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Ruthenium 1994

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Contents

1. Introduction

This review covers the coordination chemistry of ruthenium for 1994 and is based upon a search of volumes 120, 121 and 122 of *Chemical Abstracts*. Moreover, major inorganic chemistry journals have been searched individually from the period of January to December 1994. The metal complexes are classified according to the ligand type. References to most of the organometallic ruthenium complexes are excluded in this review.

2. Complexes with hydrogen donor or hydride ligands

The electronic structure and bonding of Mg_2RuH_4 and Mg_3RuH_3 have been investigated using charge iteration of the transition metal orbital parameters,

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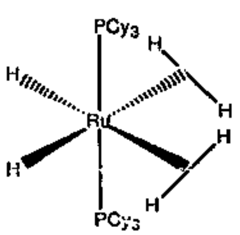
Mulliken population analyses, and second moment scaling methods. The unusual sawhorse geometry of individual d^8 RuH_4 fragment in Mg_2RuH_4 was also revealed [1]. The compound $LiMg_2RuH_7$ and its deuteride were synthesized by sintering a mixture of LiH, magnesium and ruthenium powders at 500-550°C and hydrogen (deuterium) pressure of 120-155 bar. X-ray and neutron powder diffraction revealed the existence of discrete octahedral $[Ru(II)H_6]^{4-}$ complex anions [2].

Under ambient conditions, $[RuCl_2(PPh_3)_3]$ reacted with azine phosphines to produce complexes showing strong agostic interactions between ruthenium and C-H bonds of *tert*-butyl, methyl, aryl or alkenyl groups in dynamic systems and has been examined by ^1H NMR spectroscopy at 20°C [3]. A strong B-H-Ru agostic interaction was also observed in some ruthenium derivatives of 7,8-dicarba-*nido*-undecaborate in which the sulfur atoms were connected to the cluster carbon atoms. Such interaction has been shown by ^1H and ^{11}B NMR spectroscopy to be a function of the length of the *S*,*S*′-connecting chain. Two extreme types of B-H-Ru agostic chains have also been described [4].

The compound $[RuH_2(PPh_3)_4]$ catalysed the condensation of nitrile and alcohols in the presence of 1-2 equivalents of water to give the corresponding esters and lactones [5]. In an oxygenated benzene solution of $[RuH_2(PPh_3)_4]$ and $[RuCl_2(PPh_3)_4]$, vinyltrimethylsilane underwent self-metathesis to give (*E*)-1,2-bis(silyl)ethene, 1,1-bis(silyl)ethane, 1,4-bis(silyl)but-2-enes (*E*+*Z*) and butenylsilane as well as hexamethyldisiloxane. In contrast, ruthenium complexes containing no phosphine gave stereoselectivity in only the (*E*)-product of metathesis [6].

The reaction of $[RuH_2(H_2)_2(PCy_3)_2]$ (1) with MeI or CH_2Cl_2 yielded the 16 electron complex $[RuHX(H_2)(PCy_3)_2]$ (X = I, Cl) which converted to the corresponding $[RuHX(H_2)_2(PCy_3)_2]$ under excess H_2. Moreover, (1) also reacted with thiols (RSH) to afford $[RuH(SR)(H_2)(PCy_3)_2]$ (R = Cy, Ph, CMe_3). Upon carbonylation, all complexes afforded the corresponding $[RuHX(CO)_2(PCy_3)_2]$ (X = H, I, Cl, SCy, SPh) respectively [7]. Under the same conditions, (1) produced $[RuH_2(N_2)_2(PCy_3)_2]$, $[RuH(O_2CH)(H_2)(PCy_3)_2]$, $[RuH_2(S_2CH_2)(PCy_3)_2]$, $[RuH(H_2)(NNC_3H_3)(NNHC_3H_3)(PCy_3)_2]$ and $[RuH(\eta^5\text{-}PhO)(PCy_3)_2]$ on reacting with N_2, CO_2, CS_2, pyrazole and phenol respectively [8]. Also, reactions of (1) with $HEPh_3$ (E = Si, Ge) led to $[RuH_2(H_2)(HEPh_3)(PCy_3)_2]$, the chemical reactivity of which towards N_2 or H_2 has been investigated [9].

The complexes *trans*-$[RuH(H_2)L_2]BF_4$ [L = $P(C_6H_4\text{-}4\text{-}R)_2(CH_2)_2P(C_6H_4\text{-}4\text{-}R)_2$,

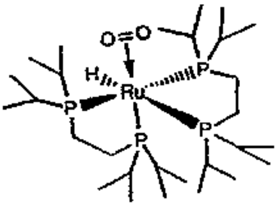


(1)

$R = CF_3$ or OMe] were synthesized by the reaction of RuH_2L_2 with HBF_4; the effects of the ligand and metal on the pK_a values of the dihydrogen ligand were also described [10].

