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10. Ruthenium 1992

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of ruthenium for 1992 and is based upon a search of volumes 116, 117 and 118 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched independently from the period of January to December 1992. The metal complexes are classified according to the ligand type. Most of the organometallic ruthenium complexes are not covered in this article as they are periodically reviewed in *J. Organometal. Chem.*

Compounds are classified according to donor atoms in the ligands but are not separated according to the oxidation state of the ruthenium centre.

10.1 Complexes with hydrogen donor or hydride ligands

The compounds Mg_2RuH_4 and Mg_2RuD_4 were synthesized and characterized by X-ray and neutron powder diffraction and were found to contain a diamagnetic $[RuH_4]^{4-}$ complex anion [1]. Mg_3RuH_3 and Mg_3RuD_3 were also synthesized and similarly characterized but were found to contain $[Ru_2D_6]^{12-}$ dianions [2].

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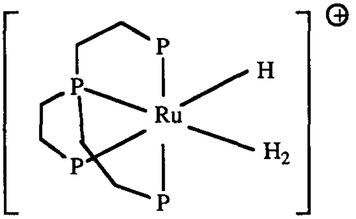
The barrier to rotation of the dihydrogen ligand in $[RuH(\eta^2\text{-}H_2)PP_3]BPh_4$ (**1**) was found to be lower than the Fe analogue from inelastic neutron scattering studies of the dihydrogen rotation energy levels which showed that the Fe centre was a better back-donor than Ru [3]. Depending on the substrate to metal complex ratio, the same complex (**1**) was found to react with phenylacetylene to give $[(PP_3)Ru\text{-}\{C(H){=}C(H)Ph\}]^+$ (**2**), $[(PP_3)Ru({\equiv}CPh)]BPh_4.thf$ (**3**) and (E)-$[(PP_3)Ru(\eta^3\text{-}PhC_3CHPh)]BPh_4$, with the last one being isolated as geometric isomers (**4a, b**) ($PP_3{=}P(CH_2CH_2PPh_2)_3$). Kinetic studies on selective hydrogenation of phenylacetylene to styrene with (**1**) as a catalyst precursor were carried out. These studies showed that (**2**), (**3**) (**4a**) and (**4b**) were important side intermediates in the catalysis cycle [4]. The electronic structures of some complexes of the type $RuL_4H(H_2)^+$ and $IRuL_2H(H_2)$ (L = phosphine) have been studied by Extended Hückel and ab initio calculations [5].



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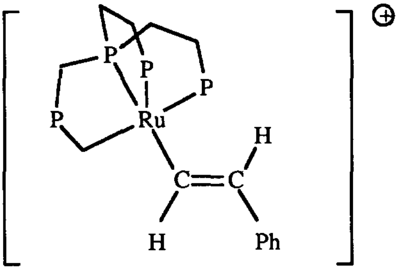

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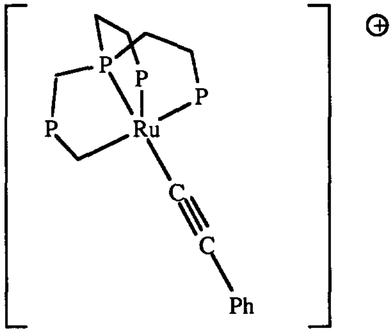
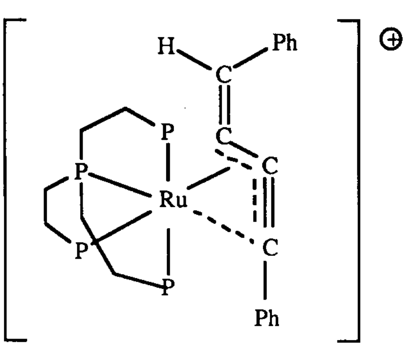


(**3**)

$RuH_2(L)(triphos)$ (triphos = $PPh(CH_2CH_2PPh_2)_2$; L = CO, $P(OCH_2)_3CEt$ or PMe_2Ph) were prepared from the corresponding $RuCl_2(L)(triphos)$ complexes. The dihydrogen complexes were in turn reacted to produce $[Ru(H)(\eta^2\text{-}H_2)\text{-}(L)(triphos)]^+$ and $[RuH(MeCN)(L)(triphos)]BF_4$ (L = $P(OCH_2)_3CEt$ or PMe_2Ph) [6]. $[RuH_2(H_2)_2\text{-}(PCy_3)_2]$ (Cy = cyclohexyl) reacted with various acids to give $[(\eta^6\text{-}C_6H_5CH_3)RuH\text{-}(PCy_3)_2]BF_4$, $RuH(\eta^2\text{-}H_2)(OCOR)(PCy_3)_2$ (R = CF_3, Me or Ph), $RuH_2(OCOCF_3)_2\text{-}(PCy_3)_2$, $RuH(H_2)(OAc)(PCy_3)_2{\cdot}AcOH$, $RuH_2(OAc)(PCy_3)_2(OSO_2CF_3)$ and $[RuH_2(OAc)(PCy_3)_2(Sol)](OSO_2CF_3)$(Sol = polar solvent) [7].



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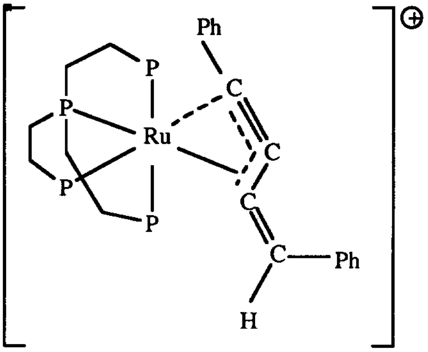

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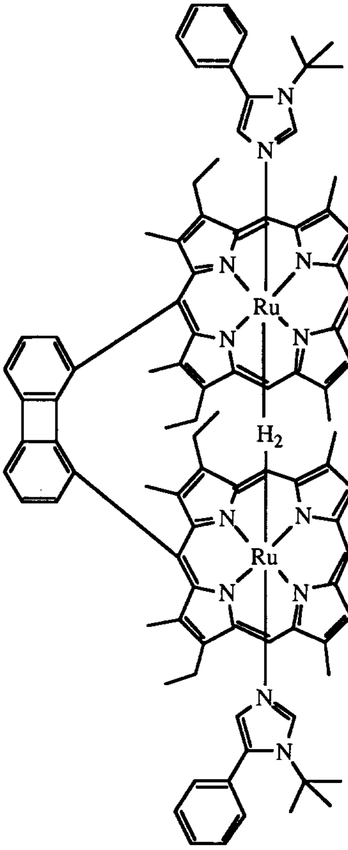


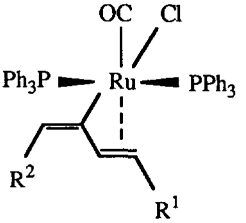
(5)

The complex Ru(OEP)(L)(H_2) (OEP = octaethylporphyrinatodiamine, L = thf or *Im = 1-tert-butyl-5-phenylimidazole) and the Os analogues were synthesized, characterised and studied with ^1H NMR spectroscopy. The first dimetallic bridging dihydrogen complex, $Ru_2(DPB)$-$(*Im)_2(H_2)$ (5) was also prepared [8].

Under different conditions, $RuCl_2(PPh_3)(isoPFA)$ or $RuCl_2(PPh_3)(PPFA)$ reacted with dihydrogen to give $L_2(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H)(PPh_3)_2$ (L_2 = isoPFA or $(PPh_3)_2$), $Ru(H)Cl_2(PPh_3)(PPFA{\cdot}H)(BuOH)$ or $RuH(Cl)(PPh_3)(isoPFA)$, with some of them having been characterized by X-ray crystallography (isoPRA = $(\eta\text{-}C_5H_5)Fe\text{-}(\eta\text{-}C_5H_3(CHMeNMe_2)P^iPr_2\text{-}1,2)$; PPFA = $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3\text{-}(CHMeNMe_2)PPh_2\text{-}1,2))$ [9].

$[RuH(\eta^2\text{-}H_2)L_4]BF_4$ reacted under various conditions to give $[RuH(NO)L_4](PF_6)_2$, $[Ru(NO)L_4](PF_6)$, $[Ru(CNR)_4L_2]^{2+}$ (R = 4-MeC_6H_4 or 4-$MeOC_6H_4$), $[Ru(NO)(CO)_2L_2]^+$ or $[RuBr_2(NO)L_3]^+$ (L = $P(OEt)_2Ph$) [10]. The Fe and Os analogues were also studied. $[Ru_2H(\mu\text{-}H)Cl(Me_4[14]aneS_4)_2]Cl$ and *trans*-$RuH(Cl)(syn\text{-}Me_4[14]aneS_4)$ were synthesized. From IR and ^1H NMR spectroscopies and X-ray crystallography, the former was found to display a single and unsupported Ru-H-Ru bond ($Me_4[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane) [11]. $[RuH(CO)(PPh_3)([9]aneS_3)]PF_6$ was prepared from $[RuH_2(CO)(PPh_3)_3]$ ([9]ane S_3 = 1,4,7-trithiacyclononane) [12]. Intramolecular ligand exchange in the latter was demonstrated by NOESY (Nuclear Overhauser Effect Spectroscopy) [13].

$RuHCl(CO)(PPh_3)_3$ reacted with various alkynes to give $RuCl(CO)(PPh_3)_2$-(*trans*-$R^1CH{=}CHC{=}CR^2$) ($R^1 = R^2 = SiMe_3$ (6), or CMe_3 (7); $R^1 = SiMe_3$, R^2 = Me (8); R^1 = Et, R^2 = CMe_3 (9)) with the following general structure [14]:



(6) - (9)

$RuHCl(CO)(PPh_3)_3$ also catalysed hydrogenation of ring-opened polymers to give a new polymer [15]. The thio-analogue, $RuHCl(CS)(PPh_3)_3$ or $RuPhCl(CS)(PPh_3)_2$ were used to prepare $Ru(SiMe_2Cl)Cl(CS)(PPh_3)_2$, which further reacted to give $Ru(\eta^2\text{-}C[S]SiMe_2X)Cl(CO)(PPh_3)_2$ (X = Cl), where the ethoxy analogue (X = OEt) was prepared from the corresponding ethoxylsilyl complex [16].

$[Ru(CO)(NO_2)(OAc)(PPh_3)_2]$ was believed to form from a C-N bond cleavage, when $[RuH(OAc)(CO)(PPh_3)_2]$ reacted with β-nitrostyrene [17]. The kinetics and mechanism of hydrogenation of benzaldehyde, catalysed by $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ was studied in reference [18].

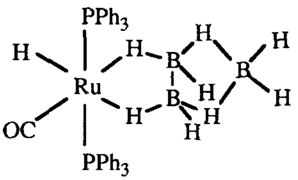
$RuHX(CO)(p\text{-}tert\text{-}Bu_2Me)_2$ (X = I, Cl, OPh, NHPh, OCH_2CF_3, OH, $OSiPh_3$, $OSiPhMe_2$ or $OSiMe_3$) were synthesized and characterized by multinuclear NMR spectroscopy and also by X-ray crystallography for X = $OSiPh_3$. The relative electron donor power of X in these compounds, as well as $RuHX(CO)(py)(p\text{-}tert\text{-}Bu_2Me)_2$, were studied [19].

$RuH(NO)P_3$ (P_3 = $(Cy_2PCH_2CH_2CH_2)_2PhP$, cyttp; $(Ph_2PCH_2CH_2CH_2)_2$-PPh, ttp; $(Ph_2PCH_2CH_2)_2PhP$, etp) were prepared and characterized. They were found to have similar trigonal bipyramidal structure with linear NO groups. The X-ray structure for $RuH(NO)(cyttp)_3$ has been determined [20]. The P_3-ligands minimized the number of isomers in the monophosphine analogues and froze the fluxionality. The fluxional behaviour of $RuH(NO)(ttp)_3$ was further studied [21].

The complex $[RuH_2(PPh_3)_4]$ was found to catalyse reactions of azulenes and dimethylacetylenedicarboxylate (ADM) [22] and additions of haloalkanes to alkenes [23]. The latter reaction was also catalysed by $[RuH_3(SiMe_2Ph)(PPh_3)_3]$. $[RuH_2(PPh_3)_4]$ was also an oxidant in the formation of 6β-lactone form 6α-lactone [24].

The photochemistry of *cis*-$Ru(dmpe)_2H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) was studied by IR, UV/VIS and NMR spectroscopic methods in matrices and in solution [25].

$[RuH(B_3H_8)(CO)(PPh_3)_2]$ (**10**) was prepared from either $[RuClH(CO)\text{-}(PPh_3)_3]$ or $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$. Its structure and reactivity have been recorded [26].

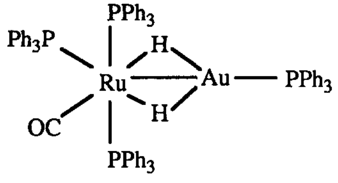


(**10**)

The complexes $[(P(CHMe_2)_3)_2(CO)HRu(\mu,\eta^4\text{-}BH_4)RuH(CO)(P(CHMe_2)_3)_2]BF_4$, $[RuH(\eta^2\text{-}O_2CR)(CO)(P(CHMe_2)_3)_2]$ (R = (S)-CH(NaphOMe)Me (**11**), (R)-CH-(OMe)Ph (**12**), (R)-$C(CF_3)(OMe)Ph$ (**13**), (S)-$CHOC(O)CH_2CH_2$ (**14**)), and $RuH(pz)(CO)(Hpz)(PCOHMe_2)_3)_2$ (Hpz = pyrazole) were prepared from $RuH(\eta^2\text{-}H_2BH_2)(CO)(PCCHMe_2)_3)_2$. These compounds were further reacted to give the cationic complexes $[RuH(CO)(MeCN)_2\text{-}(P(CHMe_2)_3)_2]^+$, $[RuH(CO)(\eta^1\text{-}Me_2CO)_2(P(CHMe_2)_3)_2]^+$, $[RuH(CO)(\eta^1\text{-}Me_2CO)\text{-}(P(CHMe_2)_3)_2]^+$, $[RuH(CO)(Hpz)_2(P(CHMe_2)_3)_2]^+$ and isomeric $RuHCl(CO)(Hpz)\text{-}(P(CHMe_2)_3)_2$ [27]. The catalytic activities of complexes (**11**)–(**14**) and their osmium analogues were studied.

The gold(I) phosphine derivative $Au(PPh_3)NO_3$ reacted with $RuH_2(CO)(PPh_3)_3$ and $RuH_4(PPh_3)_3$ to give $[AuRuH_2(CO)(PPh_3)_4]NO_3$ (**15**) and $[Au_2RuH_3(PPh_3)_5]PF_6$ (**16**) respectively [28].

The synthesis and structure of the compound $[(PP_3)RuH(\eta^1\text{-}ClTl)]PF_6$ (**17**) have been reported [29]. $Li[RuH_3(PPh_3)_3]$ reacted with $[Ir(cod)Cl]_2$ to give $(cod)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$ (**18**) as the thermodynamic product. This gave $(cod)IrH_2Ru[PPh_2(C_6H_4)](PPh_3)_2$ (**19**) upon dehydrogenation [30]. $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (**20**) reacted with MeCN and PhCN to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(MeCN)(PPh_3)_2$ (**21**) and $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (**22**); the latter further reacted to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2$ [31].



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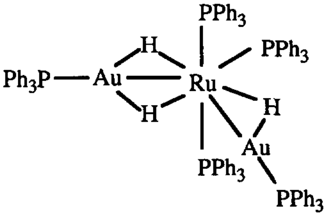

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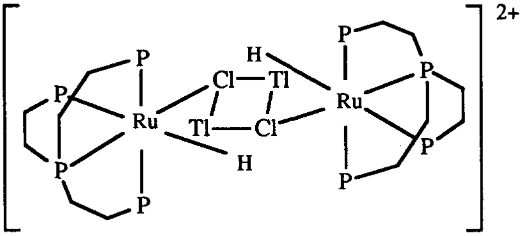

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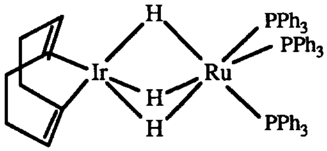

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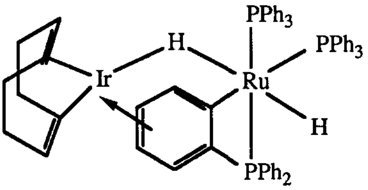

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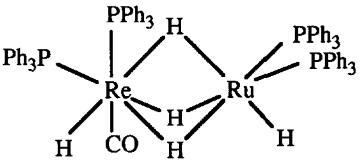

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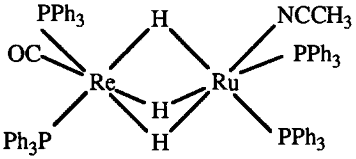

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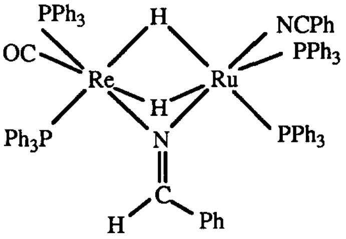

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10.2 Complexes with halide and pseudo-halide ligands

A new synthetic route has been found for RuF_4 and the structures of RuF_3, RuF_4, and RuF_5 were compared [32]. The RuF_6 cluster model was used to account for the bonding mechanism in the rutile RuO_2 structure [33]. The refined metal K-edge extended X-ray absorption fine structure data of RuF_6 and those calculated for $K[RuF_6]$ and $K_2[RuF_6]$ were compared with previous data on the 5d analogues and with X-ray crystallographic data [34].

Ruthenium trichloride was found to catalyse the oxidation of tertiary amines by hydrogen peroxide in the presence of methanol [35]. It also formed a catalyst with chromium hydroxide for fluorination of halohydrocarbons with HF [36]. A new catalyst was prepared from aqueous $RuCl_3$, TiO_2 and ammonium metavanadate(I) for manufacture of aliphatic hydrocarbons from hydrogen and carbon monoxide [37]. $RuCl_3.3H_2O$, $FeCl_3.6H_2O$ and $SnCl_2.2H_2O$ were supported on γ-alumina and reduced by $NaBH_4$ for catalysing reduction of fatty acid esters in the preparation of higher alcohols [38]. The $RuCl_3{\cdot}nH_2O$-catalysed oxidation of cyclic acetals, e.g. 2-aryl-1,3-dioxolane, by Me_3COOH under mild conditions provides a useful method for the synthesis of glycol monoesters from 1-alkenes in combination with Pd-catalysed acetalization of 1-alkenes [39]. In synthesizing 9-octadecen-1-ol from oleic acid, a new H-activated catalyst was prepared by hydrolysis of $SnCl_4$, $RuCl_3$ and $Al(OCHMe_2)_3$ in hexylene glycol-EtOH-Me_2CHOH [40]. $RuCl_3$ catalyst supported on an Al_2O_3 carrier was used in the preparation of bis(4-aminocyclohexyl)methane under high temperature and pressure [41]. Cyclohexylamines were prepared by hydrogenation of aromatic amines in the presence of Ru supported on Co hydroxide prepared from $RuCl_3$ [42].

The residual chloride ion on silica-supported ruthenium catalysts prepared from the $RuCl_3.3H_2O$ precursor showed poisoning effect of the catalysts and suppression of H chemisorption [43]. The effects of removal of Cl and a KNO_3 promoter on $RuCl_3$ precursor / MgO catalysts for NH_3 synthesis were also studied [44].

A new approach for preparing $RuCl_3$ which does not involve the use of NaOCl was tried [45]. The ^{99}Ru Mössbauer spectroscopy and magnetization studies of α- and β-$RuCl_3$ showed a conspicuous difference in the magnetic properties between the two forms due to their structural difference [46].

Studies on several syngas reactions, (catalysed by 2 forms of RuMo catalyst prepared from $RuCl_5{\cdot}1.5H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$ and SiO_2) were conducted [47]. Thin layer spectroelectrochemical techniques were employed to cause a reversible one-electron oxidation in $RuCl_6^{2-}$ anions, (Re, Os and Ir analogues were also studied), to form the corresponding pentavalent complexes at low temperature. This provided the first opportunity to examine the optical charge transfer spectra of these highly oxidized complexes of Ir and Ru [48].

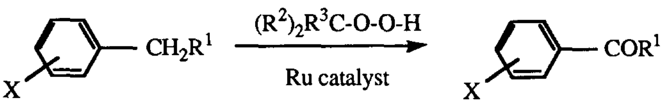
A thorough study on the effects of temperature, ionic strength and solvent isotopes on aquation and anation reactions of $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ was conducted [49]. Another ruthenium catalyst synthesized by the sol-gel process using tetraethoxysilane aluminium tri-sec-butoxide and $[RuCl_5(H_2O)]^{2-}$ was characterized and studied [50]. The electrochemical redox reactions of dimeric Ru(IV) and Ru(III) with chloride were studied by cyclic voltammetry, rotating disk electrode voltammetry and spectrometry, and the structure of the complex was discussed [51].

Supported catalysts formed from functionalized polymers containing N-P, N-O or N-N dinuclear ligands (chemically bound with $RuCl_3$) displayed high activity and selectivity in the hydrogenation of diacetone alcohol. [52]. The microstructures of polymers prepared from ring-opening metathetic catalysts $RuCl_3{\cdot}3H_2O$, $[RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$, $Ru(H_2O)_6$ di-tosylate and $W(=CH^tBu)(=NAr)[OCMe(CF_3)_2]_2$ were studied by ^1H and ^{13}C NMR spectroscopy ($C_{10}H_{16}$ = 2,7-dimethyloctadienediyl; Ar = 2,6- diisopropylphenyl) [53].

In a study of the synthesis of sorbitol via molecular hydrogenation of glucose, phosphine complex of ruthenium ($RuCl_3{:}PPh_3$ = 1:2) was found to be the most practical among the iron, rhodium and ruthenium catalysts studied. Only mild conditions of 90°C and 2 atm hydrogen pressure were used with 95% yield of sorbitol in 2 hours of reaction time [54]. The effects of temperature and variation of phosphine ligands of $RuCl_3{\cdot}xH_2O$- phosphine catalyst on selectivity for mono- or diamination of diols were studied. Selectivity towards monoamination decreased on increasing the reaction temperature but recovered by adding more phosphine ligand; it also increased by adding electron-donating and/or bulky phosphines [55].

Hydrogenated nitrile rubbers with storage stability and moldability, useful for automobile and industrial parts, were prepared by selective hydrogenation of double bonds with $RuCl_3{\cdot}3H_2O\text{-}PPh_3$ as catalysts, followed by extrusion [56]. $RuCl_3{\cdot}3H_2O\text{-}PPh_3\text{-}CaCl_2{\cdot}2H_2O$ was used as catalyst for the preparation of similar partially crosslinked-rubber with improved permanent compressive set, weather resistance and moldability [57]. Selective hydrogenations of carbon-carbon double bonds of nitrile group- containing unsaturated copolymers were catalysed by $RuCl_3$ - PPh_3 and mineral or carboxylic acids [58].

Phenyl ketones were manufactured according to the following equation:



$R^1 = C_{1\text{-}10}$ alkyl, (substituted Ph); X = lower alkyl, halo, alkoxy, OPh, H
R^2 = lower alkyl; R^3 = (halo-or NO_2-containing) Ph, lower alkyl

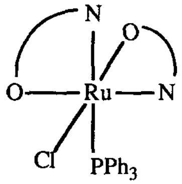
The ruthenium catalysts tried were $RuCl_2(PPh_3)_3$, $H_2Ru(PPh_3)_4$ or $RuCl_3$ hydrate, while $(R^2)_2R^3COOH$ was typically tert-butyl hydroperoxide or cumene hydroperoxide [59]. The same treatment was applied to $C_{5\text{-}15}$ branched or cyclic alkanes [60].

Compared to the homogeneous reaction, anchoring $RuCl_2(PPh_3)_3$ onto the phosphinated styrene-divinylbenzene (S-DVB) copolymers favoured *trans*-isomerization of 1-hexene and stabilized the catalyst. The solvent effects on the activity of the catalyst was also discussed [61]. The complex $RuCl_2(PPh_3)_3$ reacted with 1,4,7-trithiacyclononane (9-S3) and 1,4,8,11-tetrathiacyclotetradecane (14-S4) to give $[RuCl_2(PPh_3)(9\text{-}S3)]$ and *cis*-$[RuCl(PPh_3)(14\text{-}S4)]$; these have been characterized by X-ray analysis. In addition, the complexes $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ and $[RuClH(CS)(PPh_3)_3]$ were treated with 9-S3, giving $[RuCl(CS)(PPh_3)(9\text{-}S3)]ClO_4$ and $[RuH(CS)(PPh_3)(9\text{-}S3)]ClO_3$ [62].

The compound $RuCl_2(PPh_3)_2$ reacted with 1-hydroxy-2,4,6,8-tetra-^{t}butylphenoxazinyl (HPhenoxSQ) to give $RuCl_2(PPh_3)_2(PhenoxSQ)$ (**23**), $RuCl(PPh_3)(PhenoxSQ)_2$ (**24**) and $RuCl(PPh_3)(PhenoxSQ)(OxPhenox)$ (**25**); all three compounds were characterized spectroscopically and structurally. In addition, the first two compounds were also characterized electrochemically. An intermediate $[RuCl(PPh_3)(PhenoxSQ)_2]^-$ was proposed for the formation of (**25**). 2,4,6,8-Tetra-^{t}butylphenoxazin-1-one (PhenoxBQ) (**26**) was characterized structurally and its electrochemistry was studied [63].

The catalytic effect of the Ru complex $RuCl_2(PPh_3)_3$ was studied (together with the Pd(0) and Cu(I) catalysts) for addition reactions of tetrachloromethane to halogenated ethenes [64]. Et_3N and NH_4PF_6 were found to be effective additives for the Ru-catalysed hydrogenation of an acrylonitrile-butadiene rubber [65]. Aqueous Me_3COOH was added to a mixture of adamantane and $RuCl_2(PPh_3)_3$ in CH_2Cl_2 for over 7 hours and stirred for 1 hour to give 22.1% 1-adamantanol [66]. Glucose was transfer-hydrogenated by various alcohols in the presence of $RuCl_2(PPh_3)_3$ at 100° and normal pressure. It was interesting to note that the catalyst permanently changed to a hydridocarbonyl complex, which catalysed only disproportionation of glucose, when 2-methoxyethanol and tetrahydrofurfuryl alcohol were used [67]. An additional base like potassium carbonate was required in a similar reaction with imines and propan-2-ol [68].

Various 1,3-disubstituted 2,3-dihydroimidazol-2-ones were prepared by reaction of *N,N'*-disubstituted ureas with vicinal-diols with $RuCl_2(PPh_3)_3$ as catalyst. A typical example is shown in eqn (1) [69]. Preparation of condensed aromatic imidazoles was also catalysed by the ruthenium complex, eqn (2) [70].



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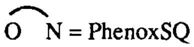

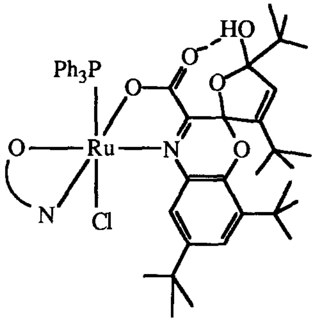

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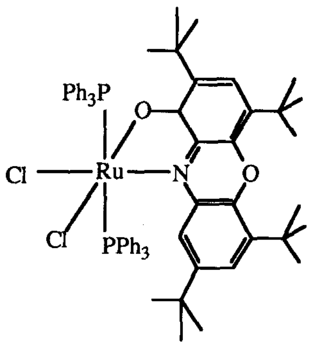

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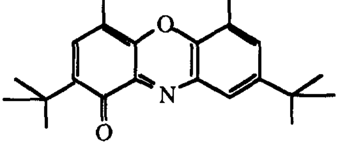

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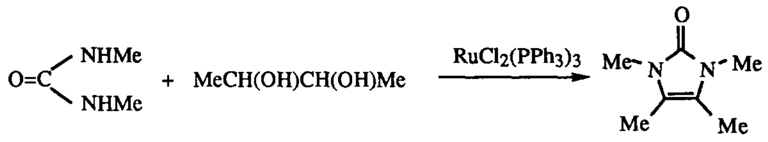
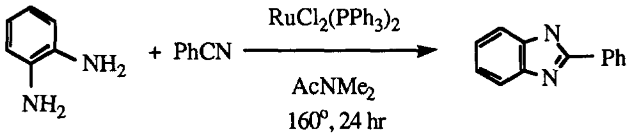


equ. (1)



equ. (2)

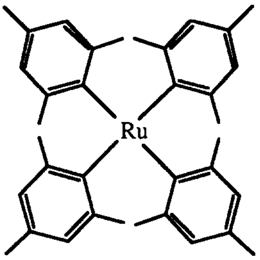
Carbamates and ureas like *N*,*N*-di-n-butyl-*N*′-phenylurea were prepared from formamides and amines or alcohols in the presence of $RuCl_2(PPh_3)_3$ [71]. Dioxygen-activated-$RuCl_2(PPh_3)_3$ catalysed metathesis of vinyl-substituted silicon compounds containing methyl, alkoxyl, phenyl, trimethylsiloxyl and silatranyl groups at silicon with 1-decene. Two proposed mechanisms involving a ruthenium-carbene intermediate as well as insertion of alkenes into the Ru-Si bond were discussed. [72]. Oxidation of alcohols by acetone was catalysed by $RuCl_2(PPh_3)_3$. Acetophenone was found to be a cocatalyst when phenylmethanol was oxidized to acetophenone, and was shown to be 30 times faster than the oxidation of 2-octanol [73].

The compound $(Ph_3P)_2Cl_2Ru{=}CHCH{=}CPh_2$, prepared with a quantitative yield from $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$, was used for polymerization of norbornene in both the presence or absence of protic solvents. A stable propagating carbene species was observed throughout the course of polymerization. This was believed to be a viable intermediate in the ring-opening metathesis polymerization of bicyclic alkenes catalysed by classical ruthenium complexes in protic solvents [74].

Chemical modification of diene-based rubber was done through catalytic hydrogenation using $RhCl(PPh_3)_3$ and $RuCl(CO)(COPh)(PPh_3)_2$ as catalysts. Plausible mechanisms were suggested with rate laws being derived [75]. $RuCl_2(CO)_2(PPh_3)_2$ was activated by contact with hydrogen, Ph_3P, thf and cyclododecatriene in an autoclave for selective hydrogenation of the cyclic polyene. Cyclododecene was obtained. An effluent containing the Ru-catalyst and the solvent was also obtained, from which the catalyst could be recycled [76].

Ruthenium (III) Schiff's base complexes $[Ru^{III}LCl_n]$ catalyse carbonylation of nitrobenzene at 160°C and 15 atm CO partial pressure in ethanol, producing phenylurethane. The catalytic activity of the complexes decreased in the following order: $K[Ru(naphoph)Cl_2]$ Schiff's base complexes > $K[Ru(naphen)Cl_2]$ > $K[Ru(naphprop)Cl_2]$ > $[Ru(naphdien)Cl]$ (naphoph = bis(naphthaldehyde)-o-phenylene-diimine; naphen = bis(naphthaldehyde)ethylenediimine; naphprop = bis(naphthaldehyde) propylenediimine; naphdien = bis(napthaldehyde)diethylene-diimine). The turnover rates after 2 hours ranged from 5 to 22 mol-product per mole-catalyst per hour [77].

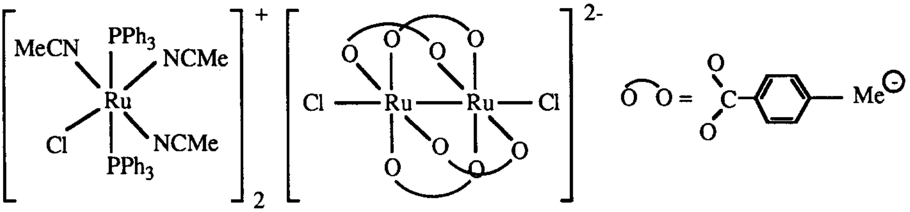
The reactions of $IrCl_3(tht)_3$ with Grignard and lithiated reagents, giving $Ir(Mes)_3$ and $Ir(Mes)_4$ respectively, and that of $RuCl_3(tht)_3$ with $Mg(Mes)_2(thf)_2$ giving $Ru(Mes)_4$ (**27**) were recorded (tht = tetrahydrothiophene; Mes = 2,4,6-trimethylphenyl). The tetramesityls were oxidized by AgO_3SCF_3 or $[NO]PF_6$ to give $[Ir^V(Mes)_4]O_3SCF_3$ and $[Ru^V(Mes)_4]PF_6$ [78].



(27)

Solid-state ^{13}C DP MAS NMR spectroscopic studies of compounds $[(Me_3Sn)_4M(CN)_6]_x$ (M = Fe, Ru and Os) revealed that the trigonal bipyramidal arrangements at Sn underwent internal rotation about the N-Sn-N axes with lifetimes on the order of 0.5 s at lower temperature [79].

The reaction of $Ru_2Cl(O_2CR)_4$ with PPh_3 in MeCN gave $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2CO_2CC_6H_4\text{-p-Me})_4]$ (**28**), $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl\text{-}(C_2CC_6H_4\text{-p-OMe})_4]$ (**29**) and $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CR)_4]$ (R = Me, Ph, C_6H_4-p-Me). The complexes were characterized from elemental analysis, magnetic and spectral data, with X-ray structures determined for (**28**) and (**29**) [80].



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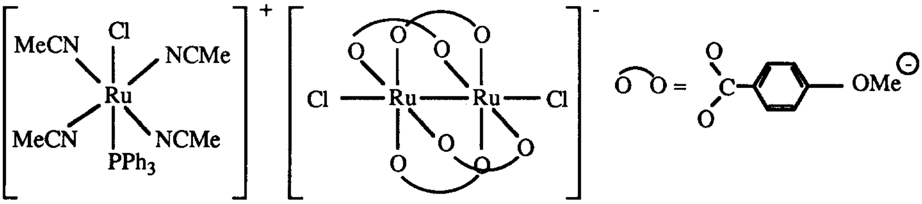
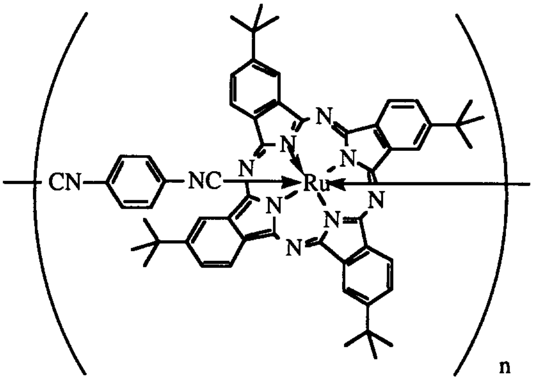


(29)

The ruthenium(II)-tin(II) cluster complexes $[NEt_4]_4[Ru(SnCl_3)_6]$ and $[NEt_4]_3[Ru(SnCl_3)_5MeCN]$, supported on $CuO\text{-}ZnO\text{-}SiO_2$, catalysed the conversion of MeOH to

AcOH and AcOMe with high selectivity. It was found that HCO_2Me formation was largely suppressed by the ruthenium catalysts [81].

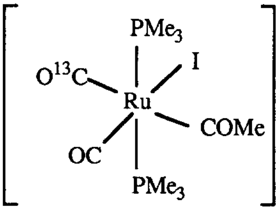
Resonant non-linear optical properties of spin-cast films of the oligomeric bridged $[^tBu_4PcRu(dib)]_n$ (**30**), axially linked by a p-diisocyanobenzene (dib) bridging ligand, were studied. Comparison with other lower-dimensional conjugated π-electron system showed that the optical properties of (**30**) were mainly determined by the 2-dimensional character of the phthalocyanine units [82].



(30)

10.3 Complexes with phosphorus donor ligands

Decarbonylation of *cis,trans*-$\{Ru(^{13}CO)(CO)(PMe_3)_2(COMe)I]$ (**31**) at −30°C was stereospecific and gave $[Ru(CO)_2(^{13}CO)(PMe_3)_2Me]^+$ (**32**). Thus, by the principle of microscopic reversibility, the reverse process of insertion was catalysed by anions [83].



