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COORDINATION
CHEMISTRY
REVIEWS

9. Ruthenium 1993

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of ruthenium for 1993 and is based upon a search of volumes 118, 119 and 120 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched independently from the period of January to December 1993. 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 elsewhere.

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

9.1 COMPLEXES WITH HYDROGEN OR HYDRIDE LIGANDS

Reaction of $[Ru(PCy_3)_2(H_2)HI]$ (**1**) with K(tpb) [tpb = tris(pyrazol-1-yl)borate (1-)] or Tl(tdmpb) [tdmpb = tris(3,5-dimethylpyrazol-1-yl)borate (1-)] yields $[Ru(\eta^3\text{-L})(PCy_3)(H_2)(H)]$ (L = tpb (**2**) or tdmpb (**3**)), *via* the intermediates *trans*-$[Ru(\eta^2\text{-L})(PCy_3)_2(H_2)H]$ (**4**). Protonation of (**2**) with $HBF_4{\cdot}Et_2O$ leads to $[Ru(tbp)(PCy_3)(OH_2)(H_2)]BF_4$ (**5**) [1].

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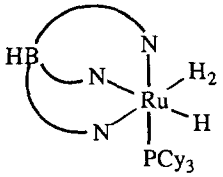

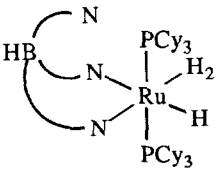

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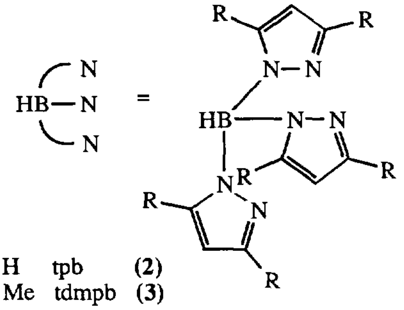
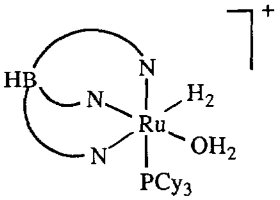


R = H tpb (2)
R = Me tdmpb (3)



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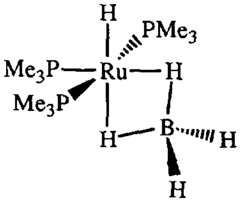
The ternary ruthenium hydride Mg_3RuH_6 (6) was prepared by reacting Mg or magnesium hydride with Ru under a hydrogen pressure of 90 bar. The structure of the rusty brown product was determined by X-ray powder diffraction methods and elastic neutron powder diffracton experiments on Mg_3RuD_6. The atomic arrangement contains two different bonding types of H atoms. One forms complex Ru-H anions, whereas the other is surrounded exclusively by Mg cations. The relation with Mg_2RuH_4 and Mg_2RuH_6 has been discussed [2]. The electronic structures of some intermetallic hydrides M_2RuH_6 (M = Mg, Ca and Sr) have been studied using *ab initio* calculations. These compounds are characterised by an octahedral coordination of the transition metal with hydrogen. These systems, which are isoelectronic and isostructural with Mg_2FeH_6, were all found to be nonconducting in agreement with experimental observations [3].

The electrochemical oxidation of $[HRuCl(dppp)_2]$ (7) was studied at a platinum electrode in dichloromethane. The CV shows two one-electron oxidation waves corresponding to the formation of Ru^{III} and Ru^{IV} species and the pH of the solution decreases during the experiments. An internal reduction of Ru^{IV} to Ru^{III} was proposed which generates the five-coordinate $[RuCl(dppp)_2]^+$ species and the X-ray structure of the complex $[RuCl(dppp)_2]PF_6$ has been reported [4].



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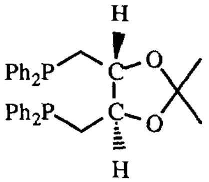

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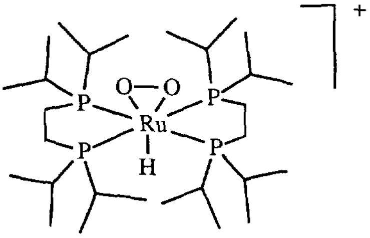
The complex *mer*-[RuH(η^2-H_2BH_2)(PMe_3)$_3$] (**8**) was prepared from the reaction of *trans*-[$RuCl_2(PMe_3)_4$] with $NaBH_4$ in MeOH. The reactions of (**8**) with CO/NEt_3, PMe_3, HON = $CHCH_3$ and CH_3OH/H_2 have been reported [5].

The agostic interaction in coordinatively unsaturated complexes [RuH(dppb)$_2$]PF_6 and [RuH(diop)$_2$]PF_6 (diop = (**9**)) has been studied by ^{1}H NMR spectroscopy. The hydrogen exchange between the agostic H in the phosphine ligand and the terminal hydride in both complexes has been reported [6]. The complex [RuH(dippe)$_2$]$^+$ (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with H_2 and O_2 to yield [RuH(η^2-H_2)(dippe)$_2$]$^+$ (**10**) and the first reported hydridodioxygen complex [RuH(η^2-O_2)(dippe)$_2$]$^+$ (**11**). The crystal structure of the BPh_4^- salt of (**11**) has been determined, showing a side-on coordination for the dioxygen in the *trans* position with respect to the hydride ligand [7]. The complexes [Ru(PMe_3)$_4$(H)(OH)] (**12**) and *trans*-[Ru(H)(OH)(dmpe)$_2$·H_2O]$_2$ (**13**) have been synthesised and characterised by X-ray diffraction studies [8].



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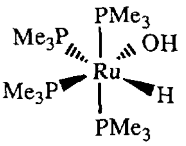

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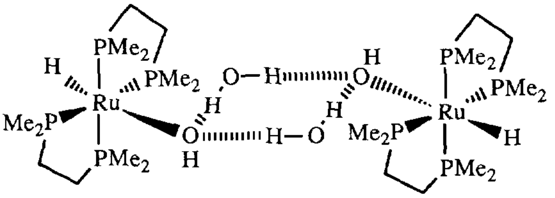

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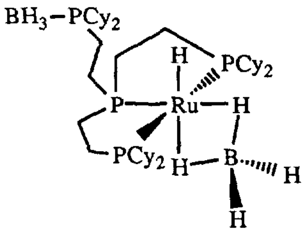
Complexes *cis*-[$RuH_2(PMe_3)_4$] (**14**) and [RuH_2(L)] (**15**) (L = P{(CH_2)$_3$$PMe_2$}$_3$) were studied by single-crystal X-ray diffraction. The structural parameters suggested a considerably higher degree of steric encumbrance in (**14**) than in (**15**). This correlates with both the ability of the P{(CH_2)$_3$PMe}$_3$Ru(0) fragment to insert across C-H bonds of non-coordinated hydrocarbons and the propensity of (Me_3P)$_4$Ru(0) to undergo spontaneous cyclometallation [9].

The Ru-H mean bond dissociation energy in [Ru(dmpe)$_2$$H_2$] (**16**) was determined by photoacoustic calorimetry to be 63.5 ± 2.0 kcal mol^{-1}. The Ru-N_2 bond energy in [Ru(dmpe)$_2$$N_2$] (**17**) was also determined to be 19.0 ± 2.0 kcal mol^{-1} [10]. The electronic structures and spectroscopic constants of RuH^+ were calculated by means of the Hartree-Fock pseudopotentials. Comparisons of these molecular characteristics with FeH^+ and OsH^+ have been made [11].

The complex *mer*-$[RuH(\eta^2\text{-}BH_4)(\eta^3\text{-}PP_3Cy{\cdot}BH_3)]$ **(18)** ($PP_3Cy = P(CH_2CH_2PCy_2)_3$) was prepared by reacting $[RuCl(PP_3Cy)]Cl$ with excess $NaBH_4$ in thf. The reaction of $[RuCl(PP_3Cy)]Cl$ with excess NaOMe in refluxing thf yields $[RuHCl(PP_3Cy)]$ **(19)**. Treatment of $[RuCl(PP_3Cy)]BPh_4$ with 1 equiv. of $NaBH_4$ under H_2 (1 atm) affords $[RuH(\eta^2\text{-}H_2)(PP_3Cy)]BPh_4$ **(20)**. The structure of **(20)** has been established by ^1H, ^{31}P and T_1 NMR spectroscopic measurements and the observation of a ^1J(HD) coupling constant of 28 Hz in the isotopomer $[RuD(HD)(PP_3Cy)]^+$ [12]. Complex **(20)** is an efficient catalyst precursor for the reduction of α,β-unsaturated ketones bearing bulky substituents at the double bond [13].



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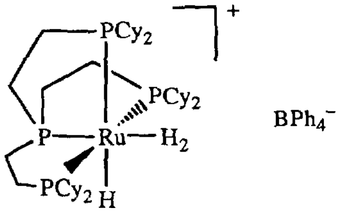

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The air-sensitive complex $[Ru(H)_2(H_2)(PPh_3)_3]$ **(21)** has been studied by far IR spectroscopy at 78 K and by ^1H NMR spectroscopy. A fluxional process occurs at room temperature and the non-equivalent nature of the hydrogens was discernible at low temperature [14]. It was found that **(21)** catalyses the addition of activated nitriles to aldehydes and ketones via the Knoevenagel condensation [15].

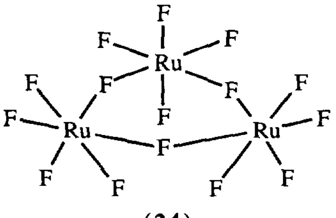
The complex $[RuH_2(PPh_3)_4]$ **(22)** catalyses the hydration of nitriles efficiently to give the corresponding amides. Under similar reaction conditions, δ-keto nitriles can be converted into the corresponding ene-lactams, which are versatile synthetic intermediates [16]. Such a ruthenium compound has also found wide catalytic applications in the manufacture of various ketones [17,18], indole derivatives [19] and glycol monoesters [20]. Moreover, **(22)** promotes C-O bond cleavage in allylic carboxylates to give the corresponding olefins at elevated temperature [21].

The preparation of anhydrous ruthenium oxide containing ruthenium polyhydride phase has been described which involves the reaction of an aqueous alkaline solution of K_2RuO_4 with a mixture containing MeOH (or EtOH) and HNO_3 at 0-100 °C [22].

9.2 COMPLEXES WITH HALIDE OR PSEUDO-HALIDE LIGANDS

Complexes $[RuBr_2(SbPh_3)_4]$ and *trans*-$[RuX_2(SbPh_3)_4]BF_4$ (X = Cl, Br) were prepared and characterised by analytical, IR and UV-VIS spectroscopies, magnetic and conductance measurements and by cyclic voltammetry. *Trans*-$[RuCl_2(SbPh_3)_4]$ **(23)** has been synthesised by the reaction of $RuCl_3{\cdot}nH_2O$ with $SbPh_3$ and characterised by a single crystal X-ray study [23].

The molecular structure of gaseous RuF_5 **(24)** at approximately 120°C has been determined by electron diffraction and found to contain mainly trimeric molecules. Each metal atom is bonded to four terminal F atoms and to two further ring F atoms in a bridging manner [24]. The preparation of monomeric molecular ruthenium oxide tetrafluoride has been reported, involving the reaction of RuF_5 with glass at ca. 300°C. Mass spectrometry and matrix-isolation IR spectroscopy have been employed to characterise this compound [25].



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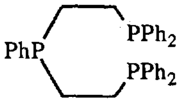
Two series of supported ruthenium catalysts were prepared and characterised. One series was obtained by exchange of silica in basic solution with $[Ru(NH_3)_6Cl_3]$, and the other by impregnation of high-area activated charcoal with $RuCl_3$ solution [26].

A method has been described for preparing polyaniline/Pt-Ru assemblies that are effective catalysts for electrochemical oxidation of MeOH or EtOH in aq. H_2SO_4. The Pt-Ru particles were deposited into polyaniline by electrochemical deposition from aq. H_2SO_4 containing K_2PtCl_6 and $K_2RuCl_5 \cdot xH_2O$. The Pt-Ru catalyst was compared to a Pt-Sn catalyst which can also be dispersed in a polyaniline matrix [27].

Complexes $[Ru_2(\mu\text{-}Cl)_3L_2]CF_3SO_3$ and $[Ru(MeCN)_3L](CF_3SO_3)_2$ (L = (**25**)) have been isolated and their X-ray crystal structures have been determined. The mononuclear complex $[RuCl_2L']$ (L' = (**26**)) was also structurally characterised by X-ray diffraction. The solution structures of these complexes have been described [28].



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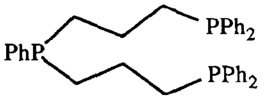

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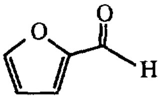

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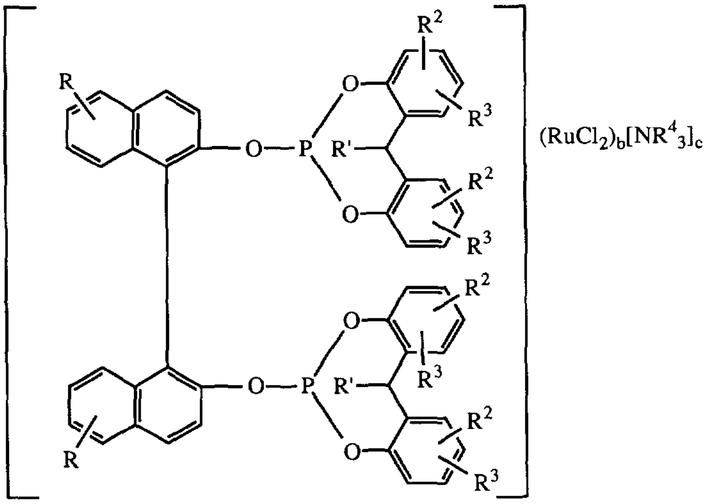
Intervalence charge transfer bands of the dinuclear mixed-valence ruthenium complexes have been studied *in situ* with the Ru(II), Ru(III) states electrochemically generated from the parent Ru(II), Ru(III) complex. The symmetrical species $[Ru_2(\mu\text{-}Cl)_3L_6]^{2+}$ (L = tertiary phosphine) and the unsymmetrical complex $[Cl(PPh_3)_2Ru(\mu\text{-}Cl)_3Ru(PPh_3)_2CS]^+$ have been discussed [29].

The synthesis and characterisation of some novel pentacoordinated Ru(II) complexes, *viz.* $[RuX_2(MPh_3)(fur)_2]$ (fur = furfural (**27**); X = Cl or Br; M = P or As) and $[RuBr_2(MPh_3)(PhCHO)_2]$ (M = P or As) have been described. The compound $[RuBr_2(PPh_3)L_2]$ (L = (**27**), benzaldehyde) can catalyse the oxidation of PPh_3 by molecular oxygen [30].

Complexes having formula (**28**) (a = 1-3; b = 1-2; c = 0-3; R = H, alkyl, aryl, halo, amino, acetylamino, sulfo; R^1, R^2, R^3 = H, C_1 to C_6 linear or branched alkyl; R^4 = straight or branched chain alkyl having 1 to 20 carbon atoms) have been used in the asymmetric hydrogenation of unsaturated organic compounds [31].



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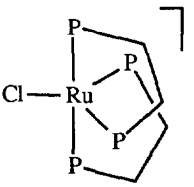

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The reaction of *trans*-[$RuCl_2(dppe)_2$] with $AgBF_4$ in thf produces the trigonal-bipyramidal complex [$RuCl(dppe)_2]BF_4$ containing cation (**29**). Both these dppe complexes were characterised by ^{31}P NMR spectroscopy and their crystal structures determined [32]. The crystal and molecular structure of *trans*-[$RuCl_2(dppe)_2$] was also determined [33]. Treatment of [$RuCl_4(PPh_3)_2]^-$ with either dppe or (**25**), in CH_2Cl_2 leads to [$RuCl_2L_2$] (L = dppe, (**25**)), both of which have been characterised by ^{31}P NMR spectroscopy. The crystal structure of [$MePPh_3$][$RuCl_4(PPh_3)_2$] was determined which reveals a *trans* octahedral geometry [34].

The reaction of [$RuCl_2(NCMe)_4$] with clotrimazole (CTZ) under mild conditions affords [$RuCl_2(CTZ)_2$], which is highly active against tropical diseases and *Trypanosoma cruzi* [35].

The thermal and photocatalytic dehydrogenation of 2-propanol with the complex [$RuCl(SnCl_3)_5]^{4-}$ have been discussed [36].

Comparison has been made between the scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) images of α-$RuCl_3$ and they show striking differences [37]. In addition, $RuCl_3$-impregnated NaY zeolite has been characterised by ^{27}Al and ^{29}Si MAS NMR [38]. Ruthenium trichloride is found to catalyse the oxidation of 1,2-ethanediol [39] and some hydroxy acids by alkaline hexacyanoferrate(III) [40], oxidation of acrylic acid by ceric sulfate [41], oxidation of alcohols by persulfate [42], preparation of mixtures of *cis*- and *trans*-$Me(CH_2)_nCH{=}CHSi(OEt)_3$ (n = 0-18) [43], oxidative transformation of alkenes to α-ketols with peracetic acid [44] and aqueous ring-opening metathesis polymerisation of *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide [45] and *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene [46].

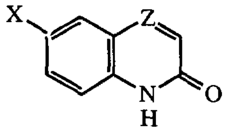
The reduction of Ru catalysts, the adsorption-desorption and the surface hydrogenation of CO on Ru/ZrO_2 and Ru/Al_2O_3 using $RuCl_3$ as precursor have been studied [47]. Moreover, fumed silica has been used as a stabiliser of precursor emulsions to prepare polymer latexes. The quaternary ammonium salts of the resulting polymer, together with $RuCl_3$, 4-*N*-Me-morph *N*-oxide and ammonium persulfate were employed in the catalytic oxidation of toluene to benzyl alcohol

[48]. An iron-ruthenium catalyst has been prepared by impregnation of calcination products of α-, β-, γ- and δ-iron oxide-hydroxides with ruthenium chloride and its activity for the water-gas shift reaction was tested [49]. An equimolar mixture of $RuCl_3$ and K_2RuCl_5 was used as the catalyst for the synthesis of homo- and copolymers of the Diels-Alder adduct of furan with maleic anhydride and of furan with dimethylacetylene dicarboxylate [50]. $RuCl_3$ also catalyses the aqueous ring-opening metathesis polymerisation of 2,3-dicarboxylic acid anhydride, 2,3-bis(methoxymethyl), and 2,3-dicarboxylic acid mono-Me ester derivatives of 7-oxanorbornene [51]. Selective hydrogenation of the C-C double bond of nitrile group-containing unsaturated copolymers by a mixture of $RuCl_3{\cdot}3H_2O$, PPh_3 and acetic acid has been reported [52]. A mixture of $RuCl_3{\cdot}3H_2O$, PPh_3 and $CaCl_2{\cdot}2H_2O$ is also found to catalyse the preparation of hydrogenated partially crosslinked nitrile rubber compositions [53].

A simple catalytic system for the oxidation of alcohols to carbonyl compounds using $RuCl_3$ and a three fold excess of aq. *tert*-butyl hydroperoxide has been described. This system is highly efficient in the case of secondary alcohols [54]. In addition, a catalyst has been prepared by reducing ruthenium(III) hydroxide, precipitated with excess NaOH from an aq. $RuCl_3$ solution, and passifying the Ru with atmospheric oxygen. Such a catalyst is useful in the manufacture of cycloalkenes by partial hydrogenation of aromatic hydrocarbons [55].

Unsupported ruthenium catalyst powders were obtained by reduction of $RuCl_3$ and RuO_2. The properties and catalytic activities of these catalysts have been studied [56].

In the presence of bases and $RuCl_3$ followed by acids, the compounds (**30**) (X = halo, C_{1-5} trihaloalkyl, NO_2; Z = N), (useful as intermediates for herbicides) have been prepared by treating quinoxalinone *N*-oxides (**30**) (Z = NO) with CO [57].



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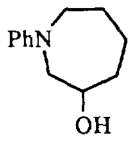

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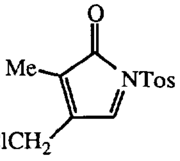
Selective oxidation of cyclohexane to cyclohexanone was carried out in a $RuCl_3$-pyridine-acetic acid-$KHSO_5$ mixture. A mechanistic study has been carried out [58]. Oxidation of butane-1,4-diol by Tl(III) in acid perchlorate medium to give $HO(CH_2)_3CHO$ is actively catalysed by $RuCl_3$ and the intermediate complex $[HO(CH_2)_3CH_2ORu^{V}Cl_3TlOH]$ has been proposed [59]. In the presence of $RuCl_3{\cdot}H_2O$-PPh_3, aromatic primary amines react with 1,2,6-hexanetriol to give selectively 1-substituted aryl-3-hydroxyperhydroazepines, e.g. (**31**), in good yields [60].

Evaluation of selected heteropolyanions (HPAs) as catalyst precursors to quinoline hydrogenation catalysts has been described. Combinations of Mo-HPA and $RuCl_3$ appear to interact synergistically and exhibit the highest activities of all the systems studied [61]. Various heterocyclic tertiary amines have been prepared by alkylation of the corresponding secondary amines in the presence of $RuCl_3$ catalyst [62]. In addition, a mixture of $RuCl_3/Sn(OEt)_4$ in EtOH catalyses the hydrogenation of $HO_2C(CH_2)_nCO_2H$ (n = 8-16) to give $HO_2C(CH_2)_nCH_2OH$ [63].

A unique route to unsaturated 2-pyrrolidinone (32) is achieved using $[RuCl_2(PPh_3)_3]$ as catalyst [64]. 1-(Trimethylsilyl)-1-alkenes of general formula $CH_3(CH_2)_nCH{=}CHSi(CH_3)_3$ where n = 3-15, have been prepared by cross metathesis of vinyltrimethylsilane with 1-alkenes catalysed by $[RuCl_2(PPh_3)_3]$ [65]. Similarly, $[RuCl_2(PPh_3)_3]$ also catalyses the stereoselective intramolecular radical addition of polyhaloacetyl functions to 2-oxazolones and the facile synthesis of statine and its 2,2-dichloro and 2,2-difluoro analogs have been reported [66]. In addition, $[RuCl_2(PPh_3)_3]$ catalyses the preparation of 2-substituted-2-oxazolines [67], hydrogenation and transfer hydrogenation of *D*-fructose [68], hydrogenation of nitrile rubber [69] and synthesis of 1-substituted-3-hydroxyperhydroazepines [70].



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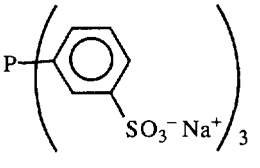

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A new method for the synthesis of five-membered lactams by $[RuCl_2(PPh_3)_3]$-catalysed chlorine atom transfer cyclisations of *N*-allylic α-chloro-α-thioacetamides and the application of this method to the synthesis of alkaloids has been described [71].

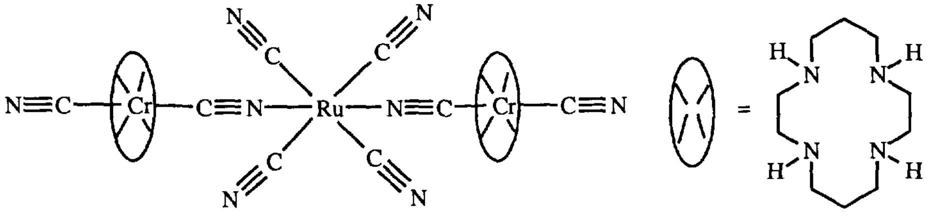
Hydroboration of cyclohexene mediated by the complex $[RuCl_3(PPh_3)_2(MeOH)]$ has been discussed [72]. Selective hydrogenations of different α,β-unsaturated aldehydes to allylic alcohols by supported aqueous phase catalyst $[RuCl_2L_3]/SiO_2$ [Na_3L = (33)] have been reported [73].

Measurement of the first hyperpolarisability of the dimetallic complex ion $[(NC)_5Ru^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^-$ (34) in solution at a wavelength of 1,064 nm gives a value greater than 10^{-27} e.s.u., which is among the largest reported for solution species [74]. The back electron transfer from the metal-to-metal charge-transfer state of (34) is ultrafast ($\tau < 0.5$ ps) and the IR frequency observed suggests that nearly a full charge transfer has occurred. The vibrational energy relaxation process of (34) has also been discussed. The femtosecond transient-absorption spectra were analysed for the metal/metal intervalence photoinduced charge-transfer reaction of (34) in different solvents and temperatures [75]. The optical electron transfer and subsequent reverse radiationless electron transfer for $[(NH_3)_5Fe^{III}(NC)Ru^{II}(CN)_5]^-$ has also been studied [76].

Photoredox reaction of a trinuclear complex $[(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5]^{3-}$ (35) has been reported (equ. 1) which is induced by a metal-to-metal charge transfer excitation from Ru(II) to the central Co(III) ion and a subsequent charge shift from the central Co(II) to the Co(III) ammine moiety [77].

$$\begin{array}{ll} [(NH_3)_5Co^{III}(\mu\text{-}NC)Co^{III}(CN)_4(\mu\text{-}CN)Ru^{II}(CN)_5]^{3-} \longrightarrow & 5NH_3 + Co^{2+} + \\ & [Co^{III}(CN)_6]^{3-} + \\ & [Ru^{III}(CN)_5(H_2O)]^{2-} \end{array} \qquad \text{(equ. 1)}$$

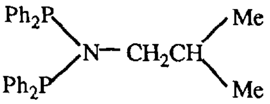
The cyano-bridged complex $[Ru(CN)_4\{Cr(cyclam)(CN)_2\}_2]$ (**36**) has been synthesised and characterised. The absorption spectrum and the excited-state charge recombination process have been discussed [78].



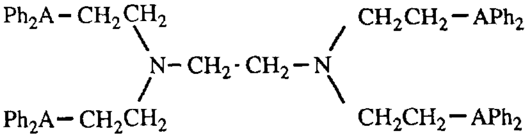
(**36**)

9.3 COMPLEXES WITH PHOSPHORUS DONOR LIGANDS

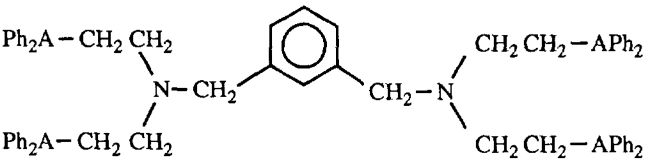
The complex *trans*-$[RuL_2Cl_2]$ (L = (**37**)) has been synthesised and characterised and its X-ray structure shows an octahedral geometry with four coordinated P atoms and two Cl atoms [79]. The reaction of $[RuCl_3(AsPh_3)_2(MeOH)]$ with the hexadentate ligands BDPE (**38**), BDAE (**39**) and BDPX (**40**) yields the dinuclear Ru(III) complexes (**41**) and (**42**). The substitution reactions of NOCl with (**41**) and (**42**) have been studied. The geometry of the complexes was established by ^{31}P NMR spectroscopy and their cyclic voltammetric behaviour have been reported [80].



