ or $Ru_4H_4(CO)_{12}$ at 140°C yields phosphido- and phosphinidene-substituted ruthenium clusters. The three clusters that have been isolated in reasonable yield include $Ru_4(CO)_8(P^tBu)_4$, $Ru_5(CO)_{15}(P^tBu)$ and $Ru_6H_2(CO)_{12}(P^tBu)_3$. The molecular structures of these clusters have been determined by X-ray crystallography [485]. The TCNE-bridged complex $[(\mu_4\text{-TCNE})\{Ru(NH_3)_5\}_4]^{8+}$ has been prepared and shown to exhibit a weak interaction between two mixed-valence ruthenium centers [486]. The facile synthesis of $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-Se})_2$ from $Fe_3(CO)_9(\mu_3\text{-Se})_2$ and $Ru_3(CO)_{12}$ or $Ru_3(CO)_9(\mu_3\text{-Se})_2$ and $Ru(CO)_4(\text{ethylene})$ has been published. Phosphine-ligand substitution has been reported to give tetraruthenium and triruthenium phosphine clusters [487]. Methods have been reported for the conversion of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}N_2Et_2)$ to $H_2Ru_4(CO)_{11}(\mu_4\text{-}\eta^2\text{-}N_2Et_2)$. XRD data on this dihydride cluster have been discussed. Alkyne insertion into one of the Ru—H bonds and H_2 reactivity of the resulting alkenyl cluster have been described [488]. The tetraosmium cluster $[Os_4H_4(CO)_{11}]^{2-}$ has been obtained with a quantitative yield from $Os_4H_4(CO)_{12}$ by chemical reduction using potassium-benzophenone ketyl. The dianion has been employed as a starting material for the synthesis of a variety of cluster compounds [489].

Decarbonylation of the 64-electron rhombic cluster $Ru_4(CO)_{13}\{\mu\text{-}P(N^iPr_2)_2\}_3$ leads to the electron-precise butterfly cluster $Ru_4(CO)_9(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-CO})\{\mu\text{-}P(N^iPr_2)_2\}_2$, which contains a $\mu_4\text{-}\eta^2\text{-CO}$ moiety within the framework cavity. Hydrogen addition occurs to give $Ru_4(CO)_9(\mu\text{-CO})(\mu_3\text{-H})\{\mu\text{-}P(N^iPr_2)_2\}\{\mu_3\text{-}P(N^iPr_2)\}$ as a result of hydrogenolysis of a phosphido ligand. Both products have been structurally characterized by X-ray methods [490]. The reaction of 1,3-diynes with the butterfly cluster *nido*-$Ru_4(CO)_{13}(\mu_3\text{-PPh})$ gives the 62-electron clusters *nido*-$Ru_4(CO)_{10}(\mu\text{-CO})\{\mu_4\text{-}\eta^1,\eta^1,\eta^2\text{-}P(Ph)C(C{\equiv}CR)CR\}$. Facile skeletal transformations involving P—C bond cleavage have been observed and reaction mechanisms for these transformations discussed. Four X-ray structures have been solved and discussed with respect to the reported reactivity [491]. The clusters $HM_3(CO)_{10}(\mu\text{-PPh}_2)$(where M ≡ Ru or Os) are precursors to the phosphinidene-capped clusters *nido*-$M_4(CO)_{13}(\mu_3\text{-PPh})$ via P—C(Ph) bond activation, reductive elimination of benzene and condensation. Both phosphinidene clusters have been characterized by NMR spectroscopy and X-ray crystallography. The use of these clusters as models for a ruthenium (100) surface has been discussed [492] (Fig. 28).

4.3. Pentanuclear clusters

The square-pyramidal cluster $Ru_5C(CO)_{15}$ reacts with cyclohexa-1,3-diene in the presence of Me_3NO to give the diene-substituted cluster $Ru_5C(CO)_{13}(\mu\text{-}\eta^2,\eta^2\text{-}C_6H_8)$.



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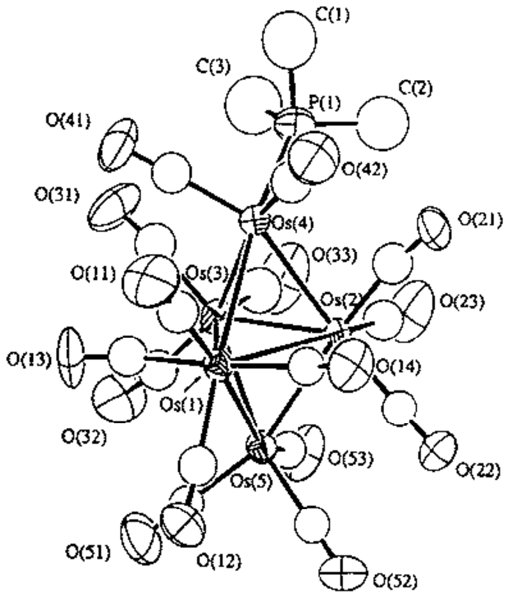
Further dehydrogenation is observed after treatment with additional Me_3NO, giving the benzene-substituted cluster $Ru_5C(CO)_{12}$(benzene). Both structures have been characterized by ^1H NMR spectroscopy, mass spectrometry and XRD analysis [493]. Cyclohexa-1,4-diene reacts with $Ru_5C(CO)_{15}$ with added Me_3NO to produce $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2,\eta^2\text{-}C_6H_8\text{-}1,4)$ and the cluster $Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2,\eta^2\text{-}C_6H_8\text{-}1,4)_2$, when additional cyclohexa-1,4-diene is used. The solid state structures have been discussed and the temperature-dependent ^1H NMR data presented [494]. A communication dealing with the synthesis and characterization of the square-pyramidal cluster $Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2,\eta^2\text{-}C_6H_8\text{-}1,4)_2$ has appeared [495].

Treatment of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with allene leads to two isomers of $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_8)(\mu\text{-}C_3H_4)(CO)_{10}$, which contain an $\eta^3{:}\eta^3$-biallyl ligand, $Ru_5(\mu_4\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}C_9H_{12})(\mu\text{-}C_3H_4)(CO)_{10}$, which contains an allene trimer, and $Ru_5(\mu_5\text{-}C_8H_8PPh_2)(\mu\text{-}PPh_2)(CO)_{11}$. This latter cluster exhibits an allene-ligated phosphino-acetylide ligand. $P(OMe)_3$ ligand substitution chemistry has been reported and the X-ray crystal structures have been presented [496]. The reactivity of thiols with $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ gives the sulfido-bridged clusters $Ru_5(\mu\text{-}H)(\mu_5\text{-}C_2PPh_2)(\mu_3\text{-}SR)(\mu\text{-}PPh_2)(CO)_{12}$ as the major isolated product. In the case of thiophenol, four additional pentaruthenium clusters have been isolated with a low yield. Included in Ref. [497] are the X-ray crystal structures of five clusters. Pyridine metallation has been observed with the cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$. The isolated clusters have been identified as $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ and $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(CO)_{12}$. The adopted polyhedral structure of each cluster has been discussed [498]. Alkene addition to the Cα atom of the C_2PPh_2 ligand in the pentaruthenium cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ has been shown to give clusters containing a $\mu\text{-}\eta^3$,P-(CHRCHCH)PPh_2 ligand, as a result of Cα–Cβ cleavage [499]. Ethylene reacts with $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ to produce two isomers of $Ru_5(\mu_4\text{-}PPh)\{\mu_4\text{-}$