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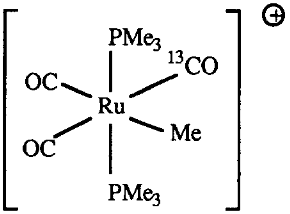


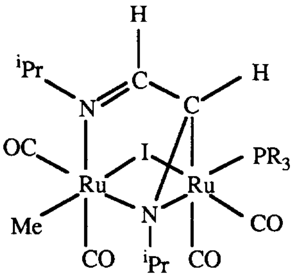
(32)

A series of acetylide compounds was prepared and characterized; the complexes included *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CR)_2$ (R = Ph (**33**), Me_3C, $SiMe_3$ (**34**), H(**35**)) and *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CC{\equiv}CR)_2$ (R = $SiMe_3$ (**36**), H (**37**)). X-ray analysis of (**33**) and (**35**) revealed a linear C_2RC_2 geometry [84]. Full characterization of (**34**), (**36**) and (**37**) by IR and Raman spectroscopy, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic studies and X-ray analysis were reported. Comparison of bond lengths between the three complexes and related acetylides suggested greater multiple-bond character in metal-to-acetylene σ bonds in (**34**), (**36**), (**37**) than in others [85].

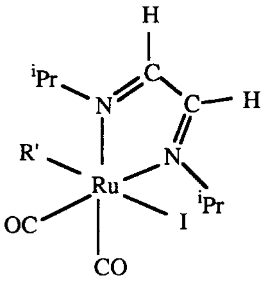
The complexes $RuXClCO(P(^iPr)_3)_2)$ and $RuXClCO(P(Cy)_3)_2$ (Cy = cyclohexyl; X = halogen) complexes were shown to be excellent catalysts for the selective hydrogenation of C=C in nitrile rubbers [86].

Seven water-soluble ruthenium complexes $(RuCl_2L_2)_2$, $RuHClL_3$, $RuH(OAc)L_3$, RuH_2L_4, $RuHIL_3$, $RuCl_2(CO)_2L_2$ and $[Ru(OAc)(CO)_2L]_2$ ($L = P(C_6H_4\text{-m-}SO_3Na)_3.3H_2O$) were synthesized and characterized. In solution, they were shown through spectroscopic investigation to have the same structures as their organosoluble analogues ($L = PPh_3$) [87]. The complexes were then tested in the catalytic hydrogenation of propionaldehyde, with their catalytic performances compared to their organosoluble analogues. The effect of both cation and anion additions had been investigated and the mechanism of hydrogenation has been discussed [88].

The 17-electron radical $[Ru(CO)_3(PCy_3)_2]^+$ and its iron and osmium analogues were prepared from $M(CO)_3(PCy_3)_2$ (M = Fe, Ru and Os). Their halide-induced disproportionation was probed by double potential step chronocoulometry, rotating-ring-disk electrochemistry, bulk coulometry, and cyclic voltammetry. Unlike the 18-electron systems, the periodic effect of the 17-electron species showed only slight variation. The role of ion pairs was studied and other thermodynamic and kinetic data were reported [89].



(38) - (42)



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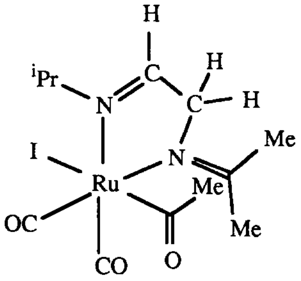

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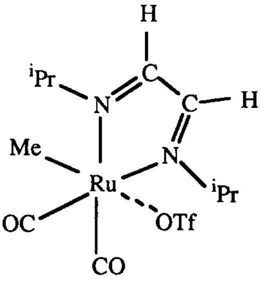
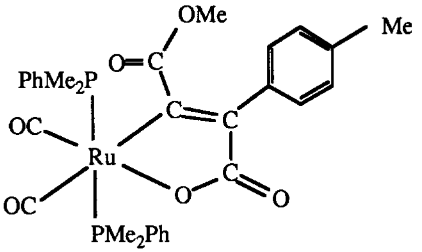
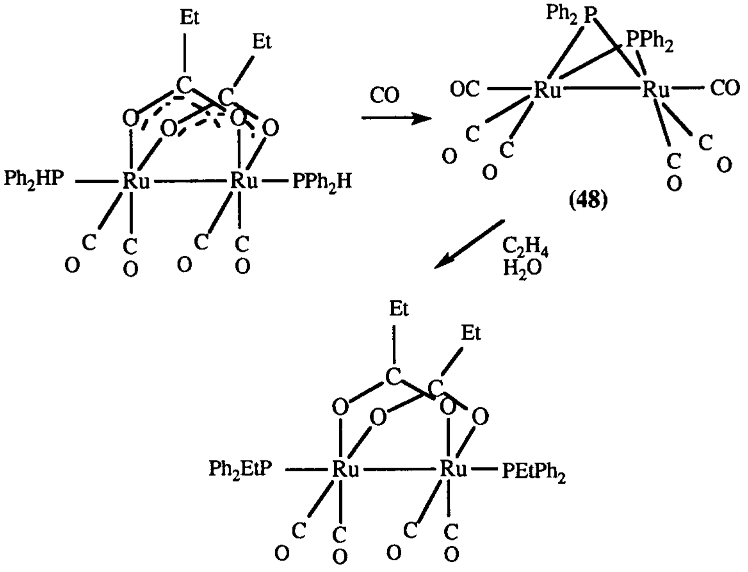


(46)

Reaction of $Ru_2(Me)(I)(CO)_4(PR_3)(^iPr\text{-DAB})$ ($^iPr\text{-DAB} = {}^iPr\text{-N=CHCH=N-}{}^iPr$; $PR_3 = PBu_3$ (**38**), PMe_2Ph (**39**), $PMePh_2$ (**40**), PPh_3 (**41**) and $P(OMe)_3$ (**42**)) with CO gave $Ru(R')(I)(CO)_2(^iPr\text{-DAB})$ (R' = Me (**43**), Ac (**44**)) and $Ru(CO)_4(PR_3)$; the more basic the phosphine, the stronger the tendency to form (**44**). Further reactions of the products gave other products including $Ru(CO)_3(PMe_2Ph)(L')$ (L' = PPh_3, $P(OPh)_3$), $Ru(Ac)(I)(CO)_2(^iPrN{=}CHCH_2N{=}CMe_2)$ (**45**), $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTf]$ (**46**), $[Ru(Ac)(CO)_2(^iPr\text{-}DAB)][OTf]$ and $[Ru(Me)(CO)_2(L)(^iPr\text{-}DAB)][OTf]$ (L = tert-BuNC, PMe_2Ph). ^{13}C labelling experiments were done to support the mechanism proposed [90].



(**47**)



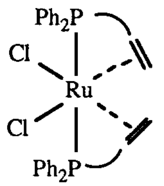
(**48**)

The compound $Ru(CO)_2(PMe_2Ph)\{MeOCOC{=}C(p\text{-}C_6H_4Me)(CO_2)\}$ (**47**) exists as discrete monomeric units in the crystal with an essentially planar 5-membered metallocycle ring [91]. Protonation of *cis-mer*-$RuH_2(CO)(cyttp)$ (cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$) with excess HX (X = BF_4, O_3SCF_3) produced an air stable complex with weakly coordinating anions, *cis-mer*-$RuX_2(CO)(cyttp)$ (X = BF_4, O_3SCF_3). X-ray structure analysis at 223 K showed that *cis-mer*-$Ru(O_3SCF_3)_2(CO)(cyttp)\cdot 1.15H_2O$ was crystallized out. Structural behaviour of the compounds in solution was investigated by variable-temperature $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopies at 178-303 K. Further reactions of the two gave *cis-mer*-$[Ru(CO)L_2(cyttp)][BF_4]_2$

(L = MeCN, CN^{t}Bu and CNCy), $[Ru(F)(CO)L'(cyttp)][BF_4]$($L'$ = H_2O, CO and CN^{t}Bu), *cis-mer*-$[Ru(CO)L''_2(cyttp)][O_3SCF_3]_2$ (L'' = MeCN, NH_3), $[Ru(CO)(P(OMe)_3)(cyttp)][O_3SCF_3]_2$, $[Ru(X')(CO)(P(OMe)_3)(cyttp)]^+$ (X' = Cl, OMe) and *cis-mer*-$RuX''_2(CO)(cyttp)$ (X'' = Me, I, H) [92].

The high yield synthesis of $[Ru_2(CO)_6(\mu\text{-}PPh_2)_2]$ (**48**) was reported and the conversion involving (**48**) and two other complexes was studied [93].

From X-ray structural analysis, $(CH_2{=}CHCH_2CH_2PPh_2)_2RuCl_2$ (**49**) was shown to have a distorted octahedral geometry [94]. Triruthenium dodecacarbonyl reacted with $Ph_2PCH_2C(O)Ph$ (L) in thf, Me_3NO to give $[Ru_3(CO)_9(L)_3]$, which further reacted with I_2 to yield $[\{Ru(\mu\text{-}I)L(CO)_2\}_2]$ (**50**). The cleavage of the iodide bridge of (**50**) by PEt_3 or L gave $[RuIL(CO)_2L']$ (L' = PEt_3 (**51**) or $Ph_2PCH_2C(O)Ph$ (**52**)). The structure of the chloride analogue of (**50**), $[\{Ru(\mu\text{-}Cl)L(CO)_2\}_2]$ was reported [95].



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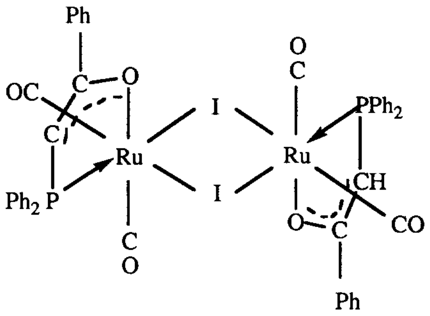

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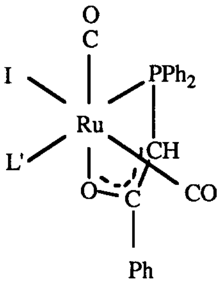
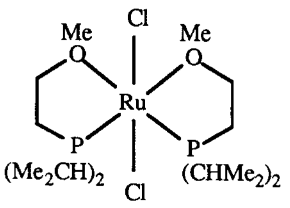


(51), (52)

The novel ether-phosphine (oxetanyl-2-methyl) diphenylphosphine (L), which has strong basic properties, was prepared and reacted with $Cl_2Ru(PPh_3)_3$ to give *trans*-$Cl_2Ru(L\text{-}O,P)_2$. The Ru-O bond in the compound was cleaved by CO, giving *trans*-$[(Cl_2Ru(CO)(L\text{-}P)(L\text{-}O,P)]$ [96]. Similar ruthenium complexes were prepared from $(Me_2CH)_2PCH_2CH_2OMe$ (L1) and $(Me_2CH)_2PCH_2C(O)OMe$ (L2), giving *trans*-$RuCl_2(P\text{-}O)_2$ ($P\text{-}O$ = L1, (**53**); $P\text{-}O$ = L2, (**54**)). Other products from further reaction of (**53**) and (**54**) under various conditions included $[RuCl_2(CO)_2(\eta^1\text{-}P\text{-}(Me_2CH)_2PCH_2CH_2OMe)_2]$, $[RuCl_2(=C=CHPh)(\eta^1\text{-}P\text{-}(Me_2CH)_2PCH_2CH_2OMe)(\eta^2\text{-}(Me_2\text{-}CH)_2PCH_2CH_2OMe)]$ (**55**), $[RuCl_2L{=}C{=}CHR)(\eta^1\text{-}P\text{-}(Me_2CH)_2PCH_2C(O)OMe)(\eta^2\text{-}(Me_2CH)_2PCH_2C(O)OMe)]$ (R = Ph, CO_2Me). The fluxional behaviour in solution was studied by ^{31}P NMR spectroscopy at various temperatures [97].



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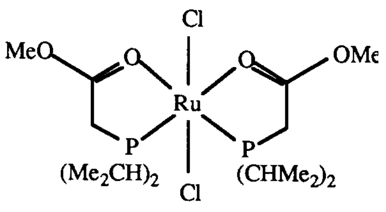
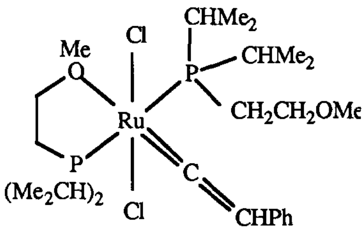


(54)

Asymmetric hydrogenation of tiglic and angelic acids was carried out by using chiral ruthenium (II) bisphosphine catalysts. Based on different results from different hydrogenation pressures, a mechanism was proposed [98].



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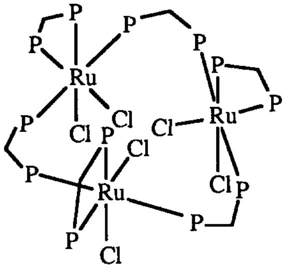

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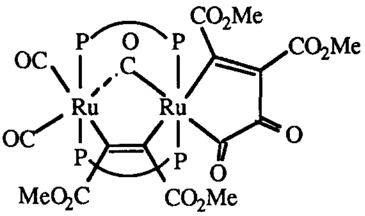

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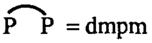

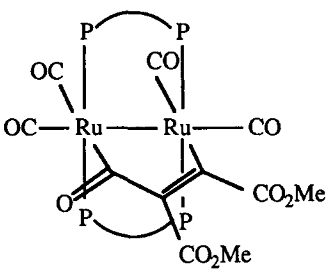

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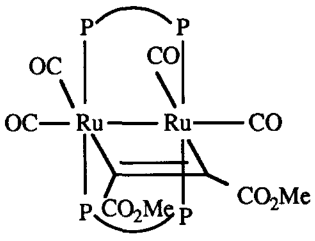


(59)

The structure of cyclo-tris-{dichloro-μ-[methylene-bis(dimethylphosphine)-$_{\kappa}$P:$_{\kappa}$P]-[methylenebis(dimethylphosphine)-$_{\kappa^2}$P]-ruthenium(II)}-ethanol-toluene (1/1/1) (**56**) was reported [99].

The reaction of Ru$_2$(dmpm)$_2$(CO)$_5$ with dimethylacetylenedicarboxylate (DMAD) gave three products in high yield at various conditions: Ru$_2$(dmpm)$_2$(CO)$_3$[μ-C$_2$(CO$_2$Me)$_2$][C(O)C(O)C$_2$(CO$_2$Me)$_2$] (**57**), Ru$_2$(dmpm)$_2$-(CO)$_4$[μ-C(O)C$_2$(CO$_2$Me)$_2$] (**58**), and

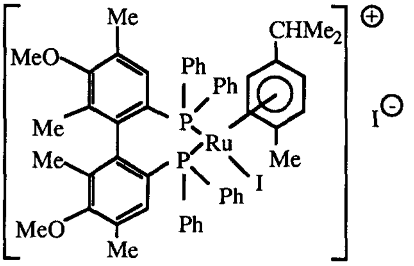
$Ru_2(dmpm)_2(CO)_4[\mu\text{-}C_2(CO_2Me)_2]$ (**59**). The X-ray crystal structures of (**57**) and (**58**) have been determined [100].

The condensation reaction of *cis*-$(dppm)_2RuCl_2$ with $Bu_3Sn\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2(OSiMe_3)$ gave $(dppm)_2Ru(Cl)C{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2(OSMe_3)$, which on protonation yielded $[(dppm)_2Ru(Cl){=}C{=}C{=}C(OMe)\text{-}CH{=}CPh_2]BF_4$ (dppm = $Ph_2PCH_2PPh_2$). Similarly, with excess $HC{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2(OSiMe_3)$, $(dppm)_2Ru[C{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2(OSiMe_3)]_2$ (**60**) and then $[(dppm)_2Ru\{[{=}C{=}C{=}C(OMe)CH{=}CPh_2\}_2](BF_4)_2$ were obtained. The X-ray structure of (**60**) was determined [101].

Kinetic and mechanistic studies of the catalytic conversion of nitroaromatics and methanol to methyl N-arylcarbamates with the homogeneous catalyst, $Ru(dppe)(CO)_3$ was conducted. The variables included CO pressure, temperature, catalyst concentration, methanol concentration and initial aniline concentration (dppe = $Ph_2PCH_2CH_2PPh_2$). The proposed mechanism was based on the characterization of the intermediates isolated: $Ru(dppe)(CO)_2\{C(O)N(Ar)O\}$, $Ru(dppe)(CO)_2\{C(O)OMe\}_2$ and $Ru(dppe)(CO)_2(OMe)_2$ [102]. Di- and trinuclear ruthenium(II) complexes containing one $Ph_2P(CH_2)_4PPh_2$ ligand per ruthenium centre were effective precursor-catalysts for the selective, homogeneous hydrogenation of benzonitrile to benzylamine, $PhCH_2N{=}CHPh$ or dibenzylamine, depending on reaction conditions [103].

The complexes $[RuCl_2(dmso)_2(bp)]$ and *cis*-$[RuCl_2(bp)_2]$ (bp = 4,4',5,5'-tetramethyl-2,2'-biphosphinine) were prepared from $[RuCl_2(dmso)_4]$. The crystal structure of the former was presented [104].

The preparation of 2R,5R-bis[(diphenyl(phosphino)hexane] ruthenium(II) diacetate and the conditions for hydrogenation of 2-(4-isobutylphenyl) propenoic acid were presented [105, 106]. Ruthenium and rhodium complexes with biphenylbisphosphine as ligand groups were prepared as catalysts for asymmetric hydrogenation and chiral amino acid synthesis. The compound (**61**) was prepared and its action on asymmetric hydrogenation of $MeCOCH_2CO_2Me$ was studied [107].



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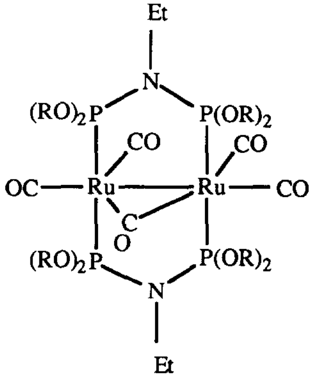
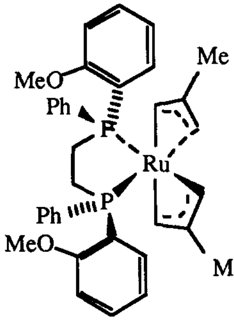
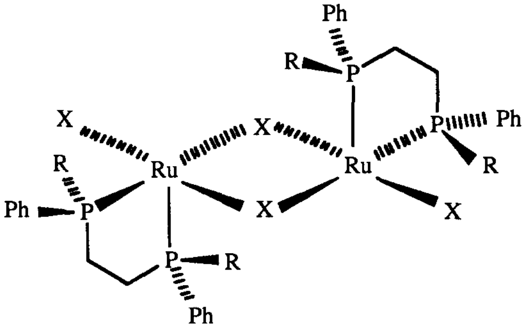


(62), (63)

Protonation of the diphosphazane ligand-bridged $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me (**62**) or ^iPr (**63**)) by HBF_4 or HPF_6 gave $[Ru_2H(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^+$. With protic acids HA, $[Ru_2A(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}A)(CO)_4\{\mu\text{-}(RO)_2P)_2NEt\}]$ were obtained ($A^- = Cl^-, Br^-, NO_3^-, FB(O)OH^-, CF_3CO_2^-$, SPh^- or HCO_3^-). The structures of $[Ru_2\{\mu\text{-}OB(F)OH\}(CO)_4\{\mu\text{-}(^iPrO)_2PNEtP(O^iPr)_2\}_2]BF_4$ and $[Ru\{\mu\text{-}SPh\}(CO)_4\{\mu\text{-}(MeO)_2PNEtP(OMe)_2\}_2]PF_6$ were determined [108]. Compounds (**62**) and (**63**) also reacted with the electron acceptors tcnx, forming $[Ru_2(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2(\eta^1\text{-}tcnx)]$ (tcnx has x = q or e; tcne = $(CN)_2C{=}C(CN)_2$; tcnq = $(CN)_2C(C_6H_4)C(CN)_2$) which contain a tcnx radical anion in both the inner and outer coordination sphere of the cation. A combined EPR/ENDOR-, UV/visible/near-IR- and IR-spectroscopic and electrochemical investigation was carried out [109].



(**64**)

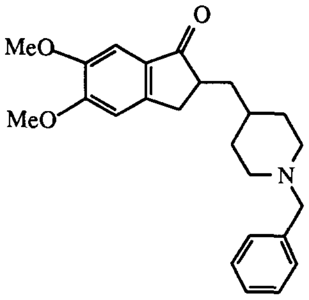


(**65**) X = Br;
(**66**) X = I

The synthesis of (R,R–DIPAMP)rutheniumbis(2-methylallyl) (**64**) and $[R,R\text{-}DIPAMP]_2Ru_2X_4$ (R = o-$MeOC_6H_4$; X = Br (**65**) or I (**66**)) was reported. They were shown to be effective catalysts for asymmetric hydrogenation of both alkene and keto groups [110]. Other similar ruthenium complexes containing allylic and diphosphine ligands were found to be homogeneous asymmetric catalysts for hydrogenation of olefinic compounds, including alkenes with carboxyl or acylamido groups. Examples given were (–)-(DIOP)RuL_2 (**67**), (+)-(BINAP)RuL_2, (–)-(CHIRAPHOS)RuL_2, (+)-(NORPHOS)-RuL_2 and (DIPAMP)$Ru(OAc)_2$. Specific conditions for hydrogenation of $MeCH{=}C\text{-}MeCO_2H$ with (**67**) (L = methylallyl) as the catalyst, which gave 100% yield of (R)-$MeCH_2\text{-}CHMeCO_2H$ were established [111].

The effect of different solvents on the structure of a few BINAP-ruthenium(II) complexes was discussed. $[RuX\{(S)\text{-}BINAP\}(arene)]Z$ (X, Z = halide and/or BF_4^-; arene = benzene or p-cymene), $[Ru\{(S)\text{-}BINAP\}(MeCN)_4]X(Z)$ (X = Z = Cl, Br, I; X = Cl, Z = BF_4^-) , $[RuX\{(S)\text{-}BINAP\}(MeCN)_3]X$ (X = Cl, Br or I) , $[RuCl_2\{(S)\text{-}BINAP\}(MeCN)_2]$ and $[Ru_3X_5\{(S)\text{-}BINAP\}_3]Z$ (X = Z = Cl, Br ; X = Cl, Z = BF_4) were observed under different conditions, with $[Ru_3Cl_5\{(S)\text{-}BINAP\}_3]BF_4$ characterized by X-ray crystallography. The relationship between the structures of the complexes and their catalytic activities for asymmetric hydrogenation of methyl 3-oxobutanoate was investigated [112]. The catalytic systems of [RuCl{(S)- or (R)-BINAP}-(benzene)]Cl and NEt_3 or with [Ru_2Cl_4{(S)- or (R)-BINAP}$_2$]·(NEt_3) (**68**), the hydrogenation of diketene $H_2C{=}C(O)CH_2C{=}O$ became highly enantioselective. Up to 97% yield of optically active 4-methyloxetan-2-one were produced with 92% enantiomeric excess [113]. The syntheses and characterization of a series of BINAP-Ru complexes were presented and their catalytic effects were widely studied. Highly stereoselective hydrogenation of methyl-2-benzamidomethyl-3-oxo-butanoate and an efficient synthesis of new chiral bis(triarylphosphine) ligands were accomplished [114].

Reduction of $ROCH_2COCH_2OR'$ in the presence of (**68**) gave (S)- and (R)-$ROCH_2CH(OH)CH_2OR'$with high enantioselectivity ($R = CH_2Ph$, $R' = CPh_3$, $(CH_2)_{17}Me$; $R = (CH_2)_{17}Me$, $R' = CPh_3$) [115]. Compound (**68**) was also shown to be a good catalyst for asymmetric hydrogenation of (Z)-$RCH{=}CFCO_2H$ to chiral RCH_2CHF-CO_2H with up to 90% enantiomeric excess, especially when the (R)-BINAP catalyst was used [116]. Another hydrogenation catalyst $RuCl_2(ArCN)_2$(BINAP) was also prepared (ArCN = benzonitrile, 2-furancarbonitrile, pentafluorobenzoinitrile). The compound had similar catalytic activities and enantioselectivities as (**68**) for hydrogenation of some prochiral acids, but it showed lower activities and selectivities for hydrogenation of β-functionalized carbonyl compounds [117]. Piperidine (**69**), a known acetylcholine esterase inhibitor useful for treating Alzheimer-type senile dementia, was prepared by asymmetric hydrogenation of (**70**) in the presence of an optically active ruthenium complex of general formula (**70a**) (either A or B was ruthenium-containing). The reaction of (**70**) with [$RuCl_4${(S)-(-)-BINAP]$_2$]·NEt_3 as catalyst was discussed [118].



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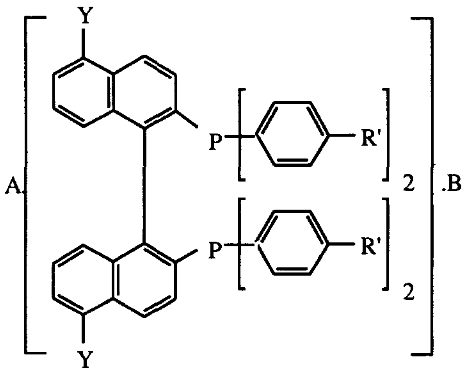

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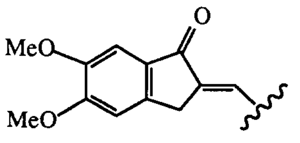
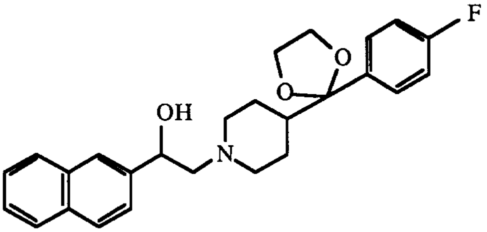


(70)

The catalytic hydrogenation of itaconic acid with $[RuH(binap)_2]PF_6$ as the catalyst was examined under a variety of conditions. The addition of Et_3N effected high enantioselectivities [119]. In specific, the (S)-BINAP enantiomer of the same compound was studied for hydrogenation of methylenesuccinic acid and (R)-2-methyl-1,3-propanedioic acid and was shown to have excellent enantioselectivities [120].

The compositions of the complexes obtained from reactions of $[RuCl_2(cod)]_n$ with various chiral diphosphine in the presence of NEt_3 varied according to the solvent used. The structures and dynamic properties of the BINAP-complexes were elucidated by the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic measurements, with X-ray diffraction analysis done for *trans*-RuHCl((R)-BINAP)$_2$ [121].

The hydrogenation of α-arylpropenoic acids proceeded with increasing enantiomeric excess with decreasing temperature and increasing pressures. The process was studied under various initial conditions with different phosphines and phosphine-Ru complexes. Thus with Et_3N and $Ru(BINAP)(OAc)_2$, 2-(6'-methoxy-2'-naphthyl) propenoic acid was hydrogenated to naproxen with 89.7% e.e. [122]. The crude product from the reaction between $[RuCl_2(C_6H_6)_2]$ and optically pure BINAP or its derivatives could be used directly for asymmetric hydrogenation of various functionalized olefins. On recrystallization, pure $Ru(BINAP)(O_2CR)_2$ (R = Me or Ph) was obtained in high yield [123].



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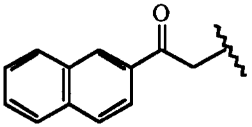


(72)

The optically active naphthylethanol (**71**) was a useful intermediate for pharmaceuticals and was prepared by asymmetric hydrogenation of acetonaphthone derivative (**72**), catalysed by Ru{(+)- or (-)-BINAP}$(O_2CR^1)(O_2CR^2)$ or Ru-$[RC_6H_4PC_{10}H_6]_2$ complexes. With $Ru(OAc)_2$[(R)-(+)-BINAP], 83.8% (R)-(**71**) of 95.1% e.e. was obtained, while (S)-(**71**) of 94% e.e. was obtained with $Ru(OAc)_2\{(S)\text{-}(-)\text{-}(p\text{-}CH_3C_6H_4PC_{10}H_6)_2\}$ [124]. $Ru(acac)_2$\{(S)-BINAP\} was prepared to catalyse hydrogenation of dehydronaproxen (L) to (S)-naproxen. It was found that the complex formed during the reaction, Ru{(S)-BINAP}(acac)(L) was much more active than any previously known catalysts for the reaction [125].

The compound $[RuCl(PPh_3)(BINAP)]_2(\mu\text{-}Cl)_2$ was prepared from ruthenium trichloride through the intermediate $[RuCl_3(PPh_3)_2(dna)](dna)$ (dna = $MeCONMe_2$) and $[RuCl(PPh_3)_2(dna)]_2(\mu\text{-}Cl)_2$ and was used for asymmetric hydrogenation of $MeCOCH_2CO_2Me$ [126]. A few mono-and dinuclear ruthenium complexes were synthesized and characterized, including $(P\text{-}P)ClRu(\mu\text{-}Cl)_3RuCl(P\text{-}P)$, $[RuCl(P\text{-}P)]_2(\mu\text{-}Cl)_2$ and $[RuCl(BINAP)]_2(\mu\text{-}Cl)_2$; the latter from [$RuCl_2$(BINAP)($PPh_3$)] (P-P = $Ph_2P(CH_2)_nPPh_2$; n = 3-6). A range of L(dppb)Ru(μ-Cl)$_3$RuCl(dppb) complexes (L = Et_3N, Me_2CO, $AcNMe_2$, MeI, PhCN, CO, N_2, H_2 and dmso) were also prepared with the dmso-analogue characterized by X-ray crystallography [127]. The enantioselective synthesis of (–)-indolizidine.223AB was mediated by a chiral (S)-BINAP-Ru catalyst for preparation of the corresponding amino alcohol from the symchiral precursors [128]. Asymmetric hydrogenation of alkenes and ketones with Ru-BINAP complexes was reviewed [129].

The water soluble complexes $RuCl_2(PTA)_4$, $RuCl_2(PTA)_4$·2HCl, $RhCl(PTA)_2$.2HCl and $RhCl(PTA)_3$ were prepared, with the first three complexes characterized by X-ray crystallography (PTA = 1,3,5-triaza-7-phosphaadamantane). $RuCl_2(PTA)_4$ was catalytically active for the conversion of unsaturated aldehydes to unsaturated alcohols [130]. The complex [α,α,α-tris{(diphenyphosphino)methyl}toluene]-ruthenium(II) dichloride was synthesized for potential use as an oxidation catalyst for homogeneous reactions [131].

The complexes *trans*-[$Ru(L\text{-}L)_2X_2$]BF_4 (X = Cl or Br; L-L = $C_6H_4(PMe_2)_2$-o), $C_6H_4(AsMe_2)_2$-o, $C_6F_4(AsMe_2)_2$-o, $Me_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCHCHAsPh_2$, $C_6H_4(PPh_2)_2$-o, $C_6F_4(PPh_2)_2$-o, $MeSCH_2CH_2SMe$, $PhSCH_2CH_2SPh$ and $PhSeCH_2CH_2SePh$) were prepared from the corresponding species [$Ru(L\text{-}L)_2X_2$]. They were characterized by spectroscopic, magnetic and electrochemical experiments. Furthermore the X-ray structure of the $C_6F_4(AsMe_2)_2$-o analogue was determined [132]. The phosphides $ThRu_2P_2$ and $URu_2P_{1\cdot894}$ were prepared by the reaction between Th and RuP, and U-Ru alloy and P respectively. Their structures were determined by X-ray crystallography and compared with several other related compounds such as $BaZn_2As_2$ [133].

10.4 Complexes with sulfur donor ligands

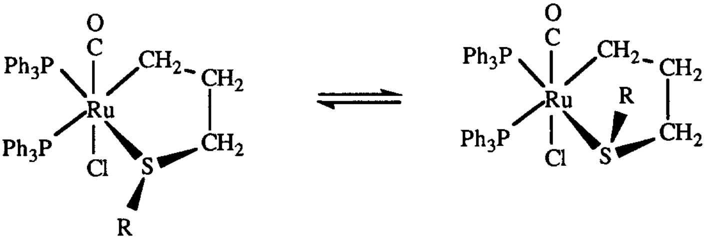
The HSO_5^- oxidation of thiols coordinated to ruthenium(III) centres proceeded cleanly via two discrete steps to give the corresponding sulfenato and sulfinato complexes. The preparation and the oxidation kinetics of several other thiolato ruthenium(III) complexes was reported [134]. The catalyst for hydrorefining petroleum fractions contained ruthenium sulfide on a non-acidic zeolite, preferably ≥1 alkali metal (e.g. Li, Na, K, Rb, Cs) and was optionally used with a conventional one [135].

Temperature-programmed reduction patterns of supported or unsupported RuS_2 crystallites clearly showed three different kinds of sulfur atom. A geometrical model based on the pyrite-type structure of RuS_2 was proposed which described qualitatively and quantitatively these sulfur species [136]. Thermodesorption and NMR spectroscopy were used to investigate the effect of desulfurization of RuS_2 on the adsorption of hydrogen [137]. The interfacial behaviour of n-RuS_2 subjected to a variety of surface treatments was investigated using the rotating-disk electrode and impedance techniques. The kinetics was studied and the results were compared with those reported for Pt and RuO_2 [138].

The first disulfido-bridged mixed-valent Ru(II)Ru(III) compound [{$Ru(MeCN)_3${$P(OMe)_3$}$_2$}$_2$(μ-S_2)](PF_6)$_3$ was prepared from [{RuCl{$P(OMe)_3$}$_2$}$_2$(μ-Cl)$_2$(μ-S_2)] and was structurally characterized. The ruthenium atoms were shown to be equivalent [139]. In turn, the latter compound was synthesized and characterized by X-ray crystallography and was shown to have a novel $Ru_2(S_2)Cl_2$ core [140]. The complex meso-[Ru(NO)('S_5')]Br was prepared from the template alkylation of $[NBu_4][Ru(NO)('S_2')_2]$ with $(BrC_2H_4)_2S$ in order to investigate the potential conversion of coordinated NO into N_2 ligands (H_2'S_2' = 1,2-benzenedithiol). Reactions of meso-[Ru(NO)('S_5')]Br with nucleophiles like azide, NH_3, $LiNH_2$ and NEt_3 were discussed [141].

The sulfur-bridged complexes $[\{Ru(TMP)_4\}_2(\mu\text{-}MS_4)](PF_6)_2$ (M = Mo or W; TMP = $P(OMe)_3$) were synthesized; the X-ray structure of the tungsten-containing species has been determined [142]. The dianion $[ReS_4]^{2-}$ was the first d^1 tetrathiometalate persistent enough to be studied with respect to charge transfer, ligand field and IR vibrational spectra via spectroelectrochemistry; however, an EPR spectrum could only be detected for the trinuclear derivative $[(bpy)_2Ru(\mu\text{-}ReS_4)Ru(bpy)_2]^{2+}$ at 4 K [143].

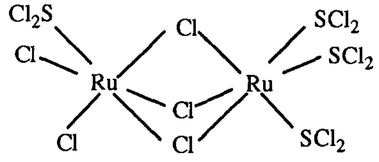
The complex *cis,cis,trans*-$Ru(SH)_2(CO)_2(PPh_3)_2$ was synthesized from $Ru(CO)_2(PPh_3)_3$ or *cis,cis,trans*-$RuH_2(CO)_2(PPh_3)_2$ and H_2S. The mechanism of the H/D exchange reactions of the product and *cis,cis,trans*-$RuH(SH)(CO)_2(PPh_3)_2$ with CD_3OD was suggested. The sole product *trans*-$RuH(SH)(dppm)_2$ was obtained from reaction of H_2S and mixture of *cis*- and *trans*-$Ru(H)_2(dppm)_2$, which further reacted to give *trans*-$Ru(SH)_2(dppm)_2$ [144]. The compounds $[Ru(CH_2CH_2CH_2SR)Cl(CO)(PPh_3)_2]$ (R = CH_3, $CH_2C_6H_5$ or $CH_2CH{=}CH_2$) were synthesized and their structural inversion behaviour was studied by variable-temperature NMR spectroscopy. The thermal product of $[Ru(CH_2CH_2CH_2SCH_3)Cl(CO)(PPh_3)_2]$ at 67°C was $[Ru_2(\mu\text{-}Cl)Cl(\mu\text{-}H)(\mu\text{-}SCH_3)(CO)_2(PPh_3)_3]$, while $[RuClH(CO)(dppe)(PPh_3)]$ reacted with allylmethyl sulfide at 110°C to afford $[Ru_2Cl_2(\mu\text{-}SMe)_2(CO)_2(dppe)_2]$; both evolved propylene [145].



