Journal of Organometallic Chemistry, 477 (1994) 219–268

Annual survey of ruthenium and osmium for the year 1992

Michael G. Richmond

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

(Received December 13, 1993)

Key words: Ruthenium; Osmium

Contents

1. Dissertations

Two ruthenium complexes have been examined as probes for higher-order structure in RNA. $[Ru(1,10\text{-}phen)_3]^{2+}$ and $[Ru(TMphen)_3]^{2+}$ display different affinities for tRNA and bind RNA by different interactions, as revealed by biophysical analyses. The reactivity of these ruthenium complexes are consistent with mediation by singlet oxygen at the nucleic acid base [1]. New osmium Schiff-base complexes have been synthesized and spectroscopically characterized. The X-ray crystal structures of $Os(O)_2[(BA)_2en]$, $Os(OCH_3)_2[(BA)_2en)]$, $Os(O)_2(SAP)py$, and $OsCl(SAP)(PPh_3)_2$ are reported [2]. The synthesis and redox properties of new ruthenium and osmium complexes bearing ancillary imine ligands have been described. Kinetic and mechanistic studies that deal with the oxidation of benzyl alcohol using $[Ru(bpy)_2(O)\{P(p\text{-}C_6H_4X)_3\}_3]^{2+}$ are reported. The mechanistic aspects of the oxidation reaction are discussed with respect to linear free energy relationships developed [3]. Proton-coupled electron transfer has been examined with several ruthenium polypyridyl complexes. The efficacy of proton-coupled electron transfer has been evaluated by using cyclic voltammetric data [4]. The synthesis and characterization of ruthenium(II) amine isocyanoborane complexes have appeared. Profound electronic changes are observed in the new complexes, as determined by UV-visible spectroscopy [5]. Chromophore-quencher complexes based on osmium have been examined for pho-

0022-328X/94/$7.00
SSDI 0022-328X(94)24341-2

toinduced electron transfer reactivity. Emission quantum yields and lifetimes have been determined, and in the case of $[Os(bpy)_2(CO)(DMABN)]^{2+}$, an emissive LLCT state has been observed [6]. Ligand loss photochemistry has been examined with thin homo- and copolymeric films of ruthenium and osmium bipyridyl complexes. The thin films, which were prepared by reductive electropolymerization, readily released $[Ru(bpy)_2]^{2+}$ fragments upon photolysis of the ruthenium–vpy bonds. Film images were obtained when masking techniques were employed [7]. Tri- and tetradentate Schiff-base ligands have been used in the synthesis of new *trans*-dioxoosmium(VI) complexes. Thiol reduction of these complexes yields the corresponding osmium(IV) complexes with *trans* thiolate ligands. The X-ray crystal structures for several of the products and cyclic voltammetric data are presented [8]. The synthesis, characterization, and photophysics of $[Ru(tpy)(bpy)L]^{n+}$ (where L = Cl, I, MeCN, or aromatic amine) are reported. The study was conducted in order to quantify the excited-state changes as a function of the ancillary ligand (L). The room temperature lifetimes for emission from the Ru^{II}-tpy MLCT excited state are reported [9]. The anionic hydride [Ru(OEP)(THF)H][K] has been synthesized by heterolytic H_2 splitting using $Ru(OEP)(THF)_2$ and base. The data suggest that dihydrogen coordination occurs, followed by deprotonation of the bound hydrogen. Support for this scenario comes from the characterization of the transient dihydrogen porphyrin complex. The reducing properties of the anionic hydride complex have been established by studying the reactivity with a suitable NAD^+ analogue. The parallels between the dihydrogen complex and hydrogenase enzymes are discussed [10]. *trans*-$Ru(TMP)(O)_2$ has been shown to catalyze the aerobic epoxidation of alkenes. Using substituted styrenes, the epoxidation data have been analyzed and found to give a Hammett ρ^+ value of -0.93. The X-ray structure of *trans*-dioxo-5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinatoruthenium(VI) has been solved. The cyclic voltammetry data are reported for many of the porphyrins studied [11]. New nitrido complexes of osmium(VI) and ruthenium(VI) have been prepared and examined as oxidants. Nitrido complexes with an ancillary chromate ligand are described. The reaction between $[M(N)(CH_2SiMe_3)_2(Cl)_2]^-$ (where M = Ru, Os) with Ag_2CrO_4 or K_2CrO_4 affords $[M(N)(CH_2SiMe_3)_2(CrO_4)]^-$. The molecular structure of the ruthenium analogue has been determined. All of these complexes are thermally stable to air and water. The kinetics for the oxidation of benzyl alcohol to benzaldehyde using $[Os(N)(CH_2SiMe_3)_2(CrO_4)]^-$ and oxygen as the secondary oxidant have been measured. The reaction is first order in both the nitrido complex and oxygen. A mechanism involving a β-elimination and oxygen insertion as the rate-limiting step is discussed [12]. A dissertation describing the synthesis, properties, and reactivity of ruthenium(II) carboxylate complexes has been published [13].

The reaction of $[OsBr_6][NBu_4]_2$ with excess PPh_3 in the presenceof $AcOH/Ac_2O$ (80:20) yields the bioctahedral complex $(\mu\text{-}Br)_3[Os(CO)(PPh_3)_2][OsBr_2(PPh_3)]$, which is ligated by the three bridging bromide ligands. This same complex reacts with MeCN to give the compounds *cis*- and *trans*-$Os(Br)_2(CO)(MeCN)(PPh_3)_2$. The *cis* isomer is kinetically favored and is shown to transform into the thermodynamically favored *trans* isomer [14]. The reactivity of the water-soluble complex $[Ru(H_2O)_6][tos]_2$ has been explored with functionalized alkenes. Complex formation, alkene isomerization, and metathesis chain transfer are reported [15]. The synthesis and characterization of mono- and bimetallic ruthenium complexes are presented. The ligand reduction potential and the steric crowding around the ruthenium control the observed redox and spectroscopic properties [16]. The complex $Ru(dmpe)_2(H)(naphthyl)$ has been examined with several substituted phenyl isocyanides as a route to indoles. The mechanistic aspects for this reaction have been investigated, and related data on N–H bond activation is reported [17]. The photochemistry of $Ru(dmpe)_2(H)_2$ has been investigated by using laser flash photolysis. Optical excitation leads to the reductive elimination of H_2 and generation of the 16-electron species $Ru(dmpe)_2$. The rate of reaction of $Ru(dmpe)_2$ with H_2 and CO has been measured and found to be close to the diffusion controlled limit. The synthesis of $Ru(CO)_2(PMe_3)_2(H)_2$ is described and the thermal reaction of this complex with alkynes has been found to give the alkenyl hydride complexes $Ru(CO)_2(PMe_3)_2(CR{=}CHR)(H)$ [18]. An improved procedure for the asymmetric hydrogenation of β-keto esters has been reported with a ruthenium catalyst [19].

The asymmetric dihydroxylation of alkenes has been studied by using new osmium(VI) to osmium(VIII) oxidants. Ligand modifications on the ancillary cinchona alkaloid ligands have led to substantially higher enantioselectivities [20]. A report on asymmetric osmium tetraoxide hydroxylation of alkenes has appeared. High enantiomeric excesses in alkene dihydroxylation were achieved when chiral *N,N'*-dialkyl-1,2-diphenylethane-1,2-diamines are employed as a chiral auxiliary. The pH requirements for alkene dihydroxylation have also been studied [21]. Mechanistic studies on the osmium-catalyzed asymmetric dihydroxylation of conjugated and non-conjugated dienes are presented [22].

The synthesis and spectroscopic characterization of the cyclic carbene complex (carbonyl)(η^5-cyclopentadienyl)(1-methoxy)ruthenacyclopentene are described [23]. Cyclometallated imine complexes have been prepared by allowing $(\eta^6\text{-}C_6R_6)Ru(PMe_3)_2(X)_2$ (where R = H, alkyl; X = Cl, I) to react with benzylidene imines. The reaction of the cyclometallated imines with nucleophiles yields amides with very high diastereoselectivity *via* a kinetically controlled process. NMR data and X-ray crystal structures are reported [24]. New $[(\text{polychlorobenzene})RuCp]^+$ complexes have been synthesized from $[CpRu(MeCN)_3]^+$. The use of these complexes in the synthesis of natural products based on vancomycin is presented [25]. The reaction between $CpRu(PPh_3)_2Cl$ and RS^- yields the corresponding thiolate complexes $CpRu(PPh_3)_2SR$. CS_2 is shown to insert into the Ru–S bond to give the thioxanthate complexes $CpRu(PPh_3)_2S_2CSR$. The X-ray crystal structures of $CpRu(PPh_3)(CO)SS(CHMe_2)$, $CpRu(PPh_3)(CO)SSS(n\text{-}C_3H_7)$, $CpRu(PPh_3(CO)SS(O)(CHMe_2)$, and $CpRu(PPh_3)(CO)SS(O)_2(4\text{-}C_6H_4Me)$ have been determined [26]. The "Cp*Ru" fragment has been allowed to react with 10,11-dimethoxyaporphine. Only one of the four possible diastereoisomeric products was isolated and whose structure was unequivocally established by X-ray crystallography [27].

The dinuclear complex $Ru_2(dmpm)_2(CO)_5$ has been obtained from the reaction between $Ru_3(CO)_{12}$, dmpm, and CO. The electron-rich nature of this dimer is demonstrated by its reactivity towards electrophiles. Non-first order ^{31}P NMR data and ten X-ray structures of $Ru_2(dmpm)_2$ A-frame complexes are discussed [28]. The synthesis, redox, and spectroelectrochemical studies of complexes of the form $[L_3m(\mu\text{-}X)_3ML_3]^{n+}$ (where M = Ru, Os; L = phosphine; X = Cl) have appeared. The nature of the metal–metal interaction is classified according to the criteria developed by Robin and Day [29].

Tercyclopentadienyl diheterotrimetallic complexes have been synthesized and their reactivity investigated. Photoisomerization studies are also included [30]. The synthesis, characterization, and reactivity studies of mixed-metal binuclear ruthenium complexes have appeared [31]. The photophysics of $Ru_3(CO)_{12}$ in fluid solution have been investigated by using time-resolved infrared spectroscopy. The transient intermediate $Ru_3(CO)_{11}$ reacts with CO and donating solvents in a second-order reaction. The second-order rate constants have been calculated [32]. The reaction of $Ru_3(CO)_{12}$ with added chloride has been studied and the rates of formation of $[Ru_3(CO)_{11}(Cl)]^-$ measured. Two possible mechanisms are discussed on the basis of the kinetic data collected [33]. P–C bond cleavage reactions have been explored in the reaction between $Ph_2PC{\equiv}CR$ (where R = Ph, ^tBu, ^iPr) and the 46-electron cluster $(\mu\text{-}H)Ru_3(CO)_9(\mu\text{-}PPh_2)$. The isolated clusters have the form $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CR)$, which result from a phosphido transfer to the cluster coupled with transfer of the hydride ligand and formation of the acetylene ligand. X-Ray crystallography has established these clusters as five-vertex *nido* clusters with a $\mu_3\text{-}\eta^2\text{-}\|$ acetylene ligand. Pyrolysis of $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}PPh_2)$ gives a range of products, of which the heptanuclear cluster $Ru_7(CO)_{18}(\mu_4\text{-}PPh)_2$ and the octanuclear cluster $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu\text{-}PPh_2)$ have been crystallographically characterized [34]. The reaction of $Ru_3(CO)_{12}$ with dppee has been examined. The synthesis of $Ru_3(CO)_9\{(PPh_2)_2CHCH_2PPh_2\}(PEt_3)$ and its reaction with other metal complexes are reported. Hydrogen activation studies have been carried out with $Ru_3(CO)_{12-2x}(dppee)_x$ (where $x = 1, 2$) [35]. The fluxional behavior of hydride ligands on tri- and tetraruthenium alkylidyne clusters have been studied by using variable-temperature ^1H and ^{13}C NMR spectroscopy. The reaction between $(\mu\text{-}H)_3Ru_3(CO)_8(MeCN)(\mu_3\text{-}CPh)$ and cyclopentadiene affords the new clusters $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}CO)(\eta^5\text{-}Cp)(\mu_3\text{-}CPh)$ and $Ru_3(CO)_6(\mu\text{-}CO)_2(\eta^5\text{-}Cp)(\mu_3\text{-}CPh)$. Hydrogenation of the latter cluster, which was also characterized by X-ray crystallography, gives the former cluster. The new cluster $(\mu\text{-}H)Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}COMe)$ has been isolated from the reaction between $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}COMe)$ with either $Ru(CO)_5$ or $Ru(CO)_4(\text{ethylene})$ and structurally characterized [36]. Ruthenium clusters containing a highly coordinated oxo, acetamidato, or sulfido ligand have been prepared. The oxo cluster $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$ has been synthesized from the oxo cluster $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ and $Ru_3(CO)_{10}(MeCN)_2$. The chemistry of the sulfido cluster $[Ru_3(CO)_9(\mu_3\text{-}S)]^{2-}$ has been investigated with the complexes $[M(CO)_3(MeCN)_3]^+$ (M = Mn, Re) and it is demonstrated that the new clusters $HRu_3M(CO)_{12}(MeCN)_2(\mu_4\text{-}S)$ can be isolated [37]. Two isomeric hydridovinyl clusters have been obtained from the reaction between $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)$ and acetylene. The solid-state structure of each isomer has been determined by X-ray diffraction analysis. When the same cluster was allowed to react with ethylene, the cluster $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$ was isolated. The reaction of diazomethane with $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)$ has also been examined, and the resulting product characterized by mass spectrometry and solution NMR techniques [38]. $Os(CO)_5$ reacts with $Os_3(CO)_{10}(\text{cyclooctene})_2$ to afford the first tetraosmium binary carbonyl cluster $Os_4(CO)_{15}$. The molecular structure of this cluster consists of a planar, "kite-like" arrangement of osmium atoms. The cluster $Os_4(CO)_{16}$, which was obtained from the reaction between CO and $Os_4(CO)_{15}$, adopts a cyclobutane-like structure. Thermolysis of $Os_4(CO)_{15}$ gives $Os_4(CO)_{14}$, which is shown to possess a pseudo-tetrahedral structure. Carbonyl mobility is still rapid at −130°C and the IR spectrum reveals only three broad carbonyl stretches. This behavior is discussed in the context of CO-exchange that occurs on the infrared time scale [39]. The new clusters $HFeRu_2(CO)_{10}(\mu\text{-}CX)$ (where X = OMe, NMe_2) have been prepared by a metal fragment exchange route. The mechanism of ligand substitution in $HFeRu_2(CO)_{10}(\mu\text{-}CNMe_2)$ has been investigated and the site of phosphine ligand attachment discussed [40]. The interaction between ruthenium and osmium clusters with magnesia has been studied both experimentally and theoretically [41]. The new platinum–osmium cluster $Pt_2Os_3(CO)_{10}(1,5\text{-}COD)_2$, $PtOs_3(CO)_8(1,5\text{-}COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$, and $PtOs_6(CO)_{22}$ have been isolated from the reaction between $Os_3(CO)_{10}(MeCN)_2$ and $Pt(1,5\text{-}COD)_2$. The reactivity of the first cluster with CO and alkynes is reported. The pyrolysis of this same cluster yields the four high nuclearity clusters $Pt_4Os_6(CO)_{22}(1,5\text{-}COD)$, $Pt_5Os_6(CO)_{21}(1,5\text{-}COD)_2$, $Pt_4Os_6(CO)_{19}(1,5\text{-}COD)_2$, and $Pt_4Os_7(CO)_{22}(1,5\text{-}COD)_2$ [42].

The results of an investigation dealing with the phases and microstructures of rapidly solidified Al–Cu–Ru face-centered icosahedral alloys are presented [43]. Metal-modified Ru(001) surfaces have been examined by using metastable quenching spectroscopy in addition to thermal desorption spectroscopy [44]. Al_2O_3 films have been prepared on Ru(001) and examined for electronic and vibrational structure [45]. The diffusion of hydrocarbon adsorbates on a Ru(001) single-crystal surface has been explored by using Laser-Induced Thermal Desorption (LITD) techniques [46]. The reaction mechanism of alcohol and aldehyde formation from syngas has been investigated with a Ru/SiO_2 catalyst [47]. Oxygen reduction and generation reactions on ruthenium metal and its pyrochlores are reported [48]. Zeolite-supported ruthenium catalysts have been synthesized and examined in the water gas shift reaction [49].

A study on the β end-point energy for the decay on neutral ^{187}Re to singly ionized ^{187}Os is reported [50]. The osmium isotopic compositions and concentrations of marine and continental sediments have been determined. Sediment osmium was analyzed by ID-SIMS [51]. A report on the osmium concentrations in modern and ancient sediments has appeared [52].

2. Mononuclear complexes

2.1. Organometallic porphyrins

The transformation of a methyl group into a carbonyl group on a ruthenium porphyrin has been observed. The reaction between $Ru(OEP)(CH_3)$ and TEMPO affords Ru(OEP)(CO). Isotopic labeling of the methyl carbon confirms that the source of carbonyl carbon is derived from the initial methyl group. The X-ray structure of Ru(OEP)(CO)(TEMPO) and pertinent spectroscopic data are presented [53]. The reactivity of $Ru(OEP)(p\text{-}XC_6H_4)_2$ complexes has been studied by cyclic voltammetry. Oxidation to $[Ru(OEP)(aryl)_2]^+$ leads to a Ru-to-N migration of an aryl group, while aryl group loss is observed from the dianion $[Ru(OEP)(aryl)_2]^{2-}$. The mechanism associated with each of these reactions is discussed [54]. The redox chemistry of $Ru(OEP)(CH_3)_2$ has been explored, and a scheme for the formation of the bridging methylene complex $[Ru(OEP\text{-}N\text{-}\mu\text{-}CH_2)(CH_3)]^+$ reported [55].

A report that includes the synthesis of $[Ru(OEP)]_2$, $Ru(OEP)(CO)(CH_3OH)$, and $Ru(OEP)(py)_2$ has appeared [56]. The metalloporphyrin hydride complexes [M(Por)(L)(H)][K] (where M = Ru, Os; Por = OEP, TMP; L = THF, 1-tert-butyl-5-phenylimidazole, PPh_3, py) have been synthesized from $[M(Por)][K]_2$. The mechanism for product formation and electrochemical studies of bimolecular H_2 elimination are described. The relationship between the porphyrin hydrides and hydrogenase enzymes and the hydrogen electrode reaction is stressed [57]. The synthesis of the stable, bridged dinitrogen complex $(\mu\text{-}N_2)Ru_2$(diporphyrinatobiphenylene)(1-tert-butyl-5-phenylimidazole$)_2$ is described. The reactivity of this complex is discussed with respect to dinitrogen reduction. The redox properties of this porphyrin have been examined by cyclic voltammetry [58]. The synthesis and spectroscopic characterization of the dihydrogen complexes $M(OEP)(L)(H_2)$ (where M = Ru, Os; L = THF, 1-tert-butyl-5-phenylimidazole) have been published. T_1 NMR data have been used to calculate the H–H bond length. Mechanisms are presented for the catalytic dihydrogen oxidation using Ru(OEP) complexes [59].

The synthesis and solution characterization of tert-butylimido complexes of osmium(VI) and ruthenium (VI) porphyrins have appeared [60]. The first (dialkylamido)ruthenium porphyrin complex $Ru(3,4,5\text{-}MeO\text{-}TPP)(NPh_2)_2$ is reported. A qualitative molecular orbital scheme that shows the π interactions between the ruthenium and nitrogen atoms is shown and discussed [61]. The synthesis and characterization of carbonyl- and dioxo-containing ruthenium/osmium tetrapropylporphycene complexes are reported [62]. New dialkoxyosmium(IV) porphyrins have been prepared from $Os(Por)(N_2)(THF)$ (where Por = Tpp, 3,4,5-MeO-TPP). Besides NMR spectroscopic data, the X-ray crystal structures of $Os(TPP)(OEt)_2$, $Os(TPP)\{OCH(CH_3)_2\}_2$, and $Os(TPP)(OPh)_2$ are presented. All three structures exhibit *trans* diaxial alkoxide groups [63].

The reaction between 2-monofluoroethyl isocyanide and 2,2,2-trifluoroethyl isocyanide with Ru(TPP)(CO)

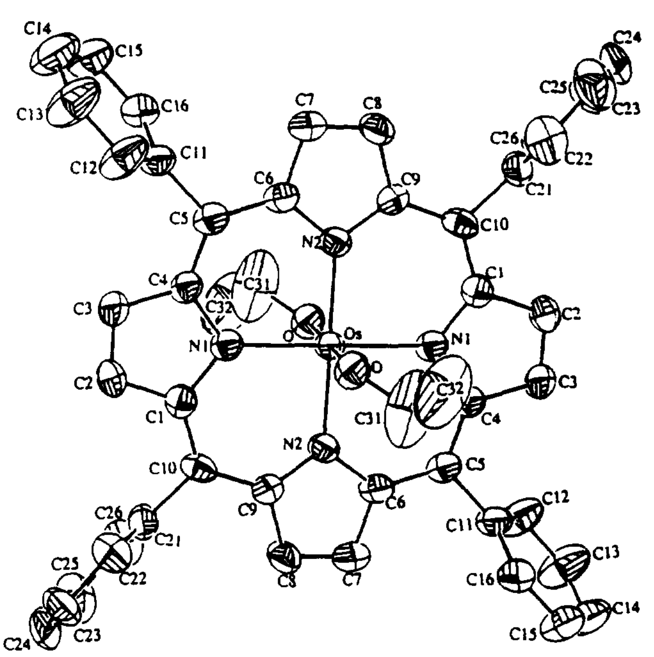

Fig. 1. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

has led to the formation of the corresponding isocyanide-substituted porphyrin complex [64]. The redox reaction between *trans*-Ru(TPP)(O)$_2$ and Fe(salmah) is reported [65]. The resonant nonlinear optical properties of films of soluble oligomeric bridged (phthalocyaninato)ruthenium(II) complexes have been investigated. The synthesis and semiconducting properties of bridged (phthalocyaninato)osmium compounds are described. The ancillary ligands used with these compounds are the bidentate nitrogen ligands pyrazine and tetrazine [67]. Several osmium porphyrin carbene complexes, Os(TPP)(=CRR′) (where R = R′ = *p*-tolyl; R = H, R′ = SiMe$_3$, CO$_2$Et), have been prepared and found to convert ethyl diazoacetate to diethyl maleate and diethyl fumarate in high yields and high stereoselectivity [68]. The use of the catalyst Ru(TMP)(O)$_2$ in alkane and alkyl alcohol oxidation has been published. The oxidant employed in these reactions is based on 2,6-dichloropyridine N-oxide [69].

2.2. Halides

The fluoride complex *cis*-OsF$_2$O$_2$ has been prepared by allowing OsO$_4$ to react with KrF$_2$ in HF [70]. Data on the magnetic exchange and zero-field splitting in the d^3 [Os^{V}Cl$_6$]$^-$ ion have been reported. DV-Xα calculations have also been carried out [71]. OsOF$_5$ has been investigated by electron spin resonance spectroscopy in several different matrices at 77 K. Hyperfine coupling to ^{189}Os and to four equivalent fluorine atoms was observed. No coupling to the axial fluorine atom was noticed [72]. Ruthenium K-edge EXAFS data for RuF$_6$ and [RuF$_6$][K] have been collected at 10 K to give the ruthenium–fluorine bond distance in each complex [73]. The reaction of AsF$_5$ with [RuF$_6$]$^{2-}$ in anhydrous HF solution affords RuF$_4$. The structure of RuF$_4$ has been determined by using synchrotron and neutron powder diffraction data [74]. A report describing the ^{99}Ru Mössbauer spectroscopic and magnetization data on black α-RuCl$_3$ and brown β-RuCl$_3$ has been published [75]. The hexachloroosmate(V) oxidation of tetrabutylammonium tert-butylcyanoacetate to *meso-* and *rac*-2,3-di-tert-butylsuccinonitrile is described. This report represents the metal ion-based oxidant that simulates the Kolbe anodic oxidation of carboxylates [76].

The structure of reduced rare-earth metal halides of the form R$_4$Br$_4$Os (where R = Y, Er) has been determined [77]. The synthesis of RuBr$_2$(DMSO)$_3$ has been investigated. The crystal structure of [*fac*-RuBr$_3$(DMSO)$_3$][NEt$_4$]·0.5MeOH is included in this report [78]. [OsBr$_6$]$^{2-}$ reacts with neat 1,2-ethanediamine to give *cis*-[Os(en-H)$_2$(en)]$^{2+}$. The spectroscopic and redox data for this and related compounds are discussed [79]. The reaction between RuCl$_3$(THF)$_3$ and Mg(mes)$_2$(THF)$_2$ yields the homoleptic mesityl complex [Ru(mes)$_4$]$^+$, whose molecular structure was determined by X-ray crystallography [80].

The ruthenatetraborane complex Ru(H)(CO)(PPh$_3$)(B$_3$H$_8$) has been prepared from the reaction between [B$_3$H$_8$][NMe$_4$] and Ru(Cl)(H)(CO)(PPh$_3$)$_3$ or [Ru(H)(CO)(MeCN)$_2$(PPh$_3$)$_2$]$^+$. The X-ray structure of the product is presented, and the reactivity towards N-halosuccinimides is reported [81].

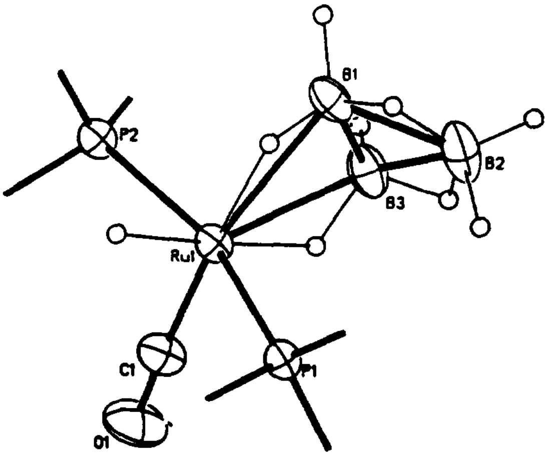

Fig. 2. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

2.3. Hydrides

The electron-rich alkene [=CN(CH$_2$Ph)CH$_2$CH$_2$N-CH$_2$Ph]$_2$ reacts with Ru(Cl)(H)(PPh$_3$)$_3$ to give the five-coordinate carbeneruthenium(II) complex Ru(Cl)-L(PPh$_3$)$_2$, which results from the ortho-metallation of one of the N-benzyl substituents. The existence of the metallocycle was established by X-ray crystallography [82]. Treatment of Ru(H)(Cl)(CO)(PPh$_3$) with [HB(1-pz)$_3$]$^-$ gives Ru{η^3-HB(1-pz)$_3$}(PPh$_3$)(CO)(H) in excellent yield. The corresponding chloride is obtained by treating the hydride with chloroform. The reactivity of the chloride complex with donor ligands is presented along with the X-ray structure of [Ru{η^3-HB(1-pz)$_3$}(PPh$_3$)(CO)(PMe$_3$)]$^+$ [83]. Kinetic data on the addition of haloalkanes to alkenes using the catalysts Ru(H)$_3$(SiMe$_2$Ph)(PPh$_3$)$_3$ and Ru(H)$_4$(PPh$_3$)$_4$ have appeared. The mechanism associated with this reaction is discussed [84]. Intramolecular ligand exchange in Ru(H)$_2$-(CO)(PPh$_3$)$_3$ has been investigated by NOESY NMR spectroscopy. A trigonal twist process is shown to be operative in the ligand exchange process [85]. The alkylhydrido complexes Os(H)(CH$_3$)(CO)$_2$(PR$_3$)$_2$ are obtained from Os(H)(η^2-BH$_4$)(CO)(PR$_3$)$_2$ when treated with the protic solvents ethanol or 2-methoxyethanol. The X-ray structure of the isopropyl phosphine complex is included, and the reactivity of the methyl moiety with electrophiles is outlined [86].

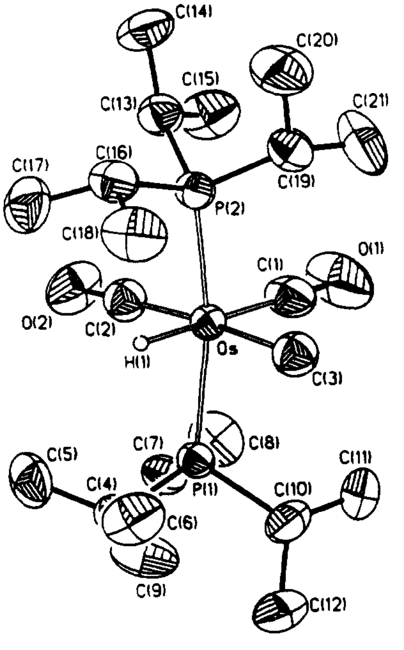

Fig. 3. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

The hydrogenation of benzylideneacetone has been explored with several dihydrogen osmium catalysts. The catalytically inactive complex *trans*-(hydride, dihydrogen)-Os(H)(Cl)(η^2-H$_2$)(CO)(P-^{i}Pr$_3$)$_2$ is also shown to isomerize to the *cis* isomer before dissociation of molecular hydrogen [87]. H$_2$ reacts with Ru(H)(Cl)-(CO)(P-^{i}Pr$_3$)$_2$ in fluid solution to produce RuH(H$_2$)-(Cl)(CO)(P-^{i}Pr$_3$)$_2$ and Ru(H)$_2$(H$_2$)(CO)(P-^{i}Pr$_3$)$_2$ when the reaction is run in the presence of KOH. The structures of these compounds have been assigned by using NMR data [88]. Phenylacetylene hydrogenation to styrene is shown to be catalyzed by the *cis*-hydrido (η^2-hydrogen)ruthenium(II) complex [Ru(H)(η^2-H$_2$)-(PP$_3$)]$^+$. Kinetic data and a reaction mechanism that involves this molecular hydrogen complex as an active catalyst are presented [89]. The reactivity of M(H)(η^2-BH$_4$)(CO)(P-^{i}Pr$_3$)$_2$ (where M = Ru, Os) towards electrophiles has been studied. The catalytic activity of related complexes in asymmetric hydrogen transfer from 2-propanol to acetophenone is described [90]. The dihydride complexes Ru(H)$_2$(L)(triphos) {where L = CO, P(OCH$_2$)$_3$CEt, PMe$_2$Ph} have been prepared from corresponding dichloride with NaBH$_4$. Protonation of these complexes with HBF$_4 \cdot$OEt$_2$ gives the η^2-dihydrogen complexes [Ru(H)(η^2-H$_2$)(L)(triphos)]$^+$, which have been confirmed by variable-temperature ^{1}H NMR T$_1$ measurements and ^{1}H$_{HD}$ coupling constants [91]. The dihydrogen complexes [M(H)(η^2-H$_2$)-(PP$_3$)]$^+$ (where M = Ru, Os) have been studied by inelastic neutron scattering experiments and the barrier to rotation of the dihydrogen ligand determined [92]. Molecular dihydrogen and hydrido complexes of ruthenium(II) with ancillary ferrocenyl-based phosphine amine ligands and monodentate phosphine ligands have been synthesized, studied by variable-temperature NMR spectroscopy, and examined by X-ray crystallography [93].

2.4. Phosphines

Several new dihydrobis(benzotriazolyl)borato complexes of ruthenium(II) have been prepared. Treatment of [H$_2$B(bta)$_2$]$^-$ with Ru(Cl)(R)(CO)(PPh$_3$)$_n$ (where $n = 3$, R = H; $n = 2$, R = aryl and alkenyl groups) furnishes the chelate complexes Ru(R)(CO)(PPh$_3$)$_2${η^2-H$_2$B(bta)} in high yield. The hydrido complex, which may also be prepared from [Ru(H)(MeCN)$_2$-(CO)(PPh$_3$)$_2$]$^+$, gives the corresponding chloride complex upon treatment with N-chlorosuccinimide [94]. The synthesis and X-ray crystal structure of Ru(Cl)(PPh$_3$)$_2${κ^3-HB(pz)$_3$} have been published. Halide displacement by [B$_3$H$_8$]$^-$ yields the ruthenatetraborane complex Ru(B$_3$H$_8$)(PPh$_3$){κ^3-HB(pz)$_3$} [95].

The reaction between the *cis* hydridochloro complex Ru(H)(Cl)(PP$_3$) with Tl(I) ions gives [Ru(ClTl)(H)-

$(PP_3)]^-$. X-Ray crystallography confirms the presence of the TlCl ligand in the product [96]. The characterization and reactivity of the unsaturated complex Ru(dmpe)$_2$ have been investigated by using matrix isolation and transient spectroscopic techniques. Optical excitation of *cis*-Ru(H)$_2$(dmpe)$_2$ generates the complex of interest. The reaction of Ru(dmpe)$_2$ with various ligands has been studied and the second-order rate constants reported for these reactions. In the case of H_2 and CO, the reaction with Ru(dmpe)$_2$ is close to the diffusion limit. The reaction chemistry is discussed and it is suggested that Ru(dmpe)$_2$ has a singlet ground state with a square-planar coordination geometry [97]. The kinetics and mechanism for the conversion of nitroaromatics and methanol to methyl N-arylcarbamates using the catalyst Ru(CO)$_3$(dppe) are presented. Aniline has been observed as a reaction byproduct as well as an intermediate in the formation of carbamate. This report includes the X-ray structure of Ru(CO)$_2$(dppe){C(O)N(Ar)O} (where Ar = *p*-C_6H_4-Cl), which was obtained from the room temperature reaction between Ru(CO)$_3$(dppe), $ArNO_2$, and CO. High-pressure CIR spectral and NMR data are also presented [98]. Ruthenium acetate complexes possessing triphosphine ligands have been synthesized. Ru(Cl)$_2$(Cyttp) reacts with AgOAc and NaOAc to yield *mer*-Ru(Cl)(OAc)(Cyttp), *fac*-Ru(Cl)(OAc)(Cyttp), or *fac*-Ru(OAc)$_2$(Cyttp) depending on the initial conditions. The molecular structure of *fac*-Ru(Cl)(OAc)(Cyttp) was determined by X-ray crystallography [99]. *cis-mer*-Ru(H)$_2$(CO)(Cyttp) reacts with excess HX (where X = BF_4, O_3SCF_3) to afford air-stable complexes with two weakly coordinated anion ligands. The X-ray structure of *cis-mer*-Ru(O_3SCF_3)$_2$(CO)(Cyttp) is reported. Variable-temperature NMR data support the existence of complexed and free X ligands. The use of these complexes in ligand substitution reactions is discussed [100].

A practical synthesis of BINAP–ruthenium(II) dicarboxy-ate complexes has appeared. The starting ruthenium complex employed in this synthesis is [Ru(Cl)$_2$(benzene)]$_2$ [101]. An improved procedure for the synthesis of [Ru(Cl)$_2$(BINAP)]$_2$ · NEt_3 and the effect of trace amounts of acid on the ruthenium(II)-BINAP catalyzed asymmetric hydrogenation of β-keto esters have been published [102]. The biphosphine complexes Ru(Cl)$_2$(DMSO)$_2$(bp) and *cis*-Ru(Cl)$_2$(bp)$_2$ have been isolated from the reaction between bp and Ru(Cl)$_2$(DMSO)$_4$. The structure of the former complex has been established by X-ray crystallography [103]. Several ruthenium(II) complexes derived from [RuX{(S)–BINAP}(arene)]$^+$ (where X = halide; arene = benzene, *p*-cymene) have been prepared and structurally characterized by X-ray crystallography. The catalytic activity of these complexes has been examined in the asymmetric hydrogenation of methyl 3-oxobutanoate [104]. The asymmetric hydrogenation of prochiral carboxylic acids and functionalized carbonyl complexes has been explored with ruthenium(II)–BINAP catalysts. The catalysts prepared for this study were Ru(Cl)$_2$(ArCN)$_2$(BINAP) (where ArCN = benzonitrile, 2-furancarbonitrile, pentafluorobenzonitrile) [105].

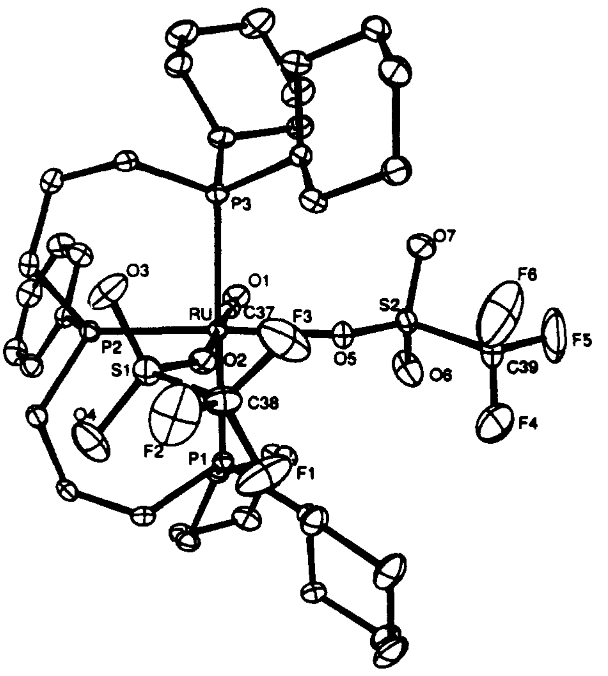

Fig. 4. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

Models for linear acetylide polymers have been examined by using ruthenium(II) phosphine complexes. The bis(acetylide) and bis(diacetylides) complexes *trans*-Ru(CO)$_2$(PEt$_3$)$_2${(C≡C)$_n$R}$_2$ (where $n = 1$, R = SiMe$_3$; $n = 2$, R = SiMe$_3$; $n = 2$, R = H) have been synthesized and fully characterized by IR and Raman spectroscopy. The solid-state structure of *trans*-Ru(CO)(PEt$_3$)$_2$(C≡CSiMe$_3$)$_2$ has been established by X-ray crystallography [106]. A report demonstrating the π stabilization of unsaturation in Ru(H)(X)(R)(P-^{t}BuMe$_2$)$_2$ (where X = halide; R = anilide, alkoxides) has appeared. Included in this report is the X-ray structure of Ru(H)(OSiPh$_3$)(CO)(P-^{t}BuMe$_2$)$_2$ [107]. The reaction between *cis*-Os(Br)$_2$(CO)$_4$ with ether–phosphine ligands yields complexes of the form Os(Br)$_2$(CO)$_2$(P–O)$_2$. The chemistry of the phosphine-substituted complexes and the properties of the corresponding chelated species Os(Br)$_2$(P–O)$_2$ are presented [108]. The X-ray structure of *cis*-Ru(Cl)$_2$(CO)(P–O)$_2$, which exhibits one chelated P–O ligand and one phosphine-coordinated P–O ligand, and the fluxional NMR behavior of this and related complexes have been published [109]. The reaction between the functionalized ether–phosphine ligand $MeO(CH_2)_2P(Ph)(CH_2)_3Si(OMe)_3$ with $Ru(Cl)_2(PPh_3)_3$ and $Ru(H)(Cl)(CO)(PPh_3)_3$ is described [110]. Butadienyl complexes have been isolated from the reaction between $Ru(H)(Cl)(CO)(PPh_3)_3$ and *trans*-R′CH=CHC≡CR″ (where R′ = R″ = $SiMe_3$, ^tBu, Me, Et). Instead of having an 18-electron configuration at the ruthenium by the normal η^3-coordination of the butadienyl ligand, these complexes are unsaturated as a result of η^1-coordination of the butadienyl ligand [111]. Carbon–nitrogen bond cleavage in β-nitrostyrene has been observed in the reaction with $Ru(H)(OAc)(CO)(PPh_3)_2$. IR data indicate that a N-bonded nitro group is present in the product which has been identified as $Ru(NO_2)(OAc)(CO)(PPh_3)_2$. The byproduct in this reaction is styrene [112]. $Os(Cl)_2(PPh_3)_3$ reacts with $P(C_6H_4SH\text{-}2)_3$ to afford the osmium(II) complex OsL. The nature of the ancillary L ligand has been determined by X-ray diffraction analysis to be a hexadentate ligand, which was formed by the oxidative coupling of two $P(C_6H_4S\text{-}2)_3$ ligands by two disulfide bonds [113]. Three isomeric products have been spectroscopically characterized when $Ru(Cl)(H)(PPh_3)_3$ was allowed to react with COT. The interconversion of two of these isomers has been studied through the use of NMR spectroscopy [114]. The synthesis, spectroscopic characterization, and redox reactivity studies on cationic ruthenium(III) complexes have appeared [115]. The ring-opening metathesis polymerization (ROMP) of norbornene by the ruthenium carbene complex $Ru(Cl)_2(PPh_3)_2(=CHCH=CPh_2)$ has been reported [116]. The new water-soluble phosphine complexes $Ru(Cl)_2(PTA)_4$ and $Ru(Cl)_2(PTA)_4 \cdot 2HCl$ have been synthesized from $RuCl_3$ and shown to be catalytically active in the hydrogenation of unsaturated aldehydes to unsaturated alcohols. The X-ray crystal structure of the former complex reveals the presence of *cis* chloro groups [117]. Several TPPTS-substituted ruthenium complexes have been synthesized and examined for their catalytic efficacy in propionaldehyde hydrogenation reactions. The kinetic data, salt effect on the reactivity, and a plausible mechanism are presented and discussed [118]. The synthesis of ruthenium complexes with ancillary TPPTS ligands is reported, and spectroscopic data on the structures of these TPPTS-substituted complexes relative to their PPh_3-substituted complexes are discussed [119].