(**37**)

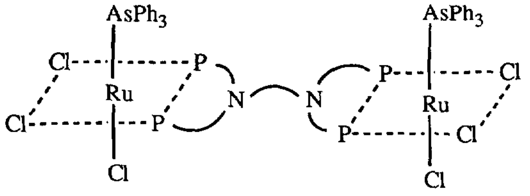


A = P (BDPE) (**38**)
A = As (BDAE) (**39**)



(BDPX) (**40**)

The novel five-coordinate Ru(II) species $[RuCl_2(PPh_3)L]$ (L = (**43**) and (**44**)) were synthesised and characterised. The solution behaviour and reactivity of these complexes towards H_2 have been described. In addition, the acetato derivatives $[RuCl(\eta^2\text{-}OAc)(PPh_3)L]$ (**45**) and $[Ru(\eta^2\text{-}OAc)_2L]$ (**46**) and the tetrahydroborato adduct $[RuH(\eta^2\text{-}BH_4)(PPh_3)L]$ (**47**) have been prepared [81].



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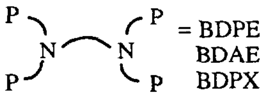

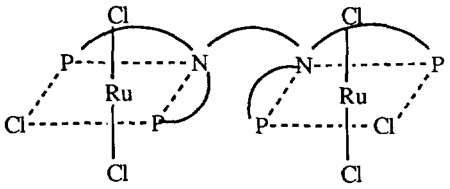

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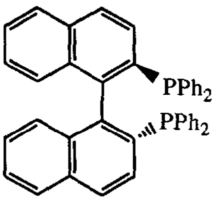
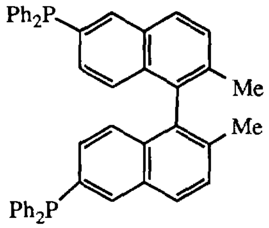


(S) - BINAP **(43)**



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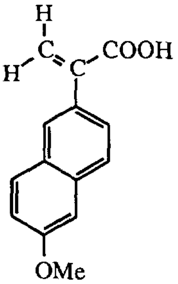

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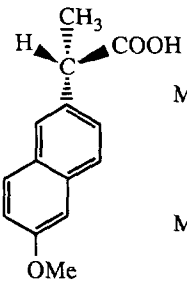

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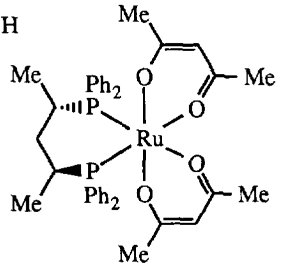

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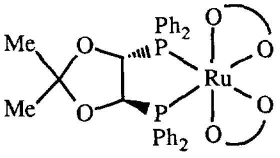
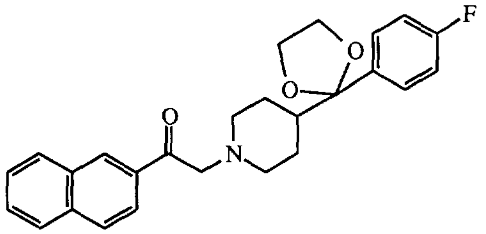


(52)

The reaction of [Ru(acac)$_3$] with (*S*)-BINAP and Zn dust in EtOH gives [Ru(acac)$_2$(*S*-BINAP)] **(48)**. Complex **(48)** was used to hydrogenate dehydronaproxen **(49)** to give 100% conversion to (S)-naproxen **(50)** in 94% enantiomeric excess (ee) [82]. Moreover, the complexes **(48)**, [Ru(acac)$_2$(SKEW)] **(51)** and [Ru(acac)$_2$(DIOP)] **(52)** were generated *in situ* by hydrogenation of a mixture of the appropriate phosphine and [Ru(acac)$_3$] in methanol. Addition of

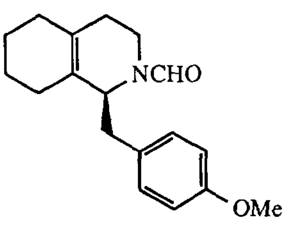
2-(4-isobutylphenyl)propenoic acid to these solutions, followed by hydrogenation affords (*S*)-(+)-ibuprofen in various ee. The crystal structure of (**52**) has been established [83].

A novel water-soluble ruthenium(II)-sulfonated-BINAP complex has been synthesised and was shown to be an excellent asymmetric hydrogenation catalyst for 2-acylamino acid precursors and methylenesuccinic acid. Effects of solvent, pressure and the addition of organic base on enantioselectivity have been described [84]. Ligand (*S*)-BINAP reacts with $[Ru(COD)Cl_2]_n$ in acetic acid to give $[Ru(S\text{-BINAP})Cl_2]_n$ (**53**) which catalyses asymmetric hydrogenation of dehydronaproxen to naproxen in 92% ee at room temperature [85]. Ruthenium-optically active phosphine complexes with (+)- or (-)-BINAP $(O_2CR^1)(O_2CR^2)$ (R^1, R^2 = lower alkyl, CF_3) were found to be effective catalysts for asymmetric hydrogenation of acetonaphthone derivatives (**54**) to give the corresponding secondary alcohols [86]. In addition, complex $[Ru_2Cl_4\{(-)\text{-Tol-BINAP}\}_2(NEt_3)]$ (Tol-BINAP = 2,2'-bis[di(p-toly)phosphino-1,1'-binaphthyl]) catalyses the preparation of optically active hydroxylamine derivatives by stereoselective hydrosilylation of nitrones [87].

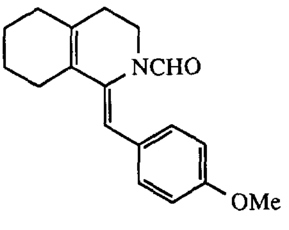


(**54**)

The compound (**55**) was prepared in 98% ee by asymmetric hydrogenation of (*Z*)-(**56**) in the presence of $[Ru\{(-)\text{-Me-BINAP}\}SnCl_6]_2(NEt_3)$ [88]. It was also found that asymmetric hydrogenation of $MeCOCH_2CO_2Me$ with *in situ* (*R*)-BINAP-Ru(II) complex afforded (*R*)-(-)-methyl 3-hydroxybutanoate in 97-98% ee [89].



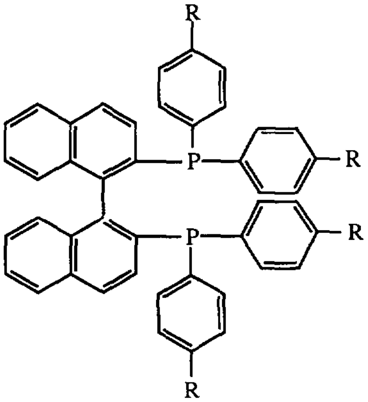
(**55**)



(**56**)

Ruthenium-BINAP complexes also catalyse enantioselective hydrogenation of 3-*o*-substituted 1,3-dihydroxypropan-2-ones [90] and stereoselective hydrogenation of 2-substituted 3-oxo carboxylic esters [91]. Asymmetric reactions catalysed by chiral Ru-BINAP complexes and their applications have been reviewed [92].

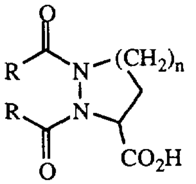
Optically active $R^1CH_2CHFCO_2H$ ($R^1 = C_{1-12}$ alkyl), useful as intermediates for ferroelectric liquid crystals were prepared by asymmetric hydrogenation of $R^1CH{=}CFCO_2H$ in the presence of $[Ru_2Cl_4L_2(NEt_3)]$ (L = (57); R = H, Me, CMe_3), $[Ru(OCOR)_2L]$ (R = lower alkyl, CF_3) or $[RuX_2L]$ (X = halo) [93].



(57)

The Ru^{II}-Sn^{II} heteronuclear cluster complex $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ has been found to be catalytically active for the isomerisation of methyl formate to acetic acid. The kinetic data for this reaction have been presented [94]. A process for the hydrogenation of a polyene to a monoene has been claimed which comprises the use of a mixture of polyene, ruthenium-triarylphosphine complex, free triarylphosphine and a sterically hindered tertiary amine promotor [95]. The tetrahydropyranyl derivatives of alcohols and phenols have been prepared efficiently in the presence of catalytic amounts of $[Ru(CH_3CN)_3(triphos)](CF_3CO_2)_2$ under mild conditions, in good to excellent yields [96]. Hydroxylation and/or ketonisation of alkanes (adamantane, cyclooctene, hexane) has also been achieved by using iodosobenzene or aq. monopersulfate in the presence of catalytic amounts of ruthenium(III)-diphosphino complexes [97].

(*R*)- or (*S*)-Stereoisomers of heterocycles (**58**) have been prepared by asymmetric hydrogenation of the corresponding unsaturated heterocycles (**59**) or their salts using optically active Ru-diphosphine complexes as catalysts [98].



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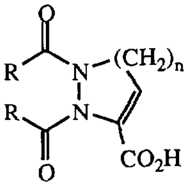
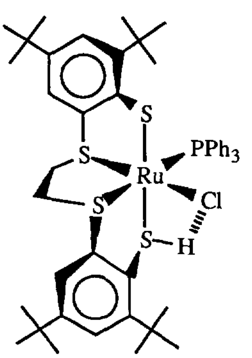


(59)

The complex $[Ru(SnCl_3)_5(PPh_3)](NEt_4)_3$ (**60**) has been found to be catalytically active in the manufacture of acetic acid and methyl acetate from methanol [99].

9.4 COMPLEXES WITH SULFUR DONOR LIGANDS

The complex $[Ru(ClH)(PPh_3)(^{\prime bu}S_4^{\prime})]$ (**61**) ($^{\prime bu}S_4^{\prime 2-}$ = 1,2-bis(2-mercapto-3,5-di-*tert*-butylphenylthio)ethane(2-)) has been isolated from the reaction of $[RuCl_2(PPh_3)_2]$ with $^{\prime bu}S_4^{\prime}$-Li_2 and HCl gas. Treatment of (**61**) with NMe_4OH gives $[Ru(PPh_3)(^{\prime bu}S_4^{\prime})]$ (**62**) which contains a coordinatively unsaturated Ru centre. Compound (**62**) reacts with Lewis bases such as N_3^-, NH_3 and N_2H_4 to afford soluble $[Ru(L)(PPh_3)(^{\prime bu}S_4^{\prime})]$ complexes (L = N_3^- (**63**), NH_3 (**64**), N_2H_4 (**65**)), which can be regarded as model compounds for the active centres of nitrogenases. Oxidation of (**65**) leads to the dinuclear diazene complex $[\mu\text{-}(N_2H_2)\{Ru(PPh_3)(^{\prime bu}S_4^{\prime})\}_2]$ (**66**), which has been characterised by an X-ray structure analysis [100].



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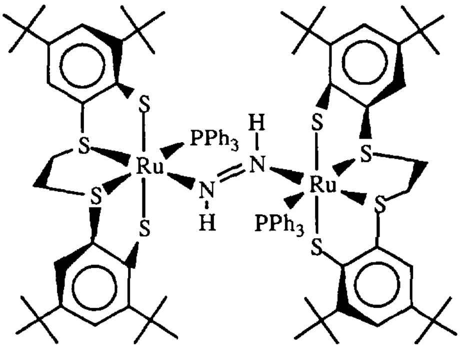
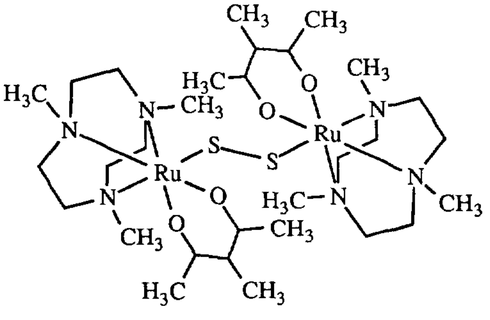


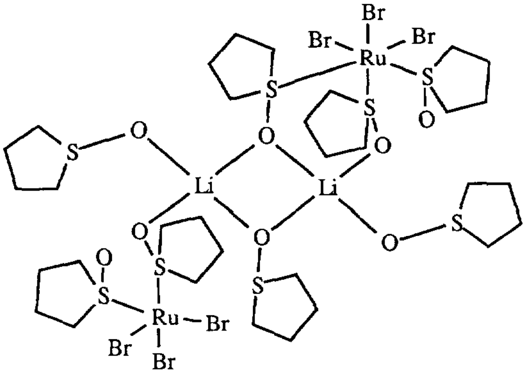
(66)

Reaction of mononuclear $[LRu(acac)(OH)]PF_6{\cdot}H_2O$ in alkaline aqueous solution with $Na_2S{\cdot}xH_2O$ yields the dinuclear species $[\{LRu(acac)\}_2(\mu\text{-}S_2)](PF_6)_2$ (**67**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), the crystal structure of which was determined. An exchange coupled dinuclear ruthenium(III) species containing an S_2^{2-} bridge is observed [101].

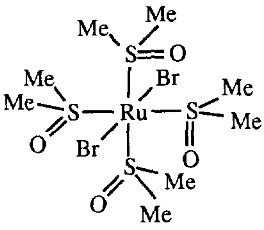


(67)

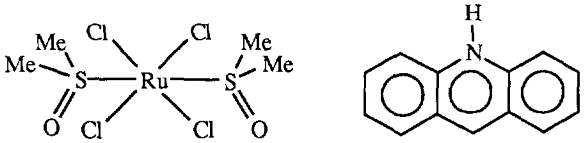
The complex $[Br_6(\text{tmso-}S)_2Ru_2(\mu_2\text{-tmso-}S,O)_2(\mu_3\text{-tmso-}S,O)_2Li_2(\text{tmso-}O)_2]$ (**68**) was isolated from solutions containing $RuCl_3{\cdot}3H_2O$, LiBr and tetramethylene sulfoxide (tmso). The crystal structure of (**68**) shows four different types of coordinated tmso ligands, including a previously unreported μ_3-type coordination. The corresponding synthesis using dmso gives *trans*-$[RuBr_2(dmso\text{-}S)_4]$ (**69**) in high yield [102]. The structure of $[(acr)H]$[*trans*-$RuCl_4(dmso\text{-}S)_2$] (**70**) has been established by X-ray crystallography and the anion has a *trans* arrangement of *S*-bonded dmso ligands [103].



(**68**)

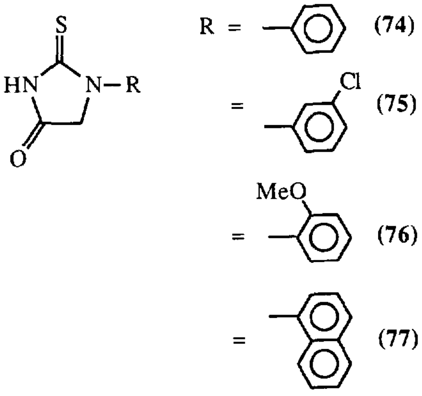


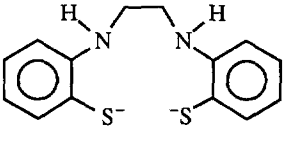
(**69**)



(**70**)

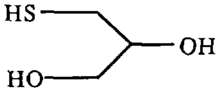
The hydrogen-ion controlled formation and reversible conversion of the two complexes $[Ru(NO)PPh_3('S_2N_2H_2')]Cl$ (**71**) and $[Ru(NO)('S_2N_2H')]_2$ (**72**) have been reported ($'S_2N_2H_2'^{2-}$ = 1,2-ethanediamine-*N*,*N*'-bis(2-benzenethiolate)(2-) (**73**)) [104]. The synthesis and spectroscopic properties of RuL_3 (LH = (**74**), (**75**), (**76**), (**77**)) have been described [105].



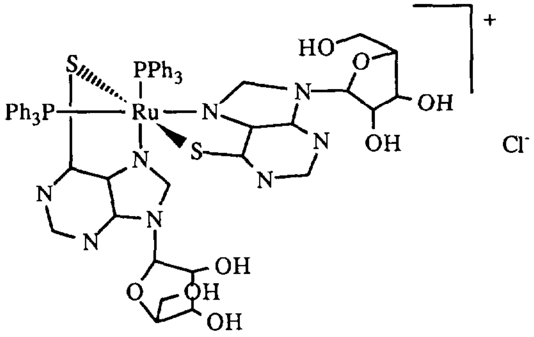


(**73**)

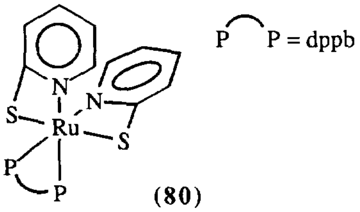
An octahedral complex $[RuLCl(H_2O)_3]$ was prepared from $RuCl_3$ and HL (HL = thiovanol (**78**)). The ligand is coordinating through the S atom and the primary alcoholic O atom [106]. The first X-ray structure of a ruthenium-nucleoside compound bis(9-β-D-ribofuranosyl-6-mercaptopurine)bis(triphenylphosphine)ruthenium(II) chloride (**79**) has been reported. The synthesis and NMR spectroscopic studies have been presented [107]. The complex [Ru(dppb)(2-Spy)$_2$] (**80**) has been structurally characterised by X-ray diffraction [108].



(**78**)



(**79**)



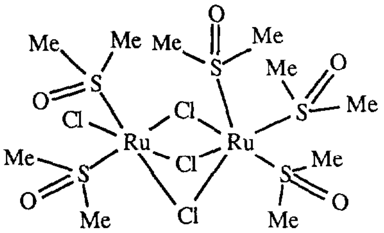
(**80**)

A novel $[Ru_2Fe_8S_6]^{8+}$ cluster (**81**) was prepared by the reaction of $[Fe_6S_6I_2(PMePh_2)_4]$ with $[RuI_2(MeCN)_4]$. The crystal structure of (**81**) shows that it is composed of a $[Fe_8S_6I_8]^{4-}$ unit and two $[Ru(SPMePh_2)(MeCN)_4]^{2+}$ complex fragments bridged via μ_5-S [109].

The sulfide RuS_2 supported on alumina has been reported to be an active catalyst in both thiophene hydrodesulfurisation [110] and hydrorefining of petroleum fractions [111]. The catalyst may be dimetallic in nature and may be used for hydrogenation and denitrogenation [112]. The adsorption and activation of thiophene on RuS_2 has been discussed [113]. The systematic changes in the catalytic activities and in adsorptive properties of RuS_2 catalysts have been investigated and correlated with S removal [114].

Heterodinuclear metal complex [*cis,cis*-$RuCl_2(dmso)_3NH_2(CH_2)_4NH_2PtCl_2$-$(NH_3)$] (**82**) is shown to form specific DNA lesions which can efficiently cross-link proteins to DNA [115]. The effect of reducing tumor-associated fibrinolytic activity by antimetastic dosages of two complexes *cis*-$[RuCl_2(dmso)_4]$ and *trans*-$[RuCl_2(dmso)_4]$ in mice bearing Lewis lung carcinoma has been reported [116].

The molecular structure of $[Ru_2(\mu\text{-}Cl)_4(dmso\text{-}S)_5]$ (**83**) has been established by X-ray crystallography and is characterised by a triple chloro-bridged diruthenium core with five terminal *S*-bonded dmso ligands [117]. The synthesis and structure of $[(dmso)H][trans\text{-}Ru(dmso)_2Cl_4]$ have been reported. The two dmso groups are *trans* to each other and are *S*-bonded to the Ru atom. The cation forms H-bonds to the O of the coordinated dmso [118].



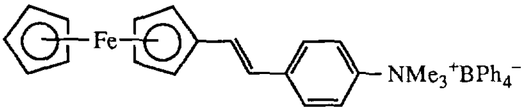
(**83**)

9.5 COMPLEXES WITH NITROGEN DONOR LIGANDS

9.5.1 Complexes with 2,2'-bipyridine ligands.

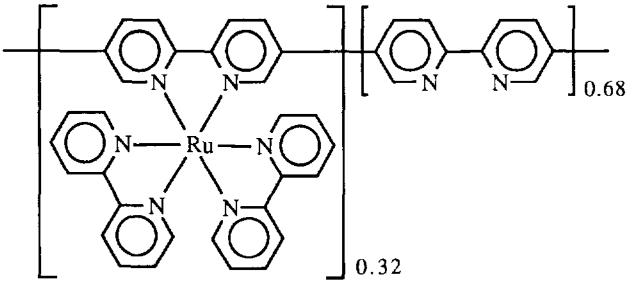
The photoinduced electron transfer and energy transfer reactions of $[Ru(bpy)_3]^{2+}$ with methylviologen or $[Os(bpy)_3]^{2+}$ as probes of interparticle ion-exchange reactions in zeolite Y have been studied by emission spectroscopy [119].

The first direct spectroscopic observation of a photoinduced electron transfer at a liquid-liquid interface was made by the surface-sensitive and surface-selective technique of optical second harmonic generation. The photoinduced electron transfer from the salt (**84**) adsorbed at the water/1,2-dichloroethane interface to photoexcited $[Ru(bpy)_3]^{2+}$ present in aqueous phase results in a large increase in the SHG response [120].



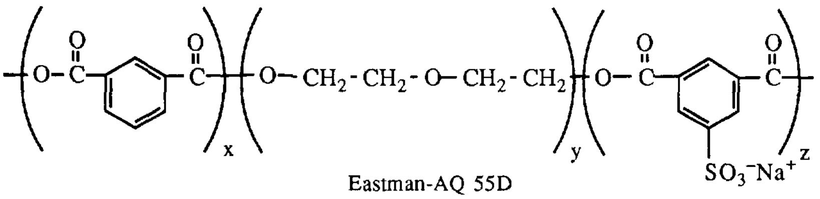
(**84**)

The preparation and characterisation of a soluble oligomeric pendant Ru(II) metal complex system (**85**) has been described. The ESR data for the reduced 1-, 2-, and 3-electron oligomer species are consistent with the data for monomeric $[Ru(bpy)_2bpy^-]^+$, $[Ru(bpy)(bpy^-)_2]^0$ and $[Ru(bpy^-)_3]^-$, indicating that the reduced species are each $S = 1/2$ ligand localised materials [121]. The electronic transfer between ligands in $[Ru(bpy^-)_3]^-$ consisting of monoanion radicals has been discussed [122]. The CO_2 reduction and water-gas-shift reaction photocatalysed by $[Ru(bpy)_3]^{2+}$ have been reviewed together with kinetic and mechanistic studies. [123]. The recoil behaviours of the central metal atoms in $[Ru(bpy)_3]^{2+}$ have been investigated in thermal neutron and Bremsstrahlung irradiation under low temperature conditions [124].

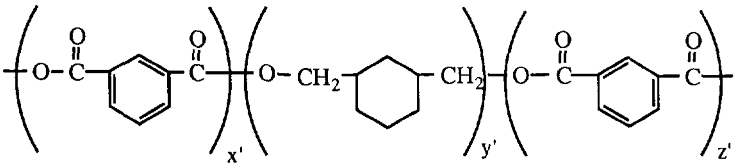


(85)

A new sandwich type photoresponsive bilayer polymer device was fabricated which uses the photochemical reaction between $[Ru(bpy)_3]^{2+}$ and methylviologen (MV^{2+}) confined in each Nafion layer. This photochemical diode generates under air a cathodic photocurrent with respect to the Ru complex-coated electrode. The photocurrent in relation to the partial mixing of the two reaction components in the membrane has been discussed [125]. In addition, another photoresponsive electrode based on the reaction between oxygen and $[Ru(bpy)_3]^{2+*}$ incorporated in a coated Nafion film on an indium tin oxide (ITO) electrode was prepared [126]. The CVs of ferrocene in CO_2 obtained with a microelectrode coated with a film of poly(ethylene oxide) containing $LiCF_3SO_3$, in the presence of $[Ru(bpy)_3](PF_6)_2$, have been discussed [127]. The mass transport of $[Ru(bpy)_3]^{2+}$ in Eastman-AQ polymer film (**86**) coated ultramicroelectrodes has been studied by non-steady-state chronoamperometry at an ultramicrodisk electrode [128]. The photoelectrochemical properties of Nafion and montmorillonite (MM) clay-coated electrodes confining $[Ru(bpy)_3]^{2+}$ have been studied in the presence of Fe^{3+} and H_2SO_4. A new photogalvanic cell was constructed using Pt/Nafion-$Ru(bpy)_3{}^{2+}$ as photoanode and Pt/MM-$Ru(bpy)_3{}^{2+}$ as photocathode [129].



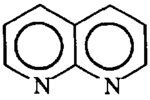
Eastman-AQ 55D



Eastman-AQ 29D

(86)

The properties of Nafion films on electrodes were studied as a function of the water content in the deposition solutions. The rate of loading and unloading of $[Ru(bpy)_3]^{2+}$ into films has been examined. Probably, $[Ru(bpy)_3]^{2+}$ exists in the films in two forms for which the mass transport proceeds by electron self-exchange or by physical diffusion [130]. In addition, cyclic voltammetry has been used to characterise the incorporation of three complexes $[RuL_3]^{2+}$ (L = bpy, phen, 1,8-naphthyridine (**87**)) into a Nafion polymer-modified glassy carbon electrode. The hydrophobicity and unflexible structure of the ligands, phen and (**87**), result in lower levels of incorporation as compared with $[Ru(bpy)_3]^{2+}$ [131].



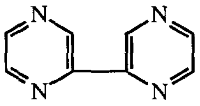
(87)

The incorporation of $[Ru(bpy)_3]^{2+}$ into the silica gel films on Pt and transparent InSn oxide electrodes has been used to modify the electrodes while the cation retains electrochemical and photoelectrochemical activity [132].

A rare example of reversible heterogeneous redox catalysis has been reported which involves the oxidation of $[Ru(bpy)_3]^{2+}$ by thallic ions in HNO_3, mediated by $RuO_2{\cdot}xH_2O$ [133]. In addition, the redox chemistry of Tl clusters in aq. solution was studied by pulse radiolysis and γ-radiolysis using $[Ru(bpy)_3]^{2+}$ as a redox indicator. $[Ru(bpy)_3]^{2+}$ reduces Tl_4^{2+} with a second-order rate constant of $(6 \pm 2) \times 10^8$ M^{-1} s^{-1} [134].

It was shown that $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ form a prototypical octupolar nonlinear system. Their quadratic nonlinear properties are not amenable to electric field-induced second harmonic generation experiments, owing to the absence of net dipole moment in the ground state [135]. A simple fiber optic oxygen sensor based on fluorescence quenching of evanescent-wave excited ruthenium complexes $[RuL_3]^{2+}$ (L = bpy or 4,7-Ph_2-phen) in sol-gel derived porous coating has been described [136]. The oxidation kinetics of $[Ru(bpy)_2(bpy\text{-}R_2)]^{2+}$ (R = $C_{19}H_{39}$) in Langmuir-Blodgett layers has been studied and the results have been compared to homogeneous oxidations by aqueous $[Ru(bpy)_3]^{3+}$ in the same reactant systems [137]. An ultrathin polymer film impregnated with an amphiphilic $[Ru(bpy)_3]^{2+}$ complex for the photocatalytic reduction of viologen has been studied and it was shown that the film had an asymmetric property [138]. Luminescence quenching of $[Ru(bpy)_3]^{2+}$ by ferrocenium derivatives of triiodide [139] and by a series of phenols at different pH has been reported [140]. A system has been described in which photoinitiated electron transfer across the interface between two immiscible electrolyte solutions containing $[Ru(bpy)_3]^{2+}$ and TCNQ has been demonstrated [141]. Luminescence oscillations were found, by fluorescence microscopy, to occur in a $[Ru(bpy)_3]^{2+}$ monolayer on the Belousov-Zhabotinskii reactor containing Ce^{4+} as a catalyst. The fluorescence image exhibits periodic bright-dark transitions due to oscillatory $Ru(bpy)_3{}^{2+}$-$Ru(bpy)_3{}^{3+}$ interconversion [142]. The photophysical properties of the three complexes $[RuL_3]^{2+}$ (L = bpy, bpz (**88**)) and $[Ru(bpz)_2(bpm)]^{2+}$ (bpm = (**89**)) have been studied in neat and mixed $MeCN$-H_2O solutions. The temperature-dependent lifetimes, room-temperature emission spectra and quantum yields were determined for the complexes [143].