The ruthenium(IV) complex $[Ru^{IV}(SR)_4(MeCN)]$ (R = 2,3,5,6-Me_4C_6H, or 2,4,6-$(Me_2CH)_3C_6H_2$) reacted to give $[Ru^{IV}(SR)_3(MeCN)_2]^+$, in which the axial RS^- ligand was selectively replaced. The osmium analogue of the Me_4C_6H complex, together with the ruthenium complexes were reduced by electrochemical and chemical means, giving $[M^{III}(SR)_3(MeCN)_2]$. The PF_6^- salt of the same complex and $[Ru^{III}(SC_6H_2{}^iPr_3\text{-}2,4,6)_3(MeCN)_2]$ were structurally characterized by X-ray crystallography [146]. The nature of Ru(II)-S(thioether) bonding has been probed by a combination of structural, spectroscopic and computational methods. $[(NH_3)_5Ru(SMeEt)](PF_6)_2$ was synthesized and characterized by X-ray crystallography, showing a substantial back-bonding in Ru(II)-S bond. Ab initio MO calculations were done for the ground state of $[(NH_3)_5Ru^{II}SMe_2]^{2+}$. The MLCT and LMCT transitions were also measured [147]. The complexes $[(SbPh_3)_3RuCl_2]$ and $[(Et_3S)_3RuCl_3]$ were prepared from $Ru(H_2O)_3Cl_3$ and $RuCl_3$ respectively [148].

The metallacarbaborane $[RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)SC_2B_9H_{10}\}(PPh_3)_2]\cdot Me_2CO$ was prepared and characterized by X-ray crystallography and FT-IR, and ^1H and ^{11}B NMR spectroscopies. The molecule contains an octahedral ruthenium(II) centre with a novel B-H→Ru agostic bond occupying the sixth coordination site [149].

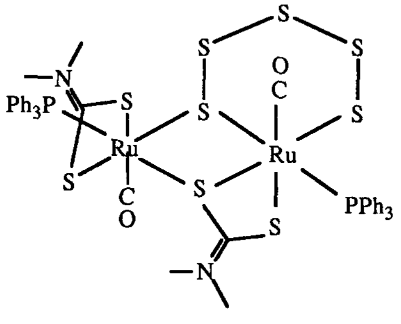
Black crystals of $Ru_2S_4Cl_{13}$ (**73**) were obtained from reaction of ruthenium and SCl_2 in closed quartz ampoules at 125°C. The crystal structure revealed the presence of dinuclear $Cl_2(SCl_2)Ru(\mu\text{-}Cl)_3Ru(SCl_2)_3$ units with unsymmetrically substituted octahedral Ru(II),(III) centres [150]. $[Ru(S_2CR)_2(PPh_3)_2]$ (R = EtO, or pyrollidinyl) reacted with tertiary phosphines to afford $[Ru(S_2CR)_2(PR_3)_2]$ and $[Ru(S_2CR)_2(P\text{-}P)]$ (P-P = dppe or dppm), with the *cis*-product dominating except for PMe_2Ph complex. The effect of the different phosphines on the ruthenium complex was analysed spectroscopically and electrochemically and the X-ray crystal structure of $[Ru(S_2COEt)_2(PMe_2Ph)_2]$ was done [151]. $[Cp(EPh_3)Ru(S_2CNCN)]$, $[(bpy)_2Ru(S_2CNCN)]$, $[Cp(EPh_3)Ru(S_2CN\text{-}CN)Ru(EPh_3)_2Cp]$, $[(bpy)_2Ru(S_2CNCN)Ru(EPh_3)_2Cp](PF_6)$ and $[(bpy)_2Ru(S_2CN\text{-}CN)Ru(bpy)_2Cl](PF_6)$ and their $[(PhCH_2)_2S_2CNCN)]$ analogues were synthesized and characterized (E = P, As or Sb) [152].



(73)

The synthesis and characterization of the unstable *trans*-(P)-$[Ru(SH)(S_2CNMe_2)(CO)(PPh_3)_2]$ and $[Ru(\mu\text{-}SH)(S_2CNMe_2)(CO)(PPh_3)]_2$ has been published, together with their X-ray crystal structures [153]. $[\{SC(NMe_2)_2\}_2]Cl_2$ was first prepared from $SC(NMe_2)_2$ (L). The reaction of $[Fe(SR)_2L_2]$ (R = 2,4,6-$^iPr_3C_6H_2$) with $[\{SC(NMe_2)_2\}_2]Cl_2$ gave $[Fe(SR)L_3]BPh_4$ and $[FeL_4](BPh_4)_2$. In addition, $[RuCl_2(CO)_2L_2]$ was also obtained and its X-ray structure was determined along with those of the other products. The structural data for $[RuCl_2(CO)_2L_2]$ showed the dual character of ligand L [154]. Novel dinuclear ruthenium compounds with S_5^{2-} and S_6^{2-} bridging ligands were prepared. X-ray analyses of these products showed that $[Ru_2(\mu\text{-}S_5)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**74**) and $[Ru_2(\mu\text{-}S_6)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**75**) coexist in the crystal lattice with the occupancy ratios of around 3 to 1 respectively; the polysulfido groups are disordered [155].

It has been shown that rhodium(III) and ruthenium(III) complexes containing dimethylsulfoxide ligands (dmso) had antitumor activity in the Lewis lung carcinoma model [156]. The reaction between the antitumour complex *trans*-$RuCl_2(dmso)_4$ and d(GpG) led to the formation of a stable compound characterized by a covalent difunctional coordination of the bases to the metal centre. Full characterization had been done by NMR spectroscopy and molecular modelling studies. The compound showed structural features which were suprisingly similar to those exhibited by the corresponding cisplatin complex, indicating that such a form of interaction with DNA was not exclusive to platinum or to metals with square planar coordination geometries [157].



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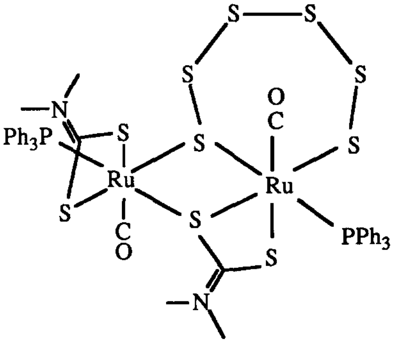

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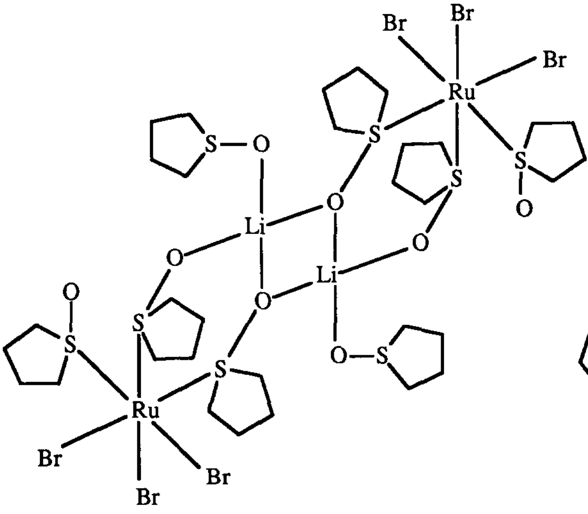

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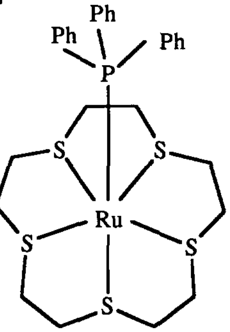
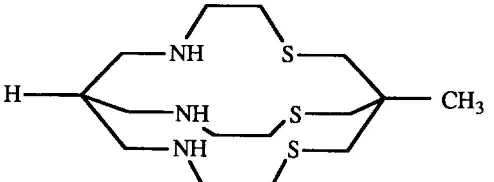


(79)

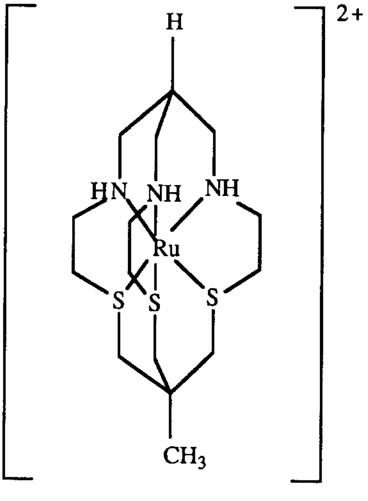
An inner sphere mechanism involving the pentacoordinate Ru(II) complex $RuCl_2[R_2S(O)]_x(R_2S)_{3-x}$ (x = 0, 1) was suggested for the auto-oxidation of sulfides to sulfoxides, using the effective Ru(II)-and Ru(III)-dmso complexes catalyst [158]. The previously reported $RuBr_2(dmso)_3$ was characterized to be a mixture of isomers, Li[*fac*-$RuCl_nBr_{3-n}(dmso)_3$] (n = 0-3). This was supported by ^1H, ^7Li and ^{37}Cl NMR spectroscopies, together with the X-ray structure of $[NEt_4]$[*fac*-$RuBr_3$-$(dmso)_3]\cdot0.5MeOH$ [159]. The synthesis of $[Br_6(tmso\text{-}S)_2\text{-}Ru_2(\mu_2\text{-}tmso\text{-}SO)_2(\mu_3\text{-}tmso\text{-}SO)_2Li_2(tmso\text{-}O)_2]$ (76) was presented. The X-ray structure revealed 4 types of coordinated tmso (tetramethylenesulfoxide) including a unique μ_3-type [160].

The high yield product $[RuCl_2(PPh_3)([9]aneS_3)]$ from $[RuCl_2(PPh_3)_3]$ and $[9]aneS_3$ (1,4,7-trithiacyclononane) was treated with $TlPF_6$ to yield $[TlCl_2Ru(PPh_3)$ - ([9]and $S_3)]_2(PF_6)_2$ (77) with a $[RuCl_2Tl_2Cl_2Ru]$ ladder. Dissolution of (**77**) in acetone precipitated TlCl, with formation of $[RuCl(PPh_3)\cdot([9]aneS_3)]_2(PF_6)_2$ (**78**). Both (**77**) and (**78**) were characterized by X-ray crystallography [161]. Using a thick-walled glass reaction vessel, $[Ru([9]aneS_3)_2](PF_6)_2$ and a number of organometallic and coordination compounds had been synthesized using microwave dielectric super-heating effects at mild temperatures and high pressure [162]. $[RhCl([15]ane S_5)](PF_6)_2$ and $[Ru(PPh_3)([15]ane S_5)](BPh_4)_2$ (**79**) were synthesized and characterized by elemental analysis and spectral methods, with the X-ray structure determined for complex (**79**) ($[15]aneS_5$ = 1,4,7,10,13-pentathia-cyclopentadecane) [163].

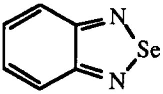
The cation $[Ru(capten)]^{2+}$ (where capten = (**80**)) (**81**) was prepared from $[Ru(dmf)_6]^{2+}$ and the free ligand. Its spectroscopic and electrochemical properties were studied [164]. $[RuCl_2(PPh_3)_3]$ reacted with DPPBT (DPPBTH = $2\text{-}Ph_2PC_6H_4SH$) to give $[HNEt_3][Ru^{II}(DPPBT)_3]$, which further oxidized to give $[Ru^{III}(DPPBT)_3]$ and then $[Ru^{II}(DPPBT)(2\text{-}Ph_2PC_6H_4SOH)(2\text{-}Ph_2PC_6H_4SO_2)]\cdot0.5H_2O$. This last species was characterized by X-ray crystallography [165]. The synthesis and characterization of $[RuHCl(CO)(RC(S)NH(CO)R')(PPh_3)_2]$ were described (R = 2-pyrrole, R' = OEt; R = 2-thiophene, R' = OEt; R = 2-pyrrole, R' = NHPh; R = 2-thiophene, R' = NHPh) [166]. The synthetic methods of $[RuCl(CH{=}CHCR_2OH)(CO)(PPh_3)_2(BSD)]$, $[RuCl\{CH{=}CHC({=}CH_2)Me\}(CO)(PPh_3)_2(BSD)]$ and $[RuCl\{CH{=}CHC_6H_9\}(CO)(PPh_3)_2(BSD)]$ were presented (BSD = (**82**)) [167].



(**80**)



(**81**)



(**82**)

10.5 Complexes with nitrogen donor ligands

10.5.1 Complexes with 2,2'-bipyridine ligands

The formation of adducts $[Cr(bpy)_3]^{3+}$, $[Cr(phen)_3]^{3+}$, $[Ru(bpy)_3]^{2+}$, (**83**), and $[Pt(bpy)(NH_3)_2]^{2+}$ with the lasalocid A anion was studied in dichloromethane solution by electronic absorption and emission spectroscopies [168]. Experimental variances in band intensities of the resonance Raman spectra of ruthenium tris(bipyridine) excited states were discussed [169]. The rate of photoreduction of methylene blue incorporated in polyaniline films was further enhanced by incorporating $[Ru(bpy)_3]^{2+}$ (**83**). The role of (**83**) on the reduction rate was quantitatively analysed by measuring the photoelectrochemical properties of the films [170]. A review on photophysical and electrochemical properties of (**83**).

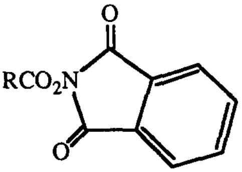
Synthetic aspects and chemistry of other ligands and dinuclear ruthenium and osmium complexes were reported [171]. A new method based on chemiluminescence of $[Ru(bpy)_3]Cl_2$ in solution was developed for the identification of Cu(III) in high-temperature superconductors [172]. A comparison of the photophysical and photochemical properties of (**83**) and tetrakis(μ-diphosphito)diplatinate (II), $[Pt_2(pop)_4]^{4-}$ was made [173]. The effects of the conformation of polymer chains on the electron transfer reactions and on the luminescence behaviour of (**83**) in aqueous solution of *cis*-Co(A)PAA and *cis*-Co(A)PMA (A = $(en)_2(OH_2)$, PAA = poly(acrylic acid), PMA = poly(methacrylic acid)) were investigated [174]. The quenching process of (**83**) by a series of ferrocene Schiff's base derivatives was shown to involve a reductive mechanism [175]. On the other hand, an electron transfer mechanism was employed when polynuclear complexes containing nitrogen and sulfur atoms of the form $M(FcCMe{=}NN{=}CSSR)_2$ (Fc = ferrocenyl) were used as quenchers [176].

The yields of singlet O_2 obtained from the reaction of the excited state of (**83**) and triplet O_2 in various solvents were measured by a steady state photolysis technique involving the trapping of the singlet O_2 [177]. The luminescence quenching of (**83**) by O_2 on porous SiO_2 and controlled porous glass studied at 253-353 K was believed to involve both the Eley-Rideal and Langmuir-Hinshelwood mechanisms [178]. The photoeffect at the liquid-liquid interface, originating from the quenching of (**83**) by O_2, and the electron transfer process occurring at the interface deriving from the quenching of excited state of (**83**) by methylviologen (MV^{2+}) were described [179]. Photoinduced electron-transfer of (**83**) and MV^{2+} in the supercages of hydrated zeolite Y and three other different zeolites (L, Y and mordenite) were studied by steady-state and time-resolved spectroscopic techniques [180, 181]. The globular particles of calcium-montmorillonite and the exchange of montmorillonite with (**83**) and MV^{2+} were observed by scanning electron microscopy [182].

The electron transfer from $Ru(bpy)_3{}^{2+}$ to cytochrome c oxidase was induced by flash photolysis in the presence of sacrificial electron donor, aniline [183]. The absolute luminescence quantum yields of $[Ru(bpy)_3]X_2$ (X = Cl or ClO_4) were determined by the thermal lens effect. The perchlorate salt was found to have a higher quantum yield [184]. The intermolecular structural and dynamic effects of (**83**) entrapped in zeolite Y cages were revealed by the spectral data [185]. The crystal structures of $[Ru(bpy)_3](PF_6)_3$ and $[Ru(bpy)_3](PF_6)_2$ were determined at 105K and were compared with the room-temperature structures [186]. Second-harmonic generation was observed with ultra thin poly(vinyl chloride) films impregnated with amphiphilic ruthenium tris(2,2'-bipyridine) complexes [187]. $Ru(bpy)_3^{2+}$ incorporated in a swelling mica-poly(vinylpyrrolidone) intercalation compound was investigated for its luminescence behaviour [188]. A polyquinoline-supported ruthenium tris(bipyridyl) complex was characterized and tested for its suitability as a photosensitizing membrane in a water photolysis cell [189]. The lifetime of the excited $Ru(bpy)_3^{2+}$ adsorbed on porous glass reflected the mobility of the molecules in the pore [190]. Polysiloxanes containing pendant $Ru(bpy)_3^{2+}$ groups were prepared and the photoluminescence characteristics were reported [191]. Similarly, another copolymer with pendant $Ru(bpy)_3^{2+}$ units and grafted on to silk was prepared and studied [192].

Electrochemiluminescence (ECL) arose from ion-annihilation reactions of $[Ru(bpy)_3](ClO_4)_2$ or diphenylanthracene in MeCN containing electrolyte and was examined at the highly efficient double-band array electrode [193]. Such ECL of the dication $[Ru(bpy)_3]^{2+}$, (**83**), in aqueous oxalate solution and in MeCN was substantially enhanced by simultaneous irradiation with 40-60 kHz ultrasound [194]. Redox reactions and electrochromism of bilayer membranes of Prussian blue and Nafion containing (**83**) coated on indium tin oxide (ITO) electrodes were studied electrochemically as well as spectrophotochemically. Both systems exhibited multi-electrochroism [195]. Polarization phenomena at an ion membrane/electrolyte interface were studied in a 4-electrode cell with $Ru(bpy)_3^{2+}$, Li^+ or Cs^+ as one electrolyte and an intermediate cation-exchanging Nafion membrane [196]. The wavelength dependence of photoinhibition and the primary process of illumination effect on the $Ru(bpy)^{2+}$-catalysed Belousov-Zhabotinskii reaction were studied [197, 198]. Chemiluminescence oscillations in the same reaction were stabilized in a continuous-flow stirred tank reactor; the marked effect of O_2 has been discussed [199].

Studies on photoelectrochemical cells with (**83**) as sensitizer in the presence of Na_2H_2edta reducing agent along with various dyes in various types of micellar media were carried out [200]. The heterogeneous kinetic parameters in both aqueous solution and non-aqueous solution (reduction of $K_3Cr(CN)_6$ in 1M KCN and $[Ru(bpy)_3]^{2+}$ in both dmf and MeCN, respectively) were obtained by fitting the second harmonic phase angle voltammograms with theoretical curves. The advantages of such a method were discussed [201]. A study on the effects of varying the conditions used for preparation of $Ru(bpy)_3^{2+}$ Langmuir-Blodgett (LB) films and for luminescence lifetime measurement was conducted [202]. The $Ru(bpy)_3^{2+}$ photosensitized reduction of $[Co(N_4)(OH_2)_2]^{3+}$ (N_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) was investigated in the networks of gelatin hydrogel and hydrosol [203]. The same reaction system was used to modify electrodes for the photoelectrocatalytic reduction of oxygen [204]. New colloidal starch-stabilized manganese-containing hydroxide catalysts for H_2O oxidation to O_2 by $Ru(bpy)_3^{3+}$ were synthesized and the selectivities were compared among the catalysts which exhibited various oxidation states for the manganese [205]. Highly efficient reductive decarboxylation of *N*-(acyloxy)-phthalimides (**84**) was achieved by visible light irradiation using $Ru(bpy)_3Cl_2$ as a sensitizer; a radial chain mechanism was involved [206].



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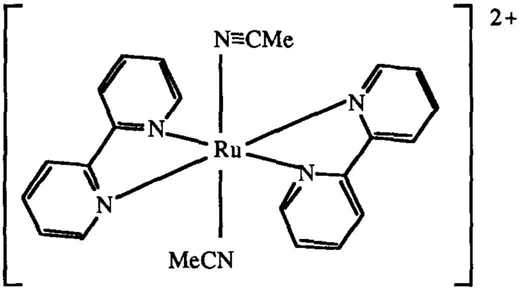

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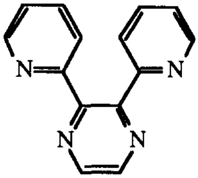
The pH-dependent metal-to-ligand charge-transfer spectra and facilitated ligand reduction of the complexes of folic acid, lumiflavin and riboflavin with $Ru(bpy)_2^{2+}$ suggested the formation of flavosemiquinone; a substantial decrease in $pK_a(NH)$ was observed [207]. The anation kinetics of *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ by 8-quinolinol, L-cysteine, acetylacetone and salicylhydroxamic acid were studied and mechanisms were proposed [208-211]. Pyrrole-$[Ru^{II}(bpy)_2Cl_2]$ was synthesized and electropolymerized on inert electrodes. The Ru(II) sites were readily converted into other complexes such as *cis*- or *trans*-$[Ru(bpy)_2(H_2O)_2]^{2+}$, $[\{Ru(bpy)_2(H_2O)\}_2O]^{4+}$ and $[Ru(bpy)_2(MeCN)_2]^{2+}$ [212]. The complex $[Ru(bpy)_2Cl_2]$ was found to catalyse the stereospecific epoxidation of oleic acid [213]. The crystal and molecular structures of *trans*-$[Ru(bpy)_2(MeCN)_2](ClO_4)_2$ **(85)** and *trans*-$[Ru(bpy)_2(NH_3)_2](ClO_4)_2$ were determined. In both, the ruthenium atom is located on a crystallographic inversion centre and the bpy ligands are in a bow conformation [214].

A series of oligomers $[(phen)(CO)_3Re(CN)\{Ru(bpy)_2(CN)\}_nRu(bpy)_2(CN)]^{(n+1)+}$ (n = 0-3) were synthesized and their electrochemical and photophysical properties were investigated. Specifically, direct evidence for long-range energy transfer in $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)Ru(bpy)_2(CN)]^{2+}$ was obtained by time-resolved resonance Raman spectroscopy [215]. The synthesis, spectroscopic, redox and photophysical properties of $[(CO)_3(bpy)ReCNRe(bpy)(CO)_3]^+$, $[(CO)_3(bpy)ReNCRu(bpy)_2CNRe(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)ReCNRu(dcbpy)_2NCRe(bpy)(CO)_3]^{2+}$ were reported (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine). A comparison was made between the N- and C-bonded isomers and between Re-Ru-Re- and Ru-Ru-Ru-polypyridyl trinuclear complexes [216]. Singly oxidized forms of $[(CN)(bpy)_2Ru^{II}\text{-}CN\text{-}Ru^{II}(dcbpy)_2\text{-}NC\text{-}Ru^{II}(bpy)_2(CN)]$ and $[(H_2O)(bpy)_2Ru^{II}\text{-}NC\text{-}Ru^{II}(dcbpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2(H_2O)]$ show intervalence transition bands in the IR spectral region. This is typical of mixed valence systems [217].

Oxidation of $PhCH_2R$ (R = Me, Et, Pr) by air or oxygen was catalysed by polymer-supported (bpy)RuL (L = bpy, phenanthroline or Ph_3P), giving the corresponding PhCOR and PhCH(OH)R with ketones as the major product [218]. The two-electron reduction of *cis*-$[Ru(bpy)_2(NCS)_2]$ and $[Ru(bpy)_2(pn)]^{2+}$ (pn = 1,2-diaminopropane) and three-electron reduction of $[Ru(bpy)_2(phen)]^{2+}$ and their reversible oxidations were studied in situ by solution UV-visible-near-IR spectroscopies. The localization of the added electron and the novel features of the ligand-to-metal charge-transfer bands of the original species were presented and discussed [219]. The synthesis and chemistry of metal complexes of nuclearity less than or equal to thirteen with Ru^{2+} and/or Os^{2+} as the metal ions, 2,3-dpp (**86**) and/or 2,5-dpp as bridging ligands, and bpy and/or 2,2'-biquinoline (**87**) as the terminal ligands were described (dpp = bis(2-pyridyl)pyrazine) [220]. The dications RuL_2Q^{2+} (L = bpy; Q = (**88**), (**89**)) were prepared and their absorption spectra, luminescence properties under different conditions and electrochemical behaviour were studied [221].



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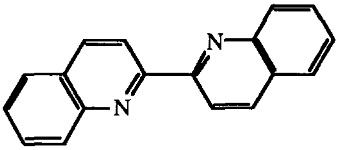

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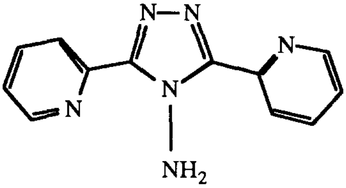

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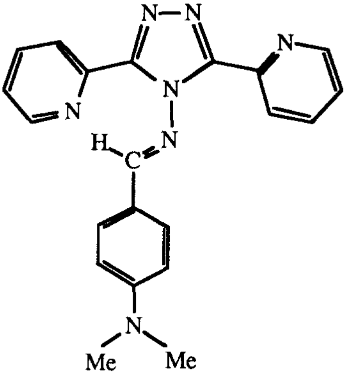

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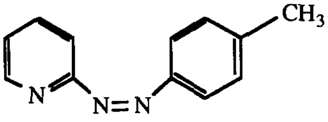
The redox behaviours of $[Ru(bpy)_3]^{2+}$, $[Ru(en)_3]^{3+}$, $[Ru(NH_3)_6]^{2+}$, $[Co(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$ immobilized in a K-carrageenan hydrogel matrix (which acted as a cation-exchange polymeric electrode coating) were described [222]. A novel synthetic approach to $[RuL_3]X_2.nH_2O$ (L = bpy, phen and tap; tap = 2-(m-tolylazo)pyridine (**90**); X = ClO_4, NO_3), $[Ru(bpy)_n(tap)_{3-n}](ClO_4)_2$ (n = 1 or 2) and some rhodium(III) complexes was presented [223]. Circularly polarized luminescence of $[RuL_3]^{2+}$-Ag^+ exciplexes in aqueous solution was studied (L = bpy, phen) [224]. The structures of $[Ru(bpy)_3](PF_6)_2$ and $[Ru(bpm)_3](PF_6)_2$ .CH_3CN were determined by X-ray diffraction (bpm = 2,2'-bipyrimidine (**91**)) [225].

The preparation of a polyimide Langmuir-Blodgett film prepared from (**92**) was described, and the photoelectrochemical characteristics of the film on indium tin oxide electrodes were studied [226]. Luminescent pH sensors based on (**92**) was tested [227]. Spectroscopic, photochemical and electrochemical properties of the series $Ru(dabp)_{3-n}(bpy)_m(BF_4)_2$ (n = 0-3, dabp = (**93**)) were studied and the steric and electronic effects were discussed [228]. High-resolution ^{1}H NMR spectra for seven ligands of the general formula bpy-4-R-4'-R_1 (L) (R, R_1 = C_nH_{2n+1}) and the corresponding ruthenium(II) complexes $[Ru(bpy)_2(L)]X_2$ (X = Cl or ClO_4) were reported. The complexation and solvent effects were discussed [229]. The donor-acceptor molecules $[RuL_2L']^{4+}$ (**94**) were prepared and the rates of photoinduced electron transfer were studied by picosecond flash photolysis/transient absorbance techniques [230].



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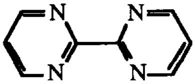

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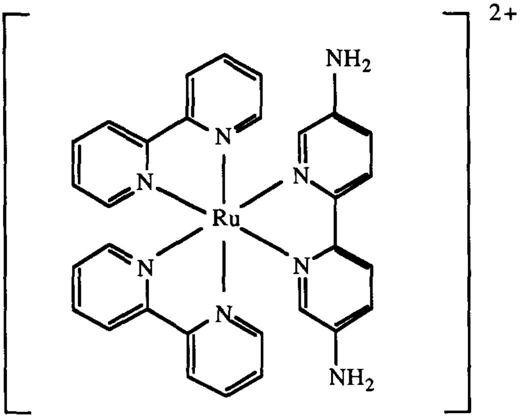

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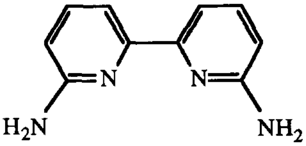

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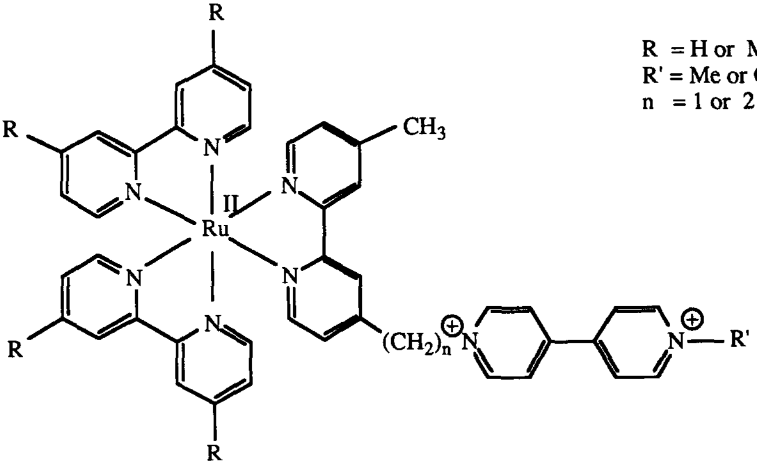
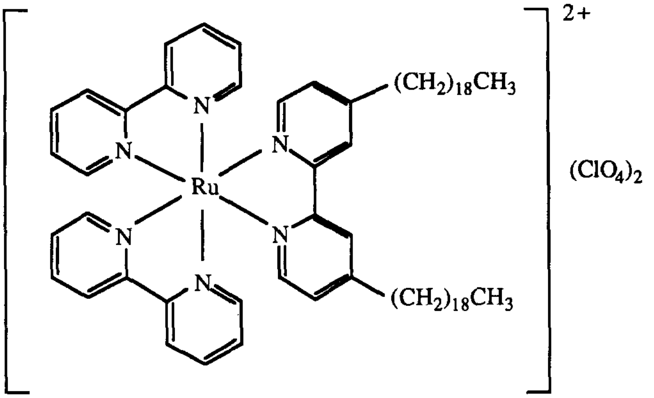


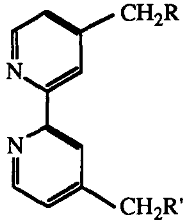
R = H or Me
R' = Me or CH_2CN
n = 1 or 2

(94)

A carbon paste electrode modified by a ruthenium(II) complex (**95**) was equipped in a fibre-optic electrochemiluminescence sensor for the determination of the oxalate ion [231]. New aniline ligands and their corresponding ruthenium and iron complexes, $[Fe(anilbpy)_3][PF_6]_2$, $[Ru(4,4'\text{-}Mebpy)_2(anilbpy)][PF_6]_2$ and $[Ru(4,4'\text{-}Mebpy)_2(bis\text{-}anilbpy)][PF_6]_2$ have been described (anilbpy = (**96**) and bis-anilbpy = (**97**), 4,4'-Mebpy = 4,4'-dimethyl-(2,2'-bipyridine) [232].



(**95**)

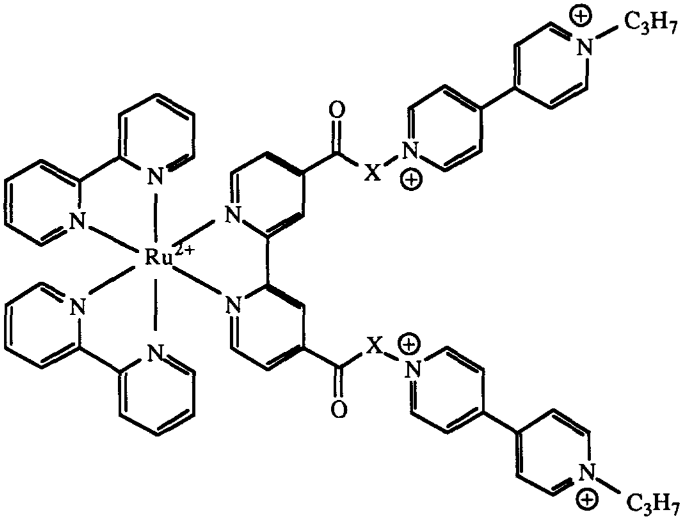


(**96**) R = NHPh, R' = H
(**97**) R = R' = NHPh

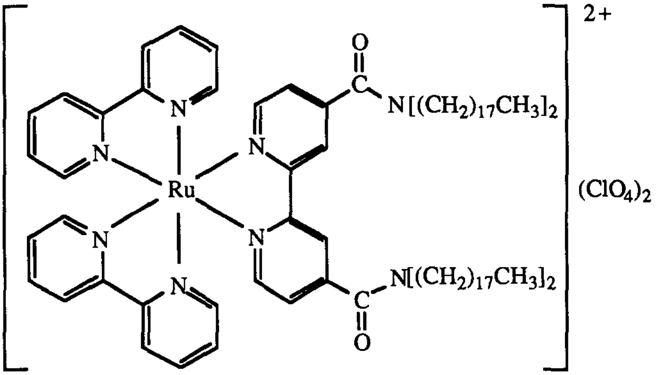
Poly(2,2'-bipyridine-5,5'-diyl), a π-conjugated electrically conducting chelate polymer, forms-electrochemically active complexes with ruthenium and nickel. The ruthenium system was studied electrochemically [233]. Using a series of electron-donating ligands (non-chromophoric or substituted 2,2'-bipyridine/phenanthroline types), the energy of the charge transfer (CT) transition was varied systematically in $[Ru(dcbpy)_2(LL)]$. The Ru→dcbpy CT was always the lowest energy transition (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) [234]. Photoluminescence and quenching of $[Ru(dcbpy)(bpy)_2]^{2+}$ in both aqueous medium and silk fibroin membrane were studied [235]. A series of novel didentate trifluoromethy-2,2'-bipyridine ligands were synthesized, with the photophysical and photochemical properties studied for $[Ru(bpy)_n(BTFMB)_{3-n}]^{2+}$ (n = 0-2; BTFMB = 4,4'- or 5,5'-bis(trifluoromethyl)-2,2'-bipyridine) [236]. A range of novel tris-(4,4'-substituted-2,2'-bipyridine) complexes of the iron triad have been synthesized and characterized electrochemically with respect to their ability to act as electron-transfer mediators for redox enzymes [237].

Complete quenching of MLCT occurred for the product $[(bpy)_2Ru(\mu\text{-}L)M(NO)ClL^*](PF_6)_2$ from the reaction of $[Ru(bpy)_2(HL)]^{2+}$ and $[ML^*(NO)Cl_2]$ (HL=4-(4-hydroxyphenyl)-2,2'-bipyridine; L* = hydrotris(3,5-dimethylpyrazolyl)borate; M = Mo or W) [238]. Two strands of an amphiphilic α-helical 22-peptide were anchored on a Ru(II) complex for the synthesis of hybrid (**98**), which was equipped with anthraquinone and viologen as a photo-induced electron transfer system embedded in bilayer membrane [239]. Electrodeposition of tungsten oxide onto the surface of glassy carbon electrodes produced a coating with significant cation exchange behaviour on which catalysts like CoTPyP or *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$

were bound to serve, respectively, as catalysts for the reduction of O_2 or various oxidation reactions (CoTPyP = cobalt(II)-meso-tetrakis(4-pyridyl)porphyrin) [240]. The trifluoromethanesulfonate salt of the porphyrin was an active catalyst in the hydrogenation of carbonyl compounds and alkenes, with water as the cocatalyst [241].



(98) X = 22-peptide chain.