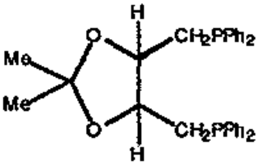
Kinetics studies of the reactions of $[Ru(Cl)H(PPh_3)_3]$ with a number of olefins have been carried out spectrophotometrically, and a dissociation mechanism was established [11]. The compound $[RuCl_2(PPh_3)_3]$ underwent substitution with the bulky diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe) (**2**) to form $[RuCl_2(dippe)_2]$ from which *cis*-$[RuH_2(dippe)_2]$ was isolated by reduction with $NaBH_4$. Complex (**2**) reacted with dihydrogen to give $[RuH(H_2)(dippe)_2][BPh_4]$ which further reacted with dioxygen to produce $[RuH(\eta^2\text{-}O_2)(dippe)_2][BPh_4]$ (**3**). The crystal structure of (**3**) was reported [12].

(2)



(3)

The complex $[RuH_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] was synthesized by reduction of *trans*-$[RuCl_2(dmpe)_2]$ which in turn protonated to afford *trans*-$[RuH(\eta^2\text{-}H_2)(dmpe)_2]^+$ [13]. In addition, intra- and inter-molecular proton dynamic exchange of *trans*-$[RuH(\eta^2\text{-}H_2)(dmpe)_2]^+$ and its isotopomers has been studied by picosecond photolysis [14]. The agostic interaction and the intramolecular hydrogen exchange in $[RuH(P\text{-}P)_2]PF_6$ [P-P = 1,4-bis(diphenylphosphino)butane (dppb), 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(di-phenylphosphino)butane (diop) (**4**), 1,3-bis(diphenylphosphino)propane (dppp)] have been examined by various NMR spectroscopic measurements. Effects of the chelate ring size on the intramolecular carbon-hydrogen bond activation were also described [15].



(4)

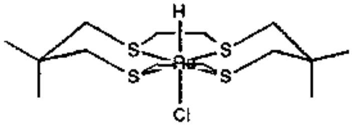
The nature of $[RuH_3(P\text{-}P)_2]$ {P-P = dppb, diop, dpmb = (1,2-bis(diphenyl phosphino)methylbenzene) and dppe (1,2-bis(diphenylphosphino)ethane)} in solution has been clarified electronically by *ab initio* MO calculations and sterically by molecular mechanics (MM) analysis [16]. The $[RuH(\eta^2\text{-}H_2)(dpbp)_2]^+$ [dpbp = 2,2'-bis(diphenylphosphino)-1,1'-biphenyl], prepared by in situ reaction of H_2 with $[RuH(dpbp)]PF_6$, exhibited intramolecular proton exchange which was shown to be related to the flexibility or rigidity of the diphosphine chelate rings. Comparisons were made with the corresponding binap analogues [binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] [17].

Ruthenium(II) hydrido complexes containing crown thioethers *trans*-[RuH(Cl)(*syn*-L)] [L = Me_4[14]aneS_4 (**5a**); Me_6[15]aneS_4 (**5b**); Me_8[16]aneS_4 (**5c**)] were synthesized by treating the corresponding dichlorides *cis*-[RuCl_2L] with $NaBH_4$ in MeOH for (**7a**) and in EtOH for (**5b**) and (**5c**). Synthesis of (**5a**) in EtOH afforded [Ru_2H(μ-H)Cl(*syn*-Me_4[14]aneS_4)$_2$]Cl (**6**) which was shown to prefer the more stable central linear Ru-H-Ru geometry by EHMO calculations and also by single crystal X-ray analysis [18].

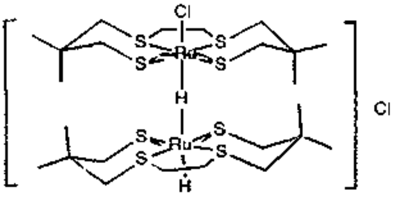
Ruthenium and osmium analogues of $[M(S_2CH)P_4]^+$, $[M\{RNC(H)S\}P_4]^+$ and $[M\{R'NC(H)NR'\}P_4]^+$ [P = $P(OMe)_3$, $P(OEt_3)_2$, $PPh(OEt)_2$; R = *p*-MeC_6H_4, Et; R′ = *p*-MeC_6H_4] were synthesized by reacting the hydride complexes $[MH(\eta^2\text{-}H_2)P_4]$ with CS_2, RNCS and R′NCNR′ respectively. The related formamido complex $[M\{PhNC(H)O\}P_4]CF_3SO_3$ was prepared by the reaction of the dihydride $[MH_2P_4]$ with phenylisocyanate in the presence of methyltriflate [19].

3. Complexes with halide and pseudohalide ligands

Fluorination of RuO_2 using various fluorinating agents ClF_3, BrF_5 and KrF_2 has been studied and the results were compared with those obtained for RuO_4 and its Os analogues. The difference between the fluorination pathway of Ru oxides and those of Os was discussed [20].