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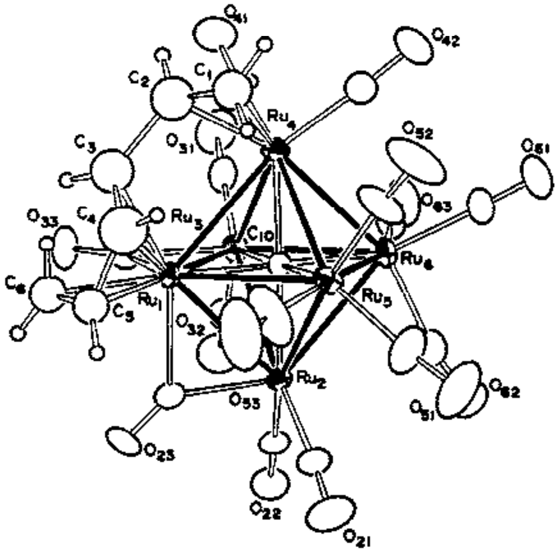
$C_2(CHCH_2)CHMe\}(\mu\text{-}PPh_2)(CO)_{12}$, which differ only in the relative locations of the μ-PPh_2 and CO groups. The X-ray structures of three cluster compounds have been presented [500]. Cyclopentadiene reacts with $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{13}$ to give $Ru_5(\mu_4\text{-}CC_{11}H_{12})(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_9$ with a high yield. The tricyclic ligand μ_4-$CC_{11}H_{12}$ results from a carbene process involving one of the C_2 acetylide carbon atoms and the cyclopentadiene ligand. The molecular structure of the product has been unequivocally determined by XRD analysis [501]. The raft cluster $Os_5(CO)_{18}$ has been synthesized from $Os_3(CO)_{10}(MeCN)_2$ and $H_2Os_3(CO)_{12}$. X-ray crystallography has confirmed the pentaosmium planar raft structure [502]. $Os(CO)_4(PMe_3)$ and $Os_4(CO)_{14}$ have been allowed to react in CH_2Cl_2 to give $Os_5(CO)_{18}(PMe_3)$. Controlled pyrolysis of this cluster has been shown to yield $Os_5(CO)_{17}(PMe_3)$, $Os_5(CO)_{15}$(axial-PMe_3) and $Os_5(CO)_{15}$(equatorial-PMe_3), depending on the reaction conditions. The X-ray structures of these pentaosmium clusters are reported [503] (Fig. 29).

4.4. Hexanuclear clusters

The isolation and structural characterization of $Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}\eta^2\text{-}EtNCSNHEt)(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)$, which has been obtained from $Ru_3(CO)_{12}$ and $SC(NHEt)_2$ at 130°C in THF, have been published. XRD data indicate that the cluster adopts an Ru_6 framework that is similar to the boat conformation of cyclohexane. When the same reaction is carried out using $SC(NHPh)_2$, the hexaruthenium cluster $Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)$ may be isolated.

The Ru_6 core in this cluster exhibits a cyclohexane-like sofa conformation [504]. Pyrolysis of $[Ru_3(CO)_{11}]_2\{\mu$-bis(diphenylphosphino)butadiyne$\}$ gives the cluster $[Ru_3(\mu\text{-}PPh_2)(CO)_9]_2(\mu_6\text{-}C_4)$; X-ray crystallography confirms the presence of the μ_6-C_4 ligand, which serves to ligate the two $Ru_3(CO)_9(\mu\text{-}PPh)_2$ cluster units [505]. ^1H, ^{13}C and ^{17}O NMR data have been reported for the carbide cluster $Ru_6C(CO)_{14}(\eta^6\text{-}C_6Me_6)$. The trends observed in the ^{13}C and ^{17}O chemical shifts have been discussed [506]. The molecular orbitals of the highly symmetrical octahedral clusters $[M_6(CO)_{18}]^{2-}$ (where $M \equiv Ru$ or Os) have been investigated by extended Hückel calculations [507]. 1,3,5-Hexatriene reacts with $Ru_6(CO)_{17}(\mu_6\text{-}C)$ to afford the clusters $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu$-s-cis,s-*cis-trans*-1,2-η^2-4,6-η^4-$CH_2CHCHCHCHCH_2)$ and $Ru_6(CO)_{14}(\mu_6\text{-}C)(\mu$-s-*trans*,s-*cis-trans*-1,2-η^2-4,6-η^4-$CH_2CHCHCHCHCH_2)$ with a low yield. Both clusters exhibit an octahedral metal core with an interstitial carbide ligand and possess a bridging hexatriene ligand. Product characterization by ^1H NMR, IR and XRD methods have been described [508] (Fig. 30).

Double deprotonation of $Os_5H_4(CO)_{11}(\eta^6$-benzene) by DBU leads to $[Os_5H_2(CO)_{11}(\eta^6\text{-benzene})]^{2-}$, which has been allowed to react with $[Os(\eta^6\text{-benzene})(MeCN)_3]^{2+}$ to give the new bis-benzene cluster $Os_6H_2(CO)_{11}(\eta^6$-benzene)$(\mu_3\text{-}\eta^2,\eta^2,\eta^2$-benzene). XRD analysis confirms the presence of a terminal benzene ring at one osmium center (η^6) and a face-capping benzene ring $(\mu_3\text{-}\eta^2,^2,\eta^2)$ [509]. The synthesis and XRD characterization of $Os_6(CO)_{12}(\eta^6\text{-benzene})_2$ have been presented [510]. Treatment of the hexaruthenium clusters $Ru_6C(CO)_{14}(\eta^6$-arene) (where arene $\equiv C_6H_6$, C_6H_5Me, $C_6H_4Me_2$-1,3, or $C_6H_3Me_3$-1,3,5) with cyclohexa-1,3-diene or cyclohexa-1,4-diene and Me_3NO gives the clusters $Ru_6C(CO)_{12}(\eta^6\text{-arene})(\mu\text{-}\eta^2,\eta^2\text{-}C_6H_8)$. Further treatment of this diene-substituted cluster with Me_3NO leads to the



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formation of the mixed-arene clusters $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\text{benzene})$. Reaction schemes for these transformations are outlined and discussed, and the X-ray structures of two of these clusters have been determined [511]. $Ru_3(CO)_{12}$ and selected arenes have been allowed to react in refluxing octane to give $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)$, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3\text{-}1,3,5)$, and $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-paracyclophane})$. The solid state structures of all three arene-substituted clusters have been crystallographically established [512]. A report describing the synthesis, XRD characterization and ^1H NMR variable-temperature study of the bis-toluene cluster $Ru_6C(CO)_{11}(\eta^6\text{-toluene})(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-toluene})$ has appeared [513]. The stepwise formation of $Ru_6C(CO)_{11}(\eta^6\text{-benzene})(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-benzene})$ from the parent carbide cluster $Ru_6C(CO)_{17}$ and 1,3- or 1,4-cyclohexadiene has been investigated. Solution characterization of the cluster intermediates and final products has been discussed, and the X-ray structures of four clusters have been presented [514]. The use of empirical packing potential energy calculations, van der Waals volume analysis and computer graphics in the study of hexaruthenium and hexaosmium carbonyl cluster anions has been described [515].