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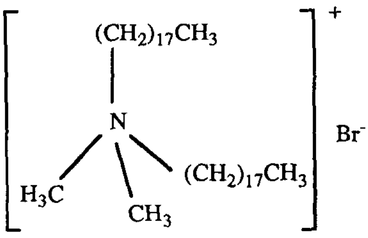
The photochemical modulation of second order nonlinear optical properties of alternate Langmuir-Blodgett films of 1:4 mixture of RuC18B (**99**) and 2C18NB (**100**), and pure 2C18NB [242]. A new type of photostable electron transfer sensitizer of crown ether-linked ruthenium coronate based (**101**) or (**102**) was prepared [243]. The synthesis and photophysical characterization of $[RuL_3]^{4-}$, $[RuL_2L']^{2-}$ (**103**), $[RuLL'_2]$ and $[RuL''_3]^{2+}$ (**104**) were reported. In all cases, the lowest excited state was associated with Ru→L' CT transition [244]. Adsorbed monolayers of (**105**) and (**106**) on both reconstructed and unreconstructed gold(III) surfaces were imaged by scanning tunnelling microscopy in dmf [245].



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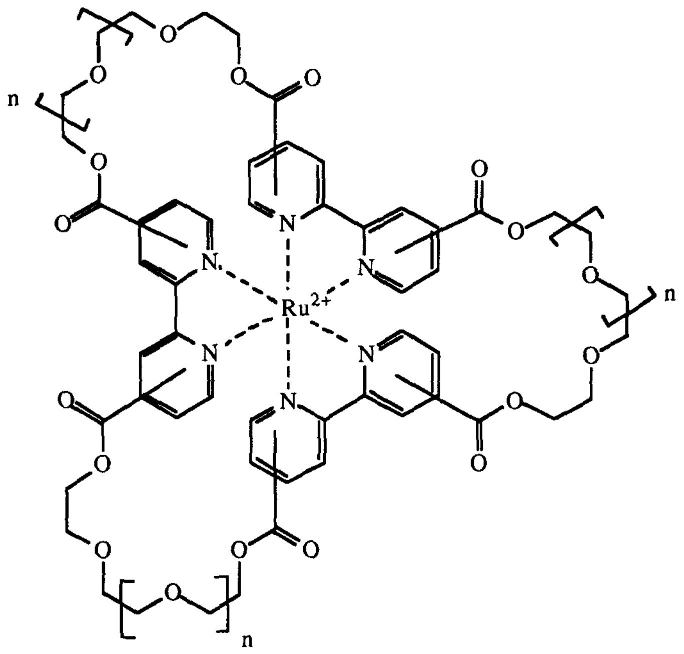
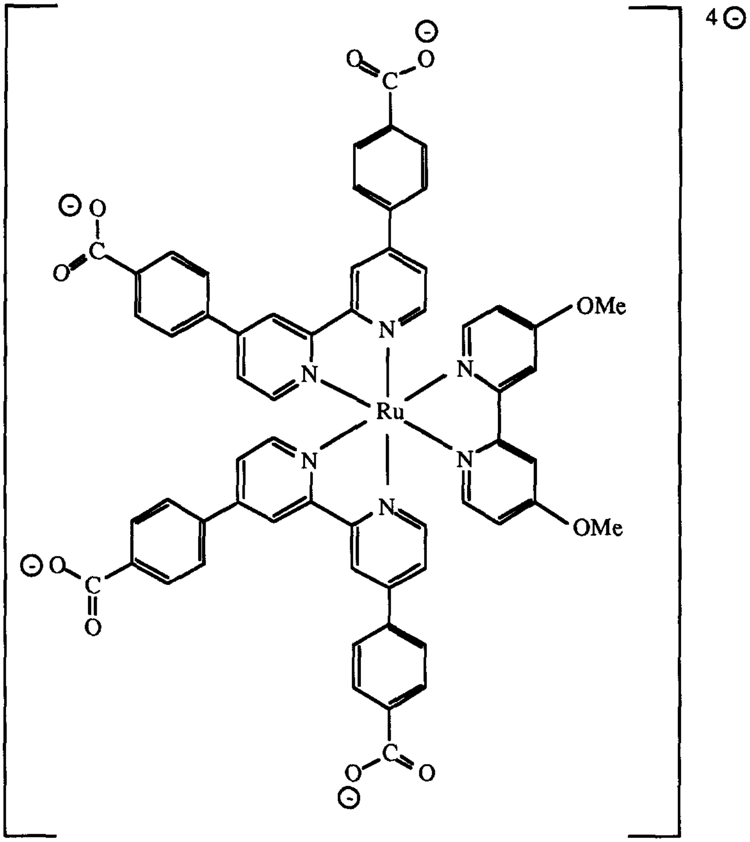


(101) n = 1
(102) n = 2

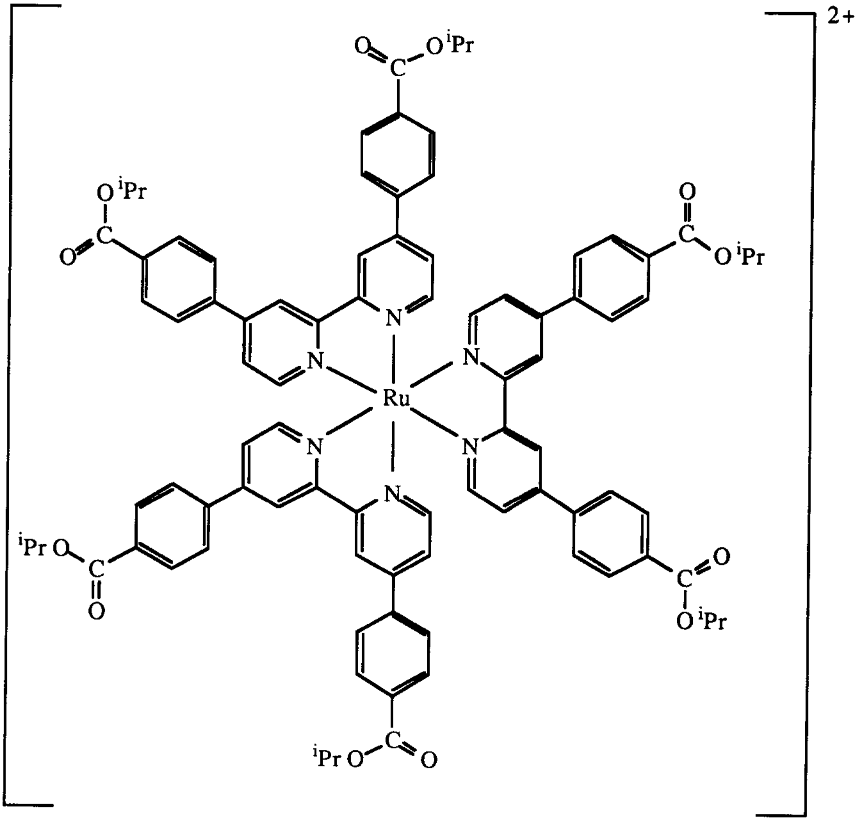
Photo-irradiation of a solution of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy = 3,3'- dimethyl-2,2'-bpy) for 10-20 s produced a long-lived intermediate with a unidentate dmbpy ligand [246]. Monolayer and multilayer Langmuir-Blodgett films of hydrophobic $[Ru(t\text{-}Mebpy)_3][ClO_4]_2$ (t-Mebpy = 4,4',5,5'-tetramethylbipyridine) dissolved in stearic acid have been formed on various substrate materials and have been studied. Comparison with the pure stearic acid films suggested a homogeneous system, and also indicated that the metal complexes were dispersed in the solution [247]. Photochemical reactions in copolymerized films of poly-*cis*-$[Ru(t\text{-}Mebpy)_2(vpy)_2]^{2+}$-$[Os(vbpy)_3]^{2+}$ (vpy = 4-vinylpyridine; vbpy = 4-methyl-4'-vinylbipyridine) on platinum electrodes result in the loss of $[Ru(t\text{-}Mebpy)_2]^{2+}$ and the creation of molecular voids [248].



(103)

The absorption and emission spectra, the emission quantum yields and the lifetimes of the MLCT excited states of $[Ru(bpy)_2(6\text{-}Mebpy)]^{2+}$, $[Ru(bpy)_2(bpy\text{-}cyclamH_2)]^{4+}$ and $[Ru(bpy)_2(bpy\text{-}cyclamNi)]^{4+}$ (**107**) were reported (6-Mebpy = 6-methylbipyridine) [249]. A similar bpy-cyclamH_2 ligand L (**108**), with the cyclam group connected directly to the 5-position of the bpy ligand, was designed for controlled and systematic polynuclear metal complex formation. The fluorescence quenching of $[Ru(bpy)_2L]^{2+}$ with a Ni^{II} or Cu^{II} ion coordinated within the cyclam cavity was reported [250].

The synthesis of a family of mono-, bis- or tris(2,2'-substituted bipyridine) complexes of a metal selected from the iron or vanadium triads has been reported [251]. Time-resolved absorption studies were performed on a series of covalently linked $Ru(bpy)_3$-donor-acceptor complexes to elucidate some intramolecular electron-transfer rates [252]. The cation $[Ru(bpy)_3L]^{2+}$ (L = (**109**), (**110**) or (**111**)) and the methylation products $[Ru(bpy)_3Q]^{n+}$ (Q = (**112**), (**113**)) were prepared and studied for electrochemical redox reactions [253]. The redox behaviour of the polypyrrole films of $[Ru(trpy)(bpy)(OH_2)]^{2+}$ complex (**114**) was exploited for preparative electrocatalytic oxidation of alcohols [254].



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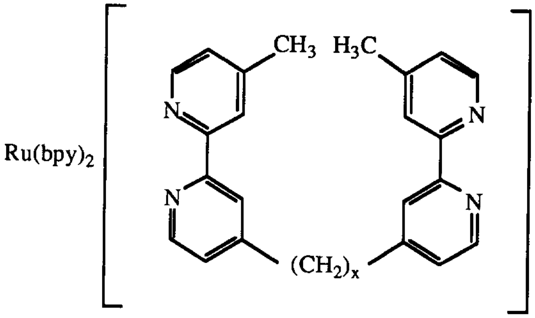
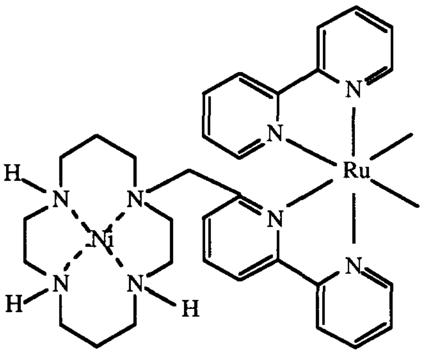


(105) x = 4; (106) x = 5



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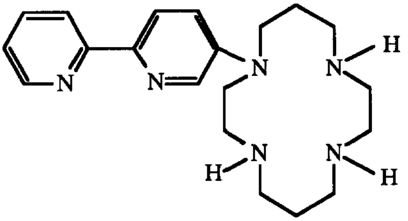

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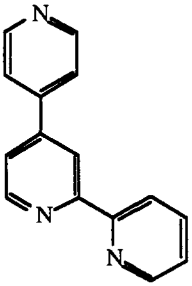

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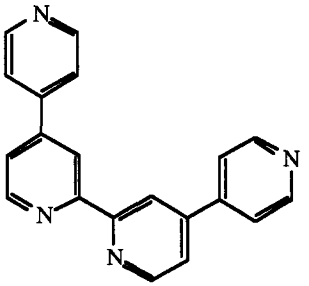

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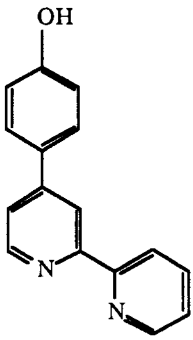
The Λ-isomer of $[Ru(bpy)_2ppz]^{2+}$ (ppz = (**115**)) promoted cleavage of plasmid DNA in the presence of copper(II), 3-mercaptopropionic acid and H_2O_2 [255]. The preparation and photophysical and photochemical properties of $[Ru(bpy)_2(py)_2](CF_3SO_3)_2$, $[Ru(bpy)_nQ_{3-n}](PF_6)_2$ (n = 0,1) and $[Ru(bpy)_2Q]$-$(CF_3SO_3)_2$ were reported (Q = 2-(2'-pyridyl)pyrimidine). This led to the design of a photostable core $[Ru(bpy)(bpz)]^{2+}$ (bpz = 2,2'-pyrazine) [256]. The photophysical and photochemical properties of $[(bpy)_2Ru(HPTN)]^{+}$ were examined in solutions of varying acidity (HPTN = 3-(pyridin-2-yl)-1,2,4-triazole) [257].

Members of a series of $Ru^{II}(bpy)_2(L)$-type complexes (where L = a monodentate coordinated pyridyltriazole) were prepared and characterized. Their coordination modes were also studied. The crystal structure of $[Ru(bpy)_2ClL']PF_6$ and the conversion of $[Ru(bpy)_2L''(MeCN)]^{2+}$ to $[Ru(bpy)_2L'']$ (L' (**116**); L'' (**117**)) were also reported [258].

The salts $[Ru^{II}(bpy)_2L^1][PF_6]$ and $[Ru^{III}L^2_2][PF_6]$ were prepared in order to study the electrochemical and spectroscopic consequences for the ruthenium centre upon stepwise replacement of pyridyl ligands by phenolates (HL^1 = 2-(2-hydroxyphenyl) pyridine, HL^2 = 6-(2-hydroxyphenyl)-2,2'-bpy) [259]. The metal-ion dependent reactivity of 2-(2-thienyl)pyridine (Hthpy) was studied for palladium, gold and ruthenium. Products such as $[(thpy)Pd(\mu OAc)Pd(thpy)]$, $[Ru(bpy)_2(Hthpy)]^{2+}$ and other gold complexes were obtained. Of note, the Hthpy ligand in the ruthenium complex was shown to be didentate, being N,S-bonded to the metal centre[260]. The electrochemistry of $[(Ru(bpy)_2)_2bpm]^{4+}$ (bpm = μ-2,2'-bipyrimidine) was investigated with complete assignments made of individual reduction steps [261]. The use of a carbon paste electrode modified with $[Ru(bpy)_2(PVP)_{10}Cl]Cl$ for the mediated detection of nitrite was described [262].



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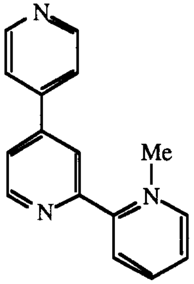

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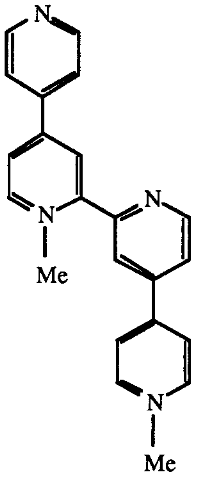

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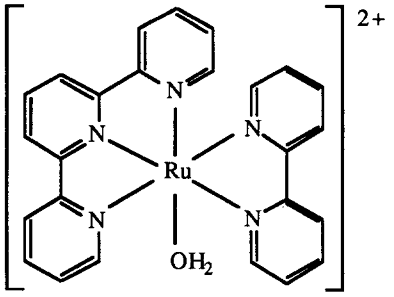

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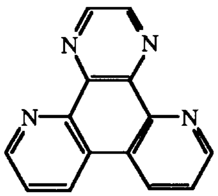

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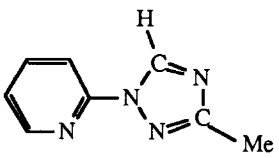

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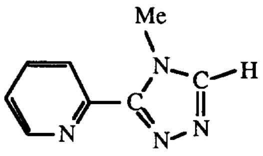

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The existence of two independent chromophores in $[Ru(bpy)_2(H_2V)]^+$ was demonstrated by comparing its resonance Raman spectra with those displayed by the $[Ru(H_2V)_3]^-$ analogue (H_2V^- = violurate anion) [263]. Synthesis and characterization of $[Ru(bpy)_2(CO)(NO_2)](PF_6)$ was reported and its reversible conversion to $[Ru(bpy)_2\text{-}(C(O)OH)(NO_2)]$ was described [264]. The kinetics of the electroanalytic reduction of CO_2 by cis–$[Os(bpy)_2(CO)H]^+$ and *cis*-$[M(bpy)_2(CO)R]^-$ (M =

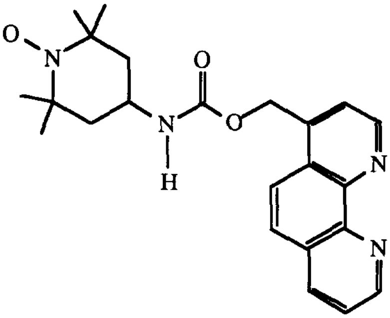
Os; R = H, Me, Ph; M = Ru, R = CHPh) were studied [265]. The molecular structure of cis-$[Ru(bpy)_2(CO)(C(O)OCH_3)](BPh_4)\cdot CH_3CN$ was determined in order to elucidate the structural difference between $[Ru(bpy)_2(CO)C(O)OH]^+$ and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ [266]. The reductive quenching of $*RuL_3{}^{2+}$ complexes (L = 4,4'-dialkylbpy) by several substituted phenolate ions was studied by the luminescence quenching technique [267]. The photochemistry of $[Ru(bpy)_3L]^{2+}$ (L = $H_2N\text{-}(CH_2)_n\text{-}NH_2$; n = 2,3) was studied for the effect of the chain length of the diamine ligands on photosubstitution reactions. A lower quantum yield for n = 2 suggested a less efficient ring reclosure process for the larger chelate ring complex [268]. A reversible three-proton three-electron couple was observed for the electrochemical oxidation of *cis*-$[Ru(bpy)_2L]^{2+}$ (L = 2,3-dimethyl-2,3-diaminobutane). The formation of *cis*-$[Ru(bpy)_2(NH{=}CMe_2)_2]^{2+}$ from the above compound and its X-ray structure were also reported [269].

A general synthetic method was developed for the preparation of tris-heteroleptic complexes of Ru (II) containing didentate polypyridyl ligands. Their photophysical and electrochemical properties were also studied [270]. Transition metal-substituted-bipyridyl complexes were applied to chemical sensor technology [271]. $Ru(bpy)_3{}^{2+}$ was used to sensitize the *trans*-membrane redox mediator for electron transfer [272].

10.5.2 Complexes with phenanthroline ligands

A study was made on the sorption of ruthenium (IV) and osmium (VIII) by silica sorbents. This study showed that bis- or tris-phen-metal (II,III) complexes were formed. A new method for the determination of the corresponding metals was proposed [273]. Scanning tunnelling microscopic studies were carried out for $[Ru(phen)_3]Cl_2$ on highly ordered pyrolytic graphite, Cu and n-doped GaAs [274]. EPR probes that structurally resemble $[Ru(phen)_3]^{2+}$ were used to monitor the binding and dynamics of these complexes with different anionic detergents in aqueous solutions [275]. Minor groove binding of $[Ru(phen)_3]^{2+}$ to the self-complementary decanucleotide duplex $[d(CGCGATCGCG)]_2$ was observed by 2-D NMR spectroscopy [276]. Equilibrium binding studies and viscosity experiments were done on the same complex with calf thymus DNA, in which classical intercalation was not observed [277].

The isomers of $[Co(acac)_2(aa)]$ (aa = amino acid) were separated by liquid chromatography on a clay column modified with optically active $[Ru(phen)_3]^{2+}$ [278]. Circularly polarized luminescence observed from racemic solutions of $[Tb(2,6\text{-}(CO_2)_2py)_3]^{3-}$ on addition of traces of resolved $[Ru(phen)_3]^{2+}$ was attributed to enantioselective quenching of the former by the latter (2,6-$(CO_2H)_2py$ = 2,6-pyridine dicarboxylic acid) [279]. A method for incorporating a diverse variety of intercalants, like ruthenium(II) phenanthroline, directly during hydrothermal synthesis of hectorite, layer-silicate clays was developed [280]. $Ru(phen)_2(phen\text{-}T)Cl_2$ and $Ru(bpy)_2(phen\text{-}T)Cl_2$ (phen-T = (**118**)) were used as EPR probes for studying interactions of the family of polypyridyl metal complexes with B-DNA [281]. The difunctional supramolecular complex. $[Ru(phen)_2(phencyclamNi)](ClO_4)_4$ (**119**) was synthesized with its spectroscopic, redox properties and catalytic behaviour in the photoreduction of CO_2 examined [282].



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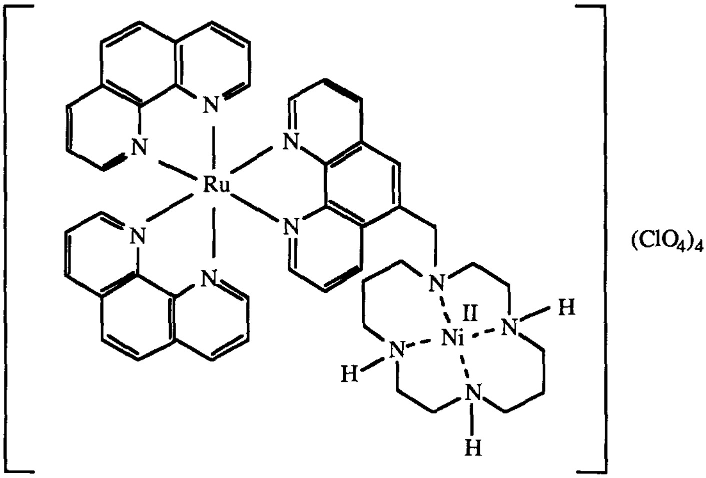
The complex dication $[Ru(phen)_2dppz]^{2+}$ and its dppz-derivative series served as molecular light switches for DNA and showed no luminescence in aqueous solution, but luminesced intensely on intercalation into DNA (dppz = (**120**)) [283-285]. The photo-induced electron transfer from nucleotides to $[Ru(tap)_3]^{2+}$ and the luminescence quenching of the latter were studied and correlated to the photosensitized cleavage of DNA by the same complex (tap = (**121**)) [286]. FAB mass spectrometry was used to characterize newly synthesized polymetallic homo- and heteronuclear complexes of Ru(II) and Rh(III) with hat (hat = (**122**)) [287]. Laser methods on the nanosecond timescale were used to investigate the decay processes following MLCT of heteroleptic complexes of Ru(II) with hat, and either bpy, tap or phen [288]. The spectroelectrochemical characteristics and the photophysical mechanisms controlling the luminescence lifetimes of a series of Ru(II)-hat complexes were presented [289].



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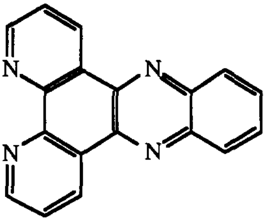

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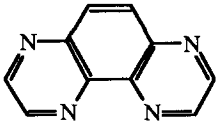

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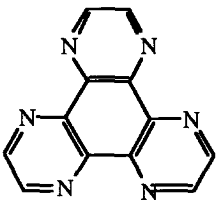
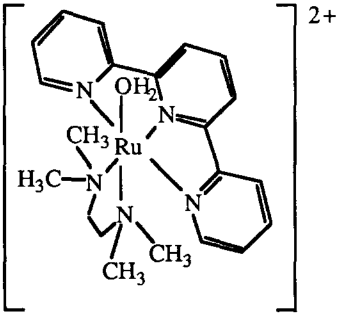


(122)

10.5.3 Complexes with other N-heterocyclic ligands

In situ spectro-cyclic voltammetry (SCV) of $[Ru(terpy)]^{2+}$ incorporated into coated Nafion membrane showed that the oxidized state and reduced state could function as water oxidation and proton reduction catalysts respectively [290]. The synthesis, spectral characterization and structure of $[RuH\text{-}(terpy)(PPh_3)_2]X$ was reported (HX = salicylic acid). [291]. The interactions of $[Ru^{II}(terpy)(bpy)(OH_2)]^{2+}$, $[Ru^{II}(terpy)(phen)(OH_2)]^{2+}$ and $[Ru^{II}(terpy)(tmen)(OH_2)]^{2+}$ (**123**) with DNA were investigated by cyclic voltammetry. The structure of the perchlorate salt of (**123**) was also reported [292]. The ligand ttpy and the complex $[\{(terpy)Ru\}_3(ttpy)](PF_6)_6$ (**124**) were prepared [293]. $[Ru(Xterpy)_2](PF_6)_2$ (**125**) was prepared together with other 4'-substituted terpyridine complexes (**126-128**); the oxidation potential and room-temperature luminescence properties of these species were studied [294].



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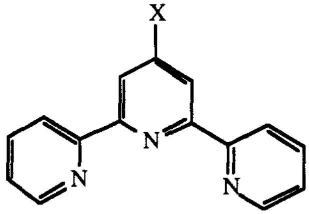
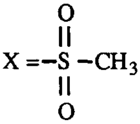
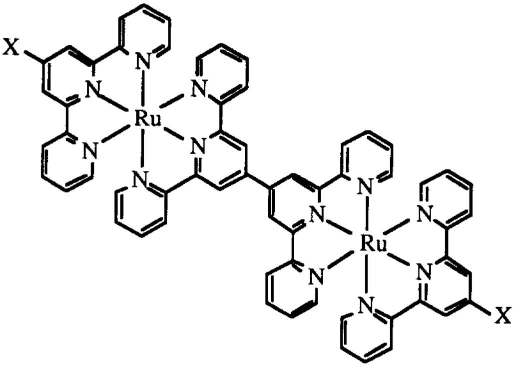




$$X = -\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-CH_3\ (\mathbf{125}),\ -Cl\ (\mathbf{126}),\ -OH\ (\mathbf{127}),$$

$-NMe_2$ (**128**)

The coordination oligomers $[(Xterpy)RuLRu(Xterpy)]^{4+}$ (**129**) and (**130**) and $[\{(Xterpy)Ru\}_3(ttpy)]^{6+}$ (**131**) were prepared and characterized for a variety of electron--donating and -withdrawing substituent groups X [295].



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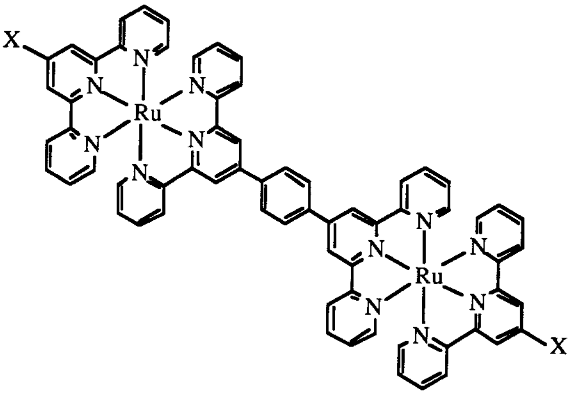

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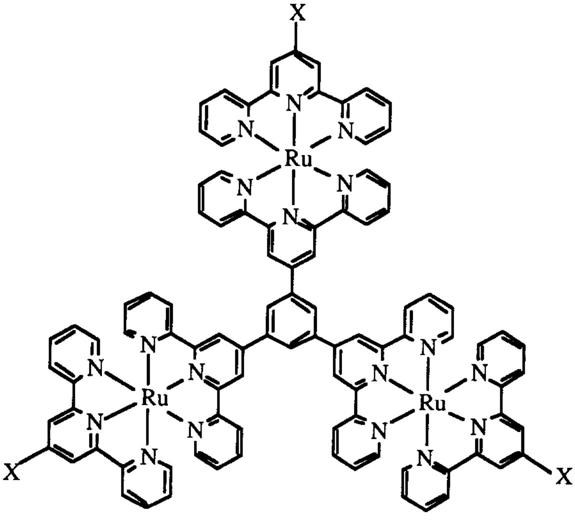

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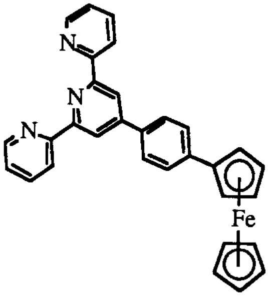
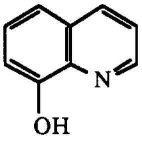


(132)

The new terpyridine ligand (**132**) was prepared by using a palladium-catalysed aromatic cross-coupling reaction. The corresponding homo- and heteroleptic complexes for the iron triad were also prepared and studied [296]. A dinuclear double stranded helical complex containing two Ru(II)-$(terpy)_2$ units $[Ru_2L_2](PF_6)_4$ (L = (6"-(p-C_6H_4OMe)-5-CH_2-2,2':6',2"-terpy)$_2$) was synthesized [297]. Complexes like $[Ru(Z)_2](PF_6)_2.H_2O$ (Z = terpyridine residue) were used in cation-exchange membranes incorporated in electrodes for determination of CO_2 concentration [298].

A one-pot, selective synthetic method for synthesizing the ruthenium-polypyridyl complexes $[RuL_3]^{2+}$, *cis*-$[RuCl_2L_2]^+$, $[RuCl_4L]^-$, (L = bpy, phen or (2-pyridine)$_2$NH), and $[RuCl_6]^{3-}$ was reported. This synthetic method was also useful for synthesizing complex pairs such as $[Ru^{III}Cl_3(terpy)]\cdot[Ru^{II}(terpy)_2]^{2+}$ and $[Ru^{III}Cl_4py_2]\cdot[Ru^{II}Cl_2py_4]$ [299]. A near quantitative yield of $[Ru_2(\mu\text{-}OAc)(\mu\text{-}R)_3Cl]$ was obtained from the reaction of $[Ru_2(OAc)_4Cl]_n$ with 6-amino-2-picoline (HR). $[Ru_2(\mu\text{-}OAc)(\mu\text{-}R)_3Cl]$ was characterized by X-ray crystallography and electrochemical methods [300]. The kinetics and mechanisms of aqua-substitution of *cis*-$[Ru(tap)_2(H_2O)_2]^{2+}$ by oxine (**133**) in EtOH/H_2O and phen in aqueous medium were studied (tap = (**90**)) [301, 302]. The emission spectrum of $[Ru(i\text{-}biq)_2](PF_6)_2$ (i-biq = (**134**)) crystal was examined and compared with that of a dilute glassy solution [303].



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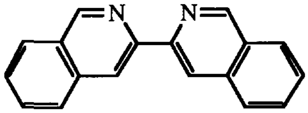
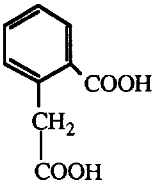


(134)

Several complexes of the formula $K[M(hp)_2L_2]$ were prepared and characterized by elemental analysis, conductometric, magnetic, IR and electronic spectral studies (M = Cr(III), Fe(III), Ru(III); hpH_2 = (**135**), L = pyridine, quinoline, isoquinoline, 2-picoline, or 4-picoline) [304].



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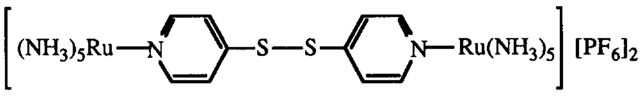
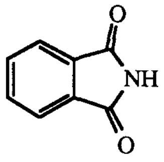


(136)

The dinuclear ruthenium complex (**136**) provided the first example of the great efficiency of the S-S bridge in conducting electrons [305]. Complexes of type $[M(IM)_3L]$ were prepared and characterized by various methods (M = Cr, Ru; HIM = (**137**), (**138**) ; L = $H_2NCH_2CH_2NHCH_2CH_2NH_2$, terpyridine); an octahedral coordination geometry was proposed [306]. Optical rotation and CD spectra along with other methods were used to characterize newly synthesized complexes $[RuLCl_2(H_2O)]$ and $K[RuL'Cl_2(H_2O)]$ (HL = 2-pyridyl-methylene-L-histidine, H_2L' = 5-methoxy- and 5-chlorosalicylidene-L-histidine) [307].



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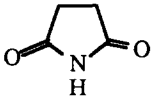

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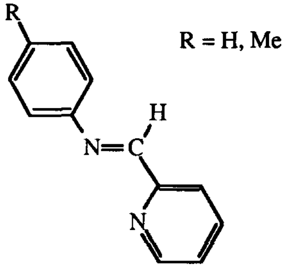
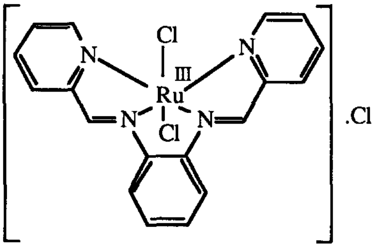


(139)

The halides $RuX_3{\cdot}nH_2O$ (X = Cl, Br) reacted to give isomeric RuX_2L_2 (L = **(139)**). The high-resolution ^1H NMR spectra of both *cis-* and *trans-*isomer were reported and completely assigned [308]. The ruthenium complexes **(140)**, **(141)** and **(142)** were synthesized from the corresponding aldehyde and amine, and were characterized by various methods. Their function as catalysts in the epoxidation of alkenes was studied using iodosylbenzene as an oxidant [309].



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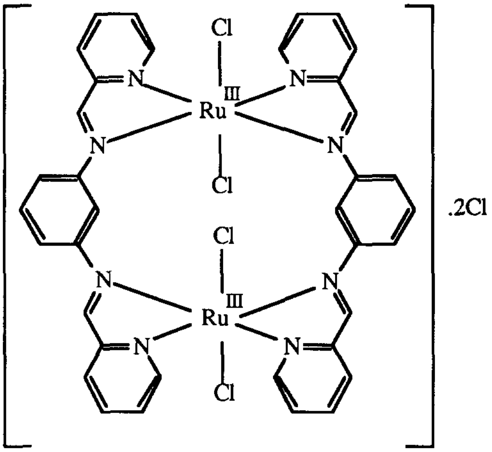
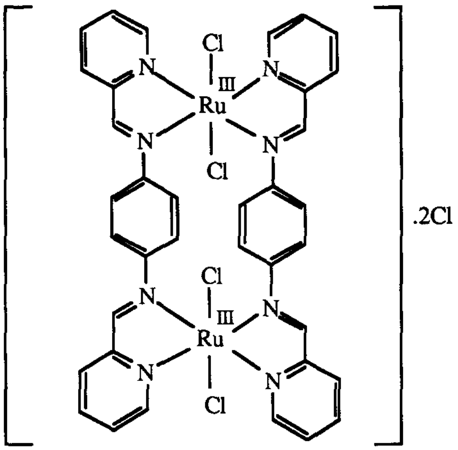


(141)

The complexes $[RuCl_2(L)(dmso)_3]$ and $[RuCl_2L_2(dmso)_2]$ were synthesized and characterized by X-ray crystallography, spectral and electrochemical methods. These complexes were found to have a distorted octahedral geometry with monodentate pyrazole (L) ligands [310]. Ligands **(143)** and **(144)** were transformed to seven other ligands including **(145)** by N-alkylations. Ruthenium(II) readily coordinated with **(143)**; some iron(III) complexes were also formed [311]. The preparation, and spectroscopic and electrochemical properties of ruthenium(II) complexes containing various combinations of **(143)** and its di- and tetra-methyl-substituted derivatives were described [312]. The ruthenium(II) pyrazolylamidine complexes, e.g. **(146)** were synthesized. The stereochemistry of the resulting complexes has been determined by NOEDIFF experiments and the X-ray structure of **(146)** was determined [313]. The reaction of $Tl(BRpz_3)$ (pz = 1-pyrazolyl; R = pz, H) and *cis*-$[RuCl_2(dmso)_4]$ gave the boron-free $[RuCl_2(pzH)(dmso)_3]$ as product, which was characterized by ^1H NMR and IR spectroscopies. $[RuCl_2(pzH)_2(dmso)_2]$ was also obtained as a minor product if excess pzH was used instead [314]. On the other hand, $Na(BHpz_3)$ reacted with $RuH(Cl)(CO)(PPh_3)_3$ to give $[Ru(\eta^3\text{-}BHpz_3)(PPh_3)(CO)H]$, which further reacted to give $[Ru(\eta^3\text{-}BHpz_3)(PPh_3)(CO)Cl]$ and $[Ru(\eta^3\text{-}BHpz)(PPh_3)(CO)(L')]PF_6$ (L' = CO, $CNCMe_3$, $P(OMe)_3$ or PMe_3). The X-ray crystal structure of $[Ru(\eta^3\text{-}BHpz)(PPh_3)(CO)(L')]PF_6$ with L' = PMe_3 was determined [315].