2.5. *Carbonyls*

Stereospecific decarbonylation of *cis,trans*-$Ru(^{13}CO_a)(CO_b)(PMe_3)_2(COMe)(I)$ occurs in the presence of [Na][BPh_4] to give $[Ru(CO_a)(CO_b)(^{13}CO_b)(PMe_3)_2(Me)]^+$ [120]. The synthesis and reactivity of hydrido, halogeno, and σ-organyl ruthenatetraboranes have been presented. The X-ray structure of $Ru(H)(B_3H_8)(CO)(PPh_3)_2$ has been solved, and sodium dialkyldithiocarbamate is shown to displace the B_3H_8 moiety from the chloro complexes [121]. Secondary amines react with $Ru(COEt)(Cl)(CO)(PPh_3)_2$ under CO and/or ethylene to yield the propionyl-carbamoyl complexes $Ru(COEt)(CONR_2)(CO)(PPh_3)_2$ (where $NR_2 = NEt_2$, $\overline{N(CH_2)_4C}H_2$, NMe_2). All new complexes have been isolated and characterized by NMR and IR spectroscopy [122]. *trans*-3,4-Bis(trifluoromethylsulfonyloxymethyl)oxolane has been allowed to react with $[Os(CO)_4][Na]_2$. The two products isolated correspond to the *cis* and *trans* forms of 3-oxo-7-osmabicyclo[3.3.0]octane, of which the molecular structure of the *cis* isomer was unequivocally established by X-ray crystallography [123]. The osmacyclobutane complex $Os(CO)_3(CH_2CD_2CH_2)$ was prepared from $[Os(CO)_4][Na]_2$ and $TsOCH_2CD_2CH_2OTs$. The mechanism for propylene extrusion has been investigated and both α- and β-hydrogen eliminations are observed. CO insertion into the osmacyclobutane ring is facile and may be a prerequisite in the propylene extrusion mechanism [124]. The synthesis and reactivity of the (isocyanide) ruthenate analogue of tetracarbonylferrate have been presented [125].

The hydrolysis of $Os(SiCl_3)(Cl)(CO)(PPh_3)_2$ affords the coordinately unsaturated trihydroxylsilyl complex $Os\{Si(OH)_3\}(Cl)(CO)(PPh_3)_2$, whose molecular structure has been determined by X-ray crystallography. Also isolated from the hydrolysis reaction is the diosmium tetrahydroxydisiloxane complex $[Os(Cl)(CO)(PPh_3)_2Si(OH)_2]_2O$. This disiloxane complex has been characterized by solution methods and X-ray diffraction analysis [126]. The mechanism of halide-induced disproportionation of $[M(CO)_3(PCy_3)_2]^+$ (where M = Ru, Os) has been studied by using double potential step chronocoulometry, rotating-ring-disk electrochemistry, bulk coulometry, and cyclic voltammetry. The role of ion pairing in the disproportionation reaction is thoroughly discussed [127]. A report on the carbonylation of the Ru–Me bond of $Ru(Me)(I)(CO)_2(^iPr\text{-}N{=}CHCH{=}N\text{-}^iPr)$ has appeared. The carbonylation reaction is shown to be catalyzed by $Ru(CO)_4L$ (where L = various phosphines and phosphites), $ZnCl_2$, and H^+. In the case of $Ru(CO)_4L$ catalysis, a binuclear intermediate is discussed. The X-ray crystal structures of $Ru\{C(O)Me\}(I)(CO)_2(^iPr\text{-}DAB)$ and $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTf]$ are presented. 1,3-Dipolar cycloaddition reactions to the C=N–M fragment of $Ru(CO)_3(^iPr\text{-}DAB)$ have been demonstrated. The X-ray crystal structures of $\overline{N(^iPr)C}$-

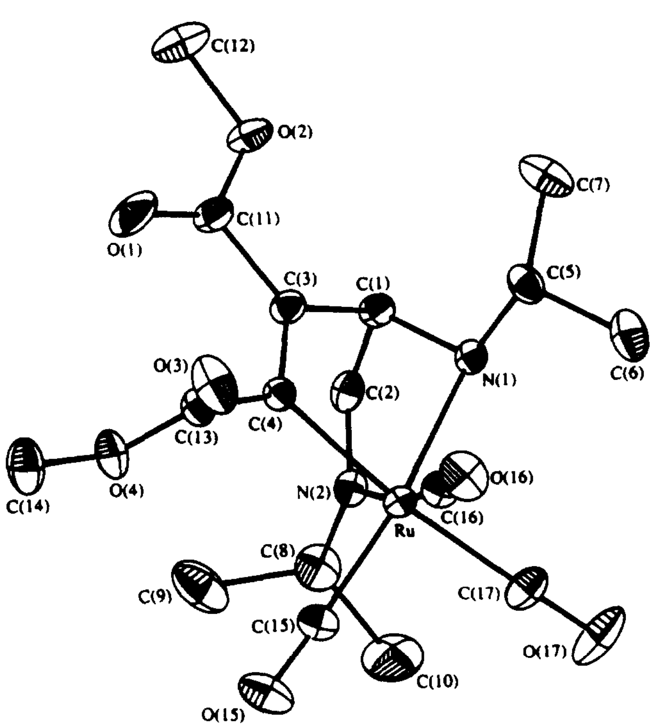

Fig. 5. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

$(O)Ru(CO)_2(PPh_3)C(CO_2Me)=C(CO_2 4\text{-}Me)C\text{-}HCH=N\text{-}(^iPr)$ and $[NH(^iPr)Ru(CO)_3C(CO_2Me)=C(CO_2Me)C\text{-}HCH=N(^iPr)]^+$ are included in this report [129].

2.6. Sulfur and oxygen ligands

The reactivity of the thiosulfate complex $[Os(O)_2(S_2O_3)_2]^{2-}$ has been investigated with organic and inorganic ligands and the vibrational spectra of the products discussed. X-Ray diffraction analysis of $[Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]^-$ reveals an octahedral geometry at the osmium center with two *trans* S-bonded thiosulfate ligands [130]. A study on the $[HSO_5]^-$ oxidation of thiols coordinated to ruthenium(III) has appeared. Included in this study are the synthesis of new (thiolato) ruthenium(III) complexes and the kinetic data related to the oxidation reaction [131].

Treatment of *cis*-$Ru(Cl)_2Me_4[14]aneS_4$ with $NaBH_4$ furnishes the new complex $[Ru_2(H)(\mu\text{-}H)(Cl)(Me_4[14]aneS_4)_2]^+$ along with *trans*-$Ru(H)(Cl)($*syn*-$Me_4[14]aneS_4)$. The former complex, which represents an example of a μ_2-hydrido complex of a crown ether without a metal–metal bond, was characterized by X-ray diffraction analysis [132]. The reaction of $Ru(Cl)_2(PPh_3)_3$ with thiacrown ethers has been examined. 1,4,7-trithiacyclononane and $Me_4[14]aneS_4$ both react with $Ru(Cl)_2(PPh_3)_3$ to give complexes derived by PPh_3 ligand substitution. The X-ray crystal structures of these products as well as the products that are formed from the reaction between $Ru(Cl)_2(CS)(OH_2)(PPh_3)_2$ and $Ru(Cl)(H)(CS)(PPh_3)_3$ with 1,4,7-trithiacyclononane are presented [133]. Treatment of $[Os(Cl)_2(4\text{-}MeC_6H_4\text{-}^iPr)]_2$ with 1,4,7-trithiacyclononane yields the bis(sandwich) complex $[Os(1,4,7\text{-trithiacyclononane})_2]^{2+}$. An alternative synthesis of this product that starts from $[Os(Cl)_6][NH_4]_2$ is also presented. The X-ray crystal structure and redox properties are discussed. The reactivity of $M(H)_2(CO)(PPh_3)_3$ (where M = Ru, Os) with 1,4,7-trithiacyclononane accompanies this report [134]. $Ru(Cl)_2(PPh_3)(1,4,7\text{-trithiacyclononane})$ has been allowed to react with $TlPF_6$ to give $[(TlCl_2)Ru(PPh_3)(1,4,7\text{-trithiacyclononane})]_2[PF_6]_2$ in CH_2Cl_2. The molecular structure of this complex has been solved by X-ray crystallography, and it is demonstrated that this product readily precipitates TlCl on dissolution in acetone and gives the chloro-bridged dimer $[Ru(Cl)(PPh_3)(1,4,7\text{-trithiacyclononane})]_2^{2+}$ [135]. Both chloride ion and phosphine ligand loss are observed in the reaction between 1,4,7-trithiacyclononane and $Ru(CH=CHR)(Cl)(CO)(PPh_3)_2$ (where R = H, ^tBu, $C_6H_4Me\text{-}4$). The isolated product, $[Ru(CH=CHR)(CO)(PPh_3)(1,4,7\text{-trithiacyclononane})]^+$, was structurally characterized by solution spectroscopic methods [136].

The complex $[Ru(CO)_3(PPh_3)_2(SMe)][BF_4]$ has been obtained from the reaction between $Ru(CO)_3(PPh_3)_2$ and $[Me_2SSMe][BF_4]$ [137]. Treatment of $Ru(Cl)(NO)(PPh_3)_2$ with thiirane-S-oxide, C_2H_2SO, yields the sulfur monoxide complex $Ru(Cl)(NO)(SO)(PPh_3)_2$, which has been shown by X-ray diffraction analysis to contain a linear nitrosyl ligand and a terminal bent sulfur monoxide group. It is demonstrated that the sulfur monoxide ligand may be oxidized to a sulfur dioxide and a sulfate group using MCPBA. These latter two complexes have been characterized by IR and NMR spectroscopies and mass spectrometry [138]. Bis(alkyl trithiocarbonato-S, S′) complexes of osmium have been synthesized and examined for geometrical isomerism. The redox properties and ESR data are included in this report. A comparison to ruthenium congeners is made and it is shown that the ruthenium congeners isomerized more rapidly [139]. The reaction of $Ru(CO)_2(pyS)_2$ with $Ru_3(CO)_{12}$ has been examined and polynuclear products have been isolated and characterized [140]. The thiocarbonyl complexes $M(SiMe_2Cl)(Cl)(CS)(PPh_3)_2$ (where M = Ru, Os) have been synthesized from $M(Ph)(Cl)(CS)(PPh_3)_2$ and $HSiMe_2Cl$. CO addition to the thiocarbonyl complexes $M(SiMe_2OEt)(Cl)(CS)(PPh_3)_2$ induces a migratory insertion reaction involving the silyl and thiocarbonyl ligands, which affords the η^2-silathioacyl complexes $M\{\eta^2\text{-}C(S)SiMe_2OEt\}(Cl)(CO)(PPh_3)_2$. The molecular structure of the

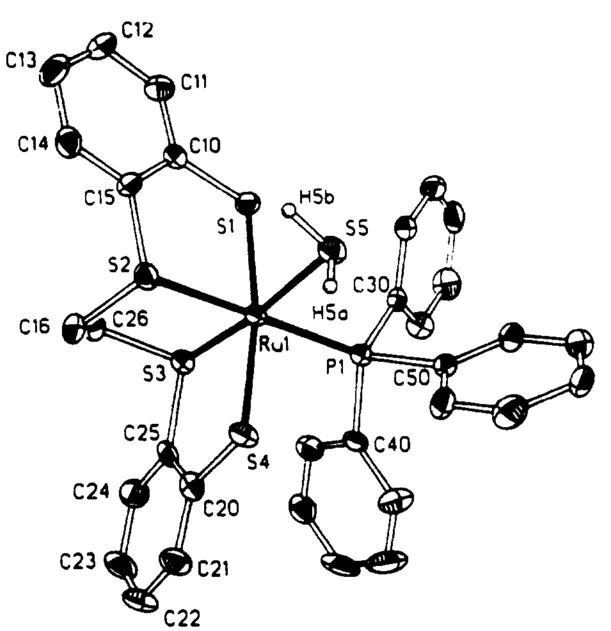

Fig. 6. Reprinted with permission from *J. Am. Chem. Soc.* Copyright 1992 American Chemical Society.

ruthenium analogue of this latter complex is presented [141]. Oxidation of thiolate ligand in $CpRuL_2(SR)$ (where $L_2 = PPh_3$, dppe, PPh_3/CO; R = Me, Ph, benzyl) by dimethyldioxirane yields the sulfone complex $CpRuL_2SO_2R$ [142]. Treatment of $Ru(CO)_2(PPh_3)_3$ or *cis,cis,trans*-$Ru(H)_2(CO)_2(PPh_3)_2$ with H_2S furnishes the complex *cis,cis,trans*-$Ru(SH)_2(CO)_2(PPh_3)_2$. X-Ray diffraction analysis confirms the structure and indicates that the mercapto protons are not involved in SH/π interactions with the phenyl rings. The same reaction was studied with $Ru(H)_2(dppm)_2$, which was shown to initially give *trans*-$Ru(H)(SH)(dppm)_2$, followed by *cis*- and *trans*-$Ru(SH)_2(dppm)_2$ upon further reaction with H_2S [143]. The structural integrity of the trigonal cores of $[M(SR)_3]^{+,\,0}$ (where M = Ru, Os; RS = S-2,3,5,6-Me_4C_6H, S-2,4,6-$^iPr_3C_6H_2$) has been explored by X-ray crystallography and electrochemical techniques [144]. Polymeric $[Ru(PPh_3)('S'_4)]_x$ [where $'S'_4$ = 1,2-bis{(2-mercaptophenyl)thio}ethane(2-)] reacts with H_2S at −70°C to give $Ru(SH_2)(PPh_3)('S'_4)$. The molecular structure of this product was determined by X-ray diffraction analysis. This is a rare example of a H_2S complex that is stabilized by hydrogen bonding with the ancillary sulfur coordination sphere. Oxidation experiments and the products that result are presented [145].

The introduction of an ethynyl group into a γ-position of a tris(β-diketonato)ruthenium(III) complex is described. The use of the ethynyl group may be used to construct homo- and heterobinuclear complexes. A stepwise two-electron oxidation and reduction through Ru^{IV}–Ru^{III} and Ru^{III}–Ru^{II} states are revealed by cyclic voltammetry for $[L_2Ru^{III}(OCMe)_24\text{-}C(\text{-}C{\equiv}C\text{-})_2C(MeCO)_2Ru^{III}L_2]$. The stabilities of mixed-valence states are discussed with respect to the comproportionation constants [146]. The redox properties of $Ru(acac)_3$ in a room-temperature molten salt have been examined. The reactivity of $[Ru(acac)_3]^-$ with the chloroaluminate molten salt is outlined [147].

The synthesis of mixed-alkyl osmium oxides of the form $(R')_2(R'')_2Os{=}O$ is described. The molecular structure of *cis*-dimethyl(2,2-dimethylpropyl)oxoosmium has been determined by X-ray diffraction analysis [148]. Osmium(VI) glycolate complexes may be alkylated in a two-step procedure to give mixed-alkyl oxoosmium complexes. The initial chelating ligands in the starting materials give square-pyramidal alkyl complexes with a *cis*-geometry (*cis* R′, R′ and R″, R″). Included in this report is the X-ray crystal structure of dimethyl(2,3-dimethylbutane-2,3-diolato)oxoosmium (VI) [149]. Dihalogen osmium(VI) complexes of pinacol have been obtained from the reaction of AlX_3 (where X = Cl, Br) with oxobis(pinacolato)osmium(VI). *Cis* alkyl groups may be subsequently introduced by reaction with dialkylzinc reagents [150]. The oxo complexes $[Os(O)_2(O_2CR)(Cl)_2]^-$ {where R = Me, Et, CH(Me)Et} and $[Ru(O)_2(O_2CR')(Cl)_2]^-$ (where R′ = Me, Et, Pr, CHF_2) have been synthesized and examined as catalytic oxidants [151]. Thermally activated ruthenium dioxide hydrate has been found to mediate the oxidation of water to oxygen by $[MnO_4]^-$ [152]. Cyclohexyl isocyanate reacts with the oxoruthenium(V) anions $[Ru(O)\{OCEt(R)C(O)O\}_2]^-$ (where R = Me, Et) to yield the amidoruthenium anions $[Ru\{NH(C_6H_{11})\}\{OCEt(R)(O)O\}_2]^-$. The reaction of dioxygen with these amido complexes has been studied [153].

A report on the regiochemistry of the bisosmylation of C_{60} has appeared [154]. The new perfluoropinacolate complex $(PFP)_2Os(O)(4\text{-}^tbutylpyridine)$ has been prepared [155]. The thermochemistry of gaseous OsO_4, OsO_3, OsO_2, and OsO, which have been generated by reaction of $O_2(g)$ with osmium, has been studied by using mass spectrometry [156]. The reaction of RuO_4 and OsO_4 with buckminsterfullerene has been explored by extended Hückel methods [157]. A report dealing with variable photon energy photoelectron spectroscopy of OsO_4 and pseudopotential calculations of the valence ionization energies of RuO_4 and OsO_4 has appeared [158]. A new model for the stereoselective dihydroxylation of alkenes by chiral diamine complexes of osmium tetraoxide has been described [159]. The catalytic oxidation of fluorinated alkenes using osmium tetraoxide has been studied [160].

The synthesis and redox chemistry of bis(*o*-benzosemiquinonato)bis(triphenylphosphine)ruthenium(II) complexes have been examined. The X-ray diffraction structure of $Ru(O_2C_6Cl_6)_2(PPh_3)_2$ is presented [161]. The preparation, characterization, and redox behavior of ruthenium complexes that bear catecholate and 2-(*m*-tolyazo)pyridine ligands are reported [162]. The charge distribution in several bis(quinone) complexes of ruthenium and osmium has been investigated. The complexes of interest have been synthesized by treating $Os(bpy)(Cl)_3$ with the desired catechol. The products, which have the form $Os(bpy)(catechol)_2$, have been examined by cyclic voltammetry and UV-vis-near-IR spectroscopy. This report presents the X-ray diffraction data for $Os(bpy)(Cl_4Cat)_2 \cdot 2C_6H_6$ [163].

2.7. Nitrogen ligands

New osmium(III) and (IV) complexes with an ancillary ethylenebis(salicylidineimine), 1,2-bis(pyridine-2-carboxamido)benzene or 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene ligand have been synthesized from *trans*-dioxoosmium(VI) complexes. The isolated complexes were observed to function as alkene oxidation catalysts using iodosylbenzene as the oxygen source [164]. The synthesis and X-ray diffraction structure of Ru(edta)(NO) are presented. This nitrosyl complex has been shown to be an excellent oxygen-atom transfer agent toward 1-hexene and cyclohexene to give hexan-2-one and cyclohexene epoxide, respectively [165]. $[Ru(Hedta)(Cl)]^-$ and $Ru(Hedta)(H_2O)$ have been allowed to react with dppm in a $H_2O/EtOH$ mixture to give Ru(Hedta)(dppm) and $Ru(H_2edta)(dppm)$. The molecular structure of the latter complex, as its DMSO and H_2O solvates, is reported [166]. The synthesis of the complexes $[Ru(Hedta)(NO)]^+$ and Ru(edta)(NO) has appeared. The use of the former complex as an efficient oxygen transfer agent for the oxidation of alkenes by dioxygen and iodosylbenzene is described. A key component of the oxidation reaction is the involvement of a ligand-mediated nitrosyl/nitro couple [167]. The details associated with the catalysis of the Diels-Alder reaction using *trans*-$[Ru(salen)(NO)(H_2O)]^+$ are described. Rate accelerations of $> 10^5$ have been measured relative to the corresponding thermal reactions [168].

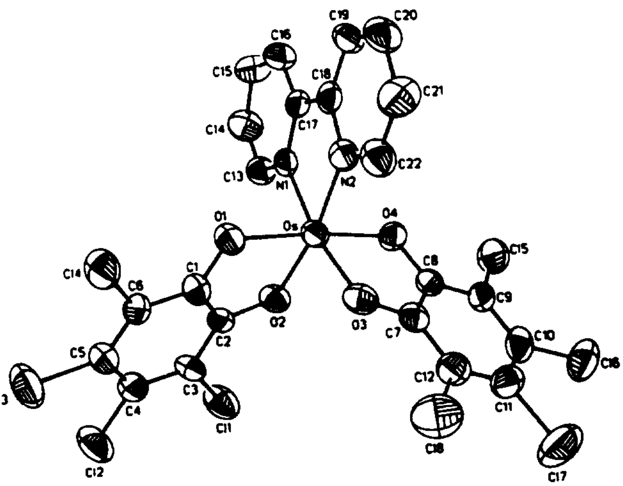

Fig. 7. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

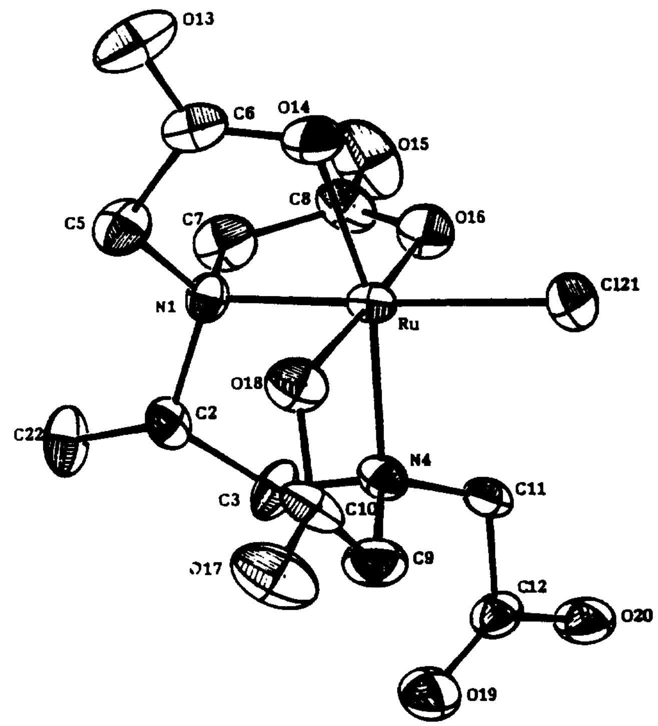

Fig. 8. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

The influence of the 5-substituent of uracils and uridines on the coordination of $[Ru(Hedta)]^-$ has been investigated by ^1H and ^{19}F NMR spectroscopy. Both cyclic voltammetry and differential-pulse polarography have been used to study the η^2 coordination of the uracils and uridines to the ruthenium center [168]. The synthesis and characterization of the ruthenium oxo complexes $[Ru(O)(edta)]^-$ and $[Ru(O)(pdta)]^-$ have appeared. Transfer of the oxo atom to saturated hydrocarbons has been studied spectrophotometrically. The X-ray crystal structures of both oxo products are presented [170].

The kinetics and mechanism of the reduction of *trans*-$[Ru^{IV}(L)(O)(H_2O)]^{2+}$ to *trans*-$[Ru^{III}(L)(OH)$-

$(H_2O)]^{2+}$ (where L = 6,7,8,9,10,11,17,18-octahydro-6, 10-dimethyl-5H-dibenzo[e,n][1,4,8,12]dioxadiaza-cyclopentadecine) by *cis*-$[Ru^{II}NH_3)_4$(isonicotinamide)$]^{2+}$ are discussed. The molecular structure of *trans*-$[Ru^{III}$-(L)(OH)$(H_2O)]^{2+}$ has been crystallographically determined. Treatment of *trans*-[Ru(L)$(Cl)_2]^+$ (where L = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with nitrite ion furnishes *trans*-[Ru(L)(O)(Cl)$]^+$ and *trans*-[Ru(L)(OH)(NO)$]^{2+}$. These products arise from the disproportionation of *trans*-[Ru(L)(Cl)$(NO_2)]^+$. The X-ray structures of the products are included in this report [172]. The synthesis and crystallographic structures of *cis*-$[Ru^{VI}(L)(O)_2]^{2+}$, *cis*-$[Ru^{V}(L)(O)_2]^+$, and *cis*-$[Ru^{II}(L)(MeCN)_2]^{2+}$ (where L = N,N,N',N'-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) have been published. The redox properties of these complexes and the oxidation of saturated hydrocarbons are discussed [173]. The mechanism of alcohol oxidation by *trans*-dioxoruthenium(VI) complexes with an ancillary nitrogen chelating ligand has appeared. The nitrogen ligands used include bpy, N,N'-dimethyl-6,7,8,9,10,11,-17,18-octahydro-5H-dibenzo[en][1,4,8,12]dioxadiazacyclopentadecine, N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17), 13,15-triene, and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. The alcohol oxidation proceeds by either a hydride or hydrogen atom abstraction process [174]. Kinetic data for alkene oxidation using a series of isostructural *trans*-dioxoruthenium(VI) complexes are reported. A linear free energy relationship between log K_2 and $E°(Ru^{VII}–Ru^{V})$ for the oxidation of styrene and norbornene has been established [175]. The synthesis and spectroscopic properties of the ruthenium complexes *trans*-Ru(Cl)(cyclam)(L) (where L = 4-picoline, py, isonicotinamide, 4-acetyl-pyridine) have been obtained from the reduction of *trans*-[Ru(cyclam)$(Cl)_2]^+$ in the presence of excess L. The redox behavior and the MLCT energies of these complexes are discussed [176].

Hydrogen displacement in [M(H)$(\eta^2-H_2)\{P(OEt)_2Ph\}_4]^+$ (where M = Ru, Os) by $[NO][PF_6]$ gives the linear nitrosyl complexes [M(H)(NO)$\{P(OEt)_2Ph\}_4]^{2+}$. Treatment of these complexes with isocyanide and CO proceeds by phosphite loss and ligand capture [177]. The single-crystal X-ray diffraction structures of *trans*-Ru(dpgh)$_2$(NO)(Cl) and *trans*-[Ru(dmgh)(dmgh$_2$)-(NO)(Cl)$]^+$ have been presented. Variable-temperature ^1H NMR spectroscopy has been used to measure the rate of proton exchange in the latter complex [178].

The synthesis and characterization of the dioxoosmium(VI) complexes *cis*-Os$(O)_2$(L) and *trans*-Os-$(O)_2$(L′) {where L = 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine; L′ = NH_2-^{t}Bu, Py, 4-tert-butylpyridine}, the nitrido complex Os(N)(L)(Cl), and the imido complexes Os(L)$(NCOCF_3)$(Cl)(O_2CCF_3) and Os(L)$(NPh)_2$ have been published [179]. Bisruthenium(II) complexes have been allowed to react with 2,6-bis(pyrazol-1-ylmethyl)-pyridine. The characterization and redox investigation of the isolated products are discussed [180]. A report on the use of the ruthenium(II) complex *trans*-Ru$(py)_4$-$(Cl)_2$ in the design of an artificial four-helix bundle metalloprotein has appeared [181]. Treatment of [Ru-$(DMSO)_6][BF_4]_2$ with 2,6-bis(*o*-methoxycarbonylphenylthiomethyl)pyridine gives a complex with a non-symmetrical tridentate ligand that possesses a benzothiophene fragment [182]. The coordination of $[Ru^{III}$(edta)-$(H_2O)]^-$ and $[Ru^{III}$(edta)$(H_2O)]^{2-}$ to poly(4-vinylpyridine) gives the corresponding poly(4-vinylpyridine)-substituted complexes. The diffusion coefficient for these complexes has been measured [183].

The synthesis and characterization of two metallacyclopentatriene complexes have been reported. When *trans*-[Os(ethylenediamine)$_2(\eta^2-H_2)(H_2O)]^{2+}$ is heated with 2-butyne, the product *cis*-$[Os(C_4Me_4)$(ethylenediamine)$_2]^{2+}$ may be isolated in near quantitative yield. The X-ray structure of the product unequivocally establishes the presence of the osmacyclopentatriene moiety. Treatment of the same reactant with 2,8-decadiyne affords *cis*-$[Os(C_{10}H_{14})$(ethylenediamine)$_2]^{2+}$ as a result of an intramolecular alkyne cyclization reaction [184]. A 1,2-hydrogen shift in the osmacyclopentatriene complex *cis*-$[Os(C_4Me_4)$(ethylenediamine)$_2]^{2+}$ furnishes the corresponding osmahexatriene complex due to the conversion of one of the carbene ligands to a coordinated alkene. The L-histidinate complexes Ru-(Cl)(L-histidine)(diene) (where diene = nbd, cod) have been prepared from the chloro-bridged polymer [Ru-(Cl)(diene)$]_n$ [186]. The synthesis and X-ray diffraction structure of $[Ru(Cl)_4$(CO)(1-methylimidazole)$]^-$ have appeared. The ruthenium(III) atom is octahedrally coordinated to four co-planar chlorine atoms [187]. A review on the coordination and organometallic chemistry of monoazadiene ruthenium complexes has been published [188]. The reaction between $[Os(Br)_6]^{2-}$ with excess tmen yields the osmium(IV) tris-chelate complex [Os(tmen-H)$_2$(tmen)$]^{2+}$. The pH dependence of the reduction potential has been determined by cyclic voltammetry [189]. Treatment of the ruthenium(II) and osmium(II) complexes $M(Cl)_2(PPh_3)_3$ with N,N'-diphenylamidines, PhN=C(R)-NHR (where R = H, Me, Et, Ph), yields the ruthenium(III) and osmium(III) products $M(Cl)_2\{PhNC(R)NPh\}(PPh_3)_2$. The X-ray structure of *trans*-$Os(Cl)_2\{PhNC(Et)NPh\}_2$ accompanies this report [190]. Excited-state proton transfer to a tris[2-(2-pyrazinyl)thiazole]ruthenium(II) cation has been examined [191]. Optically active 2-aminocarbonylpyrrolidine ligands have been introduced into ruthenium complexes. The ligands employed were (S)-2-

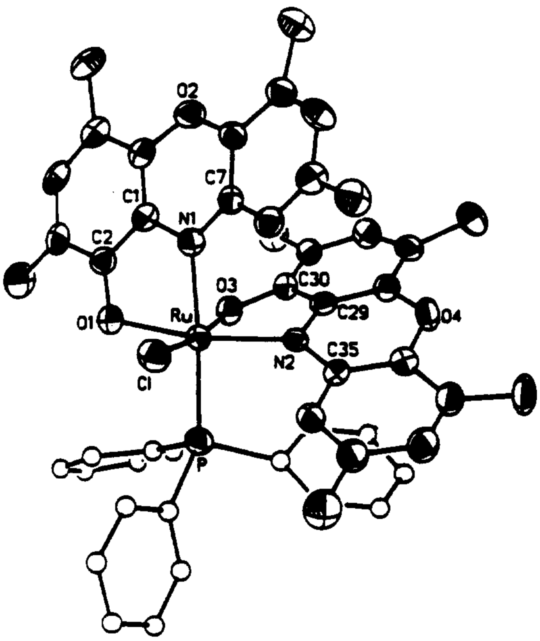

Fig. 9. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

^{t}butylaminocarbonylpyrrolidine and (S)-2-(3-triethoxysilyl) propylaminocarbonylpyrrolidine. The hydrogenation activity of the prepared complexes has been investigated [192]. The reaction between $Ru(PPh_3)_3(Cl)_2$ and HPhenoxSQ has been studied under a variety of conditions. The complexes $Ru(PPh_3)_2(Cl)_2$(PhenoxSQ) and $Ru(PPh_3)(Cl)$(PhenoxSQ$)_2$ have been isolated and characterized by spectral and electrochemical techniques. The solid-state structure of the former complex has been solved by X-ray crystallography [193].

A review dealing with electron transfer in ruthenium-modified proteins has been published [194]. Volumes of activation for intra- and intermolecular electron transfer from ruthenium(II) ammine complexes to different cytochrome C complexes have been measured by pulse radiolysis [195]. Linkage isomerization reactions in $[Ru(NH_3)_5(acetone)]^{3+/2+}$ are reported. Kinetic and thermodynamic data for the $\eta^1 \rightarrow \eta^2$ linkage isomerization in $[Ru(NH_3)_5(acetone)]^{2+}$ are presented. The redox behavior of the various isomers has been studied, and it has been observed that the hexafluoroacetone complexes exist solely in the η^2 form [196]. The coordination of $Ru(NH_3)_5$ groups to pyridine sites in a cobalt *meso*-tetrakis(4-pyridyl)porphyrin adsorbed on pyrolytic graphite has been achieved. The electrocatalysis of O_2 to H_2O has been studied [197]. Pentaammineruthenium(II) complexes of nicotinamide and isonicotinamide exhibit rapid amido to pyridyl isomerization reactivity upon reduction [198]. The incorporation of $[Ru(NH_3)_6]^{3+}$ into a poly[pyrrole-Co-{3-(pyrrol-1-y)propanesulfonate}] film is reported [199]. The theory of quasireversible electrode processes has been studied at mercury oblate spheroidal microelectrodes by using $Ru^{III}(NH_3)_6/Ru^{II}(NH_3)_6$ [200]. Zinc amalgam reduction of $[Os(NH_3)_5(MeCN)]^{3+}$ and $[Os(NH_3)_5(O_3SCF_3)]^{2+}$ in MeCN gives the complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)]^{3+}$. The spectroscopic and redox behavior of this η^2-iminium complex are described [201]. The X-ray structure and magnetic properties of $[Ru(NH_3)_6][Br][SO_4]$ have been determined [202]. Cerium(IV) oxidation of $[Os(NH_3)_5(Cl)]^{2+}$ in water gives the nitrido complex $[Os(N)(NH_3)_4]^{3+}$ in quantitative yield. Excited-state quenching of the nitrido complex by electron donors has been demonstrated and the quenching process discussed within the context of a photoinduced electron-transfer mechanism [203].

Refluxing $[Os(NH_3)_4(N_2)_2][OTf]_2$ with propylamine yields *cis*-$[Os(NH_3)_4(NH_2Pr)(N_2)]^{2+}$. Treatment of this complex with a triflic acid/bromine solution promotes nitrogen loss and formation of the corresponding triflate $[Os(NH_3)_4(NH_2Pr)(OTf)]^{2+}$, which upon zinc amalgam reduction furnishes the *cis*-iminium complex $[Os(NH_3)_4(H)(\eta^2\text{-}NH_2{=}CHEt)]^{2+}$. Cyclic voltammetric analysis for the formation of the iminium complex has allowed for the determination of the rate constant for this reaction [204]. The phenol-cyclohexadienone equilibrium for η^2-coordinated arenes in $[Os(NH_3)_5(arene)]^{2+}$ has been studied [205]. The synthesis of $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-pyrrole})]^{2+}$ and various alkylated pyrrole derivatives has been reported. Also included are the results of protonation and electrophilic addition studies [206]. The pentaamineruthenium(II) moiety has been attached to the terminally disubstituted rigid rod molecules derived from [*n*]staffane-3,3$^{(n-1)}$-dithios (where $n = 1$–4) [207]. $[Ru(NH_3)_5(H_2O)]^{2+}$ has been allowed to react with a mixture of tyrosine and valine tRNAs. Spectral, kinetic, and electrochemistrical data are discussed [208]. The theory of the feedback mode of the scanning electrochemical microscope has been examined by studying the oxidation of $[Ru(NH_3)_6]^{2+}$ [209]. The nature of ruthenium(II)-S(thioether) bonding has been investigated by a variety of techniques. The preparation, X-ray structure, and electronic spectra for $[Ru(NH_3)_5\{S(Me)(Et)\}]^{2+}$ are presented and discussed. *Ab initio* molecular orbital calculations reveal that substantial back bonding exists between the ruthenium and sulfur atoms [210].

The photochemistry of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{2+}$, and *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(CO)]^{2+}$ has been explored. Photoaquation of the thermally inert NH_3 ligand is observed, and photoaquation of CO in the latter complex is explained by considering a scheme that involves depopulation of a bonding dπ orbital and population of a σ^* orbital [211]. The synthesis, spectroscopy, and electrochemistry for *trans*-[Ru(NH$_3$)$_4$(imidazole)(isonicotinamide)]$^{3+}$ have been published. The X-ray structure of this complex reveals an octahedrally coordinated ruthenium center [212].

A report that demonstrates the use of electrochemical microscopy in the examination of counterion ejection from a Nafion coating on electrodes has appeared. It is observed that one-third of the initially present [Os(bpy)$_3$]$^{2+}$ cations are lost during the oxidation to [Os(bpy)$_3$]$^{3+}$. The characteristics of the altered cyclic voltammetric waves of [Os(bpy)$_3$]$^{3+/2+}$ and other unusual features of this film are discussed [213]. The preparation of polymers derived from [M(vbpy)$_3$][PF$_6$]$_2$ (where M = Ru, Os) by free-radical polymerization is described. The resulting polymers were fractionated according to molecular weight using size exclusion chromatography, and the diffusion coefficients determined by electrochemical methods [214]. The synthesis and photoredox pathways available to spatially restricted metallopolymeric films have appeared. The polymeric films were derived from [Ru(vbpy)$_3$]$^{2+}$ [215]. The X-ray structures of [Ru(bpy)$_3$][PF$_6$]$_2$ and [Ru(bpm)$_3$][PF$_6$]$_2$ · MeCN have been determined and a discussion on their similarities presented [216].

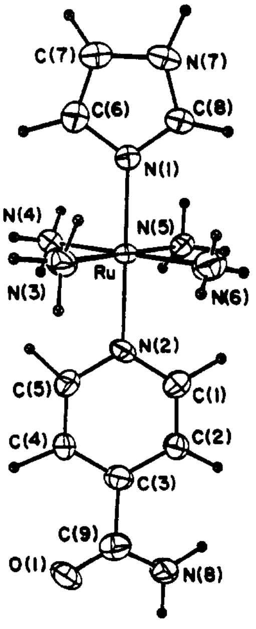

Fig. 10. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

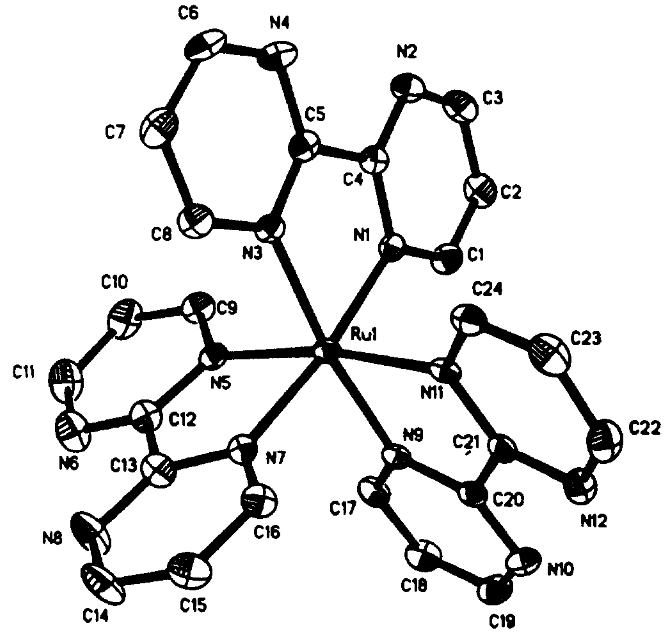

Fig. 11. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

The effect of charge separation in donor–chromophore–acceptor complexes has been explored for inverted region behavior in reverse electron transfer reactions. The electron donor is a phenothiazine moiety while the electron acceptor is a *N,N'*-diquaternary-2,2'-bpy group, both of which are covalently linked to a Ru(bpy)$_3$ moiety. Optical excitation of the Ru(bpy)$_3$ MLCT state affords a long-lived charge-separated state as a result of oxidative quenching of the Ru(bpy)$_3^{2+}$ moiety, which is followed by phenothiazine-to-ruthenium electron transfer. The Marcus inverted behavior observed has been analyzed [217]. The synthesis and photophysical properties of several complexes of ruthenium(II) containing 4,4'-di(carboxyphenyl)-2,2'-bpy and related bpy ligands are reported. Microstructures in thin polymeric films have been investigated by using copolymerized films of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$ [Os(vbpy)$_3$]$^{2+}$ on platinum electrodes. With the use of mashing techniques, spatial control of the osmium(II) complex may be achieved [219]. The synthesis and characterization of arborols containing polypyridylruthenium(II) complexes are presented. These complexes have been examined for their luminescent behavior and redox properties [220]. Underivatized amino acids have been detected by a post column chemiluminescent technique using electrogenerated [Ru(bpy)$_3$]$^{3+}$ [221]. New luminescent pH sensors based on [Ru(bpy)$_2$(5,5'-diaminomethyl-2,2'-bpy)]$^{2+}$ have been published [222]. Photoelectrocatalytic reduction of oxygen using a chemically modified electrode containing $[Ru(bpy)_3]^{2+}$ has been demonstrated [223]. The synthesis and redox behavior of a ruthenium(II)-containing poly (2,2′-bipyridine-5,5′-diyl)polymer are discussed. The catalysis of hydrogen evolution from aqueous solution has been investigated [224]. The bimolecular electron-self-exchange reaction between osmium(II) and osmium(III) sites in bipyridine redox polymer films has been examined and the rate constants discussed [225]. The redox properties of polypyridyl complexes immobilized in a κ-carrageenan hydrogel matrix are reported. The data presented support a dual-mode mechanism that involves physical diffusion and electron hopping for charge propagation [226]. The electron-transfer quenching of the MLCT excited state of $[Ru(bpy)_3]^{2+}$ by intra zeolitic methylviologen ions has been studied by steady-state and time-resolved spectroscopic techniques. This rate of quenching was shown to be dependent on the diffusion of methylviologen ions within the zeolite channels [227]. A photophysical examination of intramolecular transfer of triplet energy in a polypyridylruthenium(II) complex that is covalently attached to a pyrene moiety has been reported [228]. The primary process of illumination on the $[Ru(bpy)_3]^{2+}$-catalyzed Belousov-Zhabotinskii reaction has been determined [229]. Scanning tunneling microscopy data for adsorbed monolayers of $[Ru(bpy)_2\{bpy\text{-}(CH_2)_x\text{-}bpy\}]^{2+}$ (where $x = 4, 5$) on Au(III) are discussed with respect to the spatial distribution of ruthenium [230]. The spectral properties of $[Ru(bpy)_3]^{2+}$ synthesized within zeolite Y cages have been published [231]. A study dealing with the $[Ru(bpy)_3]^{2+}$-sensitized, photoinduced *trans*membrane electron transfer reactions has appeared [232]. The synthesis of tris-2,2′-bipyridyl macrobicyclic cryptand molecules containing externally coordinated ruthenium(II) cations has been described [233]. Nitroxide-labeled ruthenium(II)-polypyridyl complexes have been synthesized and investigated as EPR probes in the study of organized systems [234]. The photoinduced electron transfer between $[Ru(bpy)_3]^{2+}$ and methylviologen in the supercages of hydrated zeolite Y has been explored. The size of $[Ru(bpy)_3]^{2+}$ ensures that it remains trapped within the supercages, but the migration of methylviologen through the zeolite framework facilitates electron transfer in neighboring cages. Time-resolved resonance Raman spectroscopy has been used in the study of the electron-transfer reaction [235]. Photoinduced electron transfer in covalently linked ruthenium tris(bipyridyl)-viologen molecules has been investigated and data presented that support back electron transfer in the Marcus inverted region. The rates of photoinduced electron transfer were measured by picosecond flash photolysis/transient absorbance techniques [236].