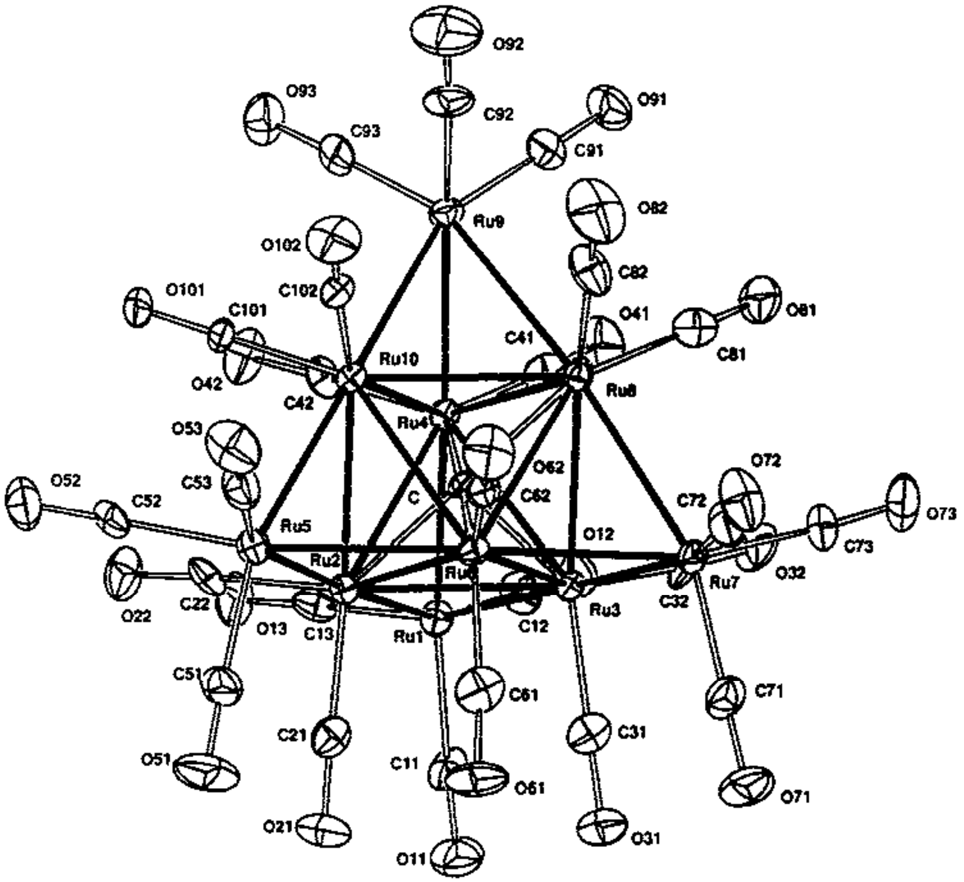
4.5. *Higher nuclearity clusters*

The octaosmium cluster $Os_8C(CO)_{22}$ has been obtained from the solid state vacuum pyrolysis of $Os_3H_3(CO)_9(\mu_3\text{-COMe})$. XRD analysis indicates that the carbido-carbon is encapsulated in a trigonal prismatic cavity within the polyhedral core [516]. 2,4,6-Trimercapto-1,3,5-triazine reacts with $Os_3(CO)_{10}(MeCN)_2$ to give the nonaosmium cluster $[Os_3H(CO)_{10}]_3(S_3C_3N_3)$, which contains three linked osmium triangles possessing thiolate and hydride bridges across a common edge [517]. The first example of an oxo-bridged osmium cluster has been published. Vacuum pyrolysis of $Os_3H(CO)_{10}(\mu\text{-OH})$ gives the undeca cluster $Os_{11}(CO)_{30}(\mu_4\text{-O})_3$, which reveals a tri-edge-bridged bicapped trigonal prismatic osmium core by XRD analysis [518]. Polymeric $[\{Ru(CO)_4\}_n]$ has been analyzed by X-ray powder diffraction methods using a Rietveld procedure. The staggered trans-D_{4h} $Ru(CO)_4$ units are discussed with respect to strain and particle-size-broadening effects [519]. Pyrolysis of $Ru_3(\mu\text{-H})(\mu\text{-NC}_5H_4)(CO)_{10}$ gives $[Ru_2(\mu\text{-H})(\mu\text{-NC}_5H_4)_2(CO)_2(NC_5H_4)_2]\text{-}[Ru_{10}(\mu\text{-H})(\mu_6\text{-C})(CO)_{24}]$ with a high yield. XRD analysis indicates that the hydrido ligand, which was believed to reside in an interstitial tetrahedral site, possibly bridges an Ru—Ru bond external to the cluster core [520] (Fig. 31).

4.6. *Mixed-metal clusters*

4.6.1. *Clusters containing main group atoms*

Treatment of $Ru_3H(CO)_9(B_2H_5)$ with PPh_3 gives the corresponding phosphine-substituted cluster $Ru_3H(CO)_8(PPh_3)(B_2H_5)$ with a good yield. The nido polyhedral core has been confirmed by X-ray crystallography. When the above thermolysis is conducted under UV light, the reaction proceeds by way of borane abstraction, giving mono-, bis- and tris-phosphine-substituted $Ru_3(CO)_9(BH_5)$ [521]. Reaction of $[Ru_3(CO)_9(B_2H_5)][PPN]$ with $Ru_3(CO)_{10}(MeCN)_2$ leads to the octahedral



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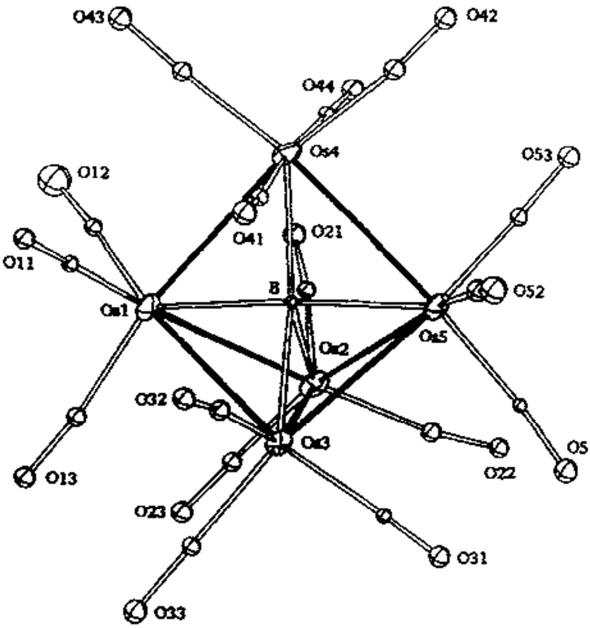
$[Ru_6(CO)_{17}B]^-$ and trigonal-prismatic $[Ru_6H_2(CO)_{18}B]^-$ boride cluster anions. It has been shown that the nature of the product is not determined by the size of the interstitial atom. The reactivity of these anions with various electrophilic gold reagents has been explored and the resulting Ru—Au clusters have been characterized [522]. The 62-electron butterfly cluster $Ru_4(CO)_{10}Cp^*BH_2$ and the 78-electron cluster $H_2Ru_5(CO)_{13}Cp^*BH_2$ have been isolated from the reaction of $[Ru_3(CO)_9(BH_4)][PPN]$ with $[Cp^*RuCl_2]_n$ in CH_2Cl_2 solution. When the same reaction was carried out in THF, only the latter cluster was isolated. X-ray crystallography of this pentaruthenium cluster reveals the existence of a spiked-butterfly framework [523]. The osmaboride clusters $HOs_5(CO)_6B$ and $HOs_4(CO)_{12}BH_2$ have been synthesized from $H_3Os_3(CO)_9BCO$ in refluxing toluene. Both clusters have been structurally characterized by X-ray crystallography, revealing a bridged butterfly metal core and a butterfly metal core for these clusters respectively (Fig. 32). ^1H and ^{11}B NMR data and cluster deprotonation studies have been presented [524].