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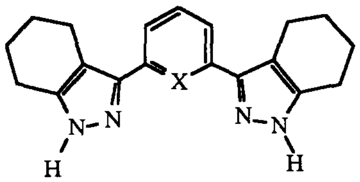
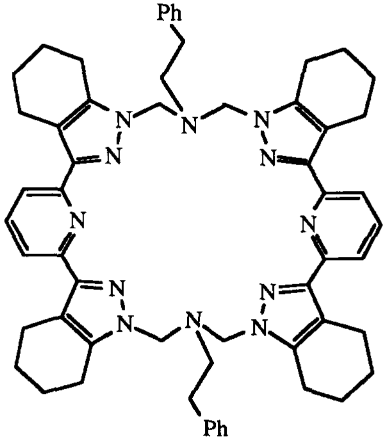


(143) X = N; **(144)** X = CH



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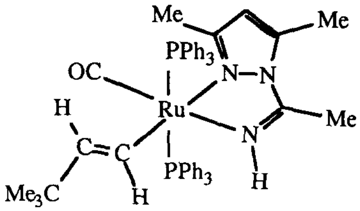
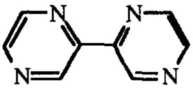


(146)

The compounds $[(Ru_2(chp)_4)_2(pyz)](BF_4)_2$ and $[Ru_2(chp)_4(py)](BF_4)$ were prepared and characterized by X-ray crystallography and by magnetic susceptibility measurements at 5 – ≈300K (pyz = pyrazine; chpH = 6-chloro-2-hydroxypyridine) [316]. The resonance Raman spectra of $Ru(bpz)_3^{2+}$ were obtained in solutions of deuterated and non-deuterated H_2SO_4-H_2O at various concentrations (bpz = (**147**)) [317]. The reductive quenching of the same complex by ferrocene and N,N'-diphenyl-1,4-phenylenediamine due to interfacial electron transfer was also reported [318]. The resonance Raman spectra of the ^{3}MLCT excited states of Ru(II) asymmetric pyridine and pyrazine ligands were studied [319].



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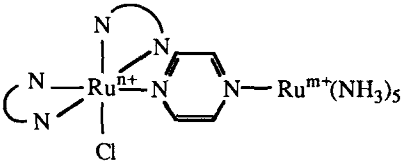
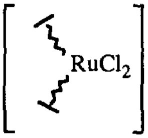
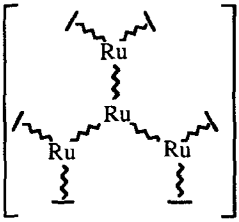


(148) m = 3, n = 2;
(149) m = 2, n = 3

= bpy



(150)



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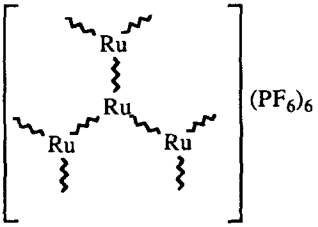
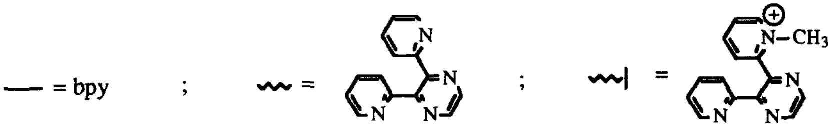
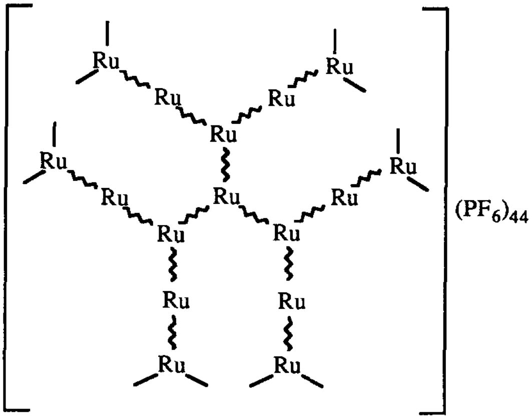


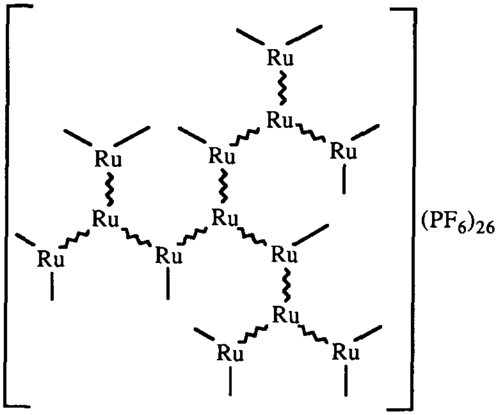
(152)



Ab initio and semi-empirical studies of electron transfer and spectra of $(NH_3)_5Ru$-pyz-$[Ru(NH_3)_5]^{4+/5+/6+}$ and $[L_5Ru^{II}$-B-$Ru^{III}L_5]$ (B = bipyridine, dipyridinemethane or dimethyldipyridine) were done [320]. The temperature dependence of the optical absorption band corresponding to the electron transfer process $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ **(148)** → $[(bpy)_2ClRu^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ **(149)** was studied and the relationships between optical and thermal electron transfer were discussed [321]. A series of ruthenium complexes **(150-153)** were prepared and their photo- and electrochemical properties were explored [322].



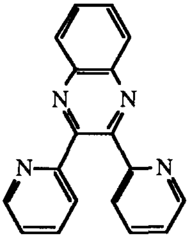
(153)



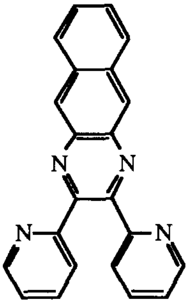
(154)

The multiruthenium complex **(154)** was synthesized and the absorption and luminescence properties and electrochemical oxidation of the compound were studied [323]. Similarly macromolecules of the form $Mc[(BL)Mi\{(BL)MpL\}_2]_3(PF_6)_{20}$ (Mc, Mi, Mp = Os or Ru; BL = μ-2,3-dpp; L = bpy or biq) and $[(L)_2M(\mu\text{-}BL)]_2M(\mu\text{-}BL)\text{-}M[(\mu\text{-}BL)M(L)_2]_2^{12+}$ (M = Os^{2+} or Ru^{2+}; BL = 2,3-dpp or 2,5-dpp; L = bpy or biq) and other Os-Ru macromolecules were synthesized and studied. In addition, the intercomponent energy transfer was investigated [324-327]. The synthesis, electrochemistry, spectroscopic and spectroelectrochemical properties of

$[(bpy)_2Os(BL)Ru(bpy)_2](PF_6)_4$ (BL = 2,3-dpp, dpq **(155)**, dpb **(156)**) were reported [328]. Photophysical studies on the mononuclear Rh(III)-polypyridyl complexes and examination of the intramolecular excited-state interactions in $[(bpy)_2Ru^{II}\text{-}(2,3\text{-}dpp)\text{-}Rh^{III}(bpy)_2]^{5+}$ using luminescence and transient absorption spectral studies were conducted [329].

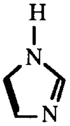


(155)



(156)

The synthesis, X-ray structure and electronic spectra of *trans*-$[(NH_3)_4Ru(im)(isn)](CF_3CO_2)_3$.MeCHOH were presented. Analogous complexes in which the imidazole ligand was derived from a peptide histidine residue that served as a non-labile surface probe in studies of electron-transfer pathways in metalloproteins (im = **(157)**; isn = **(158)**) [330]. The effects of two new ruthenium(III) complexes, *mer*-$[RuCl_3(dmso)_2Im]$ and Na[*trans*-$[RuCl_4(dmso)Im]$ were investigated on primary tumor growth and on the survival time of the mouse [331]. Specifically, the latter was further investigated for its antitumor and antimetastatic effects in mice bearing MCa mammary carcinoma [332]. Distant Fe^{2+}-Ru^{3+} electronic couplings have been determined from intramolecular electron-transfer rates in $[Ru(bpy)_2(Im)(His\text{-}X)]^{2+}$, where X = a total of 5 positions of the histidine residue in the protein [333].



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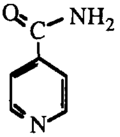
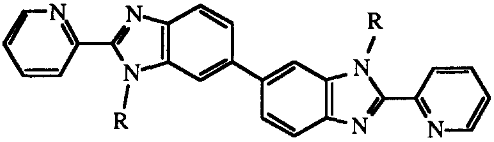
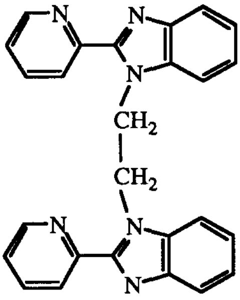


(158)

Charge transfer excited states of $[RuL_2(L'\text{-}L')]^{2+/4+}$ and $[Ru(dpimbH_2)\text{-}(bpy)_2]^{2+}$ were studied by means of emission and transient absorption spectroscopy at 77-300 K (L = bpy, 4,4'-Me_2bpy, phen; L'-L' = bpbimH_2 **(159)**, dpbime **(160)**; dpimbH_2 **(161)**) [334,335]. Intramolecular electron transfer in photoexcited $[Ru(bpy)_2(L\text{-}L)Rh(bpy)_2]^{5+}$ was investigated in the fluid solvent of a mixture of propionitrile and butyronitrile at 170-300K (L-L = dpimbH_2, bphimH_2, dmbpbim **(162)** and dpbime) [336]. The dinuclear compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-}bim)M(cod)]$ were more active catalysts for the reduction of styrene and some ketones by hydrogen-transfer reactions than the mononuclear parent [M(Hbim)(cod)] and $[RuH\text{-}(Hbim)(CO)(PPh_3)_2]$ (M = Rh, Ir; bim = 2,2'-biimidazolate) [337].



(159) R = H; **(162)** R = CH_3



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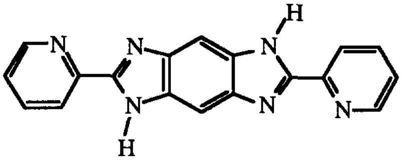
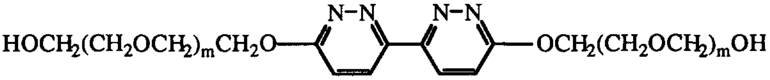
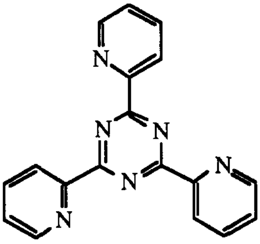


(161)

The synthesis of supramolecular complexes from $[RuL_3]Cl_2$ (L = **(163)**) and alkali and alkali earth metal ions as well as the photochemistry of the product were presented [338]. The transduction chemistry based on luminescence quenching by proton transfer to the excited tris[2-(2-pyrazinyl)thiazole]Ru(II) cation had been applied to the construction of a fibre-optic sensors for CO_2 [339].



(163) m = 2, 3



(164)

The synthesis, structural characterization, electrochemical and photophysical properties of $[(bpy)_2Ru^{II}(bpt)Rh^{III}(ppy)_2]^{2+}$ $[(bpy)_2Ru^{II}(bpt)Ir^{III}(ppy)_2]^{2+}$, $[\{Rh^{III}(ppy)_2\}_2(bpt)]^+$ and $[\{Ir^{III}(ppy)_2\}_2(bpt)]^+$ were reported (Hppy = 2-phenylpyridine; Hbpt = 3,5-bis(pyrin-2-yl)-1,2,4-triazole) [340]. The chelate complexes $[RuR(CO)(PPh_3)_2\{\eta^2\text{-}H_2B(bta)_2\}]$ and $[RuCl(CO)(PPh_3)_2\{\eta^2\text{-}H_2B(bta)_2\}]$ (R = H, 4-MeC_6H_4, 4-$MeC_6H_4CH{=}CH$, $CH{=}CHC_4H_9$, $C(C{\equiv}CPh){=}CHPh$ were synthesized [341]. A solvent extraction–spectrophotometric determination of trace amounts of Ru had been developed based on the formation of an ion association complex of Ru(III) with (**164**) and picrate [342]. The synthesis and characterization of optically active complexes $[RuCl_2(cod)L]$, $[RuCl_2(PPh_3)_2L]$ and other Co(II), Ni(II) and Rh(I) complexes were reported. These complexes showed high activity for alkene hydrogenation when anchored to a zeolite (L = (S)-2-^{t}butyl-aminocarbonyl pyrrolidine, (S)-2-(3-triethoxysilyl) propylaminocarbonylpyrrolidine) [343]. A series of ruthenium polypyridyl complexes had been covalently bound to poly(L-lysine), albumins, and immunoglobulin G using different binding modes. Their conjugation ratios and the luminescence properties were reported [344].

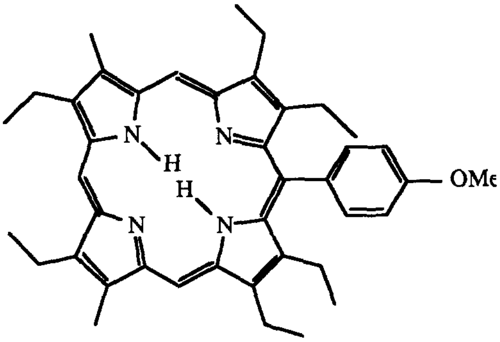
Distant heme-Ru electronic couplings had been extracted from intramolecular electron-transfer rates in Ru(his-X) (X = 33, 39, 62) derivatives of cytochrome c [345]. The complexes [RuCl(L-his)(diene)] (diene = norbornadiene, cyclooctadiene), $[RuCl(D,L\text{-}his)(PPh_3)_2]$, $[RuCl_2(L\text{-}hisme)(PPh_3)_2]$, $[RuCl(D,L\text{-}5Omet)(PPh_3)_2].CH_3OH$, $[RuCl(L\text{-}metme)_2(PPh_3)]Cl.PPh_3$ and $[RuCl_3(L\text{-}metet)(PPh_3)]$ were synthesized (L-hisme = Me L-histidinate; D,L-metH = D,L-methionine; metme = Me L-methionate; L-metet = L-methionine Et ester). X-ray analyses were carried out for four of the complexes [346]. The volumes of activation for intramolecular electron transfer in $[(NH_3)_5Ru^{II}\text{-}His33]$, horse heart ferricytochrome C (FC c), and $[(NH_3)_5Ru^{II}\text{-}His39]$, Candida krusei FC c, and that of the intermolecular reaction between $[Ru(NH_3)_6]^{2+}$ and horse heart FC c were determined by pulse radiolysis [347]. A novel metal ion-assisted self-organizing molecular process was described for the construction of a 60-residue parallel four-helix bundle metalloprotein from a 15-residue amphiphilic polypeptide upon ruthenium complexation [348]. The antiproliferative properties of six newly synthesized heterocyclic ruthenium complexes alone and in combination with cytokines against various human colon carcinoma cell lines were investigated. The most effective compounds were found to be *trans*-indazolium [tetrachloro(2H-indazole)ruthenate(III,N ^{1})] and *trans*-indazolium [tetrachlorobis(1H-indazole) ruthenate(III,N ^{2})] [349].

10.5.4 Complexes with macrocyclic ligands

The complex cations *trans*-$[Ru^{II}Cl(cyclam)L]^+$ were synthesized and their properties were investigated (L = 4-picoline, py, isn, 4-acetylpyridine; cyclam = (**165**)) [350]. The porphyrins H_2L and H_2Q and the complexes $[RuQ]_2$, $RuL(py)_2$, RuL(CO)(MeOH) along with other Re, Mo and W complexes were synthesized and studied (H_2Q = (**166**), H_2L = (**167**)) [351]. The derivatives $[RuL(O)_2]$ and $[RuL(NPh_2)_2]$ were prepared from [RuL(CO)] and were spectroscopically characterized (H_2L = meso-tetrakis(3,4,5-trimethoxyphenyl)porphyrin) [352].

The ruthenium(II) complex [RuL(CO)(EtOH)] was prepared and photochemically decarbonylated in the presence of bridging ligands such as 4,4'-azopyridine or pyrazine to produce polymers (H_2L = tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin) [353]. It was shown that $[Ru(OEP)Me_2]$ underwent irreversible oxidation and reduction to give (**168**) and $[Ru(OEP)(CH_3)(thf)]^-$, respectively (H_2OEP = (**169**)) [354]. The conversion product Ru(OEP)(CO) from Ru(OEP)Me was trapped by tempo (tempo = 2,2,6,6-tetramethyl-piperidine-1-oxyl) and analysed. The X-ray structure was determined for the trapped complex

[Ru(OEP)(CO)(tempo)] [355]. Cyclic voltammetry had been employed to study the reactivity of Ru(OEP)(p-XC_6H_4)$_2$ complexes in extreme oxidation states of [Ru(OEP)(aryl)$_2$]$^+$ and [Ru(OEP)(aryl)$_2$]$^{2-}$ (X = H, CH_3, OCH_3, Cl, F) [356].



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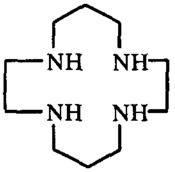

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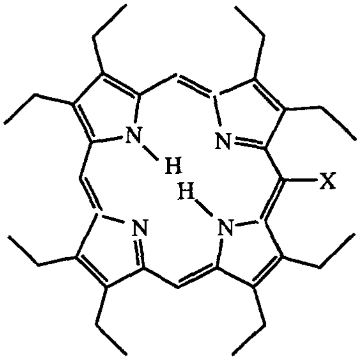
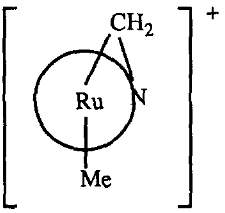


(166) X = *p*-tolyl
(169) X = H



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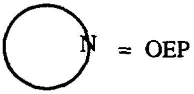
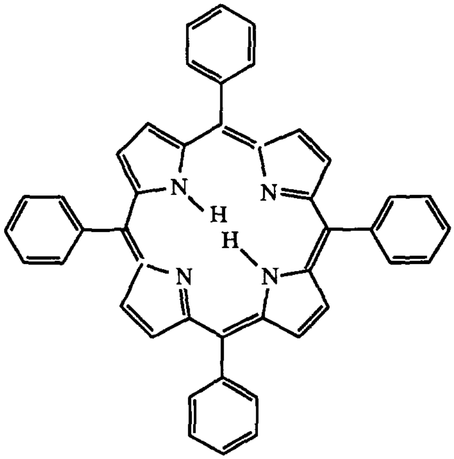
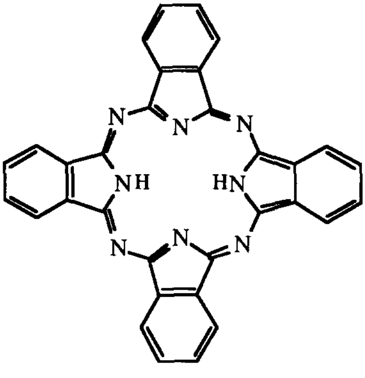


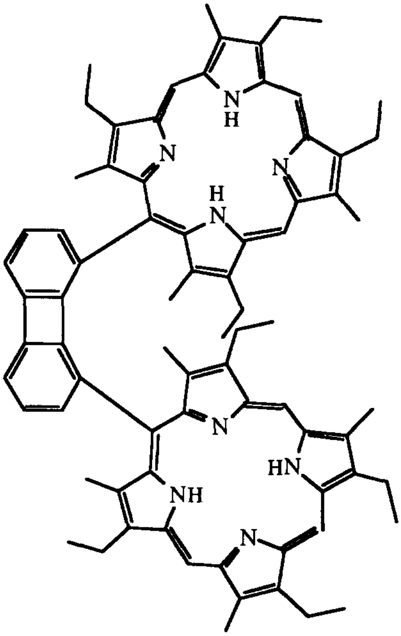


(170)

Oxidative deprotonation of [M(L)(NH$_2$CMe$_3$)$_2$] gave [M(L)(O)(NCMe$_3$)] and [Os(L)(NCMe$_3$)$_2$] (M = Os, Ru; L = meso-tetraphenylporphyrin **(170)**, meso-tetrakis(3,4,5-trimethoxyporphyrin) [357]. FCH$_2$CH$_2$NC and F$_3$CCH$_2$NC were prepared and complexed to Ru(TPP) and Fe(TPP)OSO$_2$CF$_3$ to provide information on the fluorine effect on alkyl isocyanide binding (H$_2$TPP = **(170)**) [358]. The activity of ruthenium porphyrin complex catalysts for the oxygen transfer reaction from 2,6-dichloropyridine N-oxide to substrates was enhanced by the addition of a small amount of HCl or HBr, and the catalytic abilities of dioxo, dichloro and carbonyl complexes of RuTPP(X) were discussed [359]. Ru^{II}(TCPP)(CO)(py) was bound with bovine serum albumin to give a protein-hybrid photocatalyst which could reduce Λ-(Co(acac)$_3$ enantioselectively under photoirradiation (TCPPH$_2$ = meso-tetrakis-(4-carboxyphenyl)porphyrin) [360]. Three aromatic amine-bridged coordination compounds [PcRuL]$_n$ (H$_2$Pc = **(171)**; L = p-phenylenediamine, 2,7-diaminofluorene, 4-aminopyridine) were prepared to study their properties as axial ligands in oxidation reactions [361]. The mechanism of oxidation of [(NH$_3$)$_2$Ru$_2$(DPB)L$_2$] to yield [μ-N$_2$Ru$_2$(DPB)L$_2$] was investigated (H$_4$DBP = **(172)**; L = 1-tert-butyl-5-phenylimidazole) [362]. The structural characterization and the properties of the dinitrogen complex was reported [363].



(171)



(172)

10.5.5 Complexes with ammonia and amine ligands

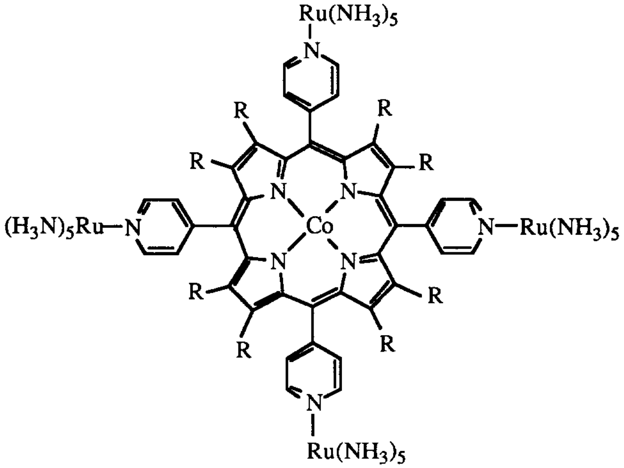
The results of an investigation of the number of multiply-charged complex ions [Ru(NH$_3$)]$^{3+}$ that could be bound onto poly{pyrrole-co[3-(pyrrol-1-yl)propane sulfonate]} films were presented along with other properties of the polymer matrix. Data were based on electrochemical quartz crystal microgravimetry and electrochemical studies of the polymer matrix [364]. The structure of $[(NH_3)_5RuCl](HSO_4)_2{\cdot}4H_2O$ was determined [365]. The encapsulation of $[Ru(NH_3)_5L]^{2+}$ (L = pyrazine, bpy) with cyclodextrins and the resulting effect on electron transfer rates to $[Co(edta)]^-$ were investigated [366]. The adduct formation of $[Ru(NH_3)_5L](PF_6)_n$ (n = 2 for L = isn, pyrazine; n = 3 for L = 4-NH_2py, 4-$N(Me)_2$py) with 18-crown-6 ether was studied spectrophotometrically and electrochemically in non-aqueous solution [367]. The properties of $(H_3N)_5Ru^{II}$-NHC(O)R (R = C_6H_5, 4-C_5H_4N, 4-C_5H_4N-$^+CH_3$) and the isomerization of the complex for R = 4-C_5H_4N and R = 2-C_5H_4N were investigated [368].

Preparations and properties of $[Ru^{II}(NH_3)_5(rcp)](BF_4)_3.mH_2O$ (rcp = N-R-n-cyanopyridinium cations; R = Me, n = 2, 3, 4; R = decyl, dodecyl, benzyl, n = 4) were reported [369]. The kinetics of the base-mediated hydrolysis of $[Os(bpy)_2\text{-}\{bpy(COOR)_2\}]^{2+}$ and $[Ru(NH_3)_5(NC_5H_4COOR)]^{2+}$ (R = Me, C_6H_{13}) were investigated by ion-pair HPLC and spectrophotometry in aqueous solution [370]. [n]Staffane-3, $3^{(n-1)}$-dithiols (n = 1-4). Their singly functionalized derivatives carrying an acetyl or $[Ru(NH_3)_5]^{2+}$, substituted were synthesized on polycrystalline gold electrodes, and the blocking properties of the films were investigated [371]. The tetra-ruthenated cobalt complex (**173**) adsorbed on pyrolytic graphite electrodes had higher catalytic power than that prepared with Nafion coatings on electrodes for the four-electron reduction of O_2 to H_2O [372]. The electrocatalytic behaviour of cobalt-porphyrin-incorporated Nafion coatings on glassy carbon electrodes with $[Ru(NH_3)_6]^{3+}$ incorporated as the mediator was studied [373]. Experiments involving the oxidation of $[Ru(NH_3)_6]^{2+}$ at Pt ultramicrodisk electrodes were done as a comparison with the theoretical predictions in scanning electrochemical microscopy (SECM) [374]. SECM experiments were carried out with a ligand Hg substrate. Kinetic parameters for the heterogeneous reduction of $[Ru(NH_3)_6]^{3+}$ at a carbon fibre by electrochemical measurements inside such a layer agreed well with those at a microdisk electrode [375].

The theory of aquasi-reversible electrode process was developed and applied to the determination of the electrode parameters of the $[Ru^{III}(NH_3)_6]/[Ru^{II}(NH_3)_6]$ electrode reaction on a Hg oblate spheroidal microelectrode [376].

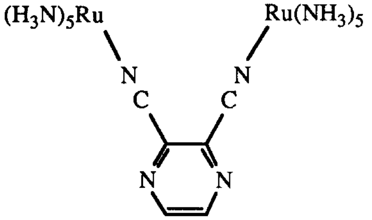
The electrode kinetics of the same redox couple electrostatically confined in montmorillonite clay / polylvinylalcohol)(PVA) composite films on graphite electrodes were examined by cyclic voltammetry and normal pulse voltammetry [377]. Electroactive $[Ru(NH_3)_6]^{3+}$ gallery cations were observed in $[Ru(NH_3)_6]^{3+}$-laponite and -montnrorillonite films supported on graphite electrodes and were compared with those of $[Fe(bpy)_3]^{2+}$ [378]. Immunoelectron microscopic study of proteoglycans in rat epiphyseal growth plate cartilage after fixation with $[Ru(NH_3)_6]Cl_3$ (RHT) was conducted [379]. Cationic dyes chemically related to RHT was used to preserve cartilage matrix proteoglycans [380]. The effect of pre-treatment on the dispersion of supported noble metal catalysts prepared from $Pt(NH_3)_4(NO_3)_2$, $Pd(NH_3)_4(NO_3)_2$, RHT, $[Rh(NH_3)_5Cl]Cl_2$ in basic solution was studied [381]. Zinc-substituted KL zeolite was loaded with RHT and served as a catalyst for aromatization of C_6 alkanes and for hydrogenation of benzene [382]. Na-Y zeolite was cation exchanged with RHT to yield a light-purple solid which was active in ammonia synthesis at atmospheric pressure [383]. The structure at 295 K and magnetic properties of $[Ru(NH_3)_6]Br(SO_4)$

were reported [384]. An article on syntheses, characterization and reactivity of ruthenium ammine complexes has been published [385].



(173)

Compounds (**174**) and (**175**) for both the +4 and +6 oxidation states were prepared and characterized [386]. The ultrafast electron transfer and vibrational energy relaxation of $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^-$ was studied using picosecond IR spectroscopy [387]. The spectroscopic and electrochemical properties of $[Bu_4N]_4[Ru(dcb)_2(CN)_2]$ and $[Re(phen)(CO)_3CNRu(NH_3)_5](PF_6)_3$, together with a series of polynuclear complexes



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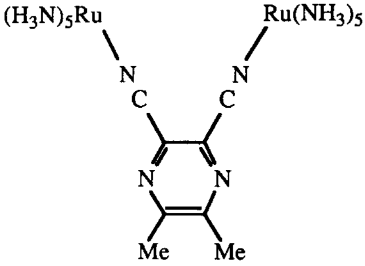

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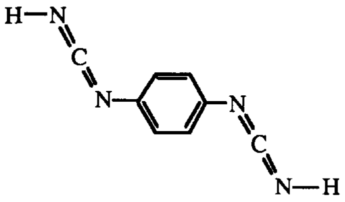
containing CN-bridged ruthenium polypyridine units were studied (H_2dcb = 2,2'-bipyridine-4,4'-dicarboxylic acid) [388]. An electrochemical variational method had been employed experimentally to examine the extent of ground-state mixing between metal-centred donor and acceptor orbitals in bridged mixed-valence complexes of the type $[L(NH_3)_4Ru\text{-}NC\text{-}Fe(CN)_5]^-$ [389]. Thermochromic effects in $[(NH_3)_5Ru^{III}(NC)Fe^{II}(CN)_5]^-$ and $[(NC)_5Fe^{III}(4,4'\text{-bpy})Fe^{II}(CN)_5]^{5-}$ were investigated [390]. The assignment of electronic transitions of $[(bpy)_2(Cl)Os^{III}(CN)Ru^{II}(NH_3)_5]^{3+}$ was done by resonance Raman excitation profiles [391].



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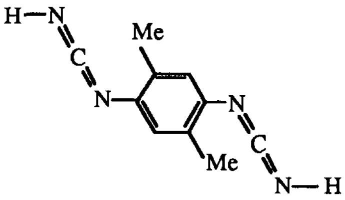

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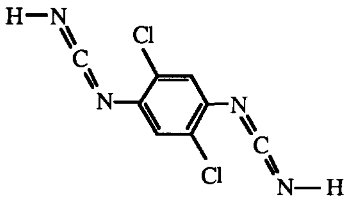

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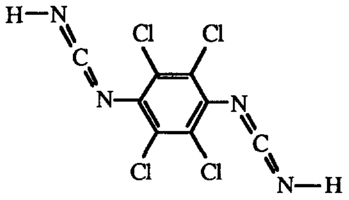

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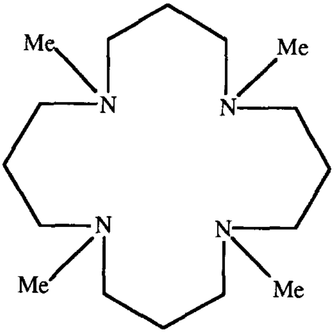
Advantage was taken for the strong amine/dmso interactions exhibited by [Cl(bpy)$_2$Os-TMB-Ru(NH$_3$)$_5$]$^{4+}$ in dmso to induce intramolecular electron transfer from Ru^{II} to Os^{III} (TMB = trimethylenebipyridine) [392]. [μ-(dicyd){(NH$_3$)$_5$Ru}$_2$](ClO$_4$)$_4$, [μ-(Me$_2$dicyd){(NH$_3$)$_5$Ru}$_2$](ClO$_4$)$_4$, [μ-(Cl$_2$dicyd){(NH$_3$)$_5$Ru}$_2$]Cl$_4$ and [μ-(Cl$_4$dicyd){(NH$_3$)$_5$Ru}$_2$]Cl$_4$ were synthesized and the crystal structure of the dicyd complex was determined. (dicyd = **(176)**; Me$_2$dicyd = **(177)**, Cl$_2$dicyd = **(178)**, Cl$_4$dicyd = **(179)**). Characterization of the complexes using cyclic voltammetry, spectroscopy, and magnetic susceptibility was carried out [393].

The complexes [Ru(hfac)$_2$(en)] and [Ru(hfac)(en)$_2$]PF$_6$ were synthesized to study the oxidative dehydrogenation of their 1,2-diaminoethane ligand in MeCN solutions (hfac = hexafluoroacetylacetonate ion) [394]. The complexes trans -[RuL$_2$Cl$_2$][PF$_6$] (L = en, N,N'-bis(2-aminoethyl)-1,3-propanediamine, cyclam) were prepared [395]. [Ru(L-L)(L')$_2$Cl$_2$] were prepared and characterized by elemental analyses, IR, and ^{1}H NMR spectroscopies (L-L = N,N,N',N'-tetramethylethylenediamine, 1-(thiomethyl)-2-(diphenylarsino)ethane, N-methyl-2-thiophenealdimene; L' = dmso, CO) [396]. The complex [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$(P(isoPr)$_3$)$_2$] reacted with HgX'$_2$ (where X = halides and carboxyl groups) to give [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$(P(isoPr)$_3$)$_2$HgX$_2$] adducts. The adducts further reacted with HgX'$_2$ to give [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$(P(isoPr)$_3$)$_2$Hg(μ-X')$_2$HgX$_2$] or [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$(P(isoPr)$_3$)$_2$Hg(μ-X)$_2$HgX'$_2$]. Crystal structures of [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$)(P(isoPr)$_3$)$_2$Hg(O$_2$CCF$_3$)$_2$] and [Ru$_2$(C$_{10}$H$_8$N$_2$)(CO)$_4$.(P(isoPr)$_3$)$_2$Hg(μ-Cl)$_2$HgCl$_2$] were reported [397]. The kinetics of base hydrolysis of *cis*-$[RuCl_2(en)]^+$, cis -α-$[RuCl_2(trien)]$ and *cis*-α-$[RuCl(OH)(trien)]$ were studied (trien = 1,8-diamino-3,6-diazaoctane) [398].

10.5.6 Complexes with nitrosyl and nitrate ligands

The nitrosyl complex [Ru(edta)(NO)] was prepared and characterized by physicochemical methods and X-ray analysis and was shown to be an excellent oxygen atom transfer agent [399]. $RuCl(NO)(SO)(PPh_3)_2$ was synthesized and structurally characterized. This complex contains a terminal linear M-N-O and bent M-S-O functionality. $RuCl(NO)(SO)(PPh_3)_2$ was further oxidized to give $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$, $RuCl(NO)(SO_4)(PPh_3)_2$ and $RuCl(NO)(\eta^2\text{-}O_2)\text{-}(PPh_3)_2$ and all these species were spectrally characterized [400]. The protonation of RuH(NO)(cyttp) gave *cis*-$[RuH_2(NO)(Cyttp)]^+$ (cyttp = bis(dicyclohexylphosphinotrimethylene)). A fluxional intermediate was proposed that involved a molecular hydrogen complex [401]. The stable aquation product *trans*-$[Ru(salen)(NO)(H_2O)][SbF_6]$ was found to be an efficient catalyst for Diels-Alder reaction (H_2salen = bis(salicylidene)-ethylenediamine) [402] and Mukaiyama crossed-aldol reaction [403].

Vibronic theory was used to explain the anomalous bond angles in the hetero-ligand MXL_5 band MXL_4L' complexes and normal bond angles in $[MNOX_5]^{2-}$ (M = Os, Ru) [404]. Structural studies on K_2RuNOX_5 (X = Cl, Br, I) with the main emphasis on the lengthening of Ru-Cl axial bond and the deformation of the octahedral structure were done [405]. The salt *trans*-$[Ru(NO)(OH)(bpy)_2](ClO_4)_2$ was prepared and characterized spectroscopically and structurally [406]. The reaction products *trans*-$[RuL(O)Cl]^+$ and *trans*-$[RuL(OH)(NO)]^{2+}$ from *trans*-$[RuLCl_2]^+$ (L = (**180**)) were structurally characterized and were rationalized by the disproportionation of *trans*-$[RuL(Cl)(NO_2)]^+$ [407].



