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Annual survey of ruthenium and osmium for the year 1990

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1. Dissertations

Four dissertations dealing with mononuclear ruthenium and osmium sulfur complexes have been published. The chemistry of the ruthenium bisulfite complexes $[(bpy)_2Ru(SO_3H)_2]$, $[(terpy)(bpy)Ru(SO_3H)]^+$, $[(bpy)_2(py)Ru(SO_3H)]^+$, has been examined. The analogous osmium complexes were found to be more difficult to prepare. Electrochemical investigations of bound SO_2 are reported for $[(NH_3)_5Ru(SO_2)]Br_2$ [1]. Synthesis, characterization, and reactivity of the ruthenium-nitrosyl thiolates $[Ru(NO)(S\text{-}2,6\text{-}Me_2C_6H_3)_4]^-$ and $[Ru(NO)(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]^-$ are described. The characterization of cyclometallated products from reactions of the above ruthenium-nitrosyl thiolates is presented [2]. Studies involving ruthenium thiolate, thiol, and thioether complexes are described. The ruthenium complexes were based on $CpRuL_2(S)$ (L = phosphine or phosphate) [3]. Synthetic routes to $[Ru(S\text{–}S)_3]$ (S–S = $-S_2P\{OEt\}_2$, $-S_2CNR_2$; R = Me, Et, ^iPr) have been reported. Electrochemical studies reveal reversible one-electron oxidation and reduction steps. The reaction of tcne with selected complexes is shown to afford a coordinated tcne ligand ($tcne^-$) and an oxidized metal center (M^{3+}) [4].

The molecular structures of $Os(CO)_5$ and $Ru(CO)_5$ have been determined by electron-diffraction studies. Both molecules exhibit D_{3h} symmetry as expected. Values for bond lengths and bond angles are included [5]. A two-part dissertation describing the synthesis and characterization of new ruthenium and osmium metallaboranes and heterobinuclear dianions has been published. The former complexes are obtained from the reaction of $[M(CO)_4]^{2-}$ (M = Ru, Os) or $[CpRu(CO)_2]^-$ with $L \cdot BH_3$ (L = THF, Et_2O). The products

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* No reprints available. For previous Annual Survey see *J. Organomet. Chem.*, *432* (1992) 215.

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resemble a diborane(6) molecule with the organometallic fragment replacing a bridging hydrogen. The heterobinuclear complexes $[MM'(CO)_8]^{2-}$ (MM' = FeRu, FeOs, RuOs) have been prepared from the reaction of $[M(CO)_4]^{2-}$ with $M'(CO)_5$. Crystallographic data on the iron-ruthenium dimer, $[FeRu(CO)_8]^{2-}$, are included [6]. The carbonylmetalate anion $[InRu(CO)_2][K]$ has been prepared from the reaction of $[InRu(CO)_2]_2$ with KEt_3BH. Anion functionalization with alkyl halides gave the corresponding alkyl complexes. The carbonylation reactivity of $InRu(CO)_2Me$ and InRu $(CO)_2CH_2OMe$ is also included [7]. Reactivity studies on alkyl and aryl ruthenium(II) carbonyl complexes are described. Carbonyl insertion and reductive elimination chemistry have been studied kinetically in selected cases [8]. Photoelectron spectroscopy data on $[CpRu(NO)]_2$ and $[CpRu(NO)]_2$-μ-CH_2 have been presented [9].

Several new difluorophosphine ruthenium complexes have been synthesized and characterized by NMR spectroscopy and X-ray diffraction analysis [10]. The phosphine ligands 1-phenyldibenzophosphole and 1-phenyl-3,4-dimethyl-phosphole have been employed as ancillary ligands in the preparation of new ruthenium(II) complexes. Full solution characterization, X-ray diffraction studies, and results from the catalytic hydrogenation of 1-hexene are presented [11]. The chemistry of pentadienylruthenium complexes has been reported. Reaction of $RuCl(PPh_3)_3$ with pentadienyltributyltin gives (η^5-pentadienyl)$RuCl(PPh_3)_2$, which has been used as a starting material for the synthesis of other pentadienyl complexes. A discussion dealing with the solution dynamics of the pentadienyl ligand in selected pentadienyl complexes is included [12]. Quinodimethane and naphthoquinodimethane complexes have been synthesized from various $RuCl_2P_4$ complexes. A detailed NMR examination of $[Ru(CH_2C_4H_4CH_2)(PMe_3)_3]$ established the existence of an intermediate that contains a $\sigma^2,\pi-\pi^2$ Ru–xylidene interaction [13]. The synthesis and redox properties of several ruthenium alkynyl complexes have been reported [14]. The isonitrile complex *trans*-$RuCl_2(CNPh)_4$ has been prepared and fully characterized by solution measurements and X-ray diffraction analysis. Included in this report are halide activation studies [15]. Chalcogen- and transition metal-bridged [3]ruthenocenophanes have been synthesized and spectroscopically examined. Pyramidal chalcogen inversion and bridge reversal are responsible for the NMR fluxionality observed in solution [16].

High-valent osmium complexes containing chelating ligands with imine, imido, and nitrido moieties have been synthesized. Included in this report are the X-ray crystal structures of Os(η^4-HBA–B)($NC_6H_5NHC_6H_4$) and $[OsN(\eta^4\text{-HBA–B})]^-$ [17]. The reaction between OsO_4 and bidentate ligands in HX is reported to give six-coordinate *trans*-dioxoosmium complexes OsO_2X_2-(L–L) (L–L = diphosphines, diamines, dithioethers, and diselenoethers; X = halide). The *trans*-$[OsO_2]^{2+}$ moiety displays a characteristic ν(Os–O) stretch at *ca.* 840 cm^{-1} [18]. The photochemistry of isomeric complexes of ruthenium(II) with 2-(phenylazo)pyridine has been explored. The effect of solvent on the absorption spectra and correlation of the lowest MLCT energies with some empirical solvent parameters is discussed. It is suggested that the MLCT excited state is responsible for the observed photoreactivity [19]. Several ruthenium(II) complexes containing terpy ligands have been examined for luminescence activity. Luminescence lifetime studies reveal that the phenyl groups on the terpy ligands increase the barrier to quenching of the ^{3}MLCT state via the ^{3}d–d states [20]. The excited-state quenching of the ruthenium-containing film poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ by Co^{III} quenchers has been reported. Both static quenching and intra-polymer energy migration mechanisms are observed [21]. Electron-transfer rate constants for oxidation and reduction in horse heart *cytochrome c* with ruthenium amines and ruthenium polypyridine complexes covalently bound to the His-33 residue have been measured. Evidence is presented that supports a directional electron-transfer model [22]. The luminescent properties of silica-immobilized polypyridyl ruthenium(II) complexes have been explored by using absorption, emission, and time-resolved emission spectroscopies. Gas phase quenching studies using oxygen exhibit complex behavior as evidenced by nonlinear Stern–Volmer behavior [23]. The solvent dynamics of heterogeneous electron transfer reactions and electrogenerated chemiluminescence and electrochemistry of organized monolayers of a $Ru(bpy)_3^{2+}$-based surfactant at In-doped tin oxide have been reported [24].

The ruthenium dimer $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(Ph)H\}(CO)_6$ has been isolated from the reaction between $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ and diphenylacetylene. The dimer reacts with PPh_3 to give the corresponding monophosphine complex, $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(Ph)H\}(CO)_5PPh_3$, which has been characterized in solution and by X-ray diffraction analysis. Low-temperature ^{1}H and ^{13}C NMR measurements reveal that both *vic* and *gem* isomers are present in solution. The major isomer is assigned to the *gem* isomer [25]. The synthesis and reactivity of binuclear ruthenium(II) and osmium(II) porphyrin complexes have been described. Dimer cleavage reactions and the redox chemistry are also discussed [26]. A report on the first example of a metal-centered ligand addition to a cyclopentadienyl metal sulfide has appeared. $[(\eta^5\text{-}C_5Me_4Et)Ru]_2S_4$ is shown to react with

CO to give $[(\eta^5\text{-}C_5Me_4Et)Ru]_2S_4(CO)$, which has been fully characterized [27].

The new phenylimido trinuclear clusters $Ru_3SD(NPh)(CO)_9$ and $H_2Ru_3S(NPh)(CO)_8$ have been prepared. Included in this study are the X-ray crystal structures of $H_2Ru_3S_2(CO)_8$ and $Ru_3S(NC_6H_4Cl)(CO)_8$. Phosphine substitution studies and alkene hydrogenation results with selected clusters are described [28]. The reaction between $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and phenylacetylene gives the acetylene-bridged cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu_3\text{-}S)$ as the major product. The reactivity of other ruthenium and osmium clusters is described [29]. The synthesis and redox activation of sulfido-bridged trinuclear ruthenium clusters are presented. High turnover numbers ($\geq 50{,}000$) are observed in the electrochemically induced ETC ligand substitution reaction employing $Ru_3(CO)_9(\mu_3\text{-}S)_2$ and $Ru_3(CO)_{10}(\mu_3\text{-}S)$. Cyclic voltammetric data indicate that CO_2 is able to bind to $Ru_3(CO)_9(\mu_3\text{-}S)_2$ [30]. Ligand substitution studies and nucleophilic activation of $Ru_3(CO)_{12}$ have been investigated. Rate constants for product formation have been measured and the resulting products fully characterized by solution and solid-state techniques [31]. Anionic ruthenium and osmium polynuclear carbonyl clusters have been synthesized and their reactivity toward small molecules explored [32].

Ruthenium-supported catalysts have been investigated as Fischer–Tropsch catalysts with major emphasis on the effect of metal particle size and its relationship to catalytic activity [33]. The catalytic activity of zeolite-supported ruthenium in the presence of Fe/ZSM-5 has been explored. Catalyst characterization includes IR, XPS, ISS, XRD and pyridine chemisorption studies [34]. CO_2 conversion to methane has been studied by using intrazeolite ruthenium carbonyl catalysts. Evidence is presented that supports an active catalyst derived from interior $Ru_3(CO)_{12}$ units and surface derived catalysts only when hydrogen poor conditions exist [35]. A report on the structure and surface composition of supported Ru/Pt bimetallic catalysts is described. Also presented is a new quantitative technique that allows measurement of the enthalpies of gas–solid reactions [36]. The preparation and characterization of supported Ru/Pt bimetallic clusters have been discussed. $RuCl_3 \cdot nH_2O$ and $Ru(NH_3)_6Cl_3$ were used as starting materials for support on silica [37]. New polyquinoline-supported ruthenium redox systems have been synthesized and characterized. Polymer-modified electrodes based on these systems were found to catalyze the oxidation of selected primary alcohols to the corresponding aldehyde with high catalytic currents. Over oxidation of the product aldehydes to carboxylic acids was not observed [38]. Supported ruthenium carbonyls have been prepared from $Ru(CO)_3Cl_2(THF)$. Adsorption onto MgO, Al_2O_3, SiO_2 and NaY zeolite proceeds with less than 0.1 equivalent loss of CO. This study also includes details on the preparation of the bimetallic cluster $[RuCo_3(CO)_{12}]^-$, which is obtained from the Al_2O_3-induced disproportionation of $RuCo_2(CO)_{11}$ [39].

Thiophene hydrodesulfurization over sulfided ruthenium catalysts has been investigated [40]. XPS and SIMS have been employed in catalyst evaluation. Hydrodesulfurization catalysts prepared from Ru_xTh_x intermetallics and ThO_2-supported ruthenium systems have been prepared and fully characterized by the normal complement of surface science techniques [41].

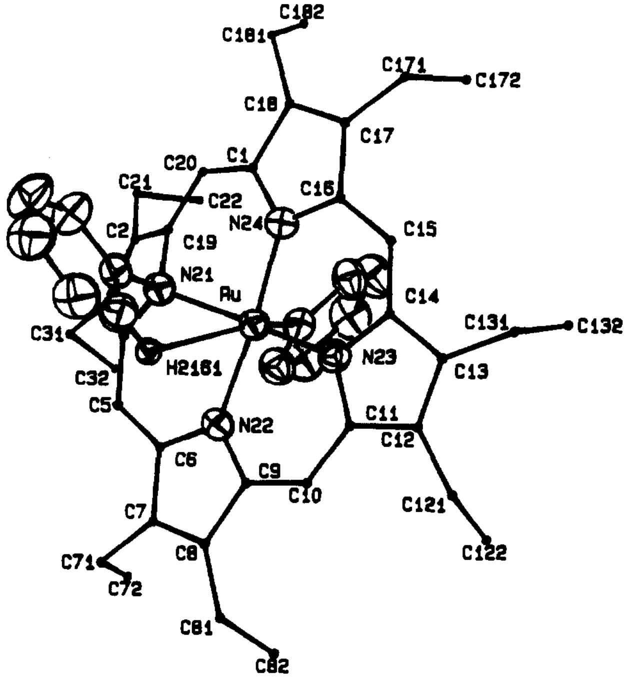
The icosahedral alloy Al–Cu–Ru was the subject of diffraction experiments [42]. A report on the laser-induced thermal desorption of methanol from a Ru (001) surface has appeared. Hydrogen and carbon monoxide diffusion on a clean Ru(001) surface have been measured and diffusion activation barriers calculated [43]. The reactivity of C_1 molecules and coadsorption of probe molecules with ammonia on a Ru (001) surface has been studied [44]. Kinetic investigations of the decomposition of formic acid on a Ru(001) surface at 130 and 310 K are described. Dissociative chemisorption proceeds by both O–H and C–O bond cleavage [45]. A study on a ruthenium cyanide surface-modified electrode has appeared [46].

2. Mononuclear complexes

2.1. Organometallic porphyrins

The first dihydrogen porphyrin complexes have been described. Reaction of [M(OEP)(H)][K] (M = Ru, Os) with benzoic acid yields the corresponding dihydrogen complex $M(OEP)(H_2)$, which exhibits an η^2-hydrogen ligand based on ^1H NMR spin–lattice relaxation measurements and examination of the $^1J_{HD}$ value from the η^2-HD complex. The hydrogen transfer reactivity of these systems resembles that of hydrogenase enzymes [47]. Confacial metallodiporphyrin complexes have been synthesized and examined as model systems involving the bimolecular reductive elimination of hydrogen [48]. The porphyrin complex $[Ru(OEP\text{-}N\text{-}C_6H_5)(C_6H_5)][BF_4]$ has been prepared by oxidation of $Ru(OEP)(C_6H_5)_2$ with $AgBF_4$. The X-ray structure of the product reveals the presence of N-bound and Ru-bound phenyl groups, consistent with the results of other "suicide adducts" of cytochrome P_{450}. The X-ray structure, which is shown below, reveals that an agostic Ru–H interaction, originating from the $N\text{–}C_6H_5$ moiety is also present [49].

The redox chemistry of $Ru(OEP)(C_6H_5)_2$ and $Ru(OEP)(C_6H_5)$ has been examined by cyclic voltamme-



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try. Rapid loss of $[C_6H_5]^-$ from $[Ru(OEP)(C_6H_5)_2]^{2-}$ gives the diamagnetic complex $[Ru(OEP)(C_6H_5)]^-$ while N-arylation is observed during oxidation. Electron-self-exchange reactions for several of the redox pairs have been determined by ^1H NMR spectroscopy [50]. The synthesis, spectroscopy, and electrochemistry of osmium(IV) and osmium(V) porphyrins are discussed. $Os(OEP)(O)_2$ was used as the starting material [51]. *m*-Chloroperoxybenzoic acid oxidation of Ru (TPP)CO and Ru(TMP)CO gives the corresponding dioxo ruthenium porphyrins, $Ru(TPP)(O)_2$ and Ru $(TMP)(O)_2$, which were then examined by resonance Raman and IR spectroscopy. Normal coordination calculations were carried out on the O=Ru=O vibrations. A mechanism involving two successive O–O bond cleavages of the oxidant is proposed in the formation of the dioxo ruthenium porphyrin complexes [52]. The origin of the excitation wavelength dependence for photoinduced CO loss in Ru(OEP)(CO) has been explored. The quantum yield for CO loss is very dependent of the excitation wavelength. Quenching studies and the results of laser flash photolysis investigations are presented [53].

A heterometallic ruthenium-osmium porphyrin complex has been synthesized by using the cofacial porphyrin ligand 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene. NMR and magnetic measurements confirm the paramagnetism associated with the Ru=Os bond [54]. The synthesis and characterization of the new porphyrin complex tetrakis(2,6-difluorophenyl)porphinato ruthenium(II) (CO)(N-MeIm) have appeared. Hydrocarbon oxidation results using the co-oxidants ^tBuOOH and hypochlorite are also presented [55].

2.2. *Halides*

Salts derived from $[Ru_2Br_9]^{3-}$ have been examined in spectroscopic and redox studies [56]. A new synthesis of RuF_6 involving fluorination of RuF_5 is reported. IR matrix studies and UV-visible vibration data are discussed [57]. Mixed fluorochloro-osmates(IV) have been studied by ^{19}F NMR spectroscopy [58].

The synthesis of *trans*-OsL_2X_4 (L = two-electron donor ligands; X = Cl, Br) complexes is presented. Cyclic voltammetric studies have defined the Os^{IV}/Os^{III} redox couples, and redox potentials correlated with the lowest charge-transfer transitions in the UV-visible spectra. The X-ray structure of *trans*-$[Os(PEt_3)_2Cl_4][Ph_4P]$ has been solved [59]. Several halogen-tetramethylene sulfoxide ruthenium(II) and ruthenium(III) complexes have been synthesized and characterized. The complexes prepared include: *cis*- and *trans*-$RuCl_2(TMSO)_4$, *cis*- and *trans*-$RuBr_2(TMSO)_4$, (TMSO)H(*trans*-$RuTMSO)_2Cl_4$), and *mer*-$RuCl_3(TMSO)_3$. The *cis* isomers, which are thermodynamically more stable, are transformed to the *trans* isomer upon optical excitation in TMSO solution. X-Ray crystallographic analysis of *cis*-$RuCl_2(TMSO)_4$ and (TMSO)-H(*trans*-$Ru(TMSO)_2Cl_4$) indicates that all TMSO ligands are S-bonded to the ruthenium center [60]. The electronic structure of $[Os(NX)Cl_5]^{2-}$ (X = S, O) and $[Os(NS)Cl_4(H_2O)]^-$ has been calculated by using CNDO/2 methodology [61].

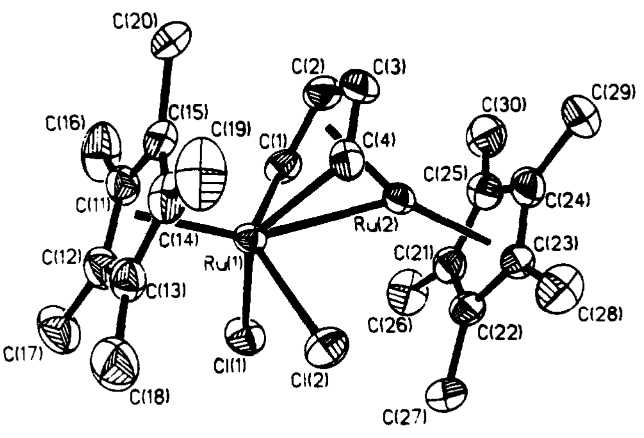
Isomerism and solution equilibria for (2,7-dimethyloctadienediyl)ruthenium(IV) complexes are presented [62]. The reaction between $RuCl_3 \cdot xH_2O$ and cyclooctadiene in the presence of zinc yields a mixture of products. Of the many products produced, $Ru_2Cl_4(C_8H_{12})_2$, $RuH(C_8H_{11})(C_6H_6)$, $Ru_3Cl_3(OCH_3)(C_8H_{12})_3$, and $Ru(C_8H_{10})(C_8H_{12})$ were isolated and structurally characterized by X-ray crystallography [63]. $RuCl_2(PPh_3)_3$ reacts with α-amino acids to give Ru(amino acid)$(PPh_3)_2$. The X-ray structures of the amino acid complexes prepared by using glycine and L-alanine are presented [64]. The σ-vinyl complex Ru(CR=CHR)-$Cl(CO)(PPh_3)_2$ (R = H, Me, Ph) reacts with [K][HB-$(pz)_3$] with chloride and PPh_3 ligand loss to give Ru-(CR=CHR)$(PPh_3)\{HB(pz)_3\}$ [65]. The reaction between $[K][H_2B(bta)_2]$ and $RuRCl(CO)(PPh_3)_2$ (R = C_6H_4-Me-4, C(C≡CPh)=CHPh) proceeds by loss of the chloride ligand to afford $RuR(CO)(PPh_3)_2\{H_2B(bta)_2\}$ in high yield [66]. Acetylene reacts with $Cp^*Ru(P^iPr_3)Cl$ or $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ to give the dinuclear ruthenacyclopentadiene complex $Cp^*Cl_2Ru(\eta^2:\eta^4\text{-}\mu_2\text{-}C_4H_4)RuCp^*$, which has been characterized by solution NMR measurements and X-ray diffraction analysis. Reaction of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with one equivalent of $HC{\equiv}CSiMe_3$ yields the monoalkyne complex $Cp_3^*Ru_3(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)(\eta^2\text{-}\mu_2\text{-}HC{\equiv}CSiMe_3)$. This complex while characterized by X-ray crystallography is unstable in solution [67].

The use of a modified microwave heating system in the synthesis of organometallic complexes has been described. Reaction times have been shortened considerably compared to the reported thermal procedures [68]. $RuCl_3 \cdot xH_2O$ and sodium periodate have been used in the oxidation of the C(6) alcohol group in benzyl 2-acetamido-3-O-[(*R*)-carboxyethyl]-2-deoxy-α-D-glucopyranoside 1′,4-lactone. The corresponding carboxylic acid was isolated in good yield [69].

2.3. Hydrides

Extended Hückel calculations have been performed on $(L)(L')(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(PR_3)_2H$ in order to study the nature of the bonding between the η^2-H moiety and the diruthenium fragment [70]. Molecular hydrogen complexes $[MH(\eta^2\text{-}H_2)P_4][BF_4]$ (M = Ru, Os; P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$) have been prepared by protonation of the neutral dihydrides MH_2P_4 at low temperature. Variable-temperature ^1H and ^{31}P NMR data, spin-lattice relaxation measurements, and J_{HD} values support the existence of the molecular hydrogen ligand. The report also deals with the reactivity of arenediazonium cations with the dihydride and molecular hydrogen complexes [71]. A report describing simultaneous photodissociation of H_2 and PMe_2Ph from $OsH_4(PMe_2Ph)_3$ has appeared. An equilibrium mixture of $Os_2H_4P_6$ and $Os_2H_4P_5$ is observed when OsH_4P_3 is photolyzed under vacuum. X-Ray diffraction results for $Os_2H_4P_5$ indicate that the dimer is composed of two octahedra that share a common edge, bridged by two hydride ligands [72].

The reaction between methyl vinyl ketone and $RuH(BH_4)(P_3)$ (P_3 = ttp, Cyttp) yields $Ru(\eta^4\text{-}CH_2{=}CHCOMe)(P_3)$. The tetrahydride RuH_4(Cyttp) has been allowed to react with 2-vinylpyridine, vinyl acetate, and methylacrylate to give a variety of products. Full solution characterization of all new products and the X-ray diffraction structure of $Ru(\eta^4\text{-}CH_2{=}CHCOMe)$(ttp) are described [73]. Thermolysis of *cis*-OsH(neopentyl)$(PMe_3)_4$ is reported to give both intramolecular and intermolecular carbon–hydrogen activation processes. The complex *fac*-$OsH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ is obtained at 80°C in cycloalkane solvent as a result of C–H bond activation of one of the coordinated PMe_3 ligands. Thermolysis in neat Me_4Si gives *cis*-$OsH(CH_2SiMe_3)(PMe_3)_4$ and the previous cyclometalated complex. Data from phosphine inhibition studies, isotope effects, and crossover experiments are presented along with a plausible mechanism which accounts for the observed C–H bond activation chemistry [74].



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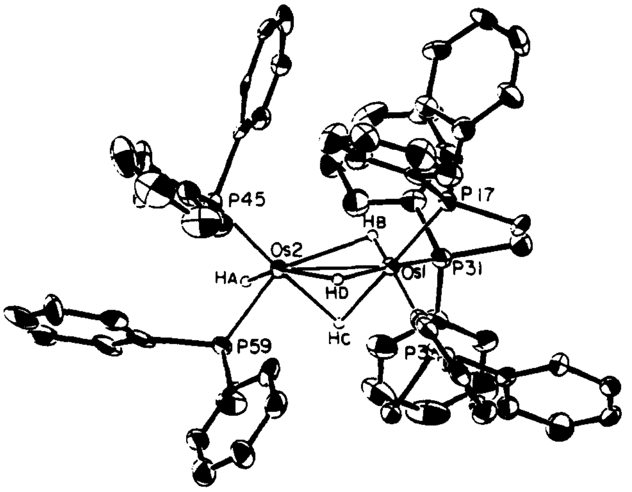
The reaction between $RuH(CO)Cl(EPh_3)_3$ (E = P, As) and 1-piperidinecarbonitrile and 1,4-piperazinecarbonitrile has been investigated [75]. The hexahydride $OsH_6(PCy_3)_2$ has been prepared by $LiAlH_4$ reduction of $Os(O)Cl_2(PCy_3)_2$ [76]. Dimethyl maleate and diethyl maleate have been allowed to react with $RuH(Cl)(CO)(PPh_3)_3$ [77]. The X-ray structure of $RuH(Cl)(CO)(PPh_3)_2(SN_2C_6H_4)$, which is obtained from $RuH(Cl)(CO)(PPh_3)_3$ and 2,1,3-benzothiadiazole, is reported [78]. Alkynes react with $RuH(Cl)(CO)(py)(PPh_3)_2$ to give the alkenyl complexes $RuCl(CO)\{(E)\text{-}HC{=}CHR\}(py)(PPh_3)_2$. The insertion reaction proceeds via a *cis*-insertion sequence [79]. The hydride complexes $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) react with



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R_2Hg compounds to afford the five-coordinate σ-complexes $RuR(Cl)(CO)(PPh_3)_2$. X-Ray results of two of the products, Ru(*p*-tolyl)(Cl)(CO)$(PPh_3)_2$ and Ru(*o*-tolyl)(Cl)(CO)$(PPh_3)_2$, are presented [80]. The effect of Group 15 donor ligands on the hydrogenation of alkynes using the catalysts $[RuHL_5]^+$ and $[RuHL_3L'_2]^+$ is reported. Hydrogenation reactivity as a function of the ligand's cone angle and added ligand is described [81].

2.4. Phosphines

Carbon–carbon bond cleavage in acetone has been explored with $Ru(PMe_3)_4(\eta^2\text{-}C_6H_4)$. Included in this report is the direct synthesis and spectroscopic characterization of an intermediate oxametallacyclobutane complex [82]. In a related study, the synthesis and spectral characterization of $Ru(PMe_3)_4(Me)\{OC(CH_2)Me\}$ are reported. $Ru(PMe_3)_4(Me)\{OC(CH_2)Me\}$ is unique in that it exists as an equilibrium mixture of oxygen- and carbon-bound transition-metal enolates. Thermolysis of the enolate mixture furnishes methane and an η^4-oxatrimethylenemethane complex [83]. Phosphorus–carbon cleavage of coordinated PMe_3 in $Ru(PMe_3)_4(OC_6H_4Me)_2$ occurs under thermolysis conditions to yield the dimethylarylphosphinite complex $Ru(PMe_3)_3(\eta^2\text{-}PMe_2OC_6H_3)(OC_6H_4Me)$. The same product is also obtained when the orthometallated complex $Ru(PMe_3)_4(\eta^2\text{-}OC_6H_3Me)$ is treated with *p*-cresol. The structure of the dimethylarylphosphinite complex has been established by X-ray diffraction analysis [84].

The effect of solution on the structure of $RuCl_2$(Cyttp) has been noted. In non-polar solvents, *mer*-$RuCl_2$(Cyttp) and *fac*-$RuCl_2$(Cyttp) are present in equal amounts while the same two isomers, plus $[Ru_2Cl_3(Cyttp)_2][Cl]$, are present in halogenated solvents. In more polar solvents such as AcOH and $MeNO_2$, the major isomer exists as a 1:1 electrolyte [85]. The reactivity of $Ru(CO)_2$(triphos) (triphos = ttp, Cyttp, etp) toward I_2 and MeI has been investigated by using NMR and IR spectroscopy [86]. The hydride complexes $MH(Cl)(CO)(PPh_3)_3$ (M = Ru, Os) react with benzotriazole to give a pair of geometric isomers $MH(Cl)(CO)(PPh_3)_2$(Hbta). Reaction of $MH_2(CO)(PPh_3)_3$ with excess benzotriazole yields the complex MH(bta ··· H–bta)benzotriazole–benzotriazolate pair that functions as an NN′ chelating ligand [87]. The X-ray structure of $Ru(PPh_3)_2(\mu\text{-}ClC_6H_4CO_2)Cl_2$ has been reported. The carboxylate complex, which was obtained from the reaction between $Ru(PPh_3)_3Cl_2$ and MCPBA, exhibits a quasi-reversible reduction at −0.4 V *vs.* SCE [88]. Octahedral and trigonal-pyramidal osmium(II) complexes containing the bidentate ligand dcpe have been synthesized and spectroscopically characterized. Addition reactions to the five-coordinate osmium and ruthenium complexes are presented [89]. HNO_3/HBF_4 oxidation of the complexes *mer*-OsL_3X_3 (L = phosphines, $AsEt_3$; X = Cl, Br) furnishes *mer*-$[OsL_3X_3][BF_4]$. The osmium(IV) complexes have been characterized by NMR and IR spectroscopy, and magnetic and conductance measurements. Cyclic voltammetric data reveal that the *mer*-$[OsL_3X_3]^{0/+}$ oxidation couple is reversible [90]. The lithium salts of 1,2,3-trimethyl-, 1,2,3,4-tetramethyl-, or 1,2,4,5-tetramethylbenzene have been allowed to react with $RuCl_2L_4$ (L = PMe_3, $PMePh_2$). Spectroscopic data indicate that the *o*-xylidene moieties are best described as methyl-substituted *o*-quinodimethanes [91]. The synthesis and reactivity of osmium phosphido complexes, $Os(\eta^2\text{-}L)(PH_2)(CO)(PPh_3)_2$ (L = AcO, Me_2CS_2, acac, NO_2), have been reported. The X-ray structure of $Os(\eta^2\text{-}OAc)(PH_2AuI)(CO)(PPh_3)_2$, which was obtained from the reaction with AuI, is included [92].

The fluxional behavior of bis- and tris-(ether phosphine) ruthenium(II) chloro and acetate complexes has been published [93]. Methanol carbonylation has been explored by using a catalyst prepared from $RuCl_2(PPh_3)_3$ and the ether phosphine ligand $Ph_2PCH_2C_4H_7O_2$ [94]. The use of methylenebis(1,3,2-dithiaphospholane) and (methylimino)bis(1,3,2-dithiaphospholane) as an ancillary ligand in ruthenium complexes is described [95].

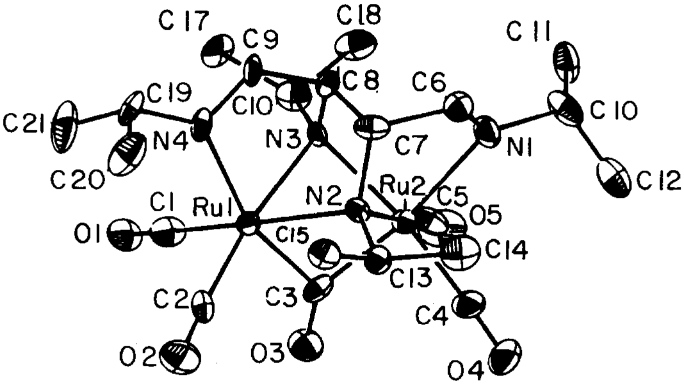
2.5. Carbonyls

The molecular structure of $Ru(CO)_5$ has been established by gas-phase electron diffraction analysis. The diffraction data reveal that $Ru(CO)_5$ adopts a trigonal-bipyramidal structure with the axial Ru–C bonds only slightly shorter than the equatorial Ru–C bonds [96]. An IR spectroscopic study of the transients derived from the photolysis of gas-phase $Os(CO)_5$ has been presented. The major photoproducts, $Os(CO)_4$ and $Os(CO)_3$, have been detected by using transient IR spectroscopic techniques. IR absorptions for $Os_2(CO)_8$ and bimolecular rate constants for the reaction of CO with these coordinatively unsaturated monomeric osmium fragments are included in the report [97]. The mechanism for the conversion of $Ru(CO)_5$ into $Ru_3(CO)_{12}$ in cyclohexane solvent has been examined. CO is lost, giving $Ru(CO)_4$ as the initial step, which is followed by a series of fast reactions to yield the trimer $Ru_3(CO)_{12}$. Activation parameters for the trimerization reaction and the equilibrium are reported [98]. The thermal behavior of $Ru(CO)_2(MeCO_2)_2(PBu_3)_2$ and related ruthenium carbonyls has been investigated by IR spectroscopy [99].

The synthesis and characterization of the polychalcogenide complex $[Ru(CO)_2(Se_4)_2]^{2-}$ are described. X-Ray diffraction analysis has unequivocally shown that $[Ru(CO)_2(Se_4)_2][Et_4N]_{1.5}[Na]_{0.5}$ consists of noninteracting Et_4N^+ cations and interacting Na^+ and $[Ru(CO)_2(Se_4)_2]^{2-}$ ions. The ruthenium center adopts an octahedral geometry with two *cis* carbonyl groups [100]. A report dealing with the synthesis and reactivity of the digermylruthenium complexes $\overline{Me_2Ge(CH_2)_n\text{-}Ge(Me_2)Ru}(CO)_4$ ($n = 1, 2$) has been published [101]. The reaction between $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ and $Ru(CO)_2L(\eta^4\text{-cot})$ ($L = CO, PPh_3$) proceeds to give $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8R)]^+$ (R = allyl) as a result of allylic alkylation of the cot ligand. The X-ray crystal structure of the 2-methylallyl complex and the results of variable-temperature NMR studies are also discussed [102]. $Os(CO)_2(PPh_3)_2$ reacts with di-*p*-tolyldiazomethane at 80°C to yield $\overline{OsH(CO)_2[(C_6H_3\text{-}p\text{-}Me)(p\text{-tolyl})C}NNC(p\text{-tolyl})_2](PPh_3)$ in high yield. The structure of this metallocycle, which possesses a ketazine ligand bound to the osmium center via nitrogen and the *ortho*-carbon of a *p*-tolyl moiety, has been established by X-ray diffraction analysis [103]. Diphenylbutadiyne and bis(phenylethynyl)mercury have been allowed to react with $RuH(Cl)(CO)(PPh_3)_3$. The major product with the former reagent is the coordinately unsaturated σ-vinyl complex $Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)Cl(PPh_3)_2$, which results from alkyne insertion into the Ru–H bond. Use of $Hg(C{\equiv}CPh)_2$ proceeds similarly to give the same products [104]. The reaction between pyrazole and $RuH(CO)(Cl)(PR_3)_n$ ($R = Ph$, $n = 3$; $R = {}^iPr$, $n = 2$) has been investigated. The resulting pyrazole complexes were used in the synthesis of heterobimetallic complexes [105].

The ruthenium complexes $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2$ and $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2L$ (L = py, Me_2Hpz) react with one equiv. of ${}^tBuNC$ to give the corresponding substitution product, $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2({}^tBuNC)$. Use of excess ${}^tBuNC$ yields the insertion product, $[Ru\text{–}\{\eta^1\text{-}C(O)CH{=}CHR\}({}^tBuNC)_3(PPh_3)_2][Cl]$ [106]. A detailed study on the kinetics and mechanism of the hydrogenolysis of the acyl complex dicarbonylchloronorbornenoylbis(triphenylphosphine)ruthenium(II), $Ru(CO)_2Cl\{\eta^1\text{-}C(O)C_7H_9\}(PPh_3)_2$, has been presented. The mechanism for the formation 2-norbornene-5-carboxaldehyde and the Ru–P solution bond dissociation energy are discussed [107].

The alkyl/aryl complex $[(N\text{–}N)_2Ru(CO)(CH_2R)]^+$ (N–N = bidentate nitrogen ligand; R = H, ${}^tBu$, Ph) has been obtained from $(N\text{–}N_2)Ru(CO_3)$. The first step involves protonation of the carbonate complex, followed by treatment with terminal alkynes. The use of terminal alkynes as sources of carbon-alkyl and carbonyl-acyl ruthenium complexes is emphasized [108]. $Ru(CO)_5$ reacts with substituted 1,4-diaza-1,3-butadienes (R–DAB) to give $Ru(CO)_3$(R–DAB) as the major product. The product, which is extremely air-sensitive, has been fully characterized in solution using NMR spectroscopy and by FD mass spectroscopy. Optical excitation or thermolysis gives the dimeric complex $Ru_2(CO)_5$(R–ADA) as a result of C–C bond coupling. The X-ray crystal structure of the isopropyl derivative, $Ru_2(CO)_5({}^iPr\text{–ADA})$, is shown in Fig. 4 [109].