B-DNA has been examined by photophysical and EPR techniques using nitroxide-labeled ruthenium(II)-polypyridyl complexes. The complexes examined include $[Ru(1,10\text{-}phen)_2(1,10\text{-}phen\text{-}T)]^{2+}$ and $[Ru(bpy)_2(1,10\text{-}phen\text{-}T)]^{2+}$ (where T = TEMPO moiety). The TEMPO spin label is attached to the phenanthroline ligand by a carbamate moiety [237]. The enantioselective quenching of $[Tb(2,6\text{-}pyridinecarboxylate)_3]^{3-}$ by resolved $[Ru(1,10\text{-}phen)_3]^{2+}$ in methanol and water has been demonstrated and shown to be solvent dependent [238]. The effect of the ionic strength of methanol and water solutions on the enantioselective quenching of $[Tb(2,6\text{-}pyridinecarboxylate)]^{3-}$ luminescence by resolved $[Ru(1,10\text{-}phen)_3]^{2+}$ is discussed [239]. Two-dimensional NMR data on the interaction of $[Ru(1,10\text{-}phen)_3]^{2+}$ with the self-complementary decanucleotide duplex $[d(CGCGATCGCG)]_2$ provide evidence for the binding of both Δ- and Δ-$[Ru(1,10\text{-}phen)_3]^{2+}$ to the AT portion of the oligonucleotide [240].

Thin films of poly{pyrrole-$[Ru^{II}(bpy)_2(Cl)_2]$} have been prepared and the $[Ru^{II}(bpy)_2(Cl)_2]$ sites in the polymer examined for their conversion to *cis*- or *trans*-$[Ru(bpy)_2(H_2O)_2]^{2+}$,$[\{Ru(bpy)_2(H_2O)\}_2O]^{(4+)}$, and $[Ru(bpy)_2(MeCN)_2]^{2+}$. The electrocatalytic behavior of these films has been investigated [241]. The oxidation of hydroquinones by $[Ru(bpy)_2(py)(O)]^{2+}$ and $[Ru(bpy)_2(py)(OH)]^{2+}$ has been investigated. The product quinones are formed by distinct one-electron steps. The mechanistic details and the effect of pH on the rate of the reaction are discussed [242]. The synthesis and catalytic hydrogenation activity of *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(H_2O)_2]^{2+}$ are reported [243]. The synthesis and spectroscopic characterization of $[Ru(bpy)_2(CO)(NO)]^+$ are presented.The X-ray structure of this complex has been solved and the reactivity with hydroxide, which gives the corresponding metalloacid, has been examined by UV-visible spectroscopy [244].

The osmium complex *cis*-$[Os(bpy)_2(CO)(H)]^+$ functions as an electrocatalyst for the reduction of CO_2 in MeCN at glassy carbon or Pt electrodes. CO is observed as the major product under anhydrous conditions, with formate being formed in the presence of water. Digital simulation of cyclic voltammograms under the electrocatalytic conditions reveals a rate-determining step that involves the reaction between CO_2 and the direduced complex $[Os(bpy)_2(CO)(H)]^-$. The kinetics of CO_2 reduction by *cis*-$[m(bpy)_2(CO)(R)]^-$ (where M = Ru, R = benzyl; M = Os, R = H, Me, Ph) have been studied, and the observed linear correlation between ln k and the cone angle of the R group discussed [245]. Treatment of $[Ru(bpy)_2(CO)_2]^{2+}$ with 2 equiv. of $[Bu_4N][OH]$ in H_2O/EtOH yields the η^1-carboxylate complex $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)] \cdot 3H_2O$. The molecular structure was determined by X-ray

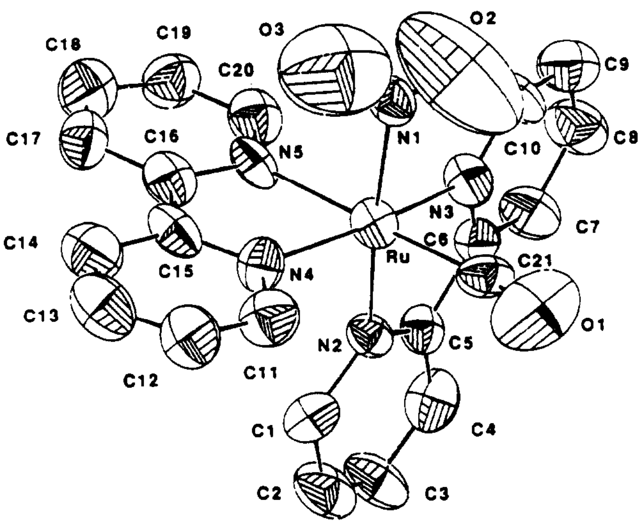

Fig. 12. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

crystallography. The initial starting material is regenerated upon treatment with acid [246]. The X-ray structure of $[Ru(bpy)_2(CO)(CO_2H)]^+$ has been determined in order to compare the structural differences between it and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$. The synthesis and characterization of *trans*-$[Ru(bpy)_2(NO)(OH)]^{2+}$ have been published. X-Ray diffraction analysis has been used to solve the molecular structure of this new complex [248]. Folic acid, lumiflavin, and riboflavin have been bound to the "$[Ru(bpy)_2]^{2+}$" fragment. The pk_a values of the heterocyclic nitrogen–H protons and the MLCT spectra have been measured [249].

The reaction between $Ru(bpy)_2(Cl)_2$ and 2-(2′-thienyl)pyridine in the presence of a chloride scavenger yields $[Ru(bpy)_2\{2\text{-}(2'\text{-thienyl})pyridine\}]^{2+}$ which contains a bidentate N,S-bonded ligand [250]. The synthesis of the trifluoromethyl-substituted ligands 4,4′-bis-(trifluoromethyl)-2,2′-bpy, 5,5′-bis(trifluoromethyl)-2,2′-bpy and their reaction with ruthenium(II) complexes are reported. The new polypyridyls have been examined by electrochemical and spectroscopic methods [251]. The synthesis and FAB mass spectrometry data of homo- and heterometallic ruthenium(II) complexes with a 1,4,5,8,9,12-hexaazatriphenylene ligand have been presented [252]. The use of the tetradentate bridging ligand 2,6-bis(2-pyridyl)benzodiimidazole as a ligand in ruthenium(II) complexes is described [253]. The electrochemistry of $[Ru(bpy)(NH_3)_4]^{2+}$ and $[Ru(1,10\text{-phen})(NH_3)_4]^{2+}$ has been investigated and estimates of electronic delocalization, which are based on partial oxidation-state markers in the Raman spectra, are discussed [254]. The synthesis and redox properties of polypyridyl complexes of ruthenium(II) containing three different bidentate ligands are presented [255]. An electrochemical study of a bpm-ligated ruthenium complex has appeared [256].The charge-transfer excited states of ruthenium(II) complexes with bridging 2,2′-bis(2-pyridyl)bibenzimidazole or 1,2-bis{2-(2-pyridyl)-benzimidazole}ethane have been examined by emission and transient absorption spectroscopy [257]. A general synthetic approach to tris(polypyridyl)-substituted ruthenium(II) complexes has been outlined [258]. The electron-transfer reactivity of pentaamineruthenium(II) complexes with either a pyrazine or bpy ligand has been explored [259]. The oxidative electropolymerization of ruthenium complexes with an aniline-substituted 2,2′-bpy has been described. The spectroscopic data for the polymer films are also discussed [260]. The photophysics and photochemical behavior of 2-(2′-pyridyl)pyrimidine and bis(pyridine)polypyridyl complexes of ruthenium(II) have been published. The MLCT-dd energy gap and the emission data have been measured and the studied complexes discussed with respect to the design of molecular assemblies [261]. Several mono- and diaquapolypyridyl complexes of ruthenium(II) have been shown to function as stereoselective binding agents to DNA [262]. A one-pot synthesis of several polypyridyl ruthenium complexes is reported [263]. The absorption spectra, luminescence properties, and electrochemistry of ruthenium(II) complexes containing bis(pyridyl)triazole ligands have been published [264]. The luminescent properties of DNA-ligated ruthenium(II) complexes with two phenanthroline ligands and a dipyridophenazine ligand have been recorded [265]. A study on the ruthenium(II) complexation to an oligonucleotide is discussed with respect to ruthenium complexes being able to function as spectroscopic probes fornucleic acid conformations [266]. The chemistry and spectroscopic properties of ruthenium complexes with pyridine and phenol ligands are discussed [267]. Several $Ru(bpy)_2$-substituted complexes containing pyridyltriazole ligands have been synthesized. The X-ray structure of $[Ru(2,2'\text{-bpy})_2(Cl)\{3\text{-methyl-1-(pyridin-2-yl)-1,2,4-triazole}\}]^{2+}$ accompanies this report [268]. The electrochemical oxidation of *cis*-$[Ru(bpy)_2(2,3\text{-dimethyl-2,3-diaminobutane})]^{2+}$ exhibits a reversible three-proton three-electron couple. C–C bond cleavage of the 2,3-dimethyl-diaminobutane ligand is observed during oxidation and the isolation of *cis*-$[Ru(bpy)_2(NH{=}CMe_2)_2]^{2+}$ reported. The identity of this oxidation product was ascertained by X-ray crystallography [269]. The enantioselective cleavage of plasmid DNA by the κ isomer of $[Ru(bpy)_2(4',7'\text{-phenanthrolino-}5',6'\text{-}:5,6\text{-pyrazine})]^{2+}$ in the presence of copper(II), 3-mercaptopropionic acid, and hydrogen peroxide has been demonstrated. The Δ isomer of this ruthenium complex is inactive [270]. The formation of supramolecular complexes of tris(6,6′-oligoethyleneglycol-3,3′-bipyridazine)ruthenium(II)has been published [271]. The excited-state interactions in ligand-bridgedchromophore-quencher ruthenium(II) complexes are reported [272]. The photophysical and photochemical properties of mixed ligand complexes of ruthenium (II) with a 3-(pyridin-2-yl)-1,2,4-triazole ligand have been examined. Temperature-dependent luminescent data indicate that the protonated complexes decay *via* population of a metal-centered excited state [273]. The photoinduced intramolecular electron transfer in several ruthenium(II) diimine donor-diquat acceptor complexes has been investigated. The data are discussed with respect to through-space and through-bond interactions [274].

The synthesis of tris(2,2′-bpy)ruthenium(II) complexes with pendant pyridyl or phenol ligands has appeared [275]. The synthesis, spectroscopic and redox characterization, and X-ray diffraction structure of $[\mathrm{Ru(H)(terpy)(PPh_3)_2}]^+$ have been published [276]. The assembly of coordination polymers and oligomers of ruthenium complexes containing terpy ligands is described [277]. The X-ray structures of the free ligands terpy and 2,6-bis(pyrazol-1-yl)pyridine are compared with the same ligands in the complexes $[\mathrm{Ru(L)(NO_2)(PMe_3)_2}]^+$ [278]. New terpy-derived coordination oligomers and polymers of ruthenium have been prepared and their redox properties investigated [279]. The luminescent $[\mathrm{Os(terpy)_2}]^{2+}$ photosensitizer has been attached to supramolecular dyads and triads and examined for electron-transfer activity with a covalently linked methylviologen acceptor group [280]. The synthesis and ruthenium complexation chemistry of 3,4-dihydroxyphenylterpyridine are presented [281]. The synthesis and redox investigation of *trans*-$[\mathrm{Ru(terpy)(O)_2(H_2O)}]^{2+}$ are reported [282]. The reactivity of *trans*-$[\mathrm{Ru(terpy)(bpy)(H_2O)}]^{2+}$, $[\mathrm{Ru(terpy)(1,10\text{-}phen)(H_2O)}]^{2+}$, and $[\mathrm{Ru(terpy)(tmen)(H_2O)}]^{2+}$ with DNA has been studied by cyclic voltammetry. DNA cleavage by an oxoruthenium(IV) species is discussed, and the molecular structure of the latter complex determined by X-ray diffraction analysis [283].

Superexchange metal–metal coupling in dinuclear pentaamineruthenium complexes tethered by a 1,4-dicyanamidobenzene ligand has been examined. The complexes were characterized by cyclic voltammetry, UV-vis-NIR spectroscopy, and magnetic susceptibility measurements. The superchange mechanism involves ruthenium(III)dπ-orbitals and the π HOMO of the bridging ligand [284]. The singly oxidized forms of the cyano-bridged complexes $[\mathrm{(CN)(bpy)_2Ru^{II}\text{-}CN\text{–}Ru^{II}(4,4'\text{-}dicarboxy\text{-}2,2'\text{-}bpy)_2\text{-}NC\text{–}Ru^{II}(bpy)_2(CN)}]$ and $[\mathrm{(H_2O)(bpy)_2Ru^{II}\text{-}NC\text{-}Ru^{II}(4,4'\text{-}dicarboxy\text{-}2,2'\text{-}bpy)_2\text{-}CN\text{–}Ru^{II}(bpy)_2(H_2O)}]$ exhibit intervalence charge transfer bands in the infrared region [285]. The temperature dependence of the intervalence transition for the transition$[\mathrm{(bpy)_2(Cl)Ru^{II}(pz)Ru^{III}(NH_3)_5}]^{4+} \rightarrow [\mathrm{(bpy)_2(Cl)Ru^{III}(pz)Ru^{II}(NH_3)_5}]^{4+}$ has been examined [286]. Data from a picosecond infrared study of ultrafast electron transfer and vibrational energy relaxation data in the mixed-valent ruthenium dimer $[\mathrm{(NC)_5Ru^{II}\text{-}CNRu^{III}(NH_3)_5}]^-$ are discussed [287]. The ability of the S–S bridge to facilitate electrical conductivity between ruthenium centers in the binuclear ruthenium complex $[\{\mathrm{Ru(NH_3)_5}\}_2\mathrm{(4,4'\text{-}dithiodipyridine)}]$ has been studied [288]. The complex *trans*-$[\mathrm{(NH_3)_4(py)Ru\text{-}pz\text{-}Ru(NH_3)_4(py)}]^{5+}$, which is a close relative of the Creutz–Taube ion, exhibits multiple intervalence bands that are dependent on the nature of the solvent and added electrolyte [289]. The synthesis, absorption and luminescence properties, and redox behavior of the tridecanuclear ruthenium complex $\mathrm{Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)(\mu\text{-}2,3\text{-}dpp)Ru\text{-}\{(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2\}_2]_3}$ have been investigated [290]. Several mixed-metal osmium (II)/ruthenium(II) bimetallic complexes have been synthesized and their electrochemical, spectroscopic, and spectroelectrochemical properties reported. The examined complexes include $[\mathrm{(bpy)_2Os(\mu\text{-}BL)Ru(bpy)_2}]^{4+}$ (where BL = the bridging ligand dpp,dpq, dpb) [291]. Resonance Raman spectra of $[\{\mathrm{(bpy)_2Ru(H_2O)}\}_2\mathrm{O}]^{4+}$ and its congeners have been recorded and pathways for water oxidation outlined [292].

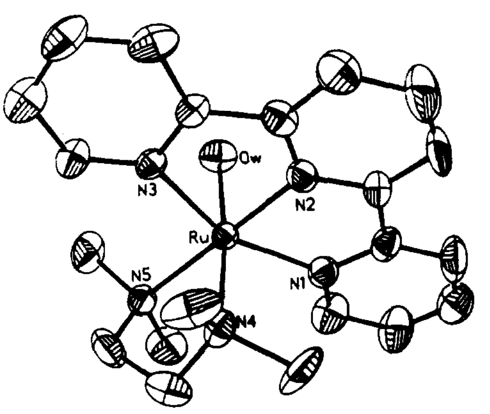

Fig. 13. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

The synthesis and resonance Raman spectral data of $[\mathrm{(bpy)_2(Cl)Os^{II}(CN)Ru^{III}(NH_3)_5}]^{3+}$,$[\mathrm{(bpy)_2(CN)Os^{II}(CN)Ru^{III}(NH_3)_5}]^{3+}$, and $[\mathrm{(bpy)_2Os^{II}\{(CN)Ru^{III}(NH_3)_5\}_2}]^{6+}$ are reported. The use of resonance Raman spectroscopy in assigning the nature of complicated and overlapping electronic transitions is discussed [293].

An electrochemical study has dealt with donor/acceptor orbital mixing and electronic coupling in the cyanide-bridged mixed-valence complexes $[(NH_3)_5Ru{-}NC{-}Fe(CN)_5]^-$ and $[t\text{-}(py\text{-}X)(NH_3)_4Ru{-}NC{-}Fe(CN)_5]^-$ (where X = py, 4-Mepy, 3-Clpy) [294]. Thermochromic effects have been investigated in the asymmetric mixed-valence complex $[(NH_3)_5Ru^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^-$ [295]. The synthesis, spectroscopic characterization, and redox properties of the triazole-bridged complexes $[(bpy)_2Ru^{II}(bpt)Rh^{III}(ppy)_2]^{2+}$ and $[(bpy)_2Ru^{II}(bpt)Ir^{III}(ppy)_2]^{2+}$ have been published. Efficient energy transfer from the higher excited states centered on the $M(ppy)_2$ moiety to the lowest energy excited state associated with the Ru(bpy) moiety is noted [296]. The reactivity of ruthenocenylbipyridines has been examined [297]. The dinuclear compounds $[(H)(CO)(PPh_3)_2Ru(\mu\text{-bim})M(COD)]$ (where M = Rh, Ir) have been studied as catalysts for the hydrogenation of cyclohexanone, styrene, and α,β-unsaturated ketones. Kinetic data have been collected and a reaction mechanism for the reaction discussed. It is suggested that the active catalyst is based on a dinuclear complex, where the ruthenium center facilitates the hydrogen transfer reaction [298]. The bifunctional supramolecule $[Ru(1,\text{-}10\text{-phen})_2(\text{phen-cyclam-Ni})]^{4+}$ has been synthesized and its spectroscopic and redox properties reported. This particular complex has been shown to function as a catalyst for the photoreduction of CO_2. In the CO_2 reduction reactions, the $Ru(1,10\text{-phen})_2$ moiety acts as a photosensitizer, and the Ni(cyclam) moiety functions as the catalytic reduction site [299]. The photophysical properties of covalently attached $[Ru(bpy)_3]^{2+}$ and $[Ni(cyclam)]^+$ are discussed [300]. Intramolecular energy transfer brin the ruthenium(II)-chromium(III) chromophore–luminophore complex $[Ru(bpy)_2\{Cr(cyclam)(CN)_2\}_2^{4+}$ has been measured and is shown to originate from a Ru(II) → Cr(III) intervalence state. Visible light absorption by the $Ru(bpy)_2^{2+}$ chromophore promotes light emission from the $Cr(cyclam)(CN)_2^+$ luminophore [301].

Luminescence and intramolecular energy-transfer processes in the cyano-bridged complexes $[(CO)_3(bpy)\text{-}Re\text{-}CN\text{-}Ru(bpy)_2\text{-}NC\text{-}Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3\text{-}bpy)Re\text{-}CN\text{-}Ru(4,4'\text{-dicarboxy-}2,2'\text{-bpy})_2\text{-}NC\text{-}Re(bpy)\text{-}CO)_3]^{2+}$ have been analyzed. Intense absorption intervalence transitions are observed in the infrared region that result from the charge transfer excited state of the partially oxidized species [302]. The extent of electronic coupling in cyano-bridged ruthenium polypyridyl complexes and the role of electronic effects on cyanide stretching frequencies have been investigated. The data on the resonance Raman spectra and time-resolved infrared measurements are reported [303]. The synthesis, luminescence data, and redox properties of hexanuclear ruthenium/osmium complexes containing the monochelating cationic ligand 2-[2-(1-methylpyridiniumyl)]-3-(2-pyridyl)pyrazine are discussed. These made-to-order complexes have unusual compositions and topologies [304]. The preparation and characterization of redox copolymers derived from $[Ru(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bpy})_3]^{2+}$ and $[Os(4\text{-vinyl-}4'\text{-methyl-}2,2'\text{-bpy})_3]^{2+}$ have been published. Luminescence experiments indicate a significant degree of energy transfer from ruthenium to osmium states in the polymer [305]. Long-range energy transfer in the oligomeric complexes $[(1,10\text{-phen})(CO)_3Re(CN)\{Ru(bpy)_2(CN)\}_nRu(bpy)_2(CN)]^{(n+1)+}$ (where $n = 0$–3) has been explored by excited-state resonance Raman spectroscopy [306]. The selective-solvation-induced intramolecular electron transfer in trimethylenebipyridine-bridged ruthenium/osmium complexes has been studied by pulsed accelerated flow spectrophotometry [307]. The synthesis and photophysical investigation of decanuclear homo- and heterometallic polypyridine complexes are presented. These supramolecular complexes exhibit relatively long-lived excited states [308]. The lifetimes of MLCT excited states of $[Ru(bpy)_2(L\text{-}L)Rh(bpy)_2]^{5+}$ [where the bridging ligand L–L = 2,6-bis(2′-pyridyl)benzdiimidazole, 2,2′-bis(2″-pyridyl)bibenzimidazole, 1,1′-dimethyl-2,2′-bis(2″-pyridyl)-6,6′-bibenzimidazole,bis{2-(2′-pyridyl)benzimidazoylethane}] have been examined by laser flash kinetic spectroscopy [309]. Optical and thermal charge-transfer processes in the three-centered, cyanide-bridged intervalent charge-transfer complexes $[Pt(NH_3)4]_2[(NC)_5M\text{-}CN\text{-}Pt(NH_3)_4\text{-}NC\text{-}m(CN)_5]$ (where M = Ru, Os) have been examined. The observed intervalence charge-transfer bands have been analyzed within the context of Marcus–Hush theory [310]. A spectroelectrochemical study of $[(bpy)_2Ru(\mu\text{-}ReS_4)Ru(bpy)_2]^{2+}$ reveals rich ligand field and IR vibrational spectral data [311].

2.8. *Alkenyl and alkylidene complexes*

The reaction of the (*E*)-alkenyl complexes $Ru(CO)(Cl)(CH{=}CHR)(PPh_3)_2$ and $Ru(CO)(Cl)(CH{=}CHR)(PPh_3)_2L$ (where L = Me_2Hpz, py) with isocyanides affords products of the form $[Ru(COCH{=}CHR)(CNR)(PPh_3)_2]^+$, which exhibit an $(E)\text{-}\alpha,\beta\text{-unsaturated-}\eta^1$-acyl ligand. The X-ray structure of $[Ru(C{\equiv}CPh)(CN\text{-}^tBu)_3(PPh_3)_2]^+$ is included [312]. Treatment of $Ru(Cl)(H)(CO)(PPh_3)_2(BSD)$ with the propargylic alcohols $HC{\equiv}CCR_2OH$ (where R = CMe_2, *cyclo*-C_6H_{11}) gives the σ-vinyl complexes $Ru(Cl)(CH{=}CHCR_2OH)(CO)(PPh_3)_2(BSD)$. The same reaction using $Ru(Cl)(H)(CO)(PPh_3)_3$, followed by treatment with BSD, yields the dehydrated σ-dienyl complexes $Ru(Cl)\{CH{=}CHC({=}CH_2)Me\}(CO)(PPh_3)_2(BSD)$ and $Ru(Cl)(CH{=}CHC_6H_9)(CO)(PPh_3)_2(BSD)$ [313]. The transfer of a vinyl ligand from mercury(II) complexes to ruthenium(II) complexes has been studied [314]. The synthesis of osmium carbene complexes by double metalation reactions involving alkoxyalkyl- and aminoalkylphosphanes has appeared [315]. The activation of diynes as a route to new bis(alkenylallenylidene)ruthenium complexes has been described [316]. The (arene)ruthenium(II) complexes $(\eta^6\text{-arene})Ru(PMe_3)(Cl)_2$ (where arene = C_6Me_6,$C_6Me_4H_2$) react with HC≡CC(R)(R′)OH, followed by metathesis with $[Na][PF_6]$, to give the cationic alkenylcarbene complexes $[(\eta^6\text{-arene})(PMe_3)(Cl)Ru{=}C(OMe)\{CH{=}C(R)(R')\}][PF_6]$. The X-ray crystal structures of several of the carbene products are presented, and mechanistic details are discussed [317]. The preparation and isolation of octahedral ruthenium(II) complexes $Ru(Cl)_2(P\text{–}O)_2$, which contain P, O-bound ligands, from the reaction between $Ru(Cl)_2(PPh_3)_3$ and $^iPr_2PCH_2CH_2OMe$ and $^iPr_2PCH_2C(O)OMe$ are described. The fluxional behavior of these complexes has been studied by variable-temperature ^{31}P NMR spectroscopy. These same complexes have been allowed to react with acetylenes to yield vinylideneruthenium(II) complexes, of which the X-ray structure of $Ru(Cl)_2(=C=CHPh)(\eta^1\text{-}^iPr_2PCH_2CH_2OMe)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)$ is discussed [318]. The catalytic activity of a well-defined diruthenium alkylidene complex in alkene polymerization reactions has been examined [319]. The synthesis and study of carbene migratory insertion reactions of a ruthenium carbene complex have appeared [320]. The σ-acetylide complex $CpRu(CO)(PPh_3)(C{\equiv}CPh)$ reacts with *trans*-$CH(CO_2Me){=}C(CN)(CO_2Me)$ to give two isomeric cyclobutenyl compounds based on $CpRu\{C{=}C(Ph)C(H)(CO_2Me)C(CN)(CO_2Me)\}(CO)(PPh_3)$. Thermal opening of the cyclobutenyl ring in both isomers occurs in a conrotatory manner to afford the same butadienyl complex $CpRu[\{C(=C(CN)(CO_2Me))\}C(Ph){=}C(H)(CO_2Me)](CO)(PPh_3)$. All four complexes have been structurally characterized by X-ray crystallography [321].

2.9. π Complexes

The synthesis and ligand exchange reaction of $[(COD)Ru(H_2O)_4][OTs]_2$ have been reported. The X-ray crystal structure of this complex reveals a highly distorted octahedral arrangement of the ligands about the ruthenium center [322]. Complexes of the form $Ru(\eta^4\text{-1,3-diene})(\eta^4\text{-COD})(nitrile)$ have been prepared from the reaction between 1,3-dienes and $Ru(\eta^6\text{-naphthalene})(\eta^4\text{-COD})$ in the presence of nitriles [323]. Treatment of $[Ru(\eta^5\text{-2,4-dimethylpentadienyl})_2(H)]^+$ with various ligands affords the complexes $[Ru(\eta^5\text{-2,4-dimethylpentadienyl})(L)_3]^+$ [324]. Disrotatory, electrocyclic closure and dehydrogenation of one of the pentadienyl ligands in $Ru(\eta^5\text{-2,4-Me}_2C_5H_5)_2$ have been observed [325]. Hydrogen migration to acyclic pentadienyl ligands has been studied in $[Ru(\eta^5\text{-2,4-dimethylpentadienyl})(\eta^4\text{-2,4-dimethylpenta-1,3-diene})(L)]^+$ {where L = ^tBuNC, CO, $P(OMe)_3$} complexes [326].

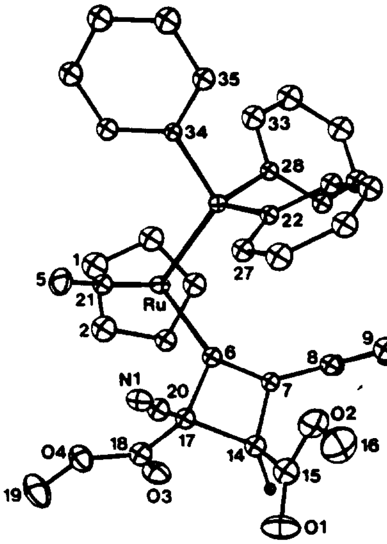

Fig. 14. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

The use of packing potential energy calculations and computer graphic analysis to study the molecular organization in crystals of ruthenocene has been discussed [327]. The synthesis and spectral characterization of the protected ethynyl ruthenocenes 1-(3-hydroxy-3-methylbut-1-ynyl)4-ruthenocene, 1,1′-bis(3-hydroxy-3-methylbut-1-ynyl)ruthenocene, and 1,3,1′-tris(3-hydroxy-3-methylbut-1-ynyl)ruthenocene have been published [328]. The synthesis of $Ru(Cp^*)(\eta^5\text{-}C_5F_5)$, which is the first transition-metal complex with a pentafluorocyclopentadienyl ligand, has appeared [329]. The reaction of 1,1′-dilithioosmocene with elemental sulfur yields the bridged osmocene compound 1,2,3-trithia[3]-osmocenophene. The X-ray structure of this complex reveals that the cyclopentadienyl rings adopt an eclipsed conformation [330]. The enantioselective reduction of benzoyl derivatives of ruthenocene has been examined as a route to carbinols and diols [331]. The synthesis and NMR examination (^1H and ^{13}C) of metallocenyldiphenylmethyl hexafluorophosphates have been investigated. Included in this report is the X-ray crystal structure of $[(Cp)Os(C_5H_4CPh_2)]^+$. The stabilization of the α-carbocationic center for diphenyl-substituted cations increased in the order Fe < Ru < Os [332]. The synthesis of the half-open metallocenes $(Cp^*)Ru(pentadienyl)$ and $(Cp^*)Ru(diene)(Cl)$ starting from $[(Cp^*)Ru(Cl)_2]_n$ is described [333]. The azaruthenocenes $[(Cp^*)Ru(\eta^5\text{-}C_4Me_4N)]$ and $[(\eta^5\text{-}C_4Me_4N)_2Ru]$ have been prepared from $[(Cp^*)Ru(Cl)_2]_n$ and (2,3,4,5-tetramethylpyrrolyl)lithium. Both azaruthenocenes have been characterized by NMR analysis and their stability is discussed [334]. A report that outlines the development of a parameter scale for substituent effects in cyclopentadienylruthenium complexes has been published [335]. The reduction of $[(\eta^5\text{-}C_4Me_4S)_2Ru][OTf]_2$ with Cp_2Co affords the neutral complex $(\eta^5\text{-}C_4Me_4S)_2Ru$, which is shown to be unstable above −20°C. Variable-temperature NMR studies reveal that the observed fluxional behavior derives from the interconversion of $\eta^5\text{-}C_4Me_4S$ and $\eta^4\text{-}C_4Me_4S$ ligands. The coordination of "$Fe(CO)_4$" to one of the sulfur atoms has been demonstrated [336]. The mercuration of $(Cp^*)_2Ru$ using mercuric acetate yields the complex pentakis(acetoxymecurio)pentamethylruthenocene. Halogenation of this complex with halide ion gives the corresponding pentahalopentamethylruthenocene (halogen = Br, I). The molecular structure of the iodo complex has been determined by X-ray diffraction analysis [337]. The synthesis of several half-open ruthenocenes of the form (Cp*)Ru(pentadienyl) have been reported and characterization by solution methods and X-ray crystallography presented [338].

The reactivity of $[(Cp^*)Ru(OMe)]_2$ with dppm has been examined and the products of hydroxy and hydrogen sulfide exchange for the methoxy groups characterized [339]. Olefin activation and allyl ligand formation have been observed when $[(Cp^*)Ru(OMe)]_2$ is allowed to react with simple olefins [340]. Treatment of $[(Cp^*)Ru(OMe)]_2$ with but-3-en-1-ol leads to exchange of the alkoxo group and formation of $[(Cp^*)Ru\{\eta^3\text{-}O(CH_2)_2\text{-}CH{=}CH_2\}]_2$, whose molecular structure has been solved by X-ray crystallography. This complex reacts with two-electron donor ligands to yield $(Cp^*)Ru(\eta^3\text{-}CH_2\text{-}CHCHCHO)L$. The butenyloxy group is transformed into an allenecarboxaldehyde upon ligand capture [341]. The reaction between $(Cp^*)Ru(P)(Cl)$ (where $P = PCy_3$, $^iPr_2PPh$) and TlOR (where $R = CH_2CF_3$) gives $(Cp^*)Ru(P)(OR)$. The X-ray crystal structure of the PCy_3 derivative is presented [342].

The reaction of $(Cp^*)Ru(^iPr_3P)(H)(\eta^2\text{-}CH{=}SiPh_2)$ with hydrosilanes occurs with an initial migration of hydride to the silene ligand, followed by the formation of disilyl hydride or silyl dihydride ruthenium(IV) complexes. The X-ray diffraction data of $(Cp^*)Ru(^iPr_3P)(H)_2(SiHClMes)$ are discussed [343]. The synthesis of donor-stabilized silylene ligands at a ruthenium center has appeared. The X-ray diffraction structure of $[(Cp^*)Ru(PMe_3)_2\{Si(STol\text{-}p)_2\}(1,10\text{-phen})][OTf]_2$ is presented in this report [344]. The ruthenium(0)-silanediyl complexes $(^tBuO)_2(HMPA)Si{=}Ru(CO)_4$, $Me_2(HMPA)Si{=}Ru(CO)_4$, $Cl_2(HMPA)Si{=}Ru(CO)_4$, $Ph_2(HMPA)Si{=}Ru(CO)_4$, and $HCl(HMPA)Si{=}Ru(CO)_4$ have been obtained from the reaction between $[Ru(CO)_4]^{2-}$ and the appropriate chlorosilane. Variable-temperature ^1H NMR data indicate that the HMPA ligand remains coordinated to the silicon center [345].

The complexes $(Cp)Ru(PPh_3)_2\{S(SO_2)R\}$ and $(Cp)Ru(PPh_3)(SO_2)\{S(SO_2)R\}$ (where $R = 4\text{-}C_6H_4Me$, n-propyl, isopropyl) have been prepared from $(Cp)Ru(PPh_3)_2(SR)$ upon treatment with SO_2. The conditions that favor these products are discussed, and the X-ray diffraction structure of $(Cp)Ru(PPh_3)(SO_2)\{S(SO_2)\text{-}4\text{-}C_6H_4Me\}$ presented [346].

The synthesis of $(Cp)Ru(PPh_3)_2(SeH)$ and $(MeCp)Ru(PPh_3)_2(SeH)$ is reported. $(Cp)Ru(PPh_3)_2(OTf)$ reacts with elemental selenium to afford $[(Cp)Ru(PPh_3)_2]_2(\mu\text{-}\eta^1, \eta^1\text{-}Se_2)(OTf)_2$. The X-ray diffraction structures of two of these products and the reduction chemistry are discussed [347]. The thiobenzaldehyde complexes $[(Cp)Ru(P_2)(\eta^2\text{-}S{=}CHC_6H_4\text{-}4\text{-}X)]^+$ (where P_2 = dppm, dppe; X = H, Cl, OMe) have been prepared by a β-hydride abstraction reaction from the corresponding thiol complex [348]. The synthesis, characterization, and reactivity of chiral half-sandwich phosphaallyl complexes have been published. The molecular structures of $[(Cp)Ru(\eta^1\text{-}Ph_2PCH{=}CH_2)(\eta^3\text{-}Ph_2PCH{=}CH_2)]^+$ and $[(Cp)Ru(Ph_2PCH{=}CH_2)_2(CO)]^+$ have been solved by crystallographic methods [349]. The reaction between $(Cp^*)Ru(bpy)(Cl)$ with different two-electron donor ligands yields $[(Cp^*Ru(bpy)(L)]^+$. The solid-state structure of the ethyl maleate complex has been solved by X-ray crystallography [350].

The oxidation of $[(Cp^*)Ru(Cl)_2]_n$ by chemical or electrochemical methods in the presence of thiophene produces $[(Cp^*)Ru(Cl)_2(\text{thiophene})_2]^+$, which has been characterized by X-ray diffraction analysis in the case of the perchlorate salt [351]. The reaction between $(Cp)Ru(PPh_3)_2(Cl)$ with ether–phosphine ligands $P \sim O$ yields $(Cp)Ru(PPh_3)(P \sim O)(Cl)$ and $(Cp)Ru(P \sim O)_2(Cl)$, of which the X-ray structure of $(Cp)Ru(Ph_2PCH_2CH_2OMe)_2(Cl)$ has been solved [352]. The complex $[(Cp)Ru(PMe_2Ph)_2(\eta^2\text{-acetylene})]^+$, which has been obtained from the reaction between $(Cp)Ru(PMe_2Ph)_2(Cl)$ and acetylene, rearranges to the vinylidene isomer, $[(Cp)Ru(PMe_2Ph)_2(C{=}CH_2)]^+$, which upon treatment with base yields the acetylide complex $(Cp)Ru(PMe_2Ph)_2(C{\equiv}CH)$. The X-ray crystal structures of the acetylene and vinylidene complexes are presented [353]. The enthalpies of protonation and ^1H NMR data for $(Cp)Os(PPh_3)_2X$, $(Cp)Os(PPh_2Me)_2X$, $[(Cp)Os(PPh_3)_2(X)(H)]^+$, and $[(Cp)Os(PPh_2Me)_2(X)(H)]^+$ (where X = H, Cl, Br, I) have been published [354]. The synthesis and X-ray diffraction study of $(Cp^*)Ru(acac)(CF_2{=}CF_2)$ have appeared. The influence of the strong π acceptor ligand $CF_2{=}CF_2$ on the

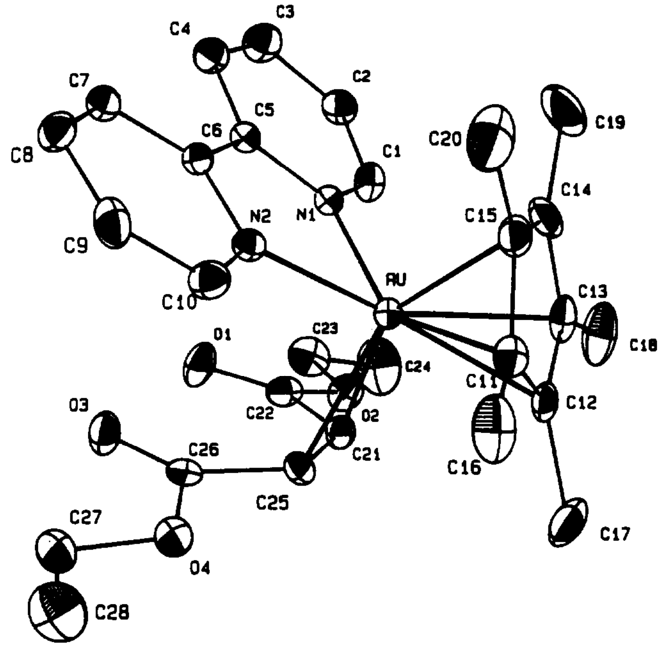

Fig. 15. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

observed low barrier to propeller rotation is discussed [355]. The conversion of (Cp and Cp*)Ru(CO)$_2$X (where X = Cl, Br) to halomethyl, alkoxymethyl, and cyanomethyl complexes is described [356]. The stereochemical aspects of the synthesis and reactivity of (diphosphine)(carbonyl)(cyclopentadienyl)ruthenium complexes have been investigated [357]. A study on the oligomerization of butadiene using the complexes (Cp or Cp*)Ru(η-butadiene)(X) (where X = Cl, Br) has appeared [358]. The thermolysis of (Cp)Ru(CO)$_2${CH(Me)Ph} in benzene solution has been examined and the Ru–CH(Me)Ph bond dissociation energy calculated [359]. The propargyl complexes (Cp)Ru(L)$_2$(CH$_2$-C≡CPh) (where L = CO, PPh$_3$) have been prepared from the reaction between [(Cp)Ru(CO)$_2$]$^-$ and PhC≡CCH$_2$Cl or PhC≡CCH$_2$Os(O)$_2$C$_6$H$_4$Me-4 and (Cp)Ru(PPh$_3$)$_2$(Cl) with PhC≡CCH$_2$MgCl. The reactivity of these propargyl complexes with acid and other transition-metal complexes is reported [360]. The reaction between [(Cp or Cp*)Ru(CO)$_2$]$^-$ with the diphosphene complexes Cp*P=PMes* and Cp*P=PCp* and the arsaphosphene complex Cp*As=PMes* has been reported to give ruthenium-substituted diphosphenes, arsaphosphenes, and tetraphospha-bicyclobutanes [361].

The "Cp*Ru$^+$" fragment has been allowed to react with cyclic chlorinated hydrocarbons to give [(Cp*)Ru(η^6-C$_6$H$_6$)]$^+$. The dechlorination reaction is discussed with respect to C–X bond reactivity (where X = Cl, O, H, C) [362]. The protonation chemistry of ruthenium and osmium diene complexes has been explored. The fluxional NMR behavior of the products and the balance between terminal and agostic hydrides are discussed [363]. The synthesis, X-ray diffraction studies, and chemical reactivity of (Cp)Ru{(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$}(Cl) have been published. The corresponding hydride and methyl complexes are obtained from [(Cp)Ru{(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$}]$^-$, which is readily synthesized by sodium naphthalide reduction of the chloro complex [364]. The resolution of tert-butyl methyl sulfoxide using the ruthenium fragment "(Cp)Ru(CO)(PPh$_3$)$^+$" has been outlined. The use of the ruthenium complex as a Lewis acid template and the resolution procedures are fully discussed [365]. The enthalpies for the formation of [(Cp*)Ru(MeCN)$_3$][OTf] and arene are reported. The factors affecting the Ru-arene bond energy are discussed, and the X-ray crystal structure of [(Cp*)Ru(η^6-C$_6$H$_5$SiMe$_3$)][OTf] presented [366]. The complex [(Cp)Ru(1-phenyl-3,4-dimethylphosphole)$_2$(MeCN)]$^+$ has been allowed to react with a wide variety of dienophiles. The scope and diastereoselectivity of these intramolecular [4 + 2] cycloadditions are discussed and many X-ray crystal structures presented [367]. The kinetic and thermodynamic acidity of η^2-dihydrogen and dihydride ligands complexes of the form [(Cp*)Ru(L)$_2$(H)$_2$]$^+$ (where L = various mono- and bidentate phosphines) has been investigated. The identity of a dihydrogen ligand in a given complex is ascertained by using T$_1$ and ^1J(HD) measurements. A single-crystal X-ray diffraction study of [(Cp*)Ru(η^2-H$_2$)(dppm)]$^+$ is included in this study [368]. The Arbuzov rearrangement of (allyloxy)phosphines catalyzed by [(Cp)Ru(MeCN)$_3$]$^+$ has been studied. The molecular structure of [(Cp)Ru{η^5-P(OCH$_2$-CH=CH$_2$)$_3$}]$^+$, which was solved by X-ray diffraction analysis, and other isolated intermediates have been used in a discussion of the reaction mechanism that is presented [369].