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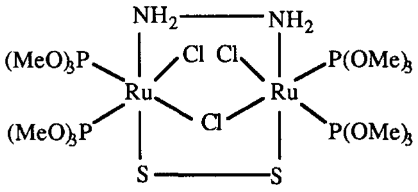
The structure of $Na_2[Ru(OH)(NO)(NO_2)_4]$ was determined by X-ray diffraction and compared with that previously obtained by neutron diffraction [408]. The activity of the dimetallic Ru-Cu catalysts supported on ZSM-5 zeolite was found to be dependent on the Ru precursor ($RuCl_3$ or $Ru(NO)(NO_3)_3$) used [409]. RuO_2/TiO_2 catalysts was synthesized by the sol-gel method using $RuCl_3{\cdot}xH_2O$, $Ru(NO)(NO_3)_3$ or $Ru(acac)_3$ as precursor. The composition and the microstructure of the catalyst were determined [410]. The effect of Ru promoters ($Ru(NO_3)_3$) on Mo/Al_2O_3 and $Co\text{-}Mo/Al_2O_3$ hydrodesulfurization catalysts was studied and was found to be better than $RuCl_3$ [411]. The synthesis of $Ru(NS)Cl_3(EPh_3)_2$ was reported (E = P, As) [412]

10.5.7 Complexes with other N- and mixed donor ligands

The catalytic activities of the dinitrogen complexes $[RuLN_2]^{n-}$ (L = aminoacetato ligands, n = 0, 1, 2) towards reduction of molecular nitrogen to ammonia were investigated [413]. The novel mixed valence Ru(II,III) complex $[RuCl(TMP)_2]_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)$ (**181**) was prepared and its properties and crystal structure were reported [414]. The theory of electrochromism for doubly degenerate states was applied to $Ru(imine)_3{}^{2+}$ complexes [415]. The synthetic routes to several ruthenium α-diimine complexes $[Ru_2(X)(I)(CO)_4(^iPr\text{-}DAB)]$ (**182**), (**183**), $[Ru(X)(Y)(CO)_2(\alpha\text{-}diimine)]$ (**184**), (**185**), $[Ru_2(Me)(I)(CO)_4\text{-}(PR_3)(^iPr\text{-}DAB)]$ and $[Ru_2(Me)(I)(CO)_3(PR_3)(^iPr\text{-}DAB)]$ (PR_3 = PPh_3, PMe_2Ph, $P(OMe)_3$) were reported. The mixed metal complexes $[FeRu(Me)(I)(CO)_4(^iPr\text{-}DAB)]$ and $[HFeRu(Me)(CO)_5(^iPr\text{-}DAB)]$ were also obtained and the crystal structures of several of the complexes were determined [416]. The complex *trans*-$[(2,6\text{-}(Me_2CH)_2(C_6H_3N)_2Ru(PMe_3)_2]$ (**186**) was synthesized and the coordination geometry was determined to be planar from the results of an X-ray diffraction study [417].



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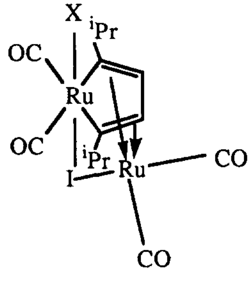
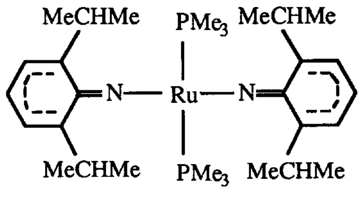


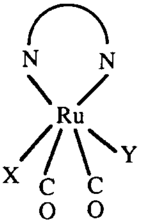
(182) X = Me
(183) X = I



(186)

The syntheses of $[Ru\{PhNC(R)NPh\}_2(CO)(PPh_3)]$, $[MX\{PhNC(R)NPh\}\text{-}(CO)(PPh_3)_2]$ and $[IrX_2\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ (M = Ru, Os; X = H, Cl; X_2 = H_2, Cl_2 or HCl) were presented [418]. Oxidative substitution of $[M^{II}Cl_2(PPh_3)_3]$ gave $[M^{III}Cl_2\{PhNCRNPh\}(PPh_3)_2]$ (M = Ru, R = H, Ph; M = Os, R = H, Me, Ph), $[Ru^{III}Cl\{PhNCRNPh\}_2(PPh_3)]$ and

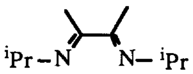
$[Os^{IV}Cl_2\{PhNCRNPh\}_2]$ (R = Me, Et or Ph); the X-ray structure of *trans*-$[OsCl_2\{PhNCEtNPh\}_2]$ has been determined [419]. $[Ru_2(PhNNNPh)_4]$, $[Ru_2(RNNNR)_4(MeCN)]$ and $[Ru_2(RNNNR)_4(MeCN)](BF_4)$ were synthesized and structurally characterized (R = p-tolyl) [420].



(184) X = Me, Y = I, $\overset{\frown}{N\ \ N}$ = ^{i}Pr-DAB

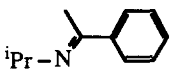
(185) X = Me, Y = I, $\overset{\frown}{N\ \ N}$ = ^{i}Pr-Pyca

^{i}Pr-DAB =

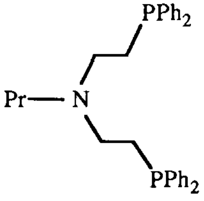


;

^{i}Pr-Pyca =



The syntheses of *trans,mer*-$[RuCl_2LZ]$ with L being a tridentate PNP- or N_2P_2-donor ligand (Z = dmso, PPh_3; PNP = **(187)**, N_2P_2 = **(188)**) were described. Other reaction products included $[Ru_2(\mu\text{-}Cl)_3(PNP)_2]BPh_4$, *trans,mer*-$[Ru(H)(\eta^1\text{-}BH_4)(PNP)(PPh_3)]$, *trans,mer*-$[RuHClL(PPh_3)]$, $[RuHL(PPh_3)]BPh_4$, and *mer*-$[RuH(CO)_2(PNP)]BPh_4$ [421].



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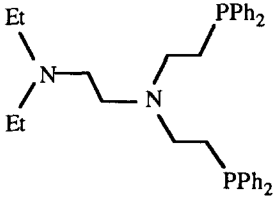

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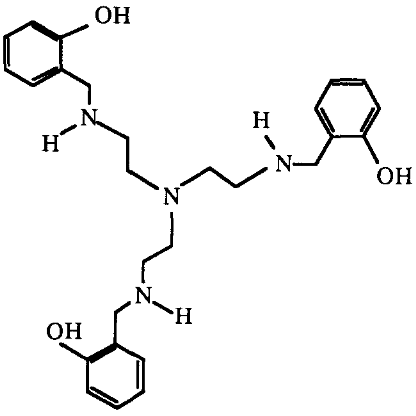

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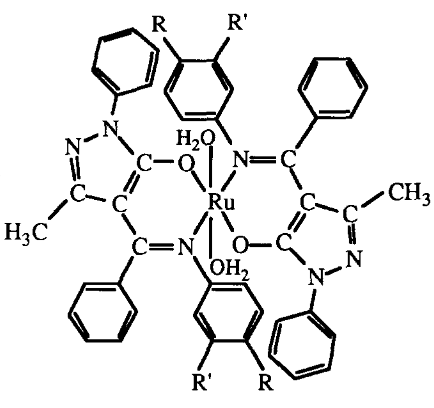

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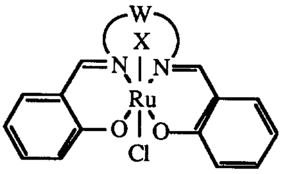
A series of Schiff's base complexes [RuL(CO)] were synthesized and characterized. The Schiff's bases L were derived from diamines and substituted salicylaldehyde [422]. Non-electrolytic low-spin [RuL] (LH_3 = (**189**)) were prepared, of which the spectral and electrochemical behaviour were investigated [423]. Schiff base complexes derived from pyrazolone [$Ru^{II}L_2(H_2O)_2$] (**190**) were prepared and characterized [424].

Ruthenium(III) Schiff's base complexes of the form (**191**) and (**192**) were prepared and their O_2 and CO affinities were studied [425, 426]. The electrochemical behaviour of the complex [Ru^{III}(Naphdien)Cl] in the presence of oxygen and organic substrates was studied [427].



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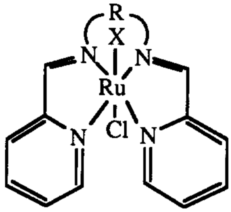
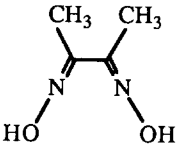


(**192**)

The crystal structure of [$Ru^{II}(dmgH_2)_3]Cl_2$ revealed a propeller-like molecule, stabilized by intermolecular hydrogen bonding ($dmGH_2$ = (**193**)) [428]. The species [$Ru(HL)_2X(NO)$] (H_2L = $dmgH_2$, $dpgH_2$ (**194**), 1,2-cyclohexanedione dioxime (**195**); X = Cl, Br, I) and [$Ru(dpgH)_2(CO)L$] (L = H_2O, py) were synthesized and spectrally characterized. Racemates were found to be present in some of the Ru^{III}–NO complexes [429]. The structures of *trans*-[$Ru(HL)_2Cl(NO)$] (H_2L = (**193**), (**194**)) and also *trans*-[$Ru(dmgH)(dmgH_2)(NO)Cl]Cl$ have previously been reported [430]. The reaction of $dmgH_2$ and *cis*-$RuCl_2(dmso)_4$ in CH_2Cl_2-MeOH mixture or dmf gave three different products, namely [$RuCl_2(dmgH_2)(dmso)_2$], [$RuCl(dmgH_2)_2(dmso)]Cl$ and [$Ru(dmgH)_2(dmso)_2$] [431].



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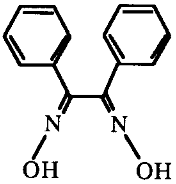

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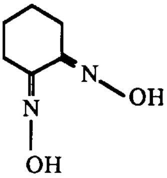


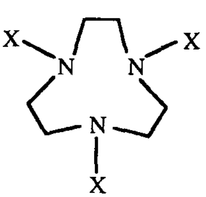
(**195**)

10.6 Complexes with oxygen donor ligands

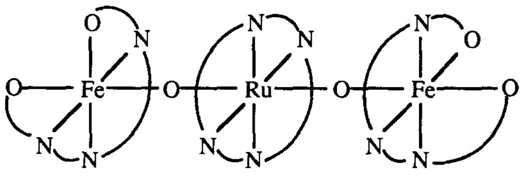
10.6.1 Complexes with oxo ligands

The preparation of [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(CH_3OH)]^+$- incorporated poly(4-vinyl pyridine) and its electrochemical activity were presented [432]. The magnetic susceptibility and ESR spectrum of the cation [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ (**196**) and its salts in the form of powders were measured over a temperature range from that of liquid helium to ambient conditions. The results were analysed using a localized model with antiferromagnetic exchange interactions [433]. Substitution reactions of py-d5 for the terminal pyridine of **(196)**, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]$ and $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(py)_2]$ had been studied in CD_3CN by following the change in ^1H NMR spectra [434]. $[Ru_2Co(\mu_3\text{-}O)(\mu_3\text{-}OAc)_6(py)_3]$ and $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}OAc)_6(py)_3]I_3$ were prepared and their physical properties were investigated [435].

The kinetics and either the mechanism or the stoichiometry of oxidation of iodide [436], 1,4-benzenediol [437] and sulfite ion [438] and reduction of bromate [439] by $[Ru_2(\mu\text{-}O)(H_2O)_2(bpy)_4]^{4+}$ **(197)** were investigated and reported. Resonance Raman spectra of **(197)** and its congeners in higher oxidation states (which were thermodynamically accessible) were obtained in aqueous solutions. An ^{18}O-isotope labelling study was performed on the oxidation of water catalysed by **(197)** [440]. The dinuclear systems $[(bpy)(H_2O)Ru(\mu\text{-}O)(\mu\text{-}bpy\text{-}(CH_2)_n\text{-}bpy)Ru(H_2O)(bpy)]$ were prepared, being stabilized by the alkyl-linked bipyridine. Their characterization and catalytic activities were presented [441]. $[\{(PPh_3)(MeCN)_2Ru\}_2(\mu\text{-}O)(\mu\text{-}OAc)_2](ClO_4)_2$ was synthesized from $[Ru_2O(OAc)_4(PPh_3)_2]$. The the X-ray structurehas been determined and spectroscopic properties have been investigated [442]. Several heterometallic oxo- and hydroxo-bridged complexes of general formula $[L'Ru(\mu\text{-}X)(\mu\text{-}AcO)_2ML]^{n+}$ and $[LRu(\mu\text{-}X)(\mu\text{-}AcO)_2CrL]^{n+}$ (L = **(198)** ; L' = **(199)**, X = O or OH; M = Co, V, Mn, Fe ; n = 2 or 3) were synthesized and studied [443]. The structure and magnetism of the redox product **(200)** were determined [444]. The kinetics of the electrocatalytic oxidation of benzyl alcohol with $[Ru^V(L)(O)]^{2+}$ (LH = **(201)**) were studied in solution and inside Nafion [445]. In addition, the kinetics and mechanism of the two-electron reduction of *trans*-$[Ru^{IV}L(O)(H_2O)]^{2+}$ to *trans*-$[Ru^{III}L(OH)(H_2O)]^{2+}$ and then *trans*-$[Ru^{III}L(H_2O)_2]^{2+}$ by *cis*-$[Ru^{II}(NH_3)_4(isn)_2]^{2+}$ and $[Ru^{II}(NH_3)_4(bpy)]^{2+}$ respectively have been investigated (L = **(202)**) [446]. Spectrophotometry was used to investigate the kinetics and mechanisms of the oxidation of hydrazine by $[RuO(H_2O)_3Cl_2]^+$ in aqueous solution [447]. The same complex and $[LRu^VO]$ (LH_4 = edtaH_4, propylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid) were observed to be excellent catalysts in the oxygen atom transfer reactions to organic substrate compared to the Fe(V) oxo complexes of the porphyrins. Thus, they act as good models for the cytochrome-P450 oxidase type reaction [448]. A review article on recent developments in the area of oxidation of primary and secondary alcohols using ruthenium oxo complexes has been published [449].



(198) X = H
(199) X = Me



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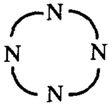
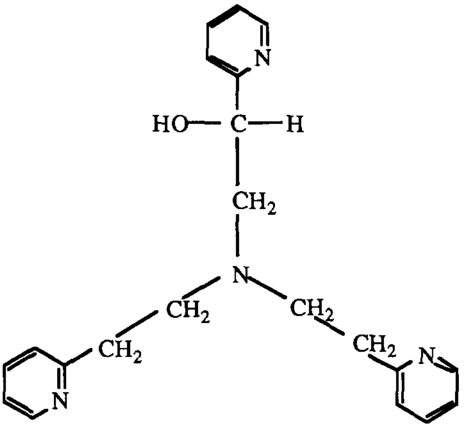
 = TPP ;  = Salicylidene amine



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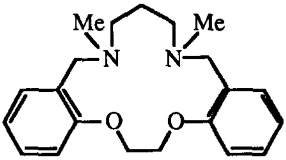
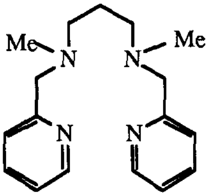


(202)

Alkene hydroxylation with catalytic systems containing the *cis*-$[Ru(O)_2]$ moiety was reported in a symposium paper [450]. The effect of driving force on the rate of oxidation of alcohols by *trans*-$[Ru^{VI}LO_2]^{2+}$ (L = $(bpy)_2$, **(202)** - **(205)**) was studied and a mechanism has been proposed [451].



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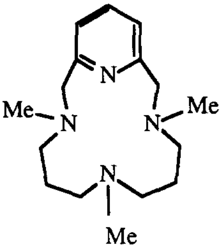

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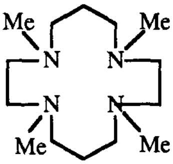

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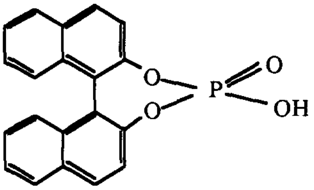
The complexes *cis*-$[Ru^{VI}LO_2]^{2+}$, *cis*-$[Ru^{V}LO_2]^{+}$ and *cis*-$[Ru^{II}L\text{-}(MeCN)_2]^{2+}$ (L = *N,N,N',N'*-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) were prepared and their structures, reactivity and electrochemistry determined [452]. The stereochemical grounds for the β-diastereofacial selection of catalytic epoxidation of unsaturated steroids by *trans*-$[Ru^{VI}O_2(TMP)]$ ($TMPH_2$ = tetramesityl porphyrin) was investigated [453]. A review article on catalytic oxidation using metalloporphyrin complexes (with an emphasis on ruthenium porphyrin complexes) via the well-characterized ruthenium(VI) dioxo species has appeared [454]. The kinetic and mechanistic study of the oxidation of the saturated hydrocarbons cyclohexane and adamantane with O_2 catalysed by Ru(III)-saloph complex supported the presence of ruthenium(IV)-superoxo complexes [455].

The formation of $(Pr_4N)[Ru\{NH(C_6H_4)\}\{OCEt(R)CO_2\}_2]$ from $(Pr_4N)[RuO\{OCEt(R)CO_2\}_2]$ has been achieved; crystallographic data are presented [456]. The compounds $(PPh_4)[OsO_2(OCOR)Cl_2]$ and $(PPh_4)[RuO_2(OCOR')Cl_2]$ were prepared and were found to function as catalytic oxidants as well as precursors to other complexes [457]. The synthesis and characterization of the four-electron oxidant *trans*-$[Ru(tpy)(O)_2(H_2O)](ClO_4)_2$ were presented; redox and spectral properties have been investigated [458].

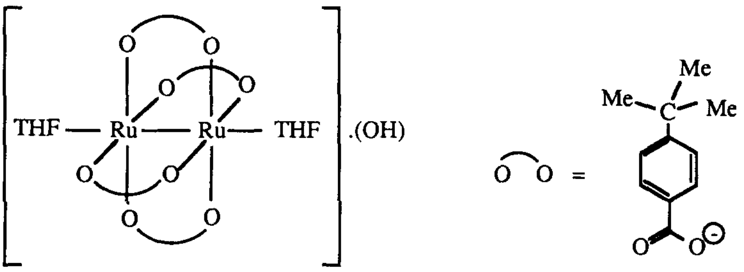
10.6.2 Complexes with carboxylate ligands

The synthesis and structure of the substitution reaction product $[Ru(OAc)(MeCN)_2(PPh_3)_2](ClO_4)$ were reported. These studies revealed a *cis*- and *trans*-geometry for the MeCN and PPh_3 ligands respectively [459]. A series of ruthenium(II) acetate complexes including *mer*-[RuCl(OAc)(cyttp)], *fac*-[RuCl(OAc)(cyttp)], *fac*-[RuCl(OAc)(ttp)] and *fac*-$[Ru(OAc)_2(ttp)]$ (cyttp = bis(dicyclohexylphosphinotrimethylene); ttp = $PhP((CH_2)_3PPh_2)_2$) were synthesized and spectroscopically characterized. Some structural data are presented [460]. Both optically active $[Ru_2(\mu\text{-}OAc)_4((+)\text{-}Phos)]\cdot 5H_2O$ and optically inactive $[Ru_2(\mu\text{-}OAc)_3((+)\text{-}Phos)((-)\text{-}Phos)]\cdot H_2O$ were prepared (PhosH = (**206**)); spectral, magnetic and electrochemical properties have been investigated [461].



(206)

The polymeric complex $[Ru_2(O_2CEt)_4(phz)](BF_4)$ (phz = phenazine) was prepared and crystallized by a diffusion technique for X-ray structure determination [462]. Low-dimensional ruthenium-containing materials featuring $[Ru(H_2O)_6]^{2+}$ or $[Ru_2(O_2CR)_4]$ (R = H, Me, Et, Pr, p-tolyl) as building blocks were characterized by ellisometry, FT-IR-ATR and UV spectroscopies, XPS, SIMS and scanning tunnelling microscopy. Specifically, polymeric $Ru_2(O_2CR)_4$-2,5-dimethyldicyano quinondiimine was synthesized, characterized and its magnetic properties were discussed [463].



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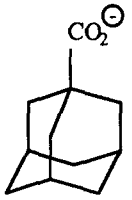
Detailed mechanistic and kinetic studies were conducted on the hydrogenation of *cis*-1,4-polybutadiene and nitrile rubber and also *cis*- to-*trans*-1,4-C=C isomerization, using $[RuCl(CO)(OCOPh)(PPh_3)_2]$ as the catalyst [464]. The complex $[Ru_2Cl(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}{}^tBu)_4]$ was prepared from $[Ru_2Cl(\mu\text{-}OAc)_4]$,and the product further reacted to give $[Ru_2(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}{}^tBu)_4(thf)_2]BF_4$ and $[Ru_2(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}{}^tBu)_4(thf)_2]OH$ (**207**). All new compounds were characterized, and the X-ray structure of (**207**) was determined [465].

The dinuclear complexes $[Ru_2(RCO_2)_4(MeOH)_2]\cdot 2MeOH$, $[Ru_2(RCO_2)_3(CO_3)(MeOH)_2]\cdot 2MeOH$ and $[Mo_2(RCO_2)_4]$.2thf were prepared and characterized by X-ray crystallography (RCO_2 = (**208**)) [466]. The catalytic effect of the diazoester-modified $[Ru_2(O_2CR)_4]$ catalysts on ring-opening polymerization of norbornene, cyclooctene or cyclopentene was investigated [467]. The synthesis, characterization and properties of $[Ru(H_2L)(H_2O)]$ and $[Ru_2L(H_2O)_2]$ were presented (H_4L = (**209**)) [468].



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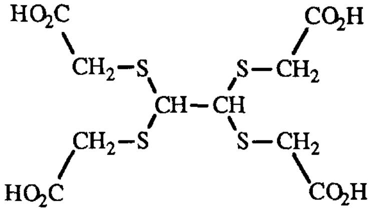

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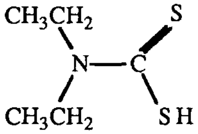
10.6.3 Complexes with edta ligands

The kinetics and mechanisms of oxidation of Me_2S [469] and epoxidation of styrene and substituted-styrene [470] catalysed by $[Ru(edta)(H_2O)]^-$ were investigated. The pH dependence of the de-aquation of $[Ru(edta)(H_2O)]^-$ by CN^- was studied with a mechanism proposed and thermodynamic data presented [471]. The crystal structure of $[Ru(Hedta)(H_2O)]$ revealed a distorted octahedral geometry with the $edtaH^{3-}$ acting as a pentadentate ligand with a free carboxyl group [470]. The catalytic effects of $[Ru(H_2O)_4Cl_2]^+$ and $[Ru(edta)(H_2O)]^-$ on oxidation and oxygenation reactions have been reviewed [472].

The electrochemical reduction of $[Ru(edtaH)(H_2O)]$ was studied at a hanging mercury drop electrode in different electrolytes by cyclic voltammetry, chrono-amperometry and chronopotentiometry [473]. The interactions of K[Ru(edtaH)Cl] with CO under various conditions yielded $[Ru(edtaH)(CO)(H_2O)]$, $K[Ru(edta)(CO)(H_2O)]$ and $K_3[\{Ru\{edta)\}_2\{\mu\text{-}OH\}]$ [474]. The characterization, kinetic and spectrochemical behaviour of $[Ru(edta)(ddtc)]^{2-}$ were presented (dttcH = (**210**)) [476]. The complexes [Ru(edtaH)(L-L)], $[Ru(edtaH_2)(L-L)]$ and $[Ru(edtaH_2)(dppm)]\cdot dmso\cdot H_2O$ were prepared and characterized (L-L = dppm, dppe, (**211**), (**212**)) [477].

Photocatalytic reduction of N_2 to NH_3 was catalysed by K[Ru(edtaH)Cl] with L-ascorbic acid acting as a sacrificial electron donor. A mechanism with $[Ru(edtaH)N_2]^-$ as an intermediate was proposed [478]. In related work, the oxo-species [Ru(edta)(O)] was proposed to be the intermediate in the photooxidation of cyclohexane and adamantane catalysed by the same complex [479]. This complex also catalysed the oxygenation reactions by O_2 of saturated and unsaturated substrates [480] and the synthesis of urea [481]. The crystal structure of K[Ru(edta)Cl_2] revealed a disorder in the lattice, showing two conformations in the free arm of the carboxylate group [482].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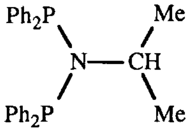
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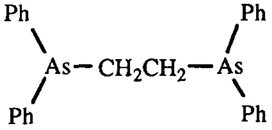
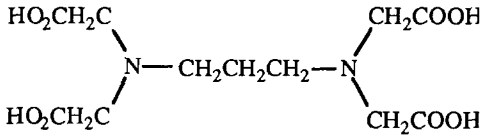

(212)

The potassium salt K[Ru(edta)(bpy)] has been synthesized and characterized. This complex was used as a photosensitizer in the photoreduction of N_2 to NH_3 [483]. [Ru^{III}(edta)(NO)] was found to be an efficient oxygen atom transfer agent for the oxidation of alkenes by O_2 and iodosylbenzene. The synthesis and characterization of the complex and [Ru^{III}(edtaH)(NO)]BF_4 were presented [484]. An efficient catalytic system for epoxidation of alkenes (*cis*-cyclooctene, styrene, *trans*-stilbene), Ru^{III}-edta-ascorbate-O_2 was devised [485]. Results of preliminary studies on concentration by ultra-filtration and re-use of a Ru^{III}-edta complex in the homogeneous catalysis were reported [486]. The retention of edta complexes of Pd(II)., Pt(II), Rh(III), Ru(IV) in reversed-phase and ion-pair chromatography on a Separon C_{18} column with the use of tertiary ammonium bromides as ion-pair reagents has been studied [487].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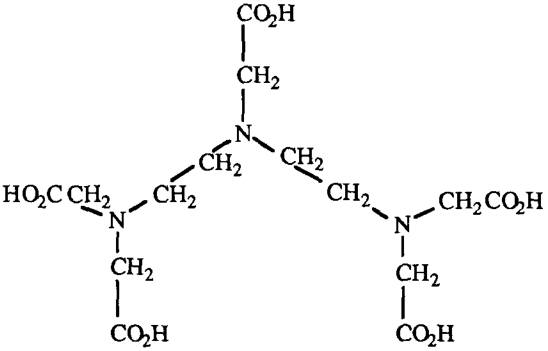
The kinetics of formation of K[RuO(edta)] and K[RuO(pdta)] at 30-50°C and the respective characterization was reported (pdtaH_4 = (**213**)). The structures of the corresponding starting materials namely K[Ru(edtaH)Cl] and K[Ru(pdtaH)Cl] were also presented [488]. The reversible binding of CO to [Ru(edtaH)(H_2O) and [Ru(pdtaH)(H_2O)] was studied in aqueous solution by spectrophotometric and electrochemical studies [489]. The crystal structure of [Ru(pdtaH)(H_2O)]·H_2O was determined and the kinetics of de-aquation of the complex by thiourea and SCN^- ion were studied [490]. The kinetics of ligand substitution reactions of [Ru(dtpaH_2)(H_2O)] (dtpaH_5 = (**214**)) were studied as a function of ligand concentration, pH, and temperature [491].

The substitution of H_2O by Cl^- and then SCN^- in [LRu^{III}(H_2O)]^n was investigated spectrophotometrically (L = $edta^{4-}$ or $edtaH^{3-}$ (**215**)) [492]. The association constants for the formation of [Ru^{II}(edtaH)L]$^-$ (L = alkene or an η^2-coordinated derivative of cytidine or uridine) were determined for 16 ligand structures [493]. The epoxidation of *cis*-stilbene and *trans*-stilbene with [Ru^{III}(edtaH)] and [$Ru^{III}(Me_2edda)]^+$ as the catalyst and Me_3COOH as the oxygen donor was investigated. A mechanism was proposed (Me_2edda^{2-} = (**216**)) [494].



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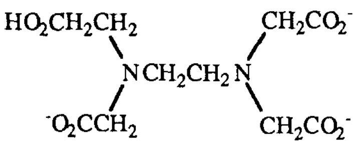

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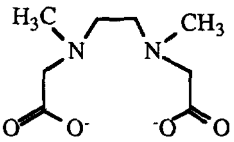
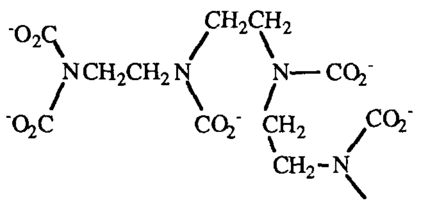


(216)

The oxidation of [Ru(edtaH)(H_2O)] was used to detect the oxidation of alcohols bearing an α-hydrogen [495]. The proton dissociation of Ru(edtaH)(LH) and $Ru_2(ttha)(LH)_2$ were measured with the use of L as probes (ttha = (**217**); L = 2-methyl-pyrazine, 4,4'-bpy) [496]. The anionic complex $[Ru_2(\mu\text{-ttha})(\mu\text{-pym})]^{2-}$ was synthesized and spectrally characterized in solution; its properties have been investigated (pym = (**218**)) [497].



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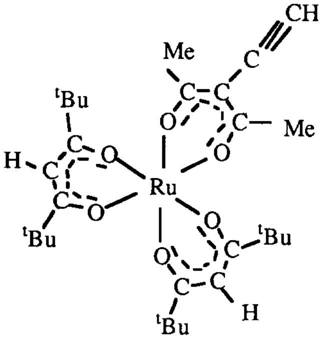
(218)

10.6.4 Complexes with other O-donor ligands

A complete kinetic and thermodynamic analysis of the linkage isomerizations of $[Ru(NH_3)_5(ace)]^{3+/2+}$ (ace = acetone) was presented. Essentially, two modes of bonding was observed for acetone: η^1 via O, or η^2 via C and O [498]. The complex $[Ru(acac)_3]$ was found to decompose in acidic melts but was stable in neutral and basic melts. Its electrochemical behaviour in room-temperature chloroaluminate molten salts was studied [499]. A review has been presented concerning the application of working electrodes and analytical procedures of chronoamperometric measurements for diffusion coefficient determination of [M(acac)$_3$] (M = Ru, Fe, Co) in MeCN [500]. [Ru(acac)$_3$] acted as a catalyst in the preparation of lactones [501], selective hydrogenation of cyclic ester [502] and co-dimerization of alpha monoalkenes and conjugated dialkenes [503]. The ethynyl complex (**219**) was found to be a useful intermediate for synthesis of homo- and heterodinuclear complexes, where the ethynyl groups were introduced through a -C≡CSiMe$_3$ intermediate. The preparations of (**220**) and (**221**) were described [504].



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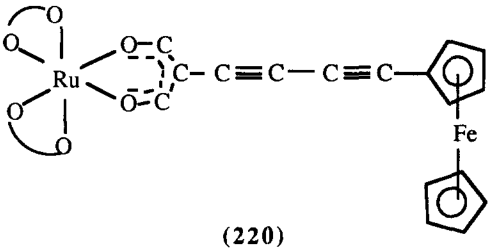

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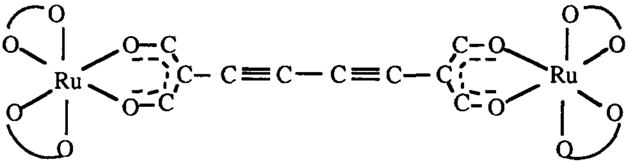
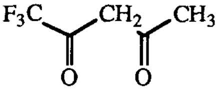
$\widehat{O\ O}$ = [^{t}Bu -C(O)CHC(O)-^{t}Bu]$^-$



(221)

A series of ruthenium and rhodium complexes containing bis-β-diketonate ligands like bis(acetacetonyl)phenylmethane, bis(dibenzolmethyl) methane and bis(benzoylacetonyl)phenylmethane, were prepared and characterized analytically and spectroscopically [505]. Other diketone complexes of the general formula [RuX$_2$(L)(EPh$_3$)$_2$] and [Ru(PPh$_3$)$_2$L$_2$] were prepared and characterized (E = As or P; X = Cl, Br; L = O,O'-donor ligands] [506, 507]. The reduction of RuL$_3$ (HL = a diketone such as (**222**), (**223**)) by ascorbate anions has been studied [508].



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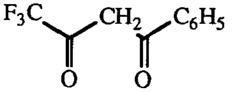
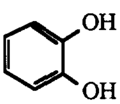


(223)

A series of ruthenium complexes containing 1,2-dioxolene ligands *trans*-$[RuQ_2(RPy)_2]^n$ (Q = dioxolene, RPy = subst. py; n = -1, 0, +1) was prepared and studied [509]. The complexes $[Ru(L)_2(PPh_3)_2].2H_2O$ (H_2L = (**224**)–(**227**)) were prepared and their chemistry was investigated [510]. The trans - to *cis*- isomerization of $Ru(R\text{-}Py)_2(L)_2$ (H_2L = (**226**)) was induced by warming with an excess of R-pyridine [511]. A coordination polymer containing Ru-η^4-o-benzoquinone was prepared [512].



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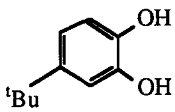

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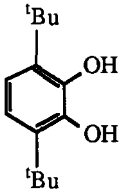

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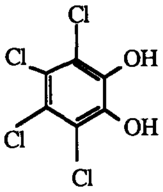
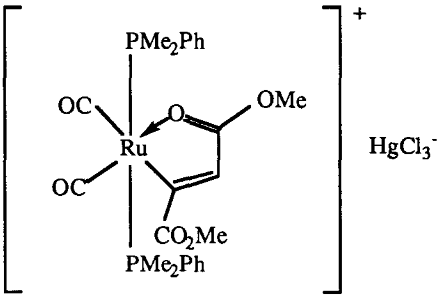


(227)

Saturated hydrocarbons such as adamantane, cyclooctane, cyclohexane, hexane and heptane were oxygenated by ᵗBuOOH or hypochlorite in the presence of the homogeneous catalysts $K_5[Ru(H_2O)PW_{11}O_{39}]$ and cis -$[Ru(H_2O)_2(dmso)_4](BF_4)_2$ [513]. The synthesis and characterization of stable ruthenium thin films from $[Ru(H_2O)_6]^{2+}$, via low-temperature aqueous solution technique were described [514]. Isomerization of alkenes is catalysed by $[Ru(H_2O)_6]^{2+}$ and produces the (E)-isomers under mild conditions [515]. Reaction of $Ru_3(CO)_{12}$ with sulfonic acids gave $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}OOS(O)R)_2(PPh_3)_2]$. The X-ray structure of this compound for R = p-tolyl has been determined [516]. A series of ruthenium-sulfato complexes was synthesized and characterized [517]. $[RuCl_3]\cdot 2dmso$ was prepared and characterized. It was found to be polymeric with bridging Cl and dmso coordinating through the oxygen donor atom [518]. Vinyl ligands were readily transferred from Ru(II) to Hg(II), with the exception of (**228**); this complex has been characterized by X-ray crystallography [519].