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2.6. *Sulfur and oxygen ligands*

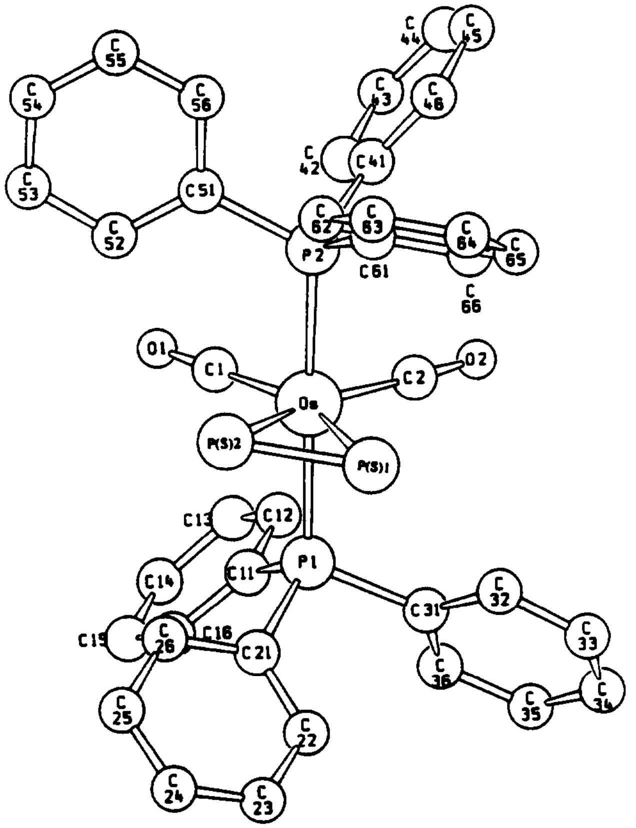
The sulfur-ligated complexes *cis*-$RuCl_2(TMSO)_4$ and *mer*-$RuX_3(TMSO)_3$ (X = Cl, Br) have been prepared and structurally characterized in the case of chloro complexes [110]. The mixed thioxanthate-phosphine complexes *cis*-$Ru(RSCS_2)_2(PPh_3)_2$ and *trans*-$[Ru(RSCS_2)_2(PPh_3)_2]^+$ have been synthesized and studied by cyclic voltammetry. The esr and UV-visible data for the 17-electron complexes *cis*-$[Ru(RSCS_2)_2(PPh_3)_2]^+$ and *trans*-$[Ru(RSCS_2)_2(PPh_3)_2]^+$ are presented [111]. Several different sulfur-containing amino acids have been allowed to react with either $[Ru(NBD)Cl_2]_n$ or $[Ru(1,5\text{-COD})Cl_2]_n$ to give Ru(diene)(amino acid)Cl_2 complexes. Crystal structures are reported for Ru(NBD)(D,L-methionine methyl ester)Cl_2, Ru(NBD)(D,L-methionine)$Cl_2 \cdot MeOH$, and Ru(NBD)(D,L-penicillamine)$Cl_2 \cdot EtOH \cdot HCl$, which exhibit bi-, tri-, and tetra-dentate coordinated S,N-, S,N,O-, and S,S,N,O- ligands, respectively [112]. A report on the redox behavior of dithiocarbonato complexes *cis*-$Ru(ROCS_2)_2(PPh_3)_2$ has appeared. One-electron oxidation yields the corresponding 17-electron *cis* complex, which is observed to isomerize to the *trans* isomer rapidly on the cyclic voltammetric time scale [113]. The chlorocarbene complex $Ru\{{=}CCl(2\text{-pyrrolyl})\}Cl_2(CO)_2(PPh_3)_2$ reacts with dimethyldithiocarbamate by chloride displacement at the carbene and metal centers. The product, a ruthenium-substituted 1-azafulvene, $\overline{Ru\{C(C_4H_3N)SCNMe_2S}\}(\mu^2\text{-}S_2CNMe_2)$-

$(CO)(PPh_3)$ has been characterized in solution by NMR measurements and its reactivity in protonation and alkylation reactions is discussed [114].

The ruthenium and osmium complexes $ML_n(PPh_3)_2(OSN{-}SO_2C_6H_4Me_4)$ have been obtained from the 16-electron complex $ML_n(PPh_3)_2$ or $ML_n(PPh_3)_3$. The sulphinylamine cumulene ligand is shown to adopt one of three possible bonding geometries, depending on the metal electron density, d-orbital occupancy, oxidation state and frontier orbital symmetry [115]. The reactivity of the *p*-tolyliminooxosulphurane complexes $Ru(CO)(L)(PPh_3)_2(OSNR)$ ($L = CO$, CNC_6H_3Me-2,6, ${}^tBuNC$; $R = p$-tolyl) and $Os(Cl)(NO)(PPh_3)_2(OSNR)$ with electrophiles has been explored. Reaction with $HSbF_6$ yields the N-protonated complexes $[Ru(OSNHR)(CO)(PPh_3)_2(CNC_6H_3Me\text{-}2,6)][SbF_6]$, which are shown to react with added nucleophiles to give the corresponding substituted η^1-sulphinamido complexes [116]. Toluene sulphonyliminooxo-λ^4-sulphurane reacts with $Os(Cl)(NO)(PPh_3)_2L$ (L = ethylene, allene, $PhC{\equiv}CPh$, $MeC{\equiv}CMe$, $CF_3C{\equiv}CCF_3$) to give the product of ethylene substitution $Os(Cl)(CO)(PPh_3)_2(OSNSO_2R)$ and by metallocycle formation to afford $Os\{C({=}CH_2)CH_2S(NSO_2R)O\}(Cl)(NO)(PPh_3)_2$. This latter product has been crystallographically characterized. The metallocycles exhibit reversible protonation chemistry at the exocyclic sulphimine moiety [117]. The synthesis and characterization of $Os(Cl)(NO)(PPh_3)_2(OSA)$ ($A = O$, CH_2, S, NR; $R = p$-tolyl, *o*-tolyl, $SO_2C_6H_4Me$-4) are reported [118].

SO_2 reacts with $(R)_{Ru}$-Ru(ncmp)(CO)(PPh_3)Me via SO_2 insertion into the Ru–Me bond to give $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3SO_2Me) with retention of configuration at the ruthenium center. Included in this reported are the X-ray crystal structures of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me and $(R)_{Ru}$-Ru(nmcp)(CO)$(PPh_3)SO_2$Me [119]. Thioxophosphane and selenoxophosphane complexes of osmium(0) have been prepared by the sequential addition of CF_3SO_3H and base to $Os(OAc)(PH_2{=}E)(CO)_2(PPh_3)_2$ (E = S, Se). ${}^{31}P\{{}^1H\}$ NMR analysis indicates that the PPh_3 groups are *trans* oriented and strongly coupled. Electrophilic reactivity studies and ab initio SCF calculations are discussed. The X-ray structure of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}PHS)$ has been solved (see Fig. 5) [120].

The reaction of the ruthenium(II) complexes $Ru(PPh_3)_2(S_4)$ and $Ru(PPh_3)_2({}^{Bu}S_4)$ with NO gas is reported. PPh_3 ligand substitution by NO and S–C bond cleavage of the S_4 and ${}^{Bu}S_4$ ligands accompany this reaction to give the (vinylthio)arenethiolate complexes $Ru(NO)(PPh_3)(S_2)(S_2{-}CH{=}CH_2)$ and $Ru(NO)(PPh_3)({}^{Bu}S_2)({}^{Bu}S_2{-}CH{=}CH_2)$, respectively. It is suggested that the reaction proceeds via 19-electron intermediates [121]. These same two complexes, $Ru(PPh_3)_2(S_4)$ and $Ru(PPh_3)_2({}^{Bu}S_4)$, have also been investigated for their reactivity toward HCl as part of a study on model reactions for oxidoreductases with metal–sulfur centers [122]. The reaction between $[Ru(arene)Cl_2]_2$ (arene = C_6H_6, C_6Me_6, 4-$MeC_6H_4^iPr$) and four molar equiv. of 1,4,6-trithiacyclononane ($[9]aneS_3$) has been found to give $[Ru([9]aneS_3)_2][BPh_4]$ upon the addition of [Na]4-$[BPh_4]$. The X-ray structure of $[Ru([9]aneS_3)_2][BPh_4] \cdot 2DMSO$ is presented along with the associated redox chemistry. The preparation and X-ray crystal structure of the hexathio complex, $[Ru([18]aneS_6)][BPh_4]$, are also described [123].



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Bis-allylic compounds have been examined as substrates in osmium tetraoxide catalyzed dihydroxylation reactions. The reported data indicate that the high diastereofacial differentiation observed may be attributed to a particular ground-state conformation [124]. A report on the stereoselective osmylation of 1,1-disubstituted alkenes has appeared [125]. The use of osmium tetraoxide in the synthesis of (+)- and (−)-pinitol has been reported [126]. Vicinal hydroxylation of alkenes using osmium tetraoxide in the presence of hexacyanoferrate as a cooxidant has been described [127]. The X-ray crystal structures of *cis*-dioxo osmium(VI) esters derived from osmium tetraoxide and cinchona alkaloids as ancillary chiral ligands are presented. The results are discussed in the context of catalytic asymmetric dihydroxylation reactions [128]. Chiral C1-oxygenated allylic silanes have been employed as substrates in catalytic osmylation reactions. The diastereofacial selectivities observed are influenced by the bulk of the silane group and the nature of the substituent on the C1-oxygen [129]. The X-ray crystal structure of an osmium(VI) bisglycolate has appeared [130].

Ruthenium tetraoxide and the stoichiometric oxidant periodic acid have been used in the oxidation of aromatic rings to carboxylic acids. The reported procedure is compatible with functional groups that are known to be acid sensitive [131].

A photochemical study on the decomposition of gaseous ruthenium tetraoxide is reported. The wavelength dependence and the nature of the primary and secondary photoproducts are discussed [132]. IR data of highly vibrationally excited osmium tetraoxide are discussed. A strong nonlinear interaction of the vibrational modes is observed and a theoretical model that explains the observed spectrum is presented [133]. A report describing sample introduction techniques for the determination of osmium isotope ratios by inductively coupled plasma mass spectrometry has appeared [134].

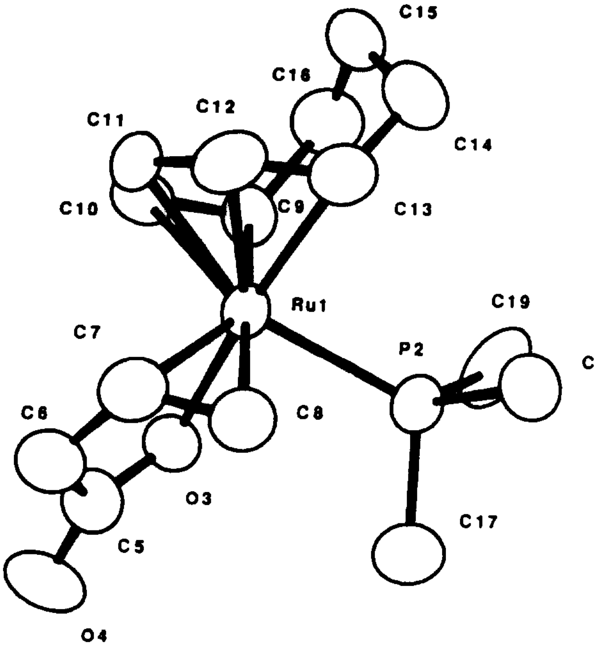
Kinetic data for the substitution of aqua and hydroxo ethylenediaminetriacetate compounds with thiocyanate and thiourea have been collected. The influence of the pendant group in the ruthenium(III) complexes studied is described [135]. The carboxylate complexes $Ru(PhCO_2)_2(PPh_3)_2(CO)_2$ and $Ru(p\text{-}MeC_6H_4CO_2)_2(PPh_3)_2(CO)_2$ have been prepared from $Ru(CO)_3(PPh_3)_2$ and the appropriate carboxylic acid. The phosphine ligands adopt a *trans* orientation in these octahedral ruthenium(II) complexes. The X-ray structure of the former complex is presented [136]. The saturated carboxylate complexes $Ru(O_2CR'')(CO)(RC{=}CHR')(PPh_3)_2$ have been synthesized from the corresponding dichloro complexes. The X-ray structure of $Ru(O_2CMe)(CO)(CH{=}CHPh)(PPh_3)_2$ reveals *trans* phosphine groups and an η^2-acetate moiety [137]. The reaction between salicylaldehyde and $RuH_2(CO)(PPh_3)_3$ and $OsH_2(CO)(PPh_3)_3$ has been studied. The *o*-hydroxybenzyl alcohol complex $Ru(OC_6H_4CO)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2 \cdot$ solvent and $Os(OC_6H_4CO)(CO)_2(PPh_3)_2$ have been characterized. The X-ray structures for the CH_2Cl_2 and MeOH solvated complexes are included [138]. A study on the reactivity of PPh_3 toward $Ru_2Cl(\mu\text{-}O_2CAr)_4$ has appeared. The chemistry associated with the mixed-valence complex $[Ru_2(\mu\text{-}OH_2)\mu\text{-}O_2CAr)^{3+}]$ is presented [139]. 3-Butenoic acid reacts with Ru(cod)(cot) in the presence of added PMe_3 to give the ruthenium(II) complex $Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})\{\eta^1(O),\eta^2(C,C')\text{-}OCOCH_2CH{=}CH_2\}(PMe_3)$. The X-ray crystal structure of the product indicates that a piano-stool coordination exists around the ruthenium center (see Fig. 6) [140].

A review article on the photochemistry and photophysics of *trans*-d^2-dioxo complexes of osmium(VI) has been published [141]. The dioxo complex $Os(O)_2(mes)_2$ has been allowed to react with a wide variety of donor ligands to give $Os(O)_2(mes)_2L_2$. The structures of several of these dioxo complexes have been solved by X-ray diffraction analysis and the redox chemistry is presented [142]. The synthesis and X-ray structure of $Os(O)_2(Me)_2(py)_2$ and the trimer $[Os(O)_2(Me)_2(py)]_3$ are described. The report also includes the electron diffraction structure of $Os(O)(Me)_4$. A flow chart for the funtionalization of osmium tetraoxide to organoosmium oxides is described [143]. Monooxo complexes of osmium(VI) and ruthenium(VI) have been prepared from $[M(O)Cl_4][Ph_4P]_2$ or $[Os(O)_2(OSiMe_3)_4][Ph_4P]_2$ using $(Me_3SiCH_2)_2Mg$. The new complexes were characterized by solution NMR measurements, and IR and UV-visible spectroscopy. Cyclic voltammetric data reveal that each compound exhibits a quasi-reversible one-electron oxidation. The molecular structure of $Os(O)(CH_2SiMe_3)_4$, as determined by X-ray diffraction analysis, reveals a distorted square pyramidal geometry about the osmium center with the four carbon ligands defining the base of the square pyramid [144]. A full paper on the comparative reactivity of isoelectronic nitrido, methylimido, and oxo osmium(VI) complexes has appeared [145]. The electronic properties of oxo/acetate-bridged ruthenium complexes have been reported [146]. The synthesis and structures of dioxoruthenium(VI) complexes have been presented. The high-yield synthesis of $Ru(O)_2(py)_2(O_2CR)_2$ (R = Me, Et, Pr, ^{i}Pr, Ph) is achieved by using barium ruthenate as a starting material. The X-ray crystal structure of the diacetate complex, $Ru(O)_2(py)_2(O_2CMe)_2$, supports the existence of a linear *trans*-dioxo moiety (see Fig. 7). Oxygen atom transfer reactivity to various substrates is discussed with respect to the long ruthenium–oxo bond lengths observed in these complexes [147].

Osmium macrocycle complexes, OsL (L = macrocycle), have been synthesized from 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclopentadecane, 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexane, and *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene. Multiple redox states and pH-dependent redox couples are observed in the *trans*-dioxo complexes. Thermal alkene oxidation reactions using *trans*-$[OsL(O)_2]^{2+}$ indicate that these complexes are poor oxidants [148]. The mechanisms of two-electron reduction of *trans*-dioxoruthenium(VI) to *trans*-aquooxoruthenium(VI) and disproportionation of *trans*-dioxoruthenium(V) have been studied [149]. The luminescent excited state of several *trans*-dioxoosmium(VI) complexes has been examined in electron-transfer quenching reactions [150].

A single-crystal neutron diffraction study of $CsRu[SO_4]_2 \cdot 12H_2O$ has appeared. The adopted structure conforms to a β alum modification [151]. Buckminsterfullerene reacts with osmium tetraoxide in the presence of pyridine to give the corresponding osmate ester as a 2:1 adduct. The carbon framework is not disrupted in this reaction [152]. Catalytic oxidation results and flow detection of carbohydrates at ruthenium dioxide modified electrodes have been published [153].

Tris(3,5-di-t-butylbenzoquinone) complexes of ruthenium and osmium have been examined for periodic trends in charge distribution of second- and third-row transition metals. Cyclic voltammetry studies indicate that both complexes exhibit two oxidations and two reductions at similar potentials. The report includes the X-ray crystal structures of the *cis* and *trans* isomers of $Ru(DBQ)_3$ and of *trans*-$Os(DBQ)_3$. Variable-temperature NMR data reveal that racemization proceeds by a trigonal twist mechanism at low temperatures while at higher temperatures structural isomerization and racemization by a rhombic twist mechanism are observed [154]. The reaction between PQQ and *cis*-$Ru(bpy)_2Cl_2$ affords a green *o*-quinone derivative with intense MLCT transitions [155]. Double chloride displacement in the chlorocarbene complex $Ru\{=CCl(pyrrolyl)\}Cl_2(CO)(PPh_3)_2$ is observed upon treatment with catechol in the presence of pyridine. The product, $Ru\{=C(OC_6H_4O)(2\text{-}N\text{-}methylpyrrolyl)I(CO)_2(PPh_3)_2$, which was obtained after reaction with MeI, has been characterized by IR spectroscopy and single-crystal X-ray diffraction analysis [156]. The synthesis and characterization of new ruthenium(II) phenolates have been presented [157]. New *trans*-(α-dioximato)ruthenium complexes have been prepared and their electronic and redox properties examined [158].



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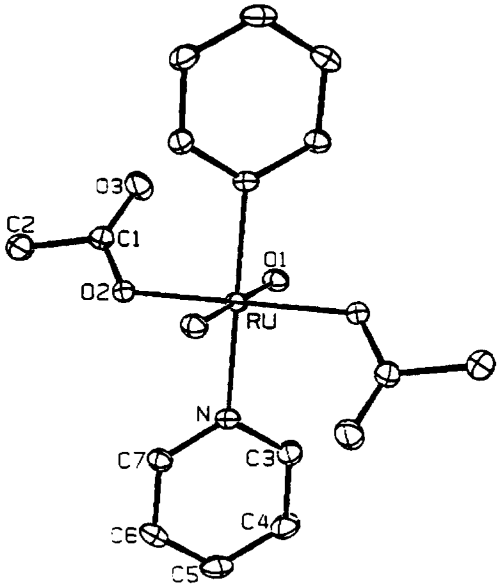

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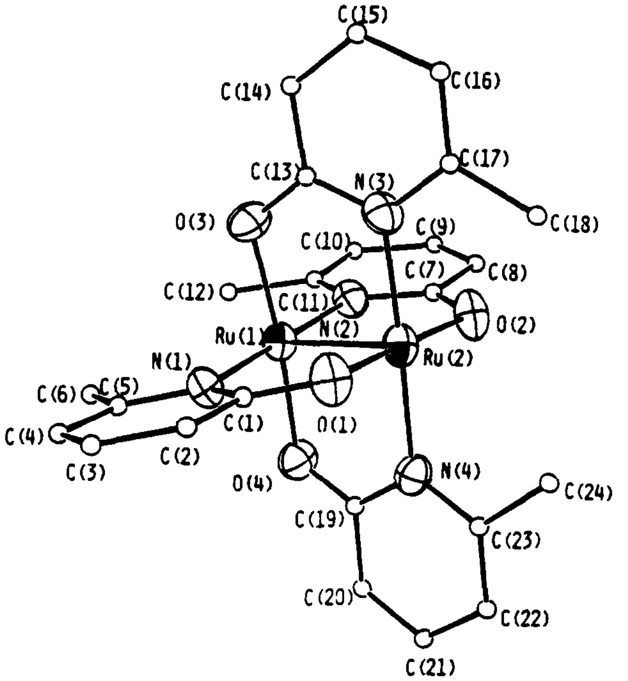
Data on the electrochemical *vs.* the self-exchange kinetics of $[Ru(hfac)_3]^{0/-}$ are discussed as a function of solvent [159]. The mixed-ligand complexes $Ru(acac)_2(tfpb)$, $Ru(acac)(tfpb)_2$, $Ru(acac)_2(hfac)$, and $Ru(dpm)_2(hfac)$ have been synthesized and explored by cyclic voltammetry. The molecular structure of $Ru(acac)(tfpb)_2$ was determined by X-ray diffraction analysis [160]. A report describing the mechanism of intramolecular rearrangements in $Ru(acac)(tfpb)_2$ has been published [161].

2.7. *Nitrogen ligands*

The X-ray crystal of $[\{Os(NH_3)_5\}_2(\eta^2:\eta^2\text{-}\mu\text{-}C_6H_6)]^{4+}$ has been published. Thermolysis of this $\eta^2:\eta^2$-μ-benzene complex gives the $\eta^2:\eta^6$-μ-benzene complex, $[\{Os(NH_3)_5\}\{Os(NH_3)_3\}(\eta^2:\eta^6\text{-}\mu\text{-}C_6H_6)]^{4+}$, which has been characterized in solution by ^1H NMR spectroscopy [162]. The 20-electron complex $Os(N\text{-}2,6\text{-}C_6H_3^iPr)_3$ has been synthesized and structurally characterized. The diffraction results reveal that the osmium center adopts a trigonal planar geometry. PMe_2Ph has been allowed to react with the imido complex to afford $Os(N\text{-}2,6\text{-}C_6H_3^iPr)_2(PMe_2Ph)_2$ and $Me_2PhP{=}NAr$ while the oxo-imido complex $OsO(N\text{-}2,6\text{-}C_6H_3^iPr)_3$ has been obtained from the reaction between the imido complex and Me_3NO [163]. *cis*-$Ru(PPh_3)_2Cl(phenox)_2$ has been synthesized and examined by cyclic voltammetry. The redox chemistry is discussed in terms of a possible model system for both oxygenase and dioxygenase metalloenzymes [164]. A report describing the preparation and reactions of $Ru(DAD)L_2(E)I$ (L_2 = CO, norbornadiene; E = R, H, COR, $SiMe_3$) has appeared. X-Ray diffraction data on $Ru(DAD)(C_7H_8)Me(I)$ indicate that the methyl group is oriented *cis* to the DAD and norbornadiene ligands [165]. Several new 2-hydroxypyridinate complexes of the form $Ru_2(Xhp)_4$ (X = 6-Me, 6-Cl, 6-Br) have been prepared and characterized by X-ray crystallography. Magnetic susceptibility measurements reveal that all three complexes are magnetically similar with a spin-triplet/orbital-singlet ground state derived from a $\delta^{*2}\pi^{*2}$ electron configuration. The X-ray structure of $Ru_2(mhp)_4$ is shown in Fig. 8 [166].

Mixed ligand complexes of ruthenium(II) edta have been synthesized from $[Ru(edtaH)Cl]^-$ by using the ligand cytosine, uracil, 2-thiocytosine, 2-aminopyrimidine and 5-aminouracil [167]. Several purine ligands have been allowed to react with $[Ru(edtaH)Cl]^-$ to give monomeric and dimeric ruthenium(II) edta complexes [168]. The reaction between $[Ru(hedta)(H_2O)]^-$ and uridine and cytidine nucleosides has been investigated. The resulting complexes, $[Ru(hedta)L]^-$ (L = uridine or cytidine ligand), were characterized by ^1H and ^{13}C NMR spectroscopy, cyclic voltammetry, and differential-pulse polarography [169]. A paper describing the electrochemical parametrization of metal complex redox potentials has appeared. Ruthenium(III)/ruthenium(II) redox couples serve as the electrochemical standard [170]. Oxidation of $[Ru(edta)(OH)_2]^-$ has been reported to give a dimeric $Ru^{III}Ru^{IV}$ ion. The low-temperature resonance Raman data and water-oxidizing properties of this dimer are discussed [171].



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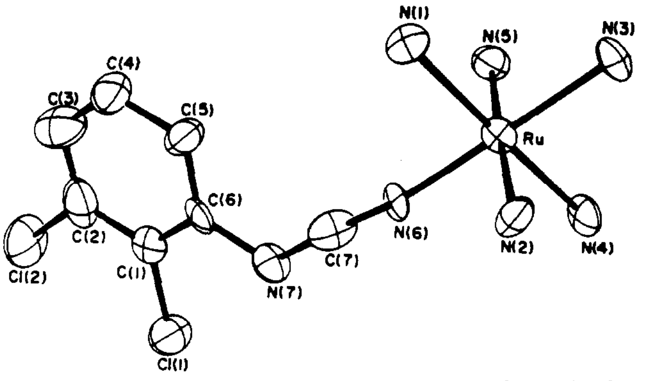
The synthesis and spectroscopic characterization of (phthalocyaninato)osmium(II) and biaxially coordinated (phthalocyaninato)osmium(II) derivatives have been published [172]. The synthesis and photoproperties of $Ru(octabutoxyphthalocyanine)(py)_2$ are presented. The triplet-state properties have been measured by laser flash photolysis and the rate constants for energy transfer from the triplet state to O_2 are reported [173].

$[Ru(CN)_6]^{4-}$ is reported to form a charge-transfer complex with 4,4′-dicyanophenyl-bipyridinium dichloride in the solid state and in solution. Thin films of this charge-transfer complex have been examined electrochemically [174]. The oxidation kinetics of ascorbic acid and 1,2- and 1,4-dihydrobenzenes by $[Ru(CN)_6]^{3-}$ have been described [175]. A mixed-valence ruthenium cyanide modified electrode has been prepared and examined in cysteine, cystine, methionine, and thiocyanate oxidation reactions [176]. The kinetics and mechanisms of electron-transfer reactions with $[Ru(CN)_6]^{4-}$ and $[Ru(CN)_6]^{3-}$ in aqueous solution have been investigated. ^{13}C NMR line-broadening experiments have been employed in the measurement of the electron self-exchange rate constant for the $[Ru(CN)_6]^{4-/3-}$ redox couple [177]. The synthesis of $[Ru(CN)_6][^nBu_4N]_3$ is described. Polymer functionalization experiments using this ruthenium cyanide complex are also presented [178].

The results of studies on long-range electron transfer in ruthenium-modified cytochrome c have appeared [179]. A report dealing with a numerical algorithm that is used to survey proteins for their electron-tunneling pathways is presented [180]. A cyclic voltammetric study of three ruthenium-modified electron-transfer proteins along with model derivatives obtained by attachment of $[Ru(NH_3)_5]^{3+/2+}$ to specific histidine residues has appeared [181]. The energetics of intramolecular electron transfer in $[Ru(NH_3)_5]^{2+}$ modified Stellacyanin are reported. Included in this report are the standard enthalpy and entropy for the protein-coordinated $[Ru(NH_3)_5(His)]^{2+/3+}$ redox couple [182].

The macrocyclic complex *cis*-$[Ru(L)(Cl)_2][ClO_4]$ has been obtained from the reaction between $[Ru(Cl)_5(H_2O)][K]_2$ and 1,4,7,10-tetramethyl-1,4,7,10-tetra-aza-cyclotridecane. The X-ray crystal structure and the UV-visible spectrum, which exhibits an intense $p_\pi(Cl)$ $d_\pi(Ru)$ charge-transfer band at 378 nm, are included [183]. The synthesis, characterization, and redox examination of *trans*-$[Ru(L)O_2]^{2+}$ have been published. The cationic dioxo complex is prepared from $[Ru(Cl)_5(H_2O)][K]$ and the ligand N,N′-dimethyl-bis(2-pyridylmethyl)propylenediamine. Oxidation results using the dioxo complex are presented [184]. A report describing the oxygenation and carbonylation studies of several ruthenium(III) Schiff base complexes has been published [185]. The synthesis, characterization, and ligand binding studies of ruthenium(III) Schiff base complexes have appeared [186]. EPR data on stable ruthenium(III) Schiff base complexes have confirmed the low-spin Ru^{III} $4d^5$ configuration associated with these complexes. The EPR results on the axially coordinated chloride and carbonyl derivatives are presented [187].

Two histidine groups in the *i* and *i* + 4 positions of a peptide have been functionalized by using $[Ru(NH_3)_4(H_2O)_2]^{2+}$. It is claimed that the resulting complex, $[Ru(NH_3)_4(L)_2]^{3+}$, can prevent helix nucleation [188]. The molecular hydrogen complex $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ has been prepared from $[Os(NH_3)_5][OTf]_3$. One-electron oxidation affords $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{3+}$, which is shown to be able to hydrogenate acetone to isopropyl alcohol. The advantages of using methanol as a reaction solvent in the preparation of $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ are discussed [189]. The effect of the magnetic field on the rate of the outer-sphere electron-transfer reaction between $[Ru(NH_3)_5]^{2+}$ and $[Co(NH_3)_6]^{3+}$ is discussed. The data reveal that the transition state of this reaction exhibits a strong coupling of the ruthenium and cobalt magnetic dipoles [190]. The nature and activation of ruthenium amines in X zeolites have been studied by using ESR and ESR modulation measurements [191]. The binding of $[Ru(NH_3)_6]^{3+}$ and $[Ru(bpy)_3]^{2+}$ to a bi-conductive polymer film has been reported [192]. A report dealing with the synthesis and electrochemistry of pterins coordinated to tetraammineruthenium(II) has appeared [193]. The $b_1^* \leftarrow b_1$ LMCT oscillator strength in $[Ru(NH_3)_5(2,3\text{-dichlorophenyl)cyanamide}(-1)]^{2+}$ has been examined as a function of solvent [194]. The new polypeptide-bridged complexes $[(NH_3)_5 4\text{-}Ru(Pro)_n Co(NH_3)_5][CF_3CO_2]_5$ (n = 0–4) have been synthesized and examined in long-range electron-transfer studies [195]. Magnetodynamic effects on outer-sphere electron-transfer reactions have been examined in the reactant pair $[Ru(NH_3)_6]^{2+}/[Co(NH_3)_6]^{2+}$ [196]. New pentaammineruthenium(II) complexes with an ancillary phenylcyanamide ligand have been synthesized and examined by cyclic voltammetry. The X-ray structure of $[Ru(NH_3)_5(2,3\text{-}Cl_2\text{-}pcyd)][SO_4] \cdot EtOH$ reveals that the cyanamide ligand is nearly coplanar as a result of strong π coupling to the ruthenium center (see Fig. 9) [197].



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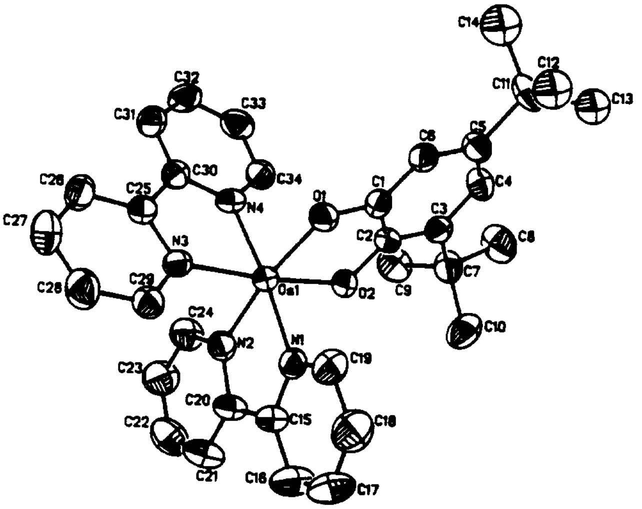
A molecular orbital study using the INDO/1 method has been carried out in order to study the interaction between *cis*-$[Ru(NH_3)(HN{=}CH{-}CH{=}NH)_2(O)]^{2+}$ and methanol. The results were discussed in the context of alcohol oxidation reactions [198]. Resonance Raman data for tris(μ-halo)bis(triammineruthenium)(II) ions are reported [199]. The reaction between $[Ru(NH_3)_4(1,10\text{-phen})]^{3+}$ and SO_3^{2-} has been examined in aqueous solution at 25°C. Sulfonation of the 1,10-phen ligand is shown to occur under acidic conditions [200]. The kinetics and mechanism of the reaction between alkyl radicals and $[Ru(NH_3)_5X]^{2+}$ (X = halides, aquo, thiocyanate, azide) have been published [201].

The photoselection spectra for a series of Ru^{II} diimine complexes have been reviewed [202]. A review article describing the energetics and dynamics of solvent reorganization in charge-transfer excited states has been published. The complex chosen was $Ru(bpy)_2(CN)_2$ and its MLCT excited state was examined in a series of aliphatic alcohols [203]. A study involving the redox regulation based on the pH-dependent hydrolysis of $[Ru(bpy)_2(2\text{-pyridinecarboxaldehyde})]^{2+}$ has appeared [204]. The ruthenium complex $[Ru(bpy)L(H_2O)]^{2+}$ (L = polypyrrole functionalized terpyridine ligand) has been prepared and electrochemically examined [205]. The use of $RuBr_3(DMSO)_3$ and *fac*- and *mer*-$[RuCl_3(DMSO)_3]$ in the synthesis of ruthenium(III) bipyridine and 1,10-phenanthroline complexes has been described [206]. Mono- and di-ferrocenyl bipyridyl ligands containing *trans* conjugated alkene linkages between the ferrocene redox centers and the 4,4′-substituted 2,2′-bipyridine ligand have been employed in the synthesis of new ruthenium(II) complexes. The redox chemistry and electrochemical polymerization reactions are described [207]. A study demonstrating a direct electrical communication between graphite electrodes and a surface adsorbed glucose oxidase/osmium(bpy)$_2$(pvp)Cl polymer system has been presented [208].

The observation of temperature-modulated photoredox reactivity and photosubstitution in [Ru(dmb)$_2$(3-Brpy)$_2$]$^{2+}$ has been noted [209]. Comparative studies on the charge distribution in [M(bpy)$_2$(quinone)]^n complexes (M = Ru, Os; $n = 0$, $+1$, $+2$) are presented. The three quinone ligands used in this study were derived from catechol, 3,5-di-t-butylcatechol, and tetrachlorocatechol. The X-ray structure of [Os(bpy)$_2$-(DBcat)][ClO$_4$] reveals that the quinone ligand is best described as a catechol on the basis of the carbon–oxygen bond lengths (see Fig. 10) [210].



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The synthesis and luminescent behavior of *cis*-[(4,4′-X$_2$-5,5′-Y$_2$-2,2′-bipyridine)Os(CO)(Cl)]$^+$ complexes (X = NEt$_2$, OMe, Me, H, Cl, Y = H; X = H, Y = Me; X = Y = Me) have been described. Linear correlation of electrochemical, ν(CO), and absorption/emission data with Hammett σ constants of the bipyridyl substituent groups are presented and are used in prediction of ground- and excited-state properties in analogous complexes [211]. Photochemical CO$_2$ reduction has been reported when [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ is used with the electron acceptors triethanolamine and 1-benzyl-1,4-dihydronicotinamide [212]. A cadmium-coated electrode containing Ru(CN)$_4$(bpy) has been prepared and examined in emission intensity and excited-state lifetime studies [213]. The X-ray structure of a ruthenium bis-2,2′,N,N′-bipyridyl ketone complex has appeared [214].

2,2′:6′,2″-Terpyridine reacts with [Os(N)X$_4$]$^-$ (X = Cl, Br) to give [Os(N)(terpy)(X)$_2$][X]. The X-ray structure of [Os(N)(terpy)(Cl)$_2$][Cl] reveals that the chloride ligands are situated *trans* to each other relative to the nitrido ligand. The nitrido ligand may be reduced by either electrochemical or chemical means in acidic solution to give the amine complex Os(NH$_3$)(terpy)Cl$_2$ [215]. The synthesis of [Ru(terpy)(tmen)(H$_2$O)]$^{2+}$ and the corresponding oxo complex has been described. The kinetics for the reaction between the oxo complex and alkenes, which affords epoxides, have been measured [216]. The synthesis of functionalized asymmetrical bis(terpyridine)osmium(II) complexes is described [217]. *trans* phosphine complexes of the form [Ru-(NO$_2$)(PR$_3$)$_2$(terpy)]$^+$ have been prepared and characterized by spectroscopic techniques and cyclic voltammetry [218]. The X-ray structure of *trans*-[Ru(NO$_2$)-(terpy)(PMe$_3$)$_2$][ClO$_4$] has been reported [219].

The reaction between *trans*-[Ru(OH)(py)$_4$(NO)]$^{2+}$ and azide ion is reported to give Ru(OH)(N$_3$)$_2$(py)$_2$-(NO) and Ru(N$_3$)$_3$(py)$_2$(NO). The ruthenium nitrosyl reactant fails to react with NH$_2$OH or OH$^-$ at pH < 13. The redox chemistry for these and other related complexes are reported along with the structural determination of *trans*-[Ru(OH)(py)$_4$(NO)][PF$_6$]$_2$ · H$_2$O, which displays *cis*-pyridines and *trans*-OH and NO groups [220]. The oxidation of *trans*-RuCl(NO$_2$)(py)$_4$ and *trans*-[Ru(NO$_2$)(H$_2$O)(py)$_4$]$^+$ is reported to give *trans*-[RuCl(O)(py)$_4$]$^+$ and *trans*-[Ru(ONO)(O)(py)$_4$]$^+$, respectively. Plausible mechanisms for these transformations are presented [221]. The eletrodeposition of ruthenium in poly(4-vinylpyridine) films on glassy carbon electrodes has been examined and studied for hydrogen evolution activity [222].