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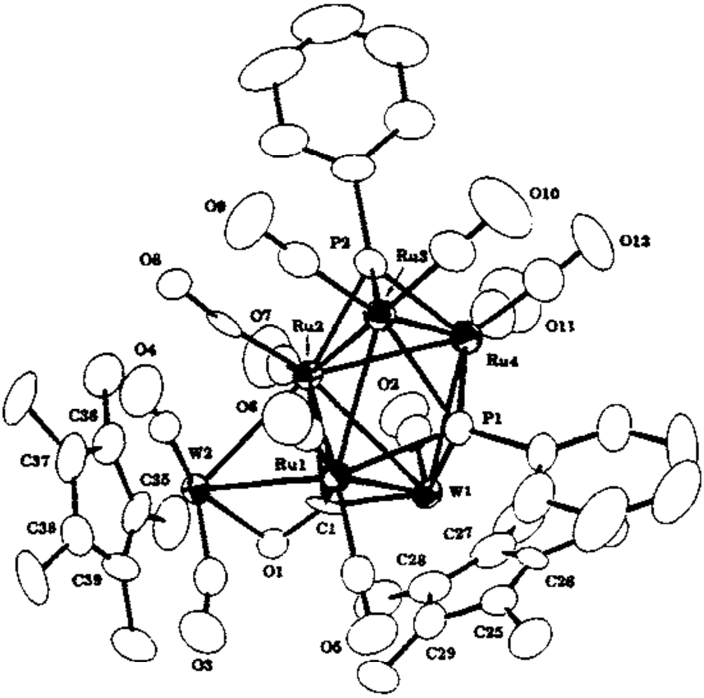
The clusters $Fe_2Ru_3(CO)_{17}(\mu_4\text{-Se})(\mu_3\text{-Se})$ and $Fe_2Ru(CO)_9(\mu_3\text{-Se})_2$ have been prepared from the room temperature reaction of $Fe_2(CO)_6(\mu_3\text{-Se})_2$ with $Ru_3(CO)_{12}$ and $Ru(CO)_4$(ethylene) respectively. The chemical reactivity of the Fe_2Ru cluster with $Fe(CO)_5$ has been described [525]. Treatment of PhSeCl with $[Os_5H(CO)_{15}]^-$ and $[Os_6H(CO)_{18}]^-$ furnishes the selenium-bridged clusters $Os_5(\mu\text{-H})(CO)_{15}(\mu_3\text{-SePh})$ and $Os_6(\mu\text{-H})(CO)_{18}(\mu_3\text{-SeH})$ respectively. Both solid state structures have been confirmed by XRD analyses [526]. The redox properties of $[\{Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu\}_2Hg]$ and $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)HgX]$ (where $X \equiv Re(CO)_5$ or $CpMo(CO)_3$) have been explored by cyclic voltammetry and coulometric methods. The nature of the products resulting from the irreversible reduction has been discussed [527]. The X-ray crystal structure of $[HgRu(CO)_4]_4$ has been solved from powder diffraction measurements. The use of X-ray powder diffraction in the determination of moderately complex organometallic complexes has been discussed [528].

4.6.2. *Clusters containing other metals*

Ruthenium compounds containing tridentate $P_3O_9^{3-}$, $Nb_2W_4O_{19}^{4-}$ and $Cp^*TiW_5O_{18}^{3-}$ ligands have been synthesized and characterized by XRD analyses [529]. The synthesis and X-ray structure of the bimetallic inorganic porphyrin analog $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 2KCl\cdot 6H_2O$ have been published [530]. Thermolysis of the phenylimido cluster $WRu_2Cp^*(CO)_7(\mu_3\text{-NPh})(CF_3CCHCF_3)$ proceeds by way of alkenyl C—H bond activation, giving the hydrido-alkyne cluster $WRu_2Cp^*(CO)_6H(\mu\text{-NPh})(CF_3C{\equiv}CCF_3)$. Carbonylation reactivity has been investigated and the X-ray crystal structures of two clusters have been reported [531]. Hydrogenation of $WRu_3L(CO)_{12}(AuPPh_3)$ (where L≡Cp or Cp*) yields the clusters $WRu_3L(CO)_{11}(\mu\text{-}H)_2(AuPPh_3)$. The polyhedral core adopted by these clusters has been established by X-ray crystallography, and the solution fluxionality of the hydride ligands has been studied by variable-temperature ^1H NMR spectroscopy [532]. Condensation of $Os_3(CO)_{10}(MeCN)_2$ with the aldehyde complex $Cp^*W(CO)_3(CH_2CHO)$ gives the ketenyl clusters $Os_3(CO)_{10}(\mu\text{-}H)\{C(O)\text{-}CH_2WCp^*(CO)_3\}$. XRD analysis confirms the pendant nature of the $Cp^*W(CO)_3$ fragment. Solid state pyrolysis of this cluster at 185 °C leads to four tetrahedral WOs_3 clusters, all of which have been isolated and characterized [533]. The ruthenium complex $Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3$ reacts with $M(CO)_6$ (where M≡Cr, Mo or W) to give a variety of compounds [534]. The reaction of $[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ with $[WS_4]^{2-}$ leads to the mixed-metal nitrido complex $[Os(N)(CH_2SiMe_3)_2(WS_4)]^-$ with a 81% yield. The reactivity of this unsaturated dimer has been explored with nucleophiles, electrophiles and the electron acceptor TCNE [535]. The X-ray structures of $Ru_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ and $Ru_2(CO)_6(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ have been solved and the unique structural features associated with these clusters discussed [536]. An isomeric mixture of W_2Ru_4 clusters has been obtained from the pyrolysis of the phosphinidene-capped cluster $Cp^*WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (Fig. 33). The square-pyramidal core (W_2Ru_4) adopted by these clusters has been established by X-ray crystallography. The reactivity of these same clusters with H_2 and CO has been reported [537].

Treatment of the electron-rich cyanide complex $CpRu(PPh_3)_2CN$ with $[Mo_6Cl^i_8\{(CF_3SO_3)^a_6]^{2-}$ affords the cyanide-bridged cluster $[Mo_6Cl^i_8\{(\mu\text{-}NC)\text{-}RU(PPh_3)_2Cp\}^a_6]^{4+}$. Intense visible absorptions are observed and shown to originate from vibronic coupling of Ru—CN charge transfer bands and cluster transitions [538]. $Re(CO)_4(PPh_3)(H)$ adds to $Os_3(CO)_{10}(\text{cyclooctene})_2$ to give $(Ph_3P)(OC)_3Re(\mu\text{-}H)Os_3(CO)_{11}$. A planar diamond-like core of the rhenium and osmiums has been shown by XRD analysis, and the location of the hydride ligand was established by use of the HYDEX program [539] (Fig. 34).