(228)

REFERENCES

1. F. Bonhomme, K. Yvon, G. Triscone, K. Jansen, G. Auffermann, P. Mueller, W. Bronger and P. Fischer, *J. Alloys Compd.*, 178 (1992) 161.
2. F. Bonhomme, K. Yvon and P. Fischer, *J. Alloys Compd.*, 186 (1992) 309.
3. J. Eckert, A. Albinati, R.P. White, C. Bianchini and M. Peruzzini, *Inorg. Chem.*, 31 (1992) 4241.
4. C. Bianchini, C. Bohanna, M.A. Esteruelas, P. Frediani, A. Meli, L.A. Oro and M. Peruzzini, *Organometallics*, 11 (1992) 3837.
5. J. F. Riehl, S.A. Jackson, M. Pelissier and O. Eisenstein, *Bull. Soc. Chim. Fr.*, 129 (1992) 221.
6. D. Michos, X.L. Luo and R.H. Crabtree, *Inorg. Chem.*, 31 (1992) 4245.
7. G. Chung, T. Arliguie and B. Chaudret, *New J. Chem.*, 16 (1992) 369.
8. J.P. Collman, P.S. Wagenknecht, J.E. Hutchison, N.S. Lewis, M.A. Lopez, R. Guilard, M. L'Her, A.A. Bothner-By and P.K. Mishra, *J. Am. Chem. Soc.*, 114 (1992) 5654.
9. C.R.S.M. Hampton, I.R. Butler, W.R. Cullen, B.R. James, J.P. Charland and J. Simpson, *Inorg. Chem.*, 31(1992) 5509.
10. G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, (1992) 1111.
11. T. Yoshida, T. Adachi, T. Tanaka and F. Goto, *J. Organomet. Chem.*, 428 (1992) C12.
12. M.N. Bell, A.J. Blake, R.M. Christie, R.O. Gould, A.J. Holder, T.I. Hyde, M. Schröder and L.J. Yellowless, *J. Chem. Soc., Dalton Trans.*, (1992) 2977.
13. G.E. Ball and B.E. Mann, *J. Chem. Soc., Chem. Commun.*, (1992) 561.
14. Y. Wakatsuki, H. Yamazaki, Y. Maruyama and I. Shimizu, *J. Organomet. Chem.*, 430 (1992) C60.
15. A. Iio, N. Oshima, Y. Ohira, M. Sakamoto and H. Oka, *Chem Abstr.* 117 (1992) 213252e.
16. C.E.F. Richard, W.R. Roper, D.M. Salter and L.J. Wright, *Organometallics* 11 (1992) 3931.
17. A. Yousfi and R. Mathieu, *J. Organomet. Chem.*, 426 (1992) C33.
18. M. Rosales, A. Gonzalez, Y. Alvarado, R. Rubio, A. Andriollo and R.A. Sanchez-Delgado, *J. Mol. Catal.*, 75 (1992) 1.
19. J. T. Poulton, K. Folting, W.E. Streib and K.G. Caulton, *Inorg. Chem.*, 31 (1992) 3190.
20. Ik-Mo Lee, D. W. Meek and J. Gallucci, *Bull. Korean Chem. Soc.*, 13 (1992) 491.
21. Ik-Mo Lee, Y. J. Kim, O. J. Cho, D.W. Meek, *Bull. Korean. Chem. Soc.*, 13 (1992) 504.
22. A.J. Rippert and H.J. Hansen, *Helv. Chim. Acta*, 75 (1992) 2219.
23. R. Davis, J.D. Furze, D.J. Cole-Hamilton and P. Pogorzelec, *J. Organomet. Chem.*, 440 (1992) 191.
24. J.L. Breton, J.J. Cejudo, A. Garcia-Granados, A. Parra and F. Rivas, *Tetrahedron Lett.*, 33 (1992) 3935.
25. C. Hall, W.D.Jones, R.J. Mawby, R. Osman, R.N. Peurtz and M.K. Whittlesey, *J. Am. Chem. Soc.*, 114 (1992) 7425.
26. N.W. Alcock, I.D. Burns, K.S. Claire and A.F. Hill, *Inorg. Chem.*, 31 (1992) 4606.
27. M.A. Esteruelas, M.P. Garcia, A.M. Lopez, L.A. Oro, N. Ruiz, C. Schluenken, C. Valero and H. Werner, *Inorg. Chem.*, 31 (1992) 5580.
28. A.M. Mueting, B.D. Alexander, P.D. Boyle, A.L. Casalnuovo, L.N. Ito, B.J. Johnson, L.H. Pignolet, M. Leeaphon and K.E. Meyer, *Inorg. Synth.*, 29 (1992) 279.
29. C. Bianchini, D. Masi, K. Linn, C. Mealli, M. Peruzzini and F. Zanobini, *Inorg. Chem.*, 31 (1992) 4036.
30. J.T. Poulton, K. Folting and K.G. Caulton, *Organometallics*, 11 (1992) 1364.
31. Z. He, D. Neibecker, N. Lugan and R. Mathieu, *Organometallics*, 11 (1992) 817.
32. W.J. Casteel, Jr., A.P. Wilkinson, H. Barrmann, R.E. Serfass and N. Bartlett, *Inorg. Chem.*, 31 (1992) 3124.
33. P.I. Sorantin and K. Schwarz, *Inorg. Chem.*, 31 (1992) 567.
34. A.K. Brisdon, J.H. Holloway, E.G. Hope, W. Levason, J.S. Ogden and A.K. Saad, *J. Chem. Soc., Dalton Trans.*, (1992) 447.
35. S. Murahashi, T. Naota, N. Miyaguchi and T. Nakato, *Tetrahedron Lett.*, 33 (1992) 6991.
36. T. Shibanuma, T. Kanemura and S. Koyama, *Chem. Abstr.*, 118 (1993) 147182z.
37. M. Saito and K. Mizuno, *Chem. Abstr.*, 118 (1993) 84214p.
38. Y. Hara and Y. Kahata, *Chem. Abstr.*, 117 (1992) 191326c.
39. S. Murahashi, Y. Oda and T. Naota, *Chem. Lett.*, (1992) 2237.
40. F. Mizukami, S. Niwa, M. Toba, K.Y. Chea, T.S. Tan and Y.M. Chiu, *Chem. Abstr.* 117 (1992) 69458g.
41. O. Immel, G. Darsow, R. Beaden, H.H. Schwarz and H. Waldmann, *Chem. Abstr.* 116 (1992) 214048j.

42. Y. Mashiba, *Chem. Abstr.*, 116 (1992) 235147f.
43. Xi Wu, B.C. Gerstein and T.S. King, *J. Catal.*, 135 (1992) 68.
44. S. Murata and K. Aika, *Appl. Catal., A*, 82 (1992) 1.
45. X. Zhou, P. Hu, Y. Ji, H. Wang and R. Gu, *Huaxue Shiji*, 14 (1992) 378, 351; *Chem. Abstr.* 118 (1993) 159739z.
46. Y. Kobayashi, T. Okada, K. Asai, M. Katada, H. Sano and F. Ambe, *Inorg. Chem.*, 31 (1992) 4570.
47. A. Juan and D.E. Damiani, *J. Catal.*, 137 (1992) 77.
48. B.J. Kennedy and G.A. Heath, *Inorg. Chim. Acta*, 195 (1992) 101.
49. M.M.T. Khan, G. Ramachandraiah and R.S. Shukla, *Polyhedron*, 11(1992) 3075.
50. T. Lopez, L. Herrera, J. Mendez-Vivar, P. Bosch, R. Gomez and R.D. Gonzalez, *J. Non-cryst. Solids*, 147-148 (1992) 773.
51. N.A. Ezerskaya and M.V. Afanaseva, *Zh. Neorg. Khim.*, 37 (1992) 2223; *Chem. Abstr.* 118 (1993) 47860a.
52. W. Zhao, L. Wang, S. Zhang and Y. Fang, *Yingyong Kexue Xuebao*, 10 (1992) 85; *Chem. Abstr.*, 118 (1993) 124036r.
53. A.D. Benedicto, B.M. Novak and R.H. Grubbs, *Macromolecules*, 25(1992) 5893.
54. T.T. Wang and J.R. Shyu, *J. Chin. Inst. Chem. Eng.*, 23 (1992) 429.
55. J.A. Marsella, *Adv. Chem. Ser.*, 230 (1992) 433.
56. N. Murai, M. Aoki and H. Hata, *Chem. Abstr.*, 118 (1993) 61337s.
57. N. Furuki and K. Mizushima, *Chem. Abstr.*, 118 (1993) 193451j.
58. N. Murai, M. Aoki and H. Hata, *Chem. Abstr.*, 118 (1993) 192552f.
59. S. Murahashi, T. Naota and Y. Oda, *Chem. Abstr.*, 118 (1993) 212676e.
60. S. Murahashi, T. Naota and Y. Oda, *Chem. Abstr.*, 118 (1993) 191190z.
61. K.S. Park and S.K. Ihm, *Chem. Abstr.*, 118 (1993) 6596a.
62. A.F. Hill, N.W. Alcock, J.C. Cannadine and G.R. Clark, *J. Organomet. Chem.*, 426 (1992) C40.
63. S. Bhattacharya and C.G. Pierpont, *Inorg. Chem.*, 31 (1992) 2020.
64. M. Kotora and M. Hajek, *J. Mol. Catal.*, 77 (1992) 51.
65. Y. Hara, K. Endo, H. Inagaki and K. Wada, *Res. Dev. Rev.-Mitsubishi Kasei Corp.* 6 (1992) 22; *Chem. Abstr.*, 119 (1993) 10234u.
66. S. Murahashi, T. Naota and Y. Oda, *Chem. Abstr.*, 118 (1993) 124060u.
67. S. Rajapopal, S. Vancheesan, J. Rajaram and J.C. Kuriacose, *J. Mol. Catal.*, 75 (1992) 199.
68. G.Z. Wang and J.E. Baeckvall, *J. Chem. Soc., Chem. Commun.*, (1992) 980.
69. T. Kondo, S. Kotachi and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, (1992) 1318.
70. M. Yamashita, Y. Imai and M. Kakimoto, *Chem. Abstr.*, 118 (1993) 80794e.
71. M.K. Faraj, *Chem. Abstr.*, 118 (1993) 80639h.
72. B. Marciniec, C. Pietraszuk and Z. Foltynowiez, *J. Mol. Catal.*, 76 (1992) 307.
73. G.Z. Wang and J.E. Baeckvall, *J. Chem. Soc., Chem. Commun.*, (1992) 337.
74. S.T. Nguyen, L.K. Johnson, R.H. Grubbs and J.W. Ziller, *J. Am. Chem. Soc.*, 114 (1992) 3974.
75. G.L. Rempel and X. Guo, *Chem. Ind. (Dekker)* 47 (1992) 105.
76. M.S. Matson and H.J. Swindell, *Chem. Abstr.*, 117 (1992) 212063g.
77. S.B. Halligudi, K.N. Bhatt, N.H. Khan and M.M.T. Khan, *J. Mol. Catal.*, 72 (1992) 139.
78. R.S. Hay-Motherwell., G. Wilkinson, B. Hussian-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1992) 3477.
79. D.C. Apperley, N.A. Davies, R.K. Harris, S. Eller, P. Schwarz and R.D. Fischer, *J. Chem. Soc., Chem. Commun.*, (1992) 740.
80. B.K. Das and A.R. Chakravarty, *Inorg. Chem.*, 31 (1992) 1395.
81. T. Yamakawa, P.K. Tsai and S. Shinoda, *Appl. Catal., A*, 92 (1992) L1.
82. A. Grund, A. Kaltbeitzel, A. Mathy, R. Schwarz, C. Bubeck, P. Vermehren and M. Hanack, *J. Phys. Chem.*, 96 (1992) 7450.
83. G. Bellachioma, G. Cardaci, A. Macchioni, G. Reichenbach, *J. Organomet. Chem.*, 427 (1992) C37.
84. Y. Sun, N.J. Taylor and A.J. Carty, *J. Organomet. Chem.*, 423 (1992) C43.
85. Y. Sun, N.J. Taylor and A.J. Carty, *Organometallics*, 11 (1992) 4293.
86. P. Martin, N.T. McManus and G.L. Rempel, *Stud. Surf. Sci. Catal.*, 73 (1992) 161.
87. E. Fache, C. Santini, F. Senocq and J.M. Basset, *J. Mol. Catal.*, 72 (1992) 331.
88. E. Fache, C. Santini, F. Senocq and J.M. Basset, *J. Mol. Catal.*, 72 (1992) 337.
89. L. Song and W.C. Trogler, *J. Am. Chem. Soc.*, 114 (1992) 3355.

90. M.J.A.Kraakman, B. De Klerk-Engels, P.P.M. De Lange, K. Vrieze, W.J.J. Smeets and A.L. Spek, *Organometallics*, 11 (1992) 3774.
91. A.J. Blake, J.R. Crook, R.J. Mawby, A.J. Reid and C.D.Reynolds, *Acta Crystallogr. Sect. C*, 18 (1992) 1411.
92. P.W. Blosser, J.C. Gallucci and A. Wojcicki, *Inorg. Chem.*, 31 (1992) 2376.
93. A. Beguin, H.C. Boettcher, G. Süss-Fink and B. Walther, *J. Chem. Soc., Dalton Trans.*, (1992) 2133.
94. A.J. Blake, T. Easton and T.A. Stephenson, *Acta Crystallogr., Sect. C*, 48 (1992) 1567.
95. P. Braunstein, S.C. Cea, M.I. Bruce, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 2539.
96. E. Lindner and A. Moeckel, *Z. Naturforsch., B: Chem. Sci.*, 47(1992) 693.
97. H. Werner, A. Stark, M. Schulz and J. Wolf, *Organometallics* , 11 (1992) 1126.
98. K. Yoshikawa, M. Murata, N. Yamamoto, K. Inoguchi and K. Achiwa, *Chem. Pharm. Bull.*, 40 (1992) 1072.
99. P.H. Van Rooyen, T.V. Terence, S. Hietkamp and N. Sparrow, *Acta Crystallogr., Sect. C*, 48 (1992) 545.
100. K.A. Johnson and W. L. Gladfelter, *Organometallics*, 11 (1992) 2534.
101. N. Pirio, D. Touchard, P.H. Dixneuf, M. Fettouhi and L. Ouahab, *Angew. Chem.*, 104 (1992) 664.
102. J.D. Gargulak, A.J. Berry, M.D. Noirot and W.L. Gladfelter, *J. Am. Chem. Soc.*, 114 (1992) 8933.
103. A.M. Joshi, K.S. MacFarlane, B.R. James and P. Frediani, *Stud. Surf. Sci. Catal.*, 73 (1992) 143.
104. D. Carmichael, P. Le Floch, L. Ricard and F. Mathey, *Inorg. Chim. Acta*, 198 (1992) 437.
105. T.S. Wu, *Chem. Abstr.*, 117 (1992) 69575t.
106. T.S. Wu, *Chem. Abstr.*, 117 (1992) 199375p.
107. K. Achinami and M. Murata, *Chem. Abstr.*, 118 (1993) 169331z.
108. J.S. Field, R.J. Haines, E. Minshall, C.N. Sampson, J. Sundermeyer and S.F. Woollam, *J. Chem. Soc., Dalton Trans.*, (1992) 2629.
109. S.E. Bell, J.S. Field, R.J. Haines, M. Moscherosch, W. Matheis and W. Kaim, *Inorg. Chem.*, 31 (1992) 3269.
110. J.P. Genet, C. Pinel, S. Mallart, S. Juge, N. Cailhol and J.A. Laffitte, *Tetrahedron Lett.*, 33 (1992) 5343.
111. J.P. Genet, S. Juge, J.A. Laffite, C. Pinel and S. Mallart, *Chem. Abstr.*, 118 (1993) 146948s.
112. K. Mashima, T. Hino and H. Takaya, *J. Chem. Soc., Dalton Trans.*, (1992) 2099.
113. T. Ohta, T. Miyake and H. Takaya, *J. Chem. Soc., Chem Commun.*, (1992) 1725.
114. H. Takaya, T. Ohta and K. Mashima, *Adv. Chem. Ser.*, 230 (1992) 123.
115. E. Cesarotti, P. Antognazza, A. Mauri, M. Pallavicini and L. Villa, *Helv. Chim. Acta*, 75 (1992) 2563.
116. M. Saburi, L. Shao, T. Sakurai and Y. Uchida, *Tetrahedron Lett.*, 33 (1992) 7877.
117. L. Shao, K. Takeuchi, M. Ikemoto, T. Kawai, M. Ogasawara, H. Takeuchi, H. Kawano and M. Saburi, *J. Organomet. Chem.*, 435 (1992) 133.
118. Y. Iimura, T. Kajima, S. Araki, H. Sugimoto, N. Kiyofuji and H. Kumobayashi, *Chem. Abstr.*, 118 (1993) 124398k.
119. M. Saburi, H. Takeuchi, M. Ogasawara, T. Tsukahara, Y. Ishii, T. Ikariya, T. Takahashi and Y. Uchida, *J. Organomet. Chem.*, 428 (1992) 155.
120. M. Saburi, M. Ohnuki, M. Ogasawara, T. Takahashi and Y. Uchida, *Tetrahedron Lett.*, 33 (1992) 5783.
121. H. Kawano, T. Ikariya, Y. Ishii, T. Kodama, M. Saburi, S. Yoshikawa, Y. Uchida and S. Akutagawa, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1595.
122. A.S.C. Chan, *Chem. Abstr.*, 117 (1992) 212145k.
123. M. Kitamura, M. Tokunaga and R. Noyori, *J. Org. Chem.*, 57 (1992) 4053.
124. N. Karibe, H. Sugimoto, K. Yamatsu, Y. Hori and H. Kumobayashi, *Chem. Abstr.*, 118 (1993) 101933s.
125. A.S.C. Chan and S.A. Laneman, *Chem. Abstr.*, 118 (1993) 147783w.
126. R. Noyori, M. Kitamura, N. Sayo, H. Kumobayashi and M.F. Giles, *Chem. Abstr.*, 117 (1992) 48916q.
127. A.M. Joshi, I.S. Thorburn, S.J. Rettig and B.R. James., *Inorg. Chim. Acta*, 198 (1992) 283.
128. D.F. Taber, P.B. Deker and L.J. Silverberg, *J. Org. Chem.*, 57 (1992) 5990.
129. S. Akutagawa, *Kagaku to Kogyo (Osaka)* 66 (1992) 528; *Chem. Abstr.*, 118 (1993) 168403n.

130. D.J. Darensbourg, F. Joo, M. Kannisto, A. Katho and J.H. Reibenspies, *Organometallics* , 11 (1992) 1990.
131. D.H. Kim, J.H. Park, S.D. Cho, *J. Korean. Chem. Soc.*, 36 (1992) 163.
132. N.R. Champness, W. Levason, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1992) 3243.
133. R.A. Glaum, J.H. Albering, W. Jeitschko and L. Boonk, *J. Alloys.Compd.*, 185 (1992) 301.
134. M.D. Johnson and D. Nickerson, *Inorg. Chem.*, 31 (1992) 3971.
135. M. Breysse, M. Cattenot, T. Des Courieres, C. Gachet and J.L. Portefaix, *Chem. Abstr.*, 118 (1993) 237421f.
136. C. Geantet, C. Calais and M. Lacroix, *C.R. Acad. Sci., Ser. II*, 315 (1992) 439; *Chem. Abstr.*, 117 (1992) 240508z.
137. M. Lacroix, S. Yuan, M. Breysse, C. Doremieux-Morin and J. Fraissard, *J. Catal.*, 138 (1992) 409.
138. H. Colell, N. Alonso-Vante and H. Tributsch, *J. Electroanal. Chem.*, 324(1992) 127.
139. T. Matsumoto and K. Matsumoto, *Chem. Lett.*, (1992) 1539.
140. T. Matsumoto and K. Matsumoto, *Chem. Lett.*, (1992) 559.
141. D. Sellmann, M. Geck and M. Moll, *Z. Naturforsch., B: Chem. Sci.*, 47 (1992) 74.
142. T. Matsumoto, K. Matsumoto and T. Sato, *Inorg. Chim. Acta*, 202 (1992) 31.
143. R. Schafer, W. Kaim, M. Moscherosch and M. Krejcik, *J. Chem. Soc., Chem. Commun.*, (1992) 834.
144. P.G. Jessop, C.L. Lee, G. Rastar, B.R. James, C.J.L. Lock and R. Faggiani, *Inorg. Chem.* 31 (1992) 4601.
145. K. Hiraki, Y. Fuchita, H. Kawabata, K. Iwamoto, T. Yoshimura and H. Kawano, *Bull. Chem. Soc. Jpn.*, 65 (1992) 3027.
146. S.P. Satsangee, J.H. Hain, Jr, P.T. Cooper and S.A. Koch, *Inorg. Chem.*, 31 (1992) 5160.
147. K. Krogh-Jespersen, X. Zhang, Y. Ding, J.D. Westbrook, J.A. Potenza and H.J. Schugar, *J. Am. Chem. Soc.*, 114 (1992) 4345.
148. T.J. Haas and U.T. Mueller-Westerhoff, *Synth. React. Inorg. Met.- Org. Chem.*, 22 (1992) 227.
149. F. Teixidor, J.A. Ayllon, C. Vinas, R. Kivekas, R. Sillanpoa and J. Casabo, *J. Chem. Soc., Chem. Commun.*, (1992) 1281.
150. M. Paulus and G. Thiele, *Z. Naturforsch., B: Chem. Sci.*, 47 (1992) 253.
151. L. Ballester, O. Esteban, A. Gutierrez, M.F. Perpinan, C. Ruiz-Valero, E. Gutierrez-Puebla and M.J. Gonzalez, *Polyhedron*, 11 (1992) 3173.
152. R. Prasad and U.C. Agarwala, *Polyhedron*, 11 (1992) 1117.
153. M. Kawano, T. Watanabe and K. Matsumoto, *Chem. Lett.*, (1992) 2389.
154. V. Bierbach, W. Barklage, W. Saak and S. Pohl, *Z. Naturorsch., B: Chem. Sci.*, 47 (1992) 1593.
155. H. Vemura, M. Kawano, T. Watanabe, T. Matsumoto and K. Matsumoto, *Inorg. Chem.*, 31 (1992) 5137.
156. S. Pacor, G. Sava, G. Mestroni and E. Alessio, *Pharmacol. Res.*, 25 (Suppl.1) (1992) 73.
157. G. Esposito, S. Cauci, F. Fogolari, E. Alessio, M. Scocchi, F. Quadrifoglio and P. Viglino, *Biochemistry*, 31 (1992) 7094.
158. R.S. Srivastava, B. Milan, E. Alessio and G. Mestroni, *Inorg. Chim. Acta*, 191 (1992) 15.
159. E. Alessio, B. Milan, M. Calligaiis and N. Bresciani-Pahon, *Inorg. Chim. Acta*, 194 (1992) 85.
160. J.S. Jaswal, D.T.T. Yapp, S.J. Rettig, B.R. James and K.A. Skov, *J. Chem. Soc., Chem. Commun.*, (1992) 1528.
161. A.J. Blake, R.M. Christie, Y.V. Roberts, M.J. Sullivan, M. Schröder and L.J. Yellowlees, *J. Chem. Soc., Chem. Commun.*, (1992) 848.
162. D.R. Baghurst and D.M.P. Mingos, J. *Chem. Soc., Dalton Trans.*, (1992) 1151.
163. A.J. Blake, G. Reid and M. Schröder, *Polyhedron*, 11 (1992) 2501.
164. P. Bernhard, D.J. Bull, W.T. Robinson and A.M. Sargeson, *Aust. J. Chem.*, 45 (1992) 1241.
165. J.R. Dilworth, Y. Zheng, S. Lu and Q. Wu, *Transition. Metal Chem, (London)*, 17 (1992) 364.
166. T. Singh and J.P. Singh, *J. Indian. Chem. Soc.*, 69 (1992) 158.
167. M.C.J. Harris and A.F. Hill, *J. Organomet. Chem.*, 438 (1992) 209.
168. R. Ballardini, M.T. Gandolfi, M.L. Moya, L. Prodi and V. Balzani, *Isr. J. Chem.*, 32 (1992) 47.
169. S. Umapathy and R.E. Hester, *Springer Proc. Phys.*, 68(Time-Resolved Vib. Spectrosc. V) (1992) 121.
170. S. Kuwabata, K. Mitsui and H. Yoneyama, *J. Electrochem. Soc.*, 139(1992) 1824.
171. R. Hage, J. G. Haasnoot, J. Reedijk and J.G. Vos, *Chemtracts: Inorg. Chem*, 4 (1992) 75.

172. R.G. Bulgakov, V.N. Yakovlev, S.P. Kuleshov, G.Y. Maistrenko, A.N. Petrov, G.A. Tolstikov and V.P. Kazakov, *Mendeleev Commun.*, (3) (1992) 84.
173. J.K. Nagle and D.M. Roundhill, *Chemtracts: Inorg. Chem.*, 4 (1992) 141.
174. Y. Kurimura, Y. Sairenchi and S. Nakayama, *Makromol. Chem., Macromol. Symp.* 59 (Int. Symp. Macromol.-Met. Complexes, 4th 1991), (1992) 199; *Chem. Abstr.* 118 (1993) 22757j.
175. C. Duan, L. Zhu and X. You, *Huaxue Xuebao*, 50 (1992) 715.
176. C. Duan, X. Xia, L. Zhu, J. You and H. Cao, *Gaodeng Xuexiao Huaxue Xuebao*, 13 (1992) 576.
177. K.O. Zahir and A. Haim, *J. Photochem. Photobiol.*, A, 63 (1992) 167.
178. J. Samuel, M. Ottolenghi and D. Avnir, *Physica A*, 191 (1992) 153; *Chem. Abstr.*, 118 (1993) 157618k.
179. O. Dvorak, A.H. De Armond and M.K. De Armond, *Langmuir*, 8 (1992) 508.
180. P.K. Dutta and W. Turbeville, *J. Phys. Chem.*, 96 (1992) 9410.
181. Y.I. Kim and T.E. Mallouk, *J. Phys. Chem.*, 96 (1992) 2879.
182. Y. Xiang, G. Villemure and C. Detellier, *Clays Clay Miner.*, 40 (1992) 362; *Chem. Abstr.*, 118 (1993) 128512r.
183. T. Nilsson, *Proc. Natl. Acad. Sci. U.S.A.*, 89 (1992) 6497; *Chem. Abstr.*, 117 (1992) 166538r.

184. J. Degen, K. Reinecke and H.H. Schmidtke, *Chem. Phys.*, 162 (1992) 419.
185. W. Turbeville, D.S. Robins and P.K. Dutta, *J. Phys. Chem.*, 96 (1992) 5024.
186. M. Biner, H.B. Buergi, A. Ludi and C.Roehr, *J. Am. Chem. Soc.*, 114 (1992) 5197.
187. T. Matsuo, H. Nakamura, T. Nakao and M. Kawazu, *Chem. Lett.*, (1992) 2363.
188. M. Ogawa, M. Inagaki, N. Kodama, K. Kuroda and C. Kato, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A.*, 216 (1992) 141.
189. S.J. Stoessel and J.K. Stille, *Macromolecules*, 25 (1992) 1832.
190. S. Yamamura, Y. Tatsu, S. Yoshikawa and T. Yazawa, *J. Photochem. Photobiol., A*, 63 (1992) 87.
191. K. Nagai, N. Nemoto, Y. Ueno, K. Ikeda and N. Takamiya, *Makromol. Chem., Macromol. Symp.*, 59 (1992) 257.
192. M. Kaneko, Makromol. Chem, *Macromol. Symp.* 59 (Int. Symp. Macromol-Met. Complexes, 4th (1991) (1992) 183.
193. J.E. Bartelt, S.M. Drew and R.M. Wightman, *J. Electrochem. Soc.*, 139 (1992) 70.
194. D.J. Waltor, S.S. Phull, D.M. Bates, J.P. Lorimer and T.J. Mason, *Ultrasonics*, 30 (1992) 186.
195. M. Kaneko, S. Teratani and K. Harashima, *J. Electroanal. Chem.*, 325(1992) 325.
196. Z. Samec, A. Trojanek and P. Vanysek, *J. Electroanal. Chem.*, 332 (1992) 349.
197. P.K. Srivastava, Y. Mori and I. Hanazaki, *Chem. Phys. Lett.*, 190 (1992) 279.
198. M. Jinguji, M. Ishihara and T. Nakazawa, *J. Phys. Chem.*, 96 (1992) 4279.
199. H.R. Weigt, *Angew. Chem.*, 104 (1992) 358.
200. S. Lingamurthy, B. Sethuram and T.N. Rao, *Transition Metal Chem., (London)*, 17 (1992) 506.
201. C. Senaratne and K.W. Hanck, *J. Electroanal. Chem.*, 338 (1992) 31.
202. M. Fujihira, M. Yanagisawa, T. Kondo and K. Suga, *Thin Solid Films*, 210 (1992) 265.
203. M. Yagi, K. Okajima and Y. Kurimura, *J. Chem. Soc., Faraday Trans.*, 88 (1992) 1411.
204. K.V. Gobi and R. Ramaraj, *J. Chem. Soc., Chem. Commun.*, (1992) 1436.
205. G.I. Elizarova, L.G. Matvienko, O.P. Taran, V.N. Parmon and V.N. Kolomiichuk, *Kinet. Catal.*, 33 (1992) 898.
206. K. Okada, K. Okubo, N. Morita and M. Oda, *Tetrahedron Lett.*, 33 (1992) 7377.
207. B. Schwederski and W. Kaim, *Inorg. Chim. Acta,* 195 (1992) 123.
208. D. Mallick and G.S. De, *Bull. Chem. Soc. Jpn.*, 65 (1992) 609.
209. D. Mallick and G.S. De, *Transition Metal Chem.*, 17 (1992) 34.
210. D. Mallick and G.S. De, *Transition Metal Chem.*, 17 (1992) 491.
211. D. Mallick and G.S. De, *Transition Metal Chem.*, 17 (1992) 521.
212. W.F. DeGiovani and A. Deronzier, *J. Chem. Soc., Chem. Commun.*, (1992) 1461.
213. J.M. Fisher, A. Fulford and P.S. Bennett, *J. Mol. Catal.*, 77 (1992) 229.
214. A.W. Cordes, B. Durham, W.T. Pennington, B. Kuntz and L. Allen, *J. Crystallog. Spectrosc. Res.*, 22 (1992) 699.
215. C.A. Bignozzi, R. Argazzi, C.G. Garcia, F. Scandola, J.R. Schoonover and T.J. Meyer, *J. Am. Chem. Soc.*, 114 (1992) 8727.
216. K. Kalyanasundaram, M. Graetzel and M.K. Nazeeruddin, *Inorg. Chem.* 31(1992) 5243.
217. K. Matsui, M.K. Nazeeruddin, R. Humphey-Baker, M. Graetzel and K. Kalyanasundaram, *J. Phys. Chem.*, 96 (1992) 10587.
218. Z. Lei and Y. Wang, Chin. Chem. Lett., 3 (1992) 267.
219. P.S. Braterman, J.I. Song and R.D. Peacock, *Spectrochim. Acta, Part A*, 48 (1992) 899.

220. G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano and V. Balzani, Perspect. *Coord. Chem.*, (1992) 153.
221. G. Giuffrida, V. Ricevuto, G. Guglielimo, S. Campagna and M. Ciano, *Inorg. Chim. Acta*, 194 (1992) 23.
222. A.L. Crumbliss, S.C. Perine, A.K. Edwards and D.P. Rillema, *J. Phys. Chem.*, 96 (1992) 1388.
223. M. Kakoti, A.K. Deb and S. Goswami, *Inorg. Chem.*, 31 (1992) 1302.
224. T. Tsubomura, O. Igarashi and M. Morita. *Chem. Lett.*, (1992) 385.
225. D.P. Rillema, D.S. Jones, C. Woods and H.A. Levy, *Inorg. Chem.*, 31(1992) 2935.
226. K. Aoki, K. Kumazawa and Y. Ohsawa, *Thin Solid Films*, 213 (1992) 295.
227. R. Grigg and W.D.J.A. Norbert, *J. Chem. Soc., Chem. Commun.*, (1992) 1300.
228. K. Araki, M. Fuse, N. Kishii and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1220.
229. Y.Z. Yousif and J.M.A. Al-Rawi, *Polyhedron*, 11 (1992) 1411.
230. E.H. Yonemoto, R.L. Riley, Y.I. Kim, S.J. Atherton, R.H. Schmehl and T.E. Mallouk, *J. Am. Chem. Soc.*, 114 (1992) 8081.
231. N. Egashira, N. Kondoh, Y. Kurauchi and K. Ohga, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* , 60 (1992) 1148; *Chem. Abstr.*, 118 (1993) 138902g.
232. C.P. Horwitz and Qi Zuo, *Inorg. Chem.*, 31 (1992) 1607.
233. T. Yamamoto, Y. Yoneda and T. Maruyama, *J. Chem. Soc., Chem Commun.*, (1992) 1652.
234. K. Kalyanasundaram and M.K. Nazeeruddin, *Chem. Phys. Lett.*, 193 (1992) 292.
235. M. Kaneko, S. Iwahata and T. Asakura, *Photochem. Photobiol.*, 55 (1992) 505; *Chem. Abstr.*, 116 (1992) 204228d.
236. M. Furue, K. Maruyama, T. Oguni, M. Naiki and M. Kamachi, *Inorg. Chem.*, 31 (1992) 3792.
237. S.M. Zakeeruddin, D.M. Fraser, M.K. Nazeeruddin and M. Graetzel, *J. Electroanal Chem.*, 337 (1992) 253.
238. A. Das, J.A. McCleverty, M.D. Ward, C.J. Jones and A.M.W. Thompson, *Polyhedron*, 11 (1992) 2119.
239. H. Mihara, N. Nishino, R. Hasegawa, T. Fujimoto, S. Usui, H. Ishida and K. Ohkubo, *Chem Lett.*, (1992) 1813.
240. J.F. Roland and F.C. Anson, *J. Electroanal. Chem.*, 336 (1992) 245.
241. C.P. Lau and L. Cheng, *Inorg. Chim. Acta*, 195 (1992) 133.
242. T. Nagamura, H. Sakaguchi and T. Matsuo, *Thin Solid Films*, 210-211 (1992) 160.
243. S. Bossmann and H. Duerr, *New J. Chem.*, 16 (1992) 769.
244. K. Kalyanasundaram, M.K. Nazeeruddin, M. Graetzel, G. Viscardi, P. Savarino and E. Barni, *Inorg. Chim. Acta*, 198 (1992) 831.
245. J.H. Schott, C.R. Arana, H.D. Abruna, H.H. Petach, C.M. Elliott and H.S. White, *J. Phys. Chem.*, 96 (1992) 5222.
246. S. Tachiyashiki, K. Nakamaru and K. Mizumachi, *Chem. Lett.*, (1992) 1119.
247. R.E. Des Enfants, II, T.A. Martinez and M.K. De Armond, *ACS Symp. Ser.*, 499 (1992) 46.
248. S. Gould, K.H. Gray, R.W. Linton and T.J. Meyer, *Inorg. Chem.*, 31 (1992) 5521.
249. E. Fujita, S.J. Milder and B.S. Brunschwig, *Inorg. Chem.*, 31 (1992) 2079.
250. S.C. Rawle, P. Moore and N.W. Alcock, *J. Chem. Soc., Chem. Commun*, (1992) 684.
251. M. Graetzel, D. Fraser, M.K. Nazeeruddin and S.H. Zakeeruddin, *Chem. Abstr.*, 118 (1993) 224387z.
252. S.L. Larson, L.F. Cooley, C.M. Elliott and D.F. Kelley, *J. Am. Chem. Soc.*, 114 (1992) 9504.
253. M.A. Hayes, C. Meckel, E. Schatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 703.
254. W.F. De Giovani and A. Deronzier, *J. Electroanal. Chem.*, 337 (1992) 285.
255. A.D. Baker, R.J. Morgan and T.C. Strekas, *J. Chem. Soc., Chem. Commun.*,(1992) 1099.
256. D.P. Rillema, C.B. Blanton, R.J. Shaver, D.C. Jackman, M. Boldaji, S. Bundy, L.A. Worl and T.J. Meyer, *Inorg. Chem.*, 31 (1992) 1600.
257. R. Wang, J.G. Vos, R.H. Schmehl and R. Hage, *J. Am. Chem. Soc.*, 114(1992) 1964.
258. B.E. Buchanan, P. Degn, J.M.P. Velasco, H.Hughes, B.S. Creaven, C. Long, J.G. Vos, R.A. Howie and R. Hage, *J. Chem. Soc., Dalton Trans.*, (1992) 1177.
259. B.M. Holligan, J.C. Jeffery, M.K. Norgett, E. Schatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 3345.
260. E.C. Constable and L.R. Sousa, *J. Organomet. Chem.*, 427 (1992) 125.
261. M. Krejcik and A.A. Vleek, *Inorg. Chem.*, 31 (1992) 2390.
262. T.J. O'Shea, D. Leech, M.R. Smyth and J.G. Vos, *Talanta*, 39 (1992) 443.
263. V.R.L. Constantino, H.E. Toma, L.F.C. De Oliveira and P.S. Santos, *J. Raman Spectrosc.*, 23 (1992) 629.
264. H. Tanaka, H. Nagao and K. Tanaka, *Inorg. Chem.*, 31 (1992) 1971.