(**5a**)



(**6**)

The compounds $[RuClL_2(P{=}O)_2]Cl$ (L = dmso, PPh_3) have been synthesized from the reaction of $[RuCl_2(dmso)_4]$ or $[RuCl_2(PPh_3)_3]$ with the bifunctional phosphino-amido ligands P=O (P=O = $Ph_2PCH_2C(O)NHR$, R = H, Me, Ph) and were characterized by IR, NMR and mass spectroscopies. Possible stereochemistries for the complexes have also been considered [21].

Ruthenium trichloride was found to catalyse the aqueous ring-opening metathesis polymerization of a number of 7-oxanorbornene derivatives containing hydroxy-, methoxy- and acetoxymethyl functionalities. The structures of the polymers were investigated by ^1H and ^{13}C NMR spectroscopies while their molar masses and molar mass distribution were measured by gel-permeation chromatography [22]. Under different conditions, $RuCl_3$ also catalysed the ring opening polymerization of *exo*-7-isopropylidenebicyclo[2,2,1]hept-2-ene-*N*-phenyl-5,6-dicarboximide, producing a high *trans*-vinylene content. The molecular weight distributions of the polymers were investigated by gel-permeation chromatography [23]. In the presence of sodium periodate, $RuCl_3$ was also an excellent catalyst for the oxidation of sulfides to sulfones [24]. In addition, electrolysis of 1,4-di-*tert*-butyl-2,5-dimethoxybenzene in the presence of water and either $RuCl_3 \cdot 3H_2O$ or $Ru(acac)_3$ afforded 2,5-di-*tert*-butyl-1,4-benzoquinone with 100% selectivity. $RuCl_3 \cdot 3H_2O$ also catalysed the oxidation of 1,4-di-*tert*-butyl-2,5-dimethoxybenzene to 2,5-di-*tert*-butyl-1,4-benzoquinone by H_2O_2 in a semblance to the Fenton reaction [25].

$RuCl_3$ reacted with imidazole (ImH) and histamine (HisH) in HCl to give $(ImH)_3[RuCl_6]$, $(HisH_2)_2[RuCl_6]Cl \cdot H_2O$ and $(ImH_2)_2[Ru_2OCl_{10}]$. All of them were characterized by IR spectroscopy with the last complex being characterized by X-ray structural analysis [26]. Substitution of the chloro ligands in $[LRuCl_3]$ (L= 1,4,7-trimethyl-1,4,7-triazacyclononane) was readily achieved in aqueous solution by X ($X = NCO^-$, NCS^- and N_3^-) and led to the formation of $LRuX_3$. Electrochemical properties of the complexes and a single crystal X-ray analysis of $LRuCl_3$ were reported [27].

The solid state structure of *trans*-$[Ru(py)_4Cl_2]$, in which the Cl-Ru-Cl moiety is linear, has been reported [28]. The optically active bis-chelated complex $[Ru(bpy)_2Cl_2]$ has been prepared by the photosubstitution of $[Ru(bpy)_3]Cl_2$ in dichloromethane. The synthetic value of the optically active $[Ru(bpy)_2Cl_2]$ as a chiral intermediate has also been exemplified by preparing a new chiral amphiphilic ruthenium(II) complex [29]. In addition, photoaquation of *trans*-$[Ru(bpy)_2Cl_2]^+$ has been undertaken and the results were compared to that of *trans*-$[Ru(en)_2Cl_2]^+$. The former was found to be less reactive towards aquation in the ground state than the latter complex, but the reverse was observed in their excited states [30].

Mean vibrational amplitudes of $[RuCl_4(SO_2)(PPh_3)_2]$ have been estimated using the method of Cyvin. Variations of the parameter with temperature have also been determined and used for characterization of the bonding within the molecule [31]. The catalytic conversion of methanol to acetic acid (or methyl acetate due to esterification) with $[RuCl_2\{P(OMe_3)\}_4]$, $[RuCl(SnCl_3)\{P(OMe_3)\}_4]$ and $[Ru(SnCl_3)_2\{P(OMe_3)\}_3]$ has been investigated. Only the last complex showed a satisfactory performance and was also active in converting paraformaldehyde or methylformate to acetic acid. Possible mechanisms for the conversion were proposed on a kinetic basis [32]. Chiral $[RuCl_4(diop)_3]$ catalysed the asymmetric isomerization of 5-methylene-1,3-dioxanes to 5-methyl-HH-1,3-dioxins under a dihydrogen atmosphere. Enantiomeric excess of up to 37.6% has been obtained [33].

4. Complexes with phosphorus donor ligands

The complex $[RuCl_2(PPh_3)_3]$ catalysed the polymerization of methyl methacrylate (MMA) in the presence of CCl_4 and methylaluminium bis(2,6-di-*tert*-butylphenoxide). The polymerization was found to proceed via the repeating radical addition of MMA to a CCl_4-derived growing end bearing a carbon-chlorine bond [34]. The same complex was also an active catalyst for the oxidative cyclocarbonylation of several allylic alcohols to the corresponding 2(5H)-furanones (7) in moderate to high yield under a CO atmosphere [35].