The directed syntheses of heterometallic clusters derived from $\{M_n(CO)_{11}\}_2\{\mu\text{-}1,4\text{-bis(diphenylphosphino)buta-}1,3\text{-diyne}\}$ (where M_n ≡ Ru_3, Os_3 or $Ru_4(\mu\text{-}H)_4$) and $Co_2(CO)_8$ have been published. All the isolated clusters were characterized by solution techniques and by X-ray crystallography in selected cases [540]. The use of the pentaruthenium cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}$, which contains the novel dicarbon ligand C_2, in the synthesis of the clusters $FeRu_5(\mu_6\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{14}$ and $Co_4Ru_5(\mu_{10}\text{-}C_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2\text{-}(\mu\text{-}CO)_7(CO)_{11}$ has been described [541]. Coupling of the carbide cluster $[Ru_5C(CO)_{14}]^{2-}$ with $[Cp^*Rh(MeCN)_3]^{2+}$ furnishes the hexanuclear cluster $Ru_5RhC(CO)_{14}(\eta^5\text{-}Cp^*)$, which undergoes decarbonylation by Me_3NO in the presence of polyenes to give the polyene-substituted clusters $Ru_5RhC(CO)_9(\eta^5\text{-}Cp^*)(\eta^5\text{-}Cp)_2$ and $Ru_5RhC(CO)_{11}(\eta^5\text{-}Cp^*)(\eta_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_6H_6)$. The molecular structures of these latter two clusters have been determined by X-ray crystallography [542]. The synthesis and electrocatalytic O_2 reduction behavior of



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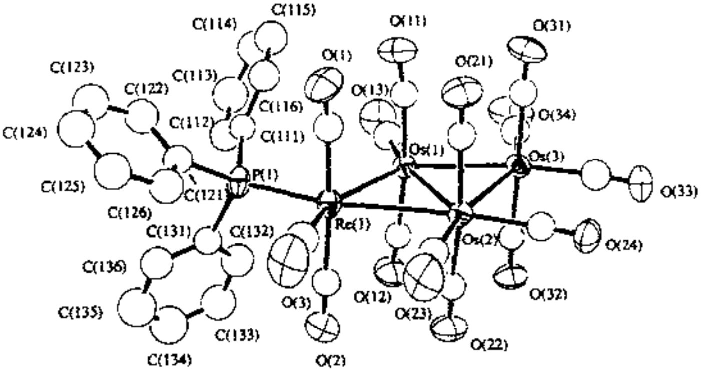

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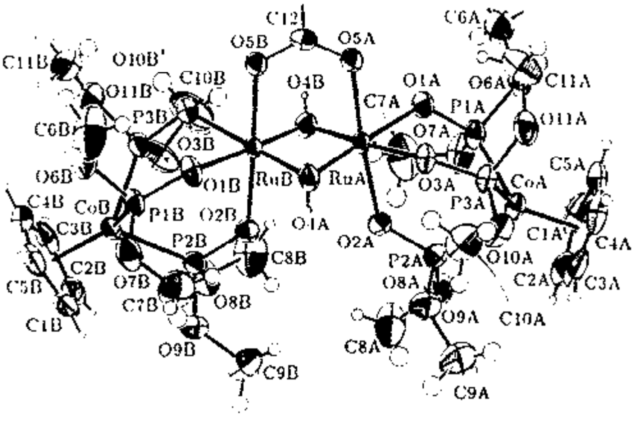
ruthenium-substituted cobalt porphyrins have been reported [543]. [(η^6-cymene)RuCl(μ-pz)$_2$Rh(CO)$_2$] reacts with alcohols in the presence of iodide to give the alkoxycarbonyl complex [(η^6-cymene)Ru(μ-I)$_2$(μ-pz)Rh(COOR)I(CO)] (where

$R \equiv Me$, Et, ${}^{n}Pr$ or ${}^{i}Pr$). The details of the solution characterization have been discussed [544]. New ruthenium oxo complexes containing the anionic tripod ligand $[CpCo\{(MeO)_2P{=}O\}_3]^-$ have been presented and the redox properties discussed. The X-ray crystal structures of several new compounds are included in [545] (Fig. 35).

The tetrametallic alkylidyne clusters $(\mu\text{-H})Ru_3M(\mu_4\text{-}\eta^2\text{-COMe})(CO)_{12}$ (where $M \equiv Fe$ or Ru) have been synthesized and characterized by X-ray crystallography. A discussion on the fluxional behavior of the ancillary CO ligands in the Ru_4 cluster has been given [546]. $Fe_6S_6I_2(PMePh_2)_4$ reacts with $RuI_2(MeCN)_4$ to give $[Ru_2Fe_8S_6]^{8+}$, whose solid state structure has been determined by XRD analysis [547]. The clusters $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$ and $\{Os_3(CO)_{11}\}(\mu\text{-dppa})\{Re_3(\mu\text{-H})_3(CO)_{11}\}$ have been prepared. Pyrolysis of the former cluster has been shown to give the pentanuclear cluster $Os_3Ru_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-PPh}_2)(CO)_{13}$. Treatment of $Re_3(\mu\text{-H})_3(CO)_{11}(dppa)$ with $Ru_3(CO)_{12}$ gives a high yield of $\{Re_3(\mu\text{-H})_3(CO)_{11}\}(\mu\text{-dppa})\{Ru_3(CO)_{11}\}$, which when heated gives the new cluster $Re_3(\mu\text{-H})_3(CO)_{11}\{PPh_2[(\mu\text{-}C_2Ru_2)(\mu\text{-PPh}_2)(CO)_6]\}$. Both pentanuclear clusters obtained from thermolysis have been crystallographically characterized [548]. The synthesis and characterization of clusters that exhibit Fe→Os bonds have been reported. $Os_3(CO)_{12}$ reacts with $Fe(C_5H_4)_2PPh$ to give, as the major product, $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PPh)Fe(C_5H_4)]$, while the cluster $Os_3(CO)_{11}(PFc_2Ph)$ (where $FcH \equiv Cp_2Fe$) gives the related product $Os_3(CO)_9[\mu_3\text{-}(C_5H_4PFc)Fe(C_5H_4)]$ in refluxing octane. Each cluster contains a closed Os_3 triangle that is capped by a ferrocenylphosphido moiety [549]. Thermolysis of $Os_3(CO)_{10}[Fc'(P^iPr_2)_2]$ (where $Fc' = (\eta\text{-}C_5H_4)_2Fe$) in octane gives six different cluster compounds, of which the crystal and molecular structures of $(\mu\text{-H})Os_3(CO)_8[\mu\text{-}(\eta\text{-}C_5H_4P^iPr_2)Fe(\eta\text{-}C_5H_4P^iPrCHMeCH_2CO)]$, $(\mu\text{-H})Os_3(CO)_9[\mu\text{-}(\eta\text{-}C_5H_4P^iPr_2)Fe(\eta\text{-}$



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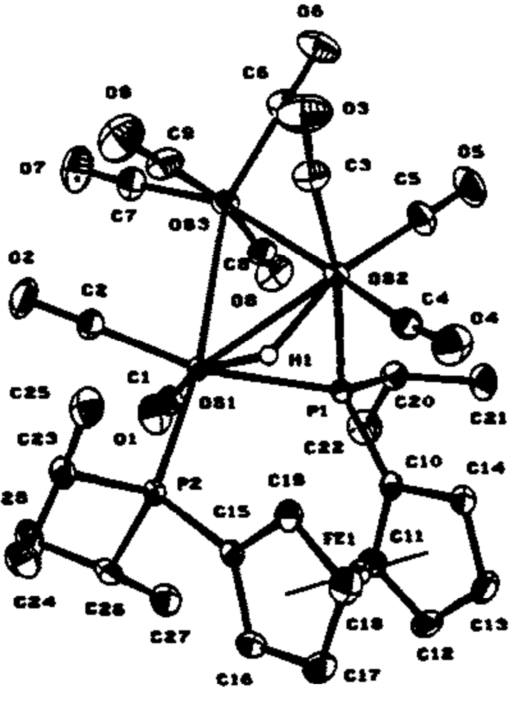
$C_5H_4P^iPr)]$ and $(\mu\text{-}H)_2Os_3(CO)_8[\eta^3\text{-}\mu\text{-}(\eta\text{-}C_5H_4P^iPr_2)Fe(\eta\text{-}C_5H_3P^iPr)]$ have been solved by X-ray crystallography [550] (Fig. 36).