A luminescence quenching study has been carried out on [Ru(bpy)$_3$]$^{2+}$ in micelles and hemimicelles as a means to gain information on the location of this Raman and luminescence probe. Stern-Volmer data for doxylstearic acid quenching of [Ru(bpy)$_3$]$^{2+}$ are included [223]. Picosecond time-resolved resonance Raman data are reported for MLCT excited states of [Ru(bpy)$_3$]$^{2+}$, [Ru(1,10-phen)$_3$]$^{2+}$, and the mixed ligand complexes of bpy and 1,10-phen [224]. Time-resolved emission spectroscopy has been employed in the spectroscopic study of [Ru(bpy)$_3$]$^{2+}$. The observed data are discussed in terms of the glass transition temperature of the medium and the counter cation [225]. A normal-coordinate analysis has been completed for the ground and ^{3}MLCT excited states of [Ru(bpy)$_3$]$^{2+}$ [226]. Homoleptic and heteroleptic ruthenium(II) bpy and bpz complexes have been investigated by resonance Raman spectroscopy [227]. Highly resolved emission data from $[Os(bpy\text{-}d_8)_3]^{2+}$ have been obtained. The three lowest excited states are blue-shifted by 32–35 cm^{-1} [228]. Exciton hopping in excited state $[Ru(bpy)_3]^{2+}$ has been examined by using picosecond polarized absorption spectroscopy. Exciton hopping is discussed in terms of solvent-mediated electron-transfer theory [229]. Vibrational frequency data have been used in the molecular structure determination of the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ [230]. The time-dependent nonradiative decay in the MLCT excited state of $[Ru(bpy)_3]^{2+}$ has been explored [231]. Bimolecular quenching of the MLCT excited triplet states of $[Ru(bpy)_3]^{2+}$, $[Ru(1,10\text{-}phen)_3]^{2+}$, and $[Ru(4,7\text{-}diphenyl\text{-}1,10\text{-}phen)_3]^{2+}$ has been studied by laser flash spectroscopy. The ΔG^0 dependence and rate of back electron transfer within the geminate radical pair are discussed in terms of nuclear rearrangement and nuclear tunneling [232]. The interchromophonic coupling model has been used in the analysis of photoselection spectra of ruthenium(II) diimine complexes [233]. The photogalvanic and photophysical behavior of ruthenium(II) diimine has been investigated in sodium lauryl sulfate solutions [234]. The effects of $HClO_4$ on the $[Ru(bpy)_3]^{2+}$-catalyzed photoreduction of phenacyl halides in MeCN are presented [235]. A study describing the photoinduced formation of spatial patterns in the Belousov-Zhabotinskii reaction has appeared. The reaction was catalyzed by $[Ru(bpy)_3]^{2+}$ [236]. The enantiopreferential DNA binding of $[Ru(1,10\text{-}phen)_3]^{2+}$ has been examined by using circular dichroism and linear dichroism spectroscopy [237]. A report describing the use of electrospray ionization as a new tool for the analysis of ionic transition-metal complexes has appeared. This technique has successfully generated intense beams of intact gas-phase cations from $[Ru(bpy)_3][Cl]_2$ and $[Ru(1,10\text{-}phen)_3][Cl]_2$ [238].

Cyclic voltammetric and electrogenerated chemiluminescent data have been used to study the electrostatic binding of $[Os(bpy)_3]^{2+}$ to calf thymus DNA. The observed ECL was greater for the DNA-bound complex [239]. The description of a novel optoelectrochemical microprobe that allows for optical and electrochemical measurements has appeared. The system was used in an ECL study involving $[Ru(bpy)_3]^{2+}$ and persulfate [240]. The electrochemiluminescence quantum yield for several ruthenium(II) diimine complexes has been measured [241].

A report on CO_2 reduction using $[Ru(bpy)_3]^{2+}$ as a catalyst has appeared. The ruthenium(II) bpy complex is activated by visible light irradiation, producing formate as the major product. CO_2 reduction derives from an intermediate Ru^I species, which is produced by reductive quenching of optically excited $[Ru(bpy)_3]^{2+}$ by added tertiary amine [242].

The kinetics and mechanism of arsenious acid oxidation by peroxodisulfate ion are presented. The rate of the reaction is accelerated by visible light excitation of $[Ru(bpy)_3]^{2+}$ [243]. The redox potentials of the azide and dithiocyanate radicals have been measured by using the reference couple $[Ru(bpy)_3]^{2+/3+}$ in a two-pulse radiolysis experiment [244]. A radiolytic study of the reaction of hydroxyl radical with $[Ru(bpy)_3]^{2+}$ has been published [245]. The kinetics of electron-transfer reactions between $[Ru(bpy)_3]^{2+}$ and several Co^{II} macrocycles have been studied by laser flash photolysis. The data have been evaluated in the context of Marcus theory [246]. Sulfite oxidation by $[Os(bpy)_3]^{3+}$ has been reinvestigated in aqueous solution at room temperature. The products from this reaction are $[SO_4]^{2-}$ and $[Os(bpy)_3]^{2+}$. The measured value of k_1 allows for an accurate evaluation of this reaction by Marcus theory [247]. The photosensitized reduction of vic-dibromo and keto compounds has been carried out by using $[Ru(bpy)_3]^{2+}$ and triethylamine as photosensitzer and electron donor, respectively [248].

A report describing the use of an optical fiber oxygen sensor, which employs the luminescent properties of $[Ru(1,10\text{-}phen)_3]^{2+}$, has appeared [249]. The rates of electron-transfer reactions of metal bound monolayers have been measured [250]. Polymer-bound ruthenium(II) and osmium(II) complexes have been examined as energy storage systems and investigated for their mixed-valence properties [251]. Thin polymeric films of poly$[Ru(bpy)_2(vpy)_2]^{2+}$, poly$[Ru(4,4'\text{-}dimethyl\text{-}bpy)_2(vpy)_2]^{2+}$, and poly$[Ru(4,4',5,5'\text{-}tetramethyl\text{-}bpy)_2(vpy)_2]^{2+}$ have been employed in imaging studies. Spatially resolved, film-based structures are obtained by photochemical ligand-loss reactions involving the deposited polymeric films [252]. $[Os(bpy)_3]^{2+}$ has been codeposited with silicotungstates to produce novel composite polynuclear films on electrodes. The catalytic properties of these new composite films are described [253]. Saveant-Andrieux theory has been used in the study of cysteine oxidation at Nafion-$[Os(bpy)_3]^{2+/3+}$ film coated glassy carbon electrodes [254]. Thin films of $[Os(bpy)_2(vpy)_2]^{2+}$ on gold electrodes have been prepared by reductive polymerization [255]. A report on clay-adsorbed $[Ru(bpy)_3]^{2+}$ enantiomers has been presented [256]. Polypyridinyl complexes of ruthenium(II) having ancillary 4,4'-dicarboxy ester–bpy ligands attached to polypyrrole films have been prepared [257]. The photoelectrochemical properties of TiO_2 electrodes in photosensitzed reactions employing $[Ru(4,4'\text{-}dicarboxylic\ acid\text{–}bpy)_3]^{2+}$ have been explored [258]. $[Ru(vbpy)_3]^{2+}$ based electrodes have been investigated in speciation studies [259]. Resonance Raman and time-resolved resonance Raman data are reported for surface interaction studies involving ruthenium(II) diimines and TiO_2 [260]. The dynamics of charge recombination from $[Ru(4,4'\text{-dicarboxylic acid–bpy})_3]^{3+}$ and transparent TiO_2 membranes are discussed [261]. Chromophore/quencher assemblies based on poly(tris[4-(2-pyrrol-1-ylethyl)-4′-methyl-bpy)]-ruthenium(II) have been prepared and examined as molecular-level photoconversion systems [262]. A glassy-carbon electrode coated with poly-$[Ru(vbpy)_3]^{2+}$ has been used to generate H_2O_2, which reacts with added Mn(TPP)Cl to produce an active olefin epoxidation reagent [263]. Polypyridine complexes of osmium (II) have been prepared and examined in three electron-hopping conductive polymer films [264]. Polymer structure and the mechanism of formation of electrochemically polymerized $[Ru(4,4'\text{-dimethyl-bpy})_3]^{2+}$ have been explored [265]. Scanning electrochemical microscopy has been used to study the surface of a Nafion-$[Os(bpy)_3]^{2+}$ thin film [266]. The redox conductance of ruthenium(II) and osmium(II) diimine complexes has been measured. The conductance data were analyzed in terms of the metal present, back-bonding ability of the ligands, and distance between localized states [267].

The optical properties of $[Ru(bpy)_3]^{2+}$ encapsulated in zeolites have been probed by using diffuse reflectance absorption, emission, Raman, and time-resolved emission and Raman spectroscopies. Data from these and other surface-science techniques reveal that the zeolite does not appreciably perturb the ground-state structure of $[Ru(bpy)_3]^{2+}$ [268].

The cations $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ have been exchanged onto clay surfaces and examined in quenching studies [269]. A stopped-flow electric dichroism study dealing with the adsorption of enantiomeric and racemic $[Ru(1,10\text{-phen})_3]^{2+}$ by colloidally dispersed montmorillonite has been published [270]. Photophysical and photochemical data for hectorite-adsorbed $[Ru(bpy)_3]^{2+}$ have been presented [271]. Clay-modified electrodes based on $[Ru(bpy)_3]^{2+}$ have been synthesized and examined electrochemically [272].

$[Ru(bpy)_2(dppz)]^{2+}$ has been examined as a spectroscopic probe for nucleic acids. The luminescence observed in the DNA-bound complex serves as a sensitive marker for DNA conformations [273]. The ECL behavior of $[Ru(bpy)_3]^{2+}$ in aqueous solutions containing persulfate has been studied. A bright orange color was observed in this experiment [274]. A comprehensive ESR study of homo- and heteroleptic mono- and dinuclear tris(α-diimine)ruthenium radical anions has been published. Fast spin exchange on the ESR time scale is reported for all of the singly reduced homoleptic complexes [275]. Photophysical data are presented that support the existence of a thermally accessible, higher lying MLCT excited state for Ru^{II} and Os^{II} polypyridyl complexes. The higher lying MLCT state, which is found 300–800 cm^{-1} above the lowest lying MLCT state, can make an appreciable contribution to nonradiative decay at room temperature [276]. Data supporting intraligand electron transfer in the excited MLCT states of mixed ligand ruthenium(II) polypyridyl complexes have been obtained by using picosecond Raman spectroscopy [277]. Novel π-conjugated complexes have been prepared from $[Ru(bpy)_3]^{2+}$ and 3,3′-diazamethylviologen. The redox chemistry of these complexes is reported along with the ESR and electronic absorption data [278]. The use of ^{99}Ru NMR spectroscopy of several ruthenium(II) polypyridyl complexes has been discussed [279]. The synthesis and characterization of 9,10-phenanthrenequinone complexes of ruthenium(II) are reported. Included in this report is the X-ray structure of $[Ru(bpy)_2(phi)][BF_4]_2$, which reveals substantial back-bonding to the ruthenium center from the phi ligand. The X-ray structure of this complex is shown in Fig. 11 [280].

Ruthenium(II) complexes with dmpt, dppt, and tpf have been prepared and examined by ^1H NMR, emission, and Raman spectroscopies. The redox data are correlated with the emission and absorption data [281]. The photophysical and electrochemical properties of $[Ru(bpy)_n(tap)_{3-n}]^{2+}$ ($n = 0–3$) have been published. The homoleptic complex $[Ru(tap)_3]^{2+}$ displays unusual photophysical behavior. Unlike similar complexes whose emission lifetimes are modulated by nonradiative deactivation from the ^3MLCT state, $[Ru(tap)_3]^{2+}$ deactivates by an intersystem crossing process to a metal-centered triplet (^3MC) state [282]. $[Os(dpp)_3]^{2+}$ and $[Os(4,4'\text{-carboxylic acid–bpy})_3]^{2+}$ have been explored for their protonation behavior in the ground

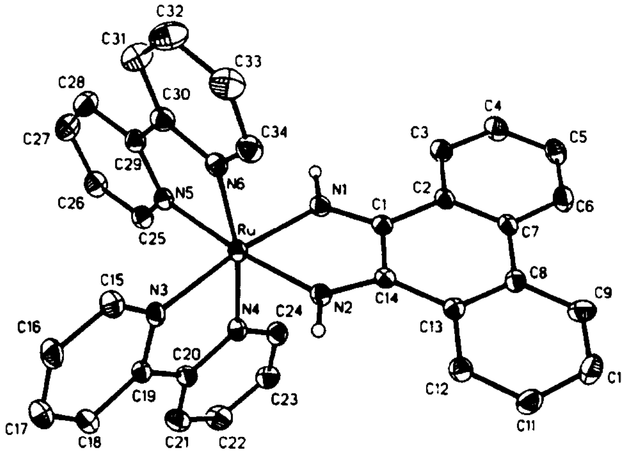
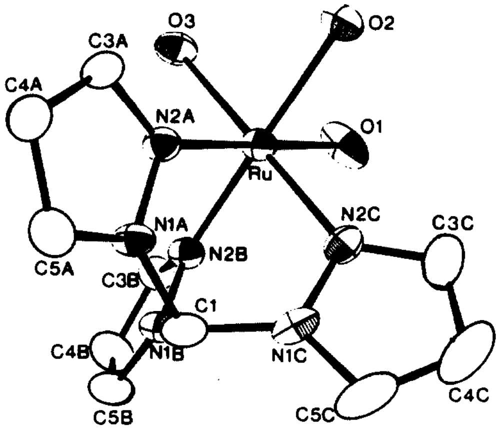


Fig. 11. Reprinted with permission from Inorg. Chem., Copyright 1990 American Chemical Society.

and excited states [283]. The synthesis, and spectroscopic and redox properties of [Ru(bpy)$_2$(3,3′-dimethyl-5,5′-bis-1,2,4-triazole)]$^{2+}$ are discussed. The pK$_a$ values of this complex have been measured by UV-visible titrations, revealing two deprotonations. The bis(triazole) ligand is reported to be a weak π-acceptor ligand [284]. The synthesis, characterization, and redox study of [Ru(bpy)$_2${3-(2-hydroxy-phenyl)-5-(pyridin-2-yl)-1,2,4-triazole}]$^{2+}$ have been published. The X-ray structure of the title compound, as the bis [PF$_6$]$^-$ salt and acetone solvate, accompanies this report [285]. Ligand–metal interactions and excited-state properties in ruthenium(II)-diimine complexes are discussed. Ligand σ- and π-bonding properties are included in this report [286].

The synthesis and coordination chemistry of 6′,6″-bis(2-pyridyl)2,2′ : 4,4″ : 2″,2‴-quaterpyridine have been published [287]. Heteroleptic [Ru(bpy)$_2$(L–L′)]$^{2+}$ and homoleptic [Ru(L–L′)$_3$]$^{2+}$ (L–L′ = new pyrazole-containing bidentate ligands) have been synthesized and fully characterized by ^{1}H and ^{13}C NMR spectroscopy. Data from CV studies are presented and discussed [288]. The complex [Ru(bpy)$_2$(dppz)]$^{2+}$ has been prepared and electrochemically examined. The photochemical properties were studied, and excited-state quenching studies have been carried out [289]. The complex Ru(pz)$_2$(pzH)$_3$(DMSO) has been obtained from the reaction between *cis*-RuCl$_2$(DMSO)$_4$ and [K][H$_2$B(pz)$_2$] as a result of B–N bond cleavage in the dihydrobis(1-pyrazolyl)borate ligand. An X-ray diffraction study confirms the identity of the ruthenium complex. In a comparative study, *cis*-RuCl$_2$(DMSO)$_4$ reacts with free pyrazole to give RuCl$_2$(pzH)$_2$(DMSO)$_2$ [290]. The acid-base chemistry of ruthenim(II) triazole complexes has been investigated. The X-ray structure of [Ru(bpy)$_2${3-methyl-5-(pyridin-2-yl)-1,2,4-triazole}]$^{2+}$ is presented and the data from luminescence titrations are discussed [291]. The reaction between RuCl$_3$ and 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole in DMF leads to [Ru(L–L′)$_2$(CO)Cl]$^+$, which exists as a mixture of isomers. Recrystallization of this mixture has allowed for the isolation of the *cis* isomer, which has been characterized by X-ray diffraction analysis. Spectroscopic and redox data reveal that the pyridyltriazole ligand is a weaker π acceptor than the bpy ligand [292]. The HPLC separation and characterization of linkage isomers of the 3-(pyridin-2-yl)-1H-1,2,4-triazole complex of Ru^{II}(bpy)$_2$ are reported [293]. The synthesis and X-ray diffraction structure of [Ru(tpm)(H$_2$O)$_3$][O$_3$SC$_6$H$_4$Me-4]$_2$ · 1.5H$_2$O have been published. The terdentate ligand tpm occupies three *cis* sites, giving rise to the observed facial isomer. The three water molecules occupy the three remaining octahedral sites. Cyclic voltammetric studies reveal the existence of Ru$^{III/II}$, Ru$^{IV/III}$, and Ru$^{V/IV}$ redox couples. One of the chelate arms opens up past the Ru^{IV} couple, resulting in the formation of a *trans*-dioxo Ru^{IV} complex (see Fig. 12) [294].



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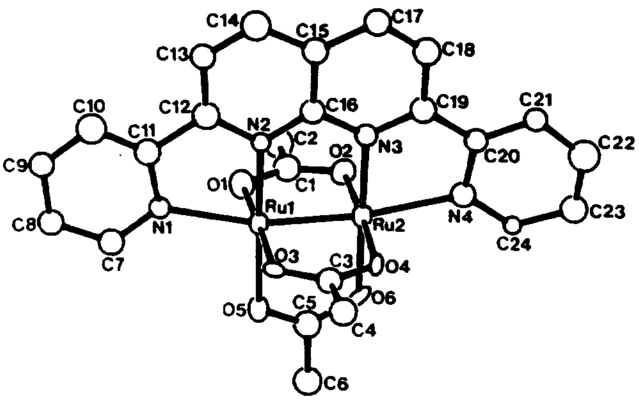
The synthesis and characterization of *cis*-[Ru(tepa)Cl$_2$]$^+$, [Ru(N$_4$O)(H$_2$O)]$^{2+}$, and [Ru(N$_4$O)(O)]$^{2+}$ are described. The latter complex reacts, after oxidation to Ru^V, with organic substrates in hydrogen atom/hydride abstraction reactions [295]. The synthesis and X-ray structure of *o*-phenylene-diaminebis(*o*-benzoquinonediamine)ruthenium(II) have been published [296]. The synthesis and ^{1}H NMR study of ruthenium (II) 2,2′-biimidazole complexes, [Ru(bpy)(2,2′-biimidazole)]$^{2+}$, have been described [297].

A vibronic coupling model for the calculation of mixed-valence line shapes in the Creutz-Taube ion has been described. It is argued that the band shape of the Creutz-Taube mixed-valence band arises from coupling to a molecular mode before and after the b$^*_{2g}$(d,π) b$_{3u}$(d,π^*) excitation [298]. Electrochromism in the near-IR absorption spectra of bridged ruthenium mixed-valence complexes has been studied [299]. The synthesis and spectroscopic examination of [(NH$_3$)$_5$Ru–L–Ru(NH$_3$)$_5$]$^{4+}$ (L = 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion) have been described. UV-vis–near-IR and electrochemical data indicate that this complex is a weakly coupled mixed-valence dimer. The X-ray structure of the dianionic ligand is included in this report [300]. A theoretical model dealing with electron transfer and energy transfer through bridged-ruthenium systems has been reported [301]. Data for electron transfer and energy transfer in bis(pentaamineruthenium) complexes that are bridged by α,ω-dipyridyl *trans*-polyenes have been published. The observed electronic spectral data have been deconvoluted into π π^*, Ru ligand, ligand Ru, and intervalence transitions [302].

A review article on intramolecular energy transfer in Ru^{II}–Ru^{II} and Ru^{II}–Cr^{III} dimers has appeared [303]. The ligand-bridged complexes $[(OC)_3ClRe\text{–}L\text{–}M(bpy)_2]^{2+}$ (M = Ru, Os; L = dpp, dpq) have been synthesized and examined by a variety of spectroscopic techniques [304]. Dimeric ruthenium-osmium complexes bridged by an asymmetric triazolate bridging ligand have been synthesized and characterized by X-ray crystallography. Intervalence charge-transfer bands are reported for these complexes [305]. Ruthenium(II)–chromium(II) and ruthenium(II)–rhodium (III) complexes with a linking cyanide ligand have been prepared and explored in photoinduced energy transfer schemes [306]. The use of $[[Ru(bpy)_2(CN)_2]_2Ru\text{-}\{bpy(CO_2)_2\}_2]^{2+}$ as an antenna-sensitized device in visible light collection is described. Emission and excitation spectra reveal that light is absorbed by the Ru $(bpy)_2(CN)_2$ antenna moieties and transmitted to the central $[Ru\text{-}\{bpy(CO_2)_2\}_2]^{2-}$ sensitized moiety [307]. Data that support an intervalence hole-transfer pathway have been published [308]. The heptanuclear complex $Ru[(\mu\text{-dpp})Ru(bpy)(\mu\text{-dpp})Ru(bpy)_2]_3^{14+}$ has been prepared and its luminescence and redox behavior explored [309]. The dpp-bridged complex $[(bpy)_2Ru(\mu\text{-dpp})Ru(bpy)_2]^{4+}$ and $[Ru(bpy)_2(dpp)]^{2+}$ have been examined by excited-state absorption spectroscopy. The redox properties, including the results from spectroelectrochemical studies, are discussed [310]. The bridged complexes $[(bpy)_2Ru\text{–}L\text{–}RhH_2(PPh_3)_2]^{3+}$ (L = bpm, dpp, dpq) have been synthesized and investigated in competitive hydrogen loss and emission after optical excitation [311]. New luminescent and redox-reactive tetranuclear ruthenium(II) polypyridyl complexes have been described [312]. Electrochemical stability constants are reported for the mixed-valence species $[(bpy)_2M(\mu\text{-bptz})M(bpy)_2]^{4+/5+/6+}$ and $[(bpy)_2M(\mu\text{-adc–Me}^{2-})M(bpy)_2]^{2+/3+/4+}$ (M = Ru, Os) [313]. The attachment of $[Ru(bpz)_3\{Fe(CN)_5\}_n]^{2-3n}$ (n = 1–6) to different electrodes is described [314]. The role of the LUMO in determining the stability of $[\{Ru(bpy)_2\}_2dpq]^{4+}$ and $[\{Ru(bpy)_2\}_2dpp]^{4+}$ has been discussed [315]. The dinuclear complexes $[Ru_2Cl_2(bpy)_2bpnp]^{2+}$ and $[Ru_2(\mu\text{-OAc})_3bpnp]^{+}$ have been synthesized and spectroscopically characterized. One-electron oxidation of the former dimer affords the corresponding mixed-valence Ru^{II}–Ru^{III} complex. The X-ray crystal structure of the latter complex is shown in this report (Fig. 13) [316].



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The ligand-bridged complex $[(4,4'\text{-dimethyl–bpy})_2Ru(\mu\text{-bbpe})Ru(4,4'\text{-dimethyl–bpy})_2]^{4+}$ has been prepared and its MLCT excited state examined for bbpe-modulated electron delocalization [317]. The symmetrical mixed-valence dimers $[(bpy)_2ClRu\text{-}4,4'\text{-bpy–Ru}(NH_3)_5]^{6+/5+/4+}$ exhibit resonance-enhanced Raman scattering in the near-IR region [318]. New ruthenium complexes containing a bridging 1,4,5,8-tetraoxonaphthalene ligand have been synthesized and examined for mixed-valence interactions [319].

A paper describing the synthesis and redox properties of bis[bis(bipyridine)ruthenium(II)]-3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl has been published [320]. The synthesis, redox properties, and X-ray crystal structure of $Ru_2(OAc)_3(dcnp)$ have been reported [321]. New cofacial bioctahedral complexes of ruthenium have appeared [322]. The preparation and properties of new ruthenium(II) complexes possessing biimidazole and bibenzimidazole ligands are described [323]. New ruthenium complexes bearing the ligand 1,3,5-tris[{(5-(ethoxycarbonyl)-2,2′-bipyridyl-5′-yl)carbonyl}-benzyl(amino)methyl]benzene have been synthesized and fully characterized [324]. The photophysics and photoredox reactivity of ligand-bridged ruthenium(II) polypyridyl dimers and their monomeric analogues have been presented [325]. The heterobimetallic complex [4-(3-ferrocenylpropyl)-4′-methyl-2,2′-bpy]bis(2,2′-bpy)-osmium dichloride has been synthesized and the diffusion coefficients of the iron and osmium centers have been determined by using electrochemical techniques. Identical diffusion coefficients were observed for the two metal centers in homogeneous solutions. However, the diffusion coefficients were observed to be unequal for a Nafion coating containing this complex. An explanation for the disparate diffusion coefficients is presented [326]. Studies of $[(H_3N)_5Co\text{–}L\text{–}Ru(edta)]^{+}$ (L = $^{-}O_2C$-4-pyridyl) incorporated as a counterion in Nafion films on glassy carbon electrodes have been reported [327].

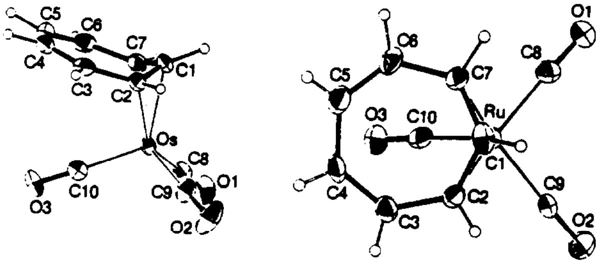
The triazenido complex $Ru_2(RNNNR)_2(CO)_6$ (R = p-tolyl) reacts with 2,2′-bpy to give $Ru_2(RNNNR)_2(CO)_4(bpy)$ and which is shown by X-ray diffraction analysis to possess a pair of non-equivalent ruthenium atoms [328].

2.8. *Alkenyl and alkylidene complexes*

Sodium cyanide reacts with the vinylidene complex $[CpRu(PMe_3)_2{=}C{=}(Me)Ph]^+$ in high stereo selectivity to give (*Z*)-$CpRu(PMe_3)_2C(CN){=}C(Me)Ph$. The (*Z*) isomer readily isomerizes under acid conditions to the (*E*) isomer [329]. $Ru(CF_3)Br(CO)_2(PPh_3)_2$ reacts with BBr_3 to give the bromoalkylidene complex $[RuBr(CO)_2\{{=}C(C_6H_4PPh_2)_2\}][BBr_4]$. This intermediate loses CO and BBr_3 on standing to furnish $RuBr_2(CO)[{=}C(C_6H_4PPh_2)_2]$. The molecular structure of this neutral alkylidene complex has been determined by X-ray crystallography [330]. The reactions of alkynes with the vinyl ester complex $CpRu\{C(CO_2Me){=}CHC(O)OMe\}(PPh_3)$ have been examined. A mechanism, which suggests either ester carbonyl group or PPh_3 displacement by the incoming alkyne, is presented. The X-ray crystal structures of two of the products are discussed [331]. A report on the carbonylation of alkenyl ruthenium complexes has appeared [332].

2.9. *π-Complexes*

Tetrafluoroethylene and maleic anhydride react with $M(CO)L(PPh_3)_3$ (M = Ru, Os; L = CO, *p*-tolyl-NC) and $OsCl(NO)(PPh_3)_3$ by phosphine loss to yield the corresponding π complex. The X-ray structure of $Ru(CF_2{=}CF_2)(CO)_2(PPh_3)_2$ exists as an equilibrating mixture of isomers in solution, possessing *cis*- and *trans*-PPh_3 groups. This equilibrium has been examined by variable-temperature NMR measurements; the Van't Hoff plot has been constructed and ΔS evaluated. While the X-ray structure of Os(maleic anhydride)$(CO)_2(PPh_3)_2$ exhibits only one crystalline form having *cis* PPh_3 groups, solution measurements reveal the presence of *cis* and *trans* isomers [333]. η^2-Bound arene complexes of pentaamineosmium(II) have been selectively hydrogenated to alkenes in the presence of Rh and Pd heterogeneous catalysts. The hydrogenation reaction is regio- and stereoselective, occurring anti to the osmium center. The structure of the 3-methoxycyclohexene complex $[Os(NH_3)_5(\eta^2\text{-}C_7H_{12}O)][OTf]_2$ has been solved by X-ray diffraction analysis [334]. The π complex $Ru\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_5H_6)$ reacts with dienes with displacement of 1,3-cyclopentadiene to give compounds of the form $Ru\{P(OMe_3)_3\}(\eta^4\text{-}C_4Ph_4)(\eta^4$-1,3-diene). A reaction mechanism is discussed and X-ray structures of several products are presented [335]. The isolation and X-ray structure of the cycloheptatrienyl anions $[(\eta^3\text{-}C_7H_7)M(CO)_3]^-$ (M = Ru, Os) are reported. Low-temperature ^1H and ^{13}C NMR data reveal that the solid-state structure is adopted in solution (Fig. 14) [336].



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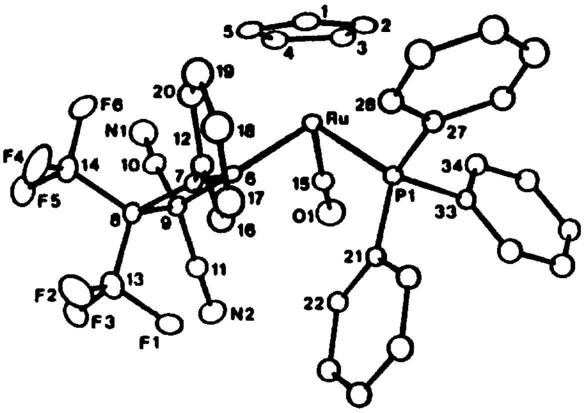
A review article dealing with the chemistry of cyclopentadienylruthenium complexes has been published [337]. The X-ray crystal structure of $[Cp^*Ru(CO)_2(H_2O)][CF_3SO_3]$, which was prepared from $Cp^*Ru(CO)_2Me$, has been presented [338]. Cyclopentadienyl complexes of ruthenium and osmium have been investigated by MS(FD) and MS(EI) spectrometry [339]. $(\eta^5\text{-}C_5Ph_5)Ru(CO)_2Br$ has been obtained from the reaction between $Ru_3(CO)_{12}$ and C_5Ph_5Br. The dicarbonyl complex has been examined in phosphine/phosphite substitution reactions. Included in this report is the X-ray crystal structure of $(\eta^5\text{-}C_5Ph_5)Ru(CO)(PPh_3)Br$ [340]. The redox properties of $(\eta^5\text{-}C_5Ph_5)Ru(CO)(L)Br$ (L = P-ligands) have been studied and the oxidized products examined by ESR spectroscopy [341]. Carbon–carbon bond formation has been observed in the coupling reaction of acetylenes and allyl alcohols using $CpRu(PPh_3)_2Cl$ as a catalyst [342]. $CpRu(SnPh_3)(CO)_2$ has been allowed to react with PhLi to furnish the carbene complex $CpRu(SnPh_3)(CO)\{{=}C(OEt)Ph\}$ after ethylation. The $SnPh_3$ group is readily displaced by iodide to give $CpRuI(CO)\{{=}C(OEt))Ph\}$, which has been structurally characterized [343]. The X-ray structure of $[CpRu(PPh_3)(NO)(Cl)][PF_6]$ is reported [344]. Ammonium hexafluorophosphate reacts with $CpRu(PPh_3)_2Cl$ and $CpRu(PPh_3)(CN^tBu)Cl$ to furnish the ammonia cations $[CpRu(PPh_3)_2(NH_3)][PF_6]$ and $[CpRu(PPh_3)(CN^tBu)(NH_3)][PF_6]$, respectively. The X-ray crystal structures of both products are presented and the spectroscopic data obtained from the $^{15}NH_3$ isotopomers are discussed [345]. Data relating to the stereoelectronic effect of the formyl ligand in $Cp^*Ru(CO)(PPhMe_2)(CHO)$ have been discussed [346].

$CpRu(PMe_3)_2(C{\equiv}CH)$ reacts with $Cp_2Zr(H)(Cl)$ to give $CpRu(PMe_3)_2CH{=}CHZr(Cl)Cp_2$, which exhibits an agostic interaction between the Zr center and the CH group that is β to the Zr, as determined by NMR and IR data [347]. The reaction of $[CpRu(CO)(MeCN)_2]^+$ with *S*-*trans*-1,3-dienes has been reported to afford stable allyl complexes [348]. γ-Oxoisocyanide ruthenium complexes have been synthesized from the reaction between $CpRu(PPh_3)_2CN$ and α,β-unsaturated ketones in the presence of HBF_4 [349]. The molecular hydrogen complexes $[CpRu(CO)L(H_2)]^+$ (L = PCy_3,



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PPh_3, PMe_2Ph, PMe_3) and $[CpRu(L\text{–}L)(H_2)]^+$ (L–L = dmpe, dmdppe, (*R*)-prophos) have been synthesized by protonation of the corresponding neutral hydride. Several of the pentamethylcyclopentadienyl derivatives have also been prepared. ^1H NMR measurements confirm the identity of the η^2-H_2 moiety. Data are presented that show that the η^2-H_2 complex, which is the kinetic product of protonation, undergoes an intramolecular isomerization to the *transoid* dihydride. The reactivity of the η^2-H_2 and dihydride complexes is discussed [350]. $[CpRu(MeCN)_3]^+$, a source of $CpRu^+$, has been allowed to react with RuBrene to give $[CpRu(RuBrene)]^+$. The effect of temperature in determining the site of attachment of the $CpRu^+$ fragment is described [351]. $CpRu(PPh_3)_2(C{\equiv}CMe)$ and $CpRu(L)_2(C{\equiv}CPh)$ {where $L_2 = (PPh_3)_2$, dppe, $(CO)(PPh_3)$} react with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene to yield the corresponding σ-cyclobutenyl complexes $CpRu\{C{=}C(R)C(CF_3)_2C(CN)_2\}(L)_2$, of which the structure of $CpRu\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(CO)(PPh_3)$ has been crystallographically characterized (Fig. 15). The reactivity of these complexes has been explored and the crystal structures of several of the products are included in this report [352].

The complexes $CpRu(PPh_3)_2SR$ (R = ^{n}Pr, ^{i}Pr, 4-C_6H_4Me) have been prepared and examined for their proclivity to participate in CS_2 insertion reactions. CO readily displaces one PPh_3 group to give the corresponding carbonyl complex. The thioxanthate complex $CpRu(PPh_3)S_2CS^nPr$ has been isolated from the reaction between $CpRu(PPh_3)_2S^nPr$ and CS_2 and fully characterized by solution and X-ray diffraction techniques [353]. The binding and activation of halocarbons by cyclopentadienylruthenium(II) complexes are reported. The halocarbon-bound complexes are best described as Ru^{II} complexes rather than Ru^{IV} products of oxidative addition. This report includes details on the X-ray crystal structure of $[CpRu(CO)(PPh_3)(IC_6H_4\text{-}p\text{-}Me)][PF_6]$ and the halocarbon displacement chemistry, which may be achieved by using inorganic and organic nucleophiles [354]. ^{187}Os NMR data have been collected for cyclopentadienylosmium complexes by using indirect heteronuclear 2D NMR spectroscopy [355]. Allylic halides oxidatively add to $(\eta^5\text{-}C_5R_5)Ru(L)_2X$ complexes (L = CO, PPh_3; R = H, Me) to give η^3-allylcomplexes of the type $CpRuX_2(\eta^3\text{-allyl})$. A pseudo-piano-stool structure is reported for $CpRuBr_2(\eta^3\text{-}C_3H_3)$, where the two bromides and two terminal carbons of the *endo*-η^3-allyl ligand define the piano stool's legs [356]. New ^1H NMR data have led to the reinterpretation of the ^1H NMR spectra of $CpRu(PPh_3)H_3$ and $Cp^*Ru(PPh_3)H_3$ [357].

The X-ray structures of $CpRu\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(MeCN)(PPh_3)$ and $[CpRu\{C{=}C(Ph)C(CF_3)_2C(CN)_2\}(PPh_3)]_2\text{-}\mu\text{-}\{(NC)_2C{=}C(CF_3)_2\}$ have been reported [358]. Open and half-open ruthenocene and osmocene complexes have been prepared and characterized by solution and X-ray diffraction methods [359]. The synthesis, structure, and reactivity of {η^4-(5e)-butadienyl}cyclopentadienylruthenium complexes are reported [360].

The complexes Cp^*RuL_2Cl (L_2 = CO, PMe_3, dienes) are readily obtained from the tetramer $[Cp^*RuCl]_4$, whose X-ray structure accompanies this report. High yields of the η^4-diene complexes are reported by using $[Cp^*RuCl]_4$ as a starting material. The X-ray structure of $Cp^*Ru(\eta^4$-S-*cis*-1,3-butadiene)I is presented [361]. The chemistry and X-ray structure of the coordinatively unsaturated complex $Cp^*Ru(acac)$ have been published. The acac complex serves as a useful precursor to a wide range of $Cp^*Ru(acac)L$ complexes [362]. The 16-electron complex $Cp^*Ru(OMe)(PCy_3)$ has been synthesized from the methoxy-bridged dimer $[Cp^*Ru(OMe)]_2$. Reaction of this PCy_3 complex with H_2 and HBF_4 affords the known trihydride $Cp^*RuH_3(PCy_3)$ and $[Cp^*Ru(C_6H_9PCy_2)]^+$ [363]. The results of a Cl/OMe exchange study using $[Cp^*Ru(OMe)]_2$, $[Cp^*RuCl]_4$, and $Cp^*Ru(COD)Cl$ have been published [364].