R^1, R^2 = aryl or alkyl group

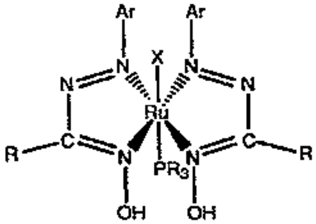
(7)

The perfluoroalkylation of aromatic and heteroaromatic compounds by perfluoroalkanesulfonyl chlorides has also been studied in the presence of $[RuCl_2(PPh_3)_3]$. Reactions of the latter complex with benzene or thiophene also proceeded smoothly to give the corresponding perfluoroalkylated compounds in good yields [36]. Moreover, hydrogenolysis of carbon tetrachloride to chloroform, and also of trichlorofluoromethane to hydrodichlorofluoromethane, was also found to be catalysed by $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(dppe)_2]$ with the former reaction proceeding to a more complete extent [37].

Chemical or electrochemical reduction of *trans*-$[RuX_2(HA)(A)]$ (X = Cl, Br; HA = RC(=NOH)N=NAr) afforded stereoretentive *trans*-$[Ru^{II}X_2(HA)(A)]^-$ which underwent mono- or disubstitution with tertiary phosphines PR_3 to give $[RuX(PR_3)(HA)(A)]$ (**8**) and $[Ru(PR_3)_2(HA)(A)]^+$ respectively. All complexes were characterized spectroscopically and electrochemically [38]. In addition, the reactions of $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) with a number of α,β-unsaturated-β-ketoamines (LL′) produced the corresponding Ru(III) complexes of general formula $[RuX_2(EPh_3)_2(LL')]$. EPR, IR spectroscopic and microanalysis data were also presented [39].

The complexes $[Ru(PPh_3)_5(ClO_4)](ClO_4)_x$ ($x = 1$ or 2), which were the first examples of Ru(II) and Ru(III) complexes comprising five PPh_3 groups coordinated to the metal, were reported along with the complexes $[Ru(PPh_3)_4(CS)_2](ClO_4)_x$ ($x = 2$ or 3) and $[Ru(PPh_3)(CS)_2(py)_2](ClO_4)_2$. All complexes were characterized by elemental analysis and physical measurements [40].

An efficient production of formic acid in a supercritical mixture of carbon dioxide and hydrogen containing a catalytic ruthenium(II) phosphine complex was achieved

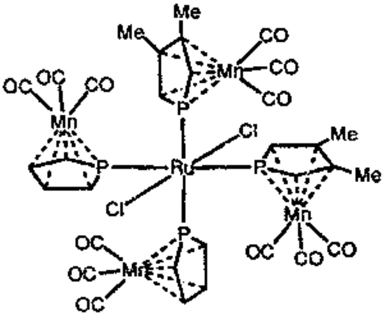


(8)

and this suggested that the supercritical fluids represented a promising medium for homogeneous catalysis [41].

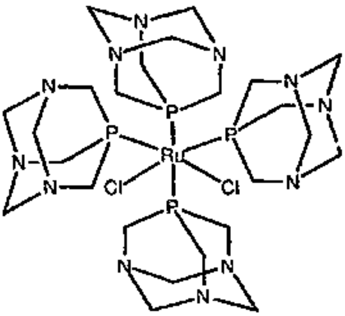
A series of ruthenium(II) chiral Schiff base complexes with nitrogen donors $[RuL(PPh_3)Y]$ and $[RuL(PPh_3)(H_2O)Y]^-$ (L = chiral Schiff base derived from L-aniline, L-valine, L-cysteine, L-arginine or L-aspartic acid with salicylaldehyde; Y = azide, bpy or phen) have been prepared and characterized. Conformational analysis with regard to the relation of the asymmetric carbon atom to the nitrogen atom donors around the metal centre was discussed [42].

Treatment of $RuCl_3 \cdot 3H_2O$ with 5-7 molar equivalents of PR_2H (R = Ph or C_6H_{11}) or $PPhH_2$ afforded *trans*-$[RuCl_2(PR_2H)_4]$ and *trans*-$[RuCl_2(PPhH_2)_4]$ in high yield. Cyclic voltammetric studies of the complexes as well as the crystal structure analysis of *trans*-$[RuCl_2(PPhH_2)_4]$ have been undertaken. The osmium analogues have also been reported [43]. In refluxing ethanol, $RuCl_3 \cdot 3H_2O$ reacted with 3,4-dimethylphosphacymantrenes (L) to give *trans*-$[RuCl_2(L)_4]$ (**9**). On the contrary, the *cis* product was afforded via the reaction of L with $[RuCl_2(dmso)_4]$ at 40°C in thf which under CO atmosphere generated *cis,cis,trans*-$[RuCl_2(CO)_2(L)_2]$. Both (**9**) and the *cis*-isomers have been structurally and spectroscopically characterized [44].