A reconstituted myoglobin with a heme bearing a photo-sensitisable $[Ru(bpy)_3]^{2+}$ pendant has been synthesised. The modified myoglobin was effectively activated by visible light irradiation to function as a dioxygen storage protein [144] and the emission of $[Ru(bpy)_3]^{2+*}$ was quenched intramolecularly in the reconstituted myoglobin [145].



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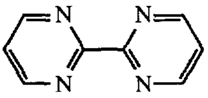

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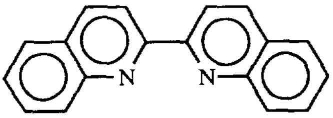


(90)

The electrochemical and electrogenerated chemiluminescence properties of a $[Ru(bpy)_3]^{2+}$-alkanethiol derivative on modified SnO_2-doped In_2O_3 and gold electrodes have been discussed [146]. Enhancement of the electrochemiluminescence of $[Ru(bpy)_3]^{2+}$ in aqueous oxalate and in MeCN containing $[Bu_4N]BF_4$ has been observed by ultrasonic irradiation [147]. The luminescence decay profiles of $[Ru(bpy)_3]^{2+}$ and pyrenetetrasulfonate in the presence of ferricyanide solubilised in cyclohexane-pentanol-sodium dodecyl sullfate quaternary water-in-oil microemulsions have been analysed in restricted spaces [148].

The photoluminescence properties of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(py)_2]^+$ have been measured as a function of pressure in three media: the crystalline solid, poly(4-vinylpyridine) and poly(acrylic acid) [149]. Measurements of the luminescence lifetime of $[Ru(bpy)_3]^{2+}$ in Nafion 117 have been used to probe the heterogeneity of the SO_3H sites in the Nafion membrane [150]. In addition, $[Ru(bpy)_3]^{2+}$-fluortetrasilicic mica-poly(vinylpyrrolidone) intercalation compounds were prepared and the luminescent behaviour of intercalated $[Ru(bpy)_3]^{2+}$ was studied [151].

The photophysical properties of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(biq)]^{2+}$(biq = (**90**)) in poly(ethylene oxide) matrices (PEO) with average molecular weights 400 and 600,000 dalton have been studied at room temperature and 77K. The results suggest that PEO-600,000 is a promising medium for studying electron and energy transfer processes having mild driving forces in the solid state at room temperature [152].

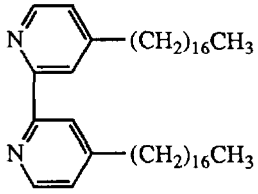
The resonance Raman and the time-resolved resonance Raman spectra have been reported for $[Ru(4\text{-}Me\text{-}bpy)_3]^{2+}$ (4-Me-bpy = 4-methyl-2,2'-bipyridine) and its methyl-deuterated analog, $[Ru(4\text{-}CD_3\text{-}bpy)_3]^{2+}$. The spectra were compared to those of $[Ru(bpy)_3]^{2+}$, $[Ru(4,4'\text{-}Me_2\text{-}bpy)_3]^{2+}$ and its methyl-deuterated analog, $[RuL_3]^{2+}$ (L = 4,4'-$(CD_3)_2$-bpy). Polarisation of the radical fragment of the ^{3}MLCT excited-states has been discussed [153]. The averaged excited state energy of (^{3}MLCT)$[Ru(bpy)_3]^{2+}$ has been found to be $(16.8 \pm 0.2) \times 10^3\ cm^{-1}$ by the photoacoustic method and $(17.0 \pm 0.6) \times 10^3\ cm^{-1}$ by the time-resolved thermal lens method [154].

A system has been reported for the storage of light energy by photoelectron transfer across a sensitised zeolite-solution interface containing $[Ru(bpy)_3]^{2+}$ as the photosensitiser donor and viologen as the acceptor in the surrounding solution [155].

The luminescence quenching of $[Ru(bpy)_3](ClO_4)_2$ by the oxopiperidine cation in sodium dodecylsulfate and aerosol OT solutions have been described [156]. Moreover, the chemiluminescence reaction of five thiazide diuretic compounds with $[Ru(bpy)_3]^{3+}$ was studied by flow injection over a range of pH values of the carrier stream [157].

The excited state absorption spectrum of $[Ru(bpy)_3]^{2+}$ in aqueous and acetonitrile solutions has been examined by three pulsed laser techniques: complete conversion of the ground state, energy transfer to anthracene and benzophenone actinometry. Reliable and reproducible values of $\varepsilon_{450} = (4.6 \pm 0.4) \times 10^3\ M^{-1}\ cm^{-1}$ were obtained by the three techniques, independent of the solution medium [158].

The kinetics of luminescence damping of $[Ru(bpy)_2(L)](ClO_4)_2$ (L = (**91**)) by quenchers of different hydrophilic-lipophilic natures in an aqueous micellar solution of cetyltrimethylammonium bromide have been measured at 303K [159].



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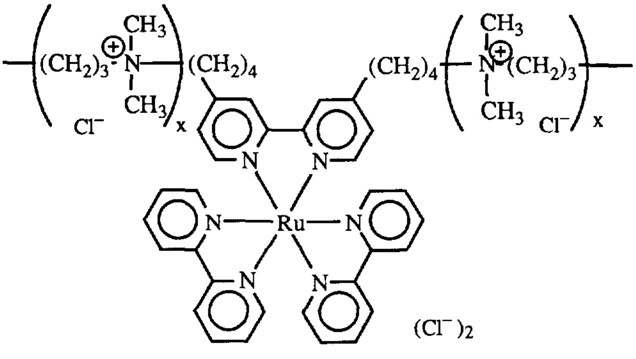
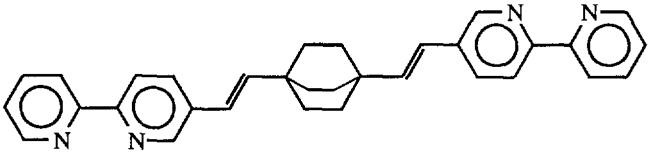


(92)

The luminescence quenching, by noncovalently attached multivalent anions, of a $[Ru(bpy)_3]^{2+}$ excited chromophore that was covalently bound to a poly(3,3-ionene) (**92**) has been reported [160].

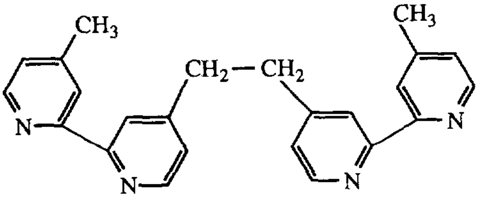
The bis(bipyridine) bridging ligand bpy-S-bpy (**93**) has been synthesised and its complexes $[(bpy)_2Ru(bpy\text{-}S\text{-}bpy)]^{2+}$ (**94**), $[(bpy)_2Ru(bpy\text{-}S\text{-}bpy)Ru(bpy)_2]^{4+}$ (**95**) and $[(bpy)_2Ru(bpy\text{-}S\text{-}bpy)Os(bpy)_2]^{4+}$ (**96**) were prepared as PF_6^- salts. Partial oxidation of the dinuclear complexes (**95**) and (**96**) by Ce(IV) in $MeCN\text{-}H_2O$ solutions leads to mixed-valence Ru(II)/Ru(III), Ru(II)/Os(III) species where the oxidised metal-based unit quenches the luminescent excited state of the unit that is not oxidised. The photoinduced energy and electron transfer processes in these supramolecular species have been discussed [161].



(93)

The mixed-valent complexes $[(bpy)_2ClRu\text{-}pz\text{-}Ru(NH_3)_5]^{4+}$ (**97**) (pz = pyrazine) and $[(4,4'\text{-}Me_2\text{-}bpy)_2ClRu\text{-}pz\text{-}Ru(NH_3)_4(4\text{-}Me\text{-}py)]^{4+}$ (**98**) were found to exist in localised and delocalised forms respectively in nitromethane. The temperature effects for localised versus delocalised optical intervalence transitions have been studied [162].

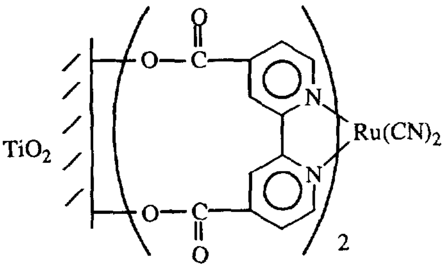
The photoinduced electron-transfer processes involving covalently-linked ruthenium and cobalt complexes $[(bpy)_2Ru(\mu\text{-}L)Co(bpy)_2]^{5+}$ (L = (**99**)) has been examined. The electronic coupling of this heterodimetallic complex has been studied [163].



(**99**)

The electrochemical behaviour of the dinuclear complex $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}CN]^+$ (**100**) and of the trinuclear complexes $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}NC\text{-}Ru^{II}\text{-}(bpy)_2\text{-}CN]^{2+}$ (**101**) and $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(DCE\text{-}bpy)_2\text{-}NC\text{-}Ru^{II}(bpy)_2\text{-}CN]^{2+}$ (**102**) (DCE-bpy = 5,5'-dicarboxyethyl-2,2'-bipyridine) is described. The experimentally determined redox series consist of nine, thirteen and fourteen redox steps for (**100**), (**101**) and (**102**) respectively [164]. Three of the redox steps in (**102**) are due to the one-electron reversible oxidations of Ru(II) to Ru(III), while the remaining eleven can be ascribed to one-electron reversible reductions centred on the bpy ligands [165]. The spectroscopic and electrochemical manifestations of a series of complexes $M[CNRu(NH_3)_5]_2$ (M = $Ru^{II}(bpy)_2$, $Co^{III}L$, $Rh^{III}(bpy)_2$ or $Rh^{III}L$; L = tetraazamacrocyclic ligand) have been reported and the contrasting donor-acceptor electronic coupling has been discussed [166].

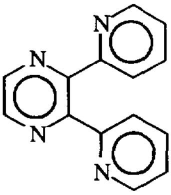
The preparation, surface attachment, optical and photoelectrochemical properties of the complexes *cis*-$[\{4,4'\text{-}(CO_2H)_2bpy\}_2Ru^{II}(CN)_2]$ (**103**) attached to sol-gel processed TiO_2 electrodes have been reported [167]. Thin Ti(IV) oxide films, deposited on SnO_2 (F-doped) and metallic (Pt, Au, Ti) electrodes by anodic oxidative hydrolysis of acidic aqueous $TiCl_3$ solutions, were spectrally sensitised to higher wavelengths by adsorption of $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}\{\mu\text{-}(NC)Ru(CN)(bpy)_2\}_2]$. The performance of an I^-/I_2 regenerative photocell based on the prepared TiO_2 photoanode has been considerably improved [168].



(**103**)

The synthesis, characterisation and spectroelectrochemical analysis of the complexes $[\{(bpy)_2Ru(BL)\}_2IrCl_2](PF_6)_5$ (BL = dpp (**104**), dpq (**105**) or dpb (**106**)) have been reported.

These complexes contain two visible light absorbing centres covalently coupled to a catalytically active central metal site [169].



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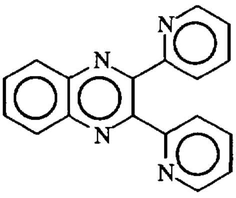

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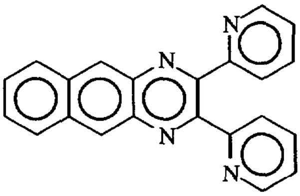
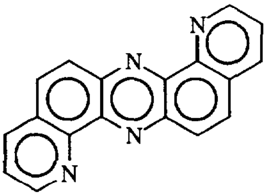


(106)

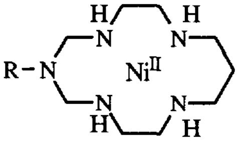
Complexes $[(bpy)_2Ru(dpop)](PF_6)_2$ and $[\{(bpy)_2Ru\}_2(dpop)](PF_6)_4$ (dpop = (**107**)) have been prepared. Their electronic absorption and emission and electrochemical properties have been studied. Overall results indicate that $[(bpy)_2Ru^{II}]$ coordination to the highly conjugated planar dpop ligand produces complexes that absorb and emit at lower energies than for complexes with similar ligands while retaining favourable electrochemical and photochemical properties for excited state energy transfer reactions [170].

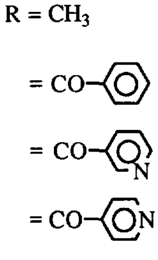


(107)

New complexes $[(bpy)_2(py)Ru^{II}\text{-}CN\text{-}Ru^{III}(NH_3)_5]^{4+}$ (**108**) and $[(bpy)_2(py)Ru^{II}\text{-}CN\text{-}Fe^{III}(CN)_5]^-$ (**109**) with a cyano bridge were prepared and their spectroscopic, electrochemical and photophysical properties have been studied. The strong asymmetric nature of (**108**), together with a strong electronic coupling indicate that the back electron transfer from the metal-to-metal charge transfer excited state of complex (**108**) probably lies in the inverted region [171].

Reaction of the metallocyclam-pyridine conjugate $Ni^{II}L^{2+}$(**110**) with *cis*-$[Ru^{II}(bpy)_2Cl_2]$, in a 2:1 ratio, gives the complex *cis*-$[(Ni^{II}L)_2Ru^{II}(bpy)_2]^{6+}$ (**111**). Cyclic voltammetry and controlled potential coulometry studies on non-aqueous solution of (**111**) have been investigated [172].



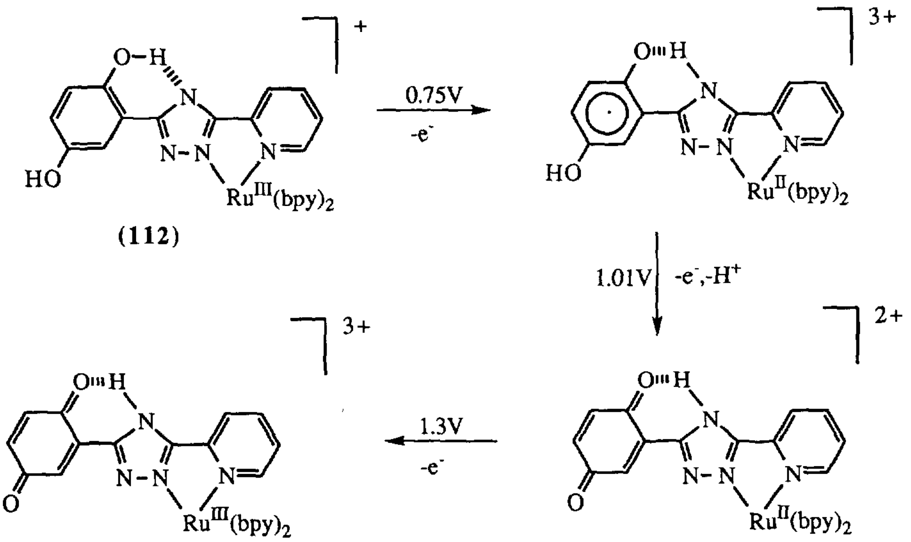


(110)

The effects of substituents on the electrochemical and spectroscopic properties of $[Ru^{II}(bpy)_2(L\text{-}L)]$ (L-L = 4,5-disubstituted *o*-benzoquinonediimines, *o*-semiquinone- diimines, *o*-phenylenediamides and *o*-phenylenediamines) have been reported. These data have been used to create a map of the orbital energies as a function of the Hammett parameter of the substituents, giving insight into the electronic behaviour of these complexes [173].

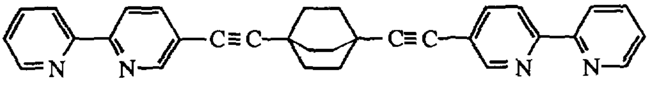
A novel ditopic ligand bpy-cyclam and its heterometallo-dinuclear complex $[Ru(bpy)_2(bpy\text{-}cyclam\text{-}Ni)](ClO_4)_4{\cdot}3H_2O$ have been synthesised and characterised. The complex was designed for use in the catalytic photoreduction of CO_2 [174].

The complex $[Ru(bpy)_2L]PF_6$ (**112**) (HL = 3-(2,5-dihyroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole) was prepared and found to exhibit electrochemically induced proton transfer between the hydroquinone moiety and the triazole. The transfer occurs intramolecularly via a H-bridge formation between the hydroquinone and triazole as shown in Scheme 1 [175].



Scheme 1

A novel ligand L = (**113**) was prepared and its reaction with $[Ru(bpy)_2Cl_2]$ to give $[Ru(bpy)_2L]^{2+}$ (**114**) and $[\{Ru(bpy)_2\}_2L]^{4+}$ (**115**) was presented. The complex $[Ru(bpy)_2LOs(bpy)_2]^{4+}$ (**116**) was also isolated. The crystal structure of (**113**) has been determined and all the complexes have been characterised by UV-VIS and luminescence spectra and electrochemical oxidation. The Ru-Os distance in (**116**) is 1.7 nm. The ligand (**113**) is the first linked bis(bipyridine) ligand with which two complex moieties are separated through a rod-shaped, rigid spacer [176].



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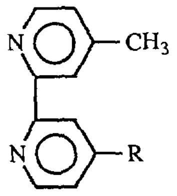
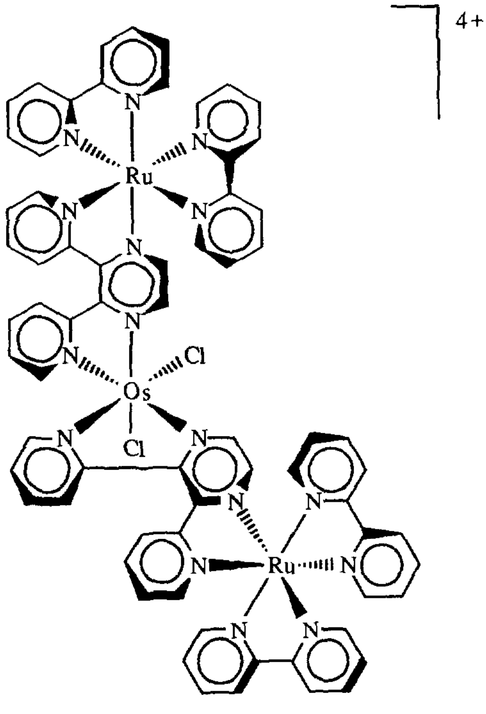


R=$C_{11}H_{23}$, $C_{18}H_{37}$, $C_{20}H_{41}$

(117)

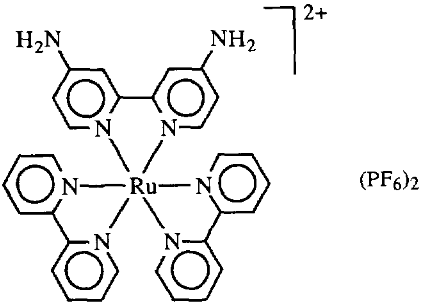
The surfactant bipyridine complexes of Ru(II) $[Ru(bpy)_2(L)]^{2+}$ (L = 4-methyl-4'-alkyl-2,2'-bipyridine (**117**)) have been prepared. These complexes exhibit lyotropic mesomorphism in water [177].



(118)

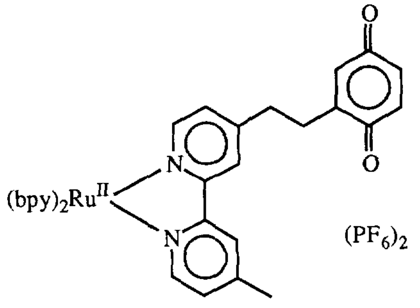
The preparation and characterisation of $[\{(bpy)_2Ru(\mu\text{-}dpp)\}_2OsCl_2]^{4+}$ (**118**), $[\{(bpy)_2Ru(\mu\text{-}dpq)\}_2OsCl_2]^{4+}$ (**119**) and $[\{(bpy)_2Ru(\mu\text{-}dpb)\}_2OsCl_2]^{4+}$ (**120**) have been reported (dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline, dpb = 2,3-bis(2-pyridyl)benzoquinoline). Cyclic voltammetric and spectroscopic studies have been discussed. The lowest lying bridging ligand-based π* orbital shifts to lower energies as the π delocalisation of the bridging ligand increases. The bridging ligand-based reductions were found to shift to more positive potentials on going from dpp to dpq to dpb [178]. The temperature and magnetic field dependence of the low-temperature emission and excitation spectra of $[Ru(bpy)_2(bpz)]^{2+}$ (bpz = (**88**)) doped into $[Zn(bpy)_3](ClO_4)_2$ have been reported [179].

The preparation and properties of the asymmetric dimetallic complex $[(bpy)_2Ru^{II}(bpm)Ru^{II}(NH_3)_4](PF_6)_4{\cdot}3H_2O$ (bpm = (**89**)) have been reported. The complex shows a low energy MLCT band at 704 nm in MeCN, whilst its mixed-valence form $[(bpy)_2Ru^{II}(bpm)Ru^{III}(NH_3)_4]^{5+}$ shows no evidence of any MLCT band in MeCN. The electrochemical study of the Ru(II)/Ru(II) complex was presented [180]. The complex $[Ru^{II}(bpy)_2L](PF_6)_2$ (**121**) was prepared from the reaction of $[Ru(bpy)_2Cl_2]$ with L (L = 5,5'-diamino-2,2'-bipyridine) in EtOH under reflux, followed by treating with saturated aq. NH_4PF_6. Complex (**121**) was polymerised with 3,3',4,4'-biphenyltetracarboxylic dianhydride in dmso to give a polyamic acid [181].

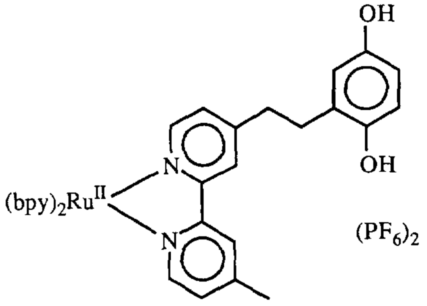


(**121**)

The redox couple of quinone-hydroquinone functional group-containing Ru bipyridyl complexes (**122**) and (**123**) represents an electrophotoswitching device which displays electrochemically reversible interconversion between a non-luminescent state (quinone-form) and a luminescent state (hydroquinone-form) [182].

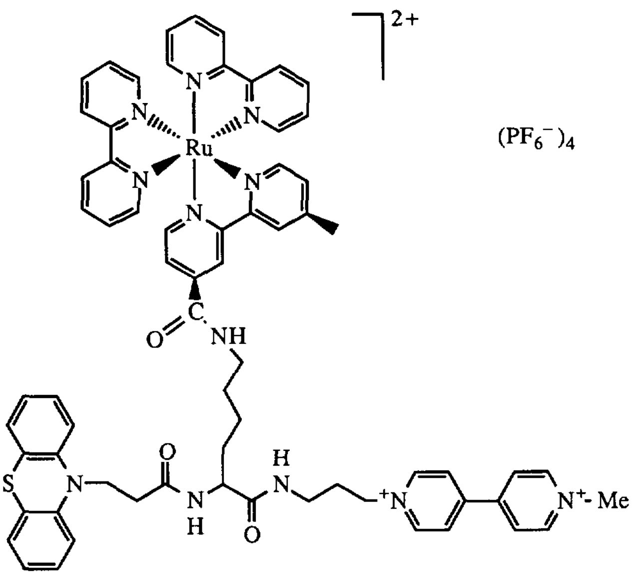


(**122**)



(**123**)

The donor-chromophore-acceptor triad (**124**) was prepared by assembly of a modified ruthenium bipyridyl chromophore $Ru^{II}(bpy)_2(L)$ (L = 4'-methyl-2,2'-bipyridyl-4'-carbonyl), an electron donor (phenothiazine) and an electron acceptor (paraquat) on a lysine scaffold utilising amide bonds. This derivatised amino acid exhibits efficient (>95%) quenching of the ruthenium MLCT excited state upon irradiation with a 420 nm laser pulse in CH_3CN. Also studied was a series of redox-active lysines and related model compounds based on polypyridyl ruthenium complexes. The photophysical characterisation of the compounds have been described [183].



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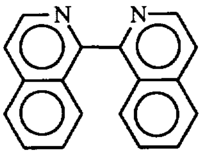
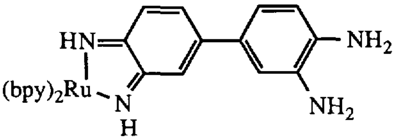


(125)

The surface-enhanced Raman scattering spectra of $[Ru(bpy)_3]^{2+}$, $[RuL_3]^{2+}$, $[Ru(bpy)_2(L)]^{2+}$ and $[Ru(bpy)(L)_2]^{2+}$ (L = 1,1'-biisoquinoline (**125**)) in aqueous silver sol have been measured [184].

The strong solvatochromic effect of the MLCT transition of the complex $[Ru(bpy)_2(L)]$ (**126**) has been studied by electronic spectrum, resonance Raman and AM1 calculations to be due to variation of the twist angle at the biphenyl linkage. Lewis acid (hydrogen bond donor) solvents cause the twist angle to approach 90°, while Lewis base (hydrogen bond acceptor) solvents favour a more coplanar conformation due to the increased contribution of resonance form (**127**) [185].



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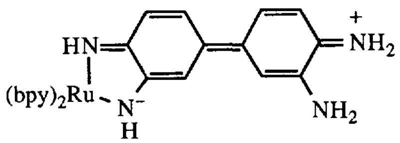
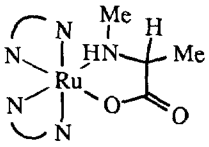


(127)

Facile dehydrogenation of α-amino acids in $[Ru(N\text{-methylalaninato})(bpy)_2]^+$ (**128**) and $[Ru(prolinato)(bpy)_2]^+$ (**129**) was achieved by anodic oxidation to yield the corresponding α-imido acidato Ru(II) complexes $[Ru\{N(R)=C(R)\text{-}CO_2\}(bpy)_2]^+$ (R = Me (**130**) or R,R = $-(CH_2)_3-$ (**131**) respectively). The X-ray structure of (**131**) has been established [186].