The base-free silylene complexes $[Cp^*Ru(PMe_3)_2{=}Si(SR)_2]^+$ (R = Et, *p*-MeC_6H_4) have been prepared by treating $Cp^*Ru(PMe_3)_2Si(SR)_3$ with Me_3SiOTf [365]. The synthesis and reactivity of ruthenium silyl and diphenylsilylene complexes have been published. ^1H NMR evidence is presented for the existence of the base-free silylene complex $[Cp^*Ru(PMe_3)_2{=}SiPh_2]^+$ in solution. The X-ray crystal structures of $Cp^*Ru(PMe_3)_2SiPh_2H$, $Cp^*Ru(PMe_3)_2SiPh_2(OTf)$, and $[Cp^*Ru(PMe_3)_2SiPh_2(MeCN)][OTf]$ are presented and their features discussed [366]. The nitro complexes $CpRu(L)_2(NO_2)$ (L = PPh_3, $\frac{1}{2}$dppe, $\frac{1}{2}$dppm, $\frac{1}{2}$dmpe) have been prepared by starting from $RuCl_3 \cdot 3H_2O$. Reaction of these nitro complexes with HPF_6 affords the cationic nitrosyl complexes $[CpRu(L)_2(NO)]^{2+}$. The spectroscopic and redox data for these complexes are reported [367]. The oxidation behavior of CpRu(CO)(PR_3)Me in MeCN (R = Ph, Cy) has been explored by using derivative cyclic voltammetry. The role of 19-electron acetonitrile complexes in the oxidatively induced Ru–methyl bond cleavage reaction is discussed [368].

1,1′-bis(chlorocarbonyl)ruthenocene has been condensed with *p*-t-butylcalix[4]arene to yield a redox-active ruthenocene-calix[4]arene dimer [369]. The dibenzothiophene (DBT) and hexahydrodibenzothiophene (HHDBT) complexes $[CpRu(DBT)]^+$, $[CpRu(HHDBT)]^+$, and $[(CpRu)_2(DBT)]^{2+}$ have been synthesized, characterized, and studied in oxidation/reduction reactions. The X-ray structure of $(CpRu)_2(DBT)$, which is obtained from the reaction between $[(CpRu)_2(DBT)]^{2+}$ and $[Et_3BH]^-$, is presented [370]. The tetramethylthiophene (tmt) complex $[(tmt)_2Ru][OTf]_2$ has been examined in base hydrolysis reactions [371]. A report dealing with the rates of electron exchange between Cp_2Ru and $[Cp_2RuBr]^+$ has been published. The effect of solvent, counter anion, and temperature were all treated as variables [372]. The rates of the atom/electron exchange process in Cp_2Os and $[Cp_2OsI]^+$ have been measured by using ^1H NMR spectroscopy [373]. 1,1′-Bis(methylthio)ruthenocene (L–L) has been used as an ancillary ligand in the preparation of $W(CO)_4(L–L)$. The X-ray crystal structure of this complex and ^1H NMR measurements of sulfur inversion are reported [374]. The X-ray crystal structure of $Cp^*Ru(OC_6H_4PPh_2)\{PPh_2(C_6H_4OH)\}$, obtained from the reaction between $PPh_2(C_6H_4OH)$ and $(Cp^*RuCl_2)_n$, has appeared [375]. The synthesis of the ruthenocene complex $(C_5H_4SiHMe_2)_2Ru$ has been described [376].

New osmium(0) and osmium(II) complexes have been obtained from $[(mes)OsCl_2]_n$. Reaction with CO affords $(mes)OsCl_2(CO)$, which serves as an intermediate to other (mes)Os complexes [377]. $(mes)OsCl_2(PMe_3)$ reacts with $NaBH_4$ or $LiAlH_4$ to yield the dihydride complex $(mes)OsH_2(PMe_3)$. When $(mes)OsH_2(PMe_3)$ is irradiated in benzene solution hydrogen is lost, giving the hydrido phenyl complex $(mes)OsH(Ph)(PMe_3)$. The X-ray structures of $[(mes)_2Os_2(\mu\text{-}H)_3]^+$ and $[(mes)OsH(\mu\text{-}H)]_2$ are included in this report [378]. Intermolecular and intramolecular C–H bond activation reactions have been described for (mesitylene)osmium complexes. Complexes of the form (mes)OsH(R)(P) (R = alkyl; P = phosphine) do not undergo alkyl hydride exchange with alkanes or arenes upon heating. It is shown that the 16-electron complexes (mes)OsL are less thermally accessible than its isolobal counterpart Cp^*IrL [379]. Several *p*-cymeneruthenium complexes have been synthesized and spectroscopically characterized. The X-ray structure of $[(MeC_6H_4{}^iPr)Ru(pz)(Hpz)_2][BF_4]$ is presented [380]. 1,1-Diphenylpenta-2,4-diyn-1-ol reacts with $(C_6Me_6)RuCl_2L$ (L = PMe_3, PMe_2Ph) to furnish the corresponding ruthenium cumulene complex. Full solution characterization and the X-ray crystal structure are described [381]. Carbon–hydrogen bond activation has been explored with $(C_6Me_6)Os(CO)H_2$ and related hexamethylbenzene complexes of osmium. Photolysis of $(C_6Me_6)Os(CO)H_2$ in hydrocarbon solvent leads to hydrogen loss and solvent C–H bond activation, giving $(C_6Me_6)Os(CO)H(R)$ (R = Ph, cyclohexyl, neopentyl) and free hexamethylbenzene. The independent synthesis and characterization of each alkyl hydride complex are presented [382]. X-Ray diffraction data for $(C_6Me_6)Os(CO)(cyclohexyl)_2$ are reported. A protonation study of arene-bis(ethylene) complexes of ruthenium and osmium has appeared. HPF_6 addition to $(arene)M(CH_2{=}CH_2)_2$ (arene = C_6Me_6, M = Ru; arene = mesitylene, M = Os) yields the corresponding monoprotonated salt. In the case of the ruthenium complex, variable-temperature ^1H and ^{13}C NMR measurements reveal the existence of a β-agostic ethyl(ethylene) cation $[(C_6Me_6)Ru(CH_2CH_2\text{-}\mu\text{-}H)(CH_2{=}CH_2)]^+$. The osmium complex $[(mes)OsH(CH_2{=}CH_2)_2]^+$ exhibits rapid ethylene ligand rotation about the metal–olefin axis. Hydrogen migration to the ethylene ligands is slow on the NMR time scale, allowing for trapping of the ethyl intermediate by external nucleophiles [383]. The phosphine-substituted complexes $(C_6Me_6)RuCl_2L$ react with excess $Mg(CH_2SiMe_3)Cl$ to yield orthometallated derivatives [384].

The synthesis and spectroscopic characterization of carbene complexes derived from $(arene)RuCl_2L$ have been described [385]. α-Amino acids have been allowed to react with $[(C_6H_6)RuCl_2]_2$ to give the corresponding coordinated amino acid complex $(C_6H_6)RuCl$(amino acid) [386]. L-Alanine and L-alanine methyl ester react with $[(C_6H_6)RuCl_2]_2$ to furnish the structurally characterized amino acid derivatives $(C_6H_6)RuCl$(amino acid). The reaction of 9-ethylguanine with the amino acid complex derived from L-alanine yields a diastereomeric mixture of products [387]. Optically active ruthenium(II) complexes with ancillary α-amino acid ligands have been synthesized. ^1H NMR measurements indicate that the epimerization of $[(p\text{-cymene})Ru(amino\ acid)(MeOH)]^+$ complexes is rapid [388].

The complexes $[CpRu(arene)]^+$ and $[(CpRu)_2(arene)]^{2+}$ (arene = naphthalene, phenanthrene, pyrene, anthracene) have been prepared and examined by cyclic voltammetry. The electrochemical data are discussed in terms of the Cp*Ru/arene interaction and stabilization of the reduction products [389]. Ruthenacyclopentane complexes have been obtained from the reaction between $(C_6Me_6)RuCl_2L$ and 1,4-dilithiobutane. The reported ruthenacyclopentane complexes react with trityl tetrafluoroborate to give η^3-allyl complexes [390]. The synthesis and reactivity of $[(C_6H_6)Ru($*para*-cyclophane$)]^{2+}$ and $[(C_6H_6)Os(acetone)_3]^{2+}$ have been investigated [391].

The reaction between $[(arene)RuCl_2]_2$ and *nido*-$[7\text{-}TeB_{10}H_{11}]^-$ is reported to give metallaheteroborane complexes [392]. A study dealing with regiospecific η-alkylation in $(arene)Ru(Et_2C_2B_3H_5)$ has appeared [393]. The metallacarborane complex $(Et_2C_2B_3H_5)Ru$(*p*-cymene) has been studied in bridge deprotonation/xylyl functionalization reactions [394]. The synthesis, structure, and redox properties of ruthenium complexes with C_2B_3 or C_3B_2 rings are presented [395]. The chemistry of tetradecker sandwich complexes containing the (cymene)Ru fragment has been published [396].

3. Dinuclear complexes

3.1. Homodinuclear complexes

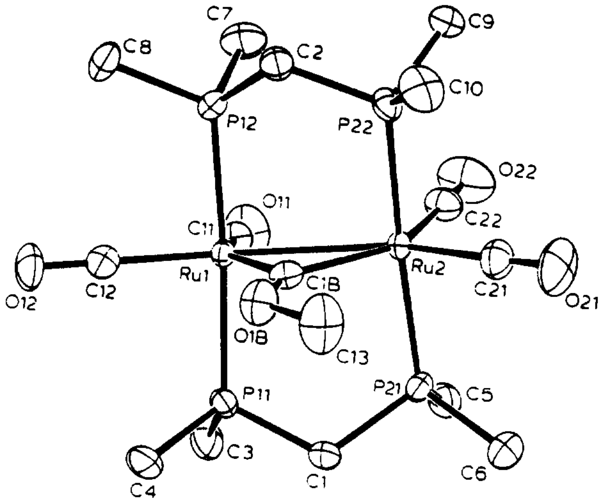
Binuclear ruthenium aquo, hydroxy, and oxo complexes with the ancillary chelating ligand $[CpCo\{(CH_3CH_2O)_2P{=}O\}_3]^-$ have been prepared and structurally characterized [397]. The dimers $Ru_2Cl(O_2CPh)_4$ and $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}OMe)_4$ react with PPh_3 in MeCN to give the diruthenium(III) complexes $[Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2]^{2+}$ and $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$, respectively. X-Ray diffraction analyses have established the molecular structure of these complexes, which are presented as models for the diiron centers in hemerythrin [398]. The X-ray crystal structure of $[Ru_2O_6(py)_4]\cdot 3.5H_2O$ has been solved. This and other pyridine-based oxo dimers have been examined in alcohol to aldehyde and ketone oxidation reactions [399].

The dimer $[Os_2Cl_8][PMePh_3]_2$ and the bromo and iodo analogues have been structurally characterized by X-ray crystallography [400]. The synthesis of an osmium–osmium triple bonded dimer that contains ancillary bromide ligands is reported [401].

The paramagnetic diruthenium complexes $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]$ ($R = {}^iPr$, Et, Cy, Bz, Ph) have been prepared from the reaction between RSNa and $[Cp^*RuCl_2]_2$. The isopropyl derivative has been structurally characterized. The reactivity of selected complexes with CO, ${}^tBuNC$, H_2, and phenylacetylene is described [402]. A one-pot synthesis of $[CpL_2Ru(\mu\text{-}CN)RuL'_2Cp]^+$ (L, L′ = PPh_3, $AsPh_3$, $SbPh_3$; L_2, L'_2 = dppe, dppm) starting from $CpRuL_2X$ and 1,3,5-triazine has been published [403]. The results of an ab initio study of the photoelectron spectra and bonding in $Ru_2(O_2CH)_4$ and $Ru_2(O_2CH)_4(NO)_2$ have appeared. The ground-state configuration of the former complex is predicted to be $\sigma^2\pi^4\delta^*\delta^{*2}\pi^{*2}$ [404]. The synthesis and NMR spectral results of the products derived from the reaction of Lewis acids and biruthenocene are discussed [405].

The pseudo-triple-decker complex $Cp_2Ru_2(\mu\text{-cyclo-}C_8H_8)$ is oxidized at ambient temperature by a two-electron process to afford the stable dication $[Cp_2Ru_2(\mu\text{-cat-}C_8H_8)]^{2+}$. Both ruthenium atoms insert into a C–C bond of the cyclooctatetraene ligand during the oxidation process. At low temperatures, the product of single-electron oxidation has been observed and shown to participate in an ECE–EEC route, which gives the dication at higher temperatures. The X-ray crystal structures of $Cp_2Ru_2(\mu\text{-cyclo-}C_8H_8)$ and $[Cp_2Ru_2(\mu\text{-cat-}C_8H_8)]^{2+}$ are included in this report [406]. Several bis(η^6-hexamethylbenzene)(η^6,η^6-$[2_n]$cyclophane)diruthenium(II,II) complexes have been synthesized. It is demonstrated that two-electron reduction leads to the formation of two cyclohexadienyl anion decks connected by a new carbon–carbon bond [407]. The synthesis and characterization of bis(η^6-hexamethylbenzene)(η^6,η^6-polycyclic aromatic)diruthenium(II,II) complexes (polycyclic aromatic = phenanthrene, 9,10-dihydrophenanthrene, biphenyl, 3,3′,5,5′-tetramethylbiphenyl, 4,5,9,10-tetrahydropyrene, triphenylene) have been presented [408]. The reaction between $(C_6Me_6)RuCl_2(PMe_3)$ and aniline in the presence of $AgBF_4$ yields the anilide-bridged diruthenium complex $[(C_6Me_6)_2Ru_2(\mu\text{-}NHPh)_3][BF_4]$ [409].

The chemistry of bis(cyclopentadienylruthenium) complexes has been reviewed [410]. The synthesis, X-ray structure, and reactivity of the ruthenium–ruthenium double-bonded complex $Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)$ have been published [411]. The interaction of $(C_3F_7)(CF_3)_2COH$ and HCl with $Cp_2Ru_2(CO)_4$ in liquid xenon solvent has been examined by IR spectroscopy [412]. The synthesis of 1,3-bis(cyclopentadienylruthenium dicarbonyl)-1,4-butadione has been reported [413]. A photochemical study of $Cp_2Ru_2(CO)_4$ and $CH_2[CpRu(CO)_2]_2$ in frozen gas matrices at 12 K has been published. Near UV-visible optical excitation of $Cp_2Ru_2(CO)_4$ produces the corresponding 17-electron radical complex as the major product along with small amounts of the triply bridged species $Cp_2Ru_2(CO)_3$ [414]. Matrix isolation techniques have been employed in the photochemical study of $Os_2(CO)_9$ and $Os_2(CO)_8(\mu\text{-}CH_2{=}CH_2)$. Optical excitation leads to ejection of CO and ethylene, respectively. Photolysis studies using plane-polarized light indicate that the dimer has C_{2v} symmetry. Extended photolysis under



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CO ultimately affords $Os(CO)_5$ [415]. The synthesis of $[M_2(CO)_8]^{2-}$ (M = Ru, Os) and $[FeRu(CO)_8]^{2-}$ has been described. The identity of the mixed-metal dimer was ascertained by X-ray crystallography [416]. The molecular structures of the arsinidene complexes $[\{CpRu(CO)_2\}]_2(\mu\text{-}CO)(\mu\text{-}AsR)$ (R = Me, Ph) have been established by X-ray diffraction analysis [417].

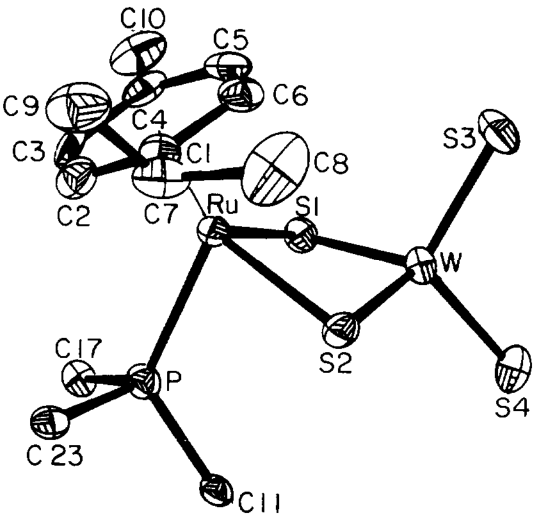
Methyl triflate reacts with $Ru_2(dmpm)_2(CO)_5$ to give two products, which have been isolated by fractional crystallization. X-Ray diffraction analysis has identified one of the products as $[Ru_2(dmpm)_2(CO)_4(\mu\text{-}COMe)]^+$ which results from methylation of the oxygen of the bridging carbonyl group. NMR spectroscopic and mass spectrometry data suggest that the other product is $[Ru_2(dmpm)_2(CO)_5(Me)]^+$ (Fig. 16) [418].

The synthesis and spectroscopic characterization of the diruthenium σ,π-vinyl complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(R){=}C(R)H\}(CO)_5(PPh_3)$ (R = Ph, p-tolyl) and $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5(PPh_3)$ have been presented. ^{13}CO labeling studies and X-ray crystal structures of the bis(tolyl) and diphenylacetylene-derived complexes are included in this study [419]. The phosphido-bridged cation $[Ru_2(CO)_8(\mu\text{-}PPh_2)]^+$ has been prepared and fully characterized. The X-ray crystal structure of this phosphido complex may be considered to be a structural analogue of $Ru_2(CO)_9$ [420]. Acetylide to acetylene transformation via C–C and C–N bond-forming sequences has been described for the edge-bound acetylide complex $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ in the presence of ^tBuNC and Et_2NH [421]. The synthesis of the σ,σ-alkyne-bridged complexes $CpRu(PMe_3)_2[\mu\text{-}\eta^1 : \eta^1\text{-}(MeO_2C)C{=}C(CO_2Me)]ML_n$ (ML_n = $CpRu(CO)_2$, $Mn(CO)_5$, $Re(CO)_5$) has been published. The X-ray structure of the bis(ruthenium) complex is discussed [422].

Dimetalloheterocyclic complexes have been obtained from the reaction between $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]^+$ (R = Me, ^iPr) and alkynes, nitrites, and carbon disulfide [423]. The synthesis of the solvent complexes $[Ru_2(CO)_5(solvent)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}]^{2+}$ (R = Me, ^iPr) has been discussed [424]. The preparation of dithiophosphinate-bridged ruthenium(I) and ruthenium(II) complexes has been described. The structure of $Ru_2(CO)_4(\mu\text{-}S_2PMe_2)_2(PPh_3)_2 \cdot \frac{1}{2}CH_2Cl_2$ accompanies this report [425]. New diruthenium(I) and diosmium(I) containing poly (pyrazolyl)borate ligands have been synthesized and examined by ^1H NMR spectroscopy for their dynamic solution behavior [426]. A report has appeared that describes the chemistry of polymeric ruthenium(I) and biruthenium(I) and biosmium(I) carboxylate-bridged complexes. The X-ray diffraction results of $Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(MeSCH_2SMe) \cdot THF$ are presented [427]. The reaction between $Ru_3(CO)_{12}$ and carboxylic acids and phosphinic acids is reported to give the carboxylate-bridged complexes $Ru_2(CO)_4(O_2CR)_2P_2$ and phosphinate-bridged species $Ru_2(CO)_4(O_2CR)_2P_2$, respectively, after treatment with added P-ligand [428]. Treatment of $Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(PBu_3)_2$ with 170 atm of H_2 at high temperature furnishes phosphine- and phosphido-substituted ruthenium carbonyl hydride clusters of varying nuclearity [429].

3.2. Heterodinuclear complexes

The propargyl-ruthenium complex $CpRu(CO)_2CH_2C{\equiv}CPh$ has been shown to react with $Fe_2(CO)_9$ to give the heterometallic-(allenylcarbonyl) complex $(OC)_3Fe\{\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2\}Ru(CO)Cp$. The molecular structure was unequivocally determined by X-ray diffraction analysis [430]. Nucleophilic attack on multisite-bound acetylides in the dimers $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (M = Ru, Os) has been investigated. Cyclohexylamine reacts at the α-carbon of the acetylide ligand [431]. $HFeRu(CO)_5(R\text{-}C{=}CH\text{-}CH{=}N^iPr)$, which is the first known heterobimetallic monoazadiene, has been synthesized from $Ru_2(CO)_6(R\text{-}C{=}CH\text{-}CH_2NR)$ and $Fe_2(CO)_9$. The X-ray crystal structure of the product is discussed with respect to its isolobal relationship to $CpFe(CO)_2H$ [432]. Heterobimetallic M–M′ complexes (M = Ru, Os; M′ = Rh, Ir, Au) with ancillary pyrazolate or imidazolate ligands are described [433]. The alkanediyl complexes $CpFe(CO)_2(CH_2)_nRu(CO)_2Cp$ (n = 3–5) have been prepared. Spectroscopic and analytical data are reported [434]. A review of the chemistry associated with heterobimetallic zirconium-ruthenium complexes has been published [435]. $CpRu(L)_2C{\equiv}CH$ (L = P-ligand) reacts with $CpWCl(CO)(PhC{\equiv}CPh)$ in the presence of the halide acceptor $TlBF_4$ to give the ruthenium-tungsten ethynyl-bridged



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complex $[Cp(L)_2Ru(\mu\text{-}C{\equiv}CH)W(PhC{\equiv}CPh)(CO)Cp]^+$, which has been fully characterized in solution and by X-ray diffraction analysis [436]. Reaction of $[(p\text{-cymene})RuCl_2]_2$ with $[WS_4]^{2-}$ yields $[(p\text{-cymene})RuCl]_2WS_4$ while $(p\text{-cymene})RuCl_2(PPh_3)$ reacts with $[WS_4]^{2-}$ to give $(p\text{-cymene})RuWS_4(PPh_3)$, which has been structurally characterized (Fig. 17) [437].

4. Polynuclear complexes

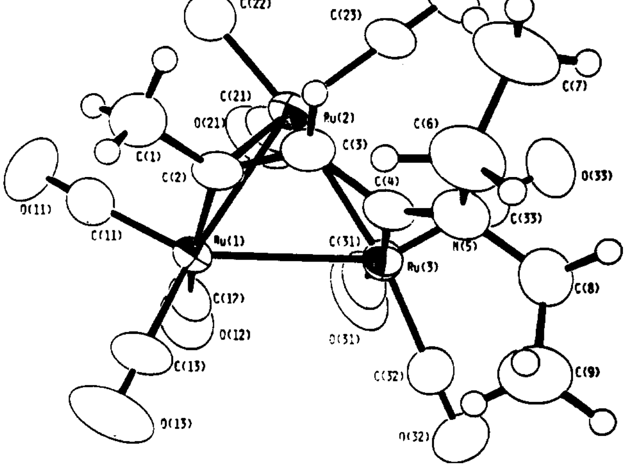
4.1. Trinuclear clusters

4.1.1. Simple and hydrocarbon ligands

A review on the mechanistic studies of the photochemical reactivity of $M_3(CO)_{12}$ (M = Ru, Os) has been published. The photochemical reactivity of $M_3(CO)_{12}$ is discussed in terms of a unified model [438]. The solid-state and dynamic solution motion exhibited by $M_3(CO)_{12}$ (M = Ru, Os) and its derivatives has been examined and interpreted by the ligand polyhedral model [439]. Carbon–nitrogen bond cleavage and carbon–carbon bond coupling in the reactions of $Ru_3(CO)_{12}$ with tertiary amines have been documented. Of the compounds described, $Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}CH_3CC(H)C{=}N(Et)_2\}$ and $Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}\eta^3\text{-}(Et)_2N{=}C(H)C(H)CCH_2\}$ have been structurally characterized by X-ray diffraction analysis (see Fig. 18). Mechanistic schemes, which account for all of the observed products, are presented [440].

The details associated with the photochemical grafting of $Os_3(CO)_{12}$ to inorganic metal oxides have been published. The physisorption of $Os_3(CO)_{12}$ to silica gel has been found to be highly dependent on the excitation wavelength [441]. The hydride clusters $M_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CMe_2NHCOR)$ (M = Ru, Os) have been obtained from the reaction between $M_3(CO)_{12}$ and $HC{\equiv}CCMe_2NHCOR$. The butterfly clusters $M_4(CO)_{11}(\mu_4\text{-}\eta^2\text{-}HC{\equiv}CMe_2NHCOR)$ have also been isolated and characterized by NMR measurements and X-ray crystallography in the case of the ruthenium cluster (R = Ph) [442]. Chiral monocarboxylic acids and $Ru_3(CO)_{12}$ react to give carboxylate-bridged diruthenium complexes [443]. A review article on edge double-bridged trinuclear ruthenium and osmium complexes has appeared [444]. The reactivity of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O{=}CNMe_2)$ with diarylacetylenes furnishes diruthenium complexes of the form $Ru_2(CO)_6(\mu\text{-}O{=}CNMe_2)\{\mu\text{-}\sigma,\pi\text{-}RC{=}CH(R)\}$ (R = aryl). The reactivity of the dinuclear products is explored [445]. The reaction between $Ru_3(CO)_{12}$ and oximes leads to fragmentation of the triruthenium cluster and formation of bisoximato-bridged diruthenium complexes of the form $Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}ONCR'R'')_2L_2$ (L = intact oxime) [446]. $Ru_3(CO)_{12}$ and bis(dimethylgermyl)alkanes react to give $Me_2Ge(CH_2)_nGe(Me)_2Ru(CO)_4$ (n = 1, 2) under photochemical or thermal conditions [447].

The observation of a dichloromethane bridging ligand has been reported in the cluster complex $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2$, which was obtained from the reaction between $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2$ and phenylacetylene and CH_2Cl_2. X-Ray diffraction analysis confirms the existence of the bridging dichloromethane ligand [448]. The ruthenium cluster $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CO)_2\}RuB_{10}H_8(OEt)_2$ has been obtained from the reaction between CO and the corresponding tetrahydride clus-



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ter [449]. The cluster $Ru_3(CO)_{10}(H)(\mu\text{-}COBH_2NMe_2)$ has been obtained as a minor product from the reaction between $Ru_3(CO)_{12-x}(MeCN)_x$ ($x = 1$, 2) and a solution of $BH_3 \cdot THF$ with added NMe_3 or $BH_3 \cdot NMe_3$. X-Ray diffraction results are presented for this cluster [450]. The synthesis and characterization of the ruthenaborane cluster $Ru_3(CO)_9B_2H_6$ have been published. The results of deprotonation studies and discussions dealing with isolobal relationships are presented [451]. 9-Chloro-9-borabicyclo[3.3.1]nonane and $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}BCO)$ react to give $Os_3(CO)_9(\mu\text{-}H)_3\{\mu_3;\eta^2\text{-}C(OBC_8H_{14})BCl\}$. An X-ray crystallographic study has established the structure of this cluster [452].

The μ_3-methylidyne cluster $[(Cp^*Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)]^+$ has been prepared from $[Cp^*RuCl_2]_2$ and $AgBF_4$ in ethanol solvent. Reductive coupling of the μ_3-methylidyne and μ_2-hydride ligands yields the dinuclear complex $[Cp^*Ru(CO)(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)Ru(CO)Cp^*]^+$. The X-ray crystal structures of these new clusters are included in this report [453]. The synthesis and characterization of trimeric tartratodiruthenium complexes are described [454].

The reaction of acid with $[Ru_3(CO)_{11}(\mu\text{-}H)]^-$ has been examined by using stopped-flow FT-IR spectroscopy. Protonation of $[Ru_3(CO)_{11}(\mu\text{-}H)]^-$ with CF_3SO_3H yields the kinetic product $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COH)$, which rapidly rearranges to $HRu_3(CO)_{11}(\mu\text{-}H)$. When CF_3CO_2H is used as the protonating agent only the latter cluster is observed. The isomerization mechanism for this kinetic to thermodynamic rearrangement is discussed and kinetic data are presented for the reductive elimination of hydrogen from the dihydride cluster [455]. The kinetics and mechanism of reductive elimination of hydrocarbon from $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CX)$ (X = Ph, Et, Cl, CO_2Me, SEt, $CHPhCH_2Ph$) have been reported. The postulated mechanism involves a series of C–H reductive eliminations, which are all preceded by a reversible migration of a bridging hydrogen in a Ru–H–Ru position to a bridging hydrogen in a Ru–H–C position. The involvement of an agostic hydrogen in the reductive elimination sequence is thoroughly discussed [456]. The kinetics of hydride fluxionality in the clusters $Ru_3(CO)_8L(\mu\text{-}H)_n(\mu_3\text{-}X)$ ($n = 1$, $X = CH_2SEt$, $L = CO$; $n = 2$, $X = CHCO_2Me$, $L = PPh_3$) are reported. The activation parameters and the results of deuterium isotope effect studies are presented [457]. The synthesis and reactivity of triruthenium and triosmium clusters possessing an agostic hydrogen bond are described. Protonation of $M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CX)$ ($M = Ru$, $X = Et$, $CHPhCH_2Ph$; $M = Os$, $X = Me$) with CF_3SO_3H yields the agostically bonded clusters $[M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}HCR)]^+$, which result from proton addition across a C–M edge [458]. The influence of π-donor substituents in determining *nido–arachno* polyhedral distortions is reported through the use of X-ray diffraction data. Structural comparisons reveal that π-donor substituents on the capping ligand are responsible for the observed polyhedral distortions. Included in this report are the X-ray crystal structures of $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CMeCMeCMe)$, $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CMeCMeCOMe)$, and $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CMeCMeCSEt)$, the former whose ORTEP diagram is shown in Fig. 19 [459].

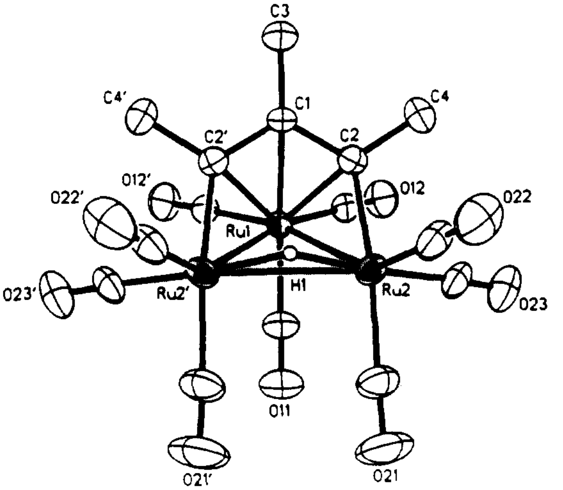


Fig. 19. Reprinted with permission from Organometallics, Copyright 1990 American Chemical Society.

The X-ray crystal structure of $Ru_3(CO)_8\{\mu\text{-}\eta^1:\eta^1:\eta^4\text{-}PhC{=}C(Ph)C(Me){=}CCH_2Me_2\}$, obtained from a regiospecific allyl–alkyne coupling reaction involving $Ru_3(CO)_9(H)(MeCCHCNMe_2)$ and diphenylacetylene, has been published. The organic ligand is bound to the triangular array of ruthenium atoms by σ–π Ru–carbon bonds and a σ Ru–nitrogen bond [460].

Kinetic data are reported for the addition of methoxide to the η^2-vinyl ligand in $Os_3(CO)_{10}(H)(CHCH_2)$ [461]. The reaction between methoxide and the clusters $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3,\eta^3\text{-}O_3ER)$ ($E = S$, $R = O$; $E = P$, $R = OH$, Ph; $E = As$, $R = Ph$) occurs at a carbonyl group to give a methoxycarbonyl species. ^{13}C NMR data have allowed the site of methoxide attack to be determined [462]. The X-ray structure of $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^1\text{-}CCO)$ has been published. A discussion of internally inconsistent Os–Os bond lengths are explained by consideration of both ordered and disordered molecular sites in the crystal [463]. The reaction between $Os_3(CO)_{10}(MeCN)_2$ and propynoic acid has been examined and found to give the cluster $Os_3(CO)_{10}(H)(CH{\equiv}CCO_2)$, which contains a μ-carboxylate group and a non-coordinated alkyne ligand. The pendant alkyne ligand has been coordinated to another trinuclear cluster by reaction with $M_3(CO)_{10}(MeCN)_2$ (M = Ru, Os). The linked clusters have been structurally characterized [464]. $[Os_3(CO)_{11}(H)]^-$ reacts with EPh_2Cl (E = P, Sb) to yield the corresponding bridged cluster, $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}EPh_2)$. The synthesis of the iodo-bridged cluster is also described. The X-ray crystal structure of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SbPh_2)$ confirms the double-bridged nature of these clusters [465]. ^{13}C Cross-polarization magic angle spinning NMR spectroscopy has been used to study the reorientational motion of the C_6H_6 and CH_2CH_2 ligands in $Os_3(CO)_8(\eta^2\text{-}CH_2{=}CH_2)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ [466].

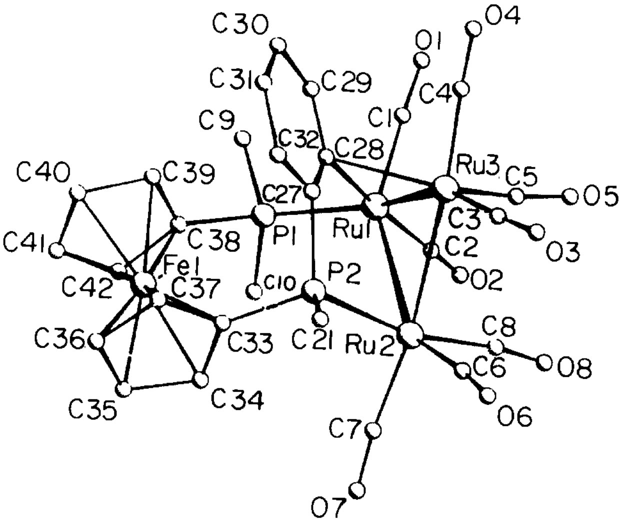
A report describing room-temperature C–H activation and transalkylation in secondary aliphatic amines with $Os_3(CO)_{10}(MeCN)_2$ has appeared. The observed products are shown to be dependent on structure and steric requirements of the amine ligand [467]. Functionalized triosmium alkylidyne clusters have been prepared from $Os_3(CO)_9(H)_3(\mu_3\text{-}CBr)$ and $AgSbF_6$ under CO, followed by the treatment with silicon and tin nucleophiles [468]. The reaction between $MeC{\equiv}CNMe_2$ and $Os_3(CO)_{10}(\mu\text{-}H)_2$ yields the cluster $Os_3(CO)_{10}\{\mu\text{-}C(Me)C(H)NMe_2\}(\mu\text{-}H)$ by the addition and insertion of the ynamine ligand into an Os–H bond. Thermolysis at 68°C yields the new cluster $Os_3(CO)_{10}\{\mu\text{-}CH(Me)CNMe_2\}(\mu\text{-}H)$ by a hydrogen shift from the NMe_2-substituted carbon to the methyl-substituted carbon. Both of these clusters have been structurally characterized. Full solution characterization and reactivity studies of these and related clusters are discussed [469]. The effect of high pressure on the vibrational frequencies of coordinated C_2 hydrocarbon ligands in triosmium clusters has been explored [470]. The synthesis and reactivity of the silyl-substituted triosmium clusters $Os_3(CO)_{11}(H)(SiR_3)$ (R = OMe, OEt, Et, Ph) have been published [471]. An IR study on the main vibrational modes of the coordinate alkyne ligand in $Os_3(CO)_{10}(\mu_3,\eta^2\text{-alkyne})$ and $Co_2Ru(CO)_9(\mu_3,\eta^2\text{-alkyne})$ is presented [472]. Thermolysis of $HOs_3(\mu\text{-}H)(CO)_{10}(^tBuNC)$ yields $Os_3(\mu\text{-}H)_2(CO)_9(^tBuNC)$ as the green isomer. Continued heating gives the known red isomers of this complex. X-Ray diffraction analysis of the green isomer reveals that the isonitrile group is axially bound to an osmium atom not associated with the bridging hydrides. The fluxionality of these isomers has been investigated by ^1H and ^{13}C NMR spectroscopy [473]. $Os_3(CO)_{10}(MeCN)_2$ reacts with 2-formylpyrrole to give the μ-acyl cluster $Os_3(CO)_{10}H(\mu_2\text{-}NHCH{=}CHCH{=}CCO)$ as a result of formyl C–H bond activation. The X-ray structure of this and related clusters is discussed in terms of tautomeric stabilization [474]. An Extended Hückel study has been carried out on the nonclassical alkyne complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}HC_2NEt_2)$. The results are compared to other 46-electron *closo* and 48-electron *nido* M_3C_2 complexes [475]. A report on the synthesis and X-ray structure of the triosmium-siloxane cage complex $Os_3(CO)_{10}(H)\{(\mu\text{-}O)Si_7O_{10}(C_6H_{11})_7\}$ has appeared [476]. Physisorbed $Os_3(CO)_{12}$ is reported to give the silica-anchored hydrido cluster $Os_3(CO)_{10}(H)(OSi\text{-})$. The cluster readily releases $Os_3(CO)_{10}(H)(OH)$ upon treatment with HF [477]. The triosmium cluster $HOs_3(CO)_{10}(OCNHCHMe_2)I_2$ has been obtained as a minor product from the reaction between $HOs_3(CO)_{10}(OCNHCHMe)_2$ and I_2. A mechanistic scheme and the ORTEP diagram of the product are presented [478]. Kinetic isotope effects on ligand migrations in $Os_3(CO)_9(\mu\text{-}X)_2\{\mu_3\text{-}\eta^2\text{-}(CH_3CH_2)_2C_2\}$ (X = H, D) are discussed. Variable-temperature NMR data indicate that alkyne migration over the face of the cluster is coupled with hydride migration [479].