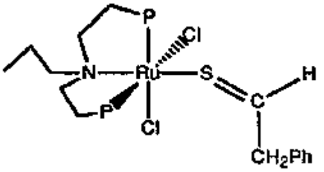
(9)

The water soluble complex $[RuCl_2(PTA)_4]$ (**10**) (PTA = 1,3,5-triaza-7-phosphaadamantane) has been synthesized by the reduction of $RuCl_3$ in the presence of PTA in ethanol. Complex (**10**) was also an effective catalyst for the regioselective conversion of aromatic/aliphatic unsaturated aldehydes to the corresponding unsaturated alcohol in a biphasic aqueous/organic medium. Detailed kinetic studies as well as some mechanistic interpretations were outlined [45].



(10)

Heating a mixture of *mer-trans*-[(PNP)$RuCl_2(PPh_3)$] [PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$] and excess phenylacetylene in refluxing thf resulted in the vinylidene *fac,cis*-[(PNP)$RuCl_2\{C{=}C(H)Ph\}$] which quantitatively converted to *fac,cis*-[(PNP)$RuCl_2\{\eta^1\text{-}S{=}CH(CH_2Ph)\}$] **(11)** under an H_2S atmosphere. Reaction of **(11)** towards 1,3-cyclopentadiene produced *fac,cis*-[(PNP)$RuCl_2\{\eta^1$-*endo*-$SC_6H_7(CH_2Ph)\}$] **(12)** which, in refluxing $CHCl_3$, generated [$Ru_2(\mu\text{-}Cl)_3(PNP)_2$]Cl via the extrusion of the phenylethanethial/cyclopentadiene adduct. Spectroscopic data have been obtained for all complexes isolated [46].



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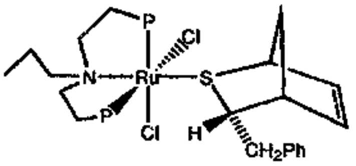
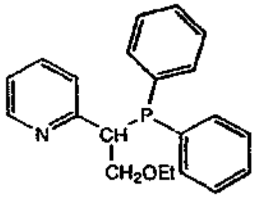


(12)

Synthesis and evaluation of the bonding properties of the tridentate ligand, [1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (pepye)] **(13)** towards [$RuCl_2(PPh_3)_3$] was accomplished, leading to two diastereoisomers of *cis*-[$RuCl_2$(pepye)$_2$] which in polar solvents converted to [RuCl(pepye)$_2$]$^+$ and subsequently to [RuCl(CO)(pepye)$_2$]BPh_4 under a CO atmosphere [47].

The adduct [RuCl(aa)(triphos)] **(14)** [triphos = bis(2-diphenylphosphinoethyl)phenylphosphine; aaH = L-alaH, L-valH] was prepared by the reaction of [$Ru_2(\mu\text{-}Cl)_3$(triphos)$_2$]Cl with the appropriate amino acid in MeOH; the geometry of the binding mode of the amino acid in the complex has been established by single crystal X-ray analysis [48]. Electrochemical reduction of the 16 electron derivatives [(PP_3)RuCl]BPh_4 [$PP_3 = P(CH_2CH_2PPh_2)_3$] generated the square-pyramidal

[(PP$_3$)RuCl]. Related ESR spectra and structural analysis of the complexes were interpreted [49].



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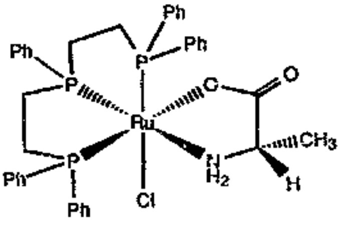


(14)

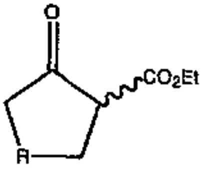
The preparation and characterization by UV-VIS and metal edge EXAFS of [(PolP-P)Ru(PPh$_3$)Cl] (PolP-P = polymer-supported diphosphine) have been carried out along with a number of related Pt, Ni and Rh complexes [50].

Asymmetric hydrogenation of 2-(ethoxycarbonyl)cyclanones (**15**) and tetralones have been examined using a series of chiral ruthenium catalysts: (*S*,*S*)-chiraphosRuBr$_2$, (*R*)-binapRuBr$_2$, (*S*)-binapRuBr$_2$ and (*R*,*R*)-diopRuBr$_2$ [51]. The complex Ru$_2$Cl$_4$[(*S*)-(-)-*p*-tolbinap]$_2$(NEt$_3$) (**16**) [*p*-tolbinap = 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl))] catalysed the enantioselective hydrosilylation of the carbon-nitrogen double bonds of nitrones with Ph$_2$SiH$_2$ to yield the corresponding optically active *N*,*N*-disubstituted hydroxylamines and up to 91% e.e. has been achieved [52]. In the presence of RuX$_2$ [(*R*)- or (*S*)-binap] (X = anionic ligand), a wide range of (*Z*)-2-acyl-1-benzylidene-1,2,3,4-tetrahydroisoquinolines (**17**) were readily hydrogenated to give the corresponding saturated products in approximately quantitatively yields. A mnemonic device for predicting the reactivity and enantiofacial selection of the ruthenium complexes upon hydrogenation was also described [53]. In addition, RuX$_2$ [(*R*) or (*S*)-binap] were active catalysts for the stereoselective asymmetric hydrogenation of α- and β-functionalized ketones [54].