A study on multiple-ligand bonding in the osmium imido complexes Os(η^6-C$_6$Me$_6$)(N-^{t}Bu) and Os{η-1,4-(CHMe$_2$)MeC$_6$H$_4$}(N-^{t}Bu) has appeared. The He I and He II photoelectron data provide evidence for a cyclopentadienyl-imido analogy [370]. The dialkylosmium(II) complexes (Mes)Os(CO)(R)$_2$ (where R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) have been synthesized from (Mes)Os(CO)(Cl)$_2$ and the Grignard reagent RMgX. The synthesis of hydrido/olefin complexes and hydride abstraction reactions are included in the report [371]. The synthesis and vibrational analysis of (arene)osmium(II) complexes have been published. The assignment of the vibrational modes are supported by polarized Raman spectra [372]. The reaction of nucleophiles (H$^-$, CN$^-$,

OH^-) with (η^6-arene)(η^6-[2.2]paracyclophane)ruthenium(II)tetrafluoroborate (where arene = benzene, *p*-cymene, 1,4-diisopropylbenzene, hexamethylbenzene) produces (η^5-cyclohexadienyl)(η^6-[2.2]paracyclophane)ruthenium(II) complexes. Similar reactions have been conducted with the osmium(II) η^6-C_6H_6 analogue and the results reported [373]. The synthesis, properties, and X-ray crystal structures of diastereomeric arene ruthenium(II)chiral Schiff-base complexes have appeared [374]. The ruthenacyclobutane complexes $\overline{\mathrm{Ru(CH_2CMe_2C}}\mathrm{H_2)}(\eta^6\text{-}C_6Me_6)(PRPh_2)$ (where R = Me, Ph) have been shown to decompose when treated with alumina [375]. The synthesis and spectroscopic characterization of (η^6-arene)ruthenium (II) trifluoromethylsulfonates and dinulear di-μ- and tri-μ-hydrido (η^6-arene)ruthenium(II) complexes are reported. The catalytic activity of these complexes in cyclohexene and 1-hexene hydrogenation reactions has been investigated [376]. The 2,6-diphenylthiophenolate anion reacts with $Ru(Cl)_2(PPh_3)_3$ to give (η^6-2,6-diphenylthiophenolate)Ru(2,6-diphenylthiophenolate)-(PPh_3), which was characterized by X-ray crystallography [377]. Areneruthenium(II) complexes with a bifunctional bridging phosphonomethylalkoxycarbene ligand have been prepared [378]. Treatment of $[(\eta^6\text{-}C_6H_6)Ru(Cl)_2]_2$ with $Cy_2PCH_2CH_2PCy_2$ in the presence of AgO_3SCF_3 gives $[(\eta^6\text{-}C_6H_6)Ru(Cl)(Cy_2PCH_2CH_2PCy_2)]^+$. This cation reacts with NaK alloy to give $(\eta^6\text{-}C_6H_6)Ru(Cy_2PCH_2CH_2PCy_2)$ and with the hydridic reagents $NaBH_4$ and $LiAlH_4$ to give the corresponding ruthenium hydride complex $[(\eta^6\text{-}C_6H_6)Ru(H)(Cy_2PCH_2CH_2PCy_2)]^+$ and $(\eta^5\text{-}C_6H_7)Ru(H)(Cy_2PCH_2CH_2PCy_2)$, respectively [379]. Intermolecular hydrogen bonding in ruthenium–hormone complexes has been examined by way of the X-ray crystal structures of α-[(Cp*)Ru(estradiol)]$^+$ and α-[(Cp*)Ru{3-O-(hydroxypropyl)estradiol}]$^+$. Strong intermolecular hydrogen bonding between the ruthenium hormone subunits is observed [380]. The reaction of $[(Cp)Ru(\eta^6\text{-}1,3\text{-}Cl_2C_6H_4)]^+$ with phenoxide nucleophiles has been studied, and the methodology for the sequential selective displacement of both chloride groups by different nucleophiles has been presented [381]. The use of areneruthenium complexes in the preparation of vancomycin has appeared [382]. A one-step synthesis of the tetramethylbenzene alkenyloxy-alkenylcarbene ruthenium(II) complexes $[(\eta^6\text{-}C_6Me_4H_2)Ru{=}C\{O(CH_2)_mCH{=}CH_2\}\{CH{=}CH(CH{=}CH)_n\text{-}R\}(Cl)(PMe_3)]^+$ (where m = 1, 2; n = 0, 1, 2) from the dichlororuthenium complex $(\eta^6\text{-}C_6Me_4H_2)Ru(Cl)_2(PMe_3)$ is reported. Also discussed is the formation of an η^5-allyl–alkene ruthenium complex [383]. Arene versus thiophene reduction and thiophene ring protonation in $[(\eta^6\text{-}C_6Me_6)$ Ru(thiophene)$]^+$ have been investigated. The redox behavior of this complex has been examined and the

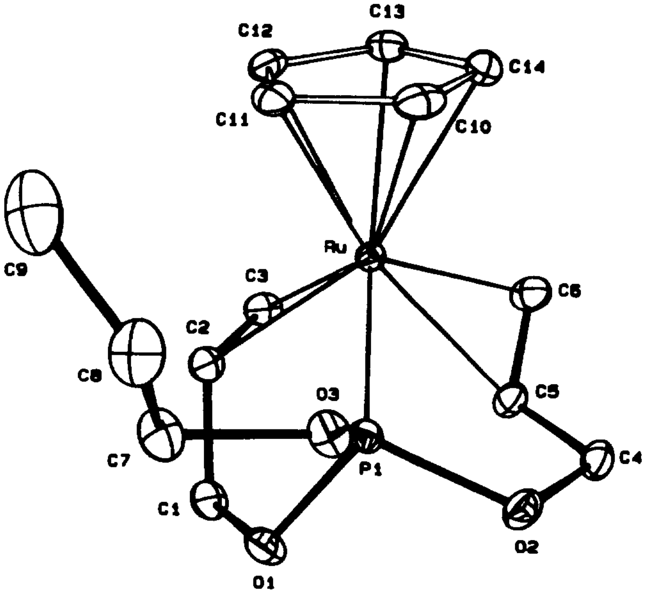

Fig. 16. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

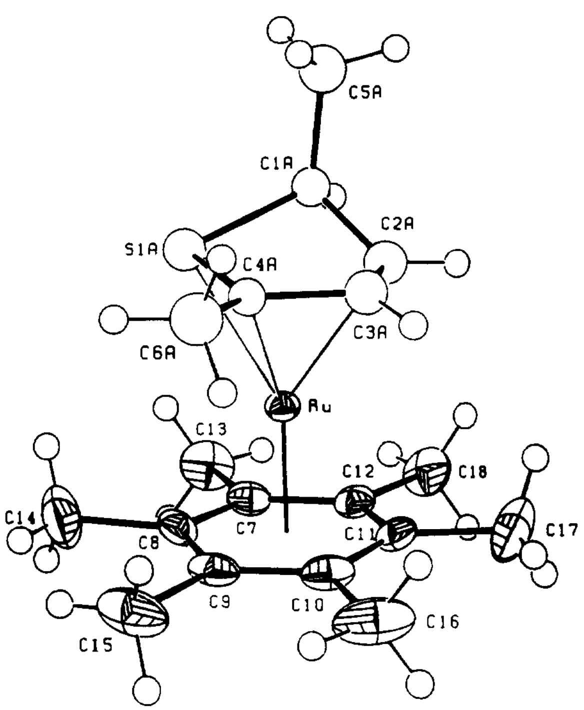

Fig. 17. Reprinted with permission from *J. Am. Chem. Soc.* Copyright 1992 American Chemical Society.

X-ray crystal structure of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2\text{-}C_4H_2\text{-}5\text{-}2\text{-}H)]^+$ presented [384].

3. Dinuclear complexes

3.1. Homodinuclear complexes

The synthesis and structural characterization of the adamantylcarboxylate-containing complexes $[Ru_2(C_{10}H_{15}CO_2)_4(MeOH)_2]\cdot 2MeOH$ and $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(MeOH)]\cdot 2MeOH$ are reported. The starting material used in the preparation of these complexes was $[Ru_2(CO_3)_4][K]_3\cdot 4H_2O$ [385]. Polymeric $[Ru_2(O_2CEt)_4(phenazine)]^+$ has been obtained from the reaction between $[Ru_2(O_2CEt)_4(H_2O)_2]^+$ and phenazine. The product has been examined by X-ray diffraction analysis and magnetic susceptibility methods [386]. The triply bridged diruthenium complexes $[Ru_2^{III}(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{2+}$ and $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{3+}$ have been synthesized and characterized by spectroscopic methods. The redox behavior has been investigated by cyclic voltammetry [387]. Treatment of $Ru_2(chp)_4Cl$ with pyridine and pyrazine gives the dinuclear complex $[Ru_2(chp)_4(py)]^+$ and the tetranuclear species $[\{Ru_2(chp)_4\}_2(pz)]^+$, respectively. The X-ray crystal structures of both complexes along with the variable-temperature magnetic susceptibility data are presented [388]. The related diruthenium triazeno complexes $Ru_2[(p\text{-tolyl})NNN(p\text{-tolyl})]_4(MeCN)$, $Ru_2(PhNNNPh)_4$, and $Ru_2[(p\text{-tolyl})NNN(p\text{-tolyl})]_4(MeCN)\cdot BF_3$ have been prepared and crystallographically examined. Magnetic susceptibility and EPR data on the latter complex confirm the existence of a π^{*3} ground state configuration [389]. Polymeric chain cleavage in $Ru_2(O_2CR)_4Cl$ has been examined and found to give the cationic–anionic complexes $[Ru(Cl)(MeCN)_3(PPh_3)_2]_2[Ru_2(Cl)_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$, $[Ru(Cl)(MeCN)_4(PPh_3)][Ru(Cl)(MeCN)_4(PPh_3)][Ru_2(Cl)_2(O_2\ CC_6H_4\text{-}p\text{-}OMe)_4]$, and $[Ru(Cl)(MeCN)_3(PPh_3)_2][Ru_2(Cl)_2(O_2CR)_4]$ (where R = Me, Ph, $C_6H_4\text{-}p\text{-}Me$). The X-ray crystal structures of the first two complexes have been solved [390]. The redox chemistry of $[Os_2(Cl)_8]^{2-}$ has been explored by using spectroelectrochemical methods, and evidence for the formation of $[Os_2(Cl)_8]^-$ and $[Os_2(Cl)_8]^0$ presented [391]. A new synthesis for $[Ru_2(CO_3)_4][M]_3\cdot n\text{-}H_2O$ (where M = Na, K) has appeared. The molecular structure of the sodium complex has been determined by X-ray crystallography. Cyclic voltammetric studies indicate that the observed one-electron oxidation is at best quasi-reversible, which explains the instability of the oxidation product in water [392].

The synthesis of 1′, 1‴-diethylbiruthenocene and 1′,1‴-dipropylbiruthenocene, from 1,1″-diacetylbiruthenocene and 1′, 1‴-dipropionylbiruthenocene, respectively, and ^1H NMR behavior of the mixed-valence halo-1′,1‴-dialkylbiruthenocenium(II, IV) salts are discussed. The rate of electron transfer between the Ru^{II} and Ru^{IV} centers in the dialkyl complexes is slow relative to the halobisruthenocenium complexes as a result of dialkyl group steric hindrance [393]. The reaction between 1,1″-biruthenocene and FeX_3 in $HX\text{–}NH_4PF_6$ (where X = Cl, Br) and I_2 has been examined. The resulting mixed-valence biruthenocenium salts have been characterized by ^{13}C CP–MAS, ^{13}C, and ^1H NMR spectroscopy [394]. The X-ray crystal structure of [1.1]ruthenocenophane has been determined in order to study the consequences of the ruthenium–ruthenium bond [395]. Single-crystal X-ray data on the [1.1] metallocenophanes$(C_5H_4\text{-}CH_2\text{-}C_5H_4)FeRu(C_5H_4\text{-}CH_2\text{-}C_5H_4)Ru_2$ have been reported. The degree of twist in these complexes is correlated with the redox potential of each complex [396].

Treatment of the dianion derived from 2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene with $[(Cp^*)Ru(Cl)]_4$ yields a diruthenium complex with a doubly bridged cyclopentadienyl ligand [397]. The reaction of O_2 with the paramagnetic polymer $[(Cp^*)Ru(Cl)_2]_n$ affords the oxo-bridged ruthenium(IV) complex $[(Cp^*)Ru(Cl)_2]_2O$, which has been cocrystallized with dibenzothiophene and examined by X-ray crystallography [398]. A report on silylene-bridged ruthenium dimers has appeared. The reaction between Ph_2SiH_2 and the coordinatively unsaturated complex $[(Cp^*)Ru(\mu\text{-}OMe)]_2$ furnishes $[(Cp^*)Ru]_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)$. The unequivocal identity of this product was established by X-ray diffraction analysis. When the same reaction is conducted with $CyMeSiH_2$, only $[(Cp^*)Ru(\mu\text{-}\eta^2\text{-}H\text{-}SiMeCy)]_2(\mu\text{-}H)(H)$ is isolated [399]. The new ruthenium complexes $[(Cp^*)Ru(OMe)]_2\{P(OMe)_3\}$, $(Cp^*)Ru\{P(OMe)_3\}_2(OMe)$, and $(Cp^*)Ru\{P(OMe)_3\}_2\{PO(OMe)_2\}$ have been isolated from the reaction between $P(OMe)_3$ and $[(Cp^*)Ru(OMe)]_2$ [400]. The molecular structure of $[(Cp^*)Ru(CO)_2]_2$ has been determined by X-ray crystallography. The complex exists as the *trans* isomer only in the solid state [401]. The μ-methylene complex $(Cp)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ and the di(μ-methylene) complex $(Cp)_2Ru(CO)_2(\mu\text{-}CH_2)_2$ have been obtained from the reaction between dihydrosilanes and $(Cp)_2Ru_2(CO)_4$ [402]. The acid-catalyzed reaction of ethylene with the Ru=Ru double-bonded μ-alkyne complex $(Cp)_2Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)$ occurs by way of ethylene C–H bond activation and alkyne-linking. The formation of the Ru≡Ru triple-bonded μ-vinyl cation $[(Cp)_2Ru_2(\mu\text{-}CO)(\mu\text{-}CR{=}CHR)]^+$ is also described [403]. The synthesis and reactivity of diruthenium μ-silyl complexes possessing three-center two-electron Ru–H–Si interactions are discussed [404]. Diphenylacetylene reacts with

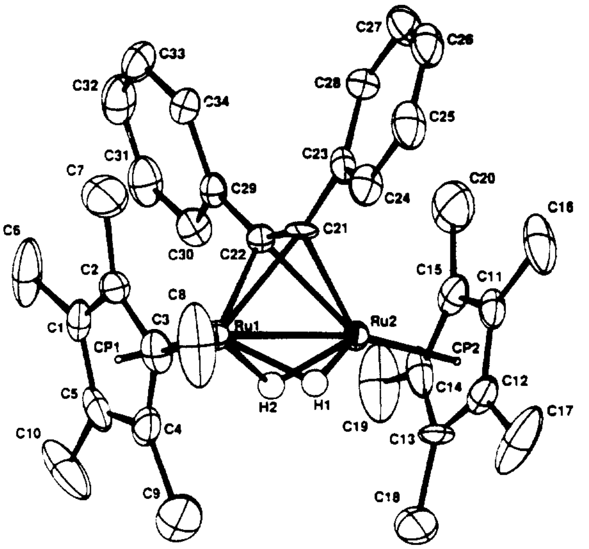

Fig. 18. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

the tetrahydride complex (Cp*)Ru(μ-H)$_4$Ru(Cp*) to afford (Cp*)Ru(μ-H)$_2$(μ-PhCCPh)Ru(Cp*). X-Ray diffraction analysis establishes the presence of the perpendicularly bridging diphenylacetylene ligand [405].

The diruthenium complex [(Cp*Ru)$_2$-η, η^6-chrysene]$^{2+}$ has been synthesized and reduced to the mixed-complex [(Cp*Ru')(Cp*Ru'')-η^6, η^6-chrysene]$^+$ using chemical and electrochemical methods. The EPR and intervalence absorption data for this mixed-valence complex are reported [406]. New dinuclear hydroxo-, methoxo-, and pyrazolate-bridged complexes of ruthenium(II) have been synthesized and characterized. The X-ray crystal structure of [{(*p*-cymene)Ru}$_2$(μ-pyrazole)(μ-OH)$_2$]$^+$ is included [407]. The synthesis and X-ray structural determination of [{(C$_6$Me$_6$)Ru}$_2$(μ-SPh)$_3$]$^+$ have been published [408]. Geometrical isomerism in 2-hydroxypyridinate and pyridine-2-thiolate complexes derived from the bis(allyl) ruthenium (IV) dimer [Ru(η^3 : η^3-C$_{10}$H$_{16}$)(Cl)(μ-Cl)]$_2$ has been investigated. The NMR properties and the X-ray crystal structures of two of the products are discussed [409]. The synthesis of the thiocyanato S,N-bridged dimer [Ru(η^3 : η^3-C$_{10}$H$_{16}$)(Cl)(μ-SCN)]$_2$ is presented and is shown to exist in two diastereomeric forms [410].

The synthesis and X-ray crystal structures of Ru$_2$(μ-S$_5$)(μ-S$_2$CNMe$_2$)(S$_2$CNMe$_2$)(CO)$_2$(PPh$_3$)$_2$ and Ru$_2$(μ-S$_6$)(μ-S$_2$CNMe$_2$)(S$_2$CNMe$_2$)(CO)$_2$(PPh$_3$)$_2$ have appeared [411]. The preparation, reactivity, and X-ray structure of the μ-hydrazine-bridged mixed-valence ruthenium(II, III) complex [Ru(Cl){P(OMe)$_3$}]$_2$(μ-Cl)(μ-N$_2$H$_4$)(μ-S$_2$) are discussed [412]. The TMSO-substituted complex (Br)$_6$(TMSO)$_2$Ru$_2$(μ_2-TMSO)$_2$(μ{3}-TMSO)$_2$(Li)$_2$(TMSO)$_2$ has been obtained from RuCl$_3$ · 3H$_2$O [413].

The electron transfer reactivity of Ru$_2$(μ-CO)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$ (where R = Me, ^{i}Pr) has been examined by using the acceptor molecule *o*-chloranil. Both electron transfer and the fission of one of the diphosphazane ligands to give Ru$_2${μ-(RO)$_2$PN(Et)C(O)}{(RO)$_2$POC$_6$Cl$_4$O}(CO)$_4${μ-(RO) $_2$PN(Et)P(OR)$_2$} are observed in the reaction. The X-ray structure of the fission product (R = Me) accompanies the report and establishes the P–O bond cleavage [414]. The protonation of the diphosphazene complexes Ru$_2$(μ-CO)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$ (where R = Me, ^{i}Pr) using HBF$_4$ or HPF$_6$ has been shown to give the terminal hydride complex [Ru$_2$(H)(CO)$_5${μ-(RP)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$, whereas the use of HX (where X = Cl, Br, NO$_3$, FBO$_2$H, CF$_3$CO$_2$) gives both terminal and bridged hydride products. The X-ray structures of two of these products and the fluxional behavior of the hydrido complexes [Ru$_2$(H)(CO)$_5${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$]$^+$ are reported [415]. The investigation of the reaction of the diphosphazane-bridged diruthenium complexes Ru$_2$(μ-CO)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_2$}$_2$ (where R = Me, ^{i}Pr) with TCNE and TCNQ by EPR/ENDOR, UV-visible and near-IR spectroscopy is presented. Cyclic voltammetric data indicate the presence of distinct reduction waves ascribed to ruthenium-coordinated and noncoordinated TCNE and TCNQ species [416]. Charge-transfer salts have been obtained from the reaction between Ru$_2$(μ-CO)(CO)$_4${μ-(RO)$_2$PN(Et)P(OR)$_3$}$_2$ (where R = Me, ^{i}Pr) and TCNQ and TCNE [417].

The synthesis, characterization, and reactivity study of the mixed-valence complexes (P–P)(Cl)Ru(μ-Cl)$_3$Ru(Cl)(P–P) have been described [418]. The diphenylphosphine complex tranforms into the diphenylphosphido complex Ru$_2$(CO)$_6$(μ-PPh$_2$)$_2$ under CO gas. The formation of the ethyldiphenylphosphine complex Ru$_2$(CO)$_4$(μ-O$_2$CEt)$_2$(PPh$_2$Et)$_2$ has been observed when the phosphido complex is allowed to react with ethylene and water. A discussion on the catalytic hydroformylation of ethylene is presented in light of the last complex [419]. Three products have been isolated from the reaction between Ru$_2$(dmpm)$_2$(CO)$_5$ and DMAD. The X-ray crystal structures of Ru$_2$(dmpm)$_2$(CO)$_3${μ-C$_2$(CO$_2$Me)$_2$}{C(O)C(O)C$_2$(CO$_2$Me)$_2$} and Ru$_2$(dmpm)$_2$(CO)$_4${μ-C(O)C$_2$(CO$_2$Me)} are included and discussed with respect to the unusual double insertion of CO observed in the former complex [420].

Hydrogenation of the central C–C bond of coordinated α-diimineligands in (H)$_2$Ru$_2$(CO)$_5$(^{i}PrN=CHCR=N-^{i}Pr) (where R = H, Me) involves C–H and Ru–H bond-making and -breaking processes. The molecular structures of $(H)_2Ru_2(CO)_5(^iPrNCH_2CH_2N\text{-}^iPr)$ and $Ru_2(CO)_6(^iPrNCH_2CH_2N\text{-}^iPr)$ have been determined by X-ray crystallography [421]. The reactivity of alkylated ruthenium α-diimine complexes toward CO and phosphines has been studied. Treatment of $Ru_2(CO)_5(^iPrDAB)$ with MeI affords the structurally characterized complex $Ru_2(Me)(I)(CO)_4(^iPrDAB)$. Here the $Ru(CO)_2(Me)$ and $Ru(CO)_2$ fragments are held together by a bridging iodide and bridging α-diimine ligand [422].

3.2. Heterodinuclear complexes

The improved synthesis of the heterometallic complex $RuMn(CO)_5(Cp)(\mu\text{-}H)(\mu\text{-}PPh_2)$ and its reactions with alkynes and phosphines have been reported. The alkyne complex $RuMn\{\mu\text{-}\sigma : \eta^2\text{-}C(Ph){=}CH(Ph)\}(\mu\text{-}PPh_2)(Cp)(CO)_4$ has been structurally characterized by X-ray crystallography [423]. The heterometallic phosphido complexes $RuFe(\mu\text{-}PPh_2)_2(CO)_6$ and $RuM(\mu\text{-}PPh_2)_2(CO)_4$ (where M = Cr, Mo, W) have been prepared by the bridge-assisted method. The hydrogenation of cyclohexanone was found to be effectively catalyzed by the RuFe dimer [424].

The nature of the metal–metal bond in the donor–acceptor complexes $(OC)_5OsM(CO)_5$ (where M = Cr, W) has been explored by *ab initio* molecular orbital calculations. The dative metal–metal bond was supported by the calculations, where the highest occupied σ-orbital of $Os(CO)_5$ and the lowest unoccupied σ-orbital of $m(CO)_5$ interact to form the observed Os–M bond [425]. The complex $(COD)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$, which is the kinetic product obtained from the reaction between $[Ru(H)_3(PPh_3)_3]^-$ and $[Ir(COD)(Cl)]_2$, isomerizes to $(COD)Ir(\mu\text{-}H)_2Ru(H)(PPh_3)_3$, with *mer* phosphine groups. The reactivity of the thermodynamic complex with H_2 and temperature-dependent ^1H NMR behavior are presented, and the X-ray crystal structure of the latter dimer solved [426]. The reaction of MeCN with $(PPh_3)_2(CO)(H)Re(\mu\text{-}H)_3Ru(H)(PPh_3)_2$ leads to $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(MeCN)(PPh_3)_2$. The reaction may be reversed by treatment with H_2. When the same reaction is examined with PhCN, only $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$, the result of nitrile hydrometalation, is observed. The terminally bound PhCN ligand is readily displaced by CO to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2$. The identity of the former hydrometalated nitrile complex has been determined by X-ray diffraction analysis [427]. The η^2-iminoacyl complex $(Cp)(PMe_3)_2RuCH{=}CHC(N\text{-}^tBu)Zr(Cl)(Cp)_2$ has been prepared from $(Cp)(PMe_3)_2RuCH{=}CHZr(Cl)(Cp)_2$ by isocyanide insertion into the Zr–C bond. The NMR properties of this complex and X-ray crystal structures of related complexes are reported [428]. CO_2 insertion into the

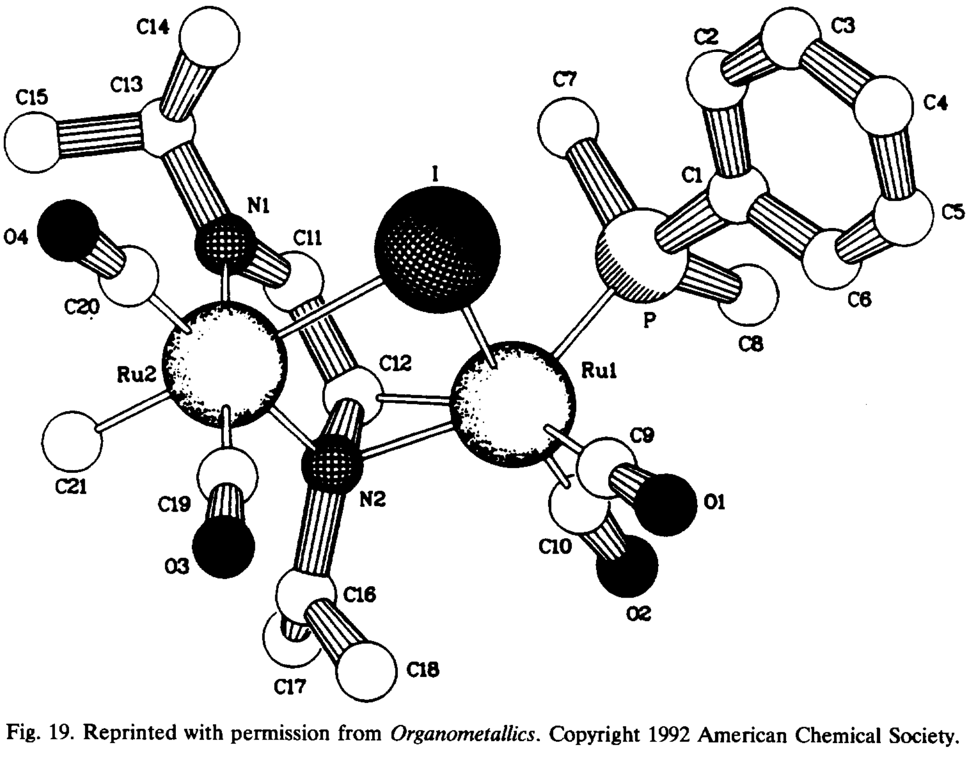

Fig. 19. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

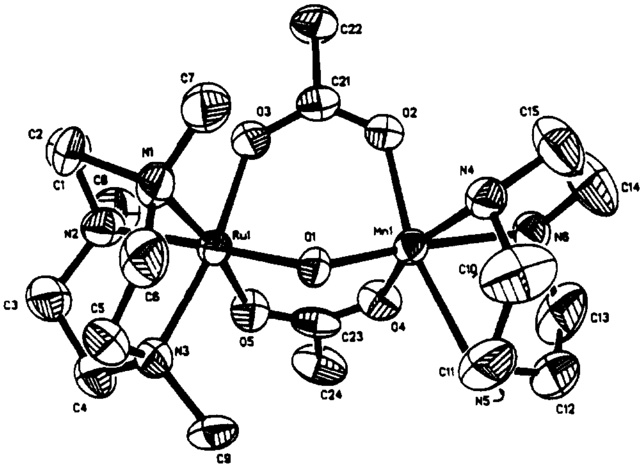

Fig. 20. Reprinted with permission from *J. Am. Chem. Soc.* Copyright 1992 American Chemical Society.

Zr–C bond of (Cp)$(PMe_3)_2RuCH{=}CHZr(Cl)(Cp)_2$ yields the carboxylate complex (Cp)$(PMe_3)_2RuCH{=}CHCO_2Zr(Cl)(Cp)_2$. The insertion chemistry with related Ru/Zr complexes containing a C_2 bridge with single, double, and triple bonds has been examined [429]. The reaction of hydrogen with $FeRu(CO)_6(\alpha$-diimine) complexes is reported to yield the highly reactive species $FeRu(H)_2(CO)_5$(diimine). The mechanism of the *trans* addition of H_2/D_2 to the central C–C bond of the coordinated 1,4-diaza-1,3-butadiene has been addressed [430]. The synthesis, crystal structures, and Mössbauer, susceptibility, and EPR data on several spin exchange coupled complexes possessing a (μ-oxo)bis(μ-acetato)ruthenium metal core have been described. The X-ray crystal structure of the RuMn derivative is shown below [431].

4. Polynuclear complexes

4.1. Trinuclear clusters

4.1.1. Simple and hydrocarbon ligands

A study on the oxidative addition of aldehydes and Schiff bases to $Ru_3(CO)_{12}$ has appeared. Both aliphatic and simple aromatic aldehydes react with $Ru_3(CO)_{12}$ to give products of the form $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}RC{=}O)$ in low yields. The oxidative addition products are favored with aromatic aldehydes that bear electron-donating groups [432]. Treatment of $Ru_3(CO)_{12}$ with pyridine at 120°C results in cluster fragmentation and formation of the *ortho*-metalated complex $Ru_2(\mu\text{-py})_2(CO)_6$. At 180°C, the complex $Ru_2(\mu\text{-py})(\mu\text{-}C_{10}H_7N_2)(CO)_5$, which contains a bridging *ortho*-metalated bpy as a result of pyridyl ligand coupling, has been isolated and structurally characterized by X-ray diffraction analysis [433]. The sugars 1,2-*o*-isopropylidene-α-D-glucofuranose and 1,2:5,6-di-*o*-isopropylidene-α-D-glucofuranose react with $Ru_3(CO)_{12}$ to yield the sugar-substituted cluster $Ru_3(CO)_8$(sugar). The catalytic properties of these new clusters have been explored [434]. $Ru_3(CO)_{12}$ reacts with sulphonic acids to furnish ruthenium complexes with μ_2-η^2-sulphonato bridges. All complexes were characterized by solution methods and in the case of $Ru_2(CO)_4\{\mu_2\text{-}\eta^2\text{-}OOS(O)(tol)\}_2(PPh_3)_2$ by X-ray crystallography [435]. The controlled pyrolysis reaction involving $Ru_3(CO)_{12}$ and tetraphenylcyclopentadienone has been shown to give $Ru_3(CO)_5(C_4Ph_4CO)_2$. The molecular structure has been established by X-ray diffraction analysis [436]. Ligand fluxionality in $M_3(CO)_{12}$ (where M = Fe, Ru, Os) and their ligand-substituted derivatives has been examined and a mechanism involving an intermediate with anticubeoctahedral geometry presented [437]. The reaction between $Ru_3(CO)_{12}$ and catechol gives a coordination polymer containing η^4-ortho-benzoquinone ligands [438].

Refluxing $Ru_3(CO)_{12}$ with 1,3-butadiene or *cis*-2-butene yields the μ_3-η^3-dimetalloallyl cluster $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta^3\text{-}CHCHCMe)(CO)_9$, which upon reaction with PPh_3 yields the corresponding mono- and bis-substituted clusters. All three of these clusters have been structurally characterized by X-ray crystallography [439]. A variable-temperature ^{13}C NMR study of $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}{}^tBu)(CO)_9$ has been conducted and three fluxional processes outlined. The phosphine derivative $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}{}^tBu)(CO)_8(PMe_2Ph)$ has also been examined by NMR spectroscopy, which revealed that the exchange of the $Ru(CO)_2(PMe_2Ph)$ group occurs by a concerted rotation, resulting in cluster enantiomerization [440]. The reaction of cyclopentadiene with $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_{9-n}(MeCN)_n$ (where $n = 1, 2$) yields the new clusters $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(Cp)$ and $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(Cp)_3$. The hydrogenation of the former cluster gives $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(Cp)$. The solid-state structures of the former two clusters have been solved by X-ray crystallography [441].

The cluster $Os_3(CO)_7(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(CH_2{=}CH_2)(MeCN)$ reacts with alkynes to give the new cluster $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2$-alkyne), where the benzene ring has migrated to a single osmium atom. The related ruthenium cluster $Ru_3(CO)_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ reacts with alkynes to give $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2RCO)$ in which CO insertion has occurred [442]. The synthesis of triosmium clusters containing benzene in a face-capping bonding mode is reported. X-Ray crystallographic data for $Os_3(CO)_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$, $Os_3(CO)_8(PPh_3)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$, and

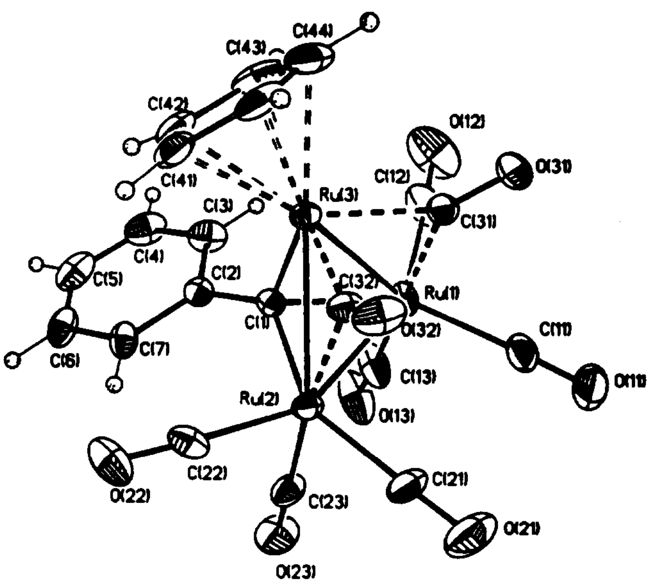

Fig. 21. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

$Os_3(CO)_8(\eta^2\text{-}CH_2{=}CH_2)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ are discussed. The bonding in the parent cluster has been studied by semiempirical molecular orbital calculations [443]. The fluxional behavior of the μ_3-arene/olefin triosmium complexes $Os_3(CO)_8(\eta^2\text{-}CH_2{=}CHR)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (where R = H, Me, Ph, ^{t}Bu) has been examined by NMR spectroscopy. Five independent fluxional processes are observed and discussed [444].

The acetonitrile cluster $Os_3(CO)_{11}(MeCN)$ reacts with excess $CNCF_3$ at room temperature to give $Os_3(CO)_{11}(\mu\text{-}CNCF_3)_2$ and $Os_3(CO)_{10}(\mu\text{-}CNCF_3)_2$. The former cluster is transformed into the latter cluster at 80°C. The X-ray crystal structures of these clusters and the role of osmium–osmium bond cleavage in the ligand substitution reaction are discussed [445,446]. Treatment of $Os_3(CO)_{11}(CNR)$ with MeCN in the presence of Me_3NO gives $Os_3(CO)_{10}(CNR)(MeCN)$. Acetonitrile displacement occurs upon treatment with two-electron donor ligands. Propynoicacid reacts with $Os_3(CO)_{10}(CNR)(MeCN)$ in CH_2Cl_2 to give the hydrido cluster $(\mu\text{-}H)Os_3(CO)_{10}(OCOC{\equiv}CH)(CNR)$, whereas in MeCN only $Os_3(CO)_{10}(\mu_2\text{-}OCOC{\equiv}CH)(\mu_2\text{-}C{=}NHR)$ was isolated [447]. The carboxamido cluster $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ has been obtained from the reaction between $Os_3(CO)_{11}(CNR)$ and primary amines. The reaction of this product with excess amine yields $Os_3(CO)_9(NH_2R')(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$. The hydrosilation of alkynes by the osmium cluster $Os_3(CO)_{10}(NCMe)\{Si(OMe)_3\}(\mu\text{-}H)$ has been examined. An isolated intermediate is used in the hydrosilation mechanism that is presented [449]. The coordination of trialkoxysilyl ligands in triosmium clusters has been studied. Treatment of $Os_3(CO)_{10}(MeCN)_2$ and $Os_3(CO)_{11}(MeCN)$ with $HSi(OR)_3$ (where R = Me, Et) affords the new clusters $Os_3(CO)_{10}(MeCN)\{Si(OR)_3\}(\mu\text{-}H)$ and $Os_3(CO)_{11}\{Si(OR)_3\}(\mu\text{-}H)$, respectively. The thermolysis reactions involving these clusters are outlined, and the X-ray crystal structures of several clusters are presented [450]. Bromine and iodine have been allowed to react with the hydrido(carboxamido)triosmium cluster $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCNHCHMe_2)$. The kinetic product of these reactions corresponds to $(\mu\text{-}X)Os_2(CO)_6(\mu\text{-}OCNHCHMe_2)(X)_2$ with two *cis* halogen ligands. A slow transformation is observed to the *trans* isomer [451]. The reaction of bis(trifluoromethyl)nitroxyl radical with $(H)_2Os_3(CO)_{10}(L)$ (where L = MeCN, PhCN) produces the stable clusters $(\mu\text{-}H)Os_3(CO)_{10}(L)\{ON(CF_3)_2\}$. X-Ray diffraction analysis reveals that the terminal $(CF_3)_2NO$ ligand occupies an axial coordination site. Variable-temperature ^{19}F NMR measurements indicate that the slowed rotation of the $(CF_3)_2N$ moiety about the Os–O bond results from steric hindrance with the ancillary carbonyl groups [452]. The X-ray crystal structures of $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}R_2C_2)(\mu\text{-}OEt)$ (where R = Me, Ph), which were obtained from the reaction between $Os_3(CO)_{10}(R_2C_2)$ and ethanol, have been published [453]. The synthesis and X-ray diffraction structure of $Os_3(CO)_{10}(\mu_3\text{-}MeO_2CC{\equiv}CCO_2Me)$ have appeared. The alkyne C–C bond is parallel to an Os–Os edge and one CO ligand is bridging. Deprotonation of $Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}COMe)$ yields the anion $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}COMe)]^-$. The reactivity of this anion and related triosmium anions is presented [455]. Trimethylsilylacetylene reacts with $Os_3(CO)_{10}(MeCN)_2$ by MeCN displacement to give $Os_3(CO)_{10}(HC{\equiv}CSiMe_3)$, which upon thermolysis undergoes decarbonylation and hydrogen migration to yield $Os_3(CO)_9(H)(C{\equiv}CSiMe_3)$. Desilylation of this last cluster is observed after silica gel chromatography, and the cluster $Os_3(CO)_9(H)(C{\equiv}CH)$ is produced [456]. Hydroboration of $(\mu\text{-}H)_2Os_3(CO)_{10}$ by diborane gives $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$ or $\{(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}C\text{-})\}_3(O_3B_3O_3)$ depending on the reaction conditions. PMe_3 reacts with the former cluster by loss of the boron-coordinated CO group to give $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BPMe_3)$. The X-ray crystal structures of several clusters are included in the report [457].

4.1.2. Phosphine ligands

The reaction of $Ru_3(CO)_{10}(\mu\text{-}dppm)$ with 1-alkynes (where R = Ph, ^{t}Bu,SiMe$_3$, C_6F_5) yields the clusters $Ru_3(\text{-}H)(\mu_3\text{-}C_2R)(CO)_7(\mu\text{-}dppm)$. Ruthenium/gold clusters have also been obtained when the gold alkyne compounds $Au(C{\equiv}CPh)(PR_3)$ were examined [458]. D-

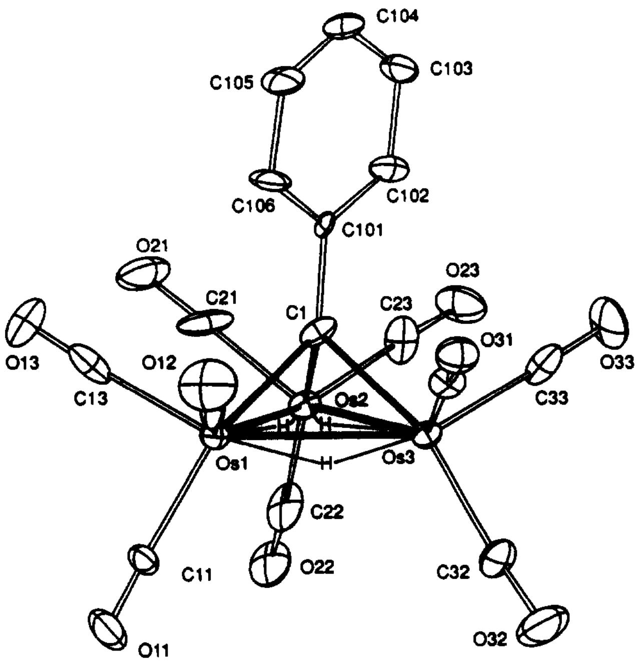

Fig. 22. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

MAD reacts with $Ru_3(CO)_{10}(\mu\text{-dppm})$ to yield four isolated complexes. The X-ray structures of three of these products have been determined [459]. The clusters $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3ER)$ (where E = P, R = Me, Ph; E = As, R = Ph) have been synthesized and spectroscopically characterized. The X-ray crystal structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu, \eta^2\text{-}O_2PPh_2)$, which was prepared from $Os_3(CO)_{10}(MeCN)_2$ and Ph_2PO_2H, is presented [460]. Triphenylphosphoranylidene, $Ph_3P\text{-}CHCHO$, reacts rapidly with $Os_3(CO)_{10}(MeCN)_2$ to give $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}Ph_3PCCHO)$ and $Os_3(CO)_{10}\text{-}(\mu\text{-H})(\mu\text{-}Ph_3PCHCO)$ as a result of C–H bond activation at the α- and β-carbons, respectively. The decarbonylation chemistry and X-ray crystal structures are discussed [461]. The synthesis and characterization of phosphinobenzyl- and aryl-silane ligands and the triosmium clusters derived from these ligands are described [462]. The ketophosphine $Ph_2PCH_2C(O)Ph$, L, and $Ru_3(CO)_{12}$ have been allowed to react with Me_3NO to give $Ru_3(CO)_9(L)_3$. Iodine reacts with this cluster by fragmentation to produce $[\overline{Ru(\mu\text{-I})\{Ph_2PCHC(O}})Ph\}(CO)_2\}(CO)_2]_2$ [463]. The reaction of $Ru_3(CO)_{12}$ with RPH_2 (where R = Ph, Cy) has been re-examined, and the role of the triruthenium clusters $Ru_3(CO)_{10}(\mu\text{-H})\text{-}(\mu\text{-PHR})$, $Ru_3(CO)_9(H)_2(\mu_3\text{-PR})$, $Ru_3(CO)_8(H)_2(\mu_3\text{-}PR)(PH_2R)$, and $Ru_3(CO)_8(H)_2(\mu\text{-PHR})_2$ in the formation of the bis-phosphinidene-capped cluster $Ru_3\text{-}(CO)_9(\mu_3\text{-PR})_2$ has been discussed. Many other related ruthenium clusters have been isolated and spectroscopically characterized [464]. The reactivity of the phosphinidene-capped, phosphido-bridged cluster $Ru_3\text{-}(CO)_7(\mu_2\text{-}PPh_2)_2(\mu_3\text{-PPh})$ with CO, $P(OMe)_3$, $NaBH_4$, and diphenylacetylene has been investigated. The molecular structure of $Ru_3(CO)_6\{P(OMe)_3\}(\mu_2\text{-}PPh_2)_2$ $(\mu_3\text{-PPh})$ has been solved by X-ray diffraction analysis [465]. The synthesis of $Ru_3(CO)_9(\eta^3\text{-tmpm})$ and its reactions with HPF_6 and $[(PPh_3)Au][OTf]$ have appeared. The X-ray crystal structure of the ruthenium/gold cluster complex formed from this last reagent is included in this report [466]. The 50-electron cluster $[Ru_3(CO)_9(\mu\text{-}PPh_2)_3][Cl]$ has been prepared from the reaction of $RuCl_3 \cdot nH_2O$ with PPh_2H and its reactivity studied. UV irradiation leads to CO loss and formation of $Ru_3(CO)_7(\mu\text{-Cl})(\mu\text{-}PPh_2)_3$. The hydrido cluster $Ru_3(CO)_7(\mu\text{-H})(\mu\text{-}PPh_2)_3$ may be isolated from both of the previous clusters during reflux in isopropyl alcohol [467]. The synthesis of $[(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-PR})]^-$ (where R = Ph, ^{t}Bu) has appeared. The course of the reaction has been investigated by low-temperature ^{31}P NMR spectroscopy and the molecular structure of $[(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-P-}^tBu)]^-$ determined by X-ray crystallography [468].