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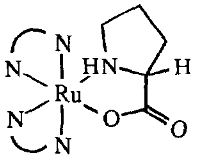

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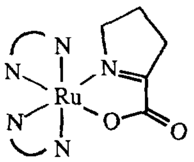

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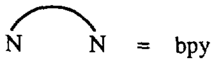
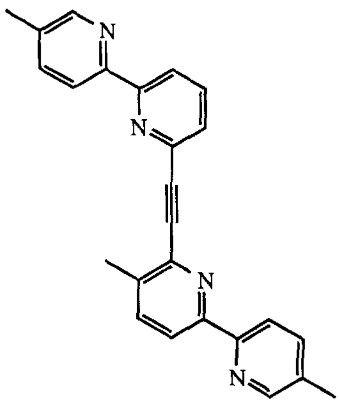


New ditopic ligands bearing two bipyridine subunits and an ethynyl or diethynyl bridge (**132**), (**133**) and (**134**) were synthesised and shown to form cationic mononuclear Ru(II), dinuclear Ru(II) and trinuclear Ru(II)-Cu(I) complexes. The fluorescence properties of the complexes have been studied [187].



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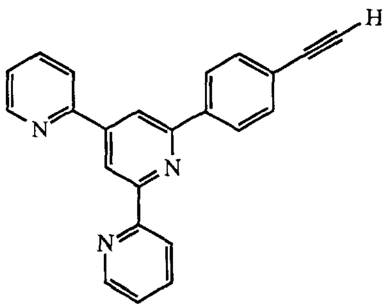

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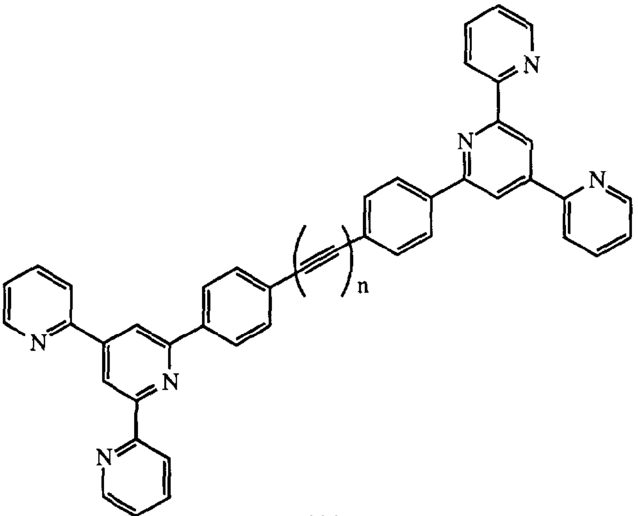
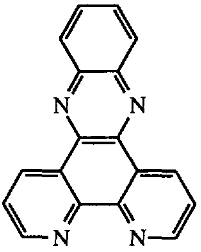


(134)

The formation of $[Ru(bpy)_2Cl_2]$ from the photosubstitution of $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$ has been reported. A radical chain reaction mechanism, initiated by homolysis of a C-Cl bond, has been suggested [188].

The chelating ligands L (L = (**135**), (**136**)) and their corresponding complexes $[Ru(bpy)_2(L)]^{2+}$ have been studied in multiply reduced states by low temperature cyclic voltammetry, UV-VIS and EPR spectroscopies. The particular composite electronic structure of the complexes with differing redox and optical orbitals is related to their light switch behaviour, i.e. to the absence of luminescence quenching in a non-aqueous environment [189].



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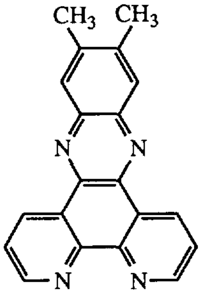
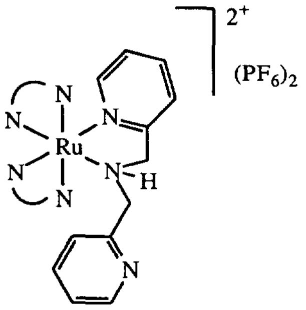


(136)

Two complexes $[Ru(bpy)_2(bpaH)](PF_6)_2$ (**137**) and $[Ru(bpy)_2(beaH)](PF_6)_2$ (**138**) were prepared and they represent suitable building blocks for polymetallic ruthenium(II) polypyridine luminophores. The complex (**137**) was characterised by X-ray crystallography and has a luminescence lifetime comparable to that of $[Ru(bpy)_3]^{2+}$ [190].



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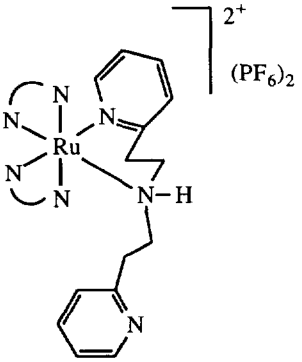

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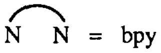
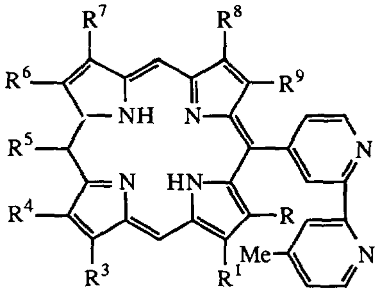


The synthesis and characterisation of *meso*-substituted porphyrins L = (**139**) and L' = (**140**) have been described. Treatment of these two ligands with an excess of *cis*-$[RuCl_2(bpy)_2]$ gives $[Ru(bpy)_2L](PF_6)_2$ and $[\{Ru(bpy)_2\}_2L'](PF_6)_4$. The cyclic voltammetry of these redox active systems has been examined [191].



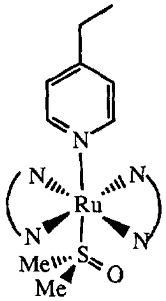
$R = R^4 = R^6 = R^9 = Me$, $R^1 = R^3 = R^7 = R^8 = Bu$, $R^5 = H$ **(139)**

$R = R^1 = R^8 = R^9 = Et$, $R^3 = R^7 = Me$, $R^4 = R^5 = Bu$,
R^5 = 4'-methyl-2,2'-bipyridin-4'-yl
(140)

The facile diastereomeric isomerisation of the complex $[Ru^{II}(bpy)_2(L)](PF_6)_2$ (L = **(125)**) has been discussed. The complex exists as a 3:1 mixture of two diastereomeric forms in acetone solutions at 25°C. However, only one of the two diastereomers crystallised from MeCN/ether and has been characterised by X-ray crystallography. The kinetics and mechanism of such isomerisation have been examined [192].

The complex *trans*-$[Ru(bpy)_2(dmso)_2](CF_3SO_3)_2 \cdot 0.5H_2O$ has been isolated and was found to react with pyridine derivatives in dmso to give *trans*-$[Ru(bpy)_2L(dmso)]PF_6 \cdot nH_2O$ (L = 4-ethylpyridine (4-Etpy) n = 0, L = 4-(dimethylamino) pyridine, n = 1.5, L = ethyl isonicotinate, n = 1). The single-crystal X-ray structure of *trans*-$[Ru(bpy)_2(4\text{-}Etpy)(dmso)] \cdot 0.5dmf$ **(141)** has been determined [193].

The photoinduced electron transfer and back electron transfer within the dinuclear complexes $[(bpy)_2Ru^{II}(L\text{-}L)Co^{III}(bpy)_2]^{5+}$ (L-L = **(142)**, **(143)** and **(144)**) have been studied [194].



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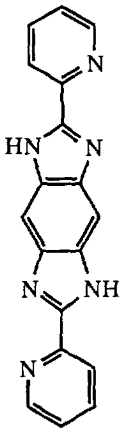

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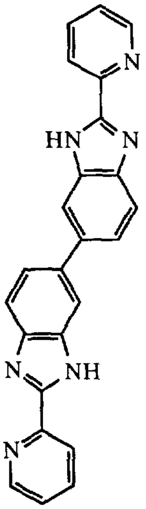

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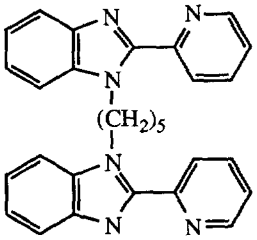
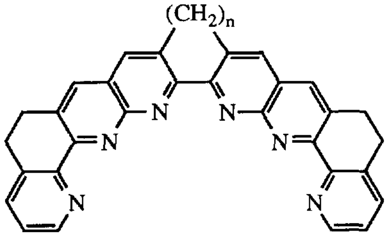


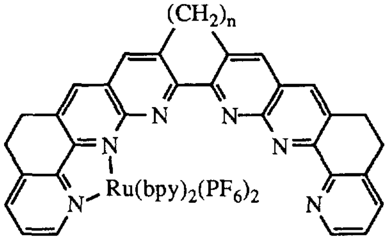
(144)

Large polyaza cavity-shaped ligands L(L = **(145)**) have been prepared. Treatment of L (X = N) with $[Ru(bpy)_2Cl_2]$ incorporates Ru(II) into a distal didentate site to give complex **(146)**. For ligands which are significantly nonplanar, a second Ru(II) or Os(II) nucleus can similarly be incorporated into the remaining distal site. The X-ray structure of the dinuclear complex $[(bpy)_2Ru(L)Ru(bpy)_2](PF_6)_4$ (n = 4, X = N) (**147**) has been determined [195].

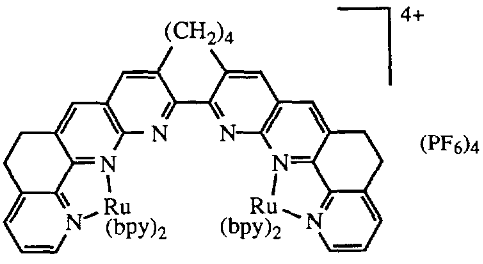


n = 2-4
x = CH,N

(**145**)

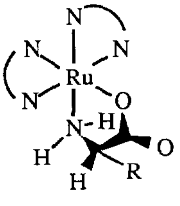


(**146**)

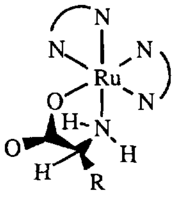


(**147**)

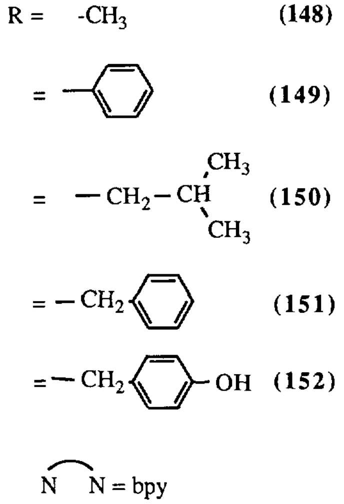
The effect of hydrophobic and hydrophilic interactions on the stability of diastereoisomers of Δ and Λ-$[Ru(L)(bpy)_2]^+$ ((**148**), L = (*S*)-alaninato; (**149**), L = (*S*)-phenylglycinato; (**150**), L = (*S*)-leucinato; (**151**), L = (*S*)-phenylalaninato; (**152**), L = (*S*)-tyrosinato) in aqueous solutions has been discussed. The hydrophilic solvation favoured the Δ-isomer in water, whereas the hydrophobic solvation preferred the Λ-isomer [196].



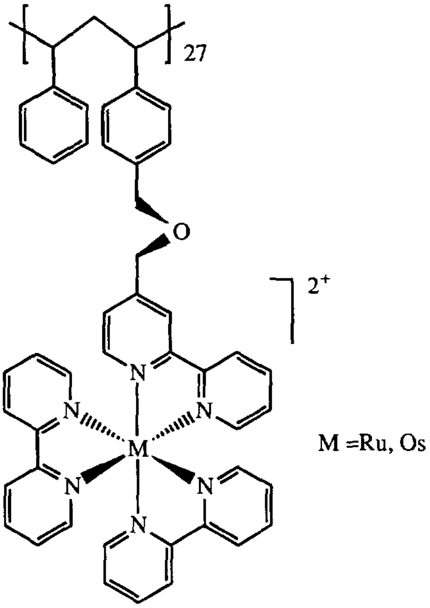
Δ - S



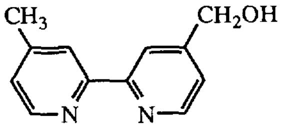
Λ - S



The polymer [p-PS-$Ru^{II}{}_{22}Os^{II}{}_{5}](PF_6)_{54}$ (**153**) (p-PS is a 1:1 copolymer of styrene and p-(chloromethyl)styrene)) was prepared by nucleophilic displacement of chloride by $[M(bpy)_2(bpyCH_2OH)]^{2+}$ (M = Ru or Os; $bpyCH_2OH$ = (**154**)) under basic conditions, in which 22 of the approximate 27 repeating units of an average strand were Ru^{II} and the remaining 5 were Os^{II}. Intrastrand electron and energy transfer between pendant sites in this derivatised copolymer have been studied by laser flash photolysis [197].



(153)



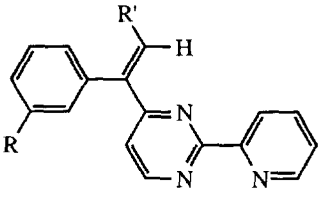
(154)

Novel biomimetic systems for the direct photoreduction of H_2O using visible light have been described. The bis-heteroleptic Ru(II) complexes $[Ru(bpy)_2(L)]Cl_2$ (L = bpy, 2-methyl-(1-(2(2'-pyridyl)-4-pyrimidyl))-1,2-phenylethene (**155**), 1-(2(2'-pyridyl)-4-pyrimidyl)-1,2-phenylethene (**156**) and 1-(2(2'-pyridyl)-4-pyrimidyl)-1,2-(4-chloro)-phenylethene (**157**)) adsorbed on a negatively charged SiO_2-TiO_2-colloid, the zwitterionic electron relay propylviologen sulfonate, TiO_2-Pt-antenna catalyst and triethanolamine sacrificial electron donor have been used as model systems [198].

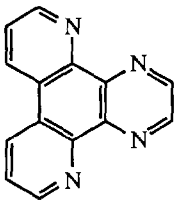
The dramatic increase in the conformational and thermal stability of a protein obtained by crosslinking an engineered metal-binding site with a $Ru^{II}(bpy)_2$ moiety has been reported. The stabilisation mechanism is similar to that of disulfide bridges and therefore involves a decrease in the conformational entropy of the unfolded state [199].

The binding of enantiomers of $[Ru(bpy)_2(ppz)]^{2+}$ (ppz = 4,7-phenanthrolino[6,5-b] pyrazine (**158**)) to calf thymus DNA has been investigated using absorption, fluorescence and resonance enhanced Raman spectroscopies [200]. In addition, the electric dichroism measurements on a solution containing DNA and optically active $[Ru(bpy)_2(phi)]^{2+}$ (phi = 9,10-

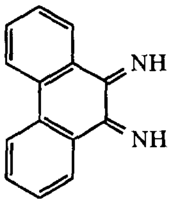
phenanthrenequinonediimine (**159**)) have been reported which indicate intercalation of the metal complex by DNA [201].



(**155**) R = H, R' = Me
(**156**) R = H, R' = H
(**157**) R = Cl, R' = H

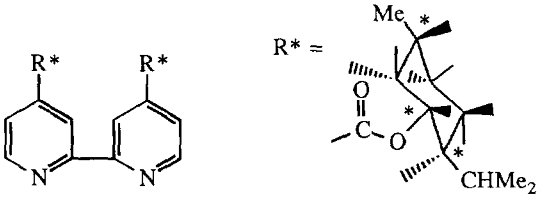


(**158**)

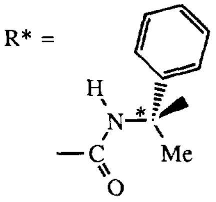


(**159**)

A novel enantioselective photoreduction of the helical substrates of *rac*-$[Co(acac)_3]$ and *rac*-$[Co(edta)]^-$ catalysed by chiral, helical complexes Δ- (or *rac*)-$[Ru(Menbpy)_3]^{2+}$ (Menbpy = 4,4'-bis[(1*R*,2*S*,5*R*)-(-)-methoxycarbonyl]2,2'-bipyridine (**160**)) and Λ-(or Δ)-[Ru{*S* or *R*)-PhEtbpy}$_3]^{2+}$ ((*S* or *R*)-PhEtbpy = 4,4'-bis[(*S*)-(-) or (*R*)-(+)-1-phenylethylaminocarbonyl]-2,2'-bipyridine (**161**)) has been reported [202]. Moreover, the racemic photocatalysts Δ- and Λ-$[Ru(Menbpy)_3]^{2+}$ were found to be active in the photoinduced asymmetric synthesis of Λ-$[Co(acac)_3]$ from $Co(acac)_2(H_2O)_2$ and Hacac [203].

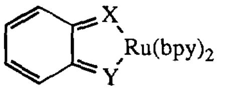


(**160**)

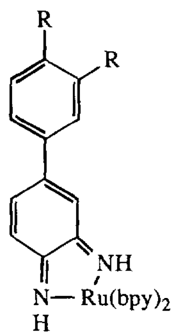


(**161**)

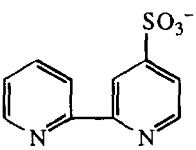
The kinetic behaviour and mechanistic study of *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ toward anation by pyridine-2-aldoxime as a function of temperature, ligand concentration, substrate complex concentration and pH have been reported [204].



(**162**) X = Y = O
(**163**) X = O; Y =NH
(**164**) X = Y =NH



(**165**)



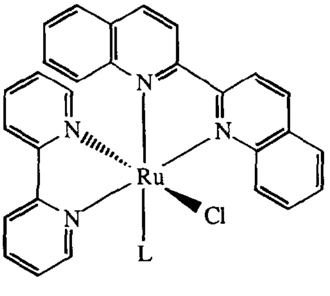
(**166**)

The water-soluble complex *cis*-$[Ru(6,6'-Cl_2-bpy)_2(OH_2)_2](CF_3SO_3)_2$ (6,6'-Cl_2-bpy = 6,6'-dichloro-2,2'-bipyridine) was found to be an effective catalyst for the hydrogenation of organic carbonyl compounds and olefins in biphasic aqueous/organic systems. The catalyst could be reused after simple decantation [205].

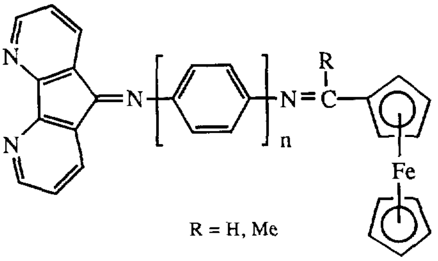
The electronic structures of some bipyridine ruthenium complexes of quinone (**162**) and a series of derivatives (**163**) and (**164**) in which the oxygen atoms of quinone are successively replaced by NH have been probed by electronic and resonance Raman spectroscopy. The electronic structures of some benzoquinoediimine species (**165**) have also been studied [206].

The synthesis, characterisation and electrochemical study of $[\{Ru(bpy)_2\}_2(\mu\text{-}OR)_2](PF_6)_2$(R = Me or Et) have been reported and the crystal structure of $[\{Ru(bpy)_2\}_2(\mu\text{-}OEt)_2](PF_6)_2{\cdot}Et_2O{\cdot}2MeCN$ has been determined [207].

The complex $[Ru(bpy)_2(bpy\text{-}5\text{-}SO_3)]Cl{\cdot}2H_2O$ (bpy-5-SO_3 = (**166**)) was synthesised and characterised. The complex is 50% more soluble than $[Ru(bpy)_3Cl_2]$ while retaining the electrochemical and photophysical properties of the tris(bpy) analog [208]. The reaction of *cis*-$[Ru(bpy)(bquin)Cl_2]$ (bquin = 2,2'-biquinoline) with imidazole (imH), 1-methylimidazole (1-mim) or 5-methylimidazole (5-mim) gives *cis*-$[Ru(bpy)(bquin)(L)Cl]PF_6$ (**167**), where substitution of only one chloride ligand takes place exclusively *trans* to bquin. The compounds *cis*-$[Ru(bpy)(bquin)L_2](PF_6)_2$ and *cis*-$[Ru(bpy)(bquin)(1\text{-}mim)(imH)](PF_6)_2$ were also isolated [209]. The preparation and electronic absorption spectra of $[Ru(L)_2Cl_2]$ (L = 1,1'-biisoquinoline) and some bipyridine and 1,10-phenanthroline ruthenium(II) complexes of 1,1'-biisoquinoline have been reported [210].



L = imH, 1-mim or 5-mim
(**167**)

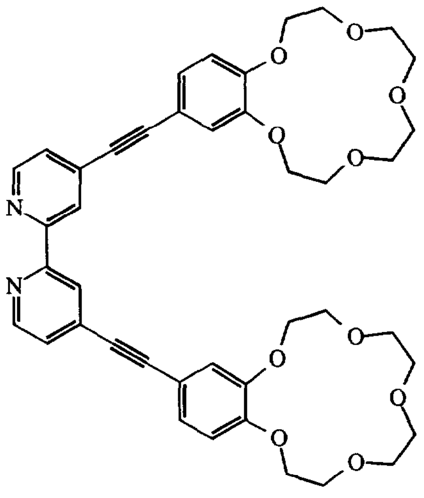


(**168**)

The luminescence systems including oxalic-acid-$Ru(bpy)^{3+}$, indole-$Ru(bpy)^{3+}$, aliphatic, tertiary amine-$Ru(bpy)^{3+}$ and ketone-$Ru(bpy)^{3+}$ have been discussed as a possible detection technique for HPLC and flow-injection analysis [211].

The ruthenium-ferrocene polynuclear complex $[Ru(bpy)(L)_2](PF_6)_2$ (L = (**168**)) has been prepared and characterised. The luminescence of the chromophore Ru(II) is quenched by the luminophor Fe(II), and an efficient intramolecular energy transfer from Ru(II) to Fe(II) occurs [212].

A new alkynyl-linked bis(benzo-15-crown-5)bipyridyl ligand (**169**) and new mono- and bis-benzo-15-crown-5 and aza-15-crown-5 bipyridyl ligands (**170**) and (**171**) have been synthesised. The corresponding $[Ru(bpy)_2L](PF_6)_2$ and $[RuL_3](PF_6)_2$ (L = (**169**), (**170**) and (**171**)) complexes were prepared and the latter electropolymerised onto optically transparent conducting glass electrodes. Electronic absorption and fluorescence-emission spectroscopic measurements have demonstrated spectrochemical recognition of Group 1 and 2 metal cations by the novel functionalised crown ethers both as solution complexes and as polymeric films [213].



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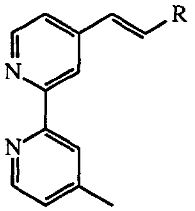

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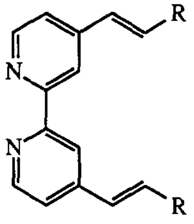

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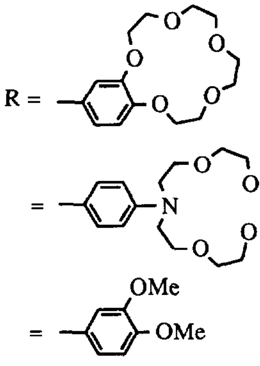
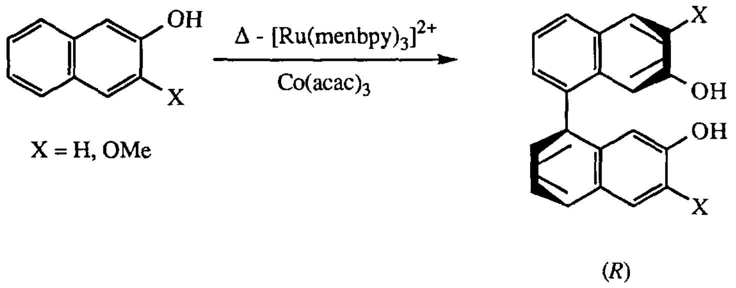


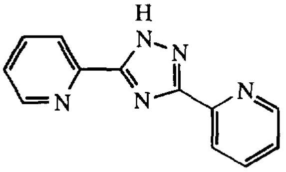
A novel photocatalytic asymmetric synthesis of (*R*)-(+)-1,1'-bi-2-naphthol (or (*R*)-(+)-1,1'-bi-3-methoxy-2-naphthol) by oxidative coupling of 2-naphthol (or 3-methoxy-2-naphthol) (equ. 2) with the chiral complex Δ-$[Ru(menbpy)_3]^{2+}$ has been reported [214].



(equ. 2)

The preparation and characterisation of $[Ru^{III}(DPA)(L)Cl]$ (DPA = 2,6-dipicolinic acid; L = bpy, en, phen) have been reported. The complexes have been used as catalysts for the oxidation of hydrocarbons using iodosylbenzene and *tert*-Bu hydroperoxide as the oxidants. The formation of the active intermediate $[Ru^{V}(DPA)(bpy)(O)]$ has been investigated in the case of L = bpy. The termination pathway of the cycle has been presented [215]. The selective oxidation of alkylbenzenes to give the corresponding ketone and alcohol has been found to be catalysed by ruthenium-polymer-bound 2,2'-bipyridine complexes [216]. Soluble redox polymers and copolymers of $[Ru(vbpy)_3(PF_6)_2]$ (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine) were prepared by radical polymerisation and characterised. The properties of these polymers have been compared to those prepared by electro-initiated polymerisation on an electrode surface. Fundamental differences between solution (homogeneous) polymerisation and (heterogeneous) electro-polymerisation have been discussed [217].

The complexes $[Ru(bpy)_2(nbpy)(ClO_4)_2]$ and $[Ru(tm\text{-}bpy)_3(ClO_4)_2]$ (nbpy = 4,4'-dinonadecyl-bpy, tm-bpy = 4,4'-5,5'-tetramethyl-bpy) were incorporated as functional species in the LB films of siloxanes. The surface area-pressure isotherms and photoluminescence measurements of the LB films were presented [218]. Polyamic acids from the reaction of dianhydrides with $[Ru(bpy)_2(L)]$ (L = 5,5'-diamino-bpy) have been used for the formationof LB films [219]. The excited state and redox properties of new $[Ru(bpy)_2(bpt)Ru(phen)_2](PF_6)_3$ and $[Ru(phen)_2(bpt)Ru(bpy)_2](PF_6)_3$ (Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole (**172**)) have been reported. Spectroelectrochemical data indicate that the Ru unit bound to the N1 site of the triazole ring is oxidised first and the lowest ^{3}MLCT state is bpy based [220]. In addition, the dinuclear complex $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$ (dpt-cy-dpt = (**173**)) has been prepared. The mono-chelating ligand (**174**) and the corresponding complex $[(bpy)_2Ru(dpt\text{-}cy)]^{2+}$ have also been synthesised. Their absorption spectra, electrochemical behaviour and luminescence properties have been studied [221].