4.1.2. Phosphine ligands

The fluxional behavior of the phosphine-substituted clusters $Os_3(CO)_9(\mu\text{-}H)_2L$ has been investigated by NMR spectroscopy. X-Ray diffraction analysis of the $^iPPr_3$ derivative reveals that the $^iPPr_3$ ligand is located at an equatorial site on the $Os(\mu\text{-}H)_2Os$ unit [480]. The cluster $Os_3(CO)_{11}(Ph_2PCH{=}CH_2)$ has been prepared from $Os_3(CO)_{12}$ and $Ph_2PCH{=}CH_2$. The same reaction using $Ru_3(CO)_{12}$ is more complex, giving $Ru_3(CO)_8(\mu\text{-}H)(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)$ as the major product. The molecular structure of this latter cluster has been unequivocally established by X-ray diffraction analysis [481]. $Os_3(CO)_{11}(MeCN)$ reacts with bis(diphenylphosphino)acetylene at room temperature to yield $[Os_3(CO)_{11}]_2(Ph_2PC{\equiv}CPPh_2)$. The X-ray structure of this cluster is presented [482]. Thermolysis of $Ru_3(CO)_{11}(PPh_3)$ in toluene is reported to give the μ_3-, μ_4-, and μ_5-benzyne complexes $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)$, $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^4\text{-}C_6H_4)$, and $Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_5\text{-}\eta^6\text{-}C_6H_4)$, respectively. X-Ray diffraction data for the last two clusters are reported. The spectroscopic data for the new clusters are discussed along with the fluxional behavior associated with benzyne rotation on the Ru_3 and Ru_4 clusters [483]. The phosphinophosphazene ligand $N_3P_3Cl_4PhPPh_2$ reacts with $Ru_3(CO)_{12}$ to furnish the monophosphine cluster $Ru_3(CO)_{11}(N_3P_3Cl_4PhPPh_2)$, which has been structurally characterized [484]. The phosphorus ylide $Ph_3P{=}CH_2$ reacts with $Ru_3(CO)_{12}$ to give $Ru_3(CO)_9(\mu\text{-}H)(OC{=}CHPPh_3)$. This initial product rearranges upon heating to yield the μ_3-capped cluster $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}CPPh_3)$. Both clusters have been characterized by X-ray diffraction analysis [485]. The phosphido-bridged cluster $[Ru_3(CO)_9(PPh_3)(\mu\text{-}PPh_2)]^-$ has been obtained from the reaction between $[Ru_3(CO)_{11}(\mu\text{-}H)]^-$ and PPh_3. It is suggested that the clusters $[HRu_3(CO)_{10}(PPh_3)]^-$ and $[HRu_3(CO)_9\text{-}$

$(PPh_3)]^-$ are probably intermediates in the reaction. The reactions of $[Ru_3(CO)_{11}(\mu\text{-H})]^-$ with other P-ligands and $AsPh_3$ are described [486]. The triosmium clusters $Os_3(CO)_9(\mu_3\text{-}C_6H_3Me)(\mu_3\text{-}AsC_6H_4Me)$ and $Os_3(CO)_8(\mu_3\text{-}C_6H_3Me)(\mu_3\text{-}AsC_6H_4Me)As(p\text{-tol})_3$ have been obtained from the reaction between $As(p\text{-tol})_3$ and $Os_3(CO)_{11}(MeCN)$ and $Os_3(CO)_{10}(MeCN)_2$, respectively [487].

$Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-ampy})$ reacts with PPh_3 or dppm to give $Ru_3(CO)_7L_2(\mu\text{-H})(\mu_3\text{-ampy})$ [488]. The effect of phosphine-ligand substitution on the mode of attachment of the triply-bridged C_6H_4 ligand in triosmium clusters has been examined. Included in this report are the X-ray crystal structures of $Os_3(CO)_9(\mu_3\text{-PMe})(C_6H_4)$ and $Os_3(CO)_8(\mu_3\text{-PMe})(PEt_3)(C_6H_4)$ [489]. $Os_3(CO)_{10}(R_2C_2)$ (R = Ph, Et, Me) reacts with Me_3NO in the presence of MeCN at low temperature to give $Os_3(CO)_9(MeCN)(R_2C_2)$. The solvent complex was next examined in reactions with alkynes and P-ligands. The X-ray structure of $Os_3(CO)_9\{P(OMe)_3\}(Ph_2C_2)$ has been determined by X-ray crystallography. A $\mu_3\text{-}\eta^2\text{-}\|$-bonding mode is observed for the diphenylacetylene ligand and the $P(OMe)_3$ ligand is shown to occupy an equatorial position at an osmium center bearing a σ-bonded acetylenic carbon [490]. A wide range of products has been reported for the thermolysis reaction between Ph_2PH and $Ru_3(CO)_{12}$ [491]. The reaction between $Os_3(CO)_{10}(\mu\text{-H})(MeCN)\{Si(OR)_3\}$ (R = Me, Et) and diphosphines has been investigated. With the ligand dppm, $Os_3(CO)_{10}(\mu\text{-H})\{Si(OR)_3\}(dppm)$ is observed as the sole product. Spectroscopic and diffraction data confirm the presence of the free, dangling phosphine group. Reaction with dppe is more complex, yielding $Os_3(CO)_{10}(\mu\text{-H})\{Si(OR)_3\}(dppe)$, $[Os_3(CO)_{10}(\mu\text{-H})\{Si(OR)_3\}]_2(\mu\text{-dppe})$, and $Os_3(CO)_{10}(dppe)$. The observed production distribution is dependent on the stoichiometry of the reaction [492]. The pyrolysis of $Ru_3(CO)_{10}(dppf)$ in cyclohexane has been reported to give six major products, most of whose structures were determined by X-ray crystallography. The X-ray structure of $Ru_3(CO)_8(\mu\text{-H})\{\mu_3\text{-PPh}(\eta^1,\eta^2\text{-}C_6H_4)(Cp)Fe(CpPPh_2)\}$ is shown in Fig. 20 [493].



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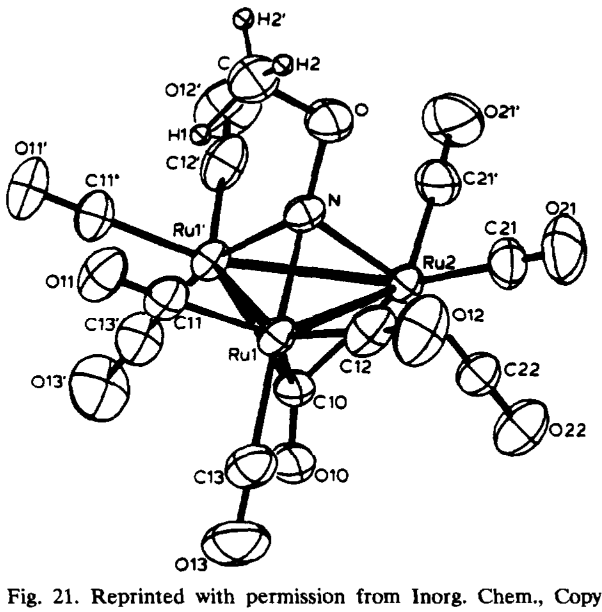
The results of a redox study on alkylidyne-capped triruthenium clusters have been published. One-electron oxidation of $Ru_3(CO)_{9-n}L_n(\mu\text{-H})_3(CX)$ (X = OMe, L = PPh_3, $n = 2, 3$; X = OMe, L = $AsPh_3$, $n = 3$; X = SEt, NMebenzyl, L = PPh_3, $n = 3$) yields the corresponding radical cation, which is shown by electrochemical criteria to be quasi-reversible. EPR data are reported for these odd-electron cluster species. The radical cations decompose in solution by loss of the capping ligand, giving $[Ru_3(CO)_9(\mu\text{-H})L_3]^+$ in the case of the tri-substituted clusters [494]. $Ru_3(CO)_{12}$ reacts with tetraethyldiphosphite at 70°C to give a mixture of at least five products. Of these products, the structure of $Ru_3(CO)_{10}\{(EtO)_2POP(OEt)_2\}$ has been solved by X-ray diffraction analysis. The diphosphite ligand occupies equatorial sites on adjacent ruthenium centers [495]. Reductive elimination of ethylene and benzene and ruthenium–ruthenium bond cleavage to give $Ru_2(CO)_6(\mu\text{-PPh}_2)(\mu\text{-PCH{=}CHC}_6H_4)$ have been observed in the thermolysis reaction of $Ru_3(CO)_8(\mu\text{-H})(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)$ [496]. Halogenation of $M_3(CO)_{10}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}$ and $M_3(CO)_8\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2$ (M = Ru, Os; R = Me, ${}^iPr$) gives cationic products as a result of M–M bond halogenation [497]. The phosphido-bridged cluster $Os_3(CO)_{10}\{\mu_2\text{-}P(C_6F_5)H\}(\mu\text{-H})$ has been isolated from the reaction between $(C_6F_5)_2PH$ and $[Os_3(CO)_{11}(\mu\text{-H})]^-$. X-Ray diffraction analysis indicates that the phosphido and hydride ligands bridge a common osmium–osmium bond [498]. The synthesis and X-ray structure of $Ru_3(CO)_6\{PPhC(Ph)C(Ph)\}(\mu\text{-PPh}_2)_2$ have been reported. The product cluster results from insertion of diphenylacetylene into one Ru–P bond in $Ru_3(CO)_7(\mu\text{-H})(\mu\text{-PPh}_2)_3$ [499]. The reactivity of $[Ru_3(CO)_8(\mu\text{-H})(\mu\text{-PPh}_2)_2]^-$ and $[Ru_3(CO)_8(\mu\text{-H})(PPh_3)(PPhC_6H_4)]^-$ with halides of the copper triad has been reported [500]. The pyrolysis of $[Ru_3(CO)_{11}]_2(Ph_2PC{\equiv}CPPh_2)$ has been studied as a method to higher nuclearity ruthenium clusters. NMR spectroscopic and X-ray crystallographic data on the Ru_4 and Ru_5 products are discussed [501].

4.1.3. Nitrogen ligands

$Ru_3(CO)_{12}$ reacts with $[N(Ph)(C_5H_4N)]^-$ to yield the nitrogen-ligated cluster $[Ru_3(CO)_9\{\mu_3\text{-}\eta^2\text{-N(Ph)}(C_5H_4N)\}]^-$. Protonation yields the corresponding hydrido cluster which has been examined for its substitutional lability. The results of cluster-assisted alkyne/ethylene dimerization studies are reported [502]. The triruthenium clusters $Ru_3(CO)_9(\mu\text{-}H)\{\mu_3\text{-}NRC(E)\text{-}NHR\}$ (E = O, S; R = H, Me, Ph) have been prepared from $Ru_3(CO)_{12}$ and the corresponding ureas and thioureas, respectively. The X-ray structure of the cluster derived from N,N′-diphenylthiourea shows that the thiourea moiety is coordinated to the metallic frame by a μ_2-sulfur linkage [503]. Site-specific protonation studies have been reported for $[Ru_3(CO)_{10}(\mu_2\text{-}NO)]^-$. Use of CF_3SO_3H yields the O-protonated cluster $Ru_3(CO)_{10}(\mu_3\text{-}NOH)$ while use of the weaker acid CF_3CO_2H leads only to $HRu_3(CO)_{10}(\mu_3\text{-}NO)$, which is the result of ruthenium–ruthenium bond protonation. An immediate O–H to Ru–H–Ru tautomerization is observed when the former cluster is treated with $[PPN][CF_3CO_2]$. *o*-Methylation using CF_3SO_3Me occurs at the nitrosyl group to yield $Ru_3(CO)_{10}(\mu_2\text{-}NOMe)$ in high yield. The X-ray structure of this cluster has been solved by using X-ray diffraction analysis (see Fig. 21) [504].

The imido clusters $Ru_3(CO)_9(\mu_3\text{-}NPh)_2$ and $Ru_3(CO)_9H_2(\mu_3\text{-}NPh)$ have been examined in alkyne reactivity studies. Diphenylacetylene reacts with the bis(imido) cluster to give the tetraruthenium cluster $Ru_4(CO)_{10}(\mu_3\text{-}NPh)_2(\eta^2\text{-}\mu_2\text{-}PhC{\equiv}CPh)$. X-Ray diffraction analysis reveals that this cluster possesses a butterfly geometry [505]. Nitrobenzene reduction has been modeled with several nitrogen-substituted clusters. The X-ray crystal structures of $Ru_3(CO)_{10}(H)(PhNH)$ and $[Ru_3(CO)_9(H)(\mu_3\text{-}NPh)]^-$ are presented. Kinetic data are reported for selected reactions [506]. $Ru_3(CO)_{12}$ reacts with benzimidazole to yield $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}bzim)$. This cluster could not be characterized directly and was, therefore, converted into the PPh_3-substituted cluster $Ru_3(CO)_9(PPh_3)(\mu\text{-}H)(\mu\text{-}bzim)$ [507]. The electronic structure of $Ru_3(CO)_6(MeC{=}CHC{=}N^iPr)_2$, which is isolobal with ruthenocene, has been investigated by using He I/He II gas-phase UV photoelectron spectroscopy and DV-Xα MO calculations [508]. The reaction between $Ru_3(CO)_{12}$ and hydrazines and hydrazones has been examined. The parent cluster of the series, $Ru_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}NHNH_2)$, has been isolated and characterized by X-ray diffraction analysis [509]. The nitrogen-bridged clusters $Ru_3(CO)_{9-x}(Ph_2PH)_x(\mu\text{-}H)(\mu\text{-}ampy)$ ($x = 1$, 2) have been prepared from $Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}ampy)$ and Ph_2PH. The mono-Ph_2PH cluster is transformed into $Ru_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}ampy)(\mu\text{-}PPh_2)$, which is predicted to have a μ_2-phosphido group that spans one of the two Ru–Ru bonds unbridged by the ampy ligand [510]. The reaction between $Ru_3(CO)_{12}$ and substituted aminopyridines has been studied [511]. The dihydride cluster $[Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}ampy)]^+$ has been synthesized from the neutral monohydride. Data from PPh_3 ligand substitution studies are discussed [512].



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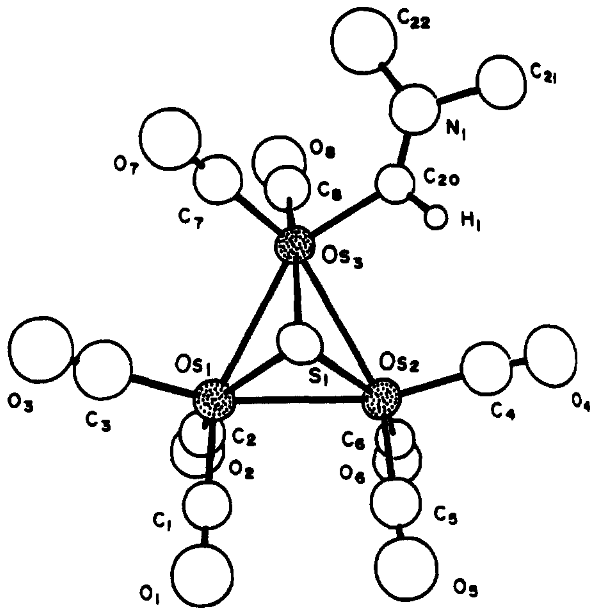
The reaction between the carbene cluster $Os_3(CO)_{11}\{C(Et)NMe_2\}$ and phenylacetylene gives $Os_3(CO)_9[\mu_3\text{-}PhC_2\{C(Et)NMe_2\}](\mu\text{-}H)$ by way of $C(Et)NMe_2$ carbene ligand transfer to the α-carbon of a bridging phenylacetylene intermediate. Both clusters were characterized by IR and NMR spectroscopy and X-ray diffraction analysis [513]. A study on the effect of pressure on the IR frequencies of the α-pyridyl ligand in $HOs_3(CO)_{10}(\mu,\eta^2\text{-}NC_5H_4)$ has appeared [514]. $Os_3(CO)_{10}(MeCN)_2$ reacts with acetone oxime, $Me_2C{=}NOH$, to yield the bridging oximato cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Me_2C{=}NO)$ as a result of O–H bond cleavage. Use of benzaldehyde oxime, $PhCH{=}NOH$, gives an isomeric mixture of $Os_3(CO)_{10}(\mu\text{-}H)(PhCH{=}NO)$, which have been separated on silica gel and characterized by IR and NMR spectroscopy. N–O Bond cleavage in $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Me_2C{=}NO)$ is observed to occur upon heating, giving $Os_3(CO)_{10}(\mu\text{-}OH)(\mu\text{-}Me_2C{=}N)$. The X-ray crystal structures of both acetone oxime-derived clusters are presented [515].

4.1.4. Sulfur ligands

The synthesis and reactivity of $Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}PyS)$ have been described. The product cluster, which is obtained from the reaction between $Ru_3(CO)_{12}$ and pyridine-2-thiol, decomposes slowly in solution to give polymeric $[Ru(pyS)(CO)_2]_n$ and $Ru(pyS)_2(CO)_2$ [516]. The triruthenium cluster $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ undergoes decarbonylation to afford the hexaruthenium clusters $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$ and $Ru_6(CO)_{14}(\mu_3\text{-}MeC_2NMe_2)(\mu_4\text{-}S)_2$ by fusion of two trinuclear clusters. Both of these products have been structurally characterized [517]. $M_3(CO)_{10}(\mu_3\text{-}S)$ (M = Ru, Os) react with $Me_2C_2NMe_2$ to give $M_2(CO)_6\{\mu\text{-}SC(NMe_2)CMe\}$ and $M_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)$ in the case of the ruthenium cluster. The osmium cluster $Os_3(CO)_{10}(\mu_3\text{-}S)$ reacts with the same ynamine to give only $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, which has been characterized by single-crystal X-ray diffraction analysis. The ynamine ligand in this latter cluster is best formulated as an (α,α-dimetallioethyl)-(dimethylamino)carbene ligand [518].

Ring opening, C–H activation, and decarbonylation in $Os_3(CO)_{11}\{S(CH_2)_3\}$ are reported to occur upon optical excitation. The isolated product, $Os_3(CO)_{10}\{\mu\text{-}SCH_2CH{=}CH_2\}(\mu\text{-}H)$, has been spectroscopically characterized and examined for its reactivity toward $PhPMe_2$ [519]. 3,3-Dimethylthietane reacts with $Os_3(CO)_{10}(MeCN)_2$ to give $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$. When this latter cluster is heated, the clusters $Os_3(CO)_9(\mu_3\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$, $Os_2(CO)_6\{\mu\text{-}S(CH_2)_2CMe\}(\mu\text{-}H)$, and $Os_4(CO)_{12}(\mu\text{-}CO)(\mu\text{-}SCH_2CMe_2CH_2)$ may be isolated [520]. The clusters $Os_3(CO)_7\{\mu\text{-}C(Et)N(Me)CH_2\}(\mu_3\text{-}S)(\mu\text{-}H)_3$ and $Os_3(CO)_8\{C(Et)NMe_2\}(\mu_3\text{-}S)(\mu\text{-}H)_2$ have been prepared from $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ and hydrogen at elevated temperature. The effect of hydrogen pressure on the product distribution is discussed. X-Ray data for several of the new clusters are reported [521]. The cluster $Os_3(CO)_8\{C(H)NMe_2\}(\mu_3\text{-}S)(\mu\text{-}H)_2$ has been obtained from the reaction between Me_3N and $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$. X-Ray crystallography reveals that the secondary (dimethylamino)carbene ligand is terminally coordinated to the μ_3-sulfido-bridged cluster (Fig. 22). This cluster is also reported to function as a catalyst in the exchange of alkyl groups between NEt_3 and N^iPr_3 [522].



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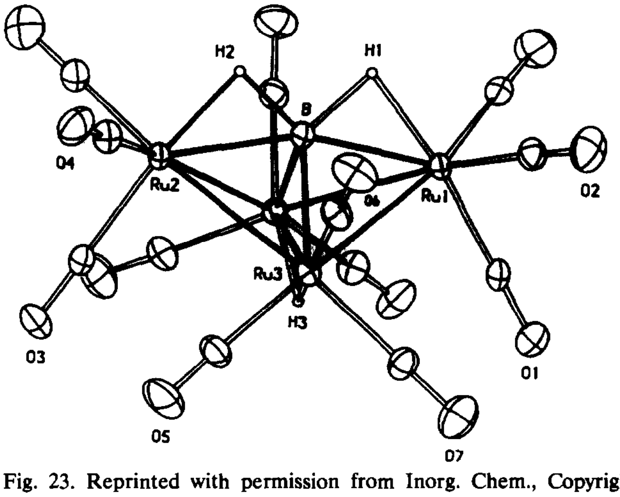
4.2. Tetranuclear clusters

A triclinic polymorph of $H_2Ru_4(CO)_{13}$ has been structurally characterized [523]. The clusters $H_4M_4(CO)_{12}$ (M = Ru, Os) have been prepared from silica-supported $M_3(CO)_{12}$ and hydrogen. Solvent extraction releases the tetranuclear cluster in high yield. The procedure described here for $H_4Os_4(CO)_{12}$ offers significant advantages over the reported solution synthesis [524]. $BH_3 \cdot THF$ reacts with $H_2Ru_4(CO)_{13}$ to furnish the butterfly cluster $HRu_4(CO)_{12}BH_2$, which has been characterized by X-ray crystallography (Fig. 23). KH is shown to sequentially deprotonate the borohydride group, giving $[HRu_4(CO)_{12}BH]^-$ and $[HRu_4(CO)_{12}B]^{2-}$. The exchange of bridging hydrides in $[HRu_4(CO)_{12}BH]^-$ has been examined by using 2-D NMR spectroscopy [525].

The chemistry of tetranuclear carbonyls of osmium has been reviewed [526]. The synthesis and structure of $Os_4(CO)_{15}L$ {where L = CO, PF_3, $P(OCH_2)_3CMe$} have been published. The structure adopted by these clusters is dependent on the electronic properties of the ancillary ligand. With either CO or PF_3 as the ancillary ligand, the cluster adopts a puckered-square osmium frame, while a spiked-triangular osmium frame is observed with the constrained phosphite ligand. The X-ray diffraction data for these three clusters are discussed [527]. $Os_4(CO)_{15}$ reacts with ^tBuNC to yield Os_4-



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$(CO)_{15}(^tBuNC)$. X-Ray diffraction analysis reveals that the 18-electron compound $Os(CO)_4(^tBuNC)$ functions as a ligand to the $Os_3(CO)_{11}$ fragment by formation of an unbridged dative Os–Os bond. The fluxional behavior of this cluster has been examined by using variable-temperature ^{13}C NMR spectroscopy [528]. The tetrahedral cluster $Os_4(CO)_{11}(H)(C_4H_5)$ has been synthesized from the pyrolysis of $Os_3(CO)_{10}(MeC{\equiv}CMe)$. X-Ray diffraction analysis reveals that an allyl ligand is present, bonding to one of the cluster faces in a μ_3-η^3 mode [529]. The cluster $Os_4(CO)_{12}(C_9H_6)$ has been isolated as one of the products from the reaction between $Os_3(CO)_{12}$ and indene. Single-crystal X-ray diffraction analysis of $HOs_4(CO)_9(C_9H_6)(C_9H_7)$ indicates that one face of the Os_4 tetrahedron is capped by an indyne ligand with μ_3-η^2-$\|$ bonding [530]. The ynamine ligand MeC_2NMe_2 reacts with $Os_4(CO)_{12}(\mu_3\text{-}S)$ to give a mixture of tri- and tetraosmium clusters. The X-ray structures of these clusters are reported [531].

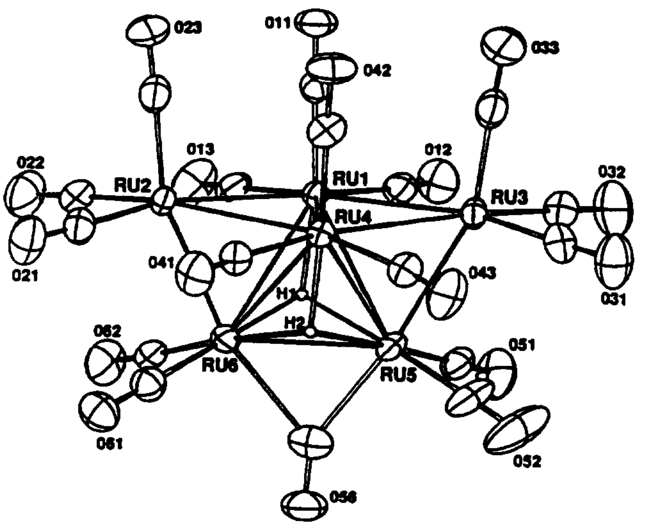
4.3. Pentanuclear clusters

A review article on the reactivity of the pentaruthenium cluster $Ru_5(CO)_{15}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$ has appeared [532]. Thermolysis of $H_2Os_5(CO)_{14}\{P(OMe)_3\}$ with excess P-ligand initially gives $H_2Os_5(CO)_{14}\{P(OMe)_3\}L$, which decarbonylates to yield $H_2Os_5(CO)_{13}\{P(OMe)_3\}L$. This latter cluster may be obtained directly from the reaction between $H_2Os_5(CO)_{14}\{P(OMe)_3\}$ and added ligand when Me_3NO is used as a decarbonylating reagent. Hydride fluxionality has been examined by using variable-temperature ^1H NMR spectroscopy. The X-ray structure of $H_2Os_5(CO)_{13}\{P(OMe)_3\}PEt_3$ is reported. The molecular polyhedron is based on a trigonal bipyramid with the $P(OMe)_3$ ligand located at an apical osmium atom and the PEt_3 ligand attached to an equatorial osmium atom of the bipyramid [533]. $Os_5(CO)_{16}$ has been prepared from the chemical oxidation of $[Os_5(CO)_{15}]^{2-}$ in the presence of CO. The reaction of $Os_5(CO)_{16}$ with Me_3NO in the presence of donor ligands leads to the corresponding mono-substituted clusters $Os_5(CO)_{15}L$. The X-ray crystal structures of $Os_5(CO)_{15}\{P(OMe)_3\}$ and $Os_5(CO)_{15}PEt_3$ are reported and in both cases the ancillary ligand is attached to one of the equatorial osmium atoms of the bipyramid [534].

4.4. Hexanuclear clusters

The hexaruthenium cluster $Ru_6(CO)_{10}(\mu\text{-}H)_6(\eta\text{-}PHBu)(\mu\text{-}PBu_2)_2(PBu_3)_2(\mu_6\text{-}P)$ has been obtained from the reaction of $Ru(CO)_2(acetone)_2(PBu_3)_2$ with hydrogen at elevated temperature. An X-ray diffraction study reveals that the cluster is based on a butterfly arrangement with two pairs of triangular wings [535]. Chemical oxidation of $[Ru_6C(CO)_{16}]^{2-}$ using either ferrocenium tetrafluoroborate or $FeCl_3$ in the presence of alkynes furnishes the cluster complexes $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}RCCR')$ (R = R' = H, Me, Et, Ph; R = H, R' = Ph; R = Me, R' = Ph). In the case of the phenylacetylene-substituted cluster $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CH)$, thermolysis in toluene gives the new cluster $Ru_6C(CO)_{15}(\mu\text{-}H)(C{\equiv}CPh)$ [536]. The clusters $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6HMe_3)$ and $HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)$ have been isolated from the thermolysis reaction between $Ru_3(CO)_{12}$ and mesitylene. The molecular structure of both clusters has been unequivocally determined by X-ray crystallography. The results of IR and ^{13}C and ^1H NMR studies are presented [537]. $[Ru_6C(CO)_{16}]^{2-}$ reacts with methyl iodide at high temperature to give $[Ru_6C(CO)_{16}(CH_3)]^-$. X-Ray diffraction data indicate that the octahedral metal core is retained. This methyl cluster reacts with CO (50 atm) to give the corresponding acetyl cluster $[Ru_6C(CO)_{16}(COMe)]^-$, which has been confirmed by X-ray diffraction analysis. The reaction between the dianionic cluster and allyl bromide is also described [538]. The 84-electron cluster $H_2Ru_6(CO)_{17}$ has been obtained from $H_2Ru_6(CO)_{18}$. X-Ray diffraction analysis indicates that the molecular polyhedron is best described as a bicapped tetrahedron (Fig. 24). When this cluster is exposed to excess CO, cluster fragmentation to tri- and tetranuclear species is observed [539].

The reaction between $P(OMe)_3$ and $Os_6(CO)_{18}$ and $Os_6(CO)_{21}$ has been examined. The ligand-substituted clusters have been isolated and characterized by solution and solid-state techniques [540]. Thiirane ring-



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opening and oligomerization reactions have been studied by using the hexaosmium clusters $Os_6(CO)_{17}(MeCN)$ and $Os_6(CO)_{16}(MeCN)_2$ [541].

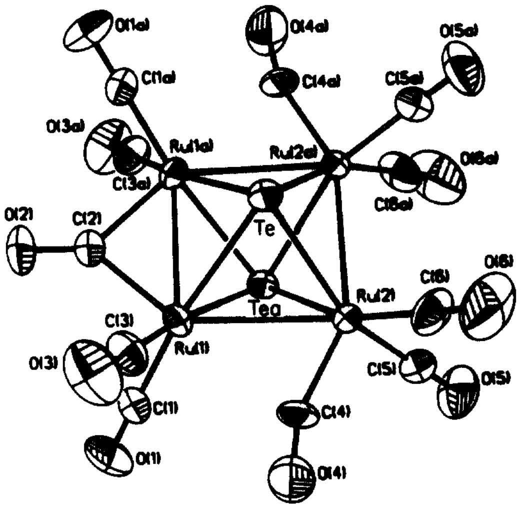
4.5. Higher nuclearity clusters

Fast atom bombardment mass spectrometry has been employed in the analysis of the osmium cluster $H_2Os_7(CO)_{22-x}$ ($x = 0$, 1, 2) [542]. The X-ray crystal structure of $[Ru_{10}(\mu_6\text{-}C)(CO)_{20}(\mu\text{-}CO)_4][Ph_3PCH_2CH_2PPh_3]\cdot 2(\text{acetone})$ has been solved and a discussion on the origin of the severely disordered structure of the bis(tetraammonium) cluster is presented [543].

4.6. Mixed-metal clusters

4.6.1. Clusters containing Main Group atoms

The ruthenaborane clusters 2,4-Me_2-(*p*-cymene)-1,2,4-$RuC_2B_8H_8$ and 2,4-Me_2-(C_6Me_6)-1,2,4-$RuC_2B_8H_8$ have been synthesized from the *nido*-dicarbaborane 5,6-Me_2-5,6-$C_2B_8H_{10}$ and $[(p\text{-cymene})RuCl_2]_2$ and $[(C_6Me_6)RuCl_2]_2$, respectively. Solution characterization details and the X-ray diffraction structure of the former ruthenaborane are presented [544]. The substitution chemistry of the bismuth-capped cluster $Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}Bi)$ has been examined. The structures of the ligand-substituted clusters have been assigned on the basis of spectroscopic measurements [545]. The oxygen atom of the unique carbonyl in $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}BCO)$ is attacked by the Lewis acids BX_3 (X = Cl, Br) to give $Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CBX_2)$. Boron-10-labeling experiments reveal that this reaction proceeds by an intramolecular boron/carbon exchange sequence. Similar reactions were also conducted with the phosphine-substituted cluster $Os_3(CO)_8(PPh_3)(\mu\text{-}H)_3(\mu_3\text{-}BCO)$. The reactivity of $Os_3(CO)_8(PPh_3)(\mu\text{-}H)_3(\mu_3\text{-}CBCl_2)$ in ligand substitution and deprotonation reactions is reported [546]. The tetraruthenium cluster $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$ has been isolated from the reaction between $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$. Reaction of $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$ with PPh_3 at room temperature affords $Ru_3(CO)_6(PPh_3)_3(\mu_3\text{-}Te)_2$ and $Ru_4(CO)_{10}(PPh_3)(\mu_4\text{-}Te)_2$ while dppm reacts to give $Ru_4(CO)_9(\mu\text{-}dppm)(\mu_4\text{-}Te)_2$. The molecular structure of each of these clusters was established by X-ray crystallography (Fig. 25) [547].



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4.6.2. Clusters containing other metals

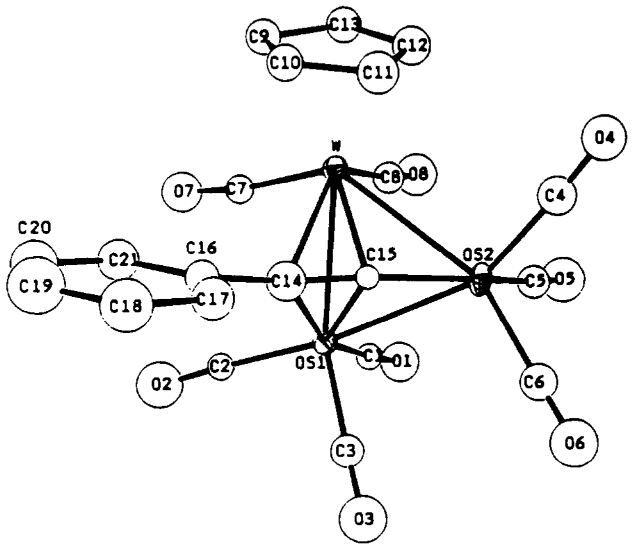
The heterometallic acetylide cluster $Cp_2Mo_2Ru_3(CO)_{10}(C{\equiv}CPh)_2$ has been synthesized from $Ru_3(CO)_{12}$ and $CpMo(CO)_3(C{\equiv}CPh)$. X-Ray diffraction analysis reveals the presence of a double butterfly polyhedron with acetylide ligands in a μ_4-η^2 bonding mode [548]. $CpW(CO)_3H$ reacts with the imido cluster $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ to give $CpWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$, which reacts with $CpW(CO)_3(C{\equiv}CPh)$ to produce $Cp_2W_2Ru_2(CO)_2(\mu\text{-}NPh)(\mu,\eta^2\text{-}CH{=}CPh)$. Use of $Cp^*W(CO)_2H$ gives the corresponding Cp* clusters [549]. Acetylide–alkyne coupling has been observed in the reaction of $CpWOs_2(CO)_8(C{\equiv}CR)$ (R = Ph, Bu) with disubstituted alkynes. The decarbonylation reagent Me_3NO was used to generate an alkyne coordination site in the WOs_3 cluster [550]. The acetylide clusters $MOs_3(CO)_{11}(C{\equiv}CPh)Cp$ (M = Mo, W) react with $CpMo(CO)_3(C{\equiv}CPh)$ to afford $MMoOs_3(CO)_{11}(CCPhCCPh)Cp_2$ as a result of head-to-tail coupling of the acetylide ligands. Variable-temperature ^1H NMR studies indicate that the C_4 chain exhibits a twisting motion in solution. The X-ray crystal structures of $Mo_2Os_3(CO)_{11}(CCPhCCPh)Cp_2$ and $MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)Cp_2$, the products of the reaction between $CpW(CO)_3(C{\equiv}CPh)$ and $MoOs_3(CO)_{11}(C{\equiv}CPh)Cp$, are presented [551]. The methoxymethylidyne cluster $(\eta^5\text{-}C_5R_5)WRu_3(CO)_{11}(\mu_3\text{-}COMe)$ (R = H, Me) has been obtained from the reaction between $Ru_3(CO)_{10}(\mu\text{-}COMe)(H)$ and $(\eta^5\text{-}C_5R_5)W(CO)_3H$. Hydrogenation in toluene leads to C–O bond scission and production of the carbido cluster $(\eta^5\text{-}C_5R_5)WRu_3(CO)_{11}(\mu_4\text{-}C)(\mu\text{-}H)$, whose structure has been solved by X-ray diffraction analysis [552]. $Os_3(CO)_{10}(MeCN)_2$ and $CpW(CO)_3(C{\equiv}CR)$ (R = Ph, Bu) react in refluxing toluene to give $CpWOs_3(CO)_{11}(C{\equiv}CR)$. $CpWOs_3(CO)_{11}(C{\equiv}CPh)$ reacts with excess ditolylacetlylene to yield $CpWOs_3(CO)_8(CO)_8(\mu_3\text{-}CPh)\{\mu_4\text{-}\eta^5\text{-}C(C_2Tol_2)_2\}$ [553]. The fluxional behavior of the coordinated acetylide ligand in $(\eta^5\text{-}C_5R_5)MM'_2(CO)_8(C{\equiv}CR')$ (M = Mo, W; M' = Ru, Os; R = H, Me; R' = Ph, C_6H_4F, C_6H_4OMe, ^tBu, Pr) has been examined by ^{13}C NMR spectroscopy. The X-ray structures of the clusters Cp-

$WOs_2(CO)_8(C{\equiv}CPh)$, $CpWRu_2(CO)_8(C{\equiv}CPh)$, and $CpMoRu_2(CO)_8(C{\equiv}CPh)$ are discussed (Fig. 26) [554].