4.1.3. Nitrogen ligands

The conjugate base derived from 2-hydroxypyridine, 2-anilinopyridine, or 2-mercaptopyridine has been examined in the reaction with $Ru_3(CO)_{12}$. The activated clusters $[Ru_3\{\mu\text{-}\eta^2\text{-}X(C_5H_4N)\}(CO)_{10}]^-$ and $[Ru_3(\mu_3\text{-}\eta^2\text{-}X\{C_5H_4N\})(CO)_9]^-$ (where X = NPh, O, S) were isolated and characterized. Similar reactions were studied by using halide-activated clusters. The above clusters were also examined for their alkyne coordination chemistry [469]. The reaction between N-tolyl-diphenylketenimine, $Ph_2C{=}C{=}N\text{-}p\text{-tolyl}$, and $Ru_3(CO)_{12}$ is reported to give $Ru_3(CO)_8(C_{21}H_{17}N)$ and $Ru_2(CO)_6\text{-}(C_{21}H_{17}N)$; the structure of the former cluster has been solved by X-ray crystallography [471]. The clusters $Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(dppm)$ and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_7(dppm)]^+$ have been isolated from the reaction between dppm and $Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9$ and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9]^+$, respectively. The structures of all products have been assigned by spectroscopic methods. Protonation ofthe former dppm-substituted cluster with $HBF_4 \cdot OEt_2$ produces a dihydride cluster that is isomeric with the latter product cluster [471]. The reaction between ureas and $Ru_3\text{-}(CO)_{12}$ has been investigated and shown to afford triruthenium clusters of the form $(\mu_2\text{-H})Ru_3(CO)_9\text{-}(\mu_3\text{-}\eta^2\text{-}R'NCONHR'')$ (where R′ = R″ = H, Me; R′ = H, R″ = Ph, *cis*-CH=CHMe, *trans*-CH=CHMe). The X-ray crystal structure of the *cis*-CH=CHMe isomer exhibits a coordinated urea moiety that functions as a tripodal handle perpendicular to the triruthenium plane [472].

Treatment of $Ru_3(CO)_{12}$ with $MeN(CMe_2C{\equiv}CH)_2$ yields the trinuclear cluster $Ru_3(CO)_8(HCCCMe_2NMeCMe_2CCHCCCMe_2)$ and a dinuclear ruthenacyclopentadiene complex. The former complex has been structurally characterized by X-ray diffraction analysis, revealing the presence of a six-carbon chain that is coordinated to three ruthenium atoms [473]. A report describing the catalytic and regioselective acylation of aromatic heterocycles using $Ru_3(CO)_{12}$ has appeared. The involvement of an ortho-metalated pyridyltriruthenium cluster is discussed [474]. The use of the edge-bridged cluster $Ru_3(\mu\text{-}C_8H_{11}N_2)(\mu\text{-}H)(CO)_9$ (where $C_8H_{11}N_2$ = 1,2-diamino-4,5-dimethylbenzene) as a catalyst for the hydrogenation of diphenylacetylene to stilbene is described. The kinetic data support catalysis arising from a mononuclear species [475]. Treatment of the clusters $Ru_3(CO)_{9-n}(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(PPh_3)_n$ (where $n = 0\text{–}2$) with Et_3SiH produces the oxidative addition products $Ru_3(CO)_{8-n}(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(PPh_3)_n(SiEt_3)$ (where $n = 0\text{–}2$). Analogous reactions are reported for Bu_3SnH. All new products have been characterized in solution by ^1H, ^{13}C, and ^{31}P NMR spectroscopies and X-ray crystallography in the case of $Ru_3(CO)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(SiEt_3)$ [476]. The reaction of diazomethane with the μ_3-imidoyl clusters $(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeC{=}NCH_2Me)Ru_3(CO)_9$, $(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2)Os_3(CO)_9$, and $(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeCH_2C{=}NCH_2CH_2CH_2CH_3)Os_3(CO)_9$ yields the clusters $(\mu\text{-}H)_2\{\mu_3\text{-}\eta^2\text{-}CH(Me)C{=}NCH_2Me\}Ru_3(CO)_9$, $(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CHC{=}NCH_2CH_2CH_2)Os_3(CO)_9$, and $(\mu\text{-}H_2)4\text{-}\{\mu_3\text{-}\eta^2\text{-}CH(MeCH_2)C{=}NCH_2CH_2Me\}Os_3(CO)_9$, respectively, as a result of CH_2 insertion into the C–M σ bond of the imidoyl ligand, followed by C–H bond activation. Solution spectroscopic data and the X-ray crystal structures of four clusters are presented [477].

Halides react with the imido cluster $Os_3(CO)_9(\mu_3\text{-}NPh)$ to afford the isomeric clusters $[Os_3(CO)_9(\mu_2\text{-}X)(\mu_3\text{-}NPh)]^-$ and $[Os_3(CO)_9(X)(\mu_3\text{-}NPh)]^-$, the ratio of which depends upon the nature of the halide. The carbonylation chemistry of these halide-substituted clusters has been investigated [478]. The cluster $Os_3(CO)_{10}(MeCN)_2$ and azetidine have been allowed to react in refluxing CH_2Cl_2 to give $Os_3(CO)_{10}(\mu\text{-}NCH_2CH_2CH_2)(\mu\text{-}H)$. The four-membered $NCH_2CH_2CH_2$ ring bridges two of the osmium atoms by the nitrogen atom. Heating this cluster at 125°C leads to the new cluster $Os_3(CO)_{10}\{\mu\text{-}N{=}C(H)Et\}(\mu\text{-}H)$ by way of ring opening and a hydrogen shift. The molecular structure was determined by X-ray crystallography [479]. The reactivity of the carbene centers in the cluster $Os_3(CO)_9\{\mu_3\text{-}C(Et)N(Me)CH\}(\mu\text{-}H)_2$ toward diphenylacetylene has been studied. At 125°C, six products were obtained. Of these, four are new clusters that have been characterized by solution methods and X-ray diffraction analysis [480].

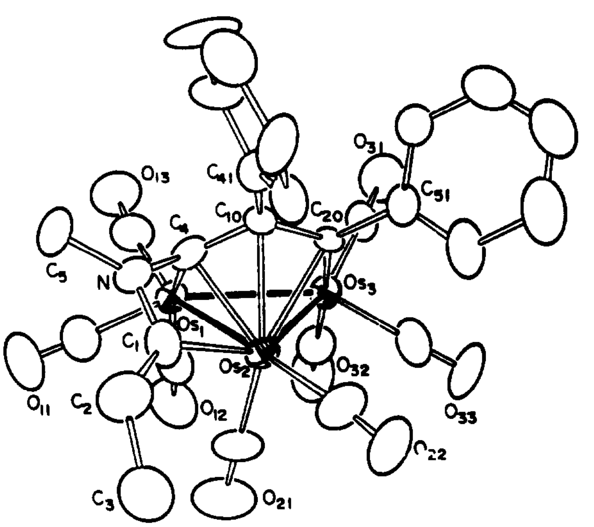

Fig. 23. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

4.1.4. *Sulfur ligands*

Treatment of $Ru_3(CO)_{12}$ with a thiourea-functionalized silica xerogel yields a surface-attached cluster whose spectroscopic properties are identical to that of $(\mu\text{-}H)Ru_3\{\mu_3\text{-}SC(NHPr)NPh\}(CO)_9$, which is obtained from the reaction between $Ru_3(CO)_{12}$ and *N*-phenyl-*N'*-propylthiourea. The molecular structure of this latter cluster has been solved by X-ray crystallography [481]. The synthesis of the trinuclear cluster $[(Cp)Ru(SR)]_3$ (where $R = {}^nPr, {}^iPr$) from $(Cp)Ru(PPh_3)_2(SR)$ is described. The clusters are formed in an aggregation reaction that proceeds by loss of the PPh_3 ligands in refluxing toluene. The X-ray structure of the n-propyl cluster accompanies this report [482]. Vacuum pyrolysis of $Ru_3(CO)_{12}$ with Ph_2Se_2 at 185°C produces the cluster $Ru_4(CO)_8(\mu_3\text{-}CO)_3(\mu_4\text{-}Se)_2$. This cluster reacts with dppp to yield the phosphine-substituted cluster $Ru_3(CO)_7(dppp)(\mu_3\text{-}Se)_2$. Both structures were determined by X-ray crystallography [483]. The reaction between $Os_3(CO)_{12}$ and the tridentate thioether [12]aneS_3 affords the clusters $Os_3(CO)_{11}([12]aneS_3)$ and $Os_4(CO)_{13}([12]aneS_3)$ while the same reaction with $Ru_3(CO)_{12}$ is much more complex. The X-ray structures of $Os_4(CO)_{13}([12]aneS_3)$ and $Ru_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)([12]aneS_3)$ are presented with this report [484]. Dppm and $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)$ have been allowed to react in refluxing toluene to give $Os_3(CO)_7(dppm)(\mu\text{-}H)_2(\mu_3\text{-}S)$. Higher reaction temperatures yield the known cluster $Os_3(CO)_8(\mu\text{-}dppm)_2$, along with the latter cluster. The protonation chemistry of these clusters has been investigated, with emphasis on the site preference for proto-

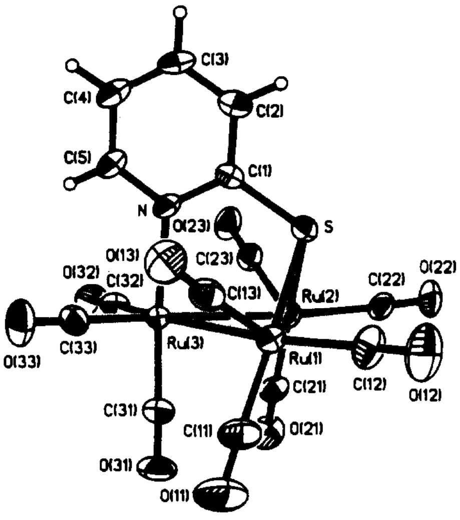

Fig. 24. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

nation and the fluxional behavior of the resulting hydride clusters. The X-ray crystal structure of $\mathrm{Os_3(CO)_7(dppm)(\mu\text{-}H)_2(\mu_3\text{-}S)}$ is discussed [485]. The cyclic polydentate thioether ligands 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane, and 1,4,7-trithiacyclononane have been allowed to react with $\mathrm{Ru_3(CO)_{12}}$. The isolated products $\mathrm{HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-}dithiacyclohexane)}$, $\mathrm{Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3,5\text{-}trithiacyclohexane)}$, and $\mathrm{Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-}trithiacyclononane)}$ have been fully characterized by solution methods and X-ray crystallography. The reactivity of these clusters towards CO and H_2 are reported [486]. $\mathrm{Ru_3(CO)_{12}}$ reacts with pyridine-2-thiol in refluxing cyclohexane to produce $\mathrm{Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9}$. X-Ray diffraction analysis reveals that the pyS ligand bridges two ruthenium centers *via* the S atom and bonds to the remaining ruthenium atom by the pyridine ring [487].

The sulfur-bridged clusters $\mathrm{Ru_3(CO)_{10}\{\mu\text{-}S(C{=}CMe_2)C(Me){=}CH_2\}(\mu\text{-}H)}$ and $\mathrm{Ru_3(CO)_9\{\mu\text{-}S(CH{=}CMe_2)C(Me){=}CH_2\}(\mu\text{-}H)}$ have been obtained from the reaction between $\mathrm{Ru_3(CO)_{12}}$ and tetramethylallene sulfide. The former product has been characterized by X-ray diffraction analysis [488]. The nucleophilic ring opening of the bridging thietane ligand in $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}\overline{SCH_2CMe_2C}H_2)}$ and $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}\overline{SCH_2CH_2C}H_2)}$ by added chloride ion proceeds by way of carbon–sulfur bond cleavage. These two clusters react with HCl to give $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)}$ and $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)}$, respectively. The molecular structures of three clusters are reported [489]. The products from the thermolysis of the 3,3-dimethylthietane-substituted clusters $\mathrm{Os_3(CO)_{11}(\overline{SCH_2CMe_2C}H_2)}$ and $\mathrm{Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2C}H_2)}$ have been isolated and characterized. Thietane ring opening reactions and the reactivity of these products towards UV light and CO have been examined. Several X-ray crystal structures are presented [490]. Optical excitation of $\mathrm{Os_3(CO)_{11}\{S(CH_2)_3\}}$ leads to decarbonylation and the formation of the isomeric clusters $\mathrm{Os_3(CO)_{10}\{\mu\text{-}S(CH_2)_2CH_2\}}$ and $\mathrm{Os_3(CO)_{10}(\mu\text{-}SCH_2CH{=}CH_2)(\mu\text{-}H)}$ as a result of C–S bond cleavage and thietane ring opening. The former cluster contains a thiametallacyclopentane ring while the latter cluster possesses a 2-propenethiolato ligand and a bridging hydride ligand. Both clusters have been crystallographically characterized and their reactivity investigated [491]. The cluster $\mathrm{Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2C}H_2)}$ reacts with a variety of nucleophiles to yield, after acidification, clusters of the form $\mathrm{Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2X)(\mu\text{-}H)}$ (where X = F, Cl, Br, I, EtO, $\mathrm{Et_2N}$, $\mathrm{Me_2N}$). The stereochemistry associated with the ring-opening reaction was explored by using $\mathrm{Os_3(CO)_{10}\{\mu\text{-}\mathit{trans}\text{-}\overline{SC(H)MeCH_2C}(H)Me\}}$ [492]. Treatment of $\mathrm{Os_3(CO)_{10}(MeCN)_2}$ with *trans*-2,4-diphenylthietane produces the isomeric clusters *cis*- and *trans*-$\mathrm{Os_3(CO)_{10}\{\mu\text{-}SC(H)PhCH_2C(H)Ph\}}$. The *cis* isomer has been characterized by X-ray diffraction analysis and found to contain a thiametalladiphenyl cyclopentane ring. Heating these isomers at 97°C leads to five cluster compounds, which have been isolated and characterized [493]. The clusters $\mathrm{Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-}SPh)}$ and $\mathrm{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-}SPh)}$ have been isolated from the reaction between $\mathrm{Os_3(CO)_{10}(MeCN)_2}$ and 1-(phenylthio)cyclobutene, $\mathrm{PhS\overline{C{=}CHCH_2C}H_2}$. When the latter cluster is treated with $\mathrm{Me_3NO}$, the new cyclobutyne-substituted cluster $\mathrm{Os_3(CO)_9(\mu\text{-}SPh)(\mu_3\text{-}\eta^2\text{-}\overline{C{\equiv}CCH_2C}H_2)(\mu\text{-}H)}$ may be isolated. The molecular structure and fluxional behavior of the hydride ligand are discussed [494].

4.2. Tetranuclear clusters

Thermolysis of $\mathrm{Ru_3(CO)_{12}}$ with the thioureas $\mathrm{SC(NHR)_2}$ (where R = Et, ^{i}Pr) produces the tetraruthenium clusters $\mathrm{Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}_2}$ and $\mathrm{Ru_4(CO)_7(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NHR)_2\}}$. The molecular structures of both of the isopropyl clusters have been solved by X-ray diffraction analysis [495]. Tetramethylthiourea reacts with $\mathrm{Ru_3(CO)_{12}}$ to give the sulfur- and diaminocarbene-substituted clusters $\mathrm{Ru_4(\mu_2\text{-}CO)_2(CO)_{9-\mathit{n}}(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_\mathit{n}}$ (where $n = 1, 2$). The X-ray crystal structures are reported and the reaction discussed with respect to the other observed products [496]. The tri-, tetra-, and pentanuclear ruthenium clusters obtained from the reaction between $\mathrm{Ru_3(CO)_{12}}$ and $\mathrm{SC(NMe_2)_2}$ are described. Included in this report are the X-ray structures of $\mathrm{Ru_4(CO)_{10}(\mu_2\text{-}CNMe_2)(\mu_3\text{-}S)\{\mu_3\text{-}SRu(CO)_3(\eta^2\text{-}CH_2NMeCNMe_2)\}}$, $\mathrm{Ru_5(CO)_{11}(\mu_2\text{-}CNMe_2)_2(\mu_4\text{-}S)_2}$, and $\mathrm{Ru_4(\mu_2\text{-}CO)_3(CO)_6(\mu_4\text{-}S)_2\text{-}}$

(η^2-$Me_2NCNMeCH_2CNMe_2$) [497]. The reaction of chloride ion with $Os_4(\mu\text{-}CO)(CO)_{12}(\mu\text{-}\overline{SCH_2CMe_2C}H_2)$ affords the cluster $[Os_4(\mu\text{-}CO)(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)]^-$. Protonation of this cluster yields the corresponding hydride cluster, which loses CO at 97°C to give $Os_4(CO)_{12}(\mu_3\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ [498].

The tetraruthenium clusters $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_5H_4(O)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_{11}$ and $Ru_4\{\mu_4\text{-}\sigma(O,P),\sigma,\eta^2\text{-}C_6H_3(CO)(PPh_2)\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ are reported as products from the reaction between 1,3-butadiene, CO, and the C_2PPh_2 ligand present in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$. X-Ray data indicate that the product Ru_4 clusters contain metalated diphenylphosphinocyclopentenone and -benzoyl ligands, respectively [499]. Hydrogen-transfer reactions and the molecular structure of one diastereomer of the 64-electron butterfly cluster $(\mu\text{-}H)_2Ru_4(CO)_8\{MeC{=}C(H)C(H)\text{-}N\text{-}{}^iPr\}_2$ are reported. Related clusters have been prepared and spectroscopically characterized [500]. The linear cluster $Ru_4(CO)_{10}\{MeC{=}C(H)C(H){=}N\text{-}{}^iPr\}_2$ reacts with CO to give $Ru_4(CO)_{14}\{MeC{=}C(H)C(H){=}N\text{-}{}^iPr\}_2$. The changes in the coordination of the ancillary MAD-yl ligands have been studied and a plausible mechanism outlined for the regioselective C–H bond activations that have been observed [501]. The transformation of $Ru_4(CO)_{13}(\mu_2\text{-}PPh_2)_2$ to $(\mu\text{-}H)Ru_4(CO)_{10}(\mu\text{-}PPh_2)\{\mu_4\text{-}\eta^1(P),\eta^1(P),\eta^1(P),\eta^1,\eta^2\text{-}(C_6H_4)PPh\}$ has been observed at elevated temperature. The molecular structure of this product supports the existence of a five-coordinate bis(aryl)phosphido bridging ligand [502]. The phosphinidene-capped cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ adds H_2 to give $(\mu\text{-}H)_2Ru_4(CO)_{12}(\mu_3\text{-}PPh)$ in quantitative yield. This cluster has been fully characterized by solution methods and by X-ray diffraction analysis [503].

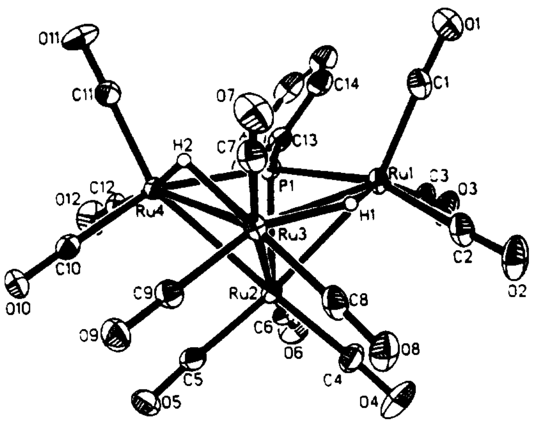

Fig. 25. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

4.3. Pentanuclear clusters

Pyrolysis of $Os(CO)_5$ yields the planar metal carbonyl cluster $Os_5(CO)_{18}$, which has a raft-like arrangement of osmium atoms as shown by X-ray crystallography [504]. The reaction between $Ru_5(CO)_{15}$ and Me_3NO in the presence of cyclohexa-1,3-diene yields the carbide cluster $Ru_5(C)(CO)_{13}(\eta^4\text{-}C_6H_8)$, which reacts with additional Me_3NO to produce the benzene-substituted clusters $Ru_5(C)(CO)_{12}(\mu_3\!:\eta^2\!:\eta^2\!:\eta^2\text{-}C_6H_6)$ and $Ru_5(CO)(CO)_{12}(\eta^6\text{-}C_6H_6)$. These latter two clusters have been characterized by spectroscopic and crystallographic methods [505]. The reactions between $Ru_5(\mu_5\text{-}CCPPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and 1,3-butadiene have been shown to give the new clusters $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$, $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$, and $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)(CO)_{11}$, the molecular structures of which have been solved by X-ray crystallography [506]. The results of a molecular orbital study on $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SH)_2(\mu\text{-}PH)_2(CO)_{11}$ indicate that the β carbon of the C_2 should behave as a nucleophile. Experimental proof that corroborates these data are presented [507]. The pentanuclear sulfido clusters $[Ru_5(CO)_{14}(S)]^{2-}$, $[Ru_5(H)(CO)_{14}(S)]^-$, and $Ru_3(H)_2(CO)_{14}(S)$ have been synthesized from the reaction between $Ru_3(CO)_{12}$ and $SC(NMe_2)_2$, depending upon the reaction conditions. The X-ray crystal structure of the dianionic cluster has been determined [508]. Ru–Ru bond cleavage has been observed in the addition of Me_2S_2 to $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$. The two isolated products $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{12}$ and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{11}$ have been analyzed by X-ray crystallography [509].

4.4. Hexanuclear clusters

The solid-state structure of the hexaruthenium carbide cluster $Ru_6(C)(CO)_{17}$ has been redetermined, and the relationship between the three known isomers of this cluster discussed [510]. The substitution of CO by P-ligands in $Ru_6(C)(CO)_{17}$ has been studied and the kinetic data reported [511]. The synthesis and X-ray structure of $Ru_6(C)(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2$ have appeared [512]. The reaction of $Ru_6(CO)(CO)_{14}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)$ with Me_3NO in the presence of 1,3-cyclohexadiene gives the mixed arene-diene cluster $Ru_6(C)(CO)_{12}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^4\text{-}C_6H_8)$, which upon further reaction with Me_3NO yields $Ru_6(C)(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\mu_3\!:\eta^2\!:\eta^2\text{-}C_6H_6)$. On standing, this latter cluster rearranges to $Ru_6(C)(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$ [513]. The clusters $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2CMe_2CH_2)_4$ and $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3\{\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2\}(\mu\text{-}H)$ have been obtained from the thermolysis reaction of $Ru_4(CO)_{12}(\mu\text{-}\overline{SCH_2CMe_2C}H_2)_2$. The former hexanuclear cluster releases $Ru_3(CO)_{12}$ and 4,4-dimethylthiobutyrolactone upon treatment with CO at elevated temperature. The X-ray crystal structures of these Ru_6 clusters are presented [514].

4.5. Higher nuclearity clusters

The reaction of $Os_3(CO)_{11}(MeCN)$ with dppa gives the linked cluster $\{Os_3(CO)_{11}\}_2(dppa)$, while the reaction between $Os_3(CO)_{10}(MeCN)_2$ and excess dppa produces the cluster complexes $\{Os_3(CO)_{10}(dppa)\}_2$, $\{Os_3(CO)_{10}(dppa)\}_3$, and $\{Os_3(CO)_{10}(dppa)\}_4$. The X-ray crystal structures of two of these products and the synthesis of gold-substituted derivatives are described [515]. The isolation and X-ray crystal structure of $[(H)Ru_7(CO)_{20}]^-$ have been published [516]. Treatment of $Os_7(H)_2(CO)_{20}$ with 2-butyne gives the cluster $Os_7(CO)_{19}(Me_2C_2)$, while $Os_7(H)_2(CO)_{19}(MeCN)$ reacts with 2-butyne to give $Os_7(H)_2(CO)_{19}(Me_2C_2)$. The spectroscopic and X-ray diffraction data for these and other clusters are discussed [517]. Hydride and carbonyl fluxionality in $[(H)M_{10}(C)(CO)_{24}]^-$ (where M = Ru, Os) has been examined by variable-temperature NMR spectroscopy [518]. The synthesis, structural characterization, and molecular organization of $(H)_2Os_{10}(C)(CO)_{24}$ in the solid state have been described. The X-ray structure reveals the presence of two bridging hydride ligands on the surface of the Os_{10} frame [519].

The thermolysis reaction involving $Ru_3(CO)_{12}$ in methanol/water affords the ruthenium cluster $[Ru_{11}(H)(CO)_{27}]^{3-}$, which is shown by X-ray crystallography to consist of two octahedra and two trigonal bipyramids that share common triangular faces [520].

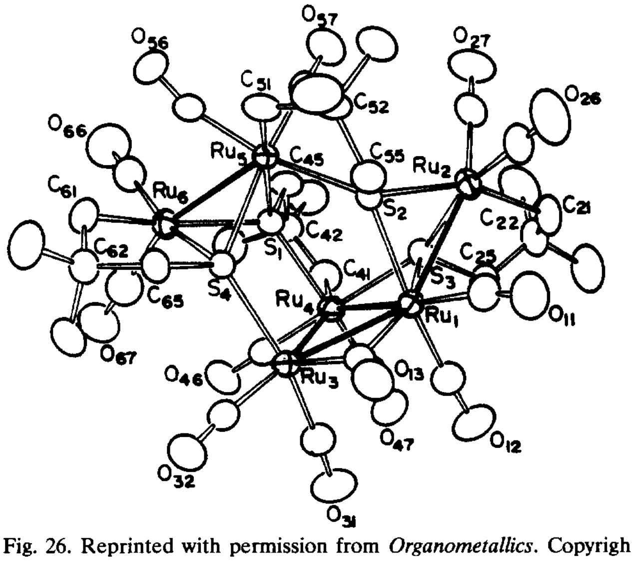

Fig. 26. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

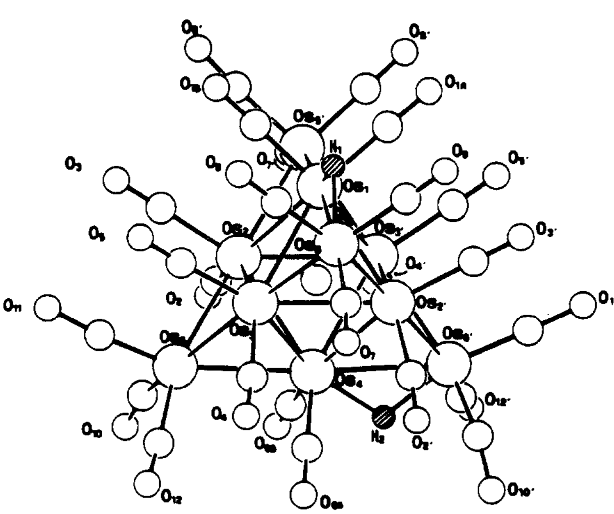

Fig. 27. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

4.6. Mixed-metal clusters

4.6.1. Clusters containing main group atoms

The reaction between $[Ru_3(CO)_9(B_2H_5)]^-$ and $Ru_3(CO)_{10}(MeCN)_2$ gives the two borido clusters $[Ru_6(H)_2(CO)_{18}(B)]^-$ and $[Ru_6(CO)_{17}(B)]^-$. The molecular structures have been solved by X-ray crystallography [521]. The agostic B–H → Ru bond in $[Ru(Cl)\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}(PPh_3)] \cdot$ acetone has been demonstrated by X-ray crystallography and NMR spectroscopy [522]. Irradiation of $(H)Ru_3(CO)_9(B_2H_5)$ with PPh_3 gives $(H)Ru_3(CO)_8(PPh_3)(B_2H_5)$, which has been shown to be an analogue of B_5H_9 by X-ray crystallography [523]. The reaction of $[(H)Ru_4(CO)_{12}(BH)]^-$ with (phosphine)gold(1) chlorides has been examined and the products characterized [524]. Treatment of $(H)Ru_4(CO)_{12}(BH)$ and $(H)(CpW)Ru_3(CO)_{11}(BH)$ with PhC≡CPh furnishes $(H)Ru_4(CO)_{12}\{BHC(Ph)C(Ph)H\}$ and $(H)(CpW)Ru_3(CO)_{11}\{BC(Ph)C(Ph)H\}$, respectively. Both products have been characterized by X-ray crystallography [525].

The synthesis and solid-state structure of $In\{Ru(CO)_2(Cp)\}_3$ have been published. X-Ray crystallography indicates that the trigonal-planar indium is bonded to three $(Cp)Ru(CO)_2$ groups by unsupported In–Ru bonds [526]. Vacuum pyrolysis of $Ru_3(CO)_{12}$ with PhSeSePh yields the selenium-containing cluster $Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_3(CO)_{11}$. The reactivity of this cluster with added dppa, $SbPh_3$, and CO has been investigated and the products characterized by X-ray diffraction analysis [527]. The synthesis and X-ray crystal structure of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ have been described [528].

4.6.2. Clusters containing other metals

The heterometallic imido clusters (L)$WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$ (where L = Cp, Cp*) react with hexafluoro-2-butyne to give (L)$WRu_2(CO)_7(\mu_3\text{-}NPh)(CF_3C\text{-}CHCF_3)$. A discussion on imido-ligand-assisted alkenyl migration and dissociative intermetallic phosphine migration is presented [529]. Decarbonylation of (Cp)$MoOs_3(CO)_{11}\{\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol\}$ with Me_3NO in the presence of H_2 yields the cluster (Cp)$MeOs_3(CO)_{10}(\mu\text{-}H)_2\{\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol\}$ in quantitative yield. Acyl C–O bond scission is observed to give three isomeric hydrido-oxo-alkylidene clusters (Cp)$MoOs_3(CO)_9(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)$ at elevated temperature [530]. The heterometallic phosphinidene clusters (Cp*)$WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ and (Cp)$WRu_2(CO)_2(\mu\text{-}H)(\mu_3\text{-}PPh)$ have been obtained from the thermolysis reaction involving $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with excess (Cp*)$W(CO)_3(H)$ and (Cp)$W(CO)_3(H)$, respectively. (Cp*)$WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ is shown to fragment under CO at elevated temperature to produce (Cp*)$WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$. The molecular structures of all three products have been assigned by X-ray diffraction data [531]. The metal fragment addition and substitution reactions of $Ru_3(CO)_9(BH_5)$ and $Ru_3(H)(CO)_9(B_2H_5)$ have been examined with $(Cp)_2M_2(CO)_6$ (where M = Mo, W). The two products that have been characterized by X-ray crystallography are (Cp)$WRu_3(H)(CO)_{11}(BH)$ and (Cp)$MoRu_3(H)_3(CO)_{11}$ [532]. Treatment of the phenylimido cluster (Cp*)$WRu_2(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)$ with hex-3-yne furnishes the cluster (Cp*)$WRu_2(CO)_6(NPh)\{C(Et)C(Et)C(CF_3)CH(CF_3)\}$. The molecular structure of this cluster, which was determined by X-ray diffraction analysis, reveals the presence of a terminal phenylimido ligand. When the same reaction was investigated with DMAD, only (Cp*)$WRu_2(CO)_6(\mu_3\text{-}NPh)\{C(CO_2Me)C(CO_2Me)C(CF_3)CH(CF_3)\}$, with a face-bridging imido ligand was isolated [533]. The reaction between $Os_3(CO)_{10}(C_2R_2)$ (where R = Tolyl, Me) and (L)$W(CO)_3(C{\equiv}CR')$ (where L = Cp, Cp*; R′ = Ph, ${}^tBu$) has been studied and found to yield a total of six WOs_3 clusters. The isolation and characterization of these clusters are reported [534]. The clusters (Cp)$MoOs_3(CO)_{11}\{\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol\}$, (Cp)$MoOs_3(CO)_{10}(\mu_3\text{-}CTol)_2(\mu\text{-}H)$, and (Cp)$MoOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol)_2(\mu\text{-}H)$ have been isolated from the room temperature reaction between (Cp)$Mo(CO)_2({\equiv}CTol)$ and $Os_3(CO)_{10}(\mu\text{-}H)_2$. The solution characterization and fluxional behavior of the first product cluster are described [536].

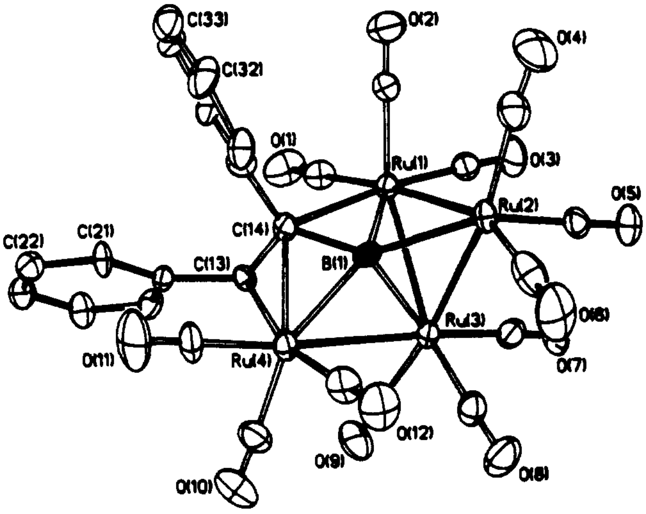

Fig. 28. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

The clusters $(OC)_5M[Os(CO)_3(PR_3)_2]_2$ {where M = Cr, Mo, W; R = Me, OMe; $R_3 = (OCH_2)_3CMe$} have been synthesized by ultraviolet irradiation of $(R_3P)(OC)_4OsM(CO)_5$ in C_6F_6. The variable-temperature NMR data are discussed and the molecular structures of several of the products determined [536]. The synthesis and X-ray diffraction structure of $(OC)_4({}^tBuNC)OsOs(CO)_3(CN\text{-}{}^tBu)W(CO)_5$ have been published. This cluster exhibits two dative metal–metal bonds in tandem (Os → Os → W) [537].

The sulfur-bridged clusters $[\{Ru(P)_4\}_2(\mu\text{-}MS_4)]^{2+}$ (where M = Mo, W; P = $P(OMe)_3$) have been synthesized and the X-ray crystal structure of the tungsten derivative determined [538]. The synthesis and reactivity of the sulfur-bridged clusters $\{(L)Ru(CO)(PPh_3)\}_2(\mu\text{-}MS_4)$ (where M = Mo, W; L = PhNCHS, $CH_2CH_2(C_5H_4N)$, $CH_2CH_2C(O)OMe$) have been presented. The molecular structures of $\{(PhNCHS)Ru(CO)(PPh_3)\}_2(\mu\text{-}MoS_4)\cdot$3acetone and the tungsten analog have been solved [539]. The reaction of $[Ru(H_2O)_6]^{2+}$ with $[PW_{11}O_{39}]^{7-}$ has been found to give, after O_2 oxidation, $[PW_{11}O_{37}Ru^{III}(H_2O)]^{4-}$. The reactivity of this complex in oxidation reactions and the redox data are discussed [540]. The cluster $Ru_3(CO)_8\{\mu_3\text{-}C_6H_4Cr(CO)_3\}(\mu_3\text{-}P\text{-}{}^tBu)$ has been obtained from the reaction between $Ru_3(CO)_{12}$ and $P\{C_6H_5Cr(CO)_3\}_2\text{-}{}^tBu$. The presence of a dative Ru → Cr bond has been confirmed by X-ray diffraction analysis [541].

Treatment of $Os_3(CO)_{10}(\text{cyclooctene})_2$ with $Re(CO)_3(PMe_3)_2(H)$ gives the new cluster $\{(OC)_3(Me_3P)_2Re(\mu\text{-}H)\}_2Os_3(CO)_{10}$, whose molecular structure has been established by X-ray crystallography [542].

A report describing the reaction between $Ru_3(CO)_{12}$ and ferrocenylacetylene has appeared. Isolated from this reaction were the clusters $Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CFc)$, $Ru_2(CO)_6\{C_4H_2(Fc)_2\}$, and $Ru_2(CO)_6\{\mu\text{-}C(H){=}C(Fc)COC(H){=}C(Fc)\}$ (where Fc = ferrocene). All three clusters were characterized by IR and NMR spectroscopies and by X-ray crystallography in case of $Ru_2(CO)_6\{C_4H_2(Fc)_2\}$ [543]. Lithioferrocene and 1,1'-dilithioferrocene have been allowed to react with (Cp)-$Ru(CO)_2(Cl)$, $(Cp^*)Ru(CO)_2(Cl)$, and $(C_6Me_6)Ru(CO)(Cl)_2$ to yield σ-bonded ferrocenyl complexes [544]. A report on iron–osmium bonding has appeared. Pyrolysis of $Os_3(CO)_{10}(PFcPh_2)_2$ and $Os_3(CO)_{11}(PFc_2Ph)$ gives $Os_3(CO)_8(H)_2\{PAr(C_6H_5)(\eta\text{-}C_5H_3)Fe(\eta\text{-}C_5H_4)\}$ (where Ar = Ph, Fc, respectively), while the thermolysis of $Os_3(CO)_{10}\{Fe(\eta\text{-}C_5H_4P\text{-}{}^iPr_2)_2\}$ furnishes the new cluster $Os_3(CO)_7(H)(P\text{-}{}^iPr)\{Fe(\eta\text{-}C_5H_4P\text{-}{}^iPr_2)(\eta\text{-}C_5H_4)\}$. The identity of these clusters has been solved by X-ray diffraction analysis [545]. Thermolysis of $Ru_3(CO)_{10}\{Fc'(P\text{-}{}^iPr_2)_2\}$ {where Fc' = $Fe(\eta\text{-}C_5H_4)_2$} gives three products, of which the structures of $Ru_3(CO)_8(\mu\text{-}H)_2\{(\eta\text{-}PC_5H_4)Fe(\eta\text{-}C_5H_4P\text{-}{}^iPr_2)\}$ and $Ru_3(CO)_8(\mu\text{-}H)(\mu\text{-}OH)\{\mu\text{-}Fe(\eta\text{-}C_5H_4P\text{-}{}^iPr_2)_2\}$ have been crystallographically determined [546]. Ferrocyne- and ferrodicyne-osmium clusters have been synthesized. Included in this report are the X-ray crystal structures of $Os_3(CO)_9\{\mu_3\text{-}(C_5H_3)Fe(C_5H_5)\}\{\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)\}$, $Os_3(H)_2(CO)_8({}^iPr_2PC_5H_2)Fe(C_5H_2P\text{-}{}^iPr_2)Os_3(H)_2(CO)_8$, and $Os_3(CO)_9(\mu_3\text{-}C_6H_4)\{\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)\}$ [547]. 1,2,4-3-Trithia[3]-ferrocenophane reacts with $Ru_3(CO)_{12}$ to yield the cluster $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$. The cluster $Fe(\eta\text{-}C_5H_4S)_2(S)Os_2(CO)_6$ was obtained when $Os_3(CO)_{12}$ was used in place of $Ru_3(CO)_{12}$. At higher temperature (> 100°C), the iron/osmium cluster was obtained along with four additional clusters. The X-ray structures of $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$ are included [548]. A report describing double metalation and iron–osmium bonding involving ferrocenyl moieties is discussed. The X-ray crystal structures of $(H)_2Os_3(CO)_8\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3P\text{-}{}^iPr_2)\}$ and $(H)_2Os_3(CO)_8\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3P(Fc)Et)\}$, which were synthesized by thermolysis of $Os_3(CO)_{11}(PFc\text{-}{}^iPr_2)$ and $Os_3(CO)_{11}(PEtFc_2)$, respectively, have been solved [549].