$Pt_2Ru_4(CO)_{18}$ reacts with diphenylacetylene in refluxing heptane to give $Pt_2Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ and $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)_3$. XRD analysis reveals that the former cluster is based on a distorted square-pyramidal core, while the Pt_3Ru_6 cluster consists of a Pt_3Ru_3 octahedral core that is capped by the remaining ruthenium atoms. The reactivity of these clusters in carbonylation reactions has been studied and the resulting products fully characterized [551]. The carbide clusters $PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)$ and $Ru_6(CO)_{13}(\mu_3\text{-}PhC_2Ph)(\mu_6\text{-}C)$ have been isolated from the reaction of $PtRu_5(CO)_{16}(\mu_6\text{-}C)$ with diphenylacetylene. The structural features of these clusters have been established by XRD measurements [552]. An example of energy capture by a $PtOs_3$ cluster has been reported. Optical excitation of $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})\{Si(OMe)_3\}(\mu\text{-}H)$ affords an isomeric cluster that differs only in the location of the bridging hydride and $Si(OMe)_3$ ligand. The activation parameters for the conversion of this metastable photoisomer back to the original cluster have been measured. The X-ray structures of these clusters are reported (Fig. 37), and a scheme outlining the observed chemistry presented and discussed [553].

Metal exchange reactions in group IB metal-substituted clusters have been



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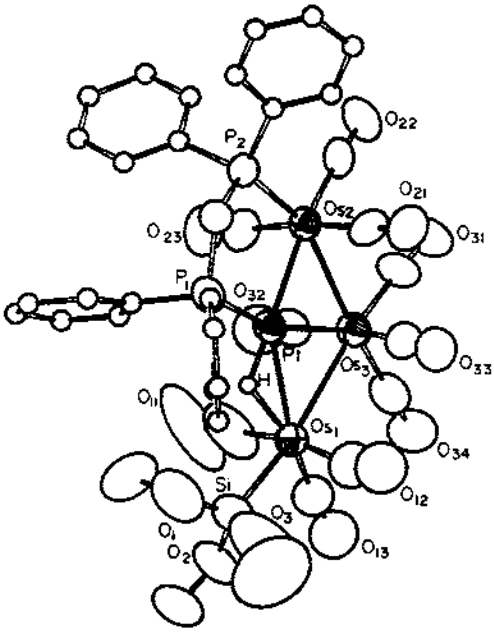

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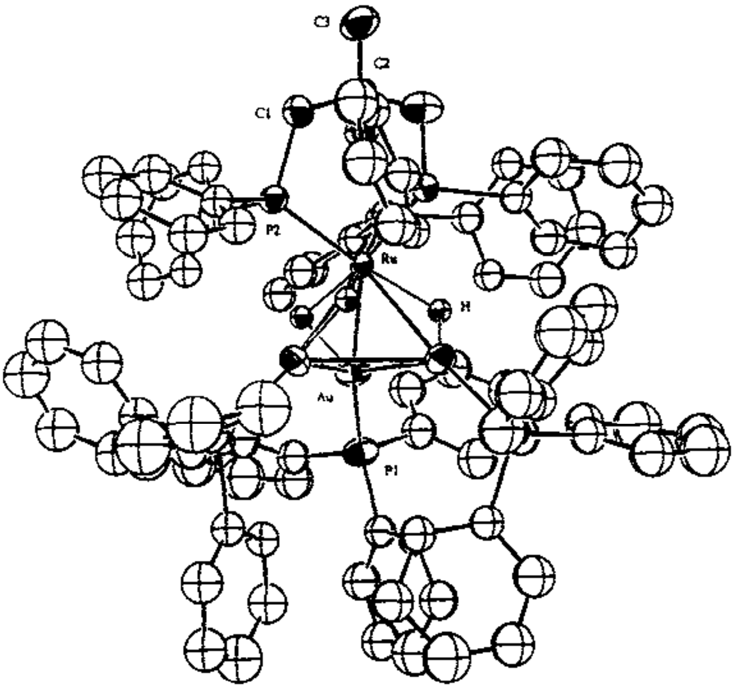
explored. The clusters $M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}$ (where $M \equiv Cu$ or Ag, $n = 1$, 2) react with $[Ag(MeCN)_4]^+$ or AuCl(thiophene) by replacement of the initial M atom(s) [554]. Treatment of the carbido cluster $[Ru_6C(CO)_{16}]^{2-}$ with $Au_2(dppm)Cl_2$ in the presence of $TlPF_6$ gives $Ru_6C(CO)_{16}Au_2$ (dppm) with a 90% yield. XRD analysis reveals that the two Au atoms bridge adjacent edges of one of the triangular faces of the Ru_6 octahedral core. The analogous cluster $[Ru_6(CO)_{18}]^{2-}$ reacts with $Au_2(dppm)Cl_2$ to give the pentaruthenium cluster $Ru_5(CO)_{15}Au_2(dppm)$. This cluster adopts a trigonal bipyramidal framework, where the Au atoms serve to cap adjacent faces of the trigonal bipyramid [555]. The carbide cluster $[Ru_5C(CO)_{14}]^{2-}$ and $Au_2(dppe)Cl_2$ have been allowed to react in the presence of $TlPF_6$ to produce $Ru_5C(CO)_{14}Au_2(dppe)$ as the major species and $[\{Ru_5C(CO)_{14}\}_2Au_2(dppe)]^{2-}$. The latter cluster is the major product when two equivalents of the carbide cluster are employed. Reaction of $[H_3Os_4(CO)_{12}]^-$ (three equivalents) with $Au_2(dppe)Cl_2$ leads to the formation of $\{H_3Os_4(CO)_{12}\}_2Au_2(dppe)$ with a good yield [556]. Theoretical and spectroscopic data on the tetrahedral cluster $[L_3Ru(\mu\text{-}H)_3(AuL')_3]^{2+}$ (where $L \equiv$ triphos; $L' \equiv PPh_3$) have been published. Also included in [557] are ^{197}Au Mössbauer data and incoherent inelastic neutron spectroscopy results that have led to the unambiguous assignment of the M–H vibrational modes. The synthesis and fluxional NMR studies of ruthenium trigold and digold hydride clusters have been discussed. The molecular structure of $[(triphos)RuH_3\{Au(PPh_3)\}_3]^{2+}$ has been determined by X-ray crystallography [558] (Fig. 38).



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5. Miscellaneous chemistry

5.1. Heterogeneous and supported complexes

The polyoxoanion-supported complexes derived from $[Ru(C_8H_{12})]^{2+}$ and $[P_3O_9]^{3-}$, $[V_4O_{12}]^{4-}$ and $[Nb_2W_4O_{19}]^{4-}$ have been examined by solution and solid state techniques [559]. The photochemistry of $H_2Ru_4(CO)_{12}$ adsorbed on silica has been investigated. The interaction of the coordinatively unsaturated photoproduct $H_2Ru_4(CO)_{12}$ with the silica support was explored by DRS UV–visible, FTIR and EXAFS spectroscopies [560]. A series of crown ether–alkali metal cation intercalation compounds containing CpRu(benzo-15-crown-5) have been synthesized [561].