The complexes [RuI(H$_8$-binap)(*p*-cymene)] (**18**) (*p*-cymene = *p*-isopropyltoluene) and [Ru(OAc)$_2$(H$_8$-binap)] (**19**) [H$_8$-binap = 2,2′-bis(diphenylphosphino)-5,5′-6,6′-7,7′-8,8′-octahydro-1,1′-binaphthyl] have been employed as efficient catalyst precursors in the stereoselective asymmetric hydrogenation of methyl 2-(benzamidomethyl)-3-oxobutanoate in up to 92% d.e. and 99% e.e. and also of geraniol in 98% optical purity [55]. Furthermore, complexes (**18**) and (**19**) have been shown to catalyse the asymmetric hydrogenation of a series of α,β-unsaturated carboxylic acids to obtain the corresponding saturated carboxylic acid in excellent enantioselectivities (86-97%). This reaction has also been applied to the syntheses of (*S*)-ibuprofen (**20**) in 97% e.e. [56]. A supported aqueous phase (SAP) asymmetric hydrogenation catalyst, SAP-Ru-binap-4SO$_3$Na, has been prepared which catalysed the asymmetric hydrogenation of 2-(6′-methoxy-2′-naphthyl)acrylic acid to naproxen in a two-phase system. The activity and enantioselectivity of the SAP catalyst were found to be dependent on the water content of the biphasic medium and the results obtained for Ru-binap-4-SO_3Na under similar conditions were compared [57].

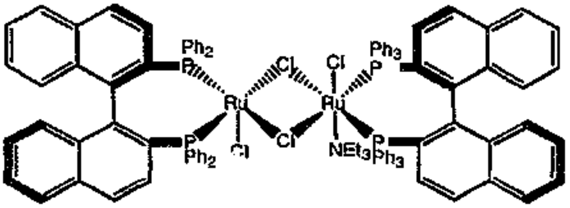
5. Complexes with sulfur donor ligands

The interactions between $RuCl_3 \cdot 3H_2O$ and polysulfone (PS) in thf afforded a dispersion medium whose behaviour has been examined by IR spectroscopy and thermal analyses. Related chemical reactivities of the Ru-containing PS films with CO, H_2, O_2, NO, D_2, N_2, C_2H_4 and particularly on the hydrogenation of ethylene, a water gas shift reaction as well as the reduction of NO, were investigated. Various ruthenium carbonyl, nitrosyl and hydride species formed in PS were characterized by IR spectroscopy and isotopic methods [58].



R = CH_2 or $(CH_2)_2$

(15)



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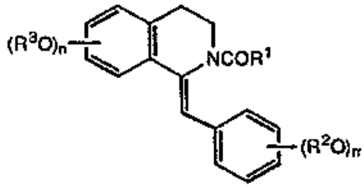
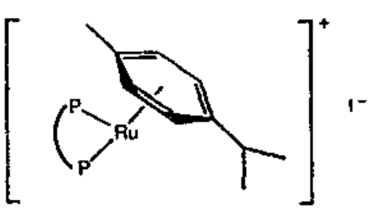


R^1, R^2, R^3 = alkyl or aryl group

(17)

The compounds $[RuHCl(CO)(py)(PPh_3)]$ and $[RuCl_2(CS)(py)(PPh_3)_2]$ reacted with β-diketones (βdk) and α,β-unsaturated-β-ketoamines (LL′) to produce a number of hexacoordinated complexes $[RuCl(CO)(py)(PPh_3)(\beta dk)]$, $[RuCl(CS)(py)(PPh_3)(\beta dk)]$, $[RuCl(CO)(py)(PPh_3)(LL')]$ and



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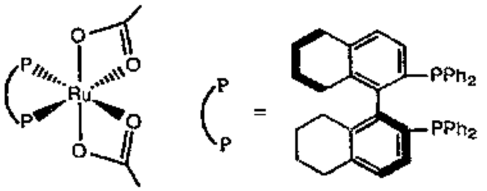

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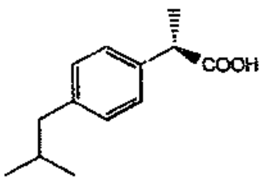

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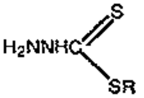
[RuCl(CS)(py)(PPh$_3$)(LL')]. All new compounds were characterized by chemical analysis, IR, electronic, ^{1}H and ^{31}P NMR spectroscopies [59]. The complexes [RuX$_2$(LL)(EPh$_3$)$_2$] [X = Cl or Br; E = P or As and LL = *S*-benzyldithiocarbazate (**21a**) or *S*-methyldithiocarbazate (**21b**)] were synthesized in which the Schiff bases were deprotonated and behaved as monoanionic didentate *NS* (*NS*$^-$) chelating ligands [60].