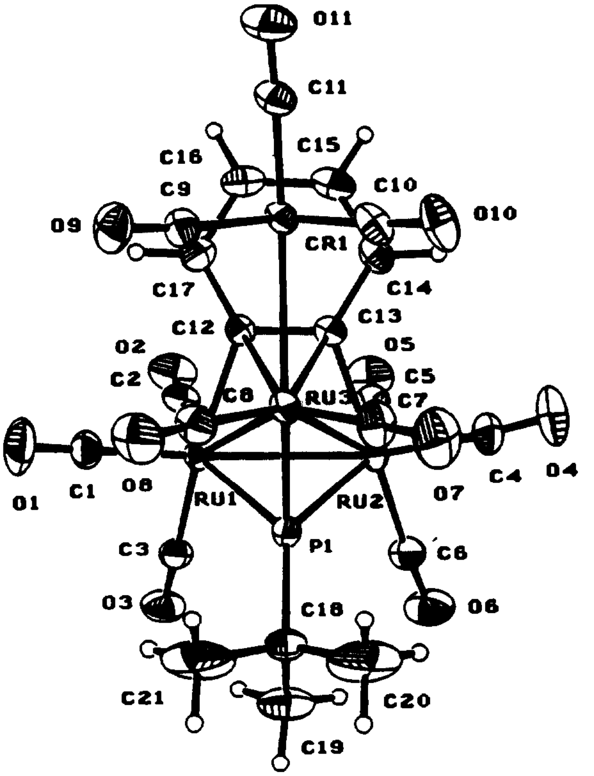

Fig. 29. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

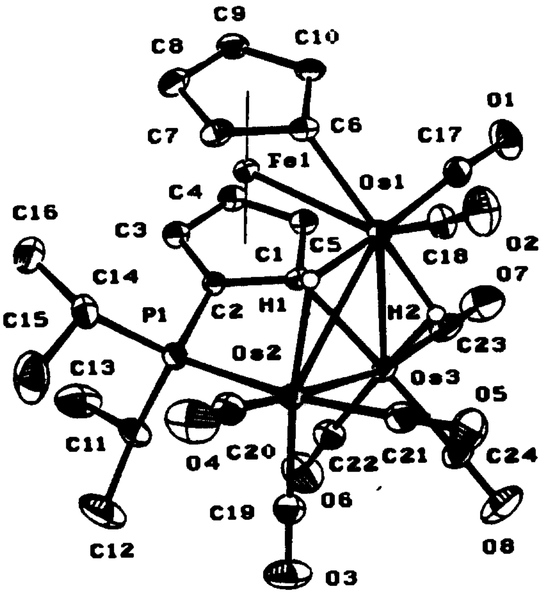

Fig. 30. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

Treatment of $Ru_3(CO)_{12}$ with $(Cp^*)Fe(CO)_2C\equiv CFe(CO)_2(Cp^*)$ gives the characterized carbide clusters $(\mu_4\text{-}C_2)(Cp^*Fe)_2Ru_2(CO)_8(\mu\text{-}CO)_2$ and $(\mu_6\text{-}C_2)_2(Cp^*\text{-}Fe)_2Ru_6(CO)_{14}(\mu\text{-}CO)_3$ [550]. The reaction between the ethynediyl complex $\{(Cp)(OC)_2Ru\}_2(\mu\text{-}C\equiv C)$ and $Fe_2(CO)_9$ yields the crystallographically characterized cluster $Fe_2Ru_2(\mu_4\text{-}C\equiv C)(\mu\text{-}CO)(CO)_8(Cp)_2$ [551]. The isolation and X-ray diffraction structure of $Fe_3Ru_5(\mu_6\text{-}C)(\mu_5\text{-}C)(\mu\text{-}PPh_2)_2(CO)_{17}$, which contains a square-pyramidal $Fe_2Ru_3(\mu_5\text{-}C)$ cluster fused to an octahedral $Fe_3Ru_3(\mu_6\text{-}C)$ cluster by a shared Fe_2Ru face, have appeared. This mixed-metal cluster is obtained from the reaction between $Fe_2(CO)_9$ and $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ [552]. Dissociative CO loss from $(H)FeOs_3(CO)_{12}$ has been observed to give the coordinatively unsaturated cluster $(H)_2FeOs_3(CO)_{11}$. UV-visible and IR spectra for the matrix-isolated $(H)_2FeOs_3(CO)_{12}$

cluster are presented and discussed with respect to the photochemistry of $(H)_2FeOs_3(CO)_{13}$ at silica surfaces [553]. Isomeric forms of $RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)$ and $RhOs_5(CO)_{15}(Cp^*)$ have been obtained from the reaction between $[Os_5(CO)_{15}]^{2-}$ and $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ and $[(Cp^*)Rh(MeCN)_3]^+$, respectively. The X-ray crystal structures of these clusters and their reaction with $(Et_3P)Au(Cl)$ are presented [554]. Treatment of $Fe(CO)_3(dppee)$ with $Ru_3(CO)_{10}(dppee)$ produces the new cluster $(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)$, which has been characterized by single-crystal X-ray diffraction analysis [555].

The mixed-metal cluster $FeRu_5(\mu_4\text{-}CCH_2)(\mu_3\text{-}SMe)(\mu\text{-}SMe)(\mu\text{-}PPh_2)_2(CO)_{13}$ has been isolated from the reaction between $Fe_2(CO)_9$ and $Ru_5(\mu_3\text{-}CCH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ [556]. Metal fragment exchange has been employed in the synthesis of $(H)FeRu_2(CO)_{10}(\mu\text{-}CX)$ (where $X = OMe$, NMe_2). Kinetic studies of substitution by PPh_3 have been conducted, and the relative rates of CO loss determined to be $FeRu_2 > Fe_3 > Ru_3$ [557].

The synthesis of the diphosphine-linked cluster $Os_3(CO)_{11}(dppm)Rh_6(CO)_{15}$ has appeared. The identity of this cluster has been determined on the basis of IR and ^{31}P NMR data [558]. Reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $(Cp)Ir(CO)_2$ leads to the new cluster $(\mu\text{-}H)_2(Cp)IrOs_3(CO)_{10}$. This cluster possesses a tetrahedral core with a semi-bridging carbonyl ligand from Ir to Os, as determined by X-ray crystallography [559]. The preparation and catalytic properties of the bimetallic complexes $[MRh_4(CO)_{15}]^{2-}$ (where M = Fe, Ru, Os) have been reported [560]. The cyclic polydentate thioether 1,3,5-trithiane has been allowed to react with $(H)_4Ru_4(CO)_{12}$, $(H)_3Ru_3Co(CO)_{12}$, and $(H)RuCo_3(CO)_{12}$. The resulting products have been characterized by solution and diffraction techniques [561]. The reactivity of $RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(Cp)$ with dppm, dppe, and dppp has been investigated. Treatment of alkynes $RC{\equiv}CR$ (where R = Ph, Et) with this cluster gives $RhRu_3(C_2R_2)(CO)_9(Cp)$ and $RhRu_2(C_2R_2)(CO)_n(Cp)$ (where $n = 7$, R = Et; $n = 8$, R = Ph) [562]. The nitrosyl-substituted cluster $RuCo_3(CO)_{11}(NO)$ has been synthesized from $[RuCo_3(CO)_{12}]^-$ and [NO][BF]. Alkyne insertion into one of the Co–Co bonds of this nitrosyl cluster affords the new cluster $RuCo_3(CO)_9(NO)(\mu_4\text{-}\eta^2\text{-}RC{\equiv}CR')$ (where R = R′ = Ph; R = Ph, R′ = H; R = R′ = H) along with a minor amount of the trinuclear cluster $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}CR')$ [563]. The tetrahedral cluster $[RuCo_3(CO)_{12}]^-$ and $(H)RuCo_3(CO)_{12}$ have been examined by solid-state ^{59}Co NMR spectroscopy [564]. The synthesis of the methoxycarbene complex derived from $(Cp^*)Co(Et_2C_2B_3H_2Cl)Ru(CO)_3$ has appeared [565]. The synthesis and characterization of the tetradecker metallacarborane sandwich complex $(Cp^*Co)(2,3\text{-}Et_2C_2B_3H_2\text{-}5\text{-}Cl)(2,3\text{-}Et_2C_2B_3H\text{-}4,5[5,6]\text{-}Cl_2)Ru$ have been reported [566]. Acidification of $[OsRh_4(CO)_{15}]^{2-}$ yields the anions $[OsRh_5(CO)_{16}]^-$ and $[OsRh_3(CO)_{12}]^-$. The X-ray structures of these anions and the ^{13}C NMR data are presented [567].

The cluster $Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_3(\mu_3\text{-}H)$ has been synthesized from the reaction of $Ru_4Pt_2(CO)_{18}$ with H_2 in refluxing heptane. This cluster has been characterized by solution techniques and X-ray diffraction analysis. Diphenylacetylene reacts with this cluster to give $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$. The molecular structure of this cluster is similar to that of the starting cluster [568]. The edge-shared bioctahedral cluster $Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$ has been prepared from the reaction of $Ru_4Pt_2(CO)_{18}$ with $Ru_4(CO)_{13}(\mu\text{-}H)_2$ and examined for its reactivity with dppe, because of its electron deficiency. The X-ray crystal structure of $Ru_8Pt_2(CO)_{23}(dppe)(\mu\text{-}H)_2$ accompanies this report [569]. The new clusters $Ru_4Pt(CO)_{13}(COD)(\mu\text{-}H)_2$, $Ru_3Pt(CO)_9(\mu\text{-}CO)(COD)(\mu\text{-}H)_2$, $Ru_4Pt_2(CO)_{11}(COD)_{11}(\mu_3\text{-}H)_2$, and $Ru_5Pt_5(CO)_{18}(COD)(\mu_3\text{-}H)_2$ have been isolated from the reaction between $Ru_4(CO)_{13}(\mu\text{-}H)_2$ and $Pt(COD)_2$. All four of these new clusters have been characterized by IR, ^1H NMR, and X-ray diffraction analyses [570]. Pyrolysis of $Pt_2Os_3(CO)_{10}(COD)_2$ under CO yields the new high-nuclearity platinum-osmium clusters $Pt_4Os_6(CO)_{22}(COD)$, $Pt_5Os_6(CO)_{21}(COD)_2$, and $Pt_4Os_6(CO)_{19}(COD)_2$. The spectroscopic data, X-ray crystal structures, and reactivity of these clusters are discussed [571].

The redox condensation of $[Os_3(CO)_9(CCO)]^{2-}$ and $Ni(CO)_4$ gives the 100-electron carbide cluster $[Os_3Ni_4(C)(CO)_{15}]^{2-}$. X-Ray diffraction analysis indicates that the carbide ligand resides in the center of a trigonal prism of two Os and four Ni atoms. The remaining Os atom caps a square face of two Ni and two Os atoms. The low-temperature ^{13}C NMR data are also discussed [572].

Redistribution reactions of $Ru_3(\mu\text{-}HgCl)(\mu_3\text{-}\eta^2\text{-}ampy)(CO)_9$ with the metal–metal bonded dimers $\{(Cp)M\text{-}(CO)_3\}_2$ (where M = Mo, W) and $Co_2(CO)_8$ give the mixed-metal clusters $\{Ru_3(\mu_3\text{-}\eta^2\text{-}ampy)(CO)_9\}(\mu_3\text{-}Hg)MLn$ {where MLn = $(Cp)M(CO)_2$, $Co(CO)_4$}. The X-ray structure of the cobalt derivative reveals that the $Hg\text{–}Co(CO)_4$ fragment bridges the same Ru–Ru edge as the amido moiety of the ampy ligand [573]. Treatment of $[RuCo_3(CO)_{12}]^-$ with $HgBr_2$ yields the pentanuclear cluster $RuCo_3(CO)_{12}(HgBr)$ and hexanuclear cluster $RuCo_3(CO)_{12}\{\mu_3\text{-}HgCo(CO)_4\}$. The mercury atom caps the Co_3 face in this latter cluster [574]. Variable-temperature ^{13}C NMR spectroscopy has been used to study the fluxional behavior of the mercury-capped decaosmium clusters $[Os_{10}(C)(CO)_{24}(HgX)]^-$ {where X = Cl, Br, I, CF_3, $(Cp)Mo(CO)_3$}. The observed mobility of the mercury fragment is discussed along with a unified model for the observed metal-core fluxionality [575]. The synthesis of the osmium clusters $[Os_{10}(C)(CO)_{24}(HgX)]^-$ (where X = Cl, Br, I) from HgX_2 and $[Os_{10}(C)(CO)_{24}]^{2-}$ and the X-ray structure of the $HgCF_3$-substituted cluster are presented [576]. Mercury extrusion from $[Os_{18}(Hg)_3(C)_2(CO)_{42}]^{2-}$ during reduction leads to $[Os_{18}(Hg)_2(C)_2(CO)_{42}]^{4-}$, which has been isolated and crystallographically characterized. The redox properties of this Os_3Hg_3 cluster and related mercury clusters have been explored by cyclic voltammetry [577]. The reaction between the carbide cluster $Ru_5(C)(CO)_{15}$ and $Hg(CF_3)(O_2CF_3)$ produces the new cluster $Ru_5(C)(CO)_{15}(HgCF_3)(O_2CCF_3)$, which is shown by X-ray diffraction analysis to contain a bridged-butterfly Ru_5 metal core [578]. The reaction between $Ru_2(1,8\text{-diaminonaphthalene})(CO)_4(P\text{-}{}^iPr_3)_2$ with HgX_2 (where X = halides, acetates, SCN, ONC) is reported to give adducts which contain mercury atoms that are bonded to two ruthenium atoms [579]. A report on the synthesis and dynamic behavior of mercury-linked clusters with methoxymethylidyne ligands has appeared. Included is the X-ray diffraction structure of $Hg\{Ru_3(\mu\text{-COMe})(CO)_{10}\}_2$ [580].

The molecular structure of $[\{Ru_4(H)(CO)_{12}B\}_2Cu_4(\mu\text{-Cl})]^{2-}$ has been solved [581]. The reaction of the soft electrophiles CuI and $[Cu(PR_3)]^+$ with $[Ru_3(CO)_9(CCO)]^{2-}$ has been investigated. The X-ray crystal structure of $[Ru_3(CuI)(CO)_9(CCO)]^{2-}$ is presented [582]. The single-crystal X-ray diffraction structure of $(OC)_3(PPh_3)_2OsAg(O_2CF_3)$ has been published and discussed as a structural model for a precursor complex in electron-transfer reactions involving organometallic complexes and silver(I) salts [583]. Phenylselenenyl chloride reacts with $[Ru_6(C)(CO)_{16}]^{2-}$ to yield $[Ru_6(C)(CO)_{15}(SePh)]^-$, which upon further reaction with $Au(PPh_3)(Cl)$ yields the cluster $Ru_6(C)(CO)_{15}(SePh)(AuPPh_3)$ [584]. The synthesis and solution properties of the boron-containing cluster $(H)Ru_4(CO)_{12}(B)\{Au(dppf)\}$ have been described. The molecular structure of this cluster has been solved by X-ray crystallography [585]. Ruthenium extrusion from the hexaruthenium cluster $Ru_6(CO)_{17}(B)\{Au(PPh_3)\}$ under CO pressure is reported to give the pentaruthenium cluster $Ru_5(CO)_{15}(B)\{Au(PPh_3)\}$. This cluster is shown to have a square-pyramidal Ru_5 core with an interstitial boron atom by X-ray diffraction analysis [586].

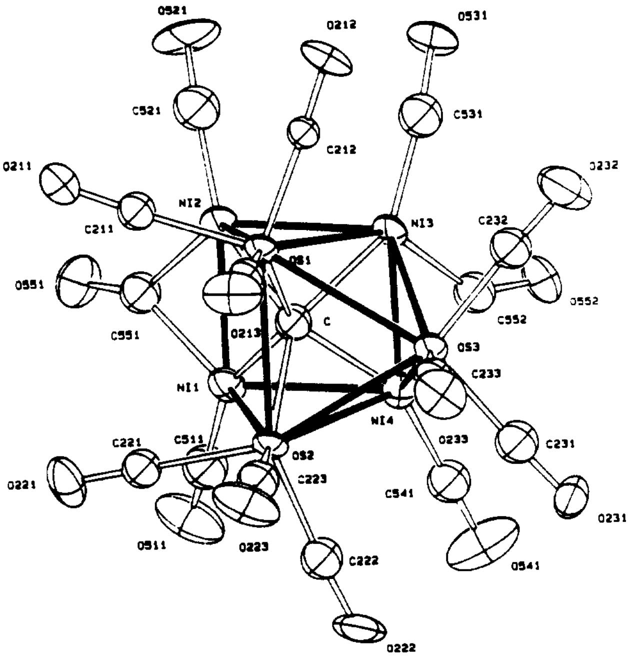

Fig. 31. Reprinted with permission from *Inorg. Chem.* Copyright 1992 American Chemical Society.

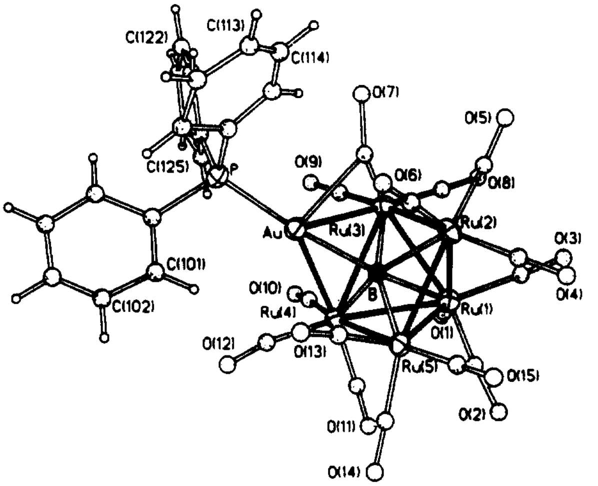

Fig. 32. Reprinted with permission from *Organometallics*. Copyright 1992 American Chemical Society.

5. Miscellaneous chemistry

5.1. Heterogeneous and supported complexes

Ruthenium has been deposited as ruthenium-red on NaY zeolites. The reduction of the ruthenium and cluster growth have been explored by the measurement of xenon adsorption on Ru and EXAFS studies [587]. The adsorption of ethylene on Ru–Y zeolites has been investigated by ^{13}C solid-state NMR spectroscopy. The rates of ethylene hydrogenation to ethane and butane are reported [588]. The low-temperature water gas shift reaction has been examined with zeolites that have been modified by $[Ru(NH_3)_6]^{3+}$. A ruthenium(II)-dicarbonyl species is reported to be the catalytically active species for this reaction [589]. The use of the xenon-adsorption method for the study of ruthenium cluster formation and growth on Y zeolites has been described [590].

The electrocatalytic properties of polypyrrole films possessing pendant cationic $[Ru(bpy)_3]^{2+}$ groups along with RuO_2 have been studied in alcohol oxidation reactions [591]. Carbon paste electrodes doped with ruthenium have been prepared and examined for electrocatalytic activity in a variety of reactions [592].

The adsorption and decomposition of monomethylamine on Ru(001) have been examined by using high-resolution electron energy loss spectroscopy and thermal desorption mass spectrometry [593]. The adsorption of diborane on clean Ru(0001), NH_3/Ru(0001), and O/Ru(0001) surfaces has been studied in connection with the synthesis of boron nitride thin films [594]. The adsorption of hydrazine on clean Ru(0001) and its coadsorption and reaction with diborane have been described [595]. The deposition of cerium onto Ru(0001) affords layer growth of the rare-earth metal [596].

^{13}C-enriched $Ru_3(CO)_{12}$ supported on the metal-oxide surfaces of γ-Al_2O_3, SiO_2, MgO, and HNa-Y zeolite has been investigated by ^{13}C MAS NMR spectroscopy. Highly mobile physisorbed clusters have been observed with the first two supports. In the case of MgO, highly fluxional hexaruthenium clusters are observed [597]. The influence of potassium as a promoter in the hydrogenation of 3-methyl-2-butenal by Ru/SiO_2 has been discussed [598]. The photochemical properties of silica-supported $(H)_2FeOs_3(CO)_{13}$ have been examined by using FT-IR and UV-visible reflectance spectroscopies. The coordinatively unsaturated cluster $(H)_2FeOs_3(CO)_{12}$ is stabilized by the silica support [599]. Adsorption of $[Os_{10}(C)(CO)_{24}]^{2-}$ onto thermally activated MgO leads to a supported decaosmium carbide cluster. Cluster characterization by EXAFS, IR spectroscopy, and UV-visible diffuse reflectance spectroscopy is described. The transmission electron microscope images of the supported cluster have been obtained [600]. The alkylation of alkenes with methane using a heterogeneous ruthenium catalyst system is presented [601]. FT-IR data have been reported for adsorbed hydrogen atoms on 2 wt % Ru/MgO catalysts [602]. Alkene homologation using methane is reported for a ruthenium-supported catalyst [603]. $Os_3(CO)_{12}$ has been supported on magnesia and examined in CO hydrogenation reactions in a flow reactor [604]. The photocatalytic reduction of N_2 to NH_3 has been examined by using surface-supported ruthenium catalysts [605]. The Si–O-supported catalysts $RuCo_3$, $RuCo_2$, Ru_3M_xC (where M = Co, Fe, Ni, Mo, Rh, Cr, Mn; $x = 1$–3) have been studied in the hydrogenation of CO to C_1–C_5 alcohols [606]. The cluster $[Ru_6(C)(CO)_{16}(Me)]^-$ has been supported on SiO_2, Al_2O_3, and TiO_2, and the supported systems characterized by EXAFS, TPD, and FT-IR spectroscopy [607]. The formation of methanol, dimethyl ether, and formaldehyde has been observed when the supported ruthenium catalysts $[Ru_6(C)(CO)_{16}(Me)]^-$/oxide are treated with syngas. Methane and hydrocarbons are the major products observed when the catalysts $[Ru_6(CO)_{18}]^{2-}$/oxide are employed [608]. The hydrogenation of nitrobenzene using polymer-supported ruthenium(II) catalysts has been examined [609].

The chemical bonding in the rutile structure of RuO_2 has been studied by *ab initio* molecular orbital calculations [610]. The phases R_3I_3Ru (where R = La, Pr, Gd, Y, Er) have been synthesized and characterized [611]. The electronic and bonding properties of RuS_2 have been examined by DV-Xα calculations [612].

5.2. CO and CO_2 reactions

The carbonylation of methanol to acetic acid has been examined by using the catalysts *trans*-$Ru(CO)_2(Cl)_2(PPh_3)_2$, *cis*-$Ru(CO)_2(Cl)_2(PPh_3)_2$, and $(H)_2Ru(CO)(PPh_3)_3$. The highest activity and selectivity were observed with the latter complex [613]. Carbonylation of nitrobenzene to methyl phenylcarbamate has been studied with the bimetallic catalysts $[MRh_4(CO)_{15}]^{2-}$ (where M = Ru, Os). The addition of bpy to the catalyst system enhances the rate and selectivity of the reaction [614]. The use of $Ru_3(CO)_{12}$ as a catalyst for the deoxygenation of 2-nitro-*N*-(phenylmethylene)benzeneamine derivatives to 2-substituted benzimidazoles has been presented [615]. A report on the ruthenium(III)-Schiff base catalyzed carbonylation of nitrobenzene to phenylurethane has appeared [616].

5.3. Oxidation reactions

Evidence for the stereoelectronic control of diastereoselectivity in osmium tetraoxide-catalyzed *cis*-dihydroxylations of sterically unbiased 3-(4-X-phenyl)-3-phenylcyclopentenes {where X = NO_2, Cl, Br, OMe, $N(Me)_2$} is reported [617]. Selective asymmetric dihydroxylation of dienes has been studied with a functionalized osmium tetraoxide catalyst [618]. A report describing a new ligand class and a process improvement in osmium-catalyzed asymmetric dihydroxylation reactions has appeared [619]. The osmium-catalyzed asymmetric dihydroxylation of enol ethers affords α-hydroxy ketones in high enantiomeric purity [620].

Alkane oxidation by molecular oxygen in the presence of acids and aldehydes with the ruthenium catalysts $RuCl_3 \cdot nH_2O$ and $Ru(Cl)_2(PPh_3)_3$ has been observed to occur with good yields [621]. The kinetics and mechanism of the oxidation of cyclohexane and adamantane by molecular oxygen have been examined with a ruthenium(III)-saloph complex [622]. *In situ* generated RuO_4 has been reported to function as a catalyst for the oxidation of nonactivated C–H bonds [623].

The use of Ru^{III}(hedta) and related complexes in the epoxidation of stilbenes is described [624]. Ruthenium(III)–Schiff base complexes have been synthesized and examined in alkene epoxidation reactions [625]. The kinetics and mechanism of styrene and substituted styrene epoxidation by oxygen and $[Ru^{III}(edta)(H_2O)]^-$ have been published [626]. The ruthenium complexes $[Ru(dimethylglyoxime)(Cl)_2]^-$, $[Ru(diphenylglyoxime)(Cl)_2]^-$, and the corresponding ruthenium(V) oxo complexes have been synthesized, characterized, and examined in the epoxidation of cyclohexene [627]. The epoxidation of oleic acid using H_2O_2 and $Ru(bpy)_2(Cl)_2$ has been described [628].

Secondary alcohols are oxidized to ketones by acetone and catalytic amounts of the ruthenium catalyst $Ru(Cl)_2(PPh_3)_3$ [629]. Allylic alcohols and terminal alkynes yield β,γ-unsaturated ketones when treated with the ruthenium catalyst $(Cp)Ru(PPh_3)_2(Cl)$ [630]. The activation and thermodynamic parameters for the homogeneous oxidation of cyclohexane to cyclohexanol, cyclohexanol to *cis*-1,3-cyclohexane diol and olefin, and cyclohexene to epoxide using the catalyst system composed of Ru^{III}(edta)-ascorbate-O_2 are reported [631]. The kinetics and mechanism for the oxidation of dimethyl sulfide by $[Ru^{III}(edta)(Cl)]^-$ and oxygen have been published [632]. Ruthenium(II) complexes have been employed as catalysts in the oxidation of saturated hydrocarbons [633]. The epoxidation of alkenes using a Ru^{III}(edta)-ascorbate-oxygen system has been presented. Detailed kinetic, catalytic, and equilibrium studies have been conducted, which have led to a proposed mechanism involving a monooxygenase model [634]. The oxidation of hydrazine using the oxoruthenium catalyst $[Ru^V(O)(H_2O)_3(Cl)_2]^+$ has appeared. A mechanism that involves a diazene intermediate that undergoes a two-electron oxidation to give N_2 is described [635]. The photooxidation of cyclohexane and adamantane using water as the oxygen source and a semiconductor catalyst system with $[Ru^{III}(edta)(Cl)]^-$ has been described [636]. A study on the oxidation of olefinic and saturated substrates using $[Ru^{III}(edta)(Cl)]^-$ has appeared. The rate and activation data are presented and a mechanism for these reactions is outlined [637]. The oxygenation of organic substrates by molecular oxygen and the ruthenium catalyst $[Ru(Cl)_2(H_2O)_4]^+$ has been explored [638]. The electrochemical behavior of the ruthenium(III)-Schiff base complex $[Ru^{III}$\{bis(2-hydroxynaphthaldehyde)diethylenetriaminato\}(Cl)] in oxidation reactions is reported [639]. The hydrocarbon compounds adamantane, cyclohexane, hexane, and heptane have been oxidized by a catalyst system composed of the ruthenium complexes $[Ru(H_2O)PW_{11}(O)_{39}]^{5-}$ and *cis*-$[Ru(H_2O)_2(DMSO)_4]^{2+}$ and t-butylhydroperoxide [640]. The oxygen-atom transfer from molecular oxygen to adamantane is catalyzed by a ruthenium(III)edta complex [641]. Alcohol dehydrogenation has been achieved with the following ruthenium complexes $[Ru(bpy)_2(2\text{-}HOCH_2py)]^{2+}$, $[Ru(bpy)_2(2\text{-}HOCD_2py)]^{2+}$, and $[Ru(bpy)_2\{2\text{-}HOCH(Me)py\}]^{2+}$. The mechanism associated with this reaction is discussed [642].

5.4. H_2 Production and hydrogenation reactions

Asymmetric hydrogen transfer reactions using ruthenium complexes have been published [643]. The enantioselective ruthenium-mediated synthesis of (−)-indolizidine 223AB has been described. The reported synthesis utilizes a symchiral aldehyde that is prepared by BINAP-ruthenium-mediated hydrogenation of a requisite β-keto ester [644]. The asymmetric hydrogenation of itaconic acid and other prochiral carboxylic acids by $[Ru(H)(binap)_2]^+$ has been investigated. ^{31}P NMR spectroscopic data are included with this report [645]. The transfer hydrogenation of α,β-unsaturated aldehydes has been examined with the ruthenium catalysts $Ru_4(CO)_8(L)_8(H)_4$ \{where $L = {}^nBu_3P$, $P(OEt)_3$, $P(OMe)_3$, PMe_3, PPh_3\} [646]. Kinetic and mechanism data are presented for the hydrogenation of benzaldehyde using the catalyst $[Ru(H)(CO)(MeCN)_2(PPh_3)_2]^+$ [647]. The alcohols 2-propanol, 2-butanol, cyclohexanol, benzyl alcohol, 1-phenylethanol, benzhydrol, 2-methoxyethanol, and tetrahydrofurfuryl alcohol have been used as reducing agents in the transfer hydrogenation of D-glucose with the catalyst system $Ru(Cl)_2(PPh_3)_3$. The major product from glucose is sorbitol, with minor amounts of glucono-1,5-lactone being observed as a side-product from a disproportionation reaction [648]. The hydrogenation of alkenes has been studied with the bulky phosphine complexes *cis*-$Ru(H)_2(dcpe)_2$ and *cis*-$Os(H)_2(dcpe)_2$. The ruthenium complex is more active in the reduction of enones to saturated ketones while the osmium complex is more active in the reduction of unactivated olefins [649]. The catalytically active species is formed by the dissociation of one of the disphosphine ligands [649]. Alkene and alkyne hydrogenation reactions have been investigated with the ruthenium complex $Ru_3(CO)_9(\mu_3\text{-ampy})(\mu\text{-H})$ [650]. Imines are hydrogenated easily under transfer hydrogenation conditions with the ruthenium catalyst $Ru(Cl)_2(PPh_3)_3$ [651].

5.5. *Other catalytic reactions*

The ruthenium-catalyzed cyclization of *N*-allyltrichloroacetamides yields trichlorinated γ-lactams. When the same catalyst is used in the cyclization of secondary *N*-allyltrichloroacetamides, good diastereoselectivity is observed [652]. The hydration of nitriles and the transformation of δ-ketonitriles to ene-lactams are reported to be catalyzed by $Ru(H)_2(PPh_3)_4$ under mild conditions [653]. The oxidative condensation of diols to 5- and 6-ring lactones has been demonstrated when ruthenium polyhydride complexes have been employed as catalysts [654]. The aqueous ring-opening metathesis polymerization (ROMP) of 7-oxa-norbornene-2,3-dicarboxylic acid dimethyl ester and norbornene with ruthenium catalysts has been described [655]. The ruthenium-catalyzed ROMP of norbornene, cyclooctene, and cyclopentene has been examined. The nature of the catalyst and the characterization of the polymer are discussed [656]. The catalytic reduction of aromatic nitro compounds using $Ru_3(CO)_{12}$ has been investigated under water gas shift conditions [657]. The dual catalytic system composed of $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ has been shown to facilitate the rearrangement of heterocyclic nitrogen ketones to lactams in good yields. Cyclization of 2,6-dimethylpiperidinyl ketones gave 5,6,7,8-tetrahydroindolizines in high yields [658]. A report describing the cyclization-reconstitutive addition of propargyl alcohols with allyl alcohols using $(Cp)Ru(PPh_3)_2(Cl)$ has appeared [659]. The synthesis of 1,3-disubstituted 2,3-dihydroimidazol-2-ones from *N*,*N'*-disubstituted ureas and *vicinal* diols is reported. Moderate to high product yields are observed with the ruthenium catalyst $Ru(Cl)_2(PPh_3)_3$ [660]. The cross-metathesis of vinyl-substituted silicon compounds with 1-decene is observed with the catalyst $Ru(Cl)_2(PPh_3)_3$ [661].

6. Abbreviations

acac	acetoacetonate
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
bpy	bipyridine
bpz	bipyrazine
BSD	2,1,3-benzoselenadiazole
bta	benzotriazol-1-yl
chp	6-chloro-2-hydroxypyridine
1,5-COD	1,5-cyclooctadiene
COT	cyclooctatriene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
cyclam	1,4,8,11-tetraazacyclotetradecane
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
DAB	1,4-diaza-1,3-butadiene
DAD	diazadiene
dcpe	$Cy_2PCH_2CH_2PCy_2$
2,5-DHT	2,5-dihydrothiophene
DMABN	4-*N*,*N*-dimethylaminobenzonitrile
DMAD	dimethyl acetylenedicarboxylate
dmgh	dimethylglyoxime
dmp	4,4'-dimethyl-2,2'-bipyridine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,1-bis(dimethylphosphino)methane
dmpt	5,6-dimethyl-3-(pyridin-2-yl)-1,2,4-triazine
dpb	2,3-di-(2'-pyridyl)(benzo[*g*]quinoline)
dpgh	diphenylglyoxime
dpp	2,3-bis(2-pyridyl)pyrazine
dppa	bis(diphenylphosphino)acetylene
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
ECL	electrogenerated chemiluminescence
Hampy	2-amino-6-methylpyridine
Hbpt	3,5-bis(pyridin-2-yl)-1,2,4-triazole
Hbta	benzotriazole
H_2DBA	1,5-diphenyl-1,3,5-pentanetrione
hedta	*N*-(hydroxyethyl)ethylenediaminetriacetate
Hfac	hexafluoroacetylacetonate
HPhenoxSQ	1-hydroxy-2,4,6,8-tetra-tert-butylphenoxazinyl
In	indenyl
$Me_4[14]aneS_4$	1,4,8,11-tetrathiocyclotetradecane
Me_2Hpz	dimethylpyrazole
1,3-Me_2lum	1,3-dimethyllumazine
mes	mesityl
MLCT	metal-to-ligand charge transfer
nbd	norbornadiene
N-MeIm	N-methylimidazole
OEP	octaethylporphyrin
pdta	propylenediaminetetraacetate
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
PTA	1,3,5-triaza-7-phosphaadamantane
py	pyridine
pz	pyrazol-1-yl
(*R*)-prophos	(*R*)-(+)-1,2-bis(diphenylphosphino) propane
saloph	bis(salicylaldehyde)-*o*-phenylenediamine
SIMS	secondary ion mass spectrometry
tap	1,4,5,8-tetraazaphenanthrene
tcne	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
tdpep	$P(CH_2CH_2PPh_2)_3$
TEMPO	2,2,6,6-tetramethylpiperidene-1-oxyl
terpy	2,2:6′,2″-terpyridine
tfpb	4,4,4-trifluoro-1-phenyl-1,3-butanedionate
tmen	*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
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

Acknowledgment

The author wishes to thank Ms. Carol N. Richmond for her typing of this review.

References

1 C.S. Chow, *Diss. Abstr.*, *53* (1992) 2836-B; DA9232169.
2 X. Shui, *Diss. Abstr.*, *53* (1992) 1843-B; DA9225924.
3 J.G. Muller, *Diss. Abstr.*, *53* (1992) 1358-B; DA9222085.
4 J.K. Blaho, *Diss. Abstr.*, *52* (1992) 4181-B; DA9202292.
5 S.D. Swieter, *Diss. Abstr.*, *52* (1992) 4190-B; DA9202055.
6 T.A. Perkins, *Diss. Abstr.*, *52* (1992) 4188-B; DA9202045.
7 S. Gould, *Diss. Abstr.*, *52* (1992) 5255-B; DA9207950.
8 W.E. Lynch, *Diss. Abstr.*, *52* (1992) 6383-B; DA9215118.
9 M.A. Billadeau, *Diss. Abstr.*, *52* (1992) 6377-B; DA9213077.
10 P.S. Wagenknecht, *Diss. Abstr.*, *52* (1992) 4724-B; DA9206874.
11 Y.-Z. Han, *Diss. Abstr.*, *53* (1992) 280-B; DA9216831.
12 N. Zhang, *Diss. Abstr.*, *52* (1992) 5837-B; DA9211056.
13 G.F. Sweigers, *Diss. Abstr.*, *53* (1992) 275-B; DA9215449.
14 I.A. Ali, *Diss. Abstr.*, *53* (1992) 2852-B; DA9230732.
15 D.V. McGrath, *Diss. Abstr.*, *53* (1992) 2859-B; DA9232204.
16 D.L. Carlson, *Diss. Abstr.*, *53* (1992) 1839-B; DA9224478.
17 G.C. Hsu, *Diss. Abstr.*, *52* (1992) 5827-B; DA9210225.
18 M.K. Whittlesey, *Diss. Abstr.*, *52* (1992) 4725-B; BRDX94365.
19 L.J. Silverberg, *Diss. Abstr.*, *52* (1992) 4738-B; DA9206337.
20 J.W. Young, Jr., *Diss. Abstr.*, *53* (1992) 1381-B; MIT Libraries.
21 M.A. Haiza, *Diss. Abstr.*, *53* (1992) 1368-B; DA9223507.
22 C.Y.-I. Park, *Diss. Abstr.*, *53* (1992) 1375-B; MIT Libraries.
23 R.L. Trace, *Diss. Abstr.*, *53* (1992) 5280-B; DA9209085.
24 G.C. Martin, *Diss. Abstr.*, *52* (1992) 4187-B; DA9202030.
25 J.-G. Park, *Diss. Abstr.*, *53* (1992) 855-B; DA9220018.
26 P.-Y. Plouffe, *Diss. Abstr.*, *53* (1992) 1359-B; DANN67854.
27 J.D.M. Atkinson, *Diss. Abstr.*, *53* (1992) 2308-B; BRD-96818.
28 K.A. Johnson, *Diss. Abstr.*, *52* (1992) 5814-B; DA9212060.
29 R.J. Sorbie, *Diss. Abstr.*, *52* (1992) 5819-B; BRD-94942.
30 R.L. Myrabo, *Diss. Abstr.*, *52* (1992) 4188-B; DA9203661.
31 W. Weng, *Diss. Abstr.*, *52* (1992) 4725-B; DA9207312.
32 D.W. Ryba, *Diss. Abstr.*, *53* (1992) 2307-B; DA9226577.
33 J.P. Lillis, *Diss. Abstr.*, *53* (1992) 2306-B; DA9226570.
34 F. van Gastel, *Diss. Abstr.*, *53* (1992) 2862-B; DANN69080.
35 N.A.E.-A. Nawar, *Diss. Abstr.*, *52* (1992) 4188-B; BRDX94045.
36 L.R. Nevinger, *Diss. Abstr.*, *53* (1992) 2307-B; DA9228071.
37 E.J. Voss, *Diss. Abstr.*, *53* (1992) 2862-B; DA9230013.
38 M. Koike, *Diss. Abstr.*, *52* (1992) 5814-B; DA9210874.
39 V.J. Johnston, *Diss. Abstr.*, *52* (1992) 5814-B; DANN59277.
40 D.S. Parfitt, *Diss. Abstr.*, *52* (1992) 5816-B; DA9210636.
41 T.B. Shay, *Diss. Abstr.*, *53* (1992) 841-B; DA9219023.
42 J.-C. Lii, *Diss. Abstr.*, *53* (1992) 1840-B; DA9224912.
43 J.E. Shield, *Diss. Abstr.*, *53* (1992) 1561-B; DA9223965.
44 C. Huang, *Diss. Abstr.*, *52* (1992) 4216-B; DA9204600.
45 B.G. Frederick, *Diss. Abstr.*, *52* (1992) 4215-B; DA9203912.
46 M.V. Arena, *Diss. Abstr.*, *52* (1992) 4741-B; DA9206731.
47 S.I. Pien, *Diss. Abstr.*, *52* (1992) 6537-B; DA9213031.
48 J. Prakash, *Diss. Abstr.*, *52* (1992) 4749-B; DA9137036.
49 G.-D. Lei, *Diss. Abstr.*, *52* (1992) 5847-B; DA9205007.
50 K. Ashktorab, *Diss. Abstr.*, *53* (1992) 2372-B; DA9226835.
51 B.K. Esser, *Diss. Abstr.*, *53* (1992) 1250-B; DA9221329.
52 G.E. Ravizza, *Diss. Abstr.*, *52* (1992) 3495-B; DA9136184.
53 J.W. Seyler, P.E. Fanwick and C.R. Leidner, *Inorg. Chem.*, *31* (1992) 3699–3700.
54 J.W. Seyler, L.K. Safford and C.R. Leidner, *Inorg. Chem.*, *31* (1992) 4300–4307.
55 J.W. Seyler, L.K. Safford, P.E. Fanwick and C.R. Leidner, *Inorg. Chem.*, *31* (1992) 1545–1547.
56 J.P. Collman, J.M. Garner, R.T. Hembre and Y. Ha, *J. Am. Chem.Soc.*, *114* (1992) 1292–1301.
57 J.P. Collman, P.S. Wagenknecht and N.S. Lewis, *J. Am. Chem. Soc.*, *114* (1992) 5665–5673.
58 J.P. Collman, J.E. Hutchison, M.A. Lopez and R. Guilard, *J. Am. Chem. Soc.*, *114* (1992) 8066–8073.
59 J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, N.S. Lewis, M.A. Lopez, R. Guilard, M. L'Her, A.A. Bothner-By and P.K. Mishra, *J. Am. Chem. Soc.*, *114* (1992) 5654–5664.
60 J.-S. Huang, C.-M. Che and C.-K. Poon, *J. Chem. Soc., Chem. Commun.*, (1992) 161–163.
61 J.-S. Huang, C.-M. Che, Z.-Y. Li and C.-K. Poon, *Inorg. Chem.*, *31* (1992) 1313–1315.
62 Z.-Y. Li, J.-S. Huang, C.-M. Che and C.K. Chang, *Inorg. Chem.*, *31* (1992) 2670–2672.
63 C.-M. Che, J.-S. Huang, Z.-Y. Li, C.-K. Poon, W.-F. Tong, T.F. Lai, M.-C. Cheng, C.-C. Wang and Y. Wang, *Inorg. Chem.*, *31* (1992) 5220–5225.

64 C. Géze, N. Legrand, A. Bondon and G. Simonneaux, *Inorg. Chim. Acta*, *195* (1992) 73–76.

65 L.D. Shulz, G.D. Fallon, B. Moubaraki, K.S. Murray and B.O. West, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 971–973.

66 A. Grund, A. Kaltbeitzel, A. Mathy, R. Schwarz, C. Bubeck, P. Vermehren and M. Hanack, *J. Phys. Chem.*, *96* (1992) 7450–7454.

67 M. Hanack, A. Gül and L.R. Subramanian, *Inorg. Chem.*, *31* (1992) 1542–1544.

68 L.K. Woo and D.A. Smith, *Organometallics*, *11* (1992) 2344–2346.

69 H. Ohtake, T. Higuchi and M. Hirobe, *J. Am. Chem. Soc.*, *114* (1992) 10660–10662.

70 K.O. Christe and R. Bougon, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 1056.

71 P.A. Reynolds, C.D. Delfs, B.N. Figgis, M.J. Henderson, B.Moubaraki and K.S. Murray, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 2309–2312.