The clusters $HRu_3(CO)_{10}\{\mu\text{-NC-Mn(CO)}_2(\eta^5\text{-}C_5H_4R)\}$ and $Ru_3(CO)_{10}\{\mu\text{-NC-Mn(CO)}_2(\eta^5\text{-}C_5H_4R)\}_2$ (R = H, Me) have been prepared from $Ru_3(CO)_{12}$ and $(\eta^5\text{-}C_5H_4R)Mn(CO)_2CN$. The X-ray structures of the methylcyclopentadienyl-substituted clusters are reported [555]. The mixed-metal carbide clusters $[MnM_3C(CO)_{13}]^-$, $[M'_2Ru_3C(CO)_{16}]^{2-}$, $[M''_3Ru_3C(CO)_{15}]^-$, and $[Ni_3Ru_3(CO)_{13}]^{2-}$ (M = Ru, Os; M′ = Cr, Mo; M″ = Co, Rh) have been synthesized in a redox-condensation scheme using the ketenylidene cluster $[M_3(CO)_9(CCO)]^{2-}$. IR and variable-temperature ^{13}C NMR data are reported, and the molecular structures of the $MnOs_3$ and Ni_3Ru_3 are discussed [556].

Regioselective alkyne insertion into the cobalt–phosphido bond of $RuCo(CO)_7(\mu_2\text{-}PPh_2)$ is reported to give $(OC)_3Ru\{\mu\text{-}\eta^3\text{-}Ph_2PCOC(R'){=}C(R'')\}Co(CO)_3$ (R′ = R″ = Ph; R′ = Ph, R″ = C≡CPh; R′ = H, R″ = Ph, R′ = H, R″ = ${}^tBu$; R′ = $SiMe_3$, R″ = H; R′ = R″ = H). These (alkenylcarbonyl)phosphine complexes undergo decarbonylation at moderate temperatures to give the (alkenyl)phosphine complexes $(OC)_4Ru\{\mu\text{-}\eta^3\text{-}Ph_2PC(R'){=}C(R'')\}Co(CO)_3$ (Fig. 27) [557].

Dimethyl- and diphenyltelluride clusters based on $HRuCo_3(CO)_{11}$ have been prepared and structurally characterized. The initial substitution step is regioselective and proceeds by replacement of an apical carbonyl group on the ruthenium atom [558]. The syntheses and X-ray structures of the dimethylselenide-substituted clusters $HRuCo_3(CO)_{11}(SeMe_2)$, $HRuCo_3(CO)_{10}(SeMe_2)_2$, and $[HRuRh_3(CO)_9]_2(SeMe_2)_2$ are reported. The latter cluster possesses two bridging 4-electron dimethylselenide ligands [559]. In a separate report, $[HRuRh_3(CO)_9]_2(SeMe_2)_2$ is shown to arise from the dimerization of $HRuRh_3(CO)_{11}(SeMe_2)$ [560]. An electrochemical investigation on the anionic clusters $[RuCo_3(CO)_{12-2n}(PhC{\equiv}CPh)_n]^-$ ($n = 0$, 1) has been carried out. The parent cluster ($n = 0$) is reported to undergo either two distinct one-electron reduction steps or a single two-electron reduction process. The particular pathway observed is dependent on the nature of the solvent. The redox tunability is discussed. The alkyne-substituted cluster undergoes two separate one-electron reduction steps in addition to an irreversible four-electron oxidation process which leads to cluster fragmentation [561].



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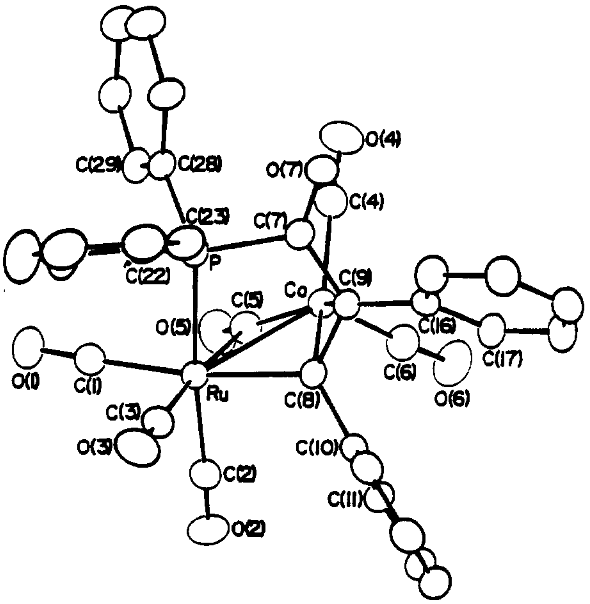

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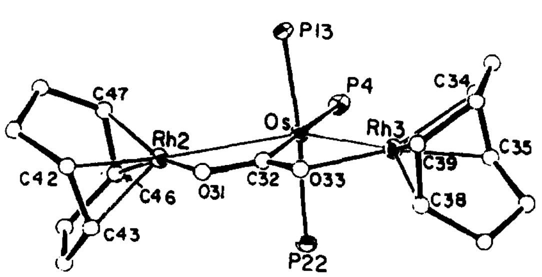
Oxidative decarbonylation of the acetylide ligand in $Co_2(CO)_6\text{-}\mu\text{-}\{CpRu(CO)(C{\equiv}CPh)\}$ is reported to give the tetrahedrane cluster $Co_2Ru(CO)_7Cp(\mu_3\text{-}CPh)$. The identity of this new cluster was established by an X-ray diffraction study. A ^{13}C-labeling study has confirmed the fate of the oxidized carbon and has enabled the presentation of a plausible reaction mechanism [562]. The unsaturated hydride-bridged cluster $Os_3(CO)_{10}(\mu\text{-}H)_2$ reacts with $CpRh(CO)_2$ in toluene to give two major products that have been identified as $CpRhOs_2(CO)_9$ and $CpRhOs_3(CO)_{10}(\mu\text{-}H)_2$; the pentanuclear cluster $CpRhOs_4(CO)_{13}(\mu\text{-}H)_2$ was also isolated, albeit in low yield. When the same reaction was conducted under an atmosphere of hydrogen, the cyclopentadienyl ligand was lost in one case and toluene coordination was observed. The two new products isolated are $RhOs_3(CO)_9(\eta^6\text{-}C_6H_5Me)(\mu\text{-}H)_3$ and $CpRhOs_3(CO)_9$-

$(\mu\text{-H})_4$ [563]. A report has described the structural trends observed in phosphine-substituted $HRuCo_xRh_{3-x}(CO)_{12}$ ($x = 0\text{–}3$) clusters [564]. The synthesis and X-ray structure of $FeRuCp(CO)_4(\mu\text{-CO})(\mu\text{-CPh=CPhH})$ have been presented. A mechanism involving $Fe(CO)_4$(acetylene) insertion into the Ru–H bond of $CpRu(CO)_2H$ is discussed [565]. Heterobimetallic M–M′ (M = Ru, Os; M′ = Rh, Ir, Au) complexes with a pyrazole or imidazole ligand have been synthesized and spectroscopically characterized by IR and NMR spectroscopy. Included in this report is the X-ray crystal structure of $(Ph_3P)_2(OC)HRu(\mu\text{-}2,2'\text{-biimidazole})Rh(1,5\text{-COD})$ [566]. X-Ray diffraction data on $Fe_2Os(CO)_{12}$ have been published [567]. Reaction between $Os_2(CO)_8(\mu\text{-CH}_2\text{=CH}_2)$ and $(C_5R_5)Rh(CO)_2$ (R = H, Me) gives the known cluster $(C_5R_5)RhOs_2(CO)_9$ in moderate yield. Both clusters exhibit fluxional carbonyl behavior which has been examined by variable-temperature ^{13}C NMR spectroscopy. The energetics for carbonyl scrambling and exchange pathways are discussed [568]. $(1,5\text{-COD})RhH_3Os(PMe_2Ph)_3$ reacts with CO_2 to give $H_2Os(CO)(PMe_2Ph)_3$, $[(1,5\text{-COD})Rh]_2OsH_2(CO_2)(PMe_2Ph)_3$ and H_2O. The X-ray crystal structure of the Rh_2Os product reveals that the CO_2 ligand serves to bind the two rhodium atoms by a single oxygen bond and the osmium atom by a carbon bond (see Fig. 28) [569].

The synthesis of ruthenium-platinum clusters with bridging methylene, methylidyne, and carbido ligands has been reported from the reaction between $Cp_2Ru_2(\mu\text{-CH}_2)(\mu\text{-CO})(CO)L$ (L = CO, MeCN) and Pt(ethylene)$(PR_3)_2$ (R = cyclohexyl, ^{i}Pr). The structures of $Ru_2Pt(\mu\text{-CH}_2)(\mu\text{-CO})(CO)_2(PCy)Cp_2$, $Ru_2Pt_2(\mu\text{-H})(\mu_4\text{-CH})(\mu\text{-CO})(CO)_2(P^iPr)_2Cp_2$, $Ru_2Pt_2(\mu\text{-H})_2(\mu_4\text{-C})(\mu\text{-CO})_2(P^iPr)_2Cp_2$ are described [570]. $Pt(1,5\text{-COD})_2$ and $Ru(CO)_5$ react at room temperature to furnish the hexanuclear cluster $[PtRu_2(CO)_9]_2$, which has been shown by X-ray crystallographic analysis to be an open cluster, consisting of two $Ru(CO)_3$ groups bonded to two Pt(CO) groups followed by two additional $Ru(CO)_3$ groups that bridge a Pt–Ru bond. This cluster undergoes ready cleavage with added dppe to give $PtRu(CO)_8$(dppe) while reaction with diphenylacetylene yields the alkyne-bridged cluster $Pt_3Ru_6(CO)_{14}(\mu\text{-PhC}_2\text{Ph})_3$ [571]. The synthesis and X-ray structure of $Pt[Ru_3(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C≡C}^t\text{Bu})(CO)_9]_2$, which was obtained from the decomposition of $Ru_3Pt(\mu\text{-H})\{\mu_4\text{-}\eta^2\text{-C≡C}^t\text{Bu}\}(CO)_9(1,5\text{-COD})$, have been reported [572]. $Pt_2Os_4(CO)_{18}$ reacts with hydrogen (100 atm) to give $Pt_2Os_5(CO)_{17}(\mu\text{-H})_6$ and $PtOs_5(CO)_{16}(\mu\text{-H})_6$. X-Ray diffraction data reveal that the former cluster is best described as a vertex-shared, Pt(1), bitetrahedron (see Fig. 29) [573].



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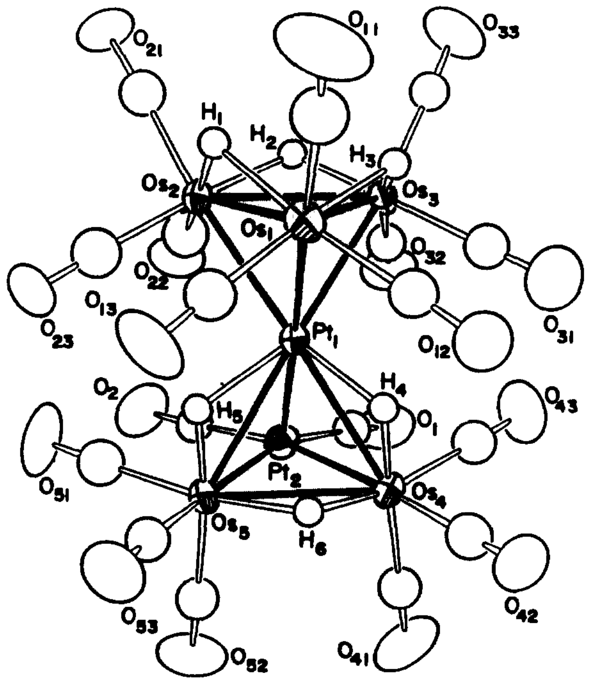

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The reaction between $[M(CO)_4(\eta^2\text{-B}_2\text{H}_5)]^-$ (M = Ru, Os) and Ph_3PAuCl leads to the heterometallic complexes $Ph_3PAuM(CO)_4(\eta^2\text{-B}_2\text{H}_5)$. NMR spectroscopy indicates that the electrophile adds to the metal and does not disturb the B_2H_5 unit [574]. The synthesis of trinuclear Ru_2M (M = Cu, Ag, Au) and pentanuclear Ru_4Au clusters starting from $Ru_2\{\mu\text{-}1,2\text{-}(NH_2)C_6H_4\}(CO)_4(PPh_3)_2$ has been described [575]. The influence of the $P(CH_2Ph)_3$ ligand on the polyhedral structures adopted by $Cu_2Ru_4(\mu_3\text{-H})_2(CO)_{12}\{\mu\text{-P}(CH_2Ph)_2(\eta^2\text{-CH}_2\text{Ph})\}$ and $Cu_2Ru_4(\mu_3\text{-H})_2(CO)_{12}\{P(CH_2Ph)_3\}$ has been investigated by X-ray crystallography [576]. Reaction of $[Ru_4(CO)_{13}]^{2-}$ with 2 equiv. of $[M(MeCN)_4]^+$ (M = Cu, Ag), followed by the addition of PPh_3, yields the mixed-metal clusters $M_2Ru_4(\mu\text{-CO})_3(CO)_{10}(PPh_3)_2$. The corresponding gold derivative is obtained by using Ph_3PAuCl as an electrophile. All of these clusters consist of a ruthenium tetrahedron that has two Ru_3 faces capped by $M(PPh_3)$ moieties [577]. The reaction of $[Ru_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ with Group 1B reagents has also been examined [578]. The synthesis of $Ru_5M_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)_2$ (M = Ag, Au) and the X-ray crystal structure of $Ru_5Au_2(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{11}(PPh_3)_2\{P(OEt)_3\}$ have been published [579]. The X-ray crystal structure and photochemical reactivity of the mercury-bridged cluster $[Os_{18}Hg_2C_2(CO)_{42}]^{2-}$ have been presented [580].

5. Miscellaneous chemistry

5.1. Heterogeneous and supported complexes

The adsorption of $Ru(CO)_3Cl_2(THF)$ onto the surface of hydroxylated metal oxides gives one of two surface $Ru(CO)_3$ species as determined by IR spectroscopy [581]. $Ru(CO)_x$ adsorbed species have been explored by ^{13}C NMR spectroscopy [582]. Solid-state NMR data on ^{13}C-enriched ethylene adsorbed on silica-supported ruthenium have been reported. Ethylene decomposition to acetylide and alkyl groups has been observed and recombination of adsorbed species is reported to yield *cis*- and *trans*-2-butene [583]. Morphology changes in ruthenium catalysts supported on $\gamma\text{-}Al_2O_3$, MgO, SiO_2, and TiO_2 have been explored by using IR and EXAFS techniques [584]. Ru/Al_2O_3 catalysts prepared from $Ru_3(CO)_{12}$ have been studied by EXAFS [585].

Surface protonation and electrochemical activity data of the rutile RuO_2 have been reported [586]. The synthesis and characterization of the ruthenium-substituted heteropolyanion $[SiRu(H_2O)W_{11}O_{39}]^{5-}$ have been published. This complex was shown to function as a catalyst in allylic oxidation, epoxidation, and oxidative cleavage reactions when a primary oxidant was present [587]. The effects of γ-radiation on CO methanation using Ru/zeolite-X catalysts have been examined by using ESR spectroscopy [588]. The use of $Ru(NO)(NO_3)_3$ as a precursor for the preparation of Ru–Cu/MgO catalysts is described [589]. A study on the atomic structure and superstructure of $\alpha\text{-}RuCl_3$ by scanning tunneling microscopy has appeared [590].

Ruthenium methanation catalysts prepared from Ru_xTh_y intermetallics have been characterized by a variety of surface science techniques [591]. The surface diffusion and desorption of pentane isomers on Ru(001) have been studied [592]. The bimetallic system Mn/Ru(001) has been prepared by vapor deposition of Mn on Ru(001). The bimetallic system was examined for its CO chemisorption reactivity [593]. The rates of hydrogen and deuterium diffusion on a Ru(0001) surface have been examined by variational transition state theory [594].

5.2. CO_2 reduction

The electrochemical reduction of CO_2 has been examined by using $[Ru(L\text{–}L)_2(CO)_2]^{2+}$ (L–L = bpy, 1,10-phen, 4,4′-Me_2bpy) and $Ru(L\text{–}L)(CO)_2Cl_2$. Reduction at -1.30 V *vs.* SCE in $MeCN/H_2O$, MeCN/MeOH, or MeOH led to the formation of formate. A working catalytic cycle is presented and individual steps are discussed [595].

5.3. Oxidation reactions

An oxygen-labeling study using $[(bpy)_2(O)Ru(O)Ru(O)(bpy)_2]^{4+}$ has been conducted in order to investigate the mechanism for dioxygen formation [596]. Primary ethers have been converted to esters or lactones by using the catalyst RuX_2L_4 (X = halide; L = DMSO; $(L)_2$ = dppp) and the co-oxidant $LiClO_4$ [597]. The oxidation of olefins by *cis*- and *trans*-ruthenium(VI)-dioxo complexes has been studied by INDO/1 molecular orbital calculations. The formation of a dioxometallacycle species represents a global minimum in the reaction between ethylene and $[cis\text{-}RuO_2]^{2+}$ [598]. INDO/1 molecular orbital calculations have been carried out as a means of studying probable intermediates in ruthenium-oxo-catalyzed epoxidations [599]. $RuCl_2(PPh_3)_3$ and the co-oxidant ^tBuOOH are reported to oxidize lactams and amides. The major product is the α-t-butyldioxy amide [600]. The oxidation of PPh_3 with NaOCl using $[Ru(edta)(O)]^-$ has been studied. The kinetics of oxoruthenium formation are reported [601]. The kinetics of oxygenation of $[Ru(edta)(H_2O)]^-$ to $[Ru(edta)(O)]^-$ using the oxidant $KHSO_5$ have been studied spectrophotometrically. The oxoruthenium complex was employed as an oxygen transfer agent in reactions with cyclohexene and cyclooctene [602]. The kinetics and mechanism of glycollic and mandelic acid oxidation by Ru^{III} and NBS have been studied [603]. Cyclohexylurethane has been obtained from the $Ru(saloph)Cl_2$-catalyzed oxidative decarbonylation of cyclohexylamine [604]. Cyclohexene epoxidation has been achieved by using a $Ru(edta)/ascorbate/H_2O_2$ system [605]. Acetaldehyde has been obtained as the sole product from acetylene using the catalyst $[Ru(edta\text{-}H)Cl]^-$ in the presence of water [606]. $RuCl_3$ and N-methylmorpholine have been reported to function as a catalytic system for the conversion of unsaturated and primary alcohols to the corresponding aldehdyes [607]. Water oxidation to give dioxygen has been reported for several ruthenium(III) complexes [608].

5.4. Hydrogen production and hydrogenation reactions

Transfer hydrogenation has been examined with the precatalysts $Ru_3(CO)_{12}$ and $Ru_4(CO)_{12}(H)_4$. Cyclohexanone has been observed as an intermediate in the conversion of cyclohex-2-en-1-one to cyclohexanol [609].

Chiral ruthenium complexes derived from (+)-diop and (+)-diphenylphosphinite-pantolactone have been synthesized and examined in asymmetric hydrogen transfer reactions [610]. The transfer hydrogenation activity of $RuH_4(PPh_3)_3$ and $RuH_2(PPh_3)_4$ has been studied [611]. $Ru_3(CO)_{12}$-catalyzed reduction of Schiff bases using syngas has been explored. Pyridine was observed to be the solvent of choice [612]. A report on the selective hydrogenation of α,β-unsaturated aldehydes using the water-soluble phosphine TPPTS and $RuCl_3$ has appeared [613]. Aromatic and aliphatic aldehydes are reduced to the corresponding alcohols using the catalyst $RuCl_2(TPPTS)_2$ and formate as the source of hydrogen [614]. A direct synthesis of ethanol from syngas has been reported with a ruthenium/[PPN][Cl] system [615]. A report describing the effects of phosphoric acid on the above catalyst system has been published [616]. The photocatalytic behavior of $[Ru(edta\text{-}H)Cl]^-$ in cyclohexene hydrogenation reactions has been described [617].

5.5. *Other catalytic reactions*

Intermolecular hydroacylation and transformylation reactions have been observed when $Ru_3(CO)_{12}$, Ru(1,5-COD)(COT), and Ru(η^5-cyclooctadienyl)$_2$ were used as catalysts [618]. Indoles have been synthesized from 2-aminophenethyl alcohols when $RuCl_2(PPh_3)_3$ was used as a catalyst [619]. 1,3-Butadiene coupling to the diazadiene ligand in $RuCl_2$(DAD) in the presence of magnesium has been reported [620]. 1-Substituted perhydroazepines have been obtained from primary amines and 1,6-hexanediol using a $RuCl_3/PPh_3$ catalyst. A plausible catalytic mechanism is presented [621]. $Ru_3(CO)_{12}$ functions as a catalyst in the reductive carbonylation of *ortho*-nitrophenylazo compounds [622].

Methyl acetate carbonylation has been examined with the catalysts $RuCl_2(PPh_3)_3$, *trans*-$Ru(CO)_2Cl_2(PPh_3)_2$, and $H_2Ru(CO)(PPh_3)_3$. The observed catalytic activity of these systems are compared with that of $RuCl_3$ [623]. The hydroformylation of 1-hexene, cyclohexene, and cyclooctene has been studied with $[Ru(saloph)Cl_2]$ as a catalyst [624]. Propylene hydroformylation has been examined with the same catalyst, and the results are compared to the analogous $Co_2(CO)_8$-catalyzed reaction [625]. Aldimines have been prepared from alkenes and cyclohexylisocyanide in the presence of hydrogen and low-valent ruthenium catalysts [626]. Dimerization of methyl acrylate and cyclotrimerization of methyl propriolate are observed with $Ru_3(CO)_{12}$ as a catalyst [627].

Reductive carbonylation of nitrobenzene in ethanol using the catalyst $[Ru(saloph)Cl_2]$ has been described [628]. Ruthenium Schiff base complexes have been investigated in preparation of phenylurethane from nitrobenzene [629]. Alcohol homologation has been explored by using ruthenium–cobalt–iodine catalyst systems [630]. A catalyst system derived from $Ru_3(CO)_{12}$ and phosphines functions to decarbonylate formates to alcohols. It is proposed that formate is activated by oxidative addition of the C–H bond to the working catalyst [631]. The coupling of alkyl formates and alkenes to esters is catalyzed by ruthenium catalysts [632]. Cyclohexene carbonylation to give cyclohexene-1-carboxaldehyde has been demonstrated by using the catalyst Ru(edta-H)(CO) in alcohol/water solvent [633]. Polymer-supported ruthenium(trimethylenediamine) complexes are reported to be active in cyclohexene hydrogenation reactions [634].

6. Abbreviations

acac	acetoacetonate
adc–Me^{2-}	1,2-diacetylhydrazido(2 –)
bbpe	*trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)-ethene
bpnp	2,7-bis(2-pyridyl)-1,8-naphthyridine
bptz	3,6-bis(2-pyridyl)-1,2,4,5-tetrazine
bta	benzotriazol-1-yl
bpy	bipyridine
bpz	bipyrazine
bzim	benzimidazole
1,5-COD	1,5-cyclooctadiene
cot	cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
DAB	1,4-diaza-1,3-butadiene
DAD	diazadiene
dcnp	1,8-naphthyridine-2,7-dicarboxylate(2 –)
dcpe	$Cy_2PCH_2CH_2PCy_2$
dmdppe	(1,1-dimethyl-2,2-diphenylphosphino) ethane
dmp	4,4′-dimethyl-2,2′-bipyridine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,1-bis(dimethylphosphino)methane
dmpt	5,6-dimethyl-3-(pyridin-2-yl)-1,2,4-triazine
dpp	2,3-bis(2-pyridyl)pyrazine
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	1,1-bis(diphenylphosphino)methane
dppt	5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine
dppz	dipyrido[3,2-*a* : 2′,3′-c]phenazine
dpq	2,3-bis(2′-pyridyl)quinoxaline
ECL	electrogenerated chemiluminescence
etp	$PhP(CH_2CH_2PPh_2)_2$

Hampy	2-amino-6-methylpyridine
Hbta	benzotriazole
hedta	N-(hydroxyethyl) ethylenediaminetriacetate
Hfac	hexafluoroacetylacetonate
Hphenox	t-butyl-substituted phenoxazinol semiquinone
Hpz	pyrazole
In	indenyl
Me$_2$Hpz	dimethylpyrazole
MLCT	metal-to-ligand charge transfer
NBD	norbornadiene
nmcp	neomenthylcyclopentadienyl
N-MeIm	N-methylimidazole
N$_4$OH	bis(2-{2-pyridyl}ethyl)(2-hydroxy-2-{2-pyridyl}ethyl)amine
OEP	octaethylporphyrin
phi	9,10-phenanthrenequinone
PPN	bis(triphenylphosphine)iminium
PQQ	4,5-dioxo-4,5-dihydro-1H-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic acid
py	pyridine
pz	pyrazol-1-yl
R–ADA	1,6-di-R-1,6-diazahexa-1,5-diene-3,di-R-aminato
(*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
tepa	tris(2-{2-pyridyl}ethyl)amine
terpy	2,2:6′,2″-terpyridine
tfpb	4,4,4-trifluoro-1-phenyl-1,3-butanedionate
tmen	N,N,N′,N″-tetramethylethylenediamine
TMP	tetramesitylporphyrin
TMSO	tetramethylene sulfoxide
tpm	tris(1-pyrazolyl)methane
TPP	tetraphenylporphyrin
TPPTS	*meta*-trisulfonated triphenylphosphine
tpt	3,5,6-tris(pyridin-2-yl)-1,2,4-triazine
ttp	PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$
vpy	vinylpyridine
XPS	X-ray photoelectron spectroscopy

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References

1 M.A. Kline, *Diss. Abstr. B, 51* (1990) 2880; DA No. 9032984.
2 S.-L. Soong, *Diss. Abstr. B, 50* (1990) 3468; DA No. 8926281.
3 R.A. Crane, *Diss. Abstr. B, 50* (1990) 5611; DA No. 9006874.
4 A.E.D. McQueen, *Diss. Abstr. B, 50* (1990) 5057; DA No. BRD-87604.
5 J. Huang, *Diss. Abstr. B, 51* (1990) 2387; DA No. 9019345.
6 T.J. Coffy, *Diss. Abstr. B, 50* (1990) 5611; DA No. 9011152.
7 M.E. Dery, *Diss. Abstr. B, 50* (1990) 2914; DA No. 8926569.
8 K.M. Stell, *Diss. Abstr. B, 51* (1990) 2365; DA No. BRDX90055.
9 A.S. Copenhaver, *Diss. Abstr. B, 50* (1990) 3464; DA No. 9000122.
10 A.M. Marr, *Diss. Abstr. B, 50* (1990) 5057; DA No. BRD-87598.
11 R. Vac, *Diss. Abstr. B, 50* (1990) 2922; DA No. 8911672.
12 D.J. Rauscher, *Diss. Abstr. B, 51* (1990) 740; DA No. 9017382.
13 N.J. Simpson, *Diss. Abstr. B, 50* (1990) 5078; DA No. BRDX87929.
14 C. Bitcon, *Diss. Abstr. B, 50* (1990) 5620; DA No. BRD-88102.
15 G.J. Miller, *Diss. Abstr. B, 51* (1990) 1258; DA No. 9022929.
16 N.J. Long, *Diss. Abstr. B, 51* (1990) 2908; DA No. BRDX90233.
17 C.J. Barner, *Diss. Abstr. B, 51* (1990) 1252; DA No. 9014375.
18 S.K. Harbron, *Diss. Abstr. B, 50* (1990) 2879; DA No. BRDX86447.
19 K. Hansongnern, *Diss. Abstr. B, 51* (1990) 2878; DA No. 9032085.
20 A.K.I. Gushurst, *Diss. Abstr. B, 51* (1990) 735; DA No. 9018835.
21 T.R. O'Toole, *Diss. Abstr. B, 50* (1990) 4526; DA No. 9007303.
22 M.-O.P. Cho, *Diss. Abstr. B, 50* (1990) 5609; DA No. 9013398.
23 E.R. Carraway, *Diss. Abstr. B, 50* (1990) 4009; DA No. 9002819.
24 X. Zhang, *Diss. Abstr. B, 50* (1990) 3962; DA No. 9005700.
25 Z. Xue, *Diss. Abstr. B, 50* (1990) 5061; DA No. 9012991.
26 G.D. Venburg, *Diss. Abstr. B, 51* (1990) 1261; DA No. 9024371.
27 A.E. Ogilvy, *Diss. Abstr. B, 51* (1990) 1258; DA No. 9021737.
28 K.J. Roesselet, *Diss. Abstr. B, 50* (1990) 3988; DA No. 9003023.
29 T.A. Wolfe, *Diss. Abstr. B, 51* (1990) 743; DA No. 9017167.
30 P.A. Eldredge, *Diss. Abstr. B, 51* (1990) 2877; DA No. 9032958.
31 T.K. Chin-Choy, *Diss. Abstr. B, 50* (1990) 3463; DA No. 9001120.
32 J.A. Krause, *Diss. Abstr. B, 50* (1990) 3465; DA No. 9001982.
33 M.W. White, Jr., *Diss. Abstr. B, 50* (1990) 3989; DA No. 8917748.
34 E.B. Zuckerman, *Diss. Abstr. B, 51* (1990) 1819; DA No. 9024420.
35 G.R. Gibson, *Diss. Abstr. B, 51* (1990) 2344; DA No. 9027214.
36 B. Rajai-Dehkordi, *Diss. Abstr. B, 50* (1990) 4121; DA No. 9003745.
37 S. Alerasool, *Diss. Abstr. B, 51* (1990) 1382; DA No. 9023211.
38 S.J. Stoessel, *Diss. Abstr. B, 50* (1990) 4544; DA No. 9007061.
39 J.J. Bergmeister, *Diss. Abstr. B, 51* (1990) 2595; DA No. 9028016.
40 R.A. Cocco, *Diss. Abstr. B, 50* (1990) 3594; DA No. 8925607.
41 C.-S. Huang, *Diss. Abstr. B, 51* (1990) 702; DA No. 9019779.
42 C.A. Guryan, *Diss. Abstr. B, 51* (1990) 1900; DA No 9024559.
43 A.A. Deckert, *Diss. Abstr. B, 50* (1990) 2941; DA No. 8925853.
44 Y. Zhou, *Diss. Abstr. B, 50* (1990) 4022; DA No. 9005702.
45 Y. Sun, *Diss. Abstr. B, 51* (1990) 1292; DA No. 9014384.
46 S.D. Clymer, *Diss. Abstr. B, 50* (1990) 4520; DA No. 9006728.
47 J.P. Collman, P.S. Wagenknecht, R.T. Hembre and N.S. Lewis, *J. Am. Chem. Soc., 112* (1990) 1294–1295.
48 J.P. Collman, J.E. Hutchison, P.S. Wagenknecht, N.S. Lewis, M.A. Lopez and R. Guilard, *J. Am. Chem. Soc., 112* (1990) 8206–8208.
49 J.W. Seyler, P.E. Fanwick and C.R. Leidner, *Inorg. Chem., 29* (1990) 2021–2023.
50 J.W. Seyler and C.R. Leidner, *Inorg. Chem., 29* (1990) 3636–3641.
51 C.-M. Che, W.-H. Leung and W.-C. Chung, *Inorg. Chem., 29* (1990) 1841–1846.

52 I.R. Paeng and K. Nakamoto, *J. Am. Chem. Soc.*, *112* (1990) 3289–3297.
53 M. Hoshino and Y. Kashiwagi, *J. Phys. Chem.*, *94* (1990) 673–678.
54 J.P. Collman and J.M. Garner, *J. Am. Chem. Soc.*, *112* (1990) 166–173.
55 S. Takagi, T.K. Miyamoto, M. Hamaguchi, Y. Sasaki and T. Matsumura, *Inorg. Chim. Acta*, *173* (1990) 215–221.
56 D. Appleby, P.B. HitCHCOck, K.R. Seddon, J.E. Turp, J.A. Zora, C.L. Hussey, J.R. Sanders and T.A. Ryan, *J. Chem. Soc., Dalton Trans.*, (1990) 1879–1887.
57 A.K. Brisdon, P.J. Jones, W. Levason, J.S. Ogden, J.H. Holloway, E.G. Hope and G. Stanger, *J. Chem. Soc., Dalton Trans.*, (1990) 715–718.
58 A.O. Alyoubi, D.J. Greenslade, M.J. Forster and W. Preetz, *J. Chem. Soc., Dalton Trans.*, (1990) 381–383.
59 R.A. Cipriano, W. Levason, R.A.S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1990) 339–347.
60 E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P. Faleschini and W.M. Attia, *Inorg. Chim. Acta*, *177* (1990) 255–265.
61 K.K. Pandey, R.B. Sharma and P.K. Pandit, *Inorg. Chim. Acta*, *169* (1990) 207–210.
62 D.N. Cox and R. Roulet, *Inorg. Chem.*, *29* (1990) 1360–1365.
63 K.-M. Frosin and L. Dahlenburg, *Inorg. Chim. Acta*, *167* (1990) 83–89.
64 W.S. Sheldrick and R. Exner, *Inorg. Chim. Acta*, *175* (1990) 261–268.
65 A.F. Hill, *J. Organomet. Chem.*, *395* (1990) C35–C38.
66 J. Cartwright, A. Harman and A.F. Hill, *J. Organomet. Chem.*, *396* (1990) C31–C34.
67 B.K. Campion, R.H. Heyn and T.D. Tilley, *Organometallics*, *9* (1990) 1106–1112.
68 D.R. Baghurst and D.M.P. Mingos, *J. Organomet. Chem.*, *384* (1990) C57–C60.
69 S.J. Hecker and M.L. Minich, *J. Org. Chem.*, *55* (1990) 6051–6054.
70 S.A. Jackson and O. Eisenstein, *Inorg. Chem.*, *29* (1990) 3910–3914.
71 P. Amendola, S. Antoniutti, G. Albertin and E. Bordignon, *Inorg. Chem.*, *29* (1990) 318–324.
72 J.W. Bruno, J.C. Huffman, M.A. Green, J.D. Zubkowski, W.E. Hatfield and K.G. Caulton, *Organometallics*, *9* (1990) 2556–2567.
73 G. Jia and D.W. Meek, J.C. Gallucci, *Organometallics*, *9* (1990) 2549–2555.
74 R.S. Shinomoto, P.J. Desrosiers, T.G.P. Harper and T.C. Flood, *J. Am. Chem. Soc.*, *112* (1990) 704–713.
75 D.S. Pandey, A. Mishra and U.C. Agarwala, *Inorg. Chim. Acta*, *172* (1990) 13–18.
76 S.W. Carr, E.H. Fowles, X.L.R. Fontaine and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1990) 573–579.
77 K. Hiraki, N. Ochi, H. Takaya, Y. Fuchita, Y. Shimokawa and H. Hayashida, *J. Chem. Soc., Dalton Trans.*, (1990) 1679–1685.
78 N.W. Alcock, A.F. Hill and M.S. Roe, *J. Chem. Soc., Dalton Trans.*, (1990) 1737–1740.
79 A. Romero, A. Santos, J. Lopez and A.M. Echavarren, *J. Organomet. Chem.*, *391* (1990) 219–223.
80 C.E.F. Rickard, W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem.*, *389* (1990) 375–388.
81 B.S. Nkosi, N.J. Coville, M.O. Albers, C. Gordon, M.M. Viney and E. Singleton, *J. Organomet. Chem.*, *386* (1990) 111–119.
82 J.F. Hartwig, R.G. Bergman and R.A. Andersen, *J. Am. Chem. Soc.*, *112* (1990) 3234–3236.
83 J.F. Hartwig, R.A. Andersen and R.G. Bergman, *J. Am. Chem. Soc.*, *112* (1990) 5670–5671.
84 J.F. Hartwig, R.G. Bergman and R.A. Andersen, *J. Organomet. Chem.*, *394* (1990) 417–432.
85 G. Jia, I. Lee, D.W. Meek and J.C. Gallucci, *Inorg. Chim. Acta*, *177* (1990) 81–88.
86 G. Jia and D.W. Meek, *Inorg. Chim. Acta*, *178* (1990) 195–201.
87 B.G. Olby, S.D. Robinson, M.B. Hursthouse and R.L. Short, *J. Chem. Soc., Dalton Trans.*, (1990) 621–627.
88 S. Chattopadhyay, N. Bag, P. Basu, G.K. Lahari and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1990) 3389–3392.
89 A. Mezzetti, A. DelZotto and P. Rigo, *J. Chem. Soc., Dalton Trans.*, (1990) 2515–2520.
90 R.A. Cipriano, W. Levason, R.A.S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1990) 2609–2616.
91 N.J. Simpson and D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, (1990) 1329–1333.
92 D.S. Bohle, G.R. Clark, C.E.F. Rickard and W.R. Roper, *J. Organomet. Chem.*, *393* (1990) 243–285.
93 G.M. McCann, A. Carvill, E. Lindner, B. Karle and H.A. Mayer, *J. Chem. Soc., Dalton Trans.*, (1990) 3107–3115.
94 E. Lindner and B. Karle, *Chem. Ber.*, *123* (1990) 1469–1473.
95 S. Kim, M.P. Johnson and D.M. Roundhill, *Inorg. Chem.* (1990) 3896–3898.
96 J. Huang, K. Hedberg, H.B. Davis and R.K. Pomeroy, *Inorg. Chem.*, *29* (1990) 3923–3925.
97 P.L. Bogdan and E. Weitz, *J. Am. Chem. Soc.*, *112* (1990) 639–644.
98 W.R. Hastings, M.R. Roussel and M.C. Baird, *J. Chem. Soc., Dalton Trans.*, (1990) 203–205.
99 P. Frediani, M. Bianchi, A. Salvini and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, (1990) 3663–3668.
100 M. Draganjac, S. Dhingra, S.-P. Huang and M.G. Kanatzidis, *Inorg. Chem.*, *29* (1990) 590–591.
101 J. Barrau and N.B. Hamida, *Inorg. Chim. Acta*, *177* (1990) 159–160.
102 N.G. Connelly, M. Gilbert, A.G. Orpen and J.B. Sheridan, *J. Chem. Soc., Dalton Trans.*, (1990) 1291–1300.
103 M.A. Gallop, C.E.F. Rickard and W.R. Roper, *J. Organomet. Chem.*, *395* (1990) 333–340.
104 A.F. Hill and R.P. Melling, *J. Organomet. Chem.*, *396* (1990) C22–C24.
105 M.P. Garcia, A.M. Lopez, M.A. Exteruelas, F.J. Lahoz and L.A. Oro, *J. Organomet. Chem.*, *388* (1990) 365–377.
106 J. Montoya, A. Santos, A.M. Echavarren and J. Ros, *J. Organomet. Chem.*, *390* (1990) C57–C60.
107 A.M. Joshi and B.R. James, *Organometallics*, *9* (1990) 199–205.
108 C. Mountassir, T.B. Hadda and H. Le Bozec, *J. Organomet. Chem.*, *388* (1990) C13–C16.
109 W.P. Mul, C.J. Elsevier, H.-W. Fruhauf, K. Vrieze, I. Pein, M.C. Zoutberg and C.H. Stam, *Inorg. Chem.*, *29* (1990) 2336–2345.
110 D.T.T. Yapp, J. Jaswal, S.J. Rettig, B.R. James and K.A. Skov, *Inorg. Chim. Acta*, *177* (1990) 199–208.
111 A. Pramanik, N. Bag, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1990) 3823–3828.
112 W.S. Sheldrick and R. Exner, *J. Organomet. Chem.*, *386* (1990) 375–387.
113 N. Bag, G.K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1990) 1557–1560.
114 G.J. Irvine, C.E.F. Rickard, W.R. Roper and L.J. Wright, *J. Organomet. Chem.*, *387* (1990) C9–C12.
115 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, *395* (1990) 195–206.
116 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, *395* (1990) 207–218.