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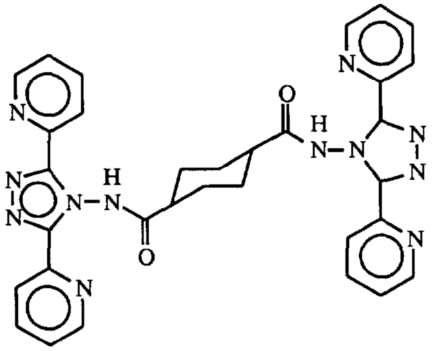

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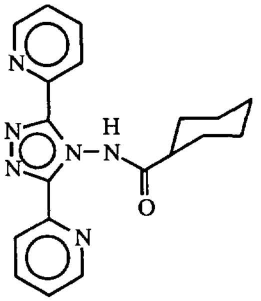
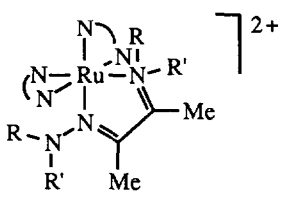


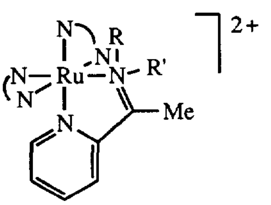
(174)

The surface enhanced resonance Raman spectra of $[Ru(bpy)_3]^{2+}$ and $[RuL_3]^{2+}$ (L = 4,4'-dimethyl-, 4,4'-diphenyl-, 4,4'-diamino- and 4,4'-diethylcarboxylate-2,2'-bipyridine) on chemically-deposited silver films have been reported [222]. Moreover, the low-energy charge-transfer transitions Ru→biq and Ru→dpp in the ligand-bridged complexes $[(bpy)_2Ru(dpp)Ru(biq)_2]^{4+}$ and $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$ (biq = (**90**)) have been assigned unambiguously based on the selective resonance enhancement of the Raman bands of the ligand biq [223]. The resonance Raman and time-resolved resonance Raman (TR^3) spectra of Ru(II) complexes with bpy and 4,4',5,5'-tetramethyl-2,2'-bipyridine have also been reported. The TR^3 spectra provide definitive evidence that the ^{3}MLCT excited-state electron density is localised on the bpy ligand in the complexes [224].

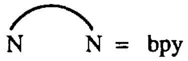
The variations in the energies and intensities of the LMCT bands in complexes of the type $[Ru(X_2\text{-}bpy)_3]^{3+}$ and $[Ru(bpy)_n(X_2\text{-}bpy)_{3-n}]^{3+}$ (X = Me, OMe, NH_2 and NMe_2) have been examined. The intensity of the LMCT band increases with increasing effective donor strength of the substituted bpy ligand, whereas the energy of the LMCT transition is much lower in mixed-ligand complexes. A quantitative analysis as a function of donor strength and Hammett substituent constants was presented [225].



	R	R'
(175)	H	Ph
(176)	Me	Ph
(177)	H	$C_6H_4Me\text{-}O$
(178)	Me	Me
(179)	H	H
(180)	CHPh	CHPh



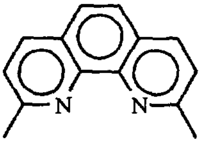
	R	R'
(181)	H	Ph
(182)	H	H



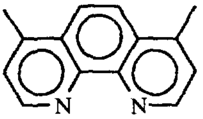
Complexes $[Ru(bpy)_2(L\text{-}L)](PF_6)_2$, (**175**)-(**182**), have been isolated from the reaction of $[Ru(bpy)_2Cl_2]$ with the appropriate ligands L-L and fully characterised. The variable temperature NMR spectra of the complexes (**175**)-(**177**) have been investigated and emission studies have been carried out. The X-ray structure of the complex $[Ru(bpy)_2\{PhNHN{=}C(Me)C(Me){=}NHPh\}](PF_6)_2$ (**175**) was determined [226].

New dinuclear complexes containing a $[Ru(terpy)(bpy)]^{2+}$ moiety bonded through cyanide to $Ru(NH_3)_5{}^{2+/3+}$ groups have been prepared and characterised by spectroscopic and electrochemical techniques. An intense metal-to-metal charge transfer transition was observed at λ_{max} = 700 nm in MeCN in the mixed-valence species $Ru^{II}\text{-}CN\text{-}Ru^{III}$ [227].

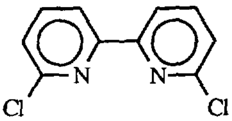
The synthesis and characterisation of $[Ru(H_2O)(N\text{-}N)(terpy)]^{2+}$ (N-N = bpy, phen, 2,9-Me_2-phen (**183**), 4,7-Me_2-phen (**184**), biq and 6,6'-Cl_2-bpy (**185**)) have been described. The rate constants for ligand substitution of H_2O for MeCN were determined for $[Ru(H_2O)(N\text{-}N)(terpy)]^{2+}$ and $[Ru(H_2O)(bpy)_2(PR_3)]^{2+}$ in pH = 2.2 $HNO_3/NaNO_3$ solution [228].



(**183**)



(**184**)



(**185**)

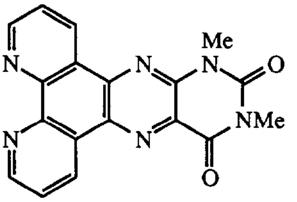
The complexes $[Ru(L)_n(L')_{3-n}\text{-}Y]$ (n = 0-3; L,L' = bpy, 4-Me-bpy, 4,4'-Me_2-bpy and 2,2'-bipyrazine) were prepared in the zeolite Y supercages and were studied by electronic absorption, electronic emission, resonance Raman and time-resolved resonance Raman spectroscopies. The effect of eliminating ligand-field-state deactivation and increasing ^{3}MLCT state lifetimes in the entrapped complexes have been discussed [229].

Absorption luminescence, quantum yields and lifetimes in a rigid alcoholic glass at 77 K have been measured for ruthenium complexes containing either 4,4'-diphenyl-2,2'-bipyridine or 4,7-diphenyl-1,10-phenanthroline as the ligands. An intrinsic lifetime, radiative rate constant and quenching rate constant have also been determined for each complex. Evidence for a near-unity efficiency for population of the emitting level following optical pumping of any upper excited state was obtained [230].

The properties and reactions of different types of charge transfer excited states (MLCT, LMCT and MMCT) of mono- and polynuclear polypyridyl complexes of Ru have been reviewed. Polynuclear complexes considered were bi- and trinuclear ones derived using dpp or CN as the bridging ligand [231]. The preparation, spectroscopic, electrochemical and photophysical properties of the complexes $[Ru(terpy)(bpy)(4,4'\text{-}bpy)]^{2+}$ (**186**) (4,4'-bpy = 4,4'-bipyridine) and $[(terpy)(bpy)Ru^{II}(4,4'bpy)Ru^{II}(NH_3)_5]^{4+}$ (**187**) have been reported. Both complexes possess the photosensitising moiety $[Ru(terpy)(bpy)]^{2+}$. Oxidation of (**187**) with bromine vapour gives $[(terpy)(bpy)Ru^{II}(4,4'\text{-}bpy)Ru^{III}(NH_3)_5]^{5+}$ [232]. The electrochemical reduction of $[Ru(2,3\text{-}dpp)_n(bpy)_{3-n}]^{2+}$ (n = 1-3; 2,3-dpp = 2,3-bis(2-pyridyl)pyrazine), which are extensively used as building blocks for the synthesis of polynuclear compounds have been investigated at −54°C in dmf solution. $[Ru(2,3\text{-dpp})_3]^{2+}$, $[Ru(2,3\text{-dpp})_2(bpy)]^{2+}$ and $[Ru(2,3\text{-dpp})(bpy)_2]^{2+}$ display 12, 10 and 8 reduction steps respectively in the potential window examined. The results have been discussed and compared with those previously reported for bpy and $[Ru(bpy)_3]^{2+}$ [233].

The apparent $pK_a{}^*$ values and the rate constants for the quenching by H^+ of the excited states of nine homo- and heteroleptic Ru(II) complexes with ligands 2,2'-bipyrimidine (bpm), 2,2'-bipyrazine (bpz) and bpy have been determined in aqueous solution. The excited state can be described as a 1-electron reduced ligand that is coordinated to a Ru(III) centre with the electron localised uniquely on the most easily reduced ligand (bpz>bpm>bpy) [234].

A new alloxazine ligand Pptd (Pptd = (**188**)) was prepared. The synthesis and characterisation of the complexes $[(bpy)_{3-n}Ru^{II}(Pptd)_n](PF_6)_2$ have been reported. Preliminary data on the pH-dependent reduction in aqueous solution of Pptd coordinated to Ru(II) in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ were presented [235].



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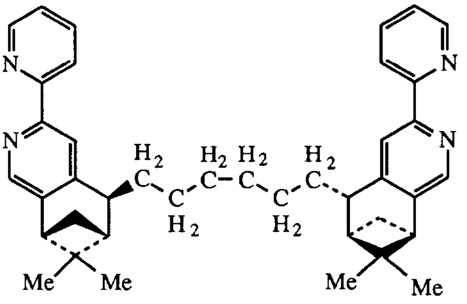


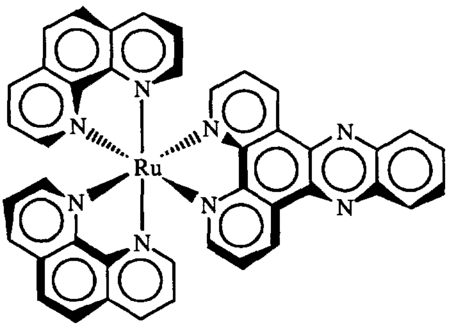
(189)

Facile stereoselective synthesis of an enantiomerically pure Δ-[Ru(L)(Q)] (L = (**189**), Q = 4,4'-Me_2-bpy) was accomplished by using a new chiral and conformationally rigid ligand L, which completely predetermines the helical chirality of the metal, yielding exclusively Δ-configuration. The structure of Δ-[Ru(chiragen[6])Q] $(CF_3SO_3)_2$ was determined by X-ray crystallography [236].

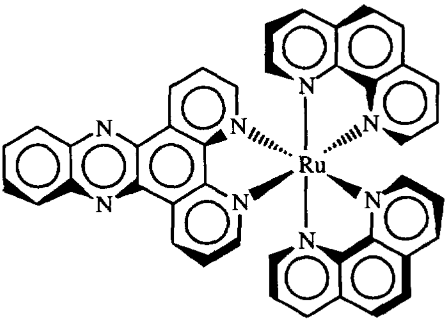
9.5.2 Complexes with phenanthroline ligands

The synthesis and characterisation of $[Ru(phen)_2(L\text{-}L)]^{2+}$ and $[Ru(4,4'\text{-}Me_2\text{-bpy})(L\text{-}L)]^{2+}$ (L-L = pyridyltriazole derivatives) have been reported. A number of coordination isomers exist for these complexes. The spectroscopic, electrochemical and acid-base properties both in the ground state and excited state of the complexes are similar to those reported for the bpy analogs [237].

The interaction of Δ- and Λ-$[Ru(phen)_3]^{2+}$ with DNA has been studied by absorbance and fluorescence methods, CD, UV melting experiments, viscosity and competition dialysis. Overall results indicated that both isomers bind to DNA by a single mode. The two isomers differ, however, in their effects on the hydrodynamic properties of DNA [238]. In addition, the interaction of the Δ and Λ enantiomers of $[Ru(phen)_2(DPPZ)]^{2+}$ (**190**) and (**191**) with DNA has been investigated by linear dichroism spectroscopy and steady-state as well as time-resolved luminescence spectroscopy. Both enantiomers were found to show luminescence in the presence of DNA. The large difference in luminescence quantum yield between the enantiomers has been discussed [239].



Λ - [Ru(phen)$_2$(DPPZ)]$^{2+}$ **(190)**



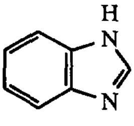
Δ- [Ru(phen)$_2$(DPPZ)]$^{2+}$ **(191)**

Comparison has been made between the enantioselective excited-state quenching of optically active Tb(III) and Dy(III) tris-complexes of 2,6-pyridinedicarboxylate by resolved [Ru(phen)$_3$]$^{2+}$. The quenching has been discussed within the contexts of a simple model involving encounter pair formation, reorientation and energy transfer [240].

The optical characteristics of [RuL$_3$](ClO$_4$)$_2$ (L = 4,7-diphenyl-1,10-phenanthroline) immobilised in a silicone rubber film have been studied with regard to its application to the measurement of oxygen. The luminescence intensity and the degree of quenching of the complex by O$_2$ were shown to be affected by the concentration of the complex in the silicone rubber film [241].

9.5.3 Complexes with other N-heterocyclic ligands

The synthesis, spectroscopic and electrochemical characterisation of [RuL$_3$](PF$_6$)$_2$ (L = benzimidazole (**192**), benzothiazole (**193**), 2-(2'-pyridyl)benzimidazole (**194**), 2,2'-dipyridylamine (**195**) and phen) have been reported. The secondary amino N of each ligand (**195**) in the complex can be deprotonated by H$^-$, and then acts as a strong nucleophile, allowing selective *N*-alkylation by alkyl halides [242].



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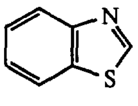

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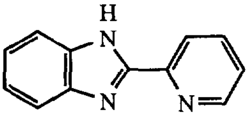

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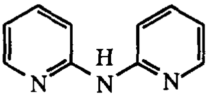
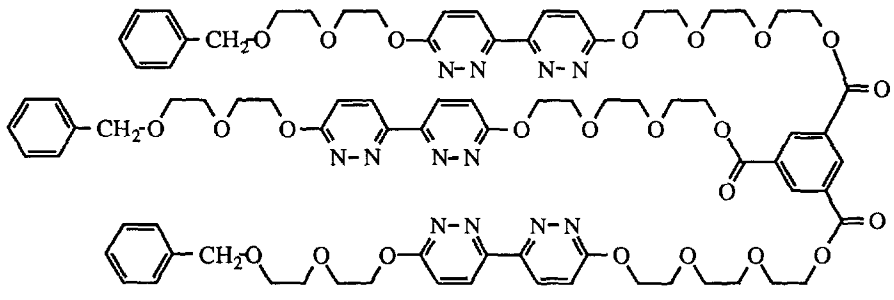


(195)

The photophysical and photochemical behaviour of a semicage bipyridazine (bpdz) Ru-podate complex (**196**) and related open-chain bpdz model complexes (**197**) have been studied and compared with those of $[Ru(bpy)_3]^{2+}$. The complexes (**196**) and (**197**) are highly photoinert relative to the photodissociation of $[Ru(bpy)_3]^{2+}$ and these highly photostable properties allow their effective use as photosensitisers in electron-transfer processes [243].



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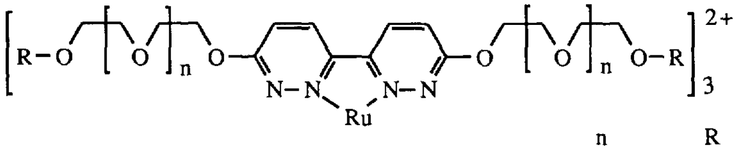
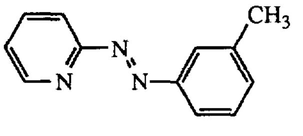


n	R
1	H
2	H
3	H
1	benzyl

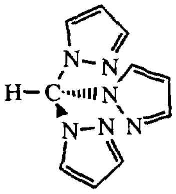
(197)

Complexes $[Ru(tap)_2Q]ClO_4$ and $[Ru(bpy)Q]ClO_4$ (tap = (**198**); HQ = 8-quinolinol) were synthesised. The complexes are diamagnetic. The spectroscopic and cyclic voltammetric studies of the complexes have been described [244]. In addition, a doubly bridged dinuclear Ru(II) complex $[Ru_2(pz)_2(tap)_4](ClO_4)_2.H_2O$ (Hpz = pyrazole) was prepared and characterised [245]. The kinetics and mechanism of the substitution reaction in *cis*-$[Ru(tap)_2(H_2O)_2]^{2+}$ by salicylaldoxime have been investigated spectrophotometrically [246].



(198)

Ruthenium-based chromophore-quencher complexes $[Ru^{II}(tpm)(bpy\text{-}PTZ)(MQ^+)]^{3+}$ and $[Ru^{II}(tpm)(bpy\text{-}PTZ)(py)]^{2+}$ were prepared and characterised (tpm = (**199**), bpy-PTZ = (**200**), MQ^+ = *N*-methyl-4,4'-bipyridinium cation). Laser flash or steady-state photolysis experiments have been presented [247].The reaction of $[RuL(Cl)(PMe_3)_2]ClO_4$ with $NaNO_2$ affords the complexes $[RuL(NO_2)(PMe_3)_2]ClO_4$ (L = (**201**)) and they were fully characterised, including by he X-ray crystal structure analysis [248].



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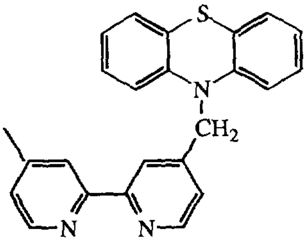

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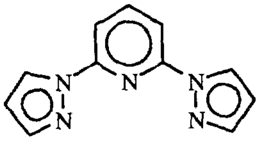
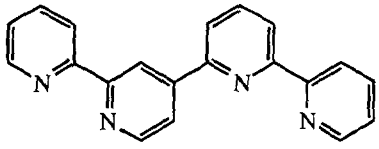


(201)

The complexes $[RuClL_2]$ and $[Ru(EPh_3)_2L_3]$ (HL = imidazole, 2-methylimidazole; E = P, As) were synthesised from $RuCl_3$ and $[Ru(EPh_3)_2Cl_3(MeOH)]$ using the reagents Me_3Si-L, which is versatile for conversion of M-Cl bonds into metal-imidazolates [249].

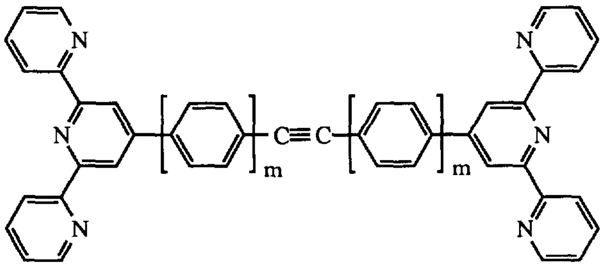
Some novel mixed ligand complexes of Ru(III) $[Ru(L)_3(L')_3]$ (L = succinimide, phthalimide; L' = isoquinoline, pyridine, 4-picoline) were prepared and characterised by elemental analyses, conductometric, magnetic, IR and electronic spectral studies [250].

A new asymmetric ligand L = **(202)** has been synthesised by reductive 2,4'-coupling of the radical anion of 2,2'-bipyridine with $LiN(CHMe_2)_2$. The ligand, confirmed by ^1H NMR spectroscopy, has two chelating bipyridyl binding sites which are inequivalent, one being much more sterically hindered than the other. The complexes $[Ru(bpy)_2(L)](PF_6)_2$, $[Ru(terpy)Cl(L)]PF_6$, $[\{Ru(bpy)_2\}_2(\mu\text{-}L)](PF_6)_4$, $[\{Ru(terpy)Cl\}_2(\mu\text{-}L)](PF_6)_2$ and $[\{Ru(bpy)_2\}(\mu\text{-}L)\{Ru(terpy)Cl\}](PF_6)_3$ could then be prepared. Their CVs have also been studied [251].



(202)

New ditopic ligands L = **(203)** and **(204)** (m = 0,1) were prepared from 4'-ethynyl-2,2':6',2"-terpyridine and 4'-(4-ethynlphenyl)-2,2':6'2"-terpyridine by couping with the corresponding triflate or bromo-substituted substrates, or by self-coupling of the ethynyl substituted precursors, respectively. These ligands were found to form rigid rod-like homonuclear and heterotrinuclear Ru(II) complexes [252]. In addition, dinuclear Ru(II) complexes containing back-to-back bis-terpyridine ligands L = **(205)** and **(206)** (n = 0,1,2) of various lengths (Ru ··· Ru distances 7-20 Å) as bridges have been prepared. Significant electronic coupling was observed in mixed-valence states, even for the systems with the longest separation [253].



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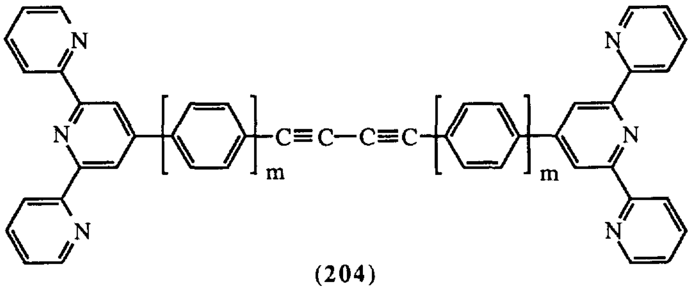

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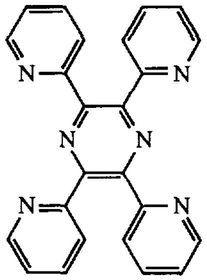
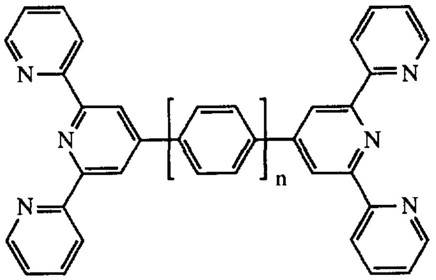
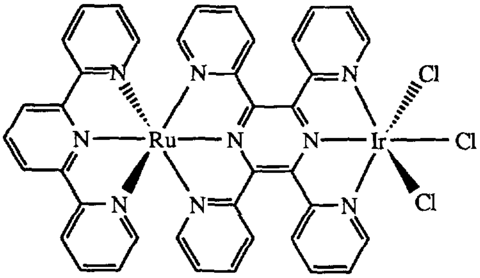




n =0, 1, 2

(205) **(206)**

The mixed-metal complex $[(\mathrm{terpy})\mathrm{Ru}(\mathrm{tpp})\mathrm{IrCl_3}]^{2+}$ (**207**) (tpp=(**205**)) and the model monometallic fragments $[\mathrm{Ir}(\mathrm{tpp})\mathrm{Cl_3}]$ and $[\mathrm{Ru}(\mathrm{terpy})(\mathrm{tpp})]^{2+}$ were prepared and their spectroscopic, electrochemical and spectroelectrochemical properties have been studied. The combination of Ru, a good light absorber, with Ir, a catalytic metal centre, into one molecule is of interest in intramolecular photosensitisation schemes [254]. Three novel dinuclear heterometallic compounds (**208**) were also synthesised where two $\mathrm{M}(\mathrm{tterpy_2})^{2+}$ (tterpy = 4'-(*p*-tolyl)-2,2':6',2"-terpyridine (**209**)) building blocks are either directly linked or connected by Ph spacers in a rigid rod-like structure. Their luminescence properties and the electronic energy transfer process through the Ph spacers were studied [255].



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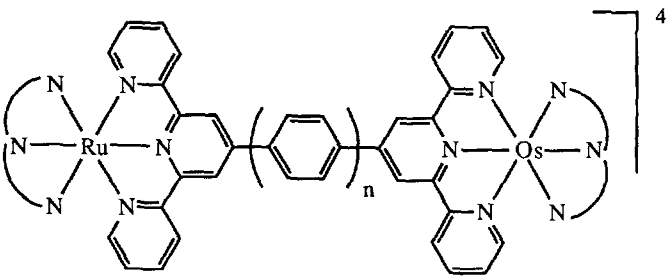
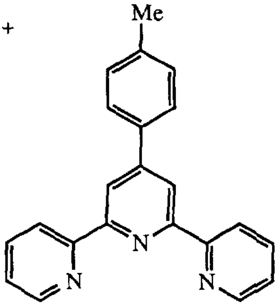


n = 0, 1, 2

(208)



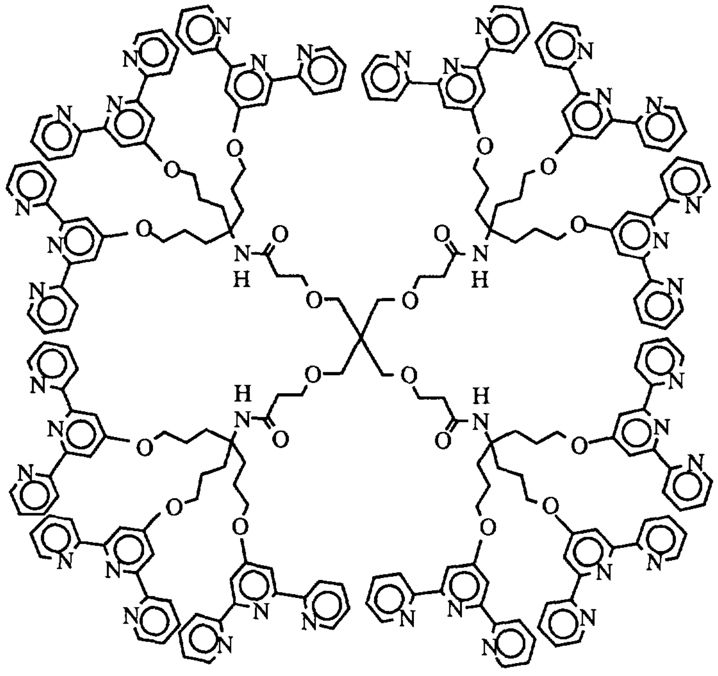
N N N = **(209)**

A cascade (dendritic) polymer (**210**) has been prepared. Incorporation of ruthenium(II)-terpy trials into the polymer gives a dodecaruthenium macromolecule, $[C\{CH_2OCH_2CH_2CONHC(CH_2CH_2CH_2OR)_3\}_4]$ (R = (**211**)) [256].

A new tridentate ligand terpy* (terpy* = (**212**)) was prepared in ≤ 50% yield from 4-*tert*-butylpyridine. The complexes $[(terpy^*)Ru(L)X]^+$ and $[(terpy^*)Ru(L)OH_2]^{2+}$ (L = bpy, bpy* = 4,4'-di-*tert*-butyl-2,2'-bipyridine) have been isolated from $[(terpy^*)RuCl_3]$ and fully characterised [257]. Moreover, 4'-ferrocenyl-2,2':6',2''-terpyridine (Fcterpy (**213**)) has been prepared from ferrocenecarboxaldehyde and 2-acetylpyridine. A single-crystal X-ray structure of (**213**) was undertaken. The synthesis, electrochemical and spectrophotometric characterisation of $[Ru(Fcterpy)_2]^{2+}$ and $[Ru(terpy)(Fcterpy)]^{2+}$ have been reported [258].

New ruthenium complexes containing two tridentate ligands (**214**) and (**215**) were synthesised and characterised by ^1H and ^{13}C NMR spectroscopy. The $[RuL_2]^{n+}$ (L = (**213**)) chelate acts as a tetrabasic acid, with pK_a of 2.5-10.7, depending on the Ru oxidation state [259].

The dinuclear complexes $[(tterpy)M(tpbp)M(tterpy)]^{2+}$ (**216**) (M = Ru(II), tterpy = (**209**), $tpbpH_2$ = 3,3',5,5'-tetrapyridylbiphenyl) have been prepared by oxidative coupling of the corresponding monomers $[M(tterpy)(dpb)]^+$ (dpbH = 1,3-di-*o*-pyridylbenzene). Spectrochemical and electrochemical properties of the monomers and dimers in different oxidation states have been described [260].