72 J.H. Holloway, E.G. Hope, J.B. Raynor and P.T. Townson, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1131–1134.

73 A.K. Brisdon, J.H. Holloway, E.G. Hope, W. Levason, J.S. Ogden and A.K. Saad, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 447–449.

74 W.J. Casteel, Jr., A.P. Wilkinson, H. Borrmann, R.E. Serfass and N. Bartlett, *Inorg. Chem.*, *31* (1992) 3124–3131.

75 Y. Kobayashi, T. Okada, K. Asai, M. Katada, H. Sano and F. Ambe, *Inorg. Chem.*, *31* (1992) 4570–4574.

76 L. Eberson and M. Nilsson, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 1041–1042.

77 P.K. Dorhout and J.D. Corbett, *J. Am. Chem. Soc.*, *114* (1992) 1697–1701.

78 E. Alessio, B. Milani, M. Calligaris and N. Bresciani-Pahor, *Inorg. Chim. Acta*, *194* (1992) 85–91.

79 P.A. Lay and A.M. Sargeson, *Inorg. Chim. Acta*, *198–200* (1992) 449–460.

80 R.S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 3477–3482.

81 N.W. Alcock, I.D. Burns, K.S. Claire and A.F. Hill, *Inorg. Chem.*, *31* (1992) 4606–4610.

82 M.A. Owen, P.L. Pye, B. Piggott and M.V. Capparelli, *J. Organomet. Chem.*, *434* (1992) 351–362.

83 N.-Y. Sun and S.J. Simpson, *J. Organomet. Chem.*, *434* (1992) 341–349.

84 R. Davis, J.D. Furze, D.J. Cole-Hamilton and P. Pogorzelec, *J. Organomet. Chem.*, *440* (1992) 191–196.

85 G.E. Ball and B.E. Mann, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 561–563.

86 M.A. Esteruelas, F.J. Lahoz, J.A. López, L.A. Oro, C. Schlunken, C. Valero and H. Werner, *Organometallics*, *11* (1992) 2034–2043.

87 M.A. Esteruelas, L.A. Oro and C. Valero, *Organometallics*, *11* (1992) 3362–3369.

88 D.G. Gusev, A.B. Vymenits and V.I. Bakhmutov, *Inorg. Chem.*, *31* (1992) 1–2.

89 C. Bianchini, C. Bohanna, M.A. Esteruelas, P. Frediani, A.Meli, L.A. Oro and M. Peruzzini, *Organometallics*, *11* (1992) 3837–3844.

90 M.A. Esteruelas, M.P. Garcia, A.M. López, L.A. Oro, N. Ruiz, C.Schlunken, C. Valero and H. Werner, *Inorg. Chem.*, *31* (1992) 5580–5587.

91 D. Michos, X.-L. Luo, and R.H. Crabtree, *Inorg. Chem.*, *31* (1992) 4245–4250.

92 J. Eckert, A. Albinati, R.P. White, C. Bianchini and M. Peruzzini, *Inorg. Chem.*, *31* (1992) 4241–4244.

93 C.R.S.M. Hampton, I.R. Butler, W.R. Cullen, B.R. James, J.-P. Charland and J. Simpson, *Inorg. Chem.*, *31* (1992) 5509–5520.

94 J. Cartwright and A.F. Hill, *J. Organomet. Chem.*, *429* (1992) 229–238.

95 N.W. Alcock, I.D. Burns, K.S. Claire and A.F. Hill, *Inorg. Chem.*, *31* (1992) 2906–2908.

96 C. Bianchini, D. Masi, K. Linn, C. Mealli, M. Peruzzini and F. Zanobini, *Inorg. Chem.*, *31* (1992) 4036–4037.

97 C. Hall, W.D. Jones, R.J. Mawby, R. Osman, R.N. Perutz and M.K. Whittlesey, *J. Am. Chem. Soc.*, *114* (1992) 7425–7435.

98 J.D. Gargulak, A.J. Berry, M.D. Noirot and W.L. Gladfelter, *J. Am. Chem. Soc.*, *114* (1992) 8933–8945.

99 G. Jia, A.L. Rheingold, B.S. Haggerty and D.W. Meek, *Inorg. Chem.*, *31* (1992) 900–904.

100 P.W. Blosser, J.C. Gallucci and A. Wojcicki, *Inorg. Chem.*, *31*(1992) 2376–2384.

101 M. Kitamura, M. Tokunaga and R. Noyori, *J. Org. Chem.*, *57* (1992) 4053–4054.

102 S.A. King, A.S. Thompson, A.O. King and T.R. Verhoeven, *J. Org. Chem.*, *57* (1992) 6689–6691.

103 D. Carmichael, P. Le Floch, L. Ricard and F. Mathey, *Inorg. Chim. Acta*, *198–200* (1992) 437–441.

104 K. Mashima, T. Hino and H. Takaya, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 2099–2107.

105 L. Shao, K. Takeuchi, M. Ikemoto, T. Kawai, M. Ogasawara, H.Takeuchi, H. Kawano and M. Saburi, *J. Organomet. Chem.*, *435* (1992) 133–147.

106 Y. Sun, N.J. Taylor and A.J. Carty, *Organometallics*, *11* (1992) 4293–4300.

107 J.T. Poulton, K. Folting, W.E. Streib and K.G. Caulton, *Inorg. Chem.*, *31* (1992) 3190–3191.

108 E. Lindner, H. Rothfuss, R. Fawzi and W. Hiller, *Chem. Ber.*, *125* (1992) 541–550.

109 E. Lindner, A. Möckel, H.A. Mayer and R. Fawzi, *Chem. Ber.*, *125* (1992) 1363–1367.

110 E. Lindner, M. Kemmler and H.A. Mayer, *Chem. Ber.*, *125* (1992) 2385–2390.

111 Y. Wakatsuki, H. Yamazaki, Y. Maruyama and I. Shimizu, *J. Organomet. Chem.*, *430* (1992) C60–C63.

112 A. Yousfi and R. Mathieu, *J. Organomet. Chem.*, *426* (1992) C33–C35.

113 J.R. Dilworth, Y. Zheng and J.R. Miller, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1757–1758.

114 G. Alibrandi and B.E. Mann, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1439–1442.

115 N.R. Champness, W. Levason, D. Pletcher and M. Webster, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 3243–3247.

116 S.T. Nguyen, L.K. Johnson, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc.*, *114* (1992) 3974–3975.

117 D.J. Darensbourg, F. Joo, M. Kannisto, A. Katho and J.H. Reibenspies, *Organometallics*, *11* (1992) 1990–1993.

118 E. Fache, C. Santini, F. Senocq and J.M. Basset, *J. Mol. Catal.*, *72* (1992) 337–350.

119 E. Fache, C. Santini, F. Senocq and J.M. Bassei, *J. Mol. Catal.*, *72* (1992) 331–336.

120 G. Bellachioma, G. Cardaci, A. Macchioni and G. Reichenbach, *J. Organomet. Chem.*, *427* (1992) C37–C40.

121 I.D. Burns, A.F. Hill, A.R. Thompsett, N.W. Alcock and K.S. Claire, *J. Organomet. Chem.*, *425* (1992) C8–C10.

122 F. Ozawa, S. Chikaoka, X.-Z. Cao and A. Yamamoto, *J. Organomet. Chem.*, *424* (1992) 173–183.

123 E. Lindner, M. Pabel, R. Fawzi and M. Steimann, *J. Organomet. Chem.*, *441* (1992) 63–74.

124 W. Fischer, R.T. Hembre, D.R. Sidler and J.R. Norton, *Inorg. Chim. Acta*, 198–200 (1992) 57–61.

125 J.A. Corella, II, R.L. Thompson and N.J. Cooper, *Angew. Chem.*, *Int. Ed. Engl.*, *31* (1992) 83–84.

126 C.E.F. Rickard, W.R. Roper, D.M. Salter and L.J. Wright, *J. Am. Chem. Soc.*, *114* (1992) 9682–9683.

127 L. Song and W.C. Trogler, *J. Am. Chem. Soc.*, *114* (1992) 3355–3361.

128 M.J.A. Kraakman, B. de Klerk-Engels, P.P.M. de Lange, K. Vrieze, W.J.J. Smeets and A.L. Spek, *Organometallics*, *11* (1992) 3774–3784.

129 M. van Wijnkoop, P.P.M. de Lange, H.-W. Frühauf, K. Vrieze, Y.Wang, K. Goubitz and C.H. Stam, *Organometallics*, *11* (1992) 3607–3617.

130 C.F. Edwards, W.P. Griffith and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, (1992) 145–151.

131 M.D. Johnson and D. Nickerson, *Inorg. Chem.*, *31* (1992) 39713974.

132 T. Yoshida, T. Adachi, T. Tanaka and F. Goto, *J. Organomet. Chem.*, *428* (1992) C12–C16.

133 A.F. Hill, N.W. Alcock, J.C. Cannadine and G.R. Clark, *J. Organomet. Chem.*, *426* (1992) C40–C43.

134 M.N. Bell, A.J. Blake, R.M. Christie, R.O. Gould, A.J. Holder, T.I. Hyde, M. Schroder and L.J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, (1992) 2977–2986.

135 A.J. Blake, R.M. Christie, Y.V. Roberts, M.J. Sullivan, M. Schroder and L.J. Yellowlees, *J. Chem. Soc., Chem. Commun.*, (1992) 848–850.

136 J. Cannadine, A. Hector and A.F. Hill, *Organometallics*, *11* (1992) 2323–2324.

137 P.M. Treichel and E.K. Rublein, *J. Oraganomet. Chem.*, *424* (1992) 71–77.

138 O. Heyke, G. Beute and I.-P. Lorenz, *J. Oraganomet. Chem.*, *440* (1992) 197–205.

139 A. Pramanik, N. Bag, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 101–105.

140 K.I. Hardcastle, B.R. Cockerton, A.J. Deeming and M. Karim, *J. Chem. Soc., Dalton Trans.*, (1992) 1607–1613.

141 C.E.F. Rickard, W.R. Roper, D.M. Salter and L.J. Wright, *Organometallics*, *11* (1992) 3931–3933.

142 W.A. Schenk, J. Frisch, W. Adam and F. Prechtl, *Inorg. Chem.*, *31* (1992) 3329–3331.

143 P.G. Jessop, C.-L. Lee, G. Rastar, B.R. James, C.J.L. Lock and R. Faggiani, *Inorg. Chem.*, *31* (1992) 4601–4605.

144 S.P. Satsangee, J.H. Hain, Jr., P.T. Cooper and S.A. Koch, *Inorg. Chem.*, *31* (1992) 5160–5161.

145 D. Sellmann, P. Lechner, F. Knoch and M. Moll, *J. Am. Chem. Soc.*, *114* (1992) 922–930.

146 Y. Kasahara, Y. Hoshino, M. Kajitani, K. Shimizu and G.P. Sato, *Organometallics*, *11* (1992) 1968–1971.

147 J. Tang, K. Shimizu and R.A. Osteryoung, *Inorg. Chem.*, *31* (1992) 2328–2333.

148 S.J. Eder, W.A. Herrmann and P. Kiprof, *J. Organomet. Chem.*, *428* (1992) 409–414.

149 W.A. Herrmann, S.J. Eder, P. Kiprof and P. Watzlowik, *J. Organomet. Chem.*, 428 (1992) 187–197.

150 W.A. Herrmann and P. Watzlowik, *J. Organomet. Chem.*, 437 (1992) 363–368.

151 W.P. Griffith and J.M. Jolliffe, *J. Chem. Soc., Dalton Trans.*, (1992) 3483–3488.

152 A. Mills, P. Douglas and T. Russell, *J. Chem. Soc., Dalton Trans.*, (1992) 1059–1064.

153 C. Redshaw, W. Clegg and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1992) 2059–2062.

154 J.M. Hawkins, A. Meyer, T.A. Lewis, U. Bunz, R. Nunlist, G.E. Ball, T.W. Ebbesen and K. Tanigaki, *J. Am. Chem. Soc.*, *114* (1992) 7954–7955.

155 W.A. Herrmann and P. Watzlowik, *J. Organomet. Chem.*, *441* (1992) 265–270.

156 D.L. Hildenbrand and K.H. Lau, *J. Phys. Chem.*, *96* (1992) 2325–2328.

157 Y.C. Fann, D. Singh and S.A. Jansen, *J. Phys. Chem.*, *96* (1992) 5817–5818.

158 J.C. Green, M.F. Guest, I.H. Hillier, S.A. Jarrettsprague, N. Kaltsoyannis, M.A. MacDonald and K.H. Sze, *Inorg. Chem.*, *31* (1992) 1588–1594.

159 Y.-D. Wu, Y. Wang and K.N. Houk, *J. Org. Chem.*, *57* (1992) 1362–1369.

160 W.A. Herrmann, S.J. Eder and W. Scherer, *Angew. Chem., Int. Ed. Engl.*, *31* (1992) 1345–1347.

161 N. Bag, G.K. Lahiri, P. Basu and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 113–117.

162 N. Bag, A. Pramanik, G.K. Lahiri and A. Chakravorty, *Inorg. Chem.*, *31* (1992) 40–45.

163 S. Bhattacharya and C.G. Pierpont, *Inorg. Chem.*, *31* (1992) 35–39.

164 W.-K. Cheng, K.-Y. Wong, W.-F. Tong, T.-F. Lai and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, (1992) 91–96.

165 M.M.T. Khan, K. Venkatasubramanian, Z. Shirin and M.M. Bhadbhade, *J. Chem. Soc., Dalton Trans.*, (1992) 1031–1035.

166 M.M.T. Khan, K. Venkatasubramanian, Z. Shirin and M.M. Bhadbhade, *J. Chem. Soc., Dalton Trans.*, (1992) 885–890.

167 M.M.T. Khan, D. Chatterjee, Z. Shirin, H.C. Bajaj, M.R.H. Siddiqui, K. Venkatasubramaniam and M.M. Bhadbhade, *J. Mol. Catal.*, *72* (1992) 271–282.

168 W. Odenkirk, A.L. Rheingold and B. Bosnich, *J. Am. Chem. Soc.*, *114*(1992) 6392–6398.

169 R.E. Shepherd, S. Zhang, F.-T. Lin and R.A. Kortes, *Inorg. Chem.*, *31* (1992) 1457–1462.

170 M.M.T. Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H.R. Abdi, D. Srinivas, M.R.H. Siddiqui, M.A. Moiz, M.M. Bhadbhade and K. Venkatasubramanian, *Inorg. Chem.*, *31* (1992) 2711–2718.

171 C.-K. Li, C.-M. Che, W.-F. Tong and T.-F. Lai, *J. Chem. Soc., Dalton Trans.*, (1992) 813–818.

172 K.-Y. Wong, C.-M. Che, W.-H. Yip, R.-J. Wang and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1992) 1417–1421.

173 C.-K. Li, C.-M. Che, W.-F. Tong, W.-T. Tang, K.-Y. Wong and T-F.Lai, *J. Chem. Soc., Dalton Trans.*, (1992) 2109–2116.

174 C.-M. Che, W.-T. Tang, W.-O. Lee, K.-Y. Wong and T.-C. Lau, *J. Chem. Soc., Dalton Trans.*, (1992) 1551–1556.

175 C.-M. Che, C.-K. Li, W.-T. Tang and W.-Y. Yu, *J. Chem. Soc., Dalton Trans.*, (1992) 3153–3158.

176 R.S. da-Silva and E. Tfouni, *Inorg. Chem.*, *31* (1992) 3313–3316.

177 G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, (1992) 1111–1116.

178 L.F. Szczepura, J.G. Muller, C.A. Bessel, R.F. See, T.S. Janik, M.R. Churchill and K.J. Takeuchi, *Inorg. Chem.*, *31* (1992) 859–869.

179 Z.-Y. Li, W.-Y. Yu, C.-M. Che, C.-K. Poon, R.-J. Wang and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1992) 1657–1661.

180 S. Mahapatra and R. Mukherjee, *J. Chem. Soc., Dalton Trans.*, (1992) 2337–2341.

181 M.R. Ghadiri, G. Soares and C. Choi, *J. Am. Chem. Soc.*, *114* (1992) 4000–4002.

182 F. Teixidor, G. Sanchez, N. Lucena, L. Escriche, R. Kivekas and J.Casabo, *J. Chem. Soc., Chem. Commun.*, (1992) 163–164.

183 R. Jiang and F.C. Anson, *J. Phys. Chem.*, *96* (1992) 452–458.

184 L. Pu, T. Hasegawa, S. Parkin and H. Taube, *J. Am. Chem. Soc.*, *114* (1992) 2712–2713.

185 L. Pu, T. Hasegawa, S. Parkin and H. Taube, *J. Am. Chem. Soc.*, *114* (1992) 7609–7610.

186 W S. Sheldrick and R. Exner, *Inorg. Chim. Acta*, *195* (1992) 1

187 A.A. Batista, L.R.V. Olmo, G. Oliva, E.E. Castellano and O.R. Nascimento, *Inorg. Chim. Acta*, *202* (1992) 37–41.

188 C.J. Elsevier, W.P. Mul and K. Vrieze, *Inorg. Chim. Acta*, *198–200* (1992) 689–703.

189 A. Patel, A. Ludi, H.-B. Bürgi, A. Raselli and P. Bigler, *Inorg. Chem.*, *31* (1992) 3405–3410.

190 T. Clark, S.D. Robinson and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 3199–3202.

191 G. Orellana, M.C. Moreno-Bondi, E. Segovia and M.D. Marazuela, *Anal. Chem.*, *64* (1992) 2210–2215.

192 A. Corma, M. Iglesias, C. del Pino and F. Sánchez, *J. Organomet. Chem.*, *431* (1992) 233–246.

193 S. Bhattacharya and C.G. Pierpont, *Inorg. Chem.*, *31* (1992) 2020–2029.

194 J.R. Winkler and H.B. Gray, *Chem. Rev.*, *92* (1992) 369–379.

195 J.F. Wishart, R. van Eldik, J. Sun, C. Su and S.S. Isied, *Inorg. Chem.*, *31* (1992) 3986–3989.

196 D.W. Powell and P.A. Lay, *Inorg. Chem.*, *31* (1992) 3542–3550.

197 C. Shi and F.C. Anson, *Inorg. Chem.*, *31* (1992) 5078–5083.

198 M.H. Chou, B.S. Brunschwig, C. Creutz, N. Sutin, A. Yeh, R.C. Chang and C.-T. Lin, *Inorg. Chem.*, *31* (1992) 5347–5348.

199 S. Basak, C.S.C. Bose and K. Rajeshwar, *Anal. Chem.*, *64* (1992) 1813–1818.

200 R.L. Birke and Z. Huang, *Anal. Chem.*, *64* (1992) 1513–1520.

201 T. Hasegawa, K.S. Kwan and H. Taube, *Inorg. Chem.*, *31* (1992) 1598–1600.

202 P.A. Reynolds, C.D. Delfs, B.N. Figgis, L.M. Engelhardt, B. Moubaraki and K.S. Murray, *J. Chem. Soc., Dalton Trans.*, (1992) 2029–2032.

203 H.-W. Lam, C.-M. Che and K.-Y. Wong, *J. Chem. Soc.*, Dalton Trans., (1992) 1411–1416.

204 J. Barrera, S.D. Orth and W.D. Harman, *J. Am. Chem. Soc.*, *114* (1992) 7316–7318.

205 M.E. Kopach, W.G. Hipple and W.D. Harman, *J. Am. Chem. Soc.*, *114* (1992) 1736–1740.

206 W.H. Myers, J.I. Koontz and W.D. Harman, *J. Am. Chem. Soc.*, *114* (1992) 5684–5692.

207 Y.S. Obeng, M.E. Laing, A.C. Friedli, H.C. Yang, D. Wang, E.W. Thulstrup, A.J. Bard and J. Michl, *J. Am. Chem. Soc.*, *114* (1992) 9943–9952.

208 M.A. McNamara and M.J. Clarke, *Inorg. Chim. Acta*, *195* (1992) 175–185.

209 A.J. Bard, M.V. Mirkin, P.R. Unwin and D.O. Wipf, *J. Phys. Chem.*, *96* (1992) 1861–1868.

210 K. Krogh-Jespersen, X. Zhang, Y. Ding, J.D. Westbrook, J.A.Potenza and H.J. Schugar, *J. Am. Chem. Soc.*, *114* (1992) 4345–4353.

211 S.E. Mazzetto, L.M. de Almeida Plicas, E. Tfouni and D.W. Franco, *Inorg. Chem.*, *31* (1992) 516–519.

212 J.F. Wishart, X. Zhang, S.S. Isied, J.A. Potenza and H.J. Schugar, *Inorg. Chem.*, *31* (1992) 3179–3181.

213 C. Lee and F.C. Anson, *Anal. Chem.*, *64* (1992) 528–533.

214 S.L. Bommarito, S.P. Lowery-Bretz and H.D. Abruna, *Inorg. Chem.*, *31* (1992) 495–502.

215 P. Subramanian, H.-T. Zhang and J.T. Hupp, *Inorg. Chem.*, *31* (1992) 1540–1542.

216 D.P. Rillema, D.S. Jones, C. Woods and H.A. Levy, *Inorg. Chem.*, *31* (1992) 2935–2938.

217 S.L. Larson, L.F. Cooley, C.M. Elliott and D.F. Kelley, *J. Am.Chem. Soc.*, *114* (1992) 9504–9509.

218 K. Kalyanasundaram, M.K. Nazeeruddin, M. Gratzel, G. Viscardi, P. Savarino and E. Barni, *Inorg. Chim. Acta*, *198–200* (1992) 831–839.

219 S. Gould, K.H. Gray, R.W. Linton and T.J. Meyer, *Inorg. Chem.*, *31* (1992) 5521–5525.

220 S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, *31* (1992) 1493–1495.

221 S.N. Brune and D.R. Bobbitt, *Anal. Chem.*, *64* (1992) 166–170.

222 R. Grigg and W.D.J.A. Norbert, *J. Chem. Soc., Chem. Commun.*, (1992) 1300–1302.

223 K.V. Gobi and R. Ramaraj, *J. Chem. Soc., Chem. Commun.*, (1992) 1436–1437.

224 T. Yamamoto, Y. Yoneda and T. Maruyama, *J. Chem. Soc., Chem. Commun.*, (1992) 1652–1654.

225 N.A. Surridge, M.E. Zvanut, F.R. Keene, C.S. Sosnoff, M. Silver and R.W. Murray, *J. Phys. Chem.*, *96* (1992) 962–970.

226 A.L. Crumbliss, S.C. Perine, A.K. Edwards and D.P. Rillema, *J.Phys. Chem.*, *96* (1992) 1388–1394.

227 Y.I. Kim and T.E. Mallouk, *J. Phys. Chem.*, *96* (1992) 2879–2885.

228 W.E. Ford and M.A.J. Rodgers, *J. Phys. Chem.*, *96* (1992) 2917–2920.

229 M. Jinguji, M. Ishihara and T. Nakazawa, *J. Phys. Chem.*, *96* (1992) 4279–4281.

230 J.H. Schott, C.R. Arana, H.D. Abruña, H.H. Petach, C.M. Elliott and H.S. White, *J. Phys. Chem.*, *96* (1992) 5222–5224.

231 W. Turbeville, D.S. Robins and P.K. Dutta, *J. Phys. Chem.*, *96* (1992) 5024–5029.

232 L. Hammarström, M. Almgren and T. Norrby, *J. Phys. Chem.*, *96* (1992) 5017–5024.

233 P.D. Beer, O. Kocian, R.J. Mortimer and P. Spencer, *J. Chem. Soc., Chem. Commun.*, (1992) 602–604.

234 M.F. Ottaviani, N.D. Ghatlia and N.J. Turro, *J. Phys. Chem.*, *96* (1992) 6075–6083.

235 P.K. Dutta and W. Turbeville, *J. Phys. Chem.*, *96* (1992) 9410–9416.

236 E.H. Yonemoto, R.L. Riley, Y.I. Kim, S.J. Atherton, R.H. Schmehl and T.E. Mallouk, *J. Am. Chem. Soc.*, *114* (1992) 8081–8087.

237 M.F. Ottaviani, N.D. Ghatlia, S.H. Bossmann, J.K. Barton, H. Durr and N.J. Turro, *J. Am. Chem. Soc.*, *114* (1992) 8946–8952.

238 R.B. Rexwinkel, S.C.J. Meskers, J.P. Riehl and H.P.J.M. Dekkers, *J. Phys. Chem.*, *96* (1992) 1112–1120.

239 R.B. Rexwinkel, S.C.J. Meskers, H.P.J.M. Dekkers and J.P. Riehl, *J. Phys. Chem.*, *96* (1992) 5725–5733.

240 M. Eriksson, M. Leijon, C. Hiort, B. Norden and A. Graslund, *J. Am. Chem. Soc.*, *114* (1992) 4933–4934.

241 W.F. De Giovani and A. Deronzier, *J. Chem. Soc., Chem. Commun.*, (1992) 1461–1463.

242 R.A. Binstead, M.E. McGuire, A. Dovletoglou, W.K. Seok, L.E. Roecker and T.J. Meyer, *J. Am. Chem. Soc.*, *114* (1992) 173–186.

243 C.P. Lau and L. Cheng, *Inorg. Chim. Acta*, *195* (1992) 133–134.

244 H. Tanaka, H. Nagao and K. Tanaka, *Inorg. Chem.*, *31* (1992) 1971–1973.

245 M.R.M. Bruce, E. Megehee, B.P. Sullivan, H.H. Thorp, T.R. O'Toole, A. Downard, J.R. Pugh and T.J. Meyer, *Inorg. Chem.*, *31* (1992) 4864–4873.

246 H. Tanaka, H. Nagao, S.-M. Peng and K. Tanaka, *Organometallics*, *11* (1992) 1450–1451.

247 H. Tanaka, B.-C. Tzeng, H. Nagao, S.-M. Peng and K. Tanaka, *Organometallics*, *11* (1992) 3171–3172.

248 T. Toyano, H. Kuroda, N. Nagao, Y. Maekawa, H. Nishimura, F.S.Howell and M. Mukaida, *Inorg. Chim. Acta*, *196* (1992) 57–63.

249 B. Schwederski and W. Kaim, *Inorg. Chim. Acta*, *195* (1992) 123–126.

250 E.C. Constable and L.R. Sousa, *J. Organomet. Chem.*, *427* (1992) 125–139.

251 M. Furue, K. Maruyama, T. Oguni, M. Naiki and M. Kamachi, *Inorg. Chem.*, *31* (1992) 3792–3795.

252 P. Didier, L. Jacquet, A.K.-D. Mesmaeker, R. Hueber and A. van Dorsselaer, *Inorg. Chem.*, *31* (1992) 4803–4809.

253 T. Ohno, K. Nozaki and M. Haga, *Inorg. Chem.*, *31* (1992) 4256–4261.

254 G.A. Mines, J.A. Roberts and J.T. Hupp, *Inorg. Chem.*, *31* (1992) 125–128.

255 G.F. Strouse, P.A. Anderson, J.R. Schoonover, T.J. Meyer and F.R. Keene, *Inorg. Chem.*, *31* (1992) 3004–3006.

256 M. Krejčík and A.A. Viček, *Inorg. Chem.*, *31* (1992) 2390–2395.

257 T. Ohno, K. Nozaki and M. Haga, *Inorg. Chem.*, *31* (1992) 548–555.

258 M. Kakoti, A.K. Deb and S. Goswami, *Inorg. Chem.*, *31* (1992) 1302–1304.

259 M.D. Johnson, V.C. Reinsborough and S. Ward, *Inorg. Chem.*, *31* (1992) 1085–1087.

260 C.P. Horwitz and Q. Zuo, *Inorg. Chem.*, *31* (1992) 1607–1613.

261 D.P. Rillema, C.B. Blanton, R.J. Shaver, D.C. Jackman, M. Boldaji, S. Bundy, L.A. Worl and T.J. Meyer, *Inorg. Chem.*, *31* (1992) 1600–1606.

262 N. Grover, N. Gupta and H.H. Thorp, *J. Am. Chem. Soc.*, *114* (1992) 3390–3393.

263 T. Togano, N. Nagao, M. Tsuchida, H. Kumakura, K. Hisamatsu, F.S. Howell, and M. Mukaida, *Inorg. Chim. Acta*, *195* (1992) 221–225.

264 G. Giuffrida, V. Ricevuto, G. Guglielmo, S. Campagna and M. Ciano, *Inorg. Chim. Acta*, *194* (1992) 23–29.

265 R.M. Hartshorn and J.K. Barton, *J. Am. Chem. Soc.*, *114* (1992) 5919–5925.

266 Y. Jenkins and J.K. Barton, *J. Am. Chem. Soc.*, *114* (1992) 8736–8738.

267 B.M. Holligan, J.C. Jeffrey, M.K. Norgett, E. Shatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 3345–3351.

268 B.E. Buchanan, P. Degn, J.M.P. Velasco, H. Hughes, B.S. Creaven, C. Long, J.G. Vos, R.A. Howie, R. Hage, J.H. van Diemen, J.G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1992) 1177–1183.

269 K.-Y. Wong, C.-M. Che, C.-K. Li, W.-H. Chiu, Z.-Y. Zhou and T.C.W. Mak, *J. Chem. Soc., Chem. Commun.*, (1992) 754–756.

270 A.D. Baker, R.J. Morgan and T.C. Strekas, *J. Chem. Soc.. Chem. Commun.*, (1992) 1099–1100.

271 H. Durr, R. Schwarz, I. Willner, E. Joselevich and Y. Eichen, *J. Chem. Soc. Chem. Commun.*, (1992) 1338–1339.

272 K. Kalyanasundaram, M. Grätzel and M.K. Nazeeruddin, *J. Phys. Chem.*, *96* (1992) 5865–5872.

273 R. Wang, J.G. Vos, R.H. Schmehl and R. Hage, *J. Am. Chem. Soc.*, *114* (1992) 1964–1970.

274 C.K. Ryu, R. Wang, R.H. Schmehl, S. Ferrere, M. Ludwikow, J.W. Merkert, C.E.L. Headford and C.M. Elliott, *J. Am. Chem. Soc.*, *114* (1992) 430–438.

275 M.A. Hayes, C. Meckel, E. Shatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 703–708.

276 A. Pramanik, N. Bag and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 97–99.

277 E.C. Constable and A.M.W.C. Thompson, *J. Chem. Soc., Dalton Trans.*, (1992) 3467–3475.

278 C.A. Bessel, R.F. See, D.L. Jameson, M.R. Churchill and K.J. Takeuchi, *J. Chem. Soc., Dalton Trans.*, (1992) 3223–3228.

279 E.C. Constable and A.M.W.C. Thompson, *J. Chem. Soc., Chem. Commun.*, (1992) 617–619.

280 J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. DeCola, L. Flamigni and V. Balzani, *Inorg. Chem.*, *31* (1992) 4112–4117.

281 C.A. Howard and M.D. Ward, *Angew. Chem., Int. Ed. Engl.*, *31* (1992) 1028–1030.

282 S.A. Adeyemi, A. Dovletoglou, A.R. Guadalupe and T.J. Meyer, *Inorg. Chem.*, *31* (1992) 1375–1383.

283 N. Grover, N. Gupta, P. Singh and H.H. Thorp, *Inorg. Chem.*, *31* (1992) 2014–2020.

284 M.A.S. Aquino, F.L. Lee, E.J. Gabe, C. Bensimon, J.E. Greedan and R.J. Crutchley, *J. Am. Chem. Soc.*, *114* (1992) 5130–5140.

285 K. Matsui, M.K. Nazeeruddin, R. Humphry-Baker, M. Gratzel and K. Kalyanasundearam, *J. Phys. Chem.*, *96* (1992) 10587–10590.

286 J.T. Hupp, G.A. Neyhart, T.J. Meyer and E.M. Kober, *J. Phys. Chem.*, *96* (1992) 10820–10830.

287 S.K. Doorn, P.O. Stoutland, R.B. Dyer and W.H. Woodruff, *J. Am. Chem. Soc.*, *114* (1992) 3133–3134.

288 I. de Sousa Moreira and D.W. Franco, *J. Chem. Soc., Chem. Commun.*, (1992) 450–451.

289 J.A. Roberts and J.T. Hupp, *Inorg. Chem.*, *31* (1992) 157–160.

290 S. Campagna, G. Denti, S. Serroni, M. Ciano, A. Juris and V. Balzani, *Inorg. Chem.*, *31* (1992) 2982–2984.

291 M.M. Richter and K.J. Brewer, *Inorg. Chem.*, *31* (1992) 1594–1598.

292 J.K. Hurst, J. Zhou and Y. Lei, *Inorg. Chem.*, *31* (1992) 1010–1017.

293 J.R. Schoonover, C.J. Timpson, T.J. Meyer and C.A. Bignozzi, *Inorg. Chem.*, *31* (1992) 3185–3186.

294 Y. Doug and J.T. Hupp, *Inorg. Chem.*, *31* (1992) 3170–3172.

295 Y. Doug and J.T. Hupp, *Inorg. Chem.*, *31* (1992) 3322–3324.

296 J.H. van Diemen, R. Hage, J.G. Haasnoot, H.E.B. Lempers, J. Reedijk, J.G. Vos, L. De Cola, F. Barigelletti and V. Balzani, *Inorg. Chem.*, *31* (1992) 3518–3522.

297 I.R. Butler, *Organometallics*, *11* (1992) 74–83.

298 M.A. Esteruelas, M.P. Garcia, A.M. Lopez and L.A. Oro, *Organometallics*, *11* (1992) 702–705.

299 E. Kimura, X. Bu, M. Shionoya, S. Wada and S. Maruyama, *Inorg. Chem.*, *31* (1992) 4542–4546.

300 E. Fujita, S.J. Milder and B.S. Brunschwig, *Inorg. Chem.*, *31* (1992) 2079–2085.

301 C.A. Bignozzi, O. Bortolini, C. Chiorboli, M.T. Indelli, M.A. Rampi and F. Scandola, *Inorg. Chem.*, *31* (1992) 172–177.

302 K. Kalyanasundaram, M. Grätzel and M.K. Nazeeruddin, *Inorg. Chem.*, *31* (1992) 5243–5253.

303 C.A. Bignozzi, R. Argazzi, J.R. Schoonover, K.C. Gordon, R.B. Dyer and F. Scandola, *Inorg. Chem.*, *31* (1992) 5260–5267.

304 S. Serroni and G. Denti, *Inorg. Chem.*, *31* (1992) 4251–4255.

305 S.L. Bommarito, S.L. Lowery-Bretz and H.D. Abruña, *Inorg. Chem.*, *31* (1992) 502–507.

306 C.A. Bignozzi, R. Argazzi, C.G. Garcia, F. Scandola, J.R. Schoonover and T.J. Meyer, *J. Am. Chem. Soc.*, *114* (1992) 8727–8729.

307 J.A. Roberts, J.C. Bebel, M.L. Absi and J.T. Hupp, *J. Am. Chem. Soc.*, *114* (1992) 7957–7958.

308 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, *114* (1992) 2944–2950.

309 K. Nozaki, T. Ohno and M. Haga, *J. Phys. Chem.*, *96* (1992) 10880–10888.

310 B.W. Pfennig and A.B. Bocarsly, *J. Phys. Chem.*, *96* (1992) 226–233.

311 R. Schäfer, W. Kaim, M. Moscherosch and M. Krejčík, *J. Chem. Soc., Chem. Commun.*, (1992) 834–835.

312 J. Montoya, A. Santos, J. Lopez, A.M. Echavarren, J. Ros and A. Romero, *J. Organomet. Chem.*, *426* (1992) 383–398.

313 M.C.J. Harris and A.F. Hill, *J. Organomet. Chem.*, *438* (1992) 209–212.

314 J.R. Crook, B. Chamberlain, R.J. Mawby, F.C.F. Körber, A.J. Reid and C.D. Reynolds, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 843–850.

315 H. Werner, B. Weber, O. Nürnberg and J. Wolf, *Angew. Chem.*, *Int. Ed. Engl.*, *31* (1992) 1025–1027.

316 N. Pirio, D. Touchard, P.H. Dixneuf, M. Fettouhi and L. Ouahab, *Angew. Chem.*, *Int. Ed. Engl.*, *31* (1992) 651–653.

317 D. Pilette, K. Ouzzine, H. Le Bozec, P.H. Dixneuf, C.E.F. Rickard and W.R. Roper, *Organometallics*, *11* (1992) 809–817.

318 H. Werner, A. Stark, M. Schultz and J. Wolf, *Organometallics*, *11* (992) 1126–1130.

319 R.L. Trace, J. Sanchez, J. Yang, J. Yin and W.M. Jones, *Organometallics*, *11* (1992) 1440–1442.

320 M.R. Gagné, R.H. Grubbs, J. Feldman and J.W. Ziller, *Organometallics*, *11* (1992) 3933–3935.

321 M.I. Bruce, D.N. Duffy, M.J. Liddell, E.R.T. Tiekink and B.K. Nicholson, *Organometallics*, *11* (1992) 1527–1536.

322 U. Kölle, G. Flunkert, R. Görissen, M.U. Schmidt and U. Englert, *Angew. Chem.*, *Int. Ed. Engl.*, *31* (1992) 440–442.

323 M.A. Bennett and X. Wang, *J. Organomet. Chem.*, *428* (1992) C17–C20.

324 T. Lumini, D.N. Cox, R. Roulet and K. Schenk, *J. Organomet. Chem.*, *434* (1992) 363–385.

325 R.U. Kirss, *Organometallics*, *11* (1992) 497–499.

326 D.N. Cox, T. Lumini and R. Roulet, *J. Organomet. Chem.*, *438* (1992) 195–207.

327 D. Braga and F. Grepioni, *Organometallics*, *11* (1992) 711–718.

328 M. Buchmeiser and H. Schottenberger, *J. Organomet. Chem.*, *441* (1992) 457–464.

329 O.J. Curnow and R.P. Hughes, *J. Am. Chem. Soc.*, *114* (1992) 5895–5897.

330 E.W. Abel, N.J. Long, A.G. Osborne, M.B. Hursthouse and M.A. Mazid, *J. Organomet. Chem.*, *430* (1992) 117–122.

331 M.N. Nefedova, I.A. Mamedyarova, P.P. Petrovski and V.I. Sokolov, *J. Organomet. Chem.*, *425* (1992) 125–130.

332 U. Tureinen, A.Z. Kreindlin, P.V. Petrovskii and M.I. Rybinskaya, *J. Organomet. Chem.*, *441* (1992) 109–116.

333 H.W. Bosch, H.-U. Hund, D. Nietlispach and A. Salzer, *Organometallics*, *11* (1992) 2087–2098.

334 W.J. Kelly and W.E. Parthun, *Organometallics*, *11* (1992) 4348–4350.

335 M.F. Ryan, A.R. Siedle, M.J. Burk and D.E. Richardson, *Organometallics*, *11* (1992) 4231–4237.

336 S. Luo, T.B. Rauchfuss and S.R. Wilson, *Organometallics*, *11* (1992) 3497–3499.

337 C.H. Winter, Y.-H. Han and M.J. Heeg, *Organometallics*, *11* (1992) 3169–3171.

338 W. Trakarnpruk, A.M. Arif and R.D. Ernst, *Organometallics*, *11* (1992) 1686–1692.

339 U. Kölle, A. Hornig and U. Englert, *J. Organomet. Chem.*, *438* (1992) 309–317.

340 U. Koelle, B.-S. Kang, T.P. Spaniol and U. Englert, *Organometallics*, *11* (1992) 249–254.

341 U. Koelle, B.-S. Kang and U. Thewalt, *Organometallics*, *11* (1992) 2893–2899.

342 T.J. Johnson, J.C. Huffman and K.G. Caulton, *J. Am. Chem. Soc.*, *114* (1992) 2725–2726.

343 B.K. Campion, R.H. Heyn and T.D. Tilley, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 1201–1203.

344 S.D. Grumbine, R.K. Chadha and T.D. Tilley, *J. Am. Chem. Soc.*, *114* (1992) 1518–1520.

345 H. Handwerker, C. Leis, S. Gamper and C. Zybill, *Inorg. Chim. Acta*, *198–200* (1992) 763–769.

346 A. Shaver and P.-Y. Plouffe, *Inorg. Chem.*, *31* (1992) 1823–1826.

347 J. Amarasekera, E.J. Houser, T.B. Rauchfuss and C.L. Stern, *Inorg. Chem.*, *31* (1992) 1614–1620.

348 W.A. Schenk, T. Stur and E. Dombrowski, *Inorg. Chem.*, *31* (1992) 723–724.

349 H.-I. Ji, J.H. Nelson, A. DeCian, J. Fischer, L. Solujic and E.B. Milosavljević, *Organometallics*, *11* (1992) 401–411.

350 G.G.A. Balavoine, T. Boyer and C. Livage, *Organometallics*, *11* (1992) 456–459.

351 B.R. Manzano, F.A. Jalon, F.J. Lahoz, B. Chaudret and D. de Montauzon, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 977–979.

352 B. de Klerk-Engels, J.H. Groen, K. Vrieze, A. Mockel, E. Lindner and K. Goubitz, *Inorg. Chim. Acta*, 195 (1992) 237–243.

353 J.R. Lomprey and J.P. Selegue, *J. Am. Chem. Soc.*, *114* (1992) 5518–5523.

354 M.K. Rottink and R.J. Angelici, *J. Am. Chem. Soc.*, *114* (1992) 8296–8298.

355 O.J. Curnow, R.P. Hughes and A.L. Rheingold, *J. Am. Chem. Soc.*, *114* (1992) 3153–3155.

356 J.L. Hubbard and W.K. McVicar, *J. Organomet. Chem.*, *429* (1992) 369–378.

357 A. Mezzetti, G. Consiglio and F. Morandini, *J. Organomet. Chem.*, *430* (1992) C15–C18.

358 K. Masuda, K. Nakano, T. Fukahori, H. Nagashima and K. Itoh, *J. Organomet. Chem.*, *428* (1992) C21–C24.

359 C. Mancuso and J. Halpern, *J. Organomet. Chem.*, *428* (1992) C8–Cll.

360 C.E. Shuchart, R.R. and A.J. Wojcicki, *J. Organomet. Chem.*, *424* (1992) 185–198.

361 P. Jutzi and S. Opiela, *J. Organomet. Chem.*, *431* (1992) C29–C32.

362 D. Rondon, X.-D. He and B. Chaudret, *J. Organomet. Chem.*, *433* (1992) C18–C21.

363 M.A. Bennett, I.J. McMahon, S. Pelling, M. Brookhart and D.M. Lincoln, *Organometallics*, *11* (1992) 127–138.

364 M.S. Keady, J.D. Koola, A.C. Ontko, R.K. Merwin and D.M. Roddick, *Organometallics*, *11* (1992) 3417–3421.

365 J.W. Faller and Y. Ma, *Organometallics*, *11* (1992) 2726–2729.

366 S.P. Nolan, K.L. Martin, E.D. Stevens and P.J. Fagan, *Organometallics*, *11* (1992) 3947–3953.

367 H.-L. Ji, J.H. Nelson, A.D. Cian, J. Fischer, L. Solujic and E.B. Milosavljevic, *Organometallics*, *11* (1992) 1840–1855.