117 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, *395* (1990) 315–326.
118 M. Herberhold and A.F. Hill, *J. Organomet. Chem.*, *387* (1990) 323–336.
119 C. Lindsay, E. Cesarotti, H. Adams, N.A. Bailey and C. White, *Organometallics*, *9* (1990) 2594–2602.
120 D.S. Bohle, C.E.F. Rickard, W.R. Roper and P. Schwerdtfeger, *Organometallics*, *9* (1990) 2068–2080.
121 D. Sellmann, I. Barth, F. Knoch and M. Moll, *Inorg. Chem.*, *29* (1990) 1822–1826.
122 D. Sellmann, I. Barth and M. Moll, *Inorg. Chem.*, *29* (1990) 176–181.
123 M.N. Bell, A.J. Blake, A.J. Holder, T.I. Hyde and M. Schroder, *J. Chem. Soc., Dalton Trans.*, (1990) 3841–3847.
124 S. Saito, Y. Morikawa and T. Moriwake, *J. Org. Chem.*, *55* (1990) 5424–5426.
125 D.A. Evans and S.W. Kaldor, *J. Org. Chem.*, *55* (1990) 1698–1700.
126 T. Hudlicky, J.D. Price, F. Rulin and T. Tsunoda, *J. Am. Chem. Soc.*, *112* (1990) 9439–9440.
127 M. Minato, K. Yamamoto and J. Tsuji, *J. Org. Chem.*, *55* (1990) 766–768.
128 R.M. Pearlstein, B.K. Blackburn, W.M. Davis and K.B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 639–641.
129 J.S. Panek and P.F. Cirillo, *J. Am. Chem. Soc.*, *112* (1990) 4873–4878.
130 M.R. Sivik, J.C. Gallucci and L.A. Paquette, *J. Org. Chem.*, *55* (1990) 391–393.
131 M.T. Nunez and V.S. Martín, *J. Org. Chem.*, *55* (1990) 1928–1932.
132 G.L. Zimmerman, S.J. Riviello, T.A. Glauser and J.G. Kay, *J. Phys. Chem.*, *94* (1990) 2399–2404.
133 O.V. Boyarkin, S.I. Ionov, A.A. Stuchebrukhov, V.N. Bagratashvili and M.S. Djidjoev, *J. Phys. Chem.*, *94* (1990) 1294–1297.
134 D.C. Gregoire, *Anal. Chem.*, *62* (1990) 141–146.
135 H.C. Bajaj and R. van Eldik, *Inorg. Chem.*, *29* (1990) 2855–2858.
136 M. Rotem, Z. Stein and Y. Shvo, *J. Organomet. Chem.*, *387* (1990) 95–101.
137 M.R. Torres, A. Perales, H. Loumrhari and J. Ros, *J. Organomet. Chem.*, *385* (1990) 379–386.
138 A. Sahajpal, S.D. Robinson, M.A. Mazid, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1990) 2119–2124.
139 B.K. Das and A.R. Chakravarty, *Inorg. Chem.*, *29* (1990) 1783–1784.
140 K. Osakada, A. Grohmann and A. Yamamoto, *Organometallics*, *9* (1990) 2092–2096.
141 V.W.-W. Yam and C.-M. Che, *Coord. Chem. Rev.*, *97* (1990) 93–104.
142 B.S. McGilligan, J. Arnold, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1990) 2465–2475.
143 W.A. Herrmann, S.J. Eder, P. Kiprof, K. Rypdal and P. Watzlowik, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 1445–1448.
144 R.W. Marshman, W.S. Bigham, S.R. Wilson and P.A. Shapley, *Organometallics*, *9* (1990) 1341–1343.
145 R.W. Marshman and P.A. Shapley, *J. Am. Chem. Soc.*, *112* (1990) 8369–8378.
146 R. Hotzelmann, K. Wieghardt, U. Florke and H.-J. Haupt, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 645–647.
147 S. Perrier, T.C. Lau and J.K. Kochi, *Inorg. Chem.*, *29* (1990) 4190–4195.
148 C.-M. Che, W.-K. Cheng and V.W.-W. Yam, *J. Chem. Soc., Dalton Trans.*, (1990) 3095–3100.
149 C.-M. Che, K. Lau, T.-C. Lau and C.-K. Poon, *J. Am. Chem. Soc.*, *112* (1990) 5176–5181.
150 V.W.-W. Yam and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, (1990) 3741–3746.
151 S.P. Best and J.B. Forsyth, *J. Chem. Soc., Dalton Trans.*, (1990) 3507–3511.
152 J.M. Hawkins, T.A. Lewis, S.D. Loren, A. Meyer, J.R. Heath, Y. Shibato and R.J. Saykally, *J. Org. Chem.*, *55* (1990) 6250–6252.
153 J. Wang and Z. Taha, *Anal. Chem.*, *62* (1990) 1413–1416.
154 S. Bhattacharya, S.R. Boone, G.A. Fox and C.G. Pierpont, *J. Am. Chem. Soc.*, *112* (1990) 1088–1096.
155 B. Schwederski, V. Kasack, W. Kaim, E. Roth and J. Jordanov, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 78–79.
156 G.J. Irvine, C.E.F. Rickard, W.R. Roper and L.J. Wright, *J. Organomet. Chem.*, *387* (1990) C5–C8.
157 N. Bag, S.B. Choudhury, A. Pramanik, G.K. Lahiri and A. Chakravorty, *Inorg. Chem.*, *29* (1990) 5013–5014.
158 J.G. Muller and K.J. Takeuchi, *Inorg. Chem.*, *29* (1990) 2185–2188.
159 M.J. Weaver, D.K. Phelps, R.M. Nielson, M.N. Golovin and G.E. McManis, *J. Phys. Chem.*, *94* (1990) 2949–2954.
160 Y. Hoshino, Y. Yukawa, T. Maruyama, A. Endo, K. Shimizu and G.P. Sato, *Inorg. Chim. Acta*, *174* (1990) 41–51.
161 Y. Hoshino, R. Takahashi, K. Shimizu, G.P. Sato and K. Aoki, *Inorg. Chem.*, *29* (1990) 4816–4820.
162 W.D. Harman, M. Gebhard and H. Taube, *Inorg. Chem.*, *29* (1990) 567–569.
163 J.T. Anhaus, T.P. Kee, M.H. Schofield and R.R. Schrock, *J. Am. Chem. Soc.*, *112* (1990) 1642–1643.
164 S. Bhattacharya, S.R. Boone and C.G. Pierpont, *J. Am. Chem. Soc.*, *112* (1990) 4561–4562.
165 W. Rohde and H. tom Dieck, *J. Organomet. Chem.*, *385* (1990) 101–111.
166 F.A. Cotton, T. Ren and J.L. Eqlin, *J. Am. Chem. Soc.*, *112* (1990) 3439–3445.
167 B.T. Khan and K. Annapoorna, *Inorg. Chim. Acta*, *171* (1990) 157–163.
168 B.T. Khan and K. Annapoorna, *Inorg. Chim. Acta*, *176* (1990) 241–246.
169 S. Zhang, L.A. Holl and R.E. Shepherd, *Inorg. Chem.*, *29* (1990) 1012–1022.
170 A.B. P Lever, *Inorg. Chem.*, *29* (1990) 1271–1285.
171 J. Zhou, W. Xi and J.K. Hurst, *Inorg. Chem.*, *29* (1990) 160–167.
172 M. Hanack and P. Vermehren, *Inorg. Chem.*, *29* (1990) 134–136.
173 B.D. Rihter, M.E. Kenney, W.E. Ford and M.A.J. Rodgers, *J. Am. Chem. Soc.*, *112* (1990) 8064–8070.
174 A. Yasuda and J. Seto, *J. Electroanal. Chem., Interfacial Electrochem.*, *283* (1990) 197–204.
175 J.M.A. Hoddenbagh and D.H. Macartney, *J. Chem. Soc., Dalton Trans.*, (1990) 615–620.
176 J.A. Cox and T.J. Gray, *Anal. Chem.*, *62* (1990) 2742–2744.
177 J.M.A. Hoddenbagh and D.H. Macartney, *Inorg. Chem.*, *29* (1990) 245–251.
178 S. Eller and R.D. Fischer, *Inorg. Chem.*, *29* (1990) 1289–1290.
179 M.J. Therien, M. Selman, H.B. Gray, I-J. Chang and J.R. Winkler, *J. Am. Chem. Soc.*, *112* (1990) 2420–2422.
180 D.N. Beratan, J.N. Onuchic, J.N. Betts, B.E. Bowler and H.B. Gray, *J. Am. Chem. Soc.*, *112* (1990) 7915–7921.
181 F.A. Armstrong, J.N. Butt, K. Govindaraju, J. McGinnis, R. Powls and A.G. Sykes, *Inorg. Chem.*, *29* (1990) 4858–4862.

182 O. Farver and I. Pecht, *Inorg. Chem., 29* (1990) 4855–4858.
183 C.-M. Che, W.-T. Tang, W.-T. Wong, H.-W. Lam and T.-F. Lai, *J. Chem. Soc., Dalton Trans.,* (1990) 2077–2079.
184 C.-M. Che, W.-T. Tang and C.-K. Li, *J. Chem. Soc., Dalton Trans.,* (1990) 3735–3739.
185 M.M.T. Khan, N.H. Khan, R.I. Kureshy and A.B. Boricha, *Inorg. Chim. Acta, 174* (1990) 175–184.1
86 M.M.T. Khan, N.H. Khan, R.I. Kureshy, A.B. Boricha and Z.A. Shaikh, *Inorg. Chim. Acta, 170* (1990) 213–223.
187 M.M.T. Khan, D. Srinivas, R.I. Kureshy and N.H. Khan, *Inorg. Chem., 29* (1990) 2320–2326.
188 M.R. Ghadiri and A.K. Fernholz, *J. Am. Chem. Soc., 112* (1990) 9633–9635.
189 W.D. Harman and H. Taube, *J. Am. Chem. Soc., 112* (1990) 2261–
190 S. Ronco and G. Ferraudi, *J. Chem. Soc., Dalton Trans.,* (1990) 887–889.
191 G.-D. Lei and L. Kevan, *J. Phys. Chem., 94* (1990) 6384–6390.
192 S. Basak, K. Rajeshwar and M. Kaneko, *Anal. Chem., 62* (1990) 1407–1413.
193 A. Abelleira, R.D. Galang and M.J. Clarke, *Inorg. Chem., 29* (1990) 633–639.
194 A.A. Saleh and R.J. Crutchley, *Inorg. Chem., 29* (1990) 2132–2135.
195 A. Vassilian, J.F. Wishart, B. van Hemelryck, H. Schwarz and S.S. Isied, *J. Am. Chem. Soc., 112* (1990) 7278–7286.
196 S. Ronco and G. Ferraudi, *Inorg. Chem., 29* (1990) 3961–3967.
197 R.J. Crutchley, K. McCaw, F.L. Lee and E.J. Gabe, *Inorg. Chem., 29* (1990) 2576–2581.
198 T.R. Cundari and R.S. Drago, *Inorg. Chem., 29* (1990) 3904–3907.
199 R.S. Armstrong, W.A. Horsfield and K.W. Nugent, *Inorg. Chem., 29* (1990) 4551–4556.
200 R. Sarala, M.A. Islam, S.B. Rabin and D.M. Stanbury, *Inorg. Chem., 29* (1990) 1133–1142.
201 D.G. Kelley, J.H. Espenson and A. Bakac, *Inorg. Chem., 29* (1990) 4996–5000.
202 M.K. De Armond, M.L. Myrick, R. Pittman and R.E. Des Enfants, II, *Coord. Chem. Rev., 97* (1990) 261–270.
203 M. Kozik, N. Sutin and J.R. Winkler, *Coord. Chem. Rev., 97* (1990) 23–34.
204 J.K. Blaho and K.A. Goldsby, *J. Am. Chem. Soc., 112* (1990) 6132–6133.
205 J.P. Collin, A. Jouaiti and J.P. Savage, *J. Electroanal. Chem., Interfacial Electrochem., 286* (1990) 75–87.
206 U.C. Sarma, S.C. Sarker, B.C. Paul and R.K. Poddar, *Inorg. Chim. Acta, 173* (1990) 195–199.
207 P.D. Beer, O. Kocian and R.J. Mortimer, *J. Chem. Soc., Dalton Trans.,* (1990) 3283–3288.
208 M.V. Pishko, I. Katakis, S.-E. Lindquist, L. Ye, B.A. Gregg and A. Heller, *Angew. Chem., Int. Ed. Eng., 29* (1990) 82–84.
209 D.W. Wright and R.H. Schmehl, *Inorg. Chem., 29* (1990) 155–157.
210 M. Haga, K. Isobe, S.R. Boone and C.G. Pierpont, *Inorg. Chem., 29* (1990) 3795–3799.
211 L.D. Ciana, W.J. Dressick, D. Sandrini, M. Maestri and M. Ciano, *Inorg. Chem., 29* (1990) 2792–2798.
212 H. Ishida, T. Terada, K. Tanaka and T. Tanaka, *Inorg. Chem., 29* (1990) 905–911.
213 C. Hidalgo-Luangdilok, A.B. Bocarsly and R.E. Woods, *J. Phys. Chem., 94* (1990) 1918–1924.
214 S. Sommerer, W.P. Jensen and R.A. Jacobson, *Inorg. Chim. Acta, 172* (1990) 3–11.
215 D.W. Pipes, M. Bakir, S.E. Vitols, D.J. Hodgson and T.J. Meyer, *J. Am. Chem. Soc., 112* (1990) 5507–5514.
216 C. Ho, C.-M. Che and T.-C. Lau, *J. Chem. Soc., Dalton Trans.,* (1990) 967–970.
217 J.-P. Collin, S. Guillerez and J.-P. Sauvage, *Inorg. Chem., 29* (1990) 5009–5010.
218 R.A. Leising, S.A. Kubow and K.J. Takeuchi, *Inorg. Chem., 29* (1990) 4569–4574.
219 R.A. Leising, S.A. Kubow, M.R. Churchill, L.A. Buttrey, J.W. Ziller and K.J. Takeuchi, *Inorg. Chem., 29* (1990) 1306–1312.
220 H. Nishimura, H. Matsuzawa, T. Togano, M. Mukaida, H. Kakihana and F. Bottomley, *J. Chem. Soc., Dalton Trans.,* (1990) 137–141.
221 H. Nagao, H. Nishimura, Y. Kitanaka, F.S. Howell, M. Mukaida and H. Kakihana, *Inorg. Chem., 29* (1990) 1693–1700.
222 K.M. Kost, D.E. Bartak, B. Kazee and T. Kuwana, *Anal. Chem., 62* (1990) 151–157.
223 J.T. Kunjappu, P. Somasundaran and N.J. Turro, *J. Phys. Chem., 94* (1990) 8464–8468.
224 Y.J. Chang, X. Xu, T. Yabe, S.-C. Yu, D.R. Anderson, L.K. Orman and J.B. Hopkins, *J. Phys. Chem., 94* (1990) 729–736.
225 H.-B. Kim, N. Kitamura and S. Tazuke, *J. Phys. Chem., 94* (1990) 1414–1418.
226 D.P. Strommen, P.K. Mallick, G.D. Danzer, R.S. Lumpkin and J.R. Kincaid, *J. Phys. Chem., 94* (1990) 1357–1366.
227 G.D. Danzer and J.R. Kincaid, *J. Phys. Chem., 94* (1990) 3976–3980.
228 H. Yersin, P. Huber and D. Braun, *J. Phys. Chem., 94* (1990) 3560–3564.
229 L.F. Cooley, P. Bergquist and D.F. Kelley, *J. Am. Chem. Soc., 112* (1990) 2612–2617.
230 P.K. Mallick, D.P. Strommen and J.R. Kincaid, *J. Am. Chem. Soc., 112* (1990) 1686–1690.
231 H.-B. Kim, N. Kitamura and S. Tazuke, *J. Phys. Chem., 94* (1990) 7401–7405.
232 T. Ohno, A. Yoshimura and N. Mataga, *J. Phys. Chem., 94* (1990) 4871–4876.
233 R.L. Blakley, M.L. Myrick, R. Pittman and M.K. De Armond, *J. Phys. Chem., 94* (1990) 4804–4809.
234 T.S. Akasheh and N.A.F. Al-Rawashdeh, *J. Phys. Chem., 94* (1990) 8594–8598.
235 S. Fukuzumi, S. Mochizuki and T. Tanaka, *J. Phys. Chem., 94* (1990) 722–726.
236 M. Jinguji, M. Ishihara and T. Nakazawa, *J. Phys. Chem., 94* (1990) 1226–1229.
237 C. Hiort, B. Norden and A. Rodger, *J. Am. Chem. Soc., 112* (1990) 1971–1982.
238 V. Katta, S.K. Chowdhury and B.T. Chait, *J. Am. Chem. Soc., 112* (1990) 5348–5349.
239 M. Rodriguez and A.J. Bard, *Anal. Chem., 62* (1990) 2658–2662.
240 L.S. Kuhn, A. Weber and S.G. Weber, *Anal. Chem., 62* (1990) 1631–1636.
241 F. Bolletta and M. Vitale, *Inorg. Chim. Acta, 175* (1990) 127–131.
242 J.-M. Lehn and R. Ziessel, *J. Organomet. Chem., 382* (1990) 157–173.
243 S. Yamazaki-Nishida and M. Kimura, *Inorg. Chim. Acta, 174* (1990) 231–235.
244 M.R. DeFelippis, M. Faraggi and M.H. Klapper, *J. Phys. Chem., 94* (1990) 2420–2424.
245 A.C. Maliyackel, W.L. Waltz, J. Lilie and R.J. Woods, *Inorg. Chem., 29* (1990) 340–348.
246 S. Lee, A. Bakac and J.H. Espenson, *Inorg. Chem., 29* (1990) 2480–2482.

247 R. Sarala and D.M. Stanbury, *Inorg. Chem.*, *29* (1990) 3456-3460.

248 I. Willner, T. Tsfania and Y. Eichen, *J. Org. Chem.*, *55* (1990) 2656-2662.

249 M.C. Moreno-Bondi, O.S. Wolfbeis, M.J.P. Leiner and B.P.H. Schaffar, *Anal. Chem.*, *62* (1990) 2377-2380.

250 J.C. Jernigan and R.W. Murray, *J. Am. Chem. Soc.*, *112* (1990) 1034-1038.

251 L.A. Worl, G.F. Strouse, J.N. Younathan, S.M. Baxter and T.J. Meyer, *J. Am. Chem. Soc.*, *112* (1990) 7571-7578.

252 S. Gould, T.R. O'Toole and T.J. Meyer, *J. Am. Chem. Soc.*, *112* (1990) 9490-9496.

253 P.J. Kulesza, G. Roslonek and L.R. Faulkner, *J. Electroanal. Chem., Interfacial Electrochem.*, *280* (1990) 233-240.

254 X. Chen, B. Xia and P. He, *J. Electroanal. Chem., Interfacial Electrochem.*, *281* (1990) 185-198.

255 R.L. McCarley, R.E. Thomas, E.A. Irene and R.W. Murray, *J. Electrochem. Soc.*, *137* (1990) 1485-1490.

256 G. Villemure and A.J. Bard, *J. Electroanal. Chem., Interfacial Electrochem.*, *283* (1990) 403-420.

257 S. Cosnier, A. Deronzier and J.F. Roland, *J. Electroanal. Chem., Interfacial Electrochem.*, *285* (1990) 133-147.

258 A. Kudo, M. Steinberg, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber and J.M. White, *J. Electrochem. Soc.*, *137* (1990) 3846-3849.

259 S.K. Cha and H.K. Abruha, *Anal. Chem.*, *62* (1990) 274-278.

260 S. Umapathy, A.M. Cartner, A.W. Parker and R.E. Hester, *J. Phys. Chem.*, *94* (1990) 8880-8885.

261 B. O'Regan, J. Moser, M. Anderson and M. Gratzel, *J. Phys. Chem.*, *94* (1990) 8720-8726.

262 A.J. Downard, N.A. Surridge, S. Gould, T.J. Meyer, A. Deronzier and J.-C. Moutet, *J. Phys. Chem.*, *94* (1990) 6754-6764.

263 H. Nishihara, K. Pressprich, R.W. Murray and J.P. Collman, *Inorg. Chem.*, *29* (1990) 1000-1006.

264 N.A. Surridge, F.R. Keene, B.A. White, J.S. Facci, M. Silver and R.W. Murray, *Inorg. Chem.*, *29* (1990) 4950-4955.

265 C.M. Elliott, C.J. Baldy, L.M. Nuwaysir and C.L. Wilkins, *Inorg. Chem.*, *29* (1990) 389-392.

266 C. Lee and A.J. Bard, *Anal. Chem.*, *62* (1990) 1906-1913.

267 H.C. Hurrell and H.D. Abruna, *Inorg. Chem.*, *29* (1990) 736-741.

268 J.A. Incavo and P.K. Dutta, *J. Phys. Chem.*, *94* (1990) 3075-3081.

269 D. Rong, Y.I. Kim and T.E. Mallouk, *Inorg. Chem.*, *29* (1990) 1531-1535.

270 M. Taniguchi, M. Kaneyoshi, Y. Nakamura, A. Yamagishi and T. Iwamoto, *J. Phys. Chem.*, *94* (1990) 5896-5900.

271 V.G. Kuykendall and J.K. Thomas, *J. Phys. Chem.*, *94* (1990) 4224-4230.

272 G. Villemure and A.J. Bard, *J. Electroanal. Chem., Interfacial Electrochem.*, *282* (1990) 107-21.

273 A.E. Friedman, J.-C. Chambron, J.-P. Sauvage, N.J. Turro and J.K. Barton, *J. Am. Chem. Soc.*, *112* (1990) 4960-4962.

274 S. Yamazaki-Nishida, Y. Harima and K. Yamashita, *J. Electroanal. Chem., Interfacial Electrochem.*, *283* (1990) 455-458.

275 W. Kaim, S. Ernst and V. Kasack, *J. Am. Chem. Soc.*, *112* (1990) 173-178.

276 R.S. Lumpkin, E.M. Kober, L.A. Worl, Z. Murtaza and T.J. Meyer, *J. Phys. Chem.*, *94* (1990) 239-243.

277 T. Yabe, L.K. Orman, D.R. Anderson, S.-C. Yu, X. Xu and J.B. Hopkins, *J. Phys. Chem.*, *94* (1990) 7128-7132.

278 W. Kaim and W. Matheis, *Chem. Ber.*, *123* (1990) 1323-1325.

279 G. Orellana, A.K.-D. Mesmaiker and N.J. Turro, *Inorg. Chem.*, *29* (1990) 882-885.

280 A.M. Pyle, M.Y. Chiang and J.K. Barton, *Inorg. Chem.*, *29* (1990) 4487-4495.

281 R. Hage, J.H. van Diemen, G. Ehrlich, J.G. Haasnoot, D.J. Stufkens, T.L. Snoeck, J.G. Vos and J. Reedjik, *Inorg. Chem.*, *29* (1990) 988-993.2

82 A. Masschelein, L. Jacquet, A.K.-D. Mesmaeker and J. Nasielski, *Inorg. Chem.*, *29* (1990) 855-860.

283 K. Kalyanasundaram and MD.K. Nazeeruddin, *Inorg. Chim. Acta*, *171* (1990) 213-216.

284 B.D. J.R. Fennema, R. Hage, J.G. Haasnoot, J. Reedijk and J.G. Vos, *Inorg. Chim. Acta*, *171* (1990) 223-228.

285 R. Hage, J.G. Haasnoot, J. Reedijk, R. Wang, E.M. Ryan, J.G. Vos, A.L. Spek and A.J.M. Duisenberg, *Inorg. Chim. Acta*, *174* (1990) 77-85.

286 T.S. Akasheh, I. Jibril and A.M. Shraim, *Inorg. Chim. Acta*, *175* (1990) 171-180.

287 E.C. Constable and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1990) 1405-1409.

288 P.J. Steel and E.C. Constable, *J. Chem. Soc., Dalton Trans.*, (1990) 1389-1396.

289 E. Amouyal, A. Homsi, J.-C. Chambron and J.-P. Sauvage, *J. Chem. Soc., Dalton Trans.*, (1990) 1841-1845.

290 M.M.T. Khan, P.S. Roy, K. Venkatasubramanian and N.H. Khan, *Inorg. Chim. Acta*, *176* (1990) 49-55.

291 B.E. Buchanan, J.G. Vos, M. Kaneko, W.J.M. van der Putten, J.M. Kelly, R. Hage, R.A.G. de Graff, R. Prins, J.G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1990) 2425-2431.

292 R.J. Forster, A. Boyle, J.G. Vos, R. Hage, A.H.J. Dijkhuis, R.A. G. de Graff, J.G. Haasnoot, R. Prins and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1990) 121-126.

293 B.E. Buchanan, R. Wang, J.G. Vos, R. Hage, J.G. Haasnoot and J. Reedijk, *Inorg. Chem.*, *29* (1990) 3263-3265.

294 A. Llobet, D.J. Hodgson and T.J. Meyer, *Inorg. Chem.*, *29* (1990) 3760-3766.

295 C.-M. Che, V.W.-W. Yam and T.C.W. Mak, *J. Am. Chem. Soc.*, *112* (1990) 2284-2291.

296 H.-Y. Cheng and S.-M. Peng, *Inorg. Chim. Acta*, *169* (1990) 23-24.

297 V. Goulle and R.P. Thummel, *Inorg. Chem.*, *29* (1990) 1767-1772.

298 S.B. Piepho, *J. Am. Chem. Soc.*, *112* (1990) 4197-4206.

299 D.H. Oh and S.G. Boxer, *J. Am. Chem. Soc.*, *112* (1990) 8161-8162.

300 M.A.S. Aquino, A.E. Bostock and R.J. Crutchley, *Inorg. Chem.*, *29* (1990) 3641-3644.

301 J.R. Reimers and N.S. Hush, *Inorg. Chem.*, *29* (1990) 4510-4513.

302 J.R. Reimers and N.S. Hush, *Inorg. Chem.*, *29* (1990) 3686-3697.

303 F. Scandola, C.A. Bignozzi, C. Chiorboli, M.T. Indelli and M.A. Rampi, *Coord. Chem. Rev.*, *97* (1990) 299-312.

304 K. Kalyanasundaram and M.K. Nazeeruddin, *J. Chem. Soc., Dalton Trans.*, (1990) 1657-1662.

305 R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, D.J.A. De Ridder and J.G. Vos, *J. Am. Chem. Soc.*, *112* (1990) 9245-9251.

306 Y. Lei, T. Buranda and J.F. Endicott, *J. Am. Chem. Soc.*, *112* (1990) 8820-8833.

307 R. Amadelli, R. Argazzi, C.A. Bignozzi and F. Scandola, *J. Am. Chem. Soc.*, *112* (1990) 7099-7103.

308 J.T. Hupp, *J. Am. Chem. Soc.*, *112* (1990) 1563-1565.

309 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chim. Acta*, *176* (1990) 175-178.

310 R.M. Berqer, *Inorg. Chem.*, *29* (1990) 1920-1924.

311 D.B. MacQueen and J.D. Petersen, *Inorg. Chem.*, *29* (1990) 2313-2320.

312 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, *29* (1990) 4750-4758.

313 W. Kaim and V. Kasack, *Inorg. Chem.*, *29* (1990) 4696-4699.

314 C. Hidalgo-Luangdilok and A.B. Bocarsly, *Inorg. Chem.*, *29* (1990) 2894–2900.

315 J.B. Cooper, D.B. MacQueen, J.D. Petersen and D.W. Wertz, *Inorg. Chem.*, *29* (1990) 3701–3705.

316 E. Binamira-Soriaga, N.L. Keder and W.C. Kaska, *Inorg. Chem.*, *29* (1990) 3167–3171.

317 S. Boyde, G.F. Strouse, W.E. Jones, Jr. and T.J. Meyer, *J. Am. Chem. Soc.*, *112* (1990) 7395–7396.

318 S.K. Doorn, J.T. Hupp, D.R. Porterfield, A. Campion and D.B. Chase, *J. Am. Chem. Soc.*, *112* (1990) 4999–5002.

319 A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, *29* (1990) 1442–1444.

320 P.R. Auburn and A.B.P. Lever, *Inorg. Chem.*, *29* (1990) 2551–2553.

321 J.-P. Collin, A. Jouaiti, J.-P. Sauvage, S.C. Kaska, M.A. McLoughlin, N.L. Keder, W.T.A. Harrison and G.D. Stucky, *Inorg. Chem.*, *29* (1990) 2238–2241.

322 P. Neubold, B.S. P.C. Della Vedova, K. Wieghardt, B. Nuber and J. Weiss, *Inorg. Chem.*, *29* (1990) 3355–3363.

323 D.P. Rillema, R. Sahai, P. Matthews, A.K. Edwards, R.J. Shaver and L. Morgan, *Inorg. Chem.*, *29* (1990) 167–175.

324 L. De Cola, P. Belser, F. Ebmeyer, F. Barigelletti, F. Vogtle, A. von Zelewsky and V. Balzani, *Inorg. Chem.*, *29* (1990) 495–499.

325 K. Kalyanasundaram and Md. K. Nazeeruddin, *Inorg. Chem.* (1990) 1888–1897.

326 C.-F. Shu and F.C. Anson, *J. Phys. Chem.*, *94* (1990) 8345–8350.

327 C.-F. Shu and F.C. Anson, *J. Am. Chem. Soc.*, *112* (1990) 9227–9232.

328 S.F. Colson, S.D. Robinson and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1990) 629–632.

329 S.G. Davies and A.J. Smallridge, *J. Organomet. Chem.*, *395* (1990) C39–C41.

330 L.M. Boyd, G.R. Clark and W.R. Roper, *J. Organomet. Chem.*, *397* (1990) 209–218.

331 M.I. Bruce, A. Catlow, M.P. Cifuentes, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, *397* (1990) 187–202.

332 M.R. Torres, A. Perales, H. Loumrhari and J. Ros, *J. Organomet. Chem.*, *384* (1990) C61–C64.

333 A.K. Burrell, G.R. Clark, C.E.F. Rickard, W.R. Roper and D.C. Ware, *J. Organomet. Chem.*, *398* (1990) 133–158.

334 W.D. Harman, W.P. Shaefer and H. Taube, *J. Am. Chem. Soc.*, *112* (1990) 2682–2685.

335 M. Crocker, M. Green, K.R. Nagle and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, (1990) 2571–2580.

336 S.T. Astley, J. Takats, J.C. Huffman and W.E. Streib, *Organometallics*, *9* (1990) 184–189.

337 M.I. Bruce, *J. Organomet. Chem.*, *400* (1990) 321–340.

338 A. Tahiri, V. Guerchais, L. Toupet and C. Lapinte, *J. Organomet. Chem.*, *381* (1990) C47–C51.

339 T. Wilczewski, *J. Organomet. Chem.*, *382* (1990) 431–443.

340 H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden and C. White, *J. Organomet. Chem.*, *387* (1990) 305–314.

341 N.G. Connelly, A.C. Lyons, I. Manners, D.L. Mercer, K.E. Richardson and P.H. Rieger, *J. Chem. Soc., Dalton Trans.*, (1990) 2451–2458.

342 B.M. Trost, G. Dyker and R.J. Kulawiec, *J. Am. Chem. Soc.*, *112* (1990) 7809–7811.

343 H. Adams, N.A. Bailey, C. Ridgway, B.F. Taylor, S.J. Walters and M.J. Winter, *J. Organomet. Chem.*, *394* (1990) 349–364.

344 F.M. Conroy-Lewis, A.D. Redhouse and S.J. Simpson, *J. Organomet. Chem.*, *399* (1990) 307–315.

345 F.M. Conroy-Lewis and S.J. Simpson, *J. Organomet. Chem.*, (1990) 83–94.

346 S.G. Davies and A.J. Smallridge, *J. Organomet. Chem.*, *397* (1990) C13–C19.

347 R.M. Bullock, F.R. Lemke and D.J. Szalda, *J. Am. Chem. Soc.*, *112* (1990) 3244–3245.

348 S.A. Benyunes, J.P. Day, M. Green, A.W. Al-Saadoon and T.L. Waring, *Angew. Chem., Int. Ed. Engl.* *29* (1990) 1416–1417.

349 W. Weigand, U. Nagel and W. Beck, *Chem. Ber.*, *123* (1990) 439–448.

350 M.S. Chinn and D.M. Heinekey, *J. Am. Chem. Soc.*, *112* (1990) 5166–5175.

351 R.S. Koefod and K.R. Mann, *J. Am. Chem. Soc.*, *112* (1990) 7287–7293.

352 M.I. Bruce, T.W. Hambley, M.J. Liddell, M.R. Snow, A.G. Swincer and E.R.T. Tiekink, *Organometallics*, *9* (1990) 96–104.

353 A. Shaver, P.-Y. Plouffe, P. Bird and E. Livingstone, *Inorg. Chem.*, *29* (1990) 1826–1831.

354 R.J. Kulawiec, J.W. Faller and R.H. Crabtree, *Organometallics*, *9* (1990) 745–755.

355 R. Benn, H. Brenneke, E. Joussen, H. Lehmkuhl and F.L. Ortiz, *Organometallics*, *9* (1990) 756–761.

356 H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-oka and K. Itoh, *Organometallics*, *9* (1990) 799–807.

357 D.M. Heinekey, N.G. Payne and C.D. Sofield, *Organometallics*, *9* (1990) 2643–2645.

358 M.I. Bruce, T.W. Hambley, M.J. Liddell, A.G. Swincer and E.R.T. Tiekink, *Organometallics*, *9* (1990) 2886–2898.

359 T.D. Newbound, L. Stahl, M.L. Ziegler and R.D. Ernst, *Organometallics*, *9* (1990) 2962–2972.

360 M. Crocker, M. Green, K.R. Nagle, A.G. Orpen, H.-P. Neumann, C.E. Morton and C.J. Schaverien, *Organometallics*, *9* (1990) 1422–1434.

361 P.J. Fagan, W.S. Mahoney, J.C. Calabrese and I.D. Williams, *Organometallics*, *9* (1990) 1843–1852.

362 U. Kolle, J. Kossakowski and G. Raabe, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 773–774.

363 B. Chaudret, A. Duteil and X.D. He, *J. Organomet. Chem.*, *391* (1990) C45–C47.

364 U. Kolle, B.-S. Kang and U. Thewalt, *J. Organomet. Chem.*, *386* (1990) 267–273.

365 D.A. Straus, S.D. Grumbine and T.D. Tilley, *J. Am. Chem. Soc.*, *112* (1990) 7801–7802.

366 D.A. Straus, C. Zhang, G.E. Quimbita, S.D. Grumbine, R.H. Heyn, T.D. Tilley, A.L. Rheingold and S.J. Geib, *J. Am. Chem. Soc.*, *112* (1990) 2673–2681.