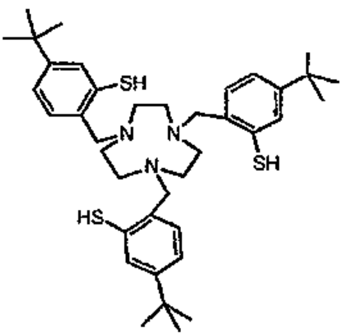


R = Me (**21a**)
= benzyl (**21b**)

Hexadentate 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane (H$_3$L) (**22**) interacted with [Ru^{II}(dmso)$_4$Cl$_2$] and K$_2$[Os^{IV}Cl$_6$] to give the complexes [LNaM^{IV}NaL] (M = Ru, Os). X-ray structural analysis revealed an octahedral M^{IV}S$_6$ central core and two trigonal-prismatic terminal LNa units with an N$_3$S$_3$ donor set; the electronic structure of the M^{IV}S$_6$ core has established a t$_{2g}^4$ (*S* = 1) electronic configuration by temperature dependent magnetic susceptibility measurements [61].

A number of mono- and dinuclear sandwiched complexes [Ru{HB(pz)$_3$}([9]aneS$_3$)][CF$_3$SO$_3$] (**23**) (pz = pyrazol-1-yl), [Ru{HC(pz)$_3$}([9]aneS$_3$)] [CF$_3$SO$_3$]$_2$, [{Ru(μ-S$_2$((NMe$_2$)([9]aneS$_3$)}$_2$](CF$_3$SO$_3$)$_2$ (**24**), [Ru(S$_2$CNMe$_2$)(PPh$_3$)([9]aneS$_3$)]-[CF$_3$SO$_3$]$_2$ and [Ru(C$_7$H$_4$NS$_2$)(PPh$_3$)([9]aneS$_3$)][CF$_3$SO$_3$] ([9]aneS$_3$ = 1,4,7-trithiacyclononane; C$_7$H$_4$NS$_2$ = 2-sulfanyl-benzothiazolate) were prepared by the reactions of [Ru(MeCN)$_3$([9]aneS$_3$)][CF$_3$SO$_3$]$_2$) and [Ru(MeCN)$_2$(PPh$_3$)-([9]aneS$_3$)][CF$_3$SO$_3$]$_2$ with Ag(CF$_3$SO$_3$) in MeCN [62].

The novel complex [{Ru(MeCN)(TMP)$_2$}$_2$(μ-S$_2$)(μ-NH$_2$NH$_2$)$_2$](CF$_3$SO$_3$)$_3$ (**25**)



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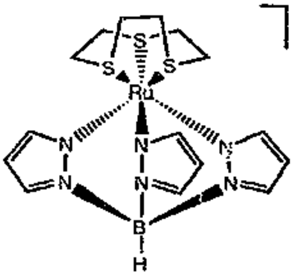

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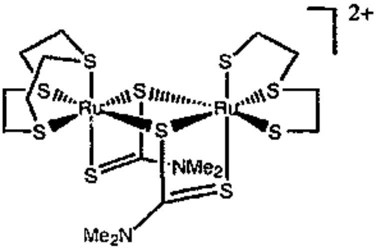

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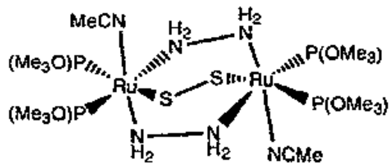
[TMP = P(OMe)$_3$] bearing two hydrazine bridges was synthesized and structurally compared to that of [{RuCl(TMP)$_2$}$_2$(μ-Cl)(μ-N$_2$H$_4$)(μ-S$_2$)] which was previously found to comprise a single hydrazine bridge [63].

Studies on the electrochemical behaviour of (1,5-dithiacyclositane-1-oxide)bis(pentaammineruthenium) (**26**) have been revisited, and the kinetic and equilibrium parameters defining the "double block" diagram were established. The associated metastable fully oxidized form (Ru^{3+}-SO/Ru^{3+}-S), the metastable fully reduced form (Ru^{2+}-OS/Ru^{2+}-S) as well as the behaviour in their mixed-valence state have also been studied quantitatively [64].

In addition, the synthesis and the electrochemical behaviour of the two linkage isomers of [RuCl$_2$(*S*-dmso)$_2$(tbpy)$_2$] (tbpy = 4-*tert*-butylpyridine) (all *cis* and *cis*,-*cis*,*trans*) were reported. The isomerization was discussed based on the competitive effects between the *S*-bound dmso and the tbpy ligand [65]. Moreover, the redox behaviour in [Ru(NH$_3$)$_5$(sulfoxide)]$^{2+/3+}$ and *cis*-[Ru(NH$_3$)$_4$(dmso)$_2$]$^{2+/3+}$ in acetone solution, where linkage isomerization Ru^{III}S→O and Ru^{II}O→S were brought about by electrochemical oxidation or reduction, were investigated. Related thermodynamic and kinetic studies have also been carried out [66].