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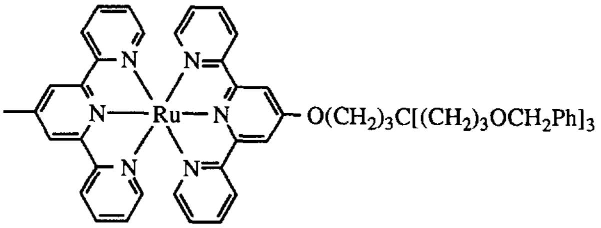

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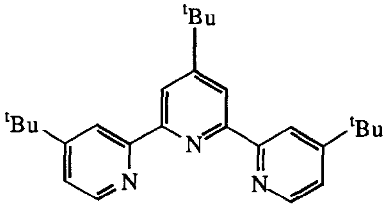

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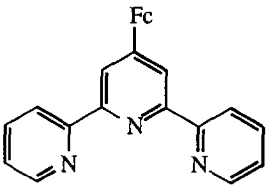

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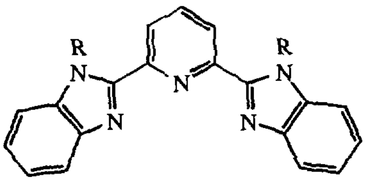
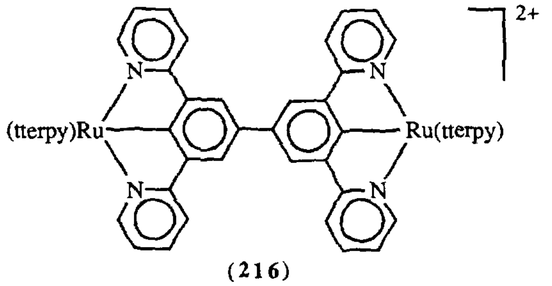
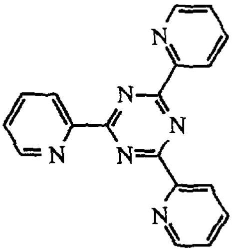


(214) R = H
(215) R = Me



(216)

Complexes based on $[Ru(terpy)(L)OH_2]^{2+}$ (L = η^2-tpt (**217**), phen, dppz (**135**), tmen (**218**)) were prepared and can all be reversibly oxidised to their $Ru^{IV}O$ forms, which are component DNA cleavage agents. In addition, $[Ru(terpy)(\eta^3\text{-tpt})]^{2+}$ was prepared, which reacts in the presence of Ag^+ to give a novel Ru_2Ag complex, $[Ru(terpy)(\eta^3\text{-tpt})](ClO_4)_2 \cdot 0.5AgClO_4 \cdot 0.5H_2O$ (**219**). The crystal structure of (**219**) was determined. The $[Ru(terpy)OH_2]^{2+}$ unit can also be attached to the tmen-AO^+ ligand (**220**) to afford an effective cleavage agent $[Ru(terpy)(tmen\text{-}AO)OH_2]^{3+}$ [261].



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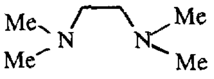

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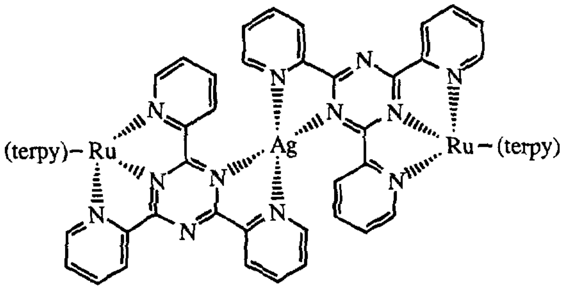

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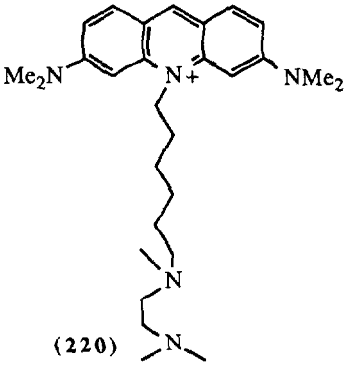
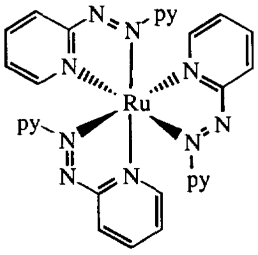


(220)

Fac- and *mer*-$[Ru(abpy)_3]^{2+}$ ((**221**) and (**222**) respectively) and two out of the three possible diastereoisomers of $[Ru(abpy)_2(bpy)]^{2+}$ (**223**)-(**225**) were isolated *via* HPLC and identified by their ^1H NMR spectra. The absence of a room-temparature EPR signal for one of the two isolated isomers of $[Ru^{II}(abpy^-)(abpy)(bpy)]^{\cdot +}$ demonstrates the structural requirements for intramolecular electron transfer [262].



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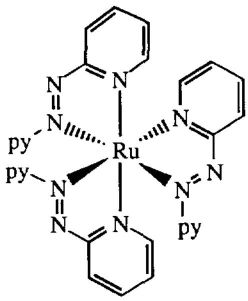

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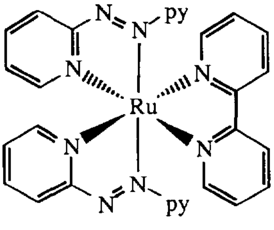

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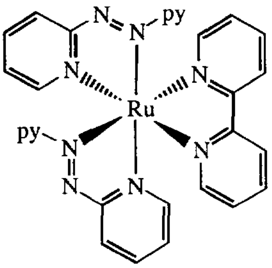

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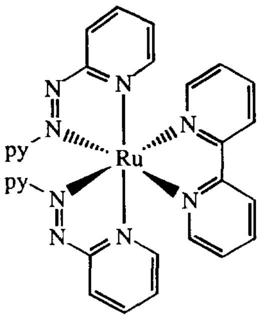
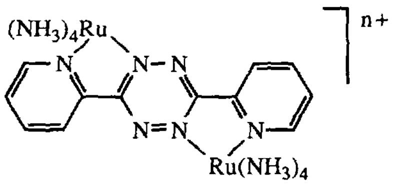


(225)

A series of dinuclear donor-acceptor complexes with helical polyproline bridges $[(4,4'\text{-bpy})_2Ru^{II}L\text{-}(Pro)_n\text{-apy-}Ru^{III}(NH_3)_5]^{5+}$ (n = 6, 7, 9) and $[(4,4'\text{-bpy})_2Ru^{II}L\text{-}(Pro)_n\text{-}Co^{III}(NH_3)_5]^{4+}$ (n = 1-6) (L = 4-carboxy-4'-methyl-2,2'-bipyridine, 4,4'-bpy = 4,4'-bipyridine, Pro = *L*-proline, apy = 4-aminopyridine) have been synthesised and characterised by absorption spectroscopy, electrochemical measurements and HPLC. The CD spectra of the complexes show a polyproline II helical structure. Intramolecular electron transfer within these complexes was studied by pulse radiolysis experiments. A weak dependence for the rate of intramolecular electron transfer versus the number of prolines has been observed [263, 264]. The solvent dependence of the intervalence charge-transfer absorption energy for $[(NH_3)_5Ru^{III}\text{-}4,4'\text{-bpy-}Ru^{II}(NH_3)_5]^{5+}$ was re-examined in the limit of infinite dilution. New data have been reported for 14 solvents [265]. On the other hand, the lamellar Hoffmann clathrate, $Ru(4,4'\text{-bpy})Ni(CN)_4$ was grown layer-by-layer on surfaces using a 3-step adsorption sequence [266]. The effect of the macrocyclic ether species (dibenzo-30-crown-10 or dibenzo-36-crown-12) and its concentration on the intervalence absorption spectra of either *trans*-$[(py)(NH_3)_4Ru^{5.5}(pz)Ru^{2.5}(NH_3)(py)]^{5+}$ or $[(NH_3)_5Ru^{2.5}(pz)Ru^{2.5}(NH_3)_5]^{5+}$ (pz = pyrazine) has been described [267]. An electrochemical approach to assessing the degree of electronic coupling in $[(NH_3)_5Ru\text{-}L\text{-}Ru(NH_3)_5]^{n+}$ (L = pyrazine or 4-cyanopyridine) has been outlined. The method relies on the comparison of electrochemical potential shifts induced at both the directly and indirectly perturbed metal sites when a ligand substitution process is carried out at one site to give $[L'(NH_3)_4Ru\text{-}L\text{-}Ru(NH_3)_5]^{n+}$ (L' = substituted pyridine) [268].

An unusually weak intervalence transition in a very stable bis chelate analog of the ruthenium mixed-valent Creutz-Taube ion, $[(NH_3)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{n+}$ (**226**) (bptz = 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine, n = 3-5) has been discussed. The UV-VIS, near-IR and EPR spectroelectrochemistry of (**226**) have been studied [269].



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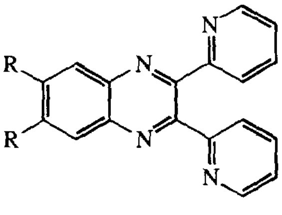
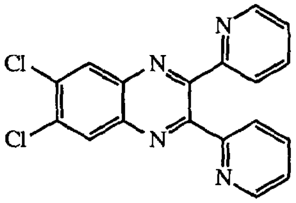


(227) R = Cl
(228) R = Me

The polyazine bridging ligands Cl_2-dpq (**227**) and Me_2-dpq (**228**) and the new complexes $[(bpy)_2Ru(BL)]^{2+}$ and $[\{(bpy)_2Ru\}_2(BL)]^{4+}$ (BL = (**227**), (**228**)) have been synthesised and their spectroscopic and electrochemical properties studied. The previously studied systems with dpp, dpq and dpb as the bridging ligands were prepared, and their properties were reported for comparison [270].



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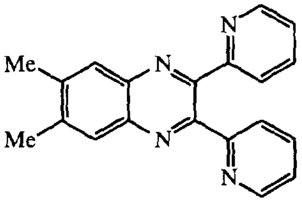


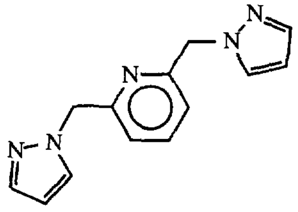
(228)

The resonance Raman and time-resolved resonance Raman spectra of ruthenium(II) complexes containing the inherently asymmetric 2-(2-pyridyl)pyrazine and its selectively deuterated analog have been reported. A detailed discussion of the spectral analysis and the potential implication of the effect for the design of practical devices were discussed [271].

The interaction of $[\{Ru(NH_3)_4\}_2(dpb)]^{4+}$ (**229**) (dpb = 2,3-di(2-pyridyl)benzo-[*g*]quinoxaline) with sonicated, dialysed calf thymus DNA was investigated in pH 7 buffer containing 115.4 mM total Na^+ ion. In the presence of a 30-fold molar base pair excess of DNA, complex (**229**) showed 29.0% hypochromicity at 317 nm and a red-shift of this band of 4.0 nm relative to the complex in buffer alone. In contrast, the related complex $[\{Ru(bpy)_2\}_2(dpb)]^{4+}$ showed essentially no spectral changes. The discrimination between the two complexes has been discussed [272].

The preparation and properties of $[Ru(H_4bpp)(MeL)](ClO_4)_2{\cdot}H_2O$ (H_4bpp = 2,6-bis(pyrazol-1-ylmethyl)pyridine (**230**), MeL = 2-pyridylethyl(2-pyridylmethyl)methylamine (**231**)) have been described, which shows a RuN_6 coordination sphere. Cyclic voltammetric study was presented [273].

The electrochemical properties of a series of dinuclear ruthenium compounds based on the bridging ligands (**172**) and 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (**232**) were discussed. The intervalence transitions of the mixed-valence dinuclear compounds have been studied using spectroelectrochemical techniques [274].



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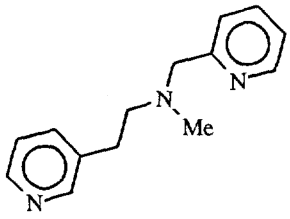

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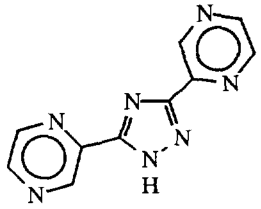
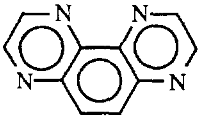


(232)

A new DNA-binding molecule, $[Ru(L)_2(POQ)]^{2+}$ (L = (**233**); POQ = (**234**)) was prepared and characterised. The spectroscopic properties of the complex were examined and compared with those of the corresponding complex without the aminochloro-quinoline moiety, $[Ru(L)_2(phen)]^{2+}$. Preliminary results on the binding characteristics of $[Ru(L)_2(POQ)]^{2+}$ to DNA and $[poly(\alpha[A\text{-}T])]_2$ from luminescence and thermal denaturation studies have been reported [275].



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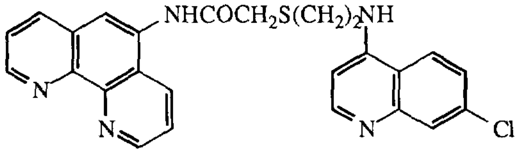
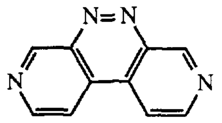


(234)

Isomeric *trans,cis*-$[Ru(CNS)_2L_2]$ (L = 2-(arylazo)pyridine; aryl = Ph, *m*-tolyl) were synthesised by a stereoretentive substitution reaction from known *trans,cis*-$[Ru(OH_2)_2L_2]^{2+}$ and studied for linkage isomerism. The most stable linkage isomer is *S,S*-bonded. Factors influencing the population of the various isomers were discussed [276].

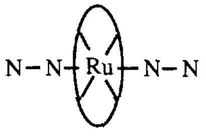
Intramolecular electron transfer has been detected in a dinuclear ruthenium complex using 2,7,9,10-tetraazaphenanthrene (**235**) as bridging ligand. The effective coupling between ruthenium sites has been determined and compared to that in the corresponding complex with 4,4'-bipyridine [277].



(235)

9.5.4 Complexes with macrocyclic ligands

The synthesis and the control of intramolecular electron transfer by a protonation/deprotonation reaction of the monomeric complexes (**236**) and the corresponding oligomers (**237**) bridged by 4,4'-azopyridine or pyrazine have been reported [278].



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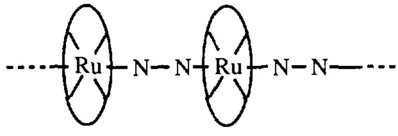

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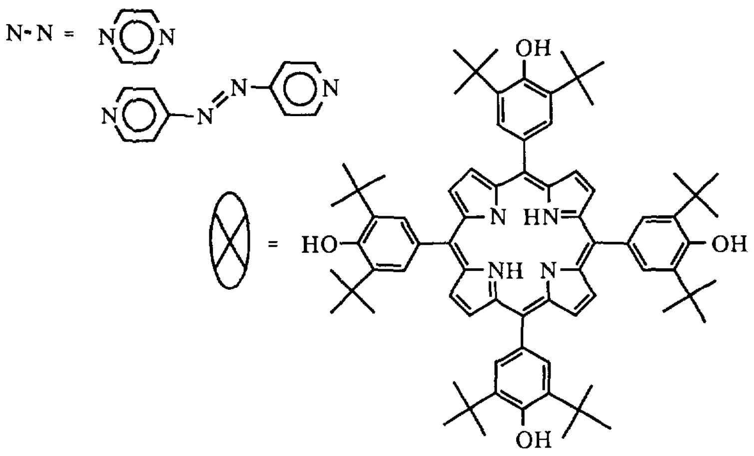
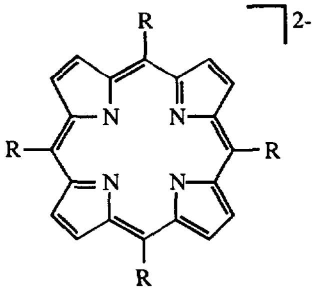
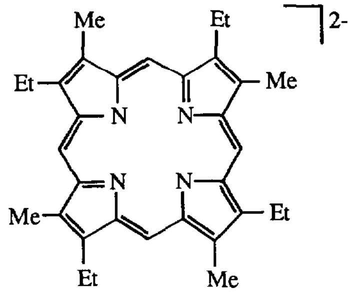


Novel dioxoruthenium(VI) porphyrin cation radicals were prepared by the stoichiometric oxidation of $Ru^{VI}(TMP)(O)_2$ and $Ru^{VI}(OEP)(O)_2$ with phenoxathiin hexachloroantimonate. The electronic structures of the oxidation products were elucidated by ^2H NMR, UV-VIS and ESR spectroscopic methods [279]. The first synthesis and electrochemical studies of metalloporphyrins containing a bound PF_3 axial ligand $[Ru(por)(PF_3)]$ (por = TPP, OEP, (**238**), (**239**) and (**240**)) have been reported. An electrochemical-initiated conversion of $[Ru^{II}(por)(PF_3)(py)]$ into $[Ru^{III}(por)(py)_2]^+$ was readily accomplished in py or CH_2Cl_2-py mixtures. This is the first such reported reaction for the oxidation of a Ru(II) porphyrin and was monitored by cyclic voltammetry and UV-VIS spectroelectrochemical methods [280].

The complex $[\{Ru^{II}(TPP)(EtO)\}_2O]$ has been used as a convenient starting material together with CS_2, $CSCl_2$ and $PhCH_2SCCl_3$ as CS precursors to afford $[Ru^{II}(TPP)(CS)L]$ (L = CS, CN, imidazole derivatives, MeCN, pyridine derivatives, toluidine, PPh_3) under reducing conditions. The chemistry and electrochemistry of these complexes were studied [281]. Metal-metal bonded dimers $[Ru(OETAP)]_2$ ($OETAPH_2$ = octaethyltetraazaporphyrin (**241**)), [(OEP)RuRu(OETAP)] and [(OEP)OsRu(OETAP)] were prepared and characterised by ^1H NMR spectroscopy and cyclic voltammetry. The chemical and electrochemical redox reactions of [(OEP)RuRu(OETAP)] and $[(OEP)RuRu(OETAP)]BF_4$ have been reported [282].



(238) $R = 4\text{-}BrC_6H_4$
(239) $R = 4\text{-}MeOC_6H_4$



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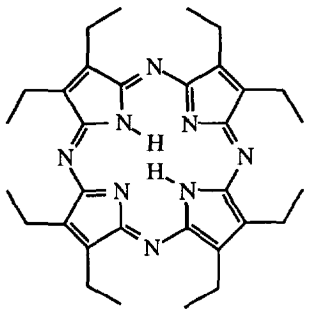
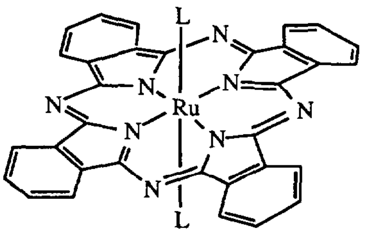


(241)

The complex $[Ru(TMP)(OH)_2]$ was isolated as air-stable violet crystals and characterised by IR and ^1H NMR spectroscopy. It was found to be paramagnetic with $\mu_{eff} \approx 2.7$ B.M. and catalytically active in the aerobic epoxidation of norbornene under mild conditions [283]. The Langmuir-Blodgett film formation and properties of a ruthenium porphyrin complex have been reported [284]. The a.c. impedance technique has been used for the measurement of electron-transfer rate constants between $[Ru^{II}(py)_2(TPP)]$ and the aqueous redox couple $[Fe(CN)_6]^{3-/4-}$ at the H_2O/1,2-dichloroethane interface [285]. Ruthenium porphyrins anchored on to polystyrene beads and silica powder have been separately tested as catalysts in the decomposition of cyclohexyl hydroperoxide [286].

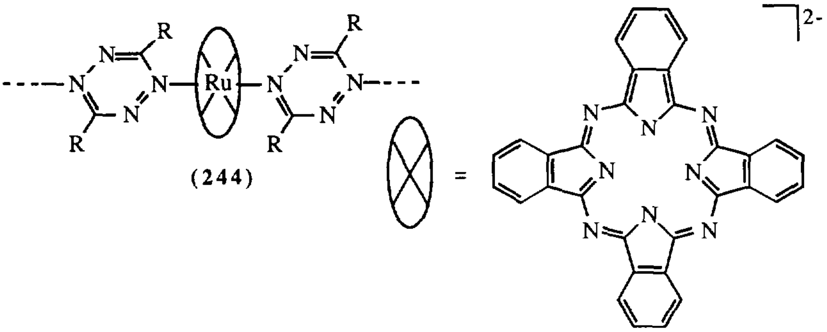


$L = PEt_2Ph$ (242)

$L = PPh_3$ (243)

The synthesis and characterisation of $[Ru(pc)(PEt_2Ph)_2]$ (242) and $[Ru(pc)(PPh_3)_2]$ (243) have been reported. The two complexes are soluble in common organic solvents [287]. In addition, the kinetic studies of the reaction of cyanide with $[Ru(pc)(dmso)_2]$ in dmf have been reported. In the presence of a large excess of CN^-, $[Ru(pc)(CN)_2]$ is formed by pseudo first-order kinetics [288].

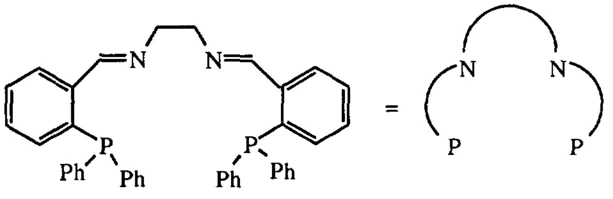
The preparation, characterisation and electrical conductivity measurements of the tetrazine-bridged phthalocyaninato ruthenium complex $[Ru(pc)(L)]_n$ (**244**) (L = tetrazine) have been described. The electrical and physical properties of this complex have been discussed with respect to the intrinsic semiconducting properties of the compound [289]. The complex $[Bu_4N][RuCl_2(pc)]$ was prepared by the reaction of $H[RuX_2(pc)]$ (X = Cl, I) with excess chloride in weakly coordinating solvents (dmf, thf). The IR and Raman spectra of the complex were studied [290].



(244)

9.5.5 Complexes with other mixed donor ligands

The reaction of $[Ru(OAc)_2(PPh_3)_2]$ with 1 equivalent of a P_2N_2 ligand (**245**) in refluxing CH_2Cl_2 gives *trans*-$[Ru(OAc)_2(P_2N_2)]$ (**246**) in moderate yield. The same reaction, when performed in refluxing toluene, affords *trans*-$[Ru(P_2N_2)Cl_2]\cdot 2H_2O$ (**247**). Both complexes were fully characterised by analytical and spectroscopic methods and the X-ray crystal structure was established for (**247**) [291].



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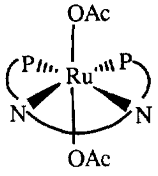
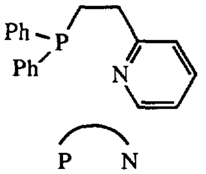


(246)

The solution behaviour of the six-coordinate species $[RuX_2(ppye)_2]$ (X = Cl, Br or I; ppye = (**248**)) has been studied by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR and UV-VIS spectroscopies and conductivity measurements. Halide dissociation from the neutral species yields the five-coordinate cations $[RuX(ppye)_2]^+$, which can dimerise to $[Ru_2X_2(ppye)_4]^{2+}$ (**249**). The crystal structure of $[Ru_2Cl_2(ppye)_4](PF_6)_2$ has been determined [292]. The synthesis and electrochemical and EPR spectroscopic properties of $[RuL_3]$, $[RuL_2(acac)]$ and $[RuL_2(bpy)](PF_6)$ (HL = (**250**)) have been reported [293].



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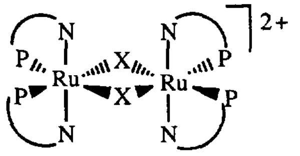

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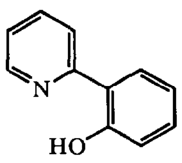
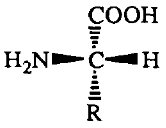


(250)

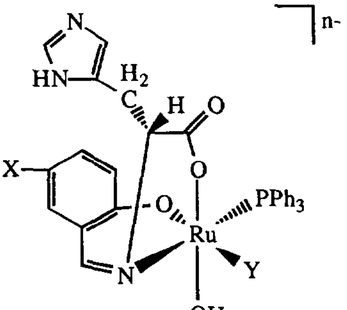
Mononuclear chiral ruthenium(II) Schiff base complexes of the type [RuL(PPh3)(H2O)2] (H_2L = chiral Schiff bases derived from salicylaldehyde and various amino acids (**251**)) have been prepared and characterised by various physical methods. The asymmetric epoxidation of styrene by these complexes and their reactions with π-acceptor ligands such as bpy and phen have been reported [294, 295].



(251)

R = $CH_2C_6H_4$-4-OH
= CH_2Ph
= CH_2CH_2SMe
= CH_3
= $CH_2CH_2CH_2NHC(=NH)NH_2$
= CH_2COOH
= CH_2SH
= CH_2OH
= $CHMe_2$

The chiral complexes Na[RuL(PPh3)N3(H2O)] (**252**), [RuL(PPh3)(imH)(H2O)] (**253**) and [RuL(PPh3)(bpy)] (**254**) were synthesised and characterised. The conformational aspects regarding the asymmetric carbon atom and the nitrogen containing ligands around the Ru(II) ion have been discussed [296].



X = H, Cl, OMe

Y = N_3^- (252) n = 1

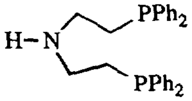
=  (253) n = 0

= bpy (254) n = 0

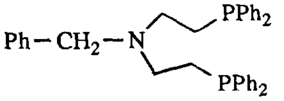
The synthesis of ruthenium(II) Schiff base complexes [RuL2Cl2]Cl (L = the carbohydrazones of salicylaldehyde, cinnamaldehyde, acetophenone and benzaldehyde) has been described. The complexes were characterised by conductivity and magnetic susceptibility measurements and XPS, IR and UV spectroscopic data [297]. Complexes [Ru(PPh3)2L2] (HL = Schiff bases formed from 2,3-dihydroxybenzaldehyde, 3,5-dibromosalicylaldehyde and salicylaldehyde) were prepared and characterised by spectroscopic and cyclic voltammetric methods.

The effective catalytic oxidation of alcohols by these complexes in the presence of *N*-Me-morph-*N*-oxide or O_2 gas as cooxidants have been reported [298]. The electrochemical behaviour in non-aqueous solution of a zeolite-encapsulated [Ru(III)(salen)] complex has been reported [299].

Chloro- and trichlorostannato complexes of Ru(II) and Ru(III) were prepared with the primary ligand (**255**) or (**256**) and PPh_3 or dmso as the secondary ligand. The complexes, characterised by IR, Raman, ^1H, ^{14}N, ^{31}P, ^{119}Sn NMR and UV-VIS spectroscopy, have a distorted octahedral geometry [300].



(255)



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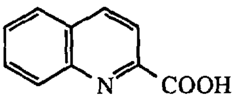


(258)

Complexes *trans*-$[Ru(quin)_2(dppm)_2]$ (**257**) and *cis*- and *trans*-$[Ru(quin)_2(PPh_3)_2]$ (H_2quin = (**258**)) were prepared and fully characterised by spectroscopic methods. The X-ray crystal structure of (**257**) reveals that it has two didentate *N,O*-quinaldinate and two monodentate dppm ligands in a *trans*-N, *trans*-O, *trans*-P arrangement [301].