367 L.F. Szczepura and K.J. Takeuchi, *Inorg. Chem.*, *29* (1990) 1772–1777.

368 T. Aase, M. Tilset and V.D. Parker, *J. Am. Chem. Soc.*, *112* (1990) 4974–4975.

369 P.D. Beer, A.D. Keefe, A.M.Z. Slawin and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, (1990) 3675–3682.

370 C.-M. Jen Wang and R.J. Angelici, *Organometallics*, *9* (1990) 1770–1777.

371 A.E. Skaugset, T.B. Rauchfuss and S.R. Wilson, *Organometallics*, *9* (1990) 2875–2876.

372 K. Kirchner, H.W. Dodgen, S. Wherland and J.P. Hunt, *Inorg. Chem.*, *29* (1990) 2381–2385.

373 K. Kirchner, L.-F. Han, H.W. Dodgen, S. Wherland and J.P. Hunt, *Inorg. Chem.*, *29* (1990) 4556–4559.

374 E.W. Abel, N.J. Long, K.H. Orrell, A.G. Osborne, V. Sik, P.A. Bates and M.B. Hursthouse, *J. Organomet. Chem.*, *394* (1990) 455–468.

375 M. Canestrari, B. Chaudret, F. Dahan, Y.-S. Haung, R. Poil-

banc, T.-C. Kim and M. Sanchez, *J. Chem. Soc., Dalton Trans.*, (1990) 1179–1182.

376 E. Colomer, R.J.P. Corriu and R. Pleixats, *J. Organomet. Chem.*, *381* (1990) C1–C6.

377 S. Stahl and H. Werner, *Organometallics*, *9* (1990) 1876–1881.

378 M. Schulz, S. Stahl and H. Werner, *J. Organomet. Chem.*, *394* (1990) 469–479.

379 M.A. Bennett and A.M.M. Weerasuria, *J. Organomet. Chem.*, *394* (1990) 481–513.

380 D. Carmona, J. Ferrer, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Elguero and M.L. Jimeno, *J. Chem. Soc., Dalton Trans.*, (1990) 1463–1476.

381 A. Romero, A. Vegas and P.H. Dixneuf, *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 215–216.

382 W.A. Kiel, R.G. Ball and W.A.G. Graham, *J. Organomet. Chem.*, *383* (1990) 481–496.

383 M.A. Bennett, I.J. McMahon and S. Pelling, *J. Organomet. Chem.*, *382* (1990) 175–184.

384 P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (1990) 1779–1792.

385 D. Devanne and P.H. Dixneuf, *J. Organomet. Chem.*, *390* (1990) 371–378.

386 R. Kramer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, *Chem. Ber.*, *123* (1990) 767–778.

387 W.S. Sheldrick and S. Heeb, *Inorg. Chim. Acta*, *168* (1990) 93–100.

388 D. Carmona, A. Mendoza, F.J. Lahoz, L.A. Oro, M.P. Lamata and E. San Jose, *J. Organomet. Chem.*, *396* (1990) C17–C21.

389 U. Koelle and M.H. Wang, *Organometallics*, *9* (1990) 195–198.

390 P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, L. Sagramora, V. Adovasio and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (1990) 179–186.

391 M.R.J. Elsegood and D.A. Tocher, *J. Organomet. Chem.*, *391* (1990) 239–245.

392 Faridoon, M. McGrath, T.R. Spalding, X.L.R. Fontaine, J.D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1990) 1819–1829.

393 J.H. Davis, Jr., M.D. Attwood and R.N. Grimes, *Organometallics*, *9* (1990) 1171–1176.

394 M.D. Attwood, J.H. Davis, Jr. and R.N. Grimes, *Organometallics*, *9* (1990) 1177–1181.

395 A. Fessenbecker, M.D. Attwood, R.F. Bryan, R.N. Grimes, M.K. Woode, M. Stephan, U. Zenneck and W. Siebert, *Inorg. Chem.*, *29* (1990) 5157–5163.

396 A. Fessenbecker, M.D. Attwood, R.N. Grimes, M. Stephan, H. Pritzkow, U. Zenneck and W. Siebert, *Inorg. Chem.*, *29* (1990) 5164–5168.

397 J.M. Power, K. Evertz, L. Henling, R. March, W.P. Schaefer, J.A. Labinger and J.E. Bercaw, *Inorg. Chem.*, *29* (1990) 5058–5065.

398 B.K. Das and A.R. Chakravarty, *Inorg. Chem.*, *29* (1990) 2078–2083.

399 A.C. Dengel, A.M. El-Hendawy, W.P. Griffith, C.A. O'Mahoney and D.J. Williams, *J. Chem. Soc., Dalton Trans.*, (1990) 737–742.

400 F.A. Cotton and K. Vidyasagar, *Inorg. Chem.*, *29* (1990) 3197–3199.

401 T.W. Johnson, S.M. Tetrick and R.A. Walton, *Inorg. Chim. Acta*, *167* (1990) 133–134.

402 S. Dev, Y. Mizobe and M. Hidai, *Inorg. Chem.*, *29* (1990) 4797–4801.

403 A. Mishra and U.C. Agarwala, *Inorg. Chim. Acta*, *170* (1990) 209–211.

404 G.E. Quelch, I.H. Hillier and M.F. Guest, *J. Chem. Soc., Dalton Trans.*, (1990) 3075–3081.

405 M. Watanabe, S. Kawata, H. Sano and I. Motoyama, *J. Organomet. Chem.*, *399* (1990) 301–306.

406 W.E. Geiger, A. Salzer, J. Edwin, W. van Philipsborn, U. Piantini and A.L. Rheingold, *J. Am. Chem. Soc.*, *112* (1990) 7113–7121.

407 K.-D. Plitzko, B. Rapko, B. Gollas, G. Wehrle, T. Weakley, D.T. Pierce, W.E. Geiger, Jr., R.C. Haddon and V. Boekelheide, *J. Am. Chem. Soc.*, *112* (1990) 6545–6556.

408 K.-D. Plitzko, G. Wehrle, B. Gollas, B. Rapki, J. Dannheim and V. Boekelheide, *J. Am. Chem. Soc.*, *112* (1990) 6556–6564.

409 G.C. Martin, G.J. Palenik and J.M. Boncella, *Inorg. Chem.*, *29* (1990) 2027–2030.

410 S.A.R. Knox, *J. Organomet. Chem.*, *400* (1990) 255–272.

411 R.E. Colborn, A.F. Dyke, B.P. Gracey, S.A.R. Knox, K.A. Macpherson, K.A. Mead and A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1990) 761–771.

412 B.V. Lokshin, A. Ginzburg and S.G. Karayan, *J. Organomet. Chem.*, *397* (1990) 203–208.

413 T.E. Bitterwolf, *J. Organomet. Chem.*, *386* (1990) 9–17.

414 P.E. Bloyce, A.K. Campen, R.H. Hooker, A.J. Rest, N.R. Thomas, T.E. Bitterwolf and J.E. Shade, *J. Chem. Soc., Dalton Trans.*, (1990) 2833–2841.

415 A. Haynes, M. Poliakoff, J.J. Turner, B.R. Bender and J.R. Norton, *J. Organomet. Chem.*, *383* (1990) 497–519.

416 N.K. Bhattacharyya, T.J. Coffy, W. Quinatana, T.A. Salupo, J.C. Bricker, T.B. Shay, M. Payne and S.G. Shore, *Organometallics*, *9* (1990) 2368–2374.

417 A.-J. DiMaio, T.E. Bitterwolf and A.L. Rheingold, *Organometallics*, *9* (1990) 551–555.

418 K.A. Johnson and W.L. Gladfelter, *Organometallics*, *9* (1990) 2101–2105.

419 Z. Xue, W.J. Sieber, C.B. Knobler and H.D. Kaesz, *J. Am. Chem. Soc.*, *112* (1990) 1825–1833.

420 D.J. Witter, S.M. Breckenridge, A.A. Cherkas, L.H. Randall, S.A. MacLaughlin, N.J. Taylor and A.J. Carty, *Organometallics*, *9* (1990) 2636–2638.

421 A.A. Cherkas, N. Hadj-Bagheri, A.J. Carty, E. Sappa, M.A. Pellinghelli and A. Tiripicchio, *Organometallics*, *9* (1990) 1887–1892.

422 J. Breimair, M. Steimann, B. Wagner and W. Beck, *Chem. Ber.*, *123* (1990) 7–10.

423 K.J. Edwards, J.S. Field, R.J. Haines, B. Homann, J. Sundermeyer and S.F. Woollam, *J. Organomet. Chem.*, *386* (1990) C1–C6.

424 J.S. Field, R.J. Haines, U. Honrath, J. Sundermeyer and S.F. Woollam, *J. Organomet. Chem.*, *395* (1990) C9–C15.

425 R.W. Hilts and M. Cowie, *Inorg. Chem.*, *29* (1990) 3349–3354.

426 M.M. de V. Steyn, E. Singleton, S. Hietkamp and D.C. Liles, *J. Chem. Soc., Dalton Trans.*, (1990) 2991–2997.

427 R.W. Hilts, S.J. Sherlock, M. Cowie, E. Singleton and M.M. de V. Steyn, *Inorg. Chem.*, *29* (1990) 3161–3167.

428 D.S. Bohle and H. Vahrenkamp, *Inorg. Chem.*, *29* (1990) 1097–1099.

429 P. Frediani, M. Bianchi, A. Salvini, F. Piacenti, S. Ianelli and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (1990) 1705–1716.

430 C.E. Suchart, G.H. Young, A. Wojcicki, M. Calligaris and G. Nardin, *Organometallics*, *9* (1990) 2417–2420.

431 A.A. Cherkas, L.H. Randall, N.J. Taylor, G.N. Mott, J.E. Yule, J.L. Guinamant and A.J. Carty, *Organometallics*, *9* (1990) 1677–1685.

432 O.C.P. Beers, C.J. Elsevier, W.P. Mul, K. Vrieze, L.P. Haming and C.H. Stam, *Inorg. Chim. Acta*, *171* (1990) 129–131.

433 M.P. Garcia, A.M. L6pez, M.A. Esteruelas, F.J. Lahoz and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1990) 3465–3472.

434 H.B. Friedrich, J.R. Moss and B.K. Williamson, *J. Organomet. Chem., 394* (1990) 313–327.

435 C.P. Casey, *J. Organomet. Chem., 400* (1990) 205–221.

436 K.G. Frank and J.P. Selegue, *J. Am. Chem. Soc., 112* (1990) 6414–6416.

437 K.E. Howard, J.R. Lockemeyer, M.A. Massa, T.B. Rauchfuss, S.R. Wilson and X. Yang, *Inorg. Chem., 29* (1990) 4385–4390.

438 P.C. Ford, *J. Organomet. Chem., 383* (1990) 339–356.

439 B.F.G. Johnson and A. Bott, *J. Chem. Soc., Dalton Trans.,* (1990) 2437–2444.

440 M. Day, S. Hajela, K.I. Hardcastle, T. McPhillips, E. Rosenberg, M. Botta, R. Gobetto, L. Milone, D. Osella and R.W. Gellert, *Organometallics, 9* (1990) 913–924.

441 S. Yamamoto, R.M. Lewis, Y. Nabata, H. Hotta and H. Kuroda, *Inorg. Chem., 29* (1990) 4342–4345.

442 G. Predieri, A. Tiripicchio, M.T. Camellini, M. Costa and E. Sappa, *Organometallics, 9* (1990) 1729–1734.

443 J.-L. Wolfender, F. Neumann and G. Suss-Fink, *J. Organomet. Chem., 389* (1990) 351–359.

444 H.D. Kaesz, *J. Organomet. Chem., 383* (1990) 413–420.

445 W. Krone-Schmidt, W.J. Sieber, N.M. Boag, C.B. Knobler and H.D. Kaesz, *J. Organomet. Chem., 394* (1990) 433–454.

446 M. Langenbahn, H. Stoeckli-Evans and G. Suss-Fink, *J. Organomet. Chem., 397* (1990) 347–358.

447 J. Barrau, N.B. Hamida and J. Satge, *J. Organomet. Chem., 395* (1990) 27–38.

448 M. Brown and J.M. Waters, *J. Am. Chem. Soc., 112* (1990) 2442–2443.

449 M. Brown, J.M. Waters, X.L.R. Fontaine and J.D. Kennedy, *J. Organomet. Chem., 390* (1990) 379–387.

450 A.K. Chipperfield, C.E. Housecroft and P.R. Raithby, *Organometallics, 9* (1990) 479–483.

451 A.K. Chipperfield, C.E. Housecroft and D.M. Matthews, *J. Organomet. Chem., 384* (1990) C38–C42.

452 D.P. Workman, H.-B. Deng and S.C. Shore, *Angew. Chem., Int. Ed. Engl., 29* (1990) 309–311.

453 T. Kakigano, H. Suzuki, M. Igarashi and Y. Moro-oka, *Organometallics, 9* (1990) 2192–2194.

454 G. Suss-Fink, J.-L. Wolfender, F. Neumann and H. Stoeckli-Evans, *Angew. Chem., Int. Ed. Engl. 29* (1990) 429–431.

455 L.R. Nevinger, J.B. Keister and J. Maher, *Organometallics, 9* (1990) 1900–1905.

456 T.P. Duggan, M.J. Golden and J.B. Keister, *Organometallics, 9* (1990) 1656–1665.

457 L.R. Nevinger and J.B. Keister, *Organometallics, 9* (1990) 2312–2321.

458 D.K. Bower and J.B. Keister, *Organometallics, 9* (1990) 2322–2327.

459 M.R. Churchill, L.A. Buttrey, J.B. Keister, J.W. Ziller, T.S. Janik and W.S. Striejewske, *Organometallics, 9* (1990) 766–773.

460 D. Osella, R. Gobetto, L. Milone, P. Zanello and S. Mangani, *Organometallics, 9* (1990) 2167–2171.

461 T. Ghazy, L.A.P. Kane-Maguire and K. Do, *J. Organomet. Chem., 390* (1990) 91–95.

462 G.R. Frauenhoff and J.R. Shapley, *J. Organomet. Chem., 397* (1990) 359–370.

463 M.R. Churchill and C. Bueno, *J. Organomet. Chem., 396* (1990) 327–338.

464 K.I. Hardcastle, T. McPhillips, A.J. Arce, Y. De Sanctis, A.J. Deeming and N.I. Powell, *J. Organomet. Chem., 389* (1990) 361–374.

465 B.F.G. Johnson, J. Lewis, A.J. Whitton and S.G. Bott, *J. Organomet. Chem., 389* (1990) 129–138.

466 D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.,* (1990) 1847–1852.

467 E. Rosenberg, S.E. Kabir, K.I. Hardcastle, M. Day and E. Wolf, *Organometallics, 9* (1990) 2214–2217.

468 M. Akita and J.R. Shapley, *Organometallics, 9* (1990) 2209–2211.

469 R.D. Adams, G. Chen and J.T. Tanner, *Organometallics, 9* (1990) 1530–1538.

470 J.L. Coffer, H.G. Drickamer, J.T. Park, R.T. Roginski and J.R. Shapley, *J. Phys. Chem., 94* (1990) 1981–1985.

471 B.F.G. Johnson, J. Lewis and M. Monari, *J. Chem. Soc., Dalton Trans.,* (1990) 3525–3529.

472 P.L. Stanghellini and R. Rossetti, *Inorg. Chem., 29* (1990) 2047–2052.

473 A.K. Ma, F.W.B. Einstein, V.J. Johnston and R.K. Pomeroy, *Organometallics, 9* (1990) 45–51.

474 M.W. Day, K.I. Hardcastle, A.J. Deeming, A.J. Arce and Y. De Sanctis, *Organometallics, 9* (1990) 6–12.

475 Z. Nomikou, J.-F. Halet, R. Hoffmann, J.T. Tanner and R.D. Adams, *Organometallics, 9* (1990) 588–595.

476 J. Liu, S.R. Wilson, J.R. Shapley and F.J. Feher, Inorg. Chem., 29 (1990) 5138-5139.

477 C. Dossi, A. Fusi, M. Pizzotti and R. Psaro, *Organometallics, 9* (1990) 1994–1995.

478 K.-L. Lu, Y.-C. Lin and Y. Wang, *Organometallics, 9* (1990) 1320–1322.

479 J. Bracker-Novak, S. Hajela, M. Lord, M. Zhang, E. Rosenberg, R. Gobetto, L. Milone and D. Osella, *Organometallics, 9* (1990) 1379–1382.

480 L.J. Farrugia, *J. Organomet. Chem., 394* (1990) 515–531.

481 R. Gobetto, E. Sappa, A. Tiripicchio, M.T. Camellini and M.J. Mays, *J. Chem. Soc., Dalton Trans.,* (1990) 807–811.

482 B.F.G. Johnson, J. Lewis, A.D. Massey, P.R. Raithby and W.T. Wong, *J. Organomet. Chem., 397* (1990) C28–C30.

483 S.A.R. Knox, B.R. Lloyd, D.A.V. Morton, S.M. Nicholls, A.G. Orpen, J.M. Vinas, M. Weber and G.K. Williams, J. Oraanomet. Chem., 394 (1990) 385-415.

484 H.R. Allcock, I. Manners, M.N. Mang and M. Parvez, *Inorg. Chem., 29* (1990) 522–529.

485 D.S. Bohle, D. Heineke, A. Tiripicchio, M.T. Camellini and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl., 29* (1990) 896–898.

486 G. Gremaud, H. Jungbluth, H. Stoeckli-Evans and G. Suss-Fink, *J. Organomet. Chem., 388* (1990) 351–364.

487 P.A. Jackson, B.F.G. Johnson, J. Lewis, A.D. Massey, D. Braga, C. Gradella and F. Grepioni, *J. Organomet. Chem., 391* (1990) 225–237.

488 P.L. Andreu, J.A. Cabeza, V. Riera, C. Bois and Y. Jeannin, *J. Organomet. Chem., 384* (1990) C25–C28.

489 A.J. Deeming, J.E. Marshall, D. Nuel, G. O'Brien and N.I. Powell, *J. Organomet. Chem., 384* (1990) 347–360.

490 M.A. Gallop, B.F.G. Johnson, R. Khattar, J. Lewis and P.R. Raithby, *J. Organomet. Chem., 386* (1990) 121–137.

491 L.M. Bullock, J.S. Field, R.J. Haines, E. Minshall, M.H. Moore, F. Mulla, D.N. Smit and L.M. Steer, *J. Organomet. Chem., 381* (1990) 429–456.

492 B.F.G. Johnson, J. Lewis, M. Monari, D. Braga, F. Grepioni and C. Gradella, *J. Chem. Soc., Dalton Trans.,* (1990) 2863–2871.

493 M.I. Bruce, P.A. Humphrey, O. bin Shawkataly, M.R. Snow, E.R.T. Tiekink and W.R. Cullen, *Organometallics, 9* (1990) 2910–2919.

494 W.G. Feighery, R.D. Allendoerfer and J.B. Keister, *Organometallics, 9* (1990) 2424–2426.

495 J.A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, *Inorg. Chim. Acta, 168* (1990) 77–82.

496 D. Belletti, A. Tiripicchio, M.T. Camellini and E. Sappa, *J. Chem. Soc., Dalton Trans.*, (1990) 703–705.

497 J.S. Field, R.J. Haines and J.A. Jay, *J. Organomet. Chem.*, *395* (1990) C16–C20.

498 H.G. Ang, W.L. Kwik, W.K. Leong, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Organomet. Chem.*, *396* (1990) C43–C46.

499 F. Van Gastel, A.J. Carty, M.A. Pellinghelli, A. Tiripicchio and E. Sappa, *J. Organomet. Chem.*, *385* (1990) C50–C54.

500 H. Jungbluth, H. Stoeckli-Evans and G. Suss-Fink, *J. Organomet. Chem.*, *391* (1990) 109–118.

501 M.I. Bruce, M.J. Liddell and E.R.T. Tiekink, *J. Organomet. Chem.*, *391* (1990) 81–107.

502 N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Liimatta and J.-J. Bonnet, *J. Am. Chem. Soc.*, *112* (1990) 8607–8609.

503 U. Bodensieck, H. Stoeckli-Evans and G. Suss-Fink, *Chem. Ber.*, *123* (1990) 1603–1606.

504 R.E. Stevens, R.D. Guettler and W.L. Gladfelter, *Inorg. Chem.*, *29* (1990) 451–456.

505 J.-S. Song, S.-H. Han, S.T. Nguyen, G.L. Geoffroy and A.L. Rheingold, *Organometallics*, *9* (1990) 2386–2395.

506 S. Bhaduri, H. Khwaja, N. Sapre, K. Sharma, A. Basu, P.G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, (1990) 1313–1321.

507 M.A. Pellinghelli, A. Tiripicchio, J.A. Cabeza and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1990) 1509–1512.

508 M. Casarin, R. Bertoncello, G.A. Rizzi, C.J. Elsevier, W.P. Mul, K. Vrieze and A. Vittadini, *J. Organomet. Chem.*, *396* (1990) 73–81.

509 T. Jenke, H. Stoeckli-Evans and G. Suss-Fink, *J. Organomet. Chem.*, *391* (1990) 395–402.

510 P.L. Andreu, J.A. Cabeza and V. Riera, *J. Organomet. Chem.*, *393* (1990) C30–C33.

511 P.L. Andreu, J.A. Cabeza, V. Riera, Y. Jeannin and D. Miguel, *J. Chem. Soc., Dalton Trans.*, (1990) 2201–2206.

512 P.L. Andreu, J.A. Cabeza, V. Riera, C. Bois and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, (1990) 3347–3353.

513 R.D. Adams and G. Chen, *Organometallics*, *9* (1990) 2882–2883.

514 J.L. Coffer, H.G. Drickamer and J.R. Shapley, *J. Phys. Chem.*, *94* (1990) 5208–5210.

515 A.J. Deeming, D.W. Owen and N.I. Powell, *J. Organomet. Chem.*, *398* (1990) 299–310.

516 P.L. Andreu, J.A. Cabeza, J.M. Fernandez-Colinas and V. Riera, *J. Chem. Soc., Dalton Trans.*, (1990) 2927–2930.

517 R.D. Adams, G. Chen, J.T. Tanner and J. Yin, *Organometallics*, *9* (1990) 1240–1245.

518 R.D. Adams, G. Chen, J.T. Tanner and J. Yin, *Organometallics*, *9* (1990) 595–601.

519 R.D. Adams and M.P. Pompeo, *Organometallics*, *9* (1990) 1718–1720.

520 R.D. Adams and M.P. Pompeo, *Organometallics*, *9* (1990) 2651–2653.

521 R.D. Adams, G. Chen, J.T. Tanner and J. Yin, *Organometallics*, *9* (1990) 1523–1529.

522 R.D. Adams, J.E. Babin, H.S. Kim, J.T. Tanner and T.A. Wolfe, *J. Am. Chem. Soc.*, *112* (1990) 3426–3435.

523 A.L. Rheingold, B.S. Haggerty, G.L. Geoffroy and S.-H. Han, *J. Organomet. Chem.*, *384* (1990) 209–216.

524 C. Dossi, R. Psaro, D. Roberto, R. Ugo and G. Zanderighi, *Inorg. Chem.*, *29* (1990) 4368–4373.

525 F.-E. Hong, D.A. McCarthy, J.P. White III, C.E. Cottrell and S.G. Shore, *Inorg. Chem.*, *29* (1990) 2874–2876.

526 R.K. Pomeroy, *J. Organomet. Chem.*, *383* (1990) 387–411.

527 F.W.B. Einstein, V.J. Johnston and R.K. Pomeroy, *Organometallics*, *9* (1990) 2754–2762.

528 F.W.B. Einstein, V.J. Johnston, A.K. Ma and R.K. Pomeroy, *Organometallics*, *9* (1990) 52–59.

529 H. Chen, B.F.G. Johnson, J. Lewis, D. Braga and F. Grepioni, *J. Organomet. Chem.*, *398* (1990) 159–164.

530 H. Chen, M. Fajardo, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Organomet. Chem.*, *389* (1990) C16–C18.

531 R.D. Adams, G. Chen, S. Sun, J.T. Tanner and T.A. Wolfe, *Organometallics*, *9* (1990) 251–260.

532 M.I. Bruce, *J. Organomet. Chem.*, *394* (1990) 365–384.

533 B.F.G. Johnson, R. Khattar, J. Lewis, P.R. Raithby and M.J. Rosales, *J. Organomet. Chem.*, *385* (1990) 387–398.

534 R. Khattar, B.F.G. Johnson, J. Lewis, P.R. Raithby and M.J. Rosales, *J. Chem. Soc., Dalton Trans.*, (1990) 2167–2174.

535 P. Frediani, M. Bianchi, A. Slavini, F. Piacenti, S. Ianelli and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (1990) 165–171.

536 S.R. Drake, B.F.G. Johnson, J. Lewis, G. Conole and Mary McPartlin, *J. Chem. Soc., Dalton Trans.*, (1990) 995–1000.

537 P.J. Bailey, M.J. Duer, B.F.G. Johnson, J. Lewis, G. Conole, M. McPartlin, H.R. Powell and C.E. Anson, *J. Organomet. Chem.*, *383* (1990) 441–461.

538 T. Chihara, K. Aoki and H. Yamazaki, *J. Organomet. Chem.*, *383* (1990) 367–385.

539 D.A. McCarthy, J.A. Krause and S.G. Shore, *J. Am. Chem. Soc.*, *112* (1990) 8587–8589.

540 A. Bott, J.G. Jeffrey, B.F.G. Johnson and J. Lewis, *J. Organomet. Chem.*, *394* (1990) 533–534.

541 R.D. Adams, G. Chen, S. Sun and T.A. Wolfe, *J. Am. Chem. Soc.*, *112* (1990) 868–869.

542 S. Naylor and M.D. Vargas, *J. Organomet. Chem.*, *386* (1990) 275–286.

543 M.R. Churchill, C. Bueno and A.L. Rheingold, *J. Organomet. Chem.*, *395* (1990) 85–103.

544 M. Bowen, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1990) 3039–3049.

545 B.F.G. Johnson, J. Lewis and A.J. Whitton, *J. Chem. Soc., Dalton Trans.*, (1990) 3129–3135.

546 D.P. Workman, D.-Y. Jan and S.G. Shore, *Inorg. Chem.*, *29* (1990) 3518–3525.

547 P. Mathur, B.H.S. Thimmappa and A.L. Rheingold, *Inorg. Chem.*, *29* (1990) 4658–4665.

548 D.-K. Hwang, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Organomet. Chem.*, *389* (1990) C7–C11.

549 Y. Chi, L.-K. Liu, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, *390* (1990) C50–C56.

550 Y. Chi, G. Huttner and W. Imhof, *J. Organomet. Chem.*, *384* (1990) 93–103.

551 C.-H. Wu, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Dalton Trans.*, (1990) 3025–3031.

552 Y. Chi, S.-H. Chuang, B.-F. Chen, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Dalton Trans.*, (1990) 3033–3037.

553 Y. Chi, C.-H. Wu, S.-M. Peng and G.-H. Lee, *Organometallics*, *9* (1990) 2305–2312.

554 D.-K. Hwang, Y. Chi, S.-M. Peng and G.-H. Lee, *Organometallics*, *9* (1990) 2709–2718.

555 B. Oswald, A.K. Powell, F. Rashwan, J. Heinze and H. Vahrenkamp, *Chem. Ber.*, *123* (1990) 243–250.

556 M.P. Jensen, W. Henderson, D.H. Johnston, M. Sabat and D.F. Shriver, *J. Organomet. Chem.*, *394* (1990) 121–143.

557 R. Regragui, P.H. Dixneuf, N.J. Taylor and A.J. Carty, *Organometallics*, *9* (1990) 2234–2242.

558 S. Rossi, J. Pursianinen and T.A. Pakkanen, *J. Organomet. Chem., 397* (1990) 81–92.

559 S. Rossi, J. Pursiainen, M. Ahlgren and T.A. Pakkanen, *J. Organomet. Chem., 393* (1990) 403–414.

560 S. Rossi, J. Pursianinen, M. Ahlgren and T.A. Pakkanen, *Organometallics, 9* (1990) 475–479.

561 R. Jund, J. Rimmelin and M. Gross, *J. Organomet. Chem., 381* (1990) 239–249.

562 W. Bernhardt and H. Vahrenkamp, *J. Organomet. Chem., 383* (1990) 357–366.

563 A. Colombie, D.A. McCarthy, J. Krause, L.-Y. Hsu, W.-L. Hsu, D.-Y. Jan and S.G. Shore, *J. Organomet. Chem., 383* (1990) 421–440.

564 J. Pursiainen, M. Ahlgren, T.A. Pakkanen and J. Valkonen, *J. Chem. Soc., Dalton Trans.*, (1990) 1147–1153.

565 R. Yanez, J. Ros, I. Moldes, R. Mathieu, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.*, (1990) 3147–3150.

566 M.P. Garcia, A.M. Lopez, M.A. Esteruelas, F.J. Lahoz and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1990) 3465–3471.

567 M.R. Churchill and J.C. Fettinger, *Organometallics, 9* (1990) 446–452.

568 J. Washington and J. Takats, *Organometallics, 9* (1990) 925–928.

569 E.G. Lundquist, J.C. Huffman, K. Folting, B.E. Mann and K.G. Caulton, *Inorg. Chem., 29* (1990) 128–134.

570 D.L. Davies, J.C. Jeffrey, D. Miguel, P. Sherwood and F.G.A. Stone, *J. Organomet. Chem., 383* (1990) 463–480.

571 R.D. Adams, G. Chen, J.-G. Wang and W. Wu, *Organometallics, 9* (1990) 1339–1341.

572 L.J. Farrugia, *Organometallics, 9* (1990) 105–110.

573 R.D. Adams, G. Chen, D.A. Katahira, J.T. Tanner and W. Wu, *Inorg. Chem., 29* (1990) 3269–3270.

574 T.J. Coffy and S.G. Shore, *J. Organomet. Chem., 394* (1990) C27–C30.

575 A. Anillo, J.A. Cabeza, R. Obeso-Rosete and V. Riera, *J. Organomet. Chem., 393* (1990) 423–429.

576 C.J. Brown, P.J. McCarthy, I.D. Salter, K.P. Armstrong, M. McPartlin and H.R. Powell, *J. Organomet. Chem., 394* (1990) 711–732.

577 S.S.D. Brown, I.D. Salter, T. Adatia and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1990) 799–805.

578 C.J. Brown, P.J. McCarthy and I.D. Salter, *J. Chem. Soc., Dalton Trans.*, (1990) 3583–3590.

579 M.I. Bruce, M.J. Liddell, M.L. Williams and B.K. Nicholson, *Organometallics, 9* (1990) 2903–2909.

580 E. Charalambous, L.H. Gade, B.F.G. Johnson, T. Kotch, A.J. Lees, J. Lewis and M. McPartlin, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1137–1139.

581 J.J. Bergmeister, III and B.E. Hanson, *Inorg. Chem., 29* (1990) 4055–4059.

582 A.M. Thayer, T.M. Duncan and D.C. Douglass, *J. Phys. Chem., 94* (1990) 2014–2020.5

83 M. Pruski, J.C. Kelzenberg, B.C. Gerstein and T.S. King, *J. Am. Chem. Soc., 112* (1990) 4232–4240.

584 T. Mizushima, K. Tohji, Y. Udagawa and A. Ueno, *J. Am. Chem. Soc., 112* (1990) 7887–7893.

585 T. Mizushima, K. Tohji, Y. Udagawa and A. Ueno, *J. Phys. Chem., 94* (1990) 4980–4985.

586 J.B. Goodenough, R. Manoharan and M. Paranthaman, *J. Am. Chem. Soc., 112* (1990) 2076–2082.

587 R. Neumann and C. Abu-Gnim, *J. Am. Chem. Soc., 112* (1990) 6025–6031.

588 V.S. Kamble, N.M. Gupta, V. Natarajan and R.M. Iyer, *J. Mol. Catal., 61* (1990) 269–281.

589 C. Crisafulli, R. Maggiore, S. Scire, L. Solarino and S. Galvagno, *J. Mol. Catal., 63* (1990) 55–63.

590 H.-J. Cantow, H. Hillebrecht, S.N. Magonov, H.W. Rotter, M. Dreschler and G. Thiele, *Angew. Chem., Int. Ed. Engl., 29* (1990) 537–541.

591 C.-S. Huang, M. Houalla, D.M. Hercules, C.L. Kibby and L. Petrakis, *J. Phys. Chem., 94* (1990) 6749–6753.

592 M.V. Arena, A.A. Deckert, J.L. Brand and S.M. George, *J. Phys. Chem., 94* (1990) 6792–6797.

593 J. Hrbek, *J. Phys. Chem., 94* (1990) 1564–1570.

594 T.N. Truong, D.G. Truhlar, J.R. Chelikowsky and M.Y. Chou, *J. Phys. Chem., 94* (1990) 1973–1981.

595 H. Ishida, K. Fujiki, T. Ohba, K. Ohkubo, K. Tanaka, T. Terada and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1990) 2155–2160.

596 D. Geselowitz and T.J. Meyer, *Inorg. Chem., 29* (1990) 3894–3896.

597 M. Bressan, A. Morvillo and G. Romanello, *Inorg. Chem., 29* (1990) 2976–2979.

598 T.R. Cundari and R.S. Drago, *Inorg. Chem., 29* (1990) 2303–2308.

599 T.R. Cundari and R.S. Drago, *Inorg. Chem., 29* (1990) 487–493.

600 S.-I. Murahashi, T. Naota, T. Kuwabara, T. Saito, H. Kumobayashi and S. Akutagawa, *J. Am. Chem. Soc., 112* (1990) 7820–7822.

601 M.M.T. Khan, D. Chatterjee, S.A. Samad and R.R. Merchant, *J. Mol. Catal., 61* (1990) 55–60.

602 M.M.T. Khan, D. Chatterjee, R.R. Merchant and A. Bhatt, *J. Mol. Catal., 63* (1990) 147–153.

603 C. Waqar, B. Singh and J.P. Sharma, *J. Mol. Catal., 60* (1990) 49–58.

604 M.M.T. Khan, S.B. Halligudi and N.S. Rao, *J. Mol. Catal., 59* (1990) 303–309.

605 M.M.T. Khan and R.S. Shulka, *J. Mol. Catal., 58* (1990) 405–413.

606 M.M.T. Khan, S.B. Halligudi and S. Shukla, *J. Mol. Catal. 58* (1990) 299–305.

607 G. Caroling, J. Rajaram and J.C. Kuriacose, *J. Mol. Catal., 58* (1990) 235–243.

608 M.M.T. Khan, G. Ramachandraiah, S.H. Mehta, S.H.R. Abdi and S. Kumar, *J. Mol. Catal., 58* (1990) 199–203.

609 S. Bhaduri, N. Sapre, K. Sharma, P.G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, (1990) 1305–1311.

610 R. Chauvin, *J. Mol. Catal., 62* (1990) 147–156.

611 Y. Lin and Y. Zhou, *J. Organomet. Chem., 381* (1990) 135–138.

612 T. Hayashi, F. Abe, T. Sakakura and M. Tanaka, *J. Mol. Catal., 58* (1990) 165–170.

613 J.M. Grosselin and C. Mercier, *J. Mol. Catal., 63* (1990) L25–L27.

614 A. Benyei and F. Joo, *J. Mol. Catal., 58* (1990) 151–163.

615 H. Ono, K. Fujiwara, M. Hashimoto, E. Sugiyama and K. Yoshida, *J. Mol. Catal., 57* (1990) 113–123.

616 H. Ono, K. Fujiwara, M. Hashimoto, H. Watanabe and K. Yoshida, *J. Mol. Catal., 58* (1990) 289–297.

617 M.M.T. Khan and N.N. Rao, *J. Mol. Catal., 58* (1990) 323–329.

618 T. Kondo, M. Akazome, Y. Tsuji and Y. Watanabe, *J. Org. Chem., 55* (1990) 1286–1291.

619 Y. Tsuji, S. Kotachi, K.-T. Huh and Y. Watanabe, *J. Org. Chem., 55* (1990) 580–584.

620 V. Rosenberger and H. tom Dieck, *Chem. Ber., 123* (1990) 83–85.

621 S.C. Shim, C.H. Doh, B.W. Woo, H.S. Kim, K.T. Huh, W.H. Park, and H. Lee, *J. Mol. Catal., 62* (1990) L11–L15.

622 M. Pizzotti, S. Cenini, R. Psaro and S. Costanzi, *J. Mol. Catal., 63* (1990) 299–304.

623 A.A. Kelkar and R.V. Chaudhari, *J. Mol. Catal., 63* (1990) L29–L31.

624 M.M.T. Khan, N.S. Rao and S.B. Halligudi, *J. Mol. Catal. 63* (1990) 137–146.

625 M.M.T. Khan, N.S. Rao and S.B. Halligudi, *J. Mol. Catal., 63* (1990) 1–4.

626 M. Tanaka and T. Hayashi, *J. Mol. Catal., 60* (1990) L5–L7.

627 C.Y. Ren, W.C. Cheng, W.C. Chan, C.H. Yeung and C.P. Lau, *J. Mol. Catal., 59* (1990) L1–L8.

628 M.M.T. Khan, S.B. Halligudi, S. Shukla and Z.A. Shaikh, *J. Mol. Catal., 57* (1990) 307–312.

629 M.M.T. Khan, S.B. Halligudi, S. Shukla and Z.A. Shaikh, *J. Mol. Catal., 57* (1990) 301–305.

630 G. Jenner and P. Andrianary, *J. Mol. Catal., 58* (199) 307–322.

631 G. Jenner, E.M. Nahmed and H. Leismann, *J. Organomet. Chem., 387* (1990) 315–321.

632 E.M. Nahmed and G. Jenner, *J. Mol. Catal., 59* (1990) L15–L19.

633 M.M.T. Khan, S.B. Halligudi, S.H.R. Abdi and S. Shukla, *J. Mol. Catal., 60* (1990) 275–281.

634 J.N. Shah, D.T. Gokak and R.N. Ram, *J. Mol. Catal., 60* (1990) 141–154.