368 C. Jia, A.J. Lough and R.H. Morris, *Organometallics*, *11* (1992) 161–171.

369 H.-L. Ji, J.H. Nelson, A. De Cian and J. Fischer, *Organometallics*, *11* (1992) 1618–1626.

370 D.S. Glueck, J.C. Green, R.I. Mechelman and I.N. Wright, *Organometallics*, *11* (1992) 4221–4225.

371 U. Wecker and H. Werner, *J. Organomet. Chem.*, *424* (1992) 199–211.

372 T. Polzer, A. Ellebracht, W. Kiefer, U. Wecker and H. Werner, *J. Organomet. Chem.*, *438* (1992) 319–328.

373 M.R.J. Elsegood, J.W. Steed and D.A. Tocher, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1797–1801.

374 S.K. Mandal and A.R. Chakravarty, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1627–1633.

375 V. Adovasio, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti and M. Nardelli, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 3385–3390.

376 M.A. Bennett and J.P. Ennett, *Inorg. Chim. Acta*, *198–200* (1992) 583–592.

377 J.R. Dilworth, Y. Zheng, S. Lu and Q. Wu, *Inorg. Chim. Acta*, *194* (1992) 99–103.

378 M. Gaye, B. Demerseman and P.H. Dixneuf, *J. Organomet. Chem.*, *424* (1992) 65–70.

379 F.L. Joslin and D.M. Roundhill, *Organometallics*, *11* (1992) 1749–1752.
380 D. Vichard, M. Gruselle, H.E. Amouri, G. Jaouen and J. Vaissermann, *Organometallics*, *11* (1992) 976–979.
381 A.J. Pearson, J.G. Park and P.Y. Zhu, *J. Org. Chem.*, *57* (1992) 3583–3589.
382 A.J. Pearson and J.G. Park, *J. Org. Chem.*, *57* (1992) 1744–1752.
383 D. Pilette, H.L. Bozec, A. Romero and P.H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, (1992) 1220–1222.
384 S. Luo, T.B. Rauchfuss and S.R. Wilson, *J. Am. Chem. Soc.*, *114* (1992) 8515–8520.
385 F.A. Cotton, L. Labella and M. Shang, *Inorg. Chim. Acta*, *197* (1992) 149–158.
386 F.A. Cotton, Y. Kim and T. Ren, *Inorg. Chem.*, *31* (1992) 2723–2726.
387 N. Gupta, S. Mukerjee, S. Mahapatra, M. Ray and R. Mukherjee, *Inorg. Chem.*, *31* (1992) 139–141.
388 F.A. Cotton, Y. Kim and T. Ren, *Inorg. Chem.*, *31* (1992) 2608–2612.
389 F.A. Cotton, L.R. Falvello, T. Ren and K. Vidyasagar, *Inorg. Chim. Acta*, *194* (1992) 163–170.
390 B.K. Das and A.R. Chakravarty, *Inorg. Chem.*, *31* (1992) 1395-1400.
391 S.F. Gheller, G.A. Heath and R.G. Raptis, *J. Am. Chem. Soc.*, *114* (1992) 7924–7926.
392 F.A. Cotton, L. Labella and M. Shang, *Inorg. Chem.*, *31* (1992) 2385–2389.
393 M. Wantanabe, T. Iwamoto, H. Sano, A. Kubo and I. Motoyama, *J. Organomet. Chem.*, *441* (1992) 309–322.
394 M. Watanabe, T. Iwamoto, S. Kawata, A. Kubo, H. Sano and I. Motoyama, *Inorg. Chem.*, *31* (1992) 177–182.
395 U.T. Mueller-Westerhoff, A.L. Rheingold and G.F. Swiegers, *Angew. Chem., Int. Ed. Engl.*, *31* (1992) 1352–1354.
396 A.L. Rheingold, U.T. Mueller-Westerhoff, G.F. Swiegers and T.J. Haas, *Organometallics*, *11* (1992) 3411–3417.
397 U. Siemeling, P. Jutzi, B. Neumann, H.-G. Stammler and M.B. Hursthouse, *Organometallics*, *11* (1992) 1328–1333.
398 K.M. Rao, C.L. Day, R.A. Jacobson and R.J. Angelici, *Organometallics*, *11* (1992) 2303–2304.
399 B.K. Campion, R.H. Heyn and T.D. Tilley, *Organometallics*, *11* (1992) 3918–3920.
400 U. Koelle, T. Ruether and W. Kläui, *J. Organomet. Chem.*, *426* (1992) 99–103.
401 A. Steiner, H. Gornitzka, D. Stalke and F.T. Edelmann, *J. Organomet. Chem.*, 431 (1992) C21–C25.
402 M. Akita, T. Oku and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, (1992) 1031–1032.
403 L.A. Brady, A.F. Dyke, S.E. Garner, V. Guerchais, S.A.R. Knox, J.P. Maher, S.M. Nicholls and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1992) 310–312.
404 H. Suzuki, T. Takao, M. Tanaka and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, (1992) 476–478.
405 H. Omori, H. Suzuki, T. Kakigano and Y. Moro-oka, *Organometallics*, *11* (1992) 989–992.
406 I. Chavez, M. Otero, E. Ramán and U. Müller, *J. Organomet. Chem.*, *427* (1992) 369–378.
407 D. Carmona, A. Mendoza, J. Ferrer, F.J. Lahoz and L.A. Oro, *J. Organomet. Chem.*, *431* (1992) 87–102.
408 H.T. Schacht, R.C. Haltiwanger and M.R. DuBois, *Inorg. Chem.*, *31* (1992) 1728–1730.
409 J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 2765–2773.
410 J.W. Steed and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 459–461.
411 H. Uemura, M. Kawano, T. Watanabe, T. Matsumoto and K. Matsumoto, *Inorg. Chem.*, *31* (1992) 5137–5139.
412 M. Kawano, C. Hoshino and K. Matsumoto, *Inorg. Chem.*, *31* (1992) 5158–5159.
413 J.S. Jaswal, D.T.T. Yapp, S.J. Rettig, B.R. James and K.A. Skov, *J. Chem. Soc., Chem. Commun.*, (1992) 1528–1529.
414 J.S. Field, R.J. Haines, J. Sundermeyer, M.W. Stewart and S.F. Woollam, *J. Chem. Soc., Dalton Trans.*, (1992) 3161–3162.
415 J.S. Field, R.J. Haines, E. Minsall, C.N. Sampson, J. Sundermeyer and S.F. Woollam, *J. Chem. Soc., Dalton Trans.*, (1992) 2629–2639.
416 S.E. Bell, J.S. Field, R.J. Haines, M. Moscherosch, W. Matheis and W. Kaim, *Inorg. Chem.*, *31* (1992) 3269–3276.
417 S.E. Bell, J.S. Field, R.J. Haines and J. Sundermeyer, *J. Organomet. Chem.*, 427 (1992) C1–C5.
418 A.M. Jochi, I.S. Thorburn, S.J. Rettig and B.R. James, *Inorg. Chim. Acta*, *198–200* (1992) 283–296.
419 A. Beguin, H.-C. Bottcher, G. Süss-Fink and B. Walther, *J. Chem. Soc.*, Dalton Trans., (1992) 2133–2134.
420 K.A. Johnson and W.L. Gladfelter, *Organometallics*, *11* (1992) 2534–2542.
421 M.J.A. Kraakman, C.J. Elsevier, K. Vrieze and A.L. Spek, *Organometallics*, *11* (1992) 4250–4260.
422 M.J.A. Kraakman, K. Vrieze, H. Kooijman and A.L. Spek, *Organometallics*, *11* (1992) 3760–3773.
423 A.J.M. Caffyn, M.J. Mays and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1992) 515–519.
424 Z. He, N. Lugan, D. Neibecker, R. Mathieu and J.-J. Bonnet, *J. Organomet. Chem.*, *426* (1992) 247–259.
425 H. Nakatsuji, M. Hada and A. Kawashima, *Inorg. Chem.*, *31* (1992) 1740–1744.
426 J.T. Poulton, K. Folting and K.G. Caulton, *Organometallics*, *11* (1992) 1364–1372.
427 Z. He, D. Neibecker, N. Lugan and R. Mathieu, *Organometallics*, *11* (1992) 817–821.
428 F.R. Lemke, D.J. Szalda and R.M. Bullock, *Organometallics*, *11* (1992) 876–884.
429 F.R. Lemke and R.M. Bullock, *Organometallics*, *11* (1992) 4261–4267.
430 M.J.A. Kraakman, K. Vrieze, K. Goubitz and M. Numan, *Inorg. Chim. Acta*, *202* (1992) 197–210.
431 R. Hotzelmann, K. Wieghardt, J. Ensling, H. Romstedt, P. Gutlich, E. Bill, U. Florke and H.-J. Haupt, *J. Am. Chem. Soc.*, *114* (1992) 9470–9483.
432 D.S. Bohle, V.F. Breidt, A.K. Powell and H. Vahrenkamp, *Chem. Ber.*, *125* (1992) 1111–1118.
433 B.R. Cockerton and A.J. Deeming, *J. Organomet. Chem.*, *426* (1992) C36–C39.
434 S. Bhaduri, N. Sapre, H. Khwaja and P.G. Jones, *J. Organomet. Chem.*, *426* (1992) C12–C15.
435 G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Organomet. Chem.*, 441 (1992) 295–308.
436 H. Adams, N.A. Bailey, P. Blenkiron and M.J. Morris, *J. Chem. Soc., Dalton Trans.*, (1992) 127–130.
437 B.F.G. Johnson, Y.V. Roberts and E. Parisini, *J. Chem. Soc., Dalton Trans.*, (1992) 2573–2578.
438 D.S. Bohle and P.A. Goodson, *J. Chem. Soc., Chem. Commun.*, (1992) 1205–1207.
439 K.M. Rao, R.J. Angelici and V.G. Young, Jr., *Inorg. Chim. Acta*, *198–200* (1992) 211–217.
440 L.J. Farrugia and S.E. Rae, *Organometallics*, *11* (1992) 196–206.
441 L.R. Nevinger, J.B. Keister, C.H. Lake and M.R. Churchill, *Organometallics*, *11* (1992) 1819–1824.
442 D. Braga, F. Grepioni, B.F.G. Johnson, E. Parisini, M. Mar-

tinelli, M.A. Gallop and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1992) 807–812.

443 M.A. Gallop, M.P. Gomez-Sal, C.E. Housecroft, B.F.G. Johnson, J. Lewis, S.M. Owen, P.R. Raithby and A.H. Wright, *J. Am. Chem. Soc.*, *114* (1992) 2502–2509.

444 M.A. Gallop, B.F.G. Johnson, J. Keeler, J. Lewis, S.J. Heyes and C.M. Dobson, *J. Am. Chem. Soc.*, *114* (1992) 2510–2520.

445 R.D. Adams, Y. Chi, D.D. DesMarteau, D. Lentz and R. Marschall, *J. Am. Chem. Soc.*, *114* (1992) 1909–1910.

446 R.D. Adams, Y. Chi, D.D. DesMarteau, D. Lentz, R. Marchall and A. Scherrmann, *J. Am. Chem. Soc.*, *114* (1992) 10822–10826.

447 K.-L. Lu, C.-J. Su, Y.-W. Lin, H.-M. Gau and Y.-S. Wen, *Organometallics*, *11* (1992) 3832–3827.

448 Y.-W. Lin, H.-M. Gau, Y.-S. Wen and K.-L. Lu, *Organometallics*, *11* (1992) 1445–1447.

449 R.D. Adams, J.E. Cortopassi and M.P. Pompeo, *Organometallics*, *11* (1992) 1–4.

450 R.D. Adams, J.E. Cortopassi and M.P. Pompeo, *Inorg. Chem.*, *31* (1992) 2563–2568.

451 K.-L. Lu, H. Lo, Y.-C. Lin and Y. Wang, *Inorg. Chem.*, *31* (1992) 4499–4502.

452 H.G. Ang, C.H. Koh and W.L. Kwik, *J. Organomet. Chem.*, *435* (1992) 1 49–155.

453 D. Braga, P. Sabatino, B.F.G. Johnson, J. Lewis and A. Massey, *Organomet. Chem.*, *436* (1992) 73–77.

454 A.J. Deeming and A.M. Senior, *J. Organomet. Chem.*, *439* (1992) 177–188.

455 B.F.G. Johnson, F.J. Lahoz, J. Lewis, N.D. Prior, P.R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, (1992) 1701–1708.

456 J. Lewis, A.D. Massey, M. Monari, B.F.G. Johnson, D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, (1992) 249–254.

457 D.-Y. Jan, D.P. Wrokman, L.-Y. Hsu, J.A. Krause and S.G. Shore, *Inorg. Chem.*, *31* (1992) 5123–5131.

458 M.I. Bruce, P.A. Humphrey, E. Horn, E.R.T. Tiekink, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *429* (1992) 207–227.

459 M.I. Bruce, P.A. Humphrey, H. Miyamae, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *429* (1992) 187–205.

460 G.R. Frauenhoff, J-C. Liu, S.R. Wilson and J.R. Shapley, *J. Organomet. Chem.*, *437* (1992) 347–361.

461 A.J. Deeming, D. Nuel, N.I. Powell and C. Whittaker, *J. Chem. Soc., Dalton Trans.*, (1992) 757–764.

462 H.G. Ang, B. Chang and W.L. Kwik, *J. Chem. Soc., Dalton Trans.*, (1992) 2161–2169.

463 P. Braunstein, S.C. Cea, M.I. Bruce, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 2539–2542.

464 A.J. Deeming, S. Doherty and N.I. Powell, *Inorg. Chim. Acta*, *198–200* (1992) 469–481.

465 J.S. Field, R.J. Haines and F. Mulla, *J. Organomet. Chem.*, 439 (1992) C56–C60.

466 J.T. Mague and C.L. Lloyd, *Organometallics*, *11* (1992) 26–34.

467 J.A. Cabeza, F.J. Lahoz and A. Martín, *Organometallics*, *11* (1992) 2754–2756.

468 S.P. Rowley, P.S. White and C.K. Schauer, *Inorg. Chem.*, *31* (1992) 3158–3161.

469 N. Lugan, F. Laurent G. Lavigne, T.P. Newcomb, E.W. Liimatta and J.-J. Bonnet, *Organometallics*, *11* (1992) 1351–1363.

470 W. Ziegler and U. Behrens, *J. Organomet. Chem.*, *427* (1992) 379–393.

471 P.L. Andreu, J.A. Cabeza, J.L. Cuyas and V. Riera, *J. Organomet. Chem.*, *427* (1992) 363–368.

472 U. Bodensieck, J. Santiago, H. Stoeckli-Evans and G. Süss-Fink, *J. Organomet. Chem.*, *433* (1992) 141–148.

473 E. Poroni, M. Costa, G. Predieri, E. Sappa and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, (1992) 2585–2590.

474 E.J. Moore, W.R. Pretzer, T.J. O'Connell, J. Harris, L. LaBounty, L. Chou and S.S. Grimmer, *J. Am. Chem. Soc.*, *114* (1992) 5888–5890.

475 J.A. Cabeza, J.M. Fernández-Colinas, A. Llamazares and V. Riera, *Organometallics*, *11* (1992) 4355–4358.

476 J.A. Cabeza, A. Llamazares, V. Riera, S. Triki and L. Ouahab, *Organometallics*, *11* (1992) 3334–3339.

477 M. Day, W. Freeman, K.I. Hardcastle, M. Isomaki, S.E. Kabir, T. McPhillips, E. Rosenberg, L.G. Scott and E. Wolf, *Organometallics*, *11* (1992) 3376–3384.

478 D.L. Ramage, G.L. Geoffroy, A.L. Rheingold and B.S. Haggerty, *Organometallics*, *11* (1992) 1242–1255.

479 R.D. Adams and G. Chen, *Organometallics*, *11* (1992) 3510–3511.

480 R.D. Adams and G. Chen, *Organometallics*, *11* (1992) 837–845.

481 E. Boroni, G. Predieri, A. Tiripicchio and M.T. Camellini, *Organometallics*, *11* (1992) 3456–3458.

482 A. Shaver, P.-Y. Plouffe, D.C. Liles and E. Singleton, *Inorg. Chem.*, *31* (1992) 997–1001.

483 B.F.G. Johnson, T.M. Layer, J. Lewis, A. Martin and P.R. Raithby, *J. Organomet. Chem.*, *429* (1992) C41–C45.

484 A.J. Edwards, B.F.G. Johnson, F.K. Khan, J. Lewis and P.R. Raithby, *J. Organomet. Chem.*, *426* (1992) C44–C48.

485 K.A. Azam, S.E. Kabir, A. Miah, M.W. Day, K.I. Hardcastle, E. Rosenberg and A.J. Deeming, *J. Organomet. Chem.*, *435* (1992) 157–167.

486 S. Rossi, K. Kallinen, J. Pursiainen, T.T. Pakkanen and T.A. Pakkanen, *J. Organomet. Chem.*, 440 (1992) 367–387.

487 A.J. Deeming, K.I. Hardcastle and M. Karim, *Inorg. Chem.*, *31* (1992) 4792–4796.

488 N. Choi, Y. Kabe and W. Ando, *Organometallics*, *11* (1992) 607–613.

489 R.D. Adams and J.A. Belinski, *Organometallics*, *11* (1992) 2488–2493.

490 R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics*, *11* (1992) 2016–2024.

491 R.D. Adams and M.P. Pompeo, *Organometallics*, *11* (1992) 2281–2289.

492 R.D. Adams and M.P. Pompeo, *Organometallics*, *11* (1992) 1460–1465.

493 R.D. Adams and M.P. Pompeo, *Organometallics*, *11* (1992) 103–111.

494 R.D. Adams, G. Chen, X. Qu, W. Wu and J.H. Yamamoto, *J. Am. Chem. Soc.*, *114* (1992) 10977–10978.

495 U. Bodensieck, J. Santiago, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, (1992) 255–259.

496 U. Bodensieck, H. Stoeckli-Evans and G. Süss-Fink, *J. Organomet. Chem.*, *433* (1992) 149–165.

497 U. Bodensieck, H. Stoeckli-Evans, G. Rheinwald and G. Süss-Fink, *J. Organomet. Chem.*, *433* (1992) 167–182.

498 R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics*, *11* (1992) 3129–3134.

499 C.J. Adams, M.I. Bruce, M.J. Liddell, B.W. Skelton and A.H. White, *Organometallics*, *11* (1992) 1182–1186.

500 W.P. Mul, C.J. Elsevier, M. van Leijen, K. Vrieze, W.J.J. Smeets and A.L. Spek, *Organometallics*, *11* (1992) 1877–1890.

501 W.P. Mul, C.J. Elsevier, K. Vrieze, W.J.J. Smeets and A.L. Spek, *Organometallics*, *11* (1992) 1891–1901.

502 J.F. Corrigan, S. Doherty, N.J. Taylor and A.J. Carty, *J. Am. Chem. Soc.*, *114* (1992) 7557–7558.

503 F. van Gastel, J.F. Corrigan, S. Doherty, N.J. Taylor and A.J. Carty, *Inorg. Chem.*, *31* (1992) 4492–4498.

504 W. Wang, F.W.B. Einstein and R.K. Pomeroy, *J. Chem. Soc., Chem. Commun.*, (1992) 1737–1738.

505 P.J. Bailey, D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, J. Lewis and P. Sabatino, *J. Chem. Soc., Chem. Commun.*, (1992) 177–178.

506 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *430* (1992) 181–196.

507 C.J. Adams, M.I. Bruce, M.J. Liddell, B.W. Skelton and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1992) 1314–1318.

508 U. Bodensieck, G. Meister, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, (1992) 2131–2132.

509 C.J. Adams, M.I. Bruce, B.W. and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1992) 26–29.

510 D. Braga, F. Grepioni, P.J. Dyson, B.F.G. Johnson, P. Frediani, M. Bianchi and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, (1992) 2565–2571.

511 A.J. Poe, D.H. Farrar and Y. Zheng, *J. Am. Chem. Soc.*, *114* (1992) 5146–5152.

512 D. Braga, F. Grepioni, S. Righi, B.F.G. Johnson, P.J. Bailey, P.J. Dyson, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, (1992) 2121–2122.

513 D. Braga, F. Grepioni, S. Righi, P.J. Dyson, B.F.G. Johnson, P.J. Bailey and J. Lewis, *Organometallics*, *11* (1992) 4042–4048.

514 R.D. Adams, J.A. Belinski and J.H. Yamamoto, *Organometallics*, *11* (1992) 3422–3426.

515 A.J. Amoroso, B.F.G. Johnson, J. Lewis, A.D. Massey, P.R. Raithby and W.T. Wong, *J. Organomet. Chem.*, *440* (1992) 219–231.

516 C.E. Housecroft, A.L. Rheingold and X. Song, *Inorg. Chem.*, *31* (1992) 4023–4025.

517 D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis and J.A. Lunniss, *J. Chem. Soc., Dalton Trans.*, (1992) 1101–1104.

518 P.J. Bailey, L.H. Gade, B.F.G. Johnson and J. Lewis, *Chem. Ber.*, *125* (1992) 2019–2023.

519 D. Braga, F. Grapioni, S. Righi, B.F.G. Johnson, P. Frediani, M. Bianchi, F. Placenti and J. Lewis, *Organometallics*, *11* (1992) 706–711.

520 P.J. Bailey, M.A. Beswick, B.F.G. Johnson, J. Lewis, P.R. Raithby and M.C.R. de Arellano, *J. Chem. Soc., Dalton Trans.*, (1992) 3159–3160.

521 C.E. Housecroft, D.M. Matthews, A.L. Rheingold and X. Song, *J. Chem. Soc., Chem. Commun.*, (1992) 842–843.

522 F. Teixidor, J.A. Ayllon, C. Vinas, R. Kivekas, R. Sillanpaa and J. Casabo, *J. Chem. Soc., Chem. Commun.*, (1992) 1281–1282.

523 C.E. Housecroft, D.M. Matthews and A.L. Rheingold, *J. Chem. Soc., Chem. Commun.*, (1992) 323–324.

524 S.M. Draper, C.E. Housecroft, J.E. Rees, M.S. Shongwe, B.S. Haggerty and A.L. Rheingold, *Organometallics*, *11* (1992) 2356–2367.

525 C.E. Housecroft, J.S. Humphrey, A.K. Keep, D.M. Matthews, N.J. Seed, B.S. Haggerty and A.L. Rheingold, *Organometallics*, *11* (1992) 4048–4056.

526 J.C. Calabrese, L.M. Clarkson, T.B. Marder, N.C. Norman and N.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1992) 3525–3529.

527 T.M. Layer, J. Lewis, A. Martin, P.R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, (1992) 3411–3417.

528 S-P. Huang and M.G. Kanatzidas, *J. Am. Chem. Soc.*, *114* (1992) 5477–5478.

529 Y. Chi, H.-F. Hsu, L.-K. Liu, S.-M. Peng and G.-H. Lee, *Organometallics*, *11* (1992) 1763–1766.

530 J.T. Park, M.-K. Chung, K.M. Chun, S.S. Yun and S. Kim, *Organometallics*, *11* (1992) 3313–3319.

531 R.-C. Lin, Y. Chi, S.-M. Peng and G.-H. Lee, *Inorg. Chem.*, *31* (1992) 3818–3824.

532 C.E. Housecroft, D.M. Matthews, A.L. Rheingold and X. Song, *J. Chem. Soc.*, Dalton Trans., (1992) 2855-2864.

533 R.–C. Lin, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, (1992) 1705–1707.

534 Y. Chi, R.-C. Lin, C.-C. Chen, S.-M. Peng and G.-H. Lee, *J. Organomet. Chem.*, 439 (1992) 347–369.

535 J.T. Park, J.-J. Cho, K.-M. Chun and S.-S. Yun, *J. Organomet. Chem.*, 433 (1992) 295–303.

536 R.J. Batchelor, H.B. Davis, F.W.B. Einstein, V.J. Johnston, R.H. Jones, R.K. Pomeroy and A.F. Ramos, *Organometallics*, *11* (1992) 3555–3565.

537 R.J. Batchelor, F.W.B. Einstein, R.K. Pomeroy and J.A. Shipley, *Inorg. Chem.*, *31* (1992) 3155–3157.

538 T. Matsumoto, K. Matsumoto and T. Sato, *Inorg. Chim. Acta*, 202 (1992) 31–36.

539 M. Kato, M. Kawano, H. Taniguchi, M. Funaki, H. Moriyama, T. Sato and K. Matsumoto, *Inorg. Chem.*, *31* (1992) 26–35.

540 C. Rong and M.T. Pope, *J. Am. Chem. Soc.*, *114* (1992) 2932–2938.

541 W.R. Cullen, S.J. Rettig and H. Zhang, *Organometallics*, *11* (1992) 1000–1002.

542 W. Wang, R.J. Batchelor, H.B. Davis, F.W.B. Einstein and R.K. Pomeroy, *Inorg. Chem.*, *31* (1992) 5150–5153.

543 A.A. Koridze, A.I. Yamovsky and Y.T. Struchkov, *J. Organomet. Chem.*, *441* (1992) 277–284.

544 M. Herberhold, W. Feger and U. Kölle, *J. Organomet. Chem.*, *436* (1992) 333–350.

545 W.R. Cullen, S.J. Rettig and T.–C. Zheng, *Organometallics*, *11* (1992) 277–283.

546 W.R. Cullen, S.J. Rettig and T.–C. Zheng, *Organometallics*, *11* (1992) 853–858.

547 W.R. Cullen, S.J. Rettig and T.-C. Zheng, *Organometallics*, *11* (1992) 928–935.

548 W.R. Cullen, A. Talaba and S.J. Rettig, *Organometallics*, *11* (1992) 3152–3156.

549 W.R. Cullen, S.J. Rettig and T.C. Zheng, *Organometallics*, *11* (1992) 3434–3439.

550 M. Akita, S. Sugimoto, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, *114* (1992) 7581–7582.

551 G.A. Koutsantonis, J.P. Selegue and J.-G. Wang, *Organometallics*, *11* (1992) 2704–2708.

552 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *Inorg. Chem.*, *31* (1992) 3336–3338.

553 S. Yamamoto, K. Asakura, A. Nitta and H. Kuroda, *J. Phys. Chem.*, *96* (1992) 9565–9568.

554 R.K. Henderson, P.A. Jackson, B.F.G. Johnson, J. Lewis and P.R. Raithby, *Inorg. Chim. Acta*, *198–200* (1992) 393–400.

555 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 3057–3058.

556 P.A. Dolby, M.M. Harding, N. Newar and A.K. Smith, *J. Chem. Soc., Dalton Trans.*, (1992) 2939–2942.

557 D.S. Parfitt, J.D. Jordan and J.B. Keister, *Organometallics*, *11* (1992) 4009–4015.

558 S.P. Tunik, M.V. Osipov and A.B. Nikolskyi, *J. Organomet. Chem.*, *426* (1992) 105–107.

559 L.-Y. Hsu, W.-L. Hsu, D.A. McCarthy, J.A. Krause, J.-H. Chung, and S.G. Shore, *J. Organomet. Chem.*, *426* (1992) 121–130.

560 F. Ragaini, S. Cenini, A. Fumagalli and C. Crotti, *J. Organomet. Chem.*, *428* (1992) 401–408.

561 S. Rossi, J. Pursiainen and T.A. Pakkanen, *J. Organomet. Chem.*, *436* (1992) 55–71.

562 J.-L. Le Grand, W.E. Lindsell, K.J. McCullough, C.H. McIntosh, and A.G. Meiklejohn, *J. Chem. Soc., Dalton Trans.*, (1992) 1089–1099.

563 P. Braunstein, F.Y. Jiao, J. Rosé, P. Granger, F. Balegroune, O. Bars and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, (1992) 2543–2550.

564 J. Hirschinger, P. Granger and J. Rosé, *J. Phys. Chem.*, *96* (1992) 4815–4820.

565 K.E. Stockman, M. Sabat, M.G. Finn and R.N. Grimes, *J. Am. Chem. Soc.*, *114* (1992) 8733–8735.

566 K.W. Piepgrass, X. Meng, M. Holscher, M. Sabat and R.N. Grimes, *Inorg. Chem.*, *31* (1992) 5202–5210.

567 A. Fumagalli, S. Martinengo, G. Ciani, M. Moret and A. Sironi, *Inorg. Chem.*, *31* (1992) 2900–2906.

568 R.D. Adams, Z. Li, P. Swepston, W. Wu and J. Yamamoto, *J. Am. Chem. Soc.*, *114* (1992) 10657–10658.

569 R.D. Adams, Z. Li, J-C. Lii and W. Wu, *J. Am. Chem. Soc.*, *114* (1992) 4918–4920.

570 R.D. Adams, Z. Li. J.-C. Lii and W. Wu, *Inorg. Chem.*, *31* (1992) 3445–3450.

571 R.D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, *31* (1992) 2556–2562.

572 G.B. Karet, R.L. Espe, C.L. Stern and D.F. Shriver, *Inorg. Chem.*, *31* (1992) 2658–2660.

573 P.L. Andreu, J.A. Cabeza, A. Llamazares, V. Riera, S. Garcia-Granda and J.F. van der Maelen, *J. Organomet. Chem.*, *434* (1992) 123–132.

574 P. Braunstein, J. Rosé, A. Tiripicchio and M.T. Camellini, *J. Chem. Soc., Dalton Trans.*, (1992) 911–920.

575 L.H. Gade, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1992) 933–937.

576 L.H. Gade, B.F.G. Johnson, J. Lewis, M. McPartlin and H.R. Powell, *J. Chem. Soc., Dalton Trans.*, (1992) 921–931.

577 L.H. Gade, B.F.G. Johnson, J. Lewis, G. Conole and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1992) 3249–3254.

578 B.F.G. Johnson, J. Lewis, P.R. Raithby, V.P. Saharan and W.T. Wong, *J. Organomet. Chem.*, 434 (1992) C10–C12.

579 J.A. Cabeza, J.M. Fernández-Colinas, S. García-Granda, V. Riera and J.F. van der Maelen, *Inorg. Chem.*, *31* (1992) 1233–1238.

580 A. Bianchini and L.J. Farrugia, *Organometallics*, *11* (1992) 540–548.

581 S.M. Draper, A.D. Hattersley, C.E. Housecroft and A.L. Rheingold, *J. Chem. Soc., Chem. Commun.*, (1992) 1365–1367.

582 A.S. Gunale, M.P. Jensen, D.A. Phillips, C.L. Stern and D.F. Shriver, *Inorg. Chem.*, *31* (1992) 2622–2626.

583 L. Song and W.C. Tolgler, *Angew. Chem.. Int. Ed. Engl.*, *31* (1992) 770–772.

584 T. Chihara and H. Yamazaki, *J. Organomet. Chem.*, *428* (1992) 169–86.

585 S.M. Draper, C.E. Housecroft and A.L. Rheingold, *J. Organomet. Chem.*, *435* (1992) 9–20.

586 C.E. Housecroft, D.M. Matthews and A.L. Rheingold, *Organometallics*, *11* (1992) 2959–2961.

587 S.J. Cho, S.M. Jung, Y.G. Shul and R. Ryoo, *J. Phys. Chem.*, *96* (1992) 9922–9927.

588 Y.S. Kye, S.X. Wu and T.M. Apple, *J. Phys. Chem.*, *96* (1992) 2632–2636.

589 G. Lei and L. Kevan, *J. Phys. Chem.*, *96* (1992) 350–357.

590 R. Ryoo, S.J. Cho, C. Pak, J.-G. Kim, S.-K. Ihm and J.Y. Lee, *J. Am. Chem. Soc.*, *114* (1992) 76–82.

591 S. Cosnier, A. Deronzier and J.-F. Roland, *J. Mol. Catal.*, *71* (1992) 303–315.

592 J. Wang, N. Naser, L. Angnes, H. Wu and L. Chen, *Anal. Chem.*, *64* (1992) 1285–1288.

593 D.F. Johnson, Y. Wang, J.E. Parmeter, M.M. Hills and W.H. Weinberg, *J. Am. Chem. Soc.*, *114* (1992) 4279–4290.

594 J.A. Rodriguez, C.M. Truong, J.S. Corneille and D.W. Goodman, *J. Phys. Chem.*, *96* (1992) 334–341.

595 C.M. Truong, J.A. Rodriguez and D.W. Goodman, *J. Phys. Chem.*, *96*(1992) 341–347.

596 A.P. Walker and R.M. Lambert, *J. Phys. Chem.*, *96* (1992) 2265–2271.

597 L. Reven and E. Oldfield, *Inorg. Chem.*, *31* (1992) 243–252.

598 A. Waghray, J. Wang, R. Oukaci and D.G. Blackmond, *J. Phys. Chem.*, *96* (1992) 5954–5959.

599 S. Yamamoto, Y. Miyamoto, R.M. Lewis, M. Koizumi, Y. Morioka, K.Asakura and H. Kuroda, *J. Phys. Chem.*, *96* (1992) 6367–6371.

600 H.H. Lamb and B.C. Gates, *J. Phys. Chem.*, *96* (1992) 1099–1105.

601 T. Koerts and R.A. van Santen, *J. Chem. Soc., Chem. Commun.*, (1992) 345–346.

602 J. Kubota and K. Aika, *J. Chem. Soc., Chem. Commun.*, (1992) 661–662.

603 T. Koerts, P.A. Leclercq and R.A. van Santen, *J. Am. Chem. Soc.*, *114* (1992) 7272–7278.

604 A.S. Fung, M.J. Kelley and B.C. Gates, *J. Mol. Catal.*, *71* (1992) 215–232.

605 M.M.T. Khan, D. Chatterjee, M. Krishnaratnam and M. Bala, *J. Mol. Catal.*, *72* (1992) 13–18.

606 F.-S. Xiao, A. Fukuoka, M. Ichikawa, W. Henderson and D.F. Shriver, *J. Mol. Catal.*, *74* (1992) 379–390.

607 Y. Izumi, T.-H. Liu, K. Asakura, T. Chihara, H. Yamazaki and Y. Iwasawa, *J. Chem. Soc., Dalton Trans.*, (1992) 2287–2297.

608 Y. Izumi, T. Chihara, H. Yamazaki and Y. Iwasawa, *J. Chem. Soc., Chem. Commun.*, (1992) 1395–1396.

609 J.N. Shah and R.N. Ram, *J. Mol. Catal.*, *77* (1992) 235–245.

610 P.I. Sorantin and K. Schwarz, *Inorg. Chem.*, *31* (1992) 567–576.

611 M.W. Payne, P.K. Dorhout, S.-J. Kim, T.R. Hughbanks and J.D. Corbett, *Inorg. Chem.*, *31* (1992) 1389–1394.

612 C. Rong, X. Qin and H. Jinglong, *J. Mol. Catal.*, *75* (1992) 253–276.

613 A.A. Kelkar, D.S. Kolhe and R.V. Chaudhari, *J. Organomet. Chem.*, *430* (1992) 111–116.

614 F. Ragaini, S. Canini, A. Fumagalli and C. Crotti, *J. Organomet. Chem.*, *428* (1992) 401–408.

615 C. Crotti, S. Cenini, F. Ragaini, F. Porta and S. Tollari, *J. Mol. Catal.*, *72* (1992) 283–298.

616 S.B. Halligudi, K.N. Bhatt, N.H. Khan and M.M.T. Khan, *J. Mol. Catal.*, *72* (1992) 139–142.

617 R.L. Halterman and M.A. McEvoy, *J. Am. Chem. Soc.*, *114* (1992) 980–985.

618 D. Xu, G.A. Crispino and K.B. Sharpless, *J. Am. Chem. Soc.*, *114* (1992) 7570–7571.

619 K.B. Sharpless, W. Amberg, Y.L. Bennani, G.A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu and X-L. Zhang, *J. Org. Chem.*, *57* (1992) 2768–2771.

620 T. Hashiyama, K. Morikawa and K.B. Sharpless, *J. Org. Chem.*, *57* (1992) 5067–5068.

621 S.-I. Murahashi, Y. Oda and T. Naota, *J. Am. Chem. Soc.*, *114* (1992) 7913–7914.

622 M.M.T. Khan, D. Chatterjee, S. Kumar, S.A.P. Rao and N.H. Khan, *J. Mol. Catal.*, *75* (1992) L49–L51.

623 A. Tengalia, E. Terranova and B. Waegell, *J. Org. Chem.*, *57* (1992) 5523–5528.

624 S. Zhang and R.E. Shepherd, *Inorg. Chim. Acta*, *193* (1992) 217–227.

625 M.J. Upadhyay, P.K. Bhattacharya, P.A. Ganeshpure and S. Satish, *J. Mol. Catal.*, *73* (1992) 277–285.

626 M.M.T. Khan, D. Chatterjee, S.D. Bhatt and A. Prakash, *J. Mol. Catal.*, 77 (1992) 23–28.

627 M.M.T. Khan, D. Chatterjee, N.H. Khan, R.I. Kureshi and K.N. Bhatt, *J. Mol. Catal.*, *77* (1992) 153–158.
628 J.M. Fisher, A. Fulford and P.S. Bennett, *J. Mol. Catal.*, *77* (1992) 229–234.
629 G.-Z. Wang and J.-E. Bäckvall, *J. Chem. Soc., Chem. Commun.*, (1992) 337–339.
630 B.M. Trost and R.J. Kulawiec, *J. Am. Chem. Soc.*, *114* (1992) 5579–5584.
631 M.M.T. Khan and R.S. Shukla, *J. Mol. Catal.*, *71* (1992) 157–175.
632 M.M.T. Khan, H.C. Bajaj and D. Chatterjee, *J. Mol. Catal.*, *71* (1992) 177–182.
633 M. Bressan and A. Morvillo, *J. Mol. Catal.*, *71* (1992) 149–155.
634 M.M.T. Rhan and R.S. Shukla, *J. Mol. Catal.*, *72* (1992) 361–372.
635 M.M.T. Khan, A.P. Rao, D. Chatterjee and S. Kumar, *J. Mol. Catal.*, *73* (1992) 17–21.
636 M.M.T. Khan, D. Chatterjee, M. Bala and K.N. Bhatt, *J. Mol. Catal.*, *73* (1992) 265–269.
637 M.M.T. Khan, A.P. Rao and S.K. Bhatt, *J. Mol. Catal.*, *75* (1992) 41–51.
638 M.M.T. Khan, A.P. Rao and S.D. Bhatt, *J. Mol. Catal.*, *75* (1992) 129–139.
639 M.M.T. Khan, S.H. Mehta, A.P. Rao and K.N. Bhatt, *J. Mol. Catal.*, *75* (1992) 245–251.
640 M. Bressan, A. Morvillo and G. Romanello, *J. Mol. Catal.*, *77* (1992) 283–288.
641 M.M.T. Khan and R.S. Shukla, *J. Mol. Catal.*, *77* (1992) 221–228.
642 M.J. Ridd, D.J. Gakowski, G.E. Sneddon and F.R. Keene, *J. Chem. Soc., Dalton Trans.*, (1992) 1949–1956.
643 G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.*, *92* (1992) 1051–1069.
644 D.F. Taber, P.B. Deker and L.J. Silverberg, *J. Org. Chem.*, *57* (1992) 5990–5994.
645 M. Saburi, H. Takeuchi, M. Ogasawara, T. Tsukahara, Y. Ishii, T. Ikariya, T. Takahashi and Y. Uchida, *J. Organomet. Chem.*, *428* (1992) 155–167.
646 S. Bhaduri, K. Sharma and D. Mukesh, *J. Chem. Soc., Dalton Trans.*, (1992) 77–81.
647 M. Rosales, A. González, Y. Alvarado, R. Rubio, A. Andriollo and T.A. Sanchez-Delgado, *J. Mol. Catal.*, *75* (1992) 1–13.
648 S. Rajagopal, S. Vancheesan, J. Rajaram and J.C. Kuriacose, *J. Mol. Catal.*, *75* (1992) 199–208.
649 E. Farnetti, M. Graziani, A. Mezzetti and A.D. Zotto, *J. Mol. Catal.*, *73* (1992) 147–155.
650 J.A. Cabeza, J.M. Fernández-Colinas, A. Llamazares and V. Riera, *J. Mol. Catal.*, *71* (1992) L7–L11.
651 G.-Z. Wang and J.E. Bäckvall, *J. Chem. Soc.. Chem. Commun.*, (1992) 980–982.
652 H. Nagashima, H. Wakamatsu, N. Ozaki, T. Ishii, M. Watanabe, T.Tajima and K. Itoh, *J. Org. Chem.*, *57* (1992) 1682–1689.
653 S.-I. Murahashi, S. Sasao, E. Saito and T. Naota, *J. Org. Chem.*, *57* (1992) 2521–2523.
654 Y. Lin, X. Zhu and Y. Zhou, *J. Organomet. Chem.*, *429* (1992) 269–274.
655 E. Zenkl and F. Seltzer, *J. Organomet. Chem.*, 76 (1992) 1–14.
656 A. Demonceau, A.F. Noels, E. Saive and A.J. Hubert, *J. Organomet. Chem.*, *76* (1992) 123–132.
657 K. Nomura, *J. Mol. Catal.*, *73* (1992) L1–L4.
658 M.D. Wang and H. Alper, *J. Am. Chem. Soc.*, *114* (1992) 7018–7024.
659 B.M. Trost and J.A. Flygare, *J. Am. Chem. Soc.*, *114* (1992) 5476–5477.
660 T. Kondo, S. Kotachi and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, (1992) 1318–1319.
661 B. Marciniec, C. Pietraszuk and Z. Foltynowicz, *J. Mol. Catal.*, *76* (1992) 307–317.