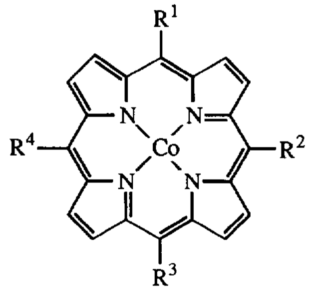
9.5.6 Complexes with ammine or amine ligands

A uniform, blue-coloured ruthenium compound film was obtained by chemical deposition in an aged solution containing $[Ru^{II}(NH_3)_6]Cl_2$. The thin film produced has been investigated by TEM, electron diffraction and electrochemical studies. The electrochromic behaviour of the film has also been reported [302]. A new approach to the characterisation of thin solid films, based on the use of scanning electrochemical microscopy, was described. The heterogeneous rate constant for the reaction of AgBr with $[Ru(NH_3)_6]^{2+}$ was determined to be 0.082 cm s^{-1} by this method [303]. The crystal structure of $[Ru(NH_3)_6](SCN)_3$ was determined at ≈295 K. The RuN_6 unit is almost of octahedral symmetry with Ru-N bond lengths of 2.109 Å and N-Ru-N angles of 89.9(5)°. The single-crystal magnetic susceptibility was obtained at 2-300 K and the ESR g tensor was derived from measurements taken at various angles of rotation about the a*, b and c axes at 77 K [304]. The self assembly properties of *N*-[(cholesteryloxy)carbonyl]-*N*'-ethylviologen and *N*-ethyl-*N*'-octadecyl viologen at the electrode surface were compared on Au in order to assess the effects of the two different hydrophobic tails. The surfactant monolayers of the cholesteryl derivative seem to be less organised than those made from the octadecyl analog, as judged from the blocking properties of the two monolayers for the reduction of water-soluble complex $[Ru(NH_3)_6]^{3+}$ [305].

A carbon fibre electrode modified with Eastman-AQ polymer film was prepared. The behaviour of $[Ru(NH_3)_6]^{3+}$ was studied by cyclic voltammetry and the linear range and the correlation coefficient are respectively 1.2×10^{-6}-1.2×10^{-5} mol dm^{-3} and 0.999 [306]. An extremely low defect density hexadecanethiol (HDT) monolayer on static Hg drop electrode (SMDE) surface has been prepared. The reduction current for $[Ru(NH_3)_6]^{3+}$ at an HDT-coated SMDE is <0.005% of that at a bare electrode. An upper limit estimate of the apparent electron transfer rate constant for $[Ru(NH_3)_6]^{3+}$ at a coated electrode was found to be 3×10^{-13} cm s^{-1}

[307]. The redox rectification by an electrochemically prepared Ir oxide film towards the $[Ru(NH_3)_6]^{3+/2+}$ redox couple has been described. Experimental studies, as a function of $[Ru(NH_3)_6]^{3+}$ concentration, solution, pH, film thickness, voltammetric sweep rate and electrode rotation rate have been reported [308]. The fast redox reactions of $[Ru(NH_3)_6]^{3+/2+}$ in aqueous solutions have been studied by carbon fibre ultramicroelectrodes at scan rates ≤11,000 V s^{-1}. The standard reaction rate constant of $[Ru(NH_3)_6]^{3+/2+}$ at the carbon fibre in aqueous solution was determined to be 1.22 ± 0.07 [309]. The formal potential of $[Ru(NH_3)_5(py)]^{3+}$ attached to Au electrodes by thiol linkages was measured in aqueous solutions with changing activities of NaCl. The influence of the Donnan potentials at the monolayer/solution interface on the apparent formal potentials measured has been described [310].

Mono-, di- and triruthenated porphyrins have been prepared by the reactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with the pyridine sites in the corresponding Co(II) porphyrins (**259**)-(**264**) adsorbed on pyrolytic graphite electrodes. The mono- and diruthenated complexes catalyse the 2-electron reduction of O_2 to H_2O_2, whereas the triruthenated complex catalyses the 4-electron reduction to H_2O [311]. It was found that similar reaction with $Co^{II}(TPyP)$ (**264**) within Nafion coatings on graphite electrodes produces the tetraruthenated porphyrins. The complex, immobilised within the polyelectrolyte coating, also acts as a catalyst for the 4-electron reduction of O_2. The results provide evidence for the intramolecular delivery of 4 electrons from the four coordinated $[Ru(NH_3)_5]^{2+}$ groups to O_2 molecules associated with the Co(II) centre of the porphyrin [312].



	R1	R2	R3	R4
(**259**)	py	Ph	Ph	Ph
(**260**)	py	py	Ph	Ph
(**261**)	py	Ph	py	Ph
(**262**)	py	py	$-C_6H_4-CF_3$	$-C_6H_4-CF_3$
(**263**)	py	py	py	Ph
(**264**)	py	py	py	py

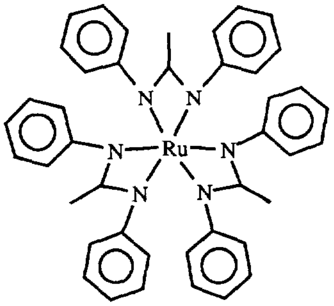
The synthesis and characterisation of the ruthenium complexes $[Ru(NH_3)_5(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4SO_2(H_2O)]^{2+}$ immobilised on divinylbenzene-vpy copolymer have been reported [313]. In addition, $[Ru(NH_3)_3(OH_2)_3](CF_3SO_3)_3$, a convenient starting material for the preparation of triamine complexes has been isolated from $[RuCl_3(NH_3)_3]$ by using F_3CSO_3H and Ag_2CO_3. The complex was characterised by microanalysis, electrochemical and spectroscopic techniques [314]. The complexes $[Ru(NH_3)_5(NCEt)](PF_6)_n$ (n = 2,3) were synthesised and characterised by microanalysis, cyclic voltammetry, UV/VIS and IR spectroscopies. The reactivities of the complexes have been discussed [315]. The air stable complexes $[(\mu_4\text{-TCNX})\{Ru(NH_3)_5\}_4](PF_6)_8$ (TCNX = TCNE, TCNQ), which contain reduced TCNX ligands, have been studied. They show spectroscopic equivalence of the four metal coordination sites on the ^1H NMR and vibrational time scales and very close lying frontier orbitals. Evidence for two weakly coupled diruthenium(II, III) subsystems has been discussed [316].

The dynamics of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ in water solution have been studied by molecular mechanical and molecular dynamical methods. A comparsion of different approaches to permit inclusion of solvation effects in quantum chemical calculations was discussed using the results from the simulations [317].

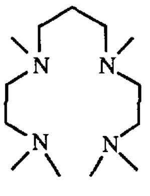
Thiols with attached redox centres $[HS(CH_2)_nCONHCH_2pyRu(NH_3)_5]^{2+/3+}$ (n = 10,11,15) readily adsorb from MeCN solutions onto gold electrodes to form electroactive monolayers. Mixed monolayers were also synthesised by co-adsorbing the electroactive thiols with diluent alkanethiols $[HS(CH_2)_nMe]$ (n = 11,15) and ω-mercaptoalkanecarboxylic acids $[HS(CH_2)_nCOOH]$ (n = 10,11,15). Cyclic voltammetry of the coated electrodes have been investigated [318]. The thermodynamics and kinetics of electron transfer were also examined as a function of aqueous electrolyte and temperature on the self-assembled monolayers [319].

The reaction of $[Ru(NH_3)_5(dpa)]^{2+}$ (dpa = 4,4'-dipyridylamine) with $[Co(edta)]^-$ were studied kinetically. The reaction was interpreted in terms of a mechanism involving the formation of an ion pair between $[Ru(NH_3)_5(dpa)]^{2+}$ and $[Co(edta)]^-$ followed by electron transfer from Ru(II) to Co(III) [320]. The synthesis of $[Co\{H_3CsarNHCH_2pyRu(NH_3)_5\}]$ (**265**), a model for a novel class of drugs, has been described. Interaction of (**265**) with calf thymus DNA and with lipopolysaccharide from *Escherichai coli C* (LPS) has been estimated from the absorption of the complex at 242 and 420nm [321]. The quenching of the intrinsic fluorescence of yeast cytochrome C peroxidase by covalently- and noncovalently-bound quenchers has also been described [322].

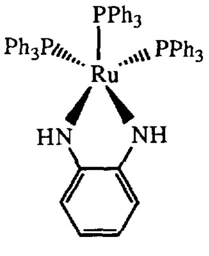
The synthesis and X-ray crystal structure of the complex $[Ru\{PhNC(Me)NPh\}_3]$ (**266**) have been reported [323]. In addition, the tertiary polyamine Ru(III) complex *trans*-$[RuCl_2L]^+$ (L = (**267**)) has been prepared. It reacts with Mg and N_2 (1 atm.) in aqueous solution at room temperature to yield the Ru(II) complex *trans*-$[RuCl(L)(N_2)]^+$ which is then converted into *trans*-$[Ru(OH)(L)(N_2)]^+$ and *trans*-$[Ru(L)(N_2)(OH_2)]^+$ [324]. The reduced Ru(II) complex was prepared by the addition of $Ti(III)Cl_3$ and the dynamics of N_2 uptake by the Ru(II) complex have been described [325].



(**266**)



(**267**)



(**269**)

Trans-$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{3+}$ (**268**) was generated by electrochemical oxidation of the corresponding *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{2+}$ ions. The oxidation is quantitative and reversible. The UV-VIS and ESR spectra of (**268**) have been measured. Upon aging, aqueous solutions of (**268**) yield *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ as the major product [326].

The X-ray crystal structure of $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$ (**269**) has been establised. The reaction of (**269**) with an excess of PR_3 (R = OMe, Me, Et) and diphosphines such as dppm, dppe and dppp have been reported. All complexes were characterised by elemental analyses and by IR and NMR spectroscopy [327].

9.5.7 Complexes with nitrosyl ligands

The bivalent nitrosyl complexes $[Ru(NO)Cl(SO_4)(L\text{-}L)]$ and $[Ru(NO)Cl(L\text{-}L)_2]SO_4$ (L-L = bpy, phen) were synthesised and characterised by analytical, IR and visible spectra, conductivity measurements and magnetic susceptibility data [328]. A mixture of *mer*- and *fac*-$[RuCl_3(en)(NO)]$ and *mer*-$[RuX_3(en)(NO)]$ (X = Br, I) were prepared from the corresponding $[RuX_5(NO)]^{2-}$ (X = Cl, Br or I) or hydrous $RuX_3{\cdot}NO$ (X = Cl or Br) and en·2HX. The complexes were fully characterised and the crystal structures of *mer*-$[RuX_3(en)(NO)]$ (X = Cl, Br, I) were determined by X-ray diffraction [329]. Photochemical reactions of $[Ru(NO)X_3(Ph_3E)_2]$ (E = P, As, Sb; X = Cl, Br, I) and $[Ru(NO)X_2(Ph_3E)_2]$ (E = P, As; X = Cl, Br, I) have been studied. Oxidation studies of the free ligands, and mass spectroscopic analysis of the gaseous reaction products were used to elucidate the nature of the oxidising agent for the complexes. The photochemical reactions of $[Ru(NO)X_3(Et_2PhP)_2]$ (X = Cl, Br, I) were also studied [330].

An emulsion containing internal latent image-type AgBr grains was prepared by adding solutions of KBr, $AgNO_2$ and $K_2[Ru(NO)Cl_5]$ to a chemically sensitised AgBr emulsion. The materials provide high contrast graduation and are useful for making colour proofs [331].

The anomalous behaviour of valence angles in *trans*-$[Ru(NO)(NH_3)_4(X)]^{2+}$ (X = Cl, Br, I), in which the σ-bonded equatorial ligands are tilted towards the multiple metal-axial ligand bond, was analysed. An explanation based on the vibronic theory of steric distortion in heteroligand systems has been presented [332]. The reversible thermal isomerisation of three geometrical isomers for $[RuCl(L)_2(NO)]$ (L = 2-methyl-8-quinolinol) in degassed DMSO at > 363K was reported [333].

The complex $[Ru(salen)(NO)(H_2O)]^+$ was found to be an efficient catalyst for the Diel-Alder reaction, but in the Mukaiyama reaction, it tends to be reduced and thereby deactivated by the silyl enol ether [334]. The oxidation reaction by the coordinated NO group in $[Ru(NO)(NO_2)(tap)_2](ClO_4)_2$ was described. The oxidative coupling of *N,N*-dimethylaniline to tetramethylbenzidine and the oxidation of $[RuCl_2(bpy)_2]$ to $[RuCl_2(bpy)_2]^+$ were studied. Results on cyclic voltammetry have been described [335]. The electrochemical and spectral properties of the $[Ru(CN)_5(NO)]^{2-}$ ion have also been reported. An IR and EPR spectroscopic study indicates dimerisation of the reduction product in solution but no cyanide splitting from electrogenerated $[Ru(CN)_5(NO)]^{3-}$ was detected [336].

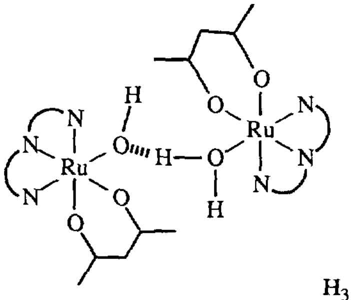
The photophysical and photochemical behaviour of a series of Ru(II) complexes *cis*-$[Ru(bpy)_2(NO)_2(X)]$ ($X = Cl^-, Br^-, CN^-, NO_2^-$) have been investigated. Complexes containing the strong field ligands py, NO_2^- or CN^- display observable emissions at room temperature which are solvent dependent. The appearance of these emissions can be controlled by pH changes via the reversible interconversion of the bound NO_2^- ligand to NO^+ since the nitrosyl complexes do not emit [337]. In addition, the transformation of $[Ru(NO)(NO_2)_4(OH)]^{2-}$ and $[Ru(NO_2)_6]^{4-}$ in aqueous alkaline $NaNO_2$ was studied by ^{15}N, ^{17}O and ^{99}Ru NMR spectroscopy. The mechanism for such reversible nitro-nitrosyl transformations has been established [338].

Both complexes *trans*-$[Ru^{IV}Cl(O)(py)_4]^+$ and *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ were generated directly by one-electron oxidation of *trans*-$[Ru^{II}Cl(NO_2)(py)_4]$. The ligand effect on the electrochemical oxidation of *trans*-$[Ru(NO_2)X(py)_4]^n$ (n = 0 for X = NO_2; n = + for X = NH_3) has been discussed [339].

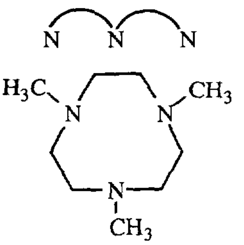
9.6 COMPLEXES WITH OXYGEN DONOR LIGANDS

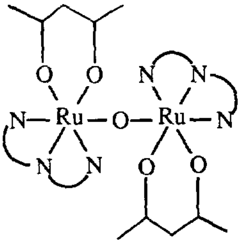
9.6.1 Complexes with oxo ligands

The synthesis and characterisation of the complexes $[LRu(acac)(OH)]PF_6{\cdot}H_2O$ (**270**), $[LRu(acac)(OMe)](BPh_4)$ (**271**), $[\{LRu(acac)\}_2(\mu\text{-}O_2H_3)](PF_6)_3$ (**272**), $[\{LRu(acac)\}_2(\mu\text{-}O)](PF_6)_2$ (**273**) and $[\{LRu^{3.5}(acac)\}_2(\mu\text{-}O)](PF_6)_3$ (**274**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) have been reported. Electronic and ESR spectra of all complexes were recorded and the magnetic properties were studied. Single-crystal X-ray structure determinations of (**270**), (**272**) and (**273**) were carried out [340].



(**272**)

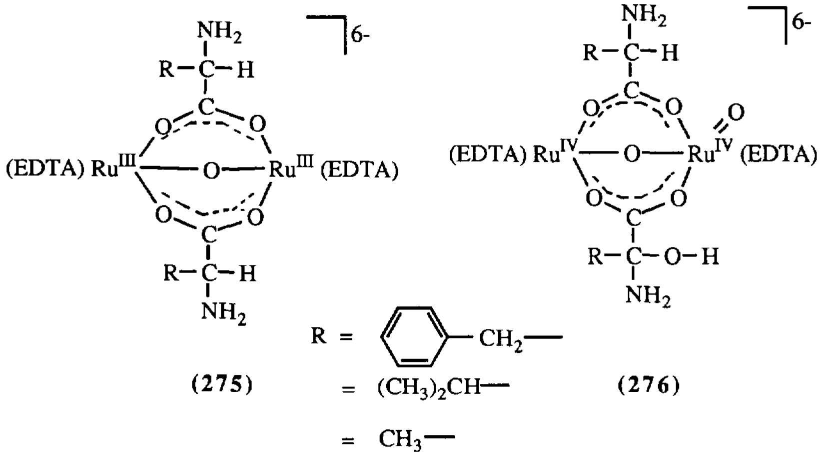




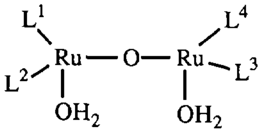
(**273**)

Stable diamagnetic $Na_6[(Ru^{III}edta)_2\text{-}\mu\text{-}L_2\text{-}\mu\text{-}oxo]$ (**275**) (HL = phenylalanine, α-alanine, valine) were prepared and characterised by elemental analysis, electrochemical and spectroscopic methods. The amino acid bridges in the presence of O_2 undergo oxidative deamination, as shown by the formation of an α-keto acid (**276**) and the liberation of NH_3. A reaction mechanism has been proposed [341].

Dimeric complexes of formula (**277**), wherein L^1, L^2, L^3 and L^4 are each a didentate ligand having ≥1 functional substituent, were described. The use of these complexes as water oxidation catalysts has been reported [342]. The kinetics of the oxidation of glutathione by $[\{Ru(H_2O)(bpy)_2\}_2O]$ (**278**) in aqueous $HClO_4$ was investigated. The rate law was determined and a mechanism consistent with the experimental results was postulated [343]. In addition, *in situ* spectrocyclic voltammetry investigations of the formation of complex (**278**) at a Nafion-coated ITO electrode was reported. Under different pH conditions, the monomeric complex *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ dimerises upon oxidation with obvious spectral changes, to yield the corresponding complex (**278**) [344].



(**275**) (**276**)

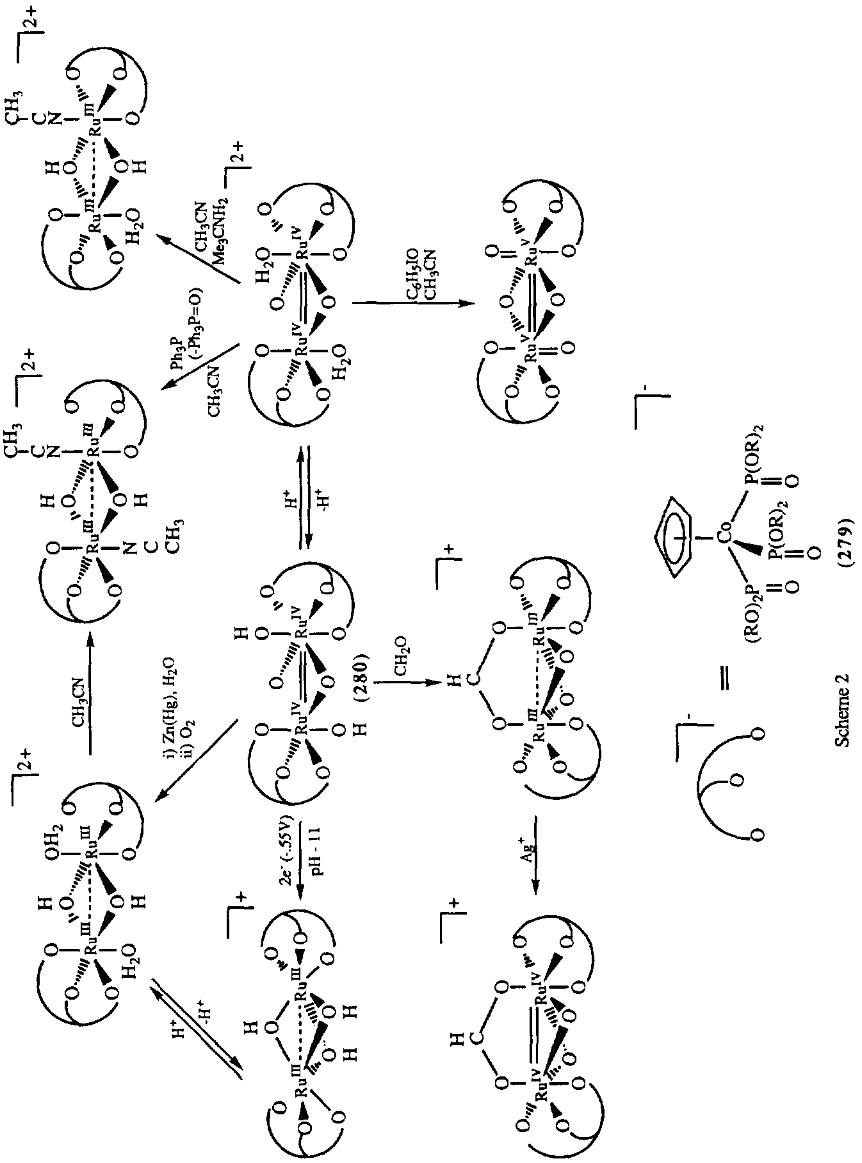


(**277**)

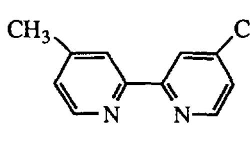
The two-phase reaction of NaL (L = (**279**)) in 1% H_2SO_4 with RuO_4 in CCl_4 affords the edge-sharing octahedral dimer (**280**). The electrocatalytic oxidation by dinuclear ruthenium complexes incorporating the anionic tripod ligand L has been described, as shown in Scheme 2. The Ru^{III}-Ru^{III} dimers were characterised by X-ray crystallography [345].

Oxidation of $[Ru^{II}(bpp)(bpy)OH_2]^{2+}$ with Ce^{IV} gives $[Ru^{IV}(bpp)(bpy)O]^{2+}$. The latter complex is paramagnetic (μ_{eff} = 2.82 B.M.) and its related complexes $[Ru(L)(L')OH_2]^{2+}$ (L = bpp, Me_4-bpp; L' = bpy, Me_2-bpy) were found to be robust catalysts for the oxidation of styrene, cyclohexene and cyclooctene with a co-oxidant such as NaOCl [346].

Electrodes coated with thin polymeric films of $^1/_3$poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$-co-$^2/_3$poly-$[Ru(vbpy)_3]^{2+}$ (vbpy = (**281**)) or poly-*cis*-$[Ru(pyr\text{-}bpy)_2(H_2O)_2]^{2+}$ (pyr-bpy = (**282**)) were prepared and characterised. In solution, oxidation of *cis*-$[Ru^{II}(bpy)_2(H_2O)_2]^{2+}$ to *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$ leads to decomposition by loss of bpy to give *trans*-$[Ru^{VI}(bpy)(O)_2(OH)_2]$. This reaction was inhibited in the polymeric film and Ru^{VI} was stabilised. Preliminary studies were made of the electrocatalytic oxidation of benzyl alcohol and of chloride ion by poly-*cis*-$[Ru(pyr\text{-}bpy)_2(H_2O)_2]^{2+}$ by rotating disk voltammetry. The mechanism for the oxidation of benzyl alcohol appears to be related to that for $[Ru(bpy)_2(py)(O)]^{2+}$ as oxidant in solution [347].


CH3CN
Me3CNH2
Ph3P
(-Ph3P=O)
CH3CN
C6H5IO
CH3CN
H+
-H+
(280)
CH2O
i) Zn(Hg), H2O
ii) O2
CH3CN
2e- (-.55V)
pH - 11
Ag+
(RO)2P
P(OR)2
Co
(279)
2+
+
-

Scheme 2



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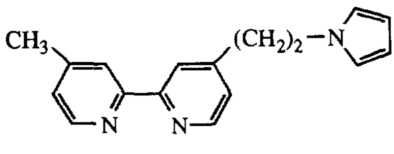

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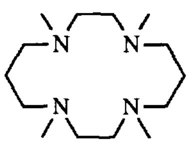


(283)

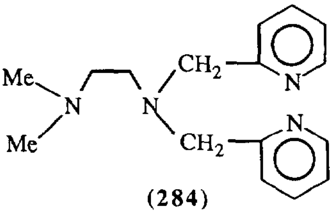
The preparation and unequivocal characterisation by X-ray crystallography of $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot 2KCl\cdot 60H_2O$ was reported. The structural results reveal a new polyoxoanion structural type, a Ru-O-Ru oxo-bridged-dimer anion that is structurally analogous to dimetallic metalloporphyrins containing a μ-oxo M-O-M bridge [348].

The kinetics of the reduction of *trans*-$[Ru(TMC)(O)_2]^{2+}$ (TMC = (**283**)) by Fe^{2+} were studied in aqueous acidic solution (equ. 3). The rate law was determined and the electron transfer mechanism was discussed [349].

$$trans\text{-}[Ru^{VI}(TMC)(O)_2]^{2+} + 2Fe^{2+} + 2H^+ \longrightarrow trans\text{-}[Ru^{IV}(TMC)O(OH_2)]^{2+} + 2Fe^{3+} \qquad \text{(equ. 3)}$$

The ruthenium complexes derived from $[Ru(tpy)(bpy)O]^{2+}$ (tpy = 2,2,2'-terpyridine) were found to be effective DNA cleavage agents both electrocatalytically and thermally. The chemistry of new families of DNA cleavage agents based on oxoruthenium(IV) has been reviewed [350]. The anion $[(terpy)(bpy)Ru(OPPh_3)]^{2-}$ was detected by ^1H NMR, FT-IR and UV-VIS spectroscopies as the intermediate complex in the rapid oxidation of PPh_3 by $[(terpy)(bpy)RuO]^{2+}$ in MeCN. A similar intermediate was observed using $[(py)(bpy)_2RuO]^{2+}$ [351]. The oxo(phosphine)-ruthenium(IV) complexes $[Ru(bpy)_2(O)PR_3](ClO_4)_2$ (R = substituted phenyl rings) cleanly oxidise sulfides to sulfoxides and in separate experiments oxidise sulfoxides to sulfones. The kinetics and mechanisms of the oxidation reactions were studied [352].

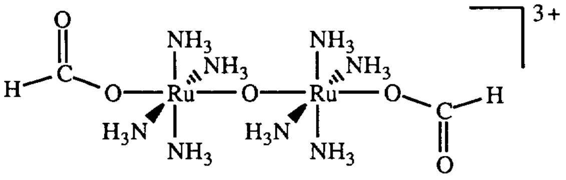
The electrocatalytic oxidation of methanol by *cis*-$[Ru^V(L)(Cl)(O)]^{2+}$ (L = (**284**)) in solution was described. The second order rate constants for the reaction between the oxo complex and MeOH, MeOD and CD_3OH were evaluated by rotating disk voltammetry. The large kinetic isotope effect for MeOH (k_H/k_D = 10) indicates the importance of α-CH bond cleavage in the transition state [353].