Ruthenium red ($[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{6+}$) and ruthenium brown ($[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{7+}$) have been shown to function as water oxidation catalysts in aqueous solution and in a Nafion membrane [562]. Temperature-programmed reduction studies have been reported for bimetallic Ru—Cu samples supported on silica gel. These same catalysts have been examined as propane hydrogenolysis catalysts [563]. Nafion- and montmorillonite-clay-coated electrodes that contain $[Ru(bpy)_3]^{2+}$ have been investigated for their photochemical properties [564]. The excited-state properties of zeolite-entrapped ruthenium(II) complexes have been examined by electronic absorption, electronic emission, resonance Raman and time-resolved resonance Raman spectroscopies [565]. The intercalation of $[Ru(bpy)_3]^{2+}$ in fluorotetrasilica mica–poly(vinylpyrrolidone) has been demonstrated and the resulting complex examined for its photoluminescence behavior [566]. The use of n-RuS_2 electrodes as oxygen evolution photocatalysts has been published [567]. The reduction of aqueous ruthenium tetraoxide as a route to hydrosols of ruthenium dioxide has been described [568]. Voltammetric electro-oxidation of ruthenium surfaces in aqueous solution has been explored by surface-enhanced Raman spectroscopy [569].

Ruthenium complexes incorporated in cellulose acetate have been prepared from $RuCl_3 \cdot 3H_2O$ and examined for their reactivity towards CO, H_2, O_2 and H_2O [570]. Anchored ruthenium porphyrins have been reported to serve as catalysts in the decomposition of cyclohexyl hydroperoxide. The supports used in these studies include polystyrene beads and silica powder [571]. The kinetics on the hydrogenation of cyclohexene using a polymer-supported ruthenium(III) complex have been reported. Catalyst recycling data have also been presented [572]. Carbonyl insertion and ethylene hydroformylation results have been reported for the carbide cluster $[Ru_6C(CO)_{16}Me]^-$ supported on silica [573]. The observation of formyl intermediates in the hydrogenation of CO by Ru(001) has been reported through the use of high-resolution electron energy loss spectroscopy [574]. EXAFS data on the reversible CO adsorption–desorption under $CO{-}H_2$ have been presented for $[Ru_6C(CO)_{16}Me]^-$ supported on MgO [575]. The hydrogenation of 3-methyl-2-butenal over $Ru{-}SiO_2$ and potassium-promoted $Ru{-}SiO_2$ has been explored by FTIR spectroscopy [576].

Inelastic neutron scattering studies have been conducted on partially desulfurized RuS_2 in order to assess the geometry and energetics of the different hydrogen adsorption sites [577]. The reactivity of O_2 and NO_2 with Zn on a Ru(001) surface has been reported [578]. A report on the hydrogenation of CO on Ru(001) as a route to formate has appeared [579]. α-$RuCl_3$ has been examined by scanning tunneling microscopy and atomic force microscopy. The differences between the data obtained with these techniques have been discussed [580]. Data on proton Knight shifts associated with chemisorbed hydrogen on Ru—Cu bimetallics have been published [581]. A paper dealing with transition-state theory for adsorption and desorption of CO on Ru(001) has appeared [582]. The electro-oxidation of methanol on a single-phase polycrystalline Pt—Ru alloy has been demonstrated. The high catalytic activity exhibited by this alloy is attributed to the bifunctional character of the alloy surface [583]. Dissociative methanethiol adsorption on Ru(0001) yields two molecular intermediates that have been characterized by XPS [584]. The decomposition of ethylidyne in the presence of coadsorbates on Ru(001) has been investigated by in-situ FTIR absorption spectroscopy. The ethylidyne fragment is present on the three-fold hollow sites of the close-packed ruthenium surface [585].

5.2. *CO and CO_2 reactions*

Reductive carbonylation of mononitroarenes and dinitroarenes by catalytic amounts of Pd clay, $Ru_3(CO)_{12}$ and bpy has been published. The selectivity of this dual-catalysis system is discussed [586]. Olefin hydroformylation by $Ru_3(CO)_{12}$ and amine modifiers has been discussed [587]. The use of the mixed-metal systems $Co_2(CO)_8$–$Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$–$Ru_3(CO)_{12}$–PPh_3 in the hydroformylation of α- and β-pinene has been described [588]. A report on the carbonylation of methanol to methyl formate using $Ru_3(CO)_{12}$ as a catalyst precursor has appeared. The effect of various promoters, phosphine ligands and solvents on the reaction has been discussed [589]. The homologation of primary alcohols by $Ru_3(CO)_{12}$, $[Bu_4P][Br]$ and HCl(aq) has been described. This reaction does not require iodine promotion or CO pressure [590].

5.3. *Oxidation reactions*

A mild procedure for the oxidative cleavage of alkenes using an oxidant derived from OsO_4 and the Jones reagent has been published. The reaction is theorized to proceed by way of an osmate ester, which is reoxidized by the added chromate [591]. The hydroxylation of (22E,24R)-5α-ergosta-2,22-dien-6-one by OsO_4 and *N*-methylmorpholine *N*-oxide has been published [592]. A discussion on the origin of enantiospecificity in olefin dihydroxylation reactions has appeared [593]. The use of alkaloid derivatives as ligands in the osmium-catalyzed asymmetric dihydroxylation of alkenes has been described [594].

The transformation of alkenes to α-ketols occurs under mild conditions using an $RuCl_3$-derived catalyst system [595]. High-valence ruthenyl species generated in situ by the electrochemical oxidation of $[Ru^{III}(H_2O)_4Cl_2]^+$ function as electrocatalysts for the oxidation of organic substrates [596]. $RuCl_3$ and ruthenium(II) complexes catalyze the oxidation of alcohols to ketones and aldehydes in the presence of aqueous persulfate. Kinetic data point to a concerted process for the bi-electronic oxygen transfer [597]. The complexes Ru^{III}(2,6-dipicolinic)(L)Cl (where L ≡ bpy, 1,10-phen or ethylenediamine) have been synthesized and characterized by solution methods and cyclic voltammetry studies. These complexes are shown to function as catalysts for the oxidation of hydrocarbons using the co-oxidants iodosylbenzene and *tert*-butylhydroperoxide [598]. Results on the electro-oxidation of naphthalene and 2-methylnaphthalene to 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone respectively using a dichromate–$RuCl_3 \cdot 3H_2O$ catalyst system have been presented [599]. Oxidative fission of the benzene ring to carbon dioxide and water has been reported for a variety of alkylbenzenes and ethylbenzene by ruthenium catalysts [600]. The mechanism associated with the epoxidation of stilbenes by Ru^{III}(Hedta)–^tBuOOH has been reconsidered [601]. The water oxidation properties of Ru red and Ru brown adsorbed on a Nafion membrane have been studied [602].

5.4. *H_2 production and hydrogenation reactions*

4-Oxoisophorone may be hydrogenated to the corresponding diketone with an enantiomeric excess of 50%, when using ruthenium(II)–BINAP complexes as the catalyst [603]. Enantioselective alkene hydrogenations have been reported with ruthenium(II)–BINAP catalysts [604]. The use of ruthenium(II)–BINAP as an asymmetric hydrogenation catalyst in the synthesis of (3R,7R,11R)- and (3S,7R,11R)-3,7,11,15-tetramethylhexadecan-1-ols has been described [605]. The dynamic kinetic resolution of 2-substituted 3-oxo carboxylic esters catalyzed by ruthenium(II)–BINAP complexes has been investigated [606].