265. M.R.M. Bruce, E. Megehee, B.P. Sullivan, H.H. Thorp, T.R. O'Tode, A. Downard, J.R. Pugh and T.J. Meyer, *Inorg. Chem.*, 31 (1992) 4864.
266. H. Tanaka, B.C. Tzeng, H.Nagao, S.M. Peng and K. Tanaka, *Organometallics*, 11 (1992) 3171.
267. S. Rajagopal, G.A. Gnanaraj, A. Mathew and C. Srinivasan, *J. Photochem. Photobiol., A*, 69 (1992) 83.
268. M.A. Ollino and A.J. Rest, *J. Photochem. Photobiol. A*, 69 (1992) 73.
269. K.Y. Wong, C.M. Che, C.K. Li, W.H. Chiu, Z.Y. Zhou and T.C.W. Mak., *J. Chem. Soc., Chem. Commun.*, (1992) 754.
270. G.F. Strouse, P.A. Anderson, J.R. Schoonover, T.J. Meyer and F.R. Keene, *Inorg. Chem.*, 31 (1992) 3004.
271. P.D. Beer, O. Kocian, R.J. Mortimer and C. Ridgway, *Analyst*, 117 (1992) 1247.
272. L. Hammarstroem, M. Almgren and T. Norrby, *J. Phys. Chem.*, 96(1992) 5017.
273. T.I. Tikhomirova, V.I. Fadeeva and G.V. Kudryavtsev, *Anal. Chim. Acta*, 257 (1992) 109.
274. K.C. Yung, T.M. Vess and M.L. Myrick, NATO ASI Ser., Ser. C, 374 (Phys, Chem. Finite Syst.: Clusters Cryst., Vol(2) (1992) 1171; *Chem. Abstr.*, 119:15800k.
275. M.F. Ottaviani, N.D. Ghatlia and N.J. Turro, *J. Phys. Chem.*, 96 (1992) 6075.
276. M. Eriksson, M. Leijon, C. Hiort, B. Norden and A. Graeslund, *J. Am. Chem. Soc.*, 114 (1992) 4933.
277. S. Satyanarayana, J. C. Dabrowiak and J.B. Chaires, *Biochemistry*, 31(1992) 9319.
278. A. Yamagishi, H. Makino, Y. Nakamura and H. Sato, *Clays Clay Miner.*, 40(1992) 359; *Chem. Abstr.*, 118 (1993) 115765a.
279. R.B. Rexwinkel, S.C.J. Meskers, J.P. Riehl and H.P.J.M. Dekkers, *J. Phys. Chem.*, 96 (1992) 1112.
280. K.A. Carrado, Ind. Eng. Chem. Res., 31 (1992) 1654; *Chem. Abstr.*, 117 (1992) 38923a.
281. M.F. Ottaviani, N.D. Ghatlia, S.H. Bossmann, J.K. Barton, H. Duerr and N.J. Turro, *J. Am. Chem. Soc.*, 114 (1992) 8946.
282. E. Kimura, X. Bu, M. Shionoya, S. Wada and S. Maruyama, *Inorg. Chem.*, 31 (1992) 4542.
283. Y. Jenkins, A.E. Friedman, N.J. Turro and J.K. Barton, *Biochemistry*, 31 (1992) 10809.
284. R.M. Hartshorn and J.K. Barton, *J. Am. Chem. Soc.*, 114 (1992) 5919.
285. Y. Jenkins and J.K. Barton, *J. Am. Chem. Soc.*, 114 (1992) 8736.
286. J.P. LeComte, A. Kirsch-De Mesmaeker, J.M. Kelly, A.B. Tossi and H. Gorner, *Photochem. Photobiol.*, 55 (1992) 681.
287. P. Didier, L. Jacquet, A. Kirsch-De Mesmaeker, R. Hurber and A. Van Dorsselaer, *Inorg. Chem.*, 31 (1992) 4803.
288. S.E.J. Bell, K.C. Gordon, J.J. McGarvey, D.I.C. Martin, A. Kirsch-De Mesmaeker and J.P. Lecomte, *Springer Proc. Phys.*, 68 (1992) 113.
289. L. Jacquet and A. Kirsch-De Mesmaeker, *J. Chem. Soc., Faraday Trans.*, 88 (1992) 2471.
290. T. Yoshida, T. Shirasagi and M. Keneko, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, 60 (1992) 1108.
291. A. Pramanik, N. Bag and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 97.
292. N. Grover, N. Gupta, P. Singh and H.H. Thorp, *Inorg. Chem.*, 31 (1992) 2014.
293. E.C. Constable and A.M.W.C. Thompson, *J. Chem. Soc., Chem. Commun.*, (1992) 617.
294. E.C. Constable and A.M.W.C. Thompson, N. Armaroli, V. Balzani, M. Maestri, *Polyhedron*, 11 (1992) 2707.
295. E.C. Constable and A.M.W.C. Thompson, *J. Chem. Soc., Dalton Trans.*, (1992) 3467.
296. J.C. Chambron and C. Coudret, J.-P. Sauvage, *New. J. Chem.*, 16 (1992) 361.
297. J.D. Crane and J.-P. Sauvage, *New J. Chem.*, 16 (1992) 649.
298. T. Shimomura, N. Koyama and H. Yamaguchi, *Chem. Abstr.*, 117 (1992) 193327c.
299. T. Togano, N. Nagao, M. Tsuchida, H. Kumakura, K. Hisamatsu, F.S. Howell and M. Mukaida, *Inorg. Chim. Acta*, 195 (1992) 221.
300. H.J. McCarthy and D.A. Tocher, *Polyhedron*, 11 (1992) 13.
301. B. Mahanti and G.S. De, *Transition Metal Chem.*, 17 (1992) 23.
302. B. Mahanti and G.S. De, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1626.
303. M. Kato, K. Sasano, M. Kimura and S. Yamauchi, *Chem. Lett.*, (1992) 1887.
304. M.S. Islam and M.M. Uddin, Pak. *J. Sci. Ind. Res.*, 35 (1992) 118; *Chem. Abstr.*, 118 (1993) 93168d.
305. I. de S. Moreira and D.W. Frauco, *J. Chem. Soc., Chem. Commun.*, (1992) 450.
306. M.S. Islam and M.M. Uddin, *Synth. React. Inorg. Met-Org. Chem.*, 22 (1992) 1303.
307. M.M.T. Khan, N.H. Khan and R.I. Kureshy, *Tetrahedron: Asymmetry*, 3 (1992) 307.
308. S. Choudhury, M. Kakoti, A.K. Deb and S. Goswami, *Polyhedron*, 11(1992) 3183.

309. M.J. Upadhyay, P.K. Bhattacharya, P.A. Ganeshpure and S. Satish, *J. Mol. Catal.*, 73 (1992) 277.
310. M.M.T. Khan, N.M. Khan, R.I. Kureshy and K. Venkatasubramanian, *Polyhedron*, 11 (1992) 431.
311. R. Dash and P.G. Potvin, *Can. J. Chem.*, 70 (1992) 2249.
312. S. Mahapatra and R. Mukherjee, *J. Chem. Soc., Dalton. Trans.*, (1992) 2337.
313. R. Prasad and U.C. Agarwala, *Bull. Chem. Soc. Jpn.*, 65 (1992) 3398.
314. K. Onishi, K. Ikemoto and K. Hiraki, *Nippon Kaguku Kaishi*, (5) (1992) 570; *Chem. Abstr.*, 116 (1992) 267933a.
315. N.Y. Sun and S.J. Simpson, *J. Organomet. Chem.*, 434 (1992) 341.
316. F.A. Cotton, Y. Kim and T. Ren, *Inorg. Chem.*, 31 (1992) 2608.
317. G.D. Danzer and J.R. Kincaid, *J. Raman Spectrosc.* 23 (1992) 681.
318. O. Dvorak, A.H. De Armond and M.K. De Armond, *Langmuir*, 8 (1992) 955.
319. G.D. Danzer and J.R. Kincaid, *Springer Proc. Phys.*, 68 (1992) 117.
320. A. Broo and S. Larsson, *Chem. Phys.*, 161 (1992) 363.
321. J.T. Hupp, G.A. Neyhart, T.J. Meyer and E.M. Kober, *J. Phys. Chem.*, 96 (1992) 10820.
322. S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano and V. Balzani, *Angew. Chem., Int. Edn Engl.*, 31 (1992) 1493.
323. S. Campagna, G. Denti, S. Serroni, M. Ciano, A. Juris and V. Balzani, *Inorg. Chem.*, 31 (1992) 2982.
324. G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 114 (1992) 2944.
325. G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 114 (1992) 7326.
326. G. Denti, S. Serroni, S. Campagna, V. Ricevuto, A. Juris, M. Ciano and V. Balzani, *Inorg. Chim. Acta*, 198 (1992) 507.
327. S. Serroni and G. Denti, *Inorg. Chem.*, 31 (1992) 4251.
328. M.M. Richter and K.J. Brewer, *Inorg. Chem.*, 31 (1992) 1594.
329. K. Kalyanasundaram, M. Graetzel and M.K. Nazeeruddin, *J. Phys. Chem.*, 96 (1992) 5865.
330. J.F. Wishart, X. Zhang, S.S. Isied, J.A. Potenza and H.J. Schugar, *Inorg. Chem.*, 31 (1992) 3179.
331. G. Sava, S. Pacor, G. Mestroni and E. Alessio, *Anti-Cancer Drugs*, 3 (1992) 25; *Chem. Abstr.*, 116 (1992) 247973k.
332. G. Sava, S. Pacor, G. Mestroni and E. Alessio, *Clin. Exp. Metastasis*, 10 (1992) 273.
333. D.S. Wuttke, M.J. Bjerrum, I.J. Chang, J.R. Winkler and H.B. Gray, *Biochim. Biophys. Acta*, 1101 (1992) 168; *Chem. Abstr.*, 118 (1993) 18166y.
334. T. Ohno, K. Nozaki and M. Haga, *Inorg. Chem.*, 31 (1992) 548.
335. T. Ohno, K. Nozaki and M. Haga, *Inorg. Chem.*, 31 (1992) 4256.
336. K. Nazaki, T. Ohno and M. Haga, *J. Phys. Chem.*, 96 (1992) 10880.
337. M.A. Esteruelas, M.P. Garcia, A.M. Lopez and L.A. Oro, *Organometallics*, 11 (1992) 702.
338. H. Duerr, R. Schwarz, I. Willner, E. Joselevich and Y. Eichen, *J. Chem. Soc., Chem. Commun.*, (1992) 1338.
339. G. Orellana, M.C. Moreno-Bondi, E. Segovia and M.D. Marazuela, *Anal. Chem.*, 64 (1992) 2210.
340. J.H. Van Diemen, R. Hage, J.G. Haasnoot, H.E.B. Lempers, J. Reedijk, J.G. Vos, L. De Cola, F. Barigelletti and V. Balzani, *Inorg. Chem.*, 31 (1992) 3518.
341. J. Cartwright and A.F. Hill, *J. Organomet. Chem.* 429 (1992) 229.
342. A. Morales, M.I. Toral, P. Richter and M. Silva, *Anal. Lett.*, 25 (1992) 1765.
343. A. Corma, M. Iglesias, C. Del. Pino and F. Sanchez, *J. Organomet. Chem.*, 431 (1992) 233.
344. E.M. Ryan, R.O' Kennedy, M.M. Feeney, J.M. Kelly and J.G. Vos, *Bioconjugate Chem.*, 3 (1992) 285.
345. H.B. Gray and J.R. Winkler, *Pure Appl. Chem.*, 64 (1992) 1257.
346. W.S. Sheldrick and R. Exner, *Inorg. Chim. Acta*, 195 (1992) 1.
347. J.F. Wishart, R. Van Eldik, J. Sun, C. Su and S.S. Isied, *Inorg. Chem.*, 31 (1992) 3986.
348. M.R. Ghadii, C. Soares and C. Choi, *J. Am. Chem. Soc.*, 114 (1992) 4000.
349. E.D. Kreuser, B.K. Keppler, W.E. Berdel, A. Piest and E. Thiel, *Semin. Oncol*, 19(2, Suppl. 3), (1992) 73; *Chem. Abstr.*, 117 (1992) 39922m.
350. R. Santana da Silva and E. Tfonni, *Inorg. Chem.*, 31 (1992) 3313.
351. J.P. Collman, J.M. Garner, R.T. Hembre and Y. Ha, *J. Am. Chem. Soc.*, 114 (1992) 1292.
352. J.S. Huang, C.M. Che, Z.Y. Li and C.K. Poon, *Inorg. Chem.*, 31 (1992) 1313.
353. J.P. Launay and V. Marvaud, *AIP Conf. Proc.*, 262 (Mol. Electron: Sci Technol) (1992) 118.

354. J.W. Seyler, L.K. Safford, P.E. Fanwick and C.R. Leidner, *Inorg. Chem.*, 31 (1992) 1545.
355. J.W. Seyler, P.E. Fanwick and C.R. Leidner, *Inorg. Chem.*, 31 (1992) 3699.
356. J.W. Seyler, L.K. Safford and C.R. Leidner, *Inorg. Chem.*, 31 (1992) 4300.
357. J.S. Huang, C.M. Che, and C.K. Poon, *J. Chem. Soc., Chem. Commun.*, (1992) 161.
358. C. Geze, N. Legrand, A. Bondon and G. Simonneaux, *Inorg. Chim. Acta*, 195 (1992) 73.
359. H. Ohtake, T. Higuchi and M. Hirobe, *J. Am. Chem. Soc.*, 114 (1992) 10660.
360. T. Hamada, H. Ishida, M. Kuwada and K. Ohkubo, *Chem. Lett.*, (7) (1992) 1283.
361. M. Hanack and Y.G. Kang, *Synth. Met.*, 48 (1992) 79.
362. J.P. Collman, J.E. Hutchison, M.S. Ennis, M.A. Lopez and R. Guilard, *J. Am. Chem. Soc.* 114 (1992) 8074.
363. J.P. Collman, J.E. Hutchison, M.A. Lopez and R. Guilard, *J. Am. Chem. Soc.*, 114 (1992) 8066.
364. S. Basak, C.S.C. Bose and K. Rajeshwar, *Anal. Chem.*, 64 (1992) 1813.
365. E. John, H.J. Schugar and J.A. Poteuza, *Acta Crystallogr., Sect. C*, 48 (1992) 1574.
366. M.D. Johnson, V.C. Reinsborough and S. Ward, *Inorg. Chem.*, 31 (1992) 1085.
367. I. Ando, D. Ishimura, M. Mitsumi, K. Ujimoto and H. Kurihara, *Polyhedron*, 11 (1992) 2335.
368. M.H. Chou, B.S. Brunschwig, C. Creutz, N. Sutin, A. Yeh, R.C. Chang and C.T. Lin, *Inorg. Chem.*, 31 (1992) 5347.
369. Z. Novais da Rocha and E. Tfouni, *Polyhedron*, 11 (1992) 2375.
370. H. Van Ryswyk, B.J. Hinds III, B.L. Simmons and D.S. Solomon, *J. Electrochem. Soc.*, 139 (1992) 3098.
371. Y.S. Obeng, M.E. Laing, A.C. Friedli, H.C. Yang, D. Wang, E.W. Thulstrup, A.J. Bard and J. Michl, *J. Am. Chem. Soc.*, 114 (1992) 9943.
372. C. Shi and F.C. Anson, *Inorg. Chem.*, 31 (1992) 5078.
373. D. Pang and Z. Wang, *J. Electroanal. Chem.*, 340 (1992) 35.
374. A.J. Bard, M.V. Mirkin, P.R Unwin and D.O. Wipf, *J. Phys. Chem.*, 96 (1992) 1861.
375. M.V. Mirkin and A.J. Bard, *J. Electrochem. Soc.*, 139 (1992) 3535.
376. R.L. Birke and Z. Huang, *Anal. Chem.* 64 (1992) 1513.
377. T. Okajima, T. Ohsaka, O. Hatozaki and N. Oyama, *Electrochim. Acta*, 37 (1992) 1865.
378. P. de S. Kaviratna and T.J. Pinnavaia, *J. Electroanal. Chem.*, 332 (1992) 135.
379. H. Hagiwara, *Histochemistry*, 98 (1992) 305.
380. E. B. Hunziker, A. Ludi and W. Herrmann, *J. Histochem. Cytochem.*, 40(1992) 909.
381. W. Zou and R.D. Gonzalez, *Catal. Today*, 15 (1992) 443.
382. J.P. Verduijn, *Chem. Abstr.*, 117 (1992) 29192j.
383. W. Mahdi, U. Sauerlandt, J. Wellenbuescher, J. Schuetze, M. Muhler, G. Ertl and R. Schloegl, *Catal. Lett.*, 14 (1992) 339.
384. P.A. Reynolds, C.D. Delfs, B.N. Figgis, L.M. Engelhardt, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, (1992) 2029.
385. D.W. Franco, *Coord. Chem. Rev.*, 119 (1992) 199.
386. E.C. Kesslen and W.B. Euler, *Polyhedron*, 11 (1992) 3109.
387. S.K. Doorn, P.O. Stoutland, R.B. Dyer and W.H. Woodruff, *J. Am. Chem. Soc.*, 114 (1992) 3133.
388. C.A. Bignozzi, R. Argazzi, J.R. Schoonover, K.C. Gordon, R.B. Dyer and F. Scandola, *Inorg. Chem.*, 31 (1992) 5260.
389. Y. Dong and J.T. Hupp, *Inorg. Chem.*, 31 (1992) 3170.
390. Y. Dong and J.T. Hupp. *Inorg. Chem.*, 31 (1992) 3322.
391. J.R. Schoonover, C.J. Timpson, T. J. Meyer and C.A. Bignozzi, *Inorg. Chem.*, 31 (1992) 3185.
392. J.A. Roberts, J.C. Babel, M.L. Absi and J.T. Hupp, *J. Am. Chem. Soc.*, 114 (1992) 7957.
393. M.A.S. Aquino, F.L. Lee, E.J. Gabe, C. Benrimon, J.E. Greedan and R.J. Crutchley, *J. Am. Chem. Soc.*, 114 (1992) 5130.
394. Y. Hoshino, F. Okuyama, A. Nanba, K. Shimizu and G.P. Sato, *Bull. Chem. Soc. Jpn.*, 65 (1992) 876.
395. C.M. Che. T.C. Lai, C.K. Poon, J. Grahtham and T.G. Richmond, *Inorg. Synth.*, 29 (1992) 164.
396. A.M. Salam, H.A. Samha, H.A. Hodali and A.M. Seyam, *Synth. React. Inorg. Met-Org. Chem.*, 22 (1992) 805.
397. J.A. Cabeza, J.M. Fernandez-Colinas, S. Garcia-Granda, V. Riera and J.F. Van der Maelen, *Inorg. Chem.*, 31 (1992) 1233.
398. J.A. Broohead and N.A. Pasha, *Transition Metal Chem.*, 17 (1992) 209.
399. M.M. T. Khan, K. Venkatasubramanian, Z. Shirin and M.M. Bhadbhade, *J. Chem. Soc., Dalton Trans.*, (1992) 1031.

400. O. Heyke, G. Beuter and I.-P.Lorenz, *J. Organomet. Chem.*, 440 (1992) 197.
401. I.M. Lee, D.W. Meek and J. Gallucci, *Bull. Korean Chem. Soc.*, 13 (1992) 498.
402. W. Odenkirk, A.L. Rheingold and B. Bosnich, *J. Am. Chem. Soc.*, 114 (1992) 6392.
403. W. Odenkirk, J. Whelan and B. Bosnich, *Tetrahedron Lett.*, 33 (1992) 5729.
404. A.A. Levin, *J. Mol. Struct.*, 272 (1992) 133.
405. R. Zarhloul, R. Faure and J.P. Deloume, *J. Crystallogr. Spectosc. Res.*, 22 (1992) 601.
406. T. Togano, H. Kuroda, N. Nagao, Y. Maekawa, H. Nishimura, F.S. Howell and M. Mukaida, *Inorg. Chim. Acta*, 196 (1992) 57.
407. K.Y. Wong, C.M. Che, W.H. Yip, R.J. Wang and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1992) 1417.
408. A. J. Blake, R.O. Gould, B.F.G. Johnson and E. Parisini, *Acta Crystallogr, Sect. C:*, C48 (1992) 982.
409. R. Maggiore, C. Crisafulli, S. Scire, L. Solarino and S. Galvagno, *React. Kinet. Catal. Lett.*, 48 (1992) 367.
410. M. Guglielmi, P. Colombo, V. Rigato, G. Battaglin, A. Boscolo-Boscoletto and A. DeBattisti, *J. Electrochem. Soc.*, 139 (1992) 1655.
411. Z. Wei, Z. Hou, X. Li and Qin Xin, *Ranliao Huaxue Xuebao*, 20 (1992) 19; *Chem. Abstr.*, 117 (1992) 215840u.
412. K.C. Jain, U.C. Agarwala, T.W. Dekleva, P. Legzdins and J.C. Oxley, *Inorg. Synth.*, 29 (1992) 161.
413. M.M.T. Khan, R.C. Bhardwaj, C. Bhardwaj and N.N. Rao, *J. Photochem. Photobiol., A*, 68 (1992) 137.
414. M. Kawano, C. Hoshino, K. Matsumoto, *Inorg. Chem.*, 31 (1992) 5158.
415. I.B. Talanina, M.A. Collins, L. Dubicki and E. Krausz, *Chem. Phys. Lett.*, 200 (1992) 318.
416. M.J.A. Kraakman, K. Vrieze, H. Kooijman and A.L. Spek, *Organometallics*, 11 (1992) 3760.
417. A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *Polyhedron*, 11 (1992) 2961.
418. T. Clark and S.D. Robinson, *Polyhedron*, 11 (1992) 993.
419. T. Clark, S.D. Robinson and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1992) 3199.
420. F.A. Cotton, L.R. Falvello, T. Ren and K. Vidyasagar, *Inorg. Chim. Acta*, 194 (1992) 163.
421. C. Bianchini, P. Innocenti, D. Masi, M. Peruzzini and F. Zanobini, *Gazz. Chim. Ital.* 122 (1992) 461 Chem. Abstr., 118 (1993) 203976a.
422. M.M.T. Khan and Z.A. Shaikh, *Indian J. Chem., Sect.A.*, 31 (1992) 191; *Chem. Abstr.*, 116 (1992) 186629d.
423. Z. Shirin and R.N. Mukherjee, *Polyhedron*, 11 (1992) 2625.
424. R.C. Maurya, D.D. Mishra and N.S. Rao, *Polyhedron*, 11 (1992) 2837.
425. M.M.T. Khan, Z.A. Shaikh, R.I. Kureshy and A.B. Boricha, *Polyhedron*, 11 (1992) 91.
426. M.M.T. Khan, S.A. Mizra, Z.A. Shaikh, C. Sreelatha, P. Paul, R.S. Shukla, D. Srinivas, A.P. Rao and S.H.R.Abdi, *Polyhedron*, 11 (1992) 1821.
427. M.M.T. Khan, S.H. Mehta, A.P. Rao and K.N. Bhatt, *J. Mol. Catal.*, 75(1992) 245.
428. M.M.T. Khan, K. Venkatasubramanian, S.H.R. Abdi, M.M. Bhadbhade and B. Tyagi, *Acta Crystallogr., Sect C*, 48(1992) 1402.
429. T. Fukuchi, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1807.
430. L.F. Szczepura, J.G. Muller, C.A. Bessel, R.F. See, T.S. Janik, M.R. Churchill and K.J. Takeuchi, *Inorg. Chem.*, 31 (1992) 859.
431. M.M.T. Khan and K. Venkatasubramanian, *Indian J. Chem., Sect.* A, 31 (1992) 17.
432. D. Akashi, H. Kido, Y. Sasaki and T. Ito, *Chem. Lett.*, (1992) 143.
433. H. Kobayashi, N. Uryu, A. Tokiwa, T. Yamaguchi and Y. Sasaki, T. Ito, *Bull. Chem. Soc. Jpn.*, 65 (1992) 198.
434. M. Abe, Y. Sasaki, A. Nagasawa and T. Ito, *Bull. Chem. Soc. Jpn.*, 65(1992) 1411.
435. T.Y. Dong, H.S. Lee, T.Y. Lee and C.F. Hsieh, *J. Chin. Chem. Soc.*, 39 (1992) 393.
436. J.F. Iyun, G.A. Ayoko and H.M. Lawal, *Transition Metal Chem. (London)*, 17 (1992) 63.
437. J.F. Iyun, G.A. Ayoko and H.M. Lawal, *Indian J. Chem., Sect. A*, 31 (1992) 943.
438. J.F. Iyun, G.A. Ayoko and Y.N. Lohdip, *Bull. Chem. Soc. Ethiop.*, 6 (1992) 1; *Chem. Abstr.*, 118 (1993) 46615n.
439. J.F. Iyun, G.A. Ayoko and Y.N. Lohdip, *Polyhedron*, 11 (1992) 2389.
440. J.K. Hurst, J. Zhou and Y. Lei, *Inorg. Chem.*, 31 (1992) 1010.
441. H.H. Petach and C.M. Elliott, *J. Electrochem. Soc.*, 139 (1992) 2217.
442. A. Syamala, B.K. Das and A.R. Chakravarty, *Polyhedron*, 11 (1992) 335.
443. R. Hotzelmann, K. Wieghardt, J. Ensling, H. Romstedt, P. Guetlich, E. Bill, U. Floerke and H.J. Haupt, *J. Am. Chem. Soc.*, 114 (1992) 9470.

444. L.D. Schulz, G.D. Fallon, B. Moubaraki, K.S. Murray and B.O. West, *J. Chem. Soc., Chem. Commun.*, (1992) 971.
445. K.Y. Wong, V.W.W. Yam and W.W.S. Lee, *Electrochim. Acta*, 37(1992) 2645.
446. C.K. Li, C.M. Che, W.F. Tong and T.F. Lai, *J. Chem. Soc., Dalton Trans.*, (1992) 813.
447. M.M.T. Khan, A.P. Rao, D. Chatterjee and S.S. Kumar, *J. Mol. Catal.*, 73 (1992) 17.
448. M.M.T. Khan, D. Chatterjee, A.P. Rao and S.H. Mehta, *Indian J. Chem., Sect. A*, 31 (1992) 146.
449. W.P. Griffith, *Chem. Soc. Rev.*, 21 (1992) 179.
450. R.S. Drago and R.H. Beer, *Prepr.-Am. Chem. Soc., Div. Pet . Chem.*, 37 (1992) 293; *Chem. Abstr.*, 116 (1992) 193522s.
451. C.M. Che, W.T. Tang, W.O. Lee, K.Y. Wong and T.C. Lau, *J. Chem. Soc., Dalton Trans.*, (1992) 1551.
452. C.K. Li, C.M. Che, W.F. Tong, W.T. Tang, K.Y. Wong and T.F. Lai, *J. Chem. Soc., Dalton Trans.*, (1992) 2109.
453. M. Tavares, R. Ramasseul, J.C. Marchon, B. Bachet, C. Brassy and J.P. Mornon, *J. Chem. Soc., Perkin. Trans. 2*, (1992) 1321.
454. B.R. James, *Chem. Ind. (Dekker)*, 47 (Catal. Org. React.) (1992) 245.
455. M.M.T. Khan, D. Chatterjee, S.S. Kumar, A.P. Rao and N.H. Khan, *J. Mol. Catal.*, 75 (1992) L49.
456. C. Redshaw, W. Clegg and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1992) 2059.
457. W.P. Griffith and J.M. Jolliffe, *J. Chem. Soc., Dalton Trans.*, (1992) 3483.
458. S.A. Adeyemi, A. Dovletoglou, A. R. Guadalupe and T.J. Meyer, *Inorg. Chem.*, 31 (1992) 1375.
459. B.K. Das and A.R. Chakravarty, *Indian J. Chem., Sect.* A, 31 (1992) 408.
460. G. Jia, A.L. Rheingold, B.S. Haggerty and D.W. Meek, *Inorg. Chem.*, 31 (1992) 900.
461. M. McCann and E. Murphy, *Polyhedron*, 11 (1992) 2327.
462. F.A. Cotton, Y. Kim and T. Ren, *Inorg. Chem.*, 31 (1992) 2723.
463. D.Q. Li, S.C. Huckett, T. Frankcom, M.T. Paffett, J.D. Fau, M.E. Hawley, S. Gottesfeld, J.D. Thompson, C.J. Burns and B.I. Swanson, *ACS Symp. Ser.* 499 (Supramol. Archir.) (1992) 33; *Chem. Abstr.*, 118 (1993) 102765a.
464. X. Guo and G.L. Rempel, Stud. Surf. Sci. Catal., 73(Prog. Catal) (1992) 135 Chem. Abstr., 117 (1992) 253071b.
465. M.C. Barrel, R. Jimenez-Aparicio, J.L. Priego, E.C. Royer, E. Gutierrez-Puebla and C.R. Valero, *Polyhedron*, 11 (1992) 2209.
466. F.A. Cotton, L. Labella and M. Shang, *Inorg. Chim. Acta*, 197 (1992) 149.
467. A. Demonceau, A.F. Noels, E. Saive and A.J. Hubert, *J. Mol. Catal.*, 76(1992) 123.
468. M.M.T. Khan, R.I. Kureshy and N.H. Khan, *Polyhedron*, 11 (1992) 1053.
469. M.M.T. Khan, H.C. Bajaj and D. Chatterjee, *J. Mol. Catal.*, 71 (1992) 177.
470. M.M.T. Khan, D. Chatterjee, S.D. Bhatt and A.P. Rao, *J. Mol. Catal.*, 77(1992) 23.
471. M.M.T. Khan, D. Chatterjee, H.C. Bajaj, K.N. Bhatt and S.S. Kumar, *Indian J. Chem. Sect. A.*, 31 (1992) 714.
472. M.M.T. Khan, K. Venkatasubramanian, H.C. Bajaj and Z. Shirin, *Indian J. Chem., Sect. A*, 31 (1992) 303.
473. M.M.T. Khan, *Indian J. Technol.*, 30 (1992) 137.
474. M.M.T. Khan, G. Ramachandraiah and A.B. Boricha, *Indian J. Chem, Sect. A*, 31 (1992) 457.
475. M.M.T. Khan, A. Hussian and M.A. Moiz., *Polyhedron*, 11 (1992) 687.
476. K. Araki, F.N. Rein, S.G. Camera and H.E. Toma, *Transition Metal Chem. (London)*, 17 (1992) 535.
477. M.M.T. Khan, K. Venkatasubramanian, Z. Shirin and M.M. Bhadbhade, *J. Chem. Soc., Dalton. Trans.*, (1992) 885.
478. M.M.T. Khan, D. Chatterjee, M. Krishnaratnam and M. Bala, *J. Mol. Catal.*, 72 (1992) 13.
479. M.M.T. Khan, D. Chatterjee, M. Bala and K.N. Bhatt, *J. Mol. Catal.*, 73(1992) 265.
480. M.M.T. Khan, A.P. Rao and S.D. Bhatt, *J. Mol. Catal.*, 75 (1992) 41.
481. M.M.T. Khan, S.B. Halligudi, and S.H.R. Abdi, *Chem. Abstr.*,118 (1993) 191201d.
482. M.M.T. Khan, M.M. Bhadbhade, K. Venkatasubramanian and M.R.H. Siddiqui, *Acta Crystallogr., Sect. C* , 48 (1992) 1202.
483. M.M.T. Khan, D. Chatterjee and M. Bala, *J. Photochem. Photobiol., A.* 67(1992) 349; *Chem. Abstr.*, 117 (1992) 242542e.
484. M.M.T. Khan, D. Chatterjee, Z. Shirin, H.C. Bajaj, M.R.H. Siddiqui, K. Venkatasubramanian and M.M. Bhadbhade, *J. Mol. Catal.*, 72 (1992) 271.
485. M.M.T. Khan and R.S. Shukla, *J. Mol. Catal.*, 72 (1992) 361.

486. S.B. Halligudi, M.M.T. Khan, N.V. Desai, R. Rangarajan and A.V. Rao, *J. Chem. Technol. Biotechnol.*, 55 (1992) 313; *Chem. Abstr.*, 118 (1993) 61888x.
487. E.M. Basova, L.G. Bondareva and V.M. Ivanov, *Zh. Anal. Khim.*, 47(1992) 1712; *Chem. Abstr.*, 118 (1993) 32266n.
488. M.M.T. Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H. R. Abdi, D. Srinivas, M.R.H. Siddiqui, M.A. Moiz, M.M. Bhadbhade and K. Venkatasubramanian, *Inorg. Chem.*, 31 (1992) 2711.
489. M.M.T. Khan, N.H. Khan, R.I. Kureshy, *Indian J. Chem., Sect. A*, 31 (1992) 883.
490. M.M.T. Khan, H.C. Bajaj, Z. Shirin and K. Venkatasubramanian, *Polyhedron*, 11 (1992) 1059.
491. M.M.T. Khan, D. Chatterjee, A.B. Boricha, R.R. Merchant, M.A. Moiz and A. Hussian., *React. Kinet. Catal. Lett.*, 46 (1992) 145.
492. M.M.T. Khan, H.C. Bajaj and D. Chatterjee, *Indian J. Chem., Sect. A*, 31 (1992) 152.
493. R.E. Shepherd and S. Zhang, *Inorg. Chim. Acta*, 191 (1992) 271.
494. S. Zhang and R.E. Shepherd, *Inorg. Chim. Acta*, 193 (1992) 217.
495. S. Zhang, L.A. Holl and R.E. Shepherd, *Transition. Metal Chem.*, 17 (1992) 390.
496. S. Zhang and R.E. Shepherd, *Transition Metal Chem.*, 17 (1992) 199.
497. S. Zhang and R.E. Shepherd, *Transition Metal Chem.*, 17 (1992) 97.
498. D.W. Powell and P.A. Lay, *Inorg. Chem.*, 31 (1992) 3542.
499. J. Tang, K. Shimizu and R.A. Osteryoung, *Inorg. Chem.*, 31 (1992) 2328.
500. H. Ikeuchi, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, 60 (1992) 693; *Chem. Abstr.*, 118 (1993) 45916z.
501. M. Otake, C.Miyazawa, K. Takahashi and H. Kaneeo, *Chem. Abstr.*, 116 (1992) 255471k.
502. Y. Hara, H. Inagaki, S. Nishimura and K. Wada, *Chem. Lett.*, (1992) 1983.
503. R.S. Myers, D.R. Mills and R.C. Michaelson, *Chem. Abstr.*, 117 (1992) 72059h.
504. Y. Kasahara, Y. Hoshino, M. Kajitani, K. Shimizu and G.P. Sato, *Organometallics*, 11 (1992) 1968.
505. G. Muthusamy, N. Jayakumar, B. Manonmani, R. Shantha and K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.*, 22 (1992) 171.
506. N. Jayakumar and K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.*, 22(1992) 349.
507. A.M. El-Hendawy, *Transition Metal Chem.*, 17 (1992) 250.
508. B. Banas and R. Grobelny, *Acta. Chim. Hung.*, 129 (1992) 159; *Chem. Abstr.*, 117 (1992) 179196c.
509. P.R. Auburn, E.S. Dodsworth, M.A. Haga, W. Liu and W.A. Nevin, Report 1991, (1992) 92 (1); *Chem. Abstr.*, 118 (1993) 182098y.
510. N. Bag, G.K. Lahiri, P. Basu and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 113.
511. Y.H. Tse, P.R.Auburn and A.B.P. Lever, *Can. J. Chem.*, 70 (1992) 1849.
512. D.S. Bohle and P.A. Goodson, *J. Chem. Soc., Chem. Commun.*, (1992) 1205.
513. M. Bressan, A. Morvillo and G. Romanello, *J. Mol. Catal.*, 77 (1992) 283.
514. D.Q. Li, D.C. Smith, B.I. Swanson, J.D. Fan, M.T. Paffett and M.E. Hawley, *Chem. Mater.*, 4 (1992) 1047.
515. T. Karlen and A. Ludi, *Helv. Chim. Acta*, 75 (1992) 1604.
516. G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Organomet. Chem.*, 441 (1992) 295.
517. S.C. Sarker and P.K. Podder, *Indian J. Chem., Sect. A*, 31 (1992) 966.
518. O.V. Rudnitskaya, I.V. Miroshnichenko and N.M. Sinitsyn, *Zh. Neorg. Khim.*, 37 (1992) 825 *Chem. Abstr.*, 117 (1992) 162850p.
519. J.R. Crook, B. Chamberlain, R.J. Mawby, F.C.F. Korber, A.J. Reid and C.D. Reynolds, *J. Chem. Soc., Dalton Trans.*, (1992) 843.