(284)

The complex $[Ru^V(O)(H_2O)_3Cl_2]^+$ was generated *in situ* by the coulombic oxidation of $[Ru^{III}(H_2O)_4Cl_2]^+$ [354]. Besides, the $[RuO_4]^-$ ion can be generated in aqueous base at pH = 10 from aquated $RuCl_3$ with excess bromate, and this reagent acts as a catalyst for various organic functionality transformations using bromate as the cooxidant. These oxidations were compared with those effected catalytically by *trans*-$[Ru(OH)_2O_3]^{2-}$ in aqueous base at pH = 14 with persulfate as cooxidant [355]. The evolution of O_2 on RuO_2 and Pt was studied at 298-180 K. The mechanism was found to proceed in a different way for RuO_2 as compared with Pt electrodes [356].

The trinuclear ruthenium complexes, Ru red $[(NH_3)_5Ru^{III}\text{-}O\text{-}Ru^{IV}(NH_3)_4\text{-}O\text{-}Ru^{III}(NH_3)_5]^{6+}$ and Ru brown $[(NH_3)_5Ru^{IV}\text{-}O\text{-}Ru^{III}(NH_3)_4\text{-}O\text{-}Ru^{IV}(NH_3)_5]^{7+}$ were studied as water oxidation catalysts in aqueous solution and in a Nafion membrane incorporated system under different pH conditons using spectrocyclic voltammetry. Experimental results show that the complexes were stabilised as water oxidation catalysts when incorporated in a Nafion membrane [357]. In addition, the efficient and stable heterogeneous catalytic systems for water oxidation utilising polymer (Nafion) membrane and Ru-red and Ru-brown can also be used to model the photosynthetic dioxygen-evolving centre [358]. The component of ruthenium red responsible for the inhibition of mitochondrial calcium ion transport has been isolated and a derivative $[\mu\text{-}O\text{-}\{(HCO_2)(NH_3)_4Ru\}_2]Cl_3$ (**285**) was characterised by X-ray diffraction, spectroscopy and electrochemistry [359].



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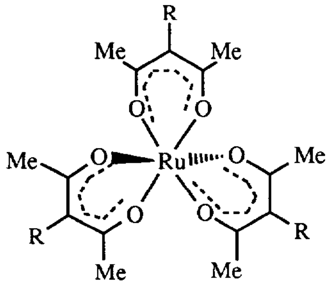
The ability of ruthenium red to reduce the autonomic reflexes and peptide release evoked by capsaicin administration in the pig *in vivo* has been described [360]. A comparison of capsazepine and ruthenium red as capsaicin antagonists in the rat isolated urinary bladder and *vas deferens* was presented [361]. It was also found that ruthenium red reduces plasma extravasation by cigarette smoke in rat airways [362] and can selectively deplete inositol 1,4,5-trisphosphate-sensitive calcium stores in permeabilised rabbit pancreatic acinar cells [363]. The effects of ruthenium red on calcium-activated current in isolated guinea pig ventricular myocytes were investigated using a single-electrode voltage-clamp system. Ruthenium red increases the amplitude of calcium current without changing the current-voltage relations [364, 365].

Barium ruthenate $[BaRu(O)_2(OH)_3]$ in acetic acid-dichloromethane oxidises alkanes at room temperature with appreciable rates and yields. The reactions are greatly accelerated in the presence of a few equivalent of Lewis acids [366].

9.6.2 *Complexes with carboxylate ligands*

The complexes $[Ru(acac)_3]$ (**286**) and $[RuL_3]$ (**287**) (HL = 3-bromo-2,4-pentanedione) have been synthesised and characterised by X-ray diffraction [367]. In addition, $[Ru^{III}Cl_2(acac)(acacH)]$ was isolated in high yield by reacting $RuCl_3$ with Hacac. The complex was used as a convenient starting material for the synthesis of $[RuCl_2(acac)(L)_2]$ (L = PPh_3, $AsPh_3$, py, MeCN, DMSO; L-L = bpy, phen) and $M_2[RuCl_4(acac)]$ (M = Me_4N, Rb, Cs) [368].

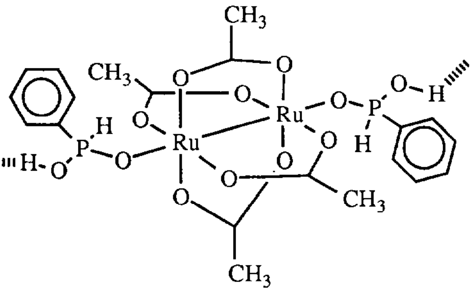


R = H (286)

R = Br (287)

The effect of the electronegativity of donor atoms on R_F values obtained by TLC on silica gel was studied with two series of [Ru^{III}(acac)$_{3-n}$(L)$_n$] (L = 1,3-diphenyl-1,3-propanedionato ion) and [Ru^{III}(acac)$_{3-n}$(L')$_n$] (L' = 3-mercapto-1,3-diphenyl-prop-2-en-1-on ion) (n = 0-3). The R_F values of the complexes increase when one O atom of a β-diketonato ligand is replaced by a less electronegative S atom. A positive linear dependence between the R_F value of the complexes and the numbers of acac substituted by L' ligands was established [369].

The base hydrolysis of [Ru(acac)$_3$] has been studied in 0.1-1M NaOH at different temperatures. The rate equation for the decomposition of [Ru(acac)$_3$] was determined [370]. The electronic structures of [Ru(acac)$_3$] and some of their derivatives with substituents in the γ-positions of the ligands have been investigated by photoelectron spectroscopy. The vertical ionisation energies were determined for the valence electrons, and the nature of the MOs corresponding to these ionisation energies were also determined [371].



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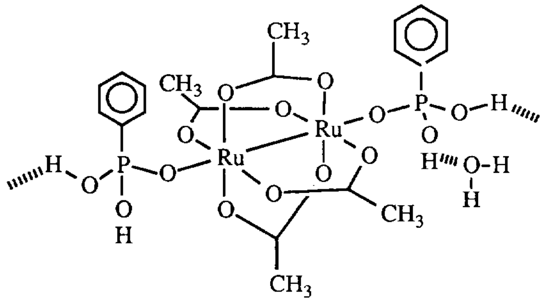
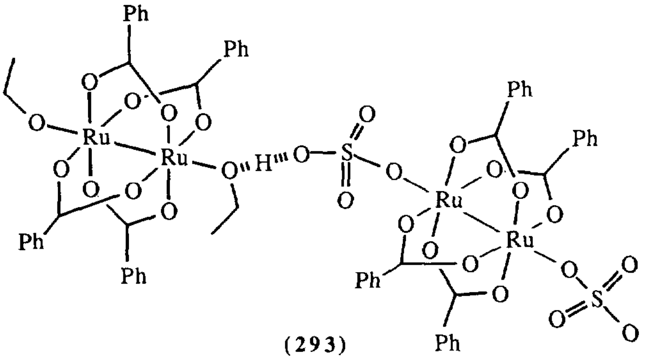


(289)

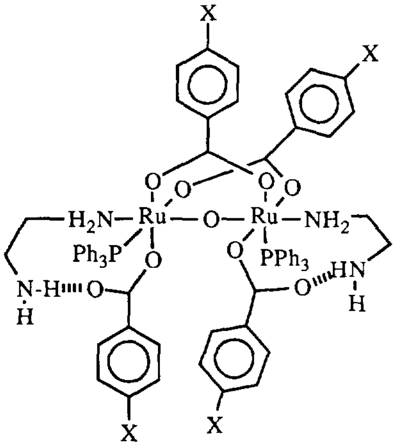
The reaction of $HPhPO_2H$ and $PhPO_3H$ with a MeOH solution of $[Ru_2(\mu\text{-}CH_3COO)_4(CH_3COO)_2]H\cdot 0.7H_2O$ at room temperature gives $[Ru_2(\mu\text{-}CH_3COO)_4(HPhPO_2)_2]$ (**288**) and $[Ru_2(\mu\text{-}CH_3COO)_4(PhPO_3H)_2]H\cdot H_2O$ (**289**) respectively. The X-ray crystal structures of both complexes have been determined. In each complex, the individual dimetallic molecules are linked together by a hydride ion which bridges the O atoms of neighouring axial ligands. The spectroscopic, magnetic and cyclic voltammetric data for the complexes have also been presented [372]. The compound $[Ru_2(\mu\text{-}CH_3COO)_4Cl]$ reacts readily with aqueous Ag_2SO_4 (2:1 molar ratio) to give $[Ru_2(\mu\text{-}CH_3COO)_4(H_2O)_2]_2(SO_4)$ (**290**). Addition of $NaBPh_4$ to an aqueous solution of (**290**) produces the ether-soluble $[Ru_2(\mu\text{-}CH_3COO)_4(H_2O)_2](BPh_4)$ (**291**). A methanol solution of (**290**) also reacts with $Ba(PhC{\equiv}CCO_2)_2\cdot H_2O$ to give $[Ru_2(\mu\text{-}CH_3COO)_4(O_2CC{\equiv}CPh)]\cdot H_2O$ (**292**). The synthesis, characterisation and X-ray crystal structure of $[Ru_2(\mu\text{-}O_2CC_6H_5)_4(C_2H_5OH)_2][Ru_2(\mu\text{-}O_2(C_6H_5)_4(HSO_4)_2]$ (**293**) have been reported. The structure of (**293**) consists of $[Ru_2(\mu\text{-}O_2CC_6H_5)_4(C_2H_5OH)_2]^+$ and $[Ru_2(\mu\text{-}O_2CC_6H_5)_4(HSO_4)_2]^-$ ions, which are linked together by H bonds into an infinite polymeric chain [373].



(**293**)

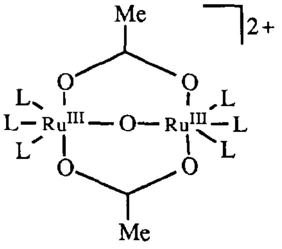
The preparation of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2(en)_2(PPh_3)_2](ClO_4)_2$ (**294**) and $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2(en)_2(PPh_3)_2](ClO_4)\cdot(CH_3CONH)$ (**295**) from $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ has been reported (R = C_6H_4-*p*-X, X = H, OMe, Me). The complex (**295**) with R = C_6H_4-*p*-OMe has been characterised by X-ray diffraction analysis. The electrochemical properties of (**294**) were investigated. The mechanistic aspects of the substitution and nucleophilic reactions in the formation of (**294**) and (**295**) were discussed [374]. The reaction of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_4(PPh_3)_2]$ with en in CH_2Cl_2 was also studied and a blue-coloured, unstable, essentially diamagnetic complex was formed. The molecular structure of the complex was proposed as $[\{(\eta^1\text{-}O_2CR)(\eta^1\text{-en})(PPh_3)Ru\}_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]$ (**296**) based on ^1H NMR spectral evidence. The electronic spectra and redox properties of the complexes have been discussed [375].

The synthesis, spectroscopic characterisation (^1H NMR, EPR and UV-VIS) and crystal structures of a novel diruthenium(III) complex $[\{(1\text{-MeIm})_3Ru\}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_2$ (**297**) and a diruthenium(III, IV) complex $[\{(1\text{-MeIm})_3Ru\}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_3\cdot 1.5H_2O$ (**298**) have been described (1-MeIm = 1-methylimidazole). The CVs of (**297**) have been studied and a previously unknown two-electron transfer process among model dimeric complexes with a "$[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)]$" core has been observed [376].

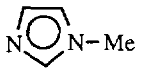


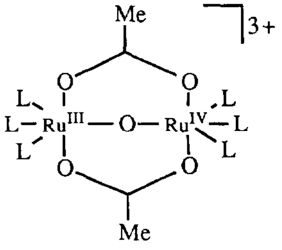
X = H, Me, OMe

(296)



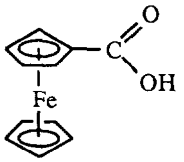
(297)

L =




(298)

Under aerobic conditions, $[RuCl_2(L)(PPh_3)_2]$ was isolated from the reaction of $RuCl_2(PPh_3)_3$ with the ligand HL (HL = (**299**)). The IR spectrum of the complex suggests the carboxylate groups of the ligand coordinate to Ru(II) through the two O donor atoms. ESR spectral data were also presented [377].



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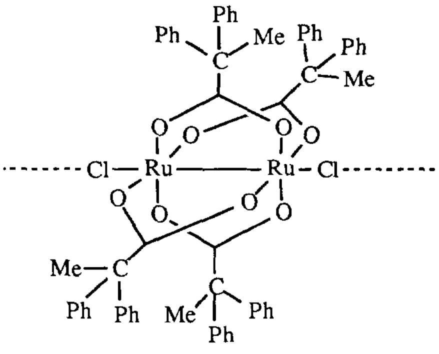
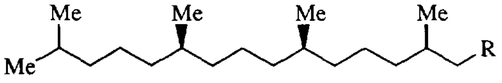


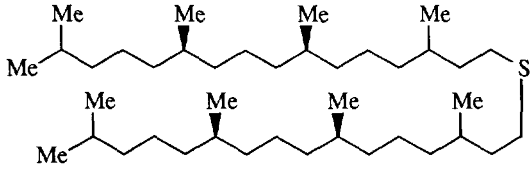
(300)

The linear-chain compound [$Ru_2(\mu\text{-}O_2CCMePh_2)_4Cl$] (**300**) was prepared by reacting [$Ru_2(\mu\text{-}CH_3COO)_4Cl$] with $MePh_2CCO_2H$ and its molecular structure was established by X-ray crystallography. The Cl^- ligand bridges the dinuclear units and these form linear chains. An anti-ferromagnetic electronic interaction between the dinuclear units with $J = -10.9\ cm^{-1}$ was observed and the magnetic moment of (**300**) at 300 K is 4.4 μB, which indicates three unpaired electrons in each dinuclear unit [378].

The synthesis and thermodynamical and structural properties of two Ru(II) carboxylates have been described. These compounds are the first examples of fully characterised metallomesogens giving an authentic columnar mesophase near room temperature in the pure state [379]. The interaction of [$Ru^{III}(CN)(\mu\text{-}CH_3COO)_3$] with human serum transferrin has been investigated through UV-VIS and CD spectroscopy. The chemical properties of the resultant ruthenium/transferrin complex were described [380]. The complex [$Ru(\mu\text{-}CH_3COO)_3$] has been used in the preparation of α,β-unsaturated nitriles and carboxylic acids [381] and manufacture of acrylonitrile dimers [382]. Besides, simple preparative-scale stereospecific syntheses of (*R*)- and (*S*)-(**301**) and the sulfide (**302**) were described using [$Ru^{II}(\mu\text{-}CH_3COO)_2\{(S)\text{-BINAP}\}$] as catalyst [383]. New catalyst systems, based on [$Ru_2(\mu\text{-}CH_3COO)_4$] were found to be highly efficient for promoting the ring opening metathesis polymerisation (ROMP) of cycloolefins. The ruthenium complexes initiate both olefin metathesis and carbene transfer reactions [384].

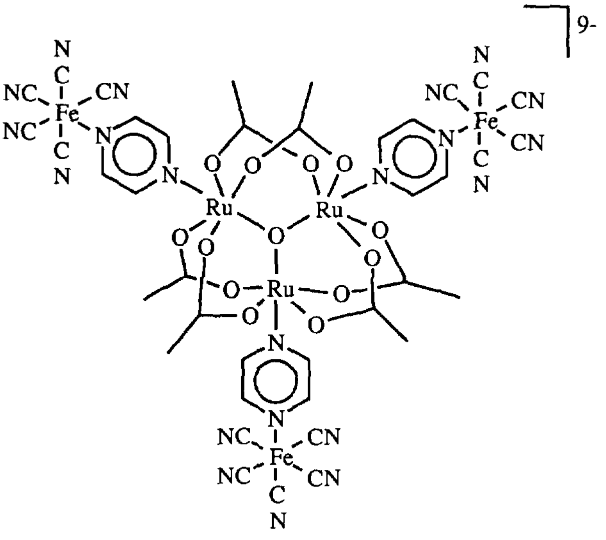


R = COOH, CH_2OH
(**301**)



(**302**)

The hexanuclear cluster [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6\text{-}\mu\text{-}(pz)_3\text{-}\{Fe(CN)_5\}_3]^{9-}$ (**303**) was prepared, characterised and employed in modified nickel electrodes. The electrochemical and spectroelectrochemical behaviour of the complex have been investigated in aqueous solution and the electrochromic properties of the modified electrodes were explored [385]. In addition, the redox reactions of the ruthenium(III,III,III) and ruthenium(III,III,II) trinuclear cluster complexes, [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3](PF_6)$ (**304**) and [$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$] (**305**), respectively in acetonitrile were studied by pulse radiolysis [386].



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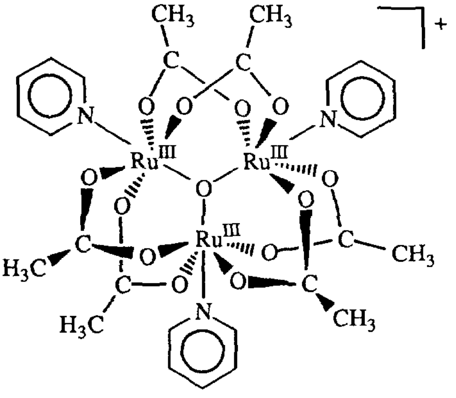


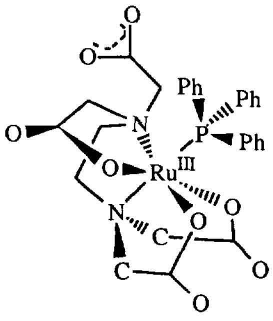
(304)

The X-ray crystal structure of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(OH_2)_3]ClO_4{\cdot}HClO_4{\cdot}H_2O$ **(306)** was reported and the structure shows a significant elongation in the Ru-O(OH_2) bond length (av. 2.091Å) when compared to that in $[Ru(OH_2)_6]^{3+}$ (2.029Å). A study of H_2O exchange and substitution by isonicotinamide on complex **(306)** in aqueous perchlorate media was carried out using ^{17}O NMR and UV-VIS spectroscopic methods [387]. The substitution reactions of CD_3OD for the coordinated water in the trinuclear complexes $[M_3(\mu\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ (M_3 = Ru_3 or Ru_2Rh) in CD_3OD have been investigated by following the acetate Me signals in the ^1H NMR spectra of the two complexes. The first-order rate constants for the first CD_3OD substitution of the complexes were determined and the *trans* labilisation effect of the central oxide ion has been discussed. On the basis of the activation parameters, a dissociative mechanism was proposed for these reactions [388]. The electrochemical and spectroelectrochemical behaviour of the complex

$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(DMSO)]^+$ have been discussed [389]. The first mixed chromium(III)-ruthenium(III) trinuclear complex $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ was prepared. The magnetic and redox behaviour indicate that d^3 Cr(III) ion acts as if isolated in the complex, and that the two d^5 Ru(III) ions are effectively coupled [390]. The cation $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(MeOH)]^+$ was found to be adsorbed as a monolayer onto the poly(2,6-bis(2-thienyl)pyridine) coated electrode in MeCN [391].

9.6.3 *Complexes with ligands derived from H_4edta*

The catalytic oxidation of tertiary phosphines PR_3 (R = p-FC_6H_4, Ph, Cy) by O_2 to the corresponding R_3PO catalysed by $Ru^{III}(edta\text{-}H)(H_2O)$ has been reported as a function of catalyst, substrate and O_2 concentration. The proposed mixed-ligand Ru^{III}-edta-PR_3 (**307**) intermediate in the catalytic oxidation cycle was isolated and its structure solved by single-crystal X-ray diffraction [392]. The synthesis and physicochemical properties (UV-VIS, IR, EPR, CV) of $K_5[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]$ (**308**) were described. The rate of formation of (**308**) is first-order with respect to both $[Ru(edta)(H_2O)]^-$ and $[Fe(CN)_6]^{4-}$ concentrations. The intervalence thermochromism for the ground-state mixed-valence complex (**308**) was discussed with reference to the data reported for the similar $[Ru^{III}(NH_3)_5(NC)Fe^{II}(CN)_5]^-$ complex [393]. The deaquation of $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ (**309**) by thiourea was studied spectrophotometrically. Rate and activation parameters were consistent with an associative interchange mechanism involving (**309**) and its deprotonated form (OH ligand) [394].



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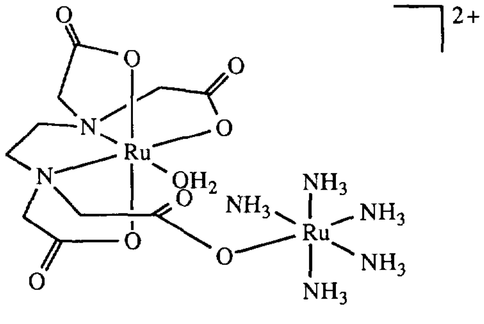
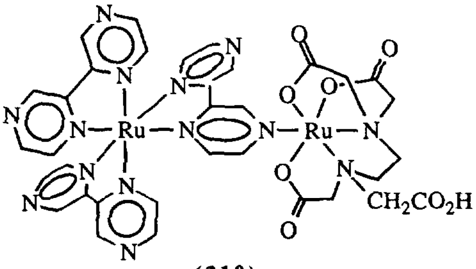


(309)

Tris(bipyrazine) ruthenium(II) forms complex (**310**) which contains $[Ru^{II/III}edta]^{2-/-}$ groups which are coordinated to the peripheral nitrogen atoms of the bipyrazine bridging ligand. The equilibrium for the formation of (**310**) and spectroelectrochemical studies have been reported [395].

The mixed ligand complexes $K[Ru^{III}(edta\text{-}H_2)(bpy)]$ and $K[Ru^{III}(edta\text{-}H_2)(phen)]$ were synthesised and characterised by physicochemical methods. Their redox and photophysical properties were studied. Surface modification of a TiO_2 semiconductor was carried out by adsorption of both complexes onto the surface of TiO_2 particles and it is found that the photoreduction of CO_2 was achieved at an energy lower than the band gap energy of TiO_2 [396].

The interaction of pentadentate Ru complex [Ru^{III}(EDTRA-H)(H_2O)] (EDTRA = (**311**)) with DMSO was investigated using spectrophotometric, electrochemical and kinetic techniques. In the presence of a large excess of DMSO, the formation of a weak *S*-bound complex [Ru^{III}(EDTRA-H)(DMSO)] was suggested [397].



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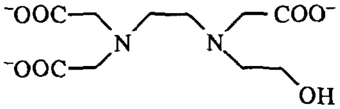
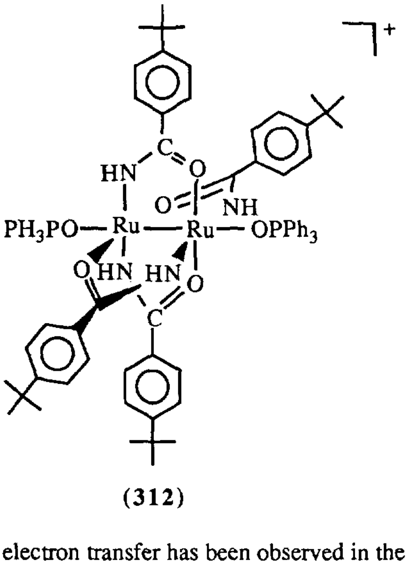


(311)

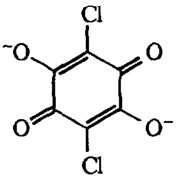
9.6.4 Complexes with other O-donor ligands

The insoluble polymeric compound [$Ru_2Cl(\mu$-$HNOCC_6H_4$-*p*-$CMe_3)_4$] was isolated and broken with $AgBF_4$ in anhydrous THF, yielding [$Ru_2(\mu$-$HNOCC_6H_4$-*p*-$CMe_3)_4(THF)_2](BF_4)$. This cationic complex reacts with Ph_3PO to give [$Ru_2(\mu$-$HNOCC_6H_4$-*p*-$CMe_3)_4(OPPh_3)_2](BF_4)$ (**312**). All complexes were fully characterised and the X-ray crystal structure of (**312**) was determined [398].



(312)

Slow intramolecular electron transfer has been observed in the dinuclear intermediate of a Ti(III)-Ru(III) redox reaction that involves dianions (**313**)-(**316**) as bridging ligands. It was found that the ligands provide small but significant cross-bridge Ru(III)-Ti(III) electronic interaction and the electronic coupling between donor and acceptor orbitals is smaller in the dihydroxyquinonate-bridged species than in the pyrazine-bridged dimers due to orbital symmetry mismatch in the former case [399].



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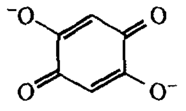

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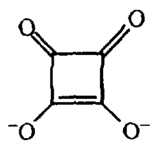

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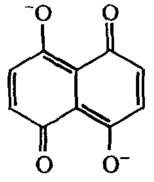
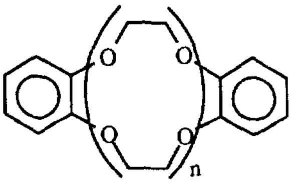


(316)

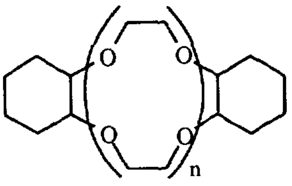
The complex $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ was prepared and its X-ray crystal structure was established. The use of highly charged sulfate and phosphate ligands facilitates the transformation of the complex to the corresponding Ru_2(III,III) complex by electrochemical oxidation [400]. In addition, the synthesis and crystal structures of $[Ru_2(\mu\text{-}SO_4)_2(\mu\text{-}OH)_2(py)_4]\cdot 8H_2O$ **(317)** and $[Ru_2(\mu\text{-}SO_4)_2(\mu\text{-}OH_2)_2(py)_4]\text{-}(CH_3COO)_2$ **(318)** have been described. The electronic configuration and the metal-metal bond order in **(317)** and **(318)** have been discussed [401]. The X-ray crystal structure of $K_2[Ru(SO_4)_2]\cdot 6H_2O$ at 160K and 295K have been determined. The resulting atomic displacement parameters were analysed in the molecular mean field approximation, and the molecular motion in the crystals has been discussed [402]. The structure of $Cs[Ru(SO_4)_2]\cdot 12D_2O$ was also determined at 15K using neutron-diffraction techniques. The influence of the stereochemistry of water coordination to Ru(III) cations on the M-O bond length and electronic structure of the cation has been discussed [403].

The charge-transfer absorption, electrochemical and NMR-NOE spectroscopic studies of monomeric and dimeric ruthenium amine guest interactions with several crown ether hosts **(319)** and **(320)** have been reported. The effects of the modification of both guest and host on the strength of second-sphere complexation have been discussed [404]. The preparation of teh complex *cis*-$[Ru(NH_3)_4\{CH_3(CO)CH_3\}_2](PF_6)_2$ from *cis*-$[Ru(NH_3)_4Cl_2]Cl$ was described and the complex was characterised by microanalysis, cyclic voltammetry and ^1H NMR spectroscopy. The substitution reactions with other monodentate and didentate ligands were reported [405].



n = 2 - 6

(319)



n = 2, 3

(320)

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