The hydrosilation of 1-octene with $(EtO)_3SiH$ using the catalyst precursor $Ru_3(CO)_{12}$ has been examined in dioxane and benzene solution. Only isomerization is observed below 60 °C, giving *trans*-2-octene as the sole product. The use of the Laine kinetic criterion in the determination of the nuclearity of the active catalyst has been described [607]. CO_2 hydrogenation gives methanol and methane as the major products when a homogeneous $Ru_3(CO)_{12}-KI$ catalyst system is employed as the catalyst precursor [608]. The hydrogenation of cinnamaldehyde using Ru—Sn/C catalysts has been described [609]. Selective hydrogenations of α,β-unsaturated aldehydes to allylic alcohols have been demonstrated with the supported aqueous-phase catalysts $RuCl_2(TPPTS)_3–SiO_2$ and $RuH_2(TPPTS)_4–SiO_2$. The chemoselectivity exhibited by these catalysts is contrasted with the analogous homogeneous catalyst systems [610]. Transfer hydrogenation of D-fructose to D-glucitol and D-mannitol has been observed with $RuCl_2(PPh_3)_3$ as the catalyst. The hydrogen sources used in this study were propan-2-ol and butan-2-ol. Solvents that promote catalyst deactivation have been discussed [611]. *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(H_2)_2]^{2+}$ functions as an efficient catalyst for the hydrogenation of organic carbonyl compounds and alkenes in biphasic media. The intermediacy of an η^2-dihydrogen complex has been discussed in the presented mechanism [612]. The transfer hydrogenation of ketones and α,β-unsaturated ketones has been examined with the cluster catalyst $[Ru_4H_3(CO)_{12}]^-$. The time-dependent concentration profiles and a plausible reaction mechanism have been presented [613]. An improvement in the rate of the transfer hydrogenation of benzaldehyde using $RuCl_2(PPh_3)_3$ has been reported when the reaction was carried out in a microwave oven [614].

Nitrobenzene reduction to aniline proceeds selectively in the presence of the catalyst system composed of aqueous methyl formate, $Ru_3(CO)_{12}$, Pd(OAc), PCy_3 and 1,10-phen. The initial products of the reaction are azoxybenzene and azobenzene, which derive from nitrobenzene deoxygenation. Hydrogenation of these products to aniline and formanilide completes the reduction reaction. The latter compound is hydrolyzed during the reaction to aniline [615]. High activity and selectivity have been reported in the $CO–H_2O$ reduction of nitrobenzene with ruthenium-phosphine catalyst systems. A correlation of the reaction rate with the electronic and steric properties of the ancillary phosphine ligand has been presented and discussed [616].

Ruthenium-catalyzed isomerization and hydrogenation reactions have been examined with 1-octene as a substrate. The nuclearity of the active catalyst has been addressed by using the Laine kinetic criterion [617]. The clusters $Ru_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ have been examined as catalysts for the hydrogenation of diphenylacetylene and isomerization of *cis*-stilbene. The isolation of the phenylacetylene-substituted cluster $Ru_3(CO)_8(PhC\equiv CPh)_2$ has been discussed [618]. The heterogeneous hydrogenation of 1-octene using silica-supported phosphido-bridged ruthenium clusters has been reported. The clusters examined include $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]$,

$Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$, $Ru_2(CO)_6[1,2\text{-}(\mu\text{-}P^tBu_2C_6H_4)]$ and $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}P^tBu_2C_6H_4)]_2$ [619].

5.5. Other catalytic reactions

A simple synthesis of γ,δ-unsaturated ketones from allylic alcohols and alkynes has appeared. The catalyst employed in these studies was CpRu(1,5-COD)Cl [620]. CpRu(1,5-COD)Cl has been found to function as a catalyst for the addition of alkenes to alkynes. The selectivity and mechanism associated with this addition reaction have been discussed [621]. A paper on the chemoselectivity in allyl alcohol isomerization reactions using the catalyst $CpRu(PPh_3)_2Cl$ has appeared. Deuterium-labeling studies have been undertaken and the data used in the formulation of the reaction mechanism [622].

The hydrosilation of allyl chloride with $(MeO)_3SiH$ has been examined with $Ru_3(CO)_{12}$ as the catalyst precursor. Good yields of chloropropylsilane have been reported [623]. Catalysis of styrene hydrosilation using $Os_3(CO)_{12}$ has been described. The observed products are the vinylsilane and the normal hydrosilation product [624].

The addition of catecholborane and 3-methyl-1,3,2-oxazaborolane to unhindered alkenes and alkynes is catalyzed by the ruthenium complexes $RuCl_2(PPh_3)_4$, $RuCl_3(PPh_3)_2(MeOH)$, $RuHCl(PPh_3)_3$, $RuH_4(PPh_3)_3$ and $RuHCl(DIOP)_2$ [625]. The dimerization of methyl acrylate proceeds to give a mixture of linear tail-to-tail dimers with a catalyst derived from $RuH(CO)Cl\{P(^iPr)_3\}_2$ and silver triflate [626]. Ethylene dimerization using the water-soluble catalyst $[Ru(H_2O)_6]^{2+}$ has been described. Two intermediates have been isolated from this reaction and characterized by NMR spectroscopy [627]. Ethylene oligomerization using the catalyst $Ru_3(CO)_{12}$ has been published [628]. The catalytic ring-closure metathesis of dienes by the ruthenium carbene complex $RuCl_2(PCy_3)_2(=CHCH=CPh_2)$ has been discussed. This particular catalytic system exhibits a diminished sensitivity to O_2 and a wide tolerance to most functional groups [629]. The synthesis and activity of single-component ruthenium olefin metathesis catalysts have appeared [630].

Nitrogen–carbon bond formation in the reductive *N*-heterocyclization of *N*-(2-nitrobenzoyl)amides to 4(3H)-quinazolinone derivatives has been reported, when $Ru_3(CO)_{12}$ is used as a catalyst [631]. The ruthenium-catalyzed cyclization of *N*-allylic-α-chloro-α-thioacetamides to alkaloids has been described. The ruthenium catalyst $RuCl_2(PPh_3)_3$ has been found to be the best catalyst for this transformation [632]. The synthesis of statine analogues by intramolecular ruthenium(II)-catalyzed cyclization of 3-[[(1S,2R)-2-{(polyhaloacetoxy)ethoxy}-1-apocamphanyl]carbonyl]-2-oxazolones has appeared. Complete diastereoselectivity is observed in these cyclizations [633]. The ruthenium–tin complex $[Ru(SnCl_3)_5PPh_3]^{3-}$ is a catalyst for the isomerization of methyl formate to acetic acid [634]. Selective deoxygenation of aromatic and *N*-heteroaromatic amidoximes to amidines was observed under CO using $Ru_3(CO)_{12}$ as a catalyst [635]. 1-Substituted-3-hydroxyperhydroazepines have been synthesized from 1,2,6-hexanetriol and primary amines in the presence of the ruthenium catalyst $RuCl_2(PPh_3)_3$ [636]. Formylation of aromatic and alkenyl iodides using the bimetallic catalyst system $PdCl_2(PPh_3)_2$–$Ru_3(CO)_{12}$ has been documented. The results have been discussed in terms of the high hydrogenolysis activity of intermediate ruthenium hydride species [637]. Regioselective and stereoselective addition of carboxylic acids to terminal alkynes gives *Z*-enol esters, when catalyzed by the ruthenium complexes $Ru\{Ph_2P(CH_2)_nPPh_2\}\{\eta^3\text{-}CH_2\text{-}C(Me){=}CH_2\}_2$ [638]. The reductive carbonylation of *o*-nitrobenzylalcohols by ruthenium–palladium catalysts has been investigated as a route to 1,4-dihydro-2*H*-3,1-benzoxazin-2-one derivatives [639]. The reaction of α-hydroxy acids with terminal alkynes yields α-hydroxy enol esters with a high selectivity, using the binuclear ruthenium complex $[Ru(\mu\text{-}O_2CR)(CO)_2(PPh_3)]_2$ as a catalyst [640]. Ru(COD)(COT) has catalyzed the allylation of carbonucleophiles with a high regioselectivity [641]. The Knoenenagel addition of cycanoacetate to aldehydes and ketones occurs with ruthenium polyhydride and dihydrogen complexes [642].

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