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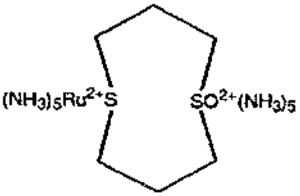

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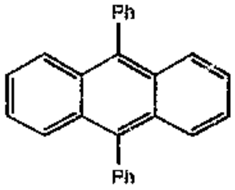
6. Complexes with nitrogen donor ligands

6.1. Complexes with 2,2'-bipyridine ligands

Reductive electrocrystallization of a solution of $[M(bpy)_3](PF_6)_2$ (M = Fe, Ru or Os) afforded their respective $[M(bpy)_3]$ neutral complexes which gave no ESR signals [67]. The crystal structure of $[Ru(bpy)_3](ClO_4)_2$ has also been determined by single crystal X-ray analysis and was structurally compared with that in $[Ru(bpy)_3](PF_6)_2$ [68]. The orientational dependences of the Zeeman effect in the lowest excited states of $[Ru(bpy)_3](PF_6)_2$ were examined by a model in which the lowest-energy charge-transfer excitation involved a metal-ligand subunit [69]. A good quality Raman spectrum of $[Ru(bpy)_3]^{2+}$ has been recorded by using 211 nm radiation generated by the sum frequency mixing of the 2^{nd} and 3^{rd} harmonics of a Nd:YLF laser in a relatively short collection time [70]. Mass spectrometric analysis of $[Ru(bpy)_3(X)_2]$ ($X = ClO_4^-$, PF_6^- and Cl^-) and its Fe analogue has also been conducted by means of Cs^+ fast ion bombardment and mass selected collision-induced dissociation (CID); relative intensities of the major desorbed ions were monitored as a function of the Cs^+ kinetic energy in the potential range of 10-30 eV [71]. In a solution containing tripropylamine, a highly oriented pyrolytic graphite (HOPG) electrode strongly adsorbed with $[Ru(bpy)_3]^{2+}$ was found to exhibit electrogenerated chemiluminescence (ECL) upon sweeping or stepping up the working potential to positive magnitude. Likewise, adsorption and ECL were found with platinum and gold electrodes [72]. The separation of a number of antihistamine drugs has been achieved by HPLC using post-column $[Ru(bpy)_3]^{2+}$ chemiluminescence (CL) detection [73]. Furthermore, ECL has been employed to evaluate the ion-annihilation reaction kinetics of the radical ions such as 9,10-diphenylanthracene (DPA) (**27**), 9,10-dimethylanthracene and $[Ru(bpy)_3]^{2+}$ in MeCN and also DPA in propylene carbonate. Diffusion-controlled ion-annihilation rates were also measured [74]. The ECL properties of $[Ru(bpy)_3]^{2+}$ have also been analysed from which information concerning the design of surface-modified ultramicroelectrodes and surface interactions influencing organic electron transfer reactions at the carbon surfaces were obtained [75]. Chemiluminescence was also found to be emitted from an ITO electrode (ITO = indium tin oxide) onto which $[Ru(bpy)_2(\text{4-methyl-4'-(1-mercaptoheptyl)-2,2'-bipyridine})(PF_6)_2]$ (**28**) was adsorbed in the presence of oxalate. The analytical properties of (**28**) with respect to its ability to form self-adsorbed monolayers on ITO and its chemical stability were discussed [76].



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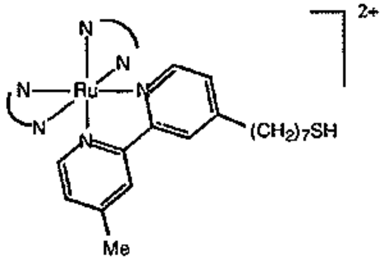

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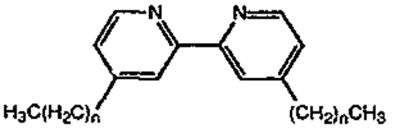
Some Ru(II)-diimine complexes, including $[Ru(bpy)_3]^{2+}$, which has been used as long-wave excitable luminescent oxygen probes, have also been studied and discussed with regard to their quenching properties, photostability and lifetimes. Incorporation of the probes into organic polymers lead to oxygen-sensitive materials for use in orbital oxygen sensing. The membranes were characterized with respect to their oxygen sensitivity, luminescence intensity, response times and stability [77]. A modified CO_2 sensor comprising the $[Ru(bpy)_3]^{2+}$/Nafion—modified Pt gauze electrode suitable for selective determination of oxalate has also been developed [78]. Oxidation of *p*-phenylenediamines by $S_2O_8{}^{2-}$ was readily achieved in the presence of $[Ru(bpy)_3]^{2+}$ which acted as photosensitizer and photocatalyst; a possible mechanism was proposed [79]. The stereoselective, photosensitized decompositions of $[Co(acac)_3]$ and $[Co(ox)_3]^{3-}$ by $[Ru(bpy)_3]^{2+}$ were disclosed. The preference of the homochiral (Δ-Δ or Λ-Λ) complex for $[Co(ox)_3]^{3-}$ was contrasted to the case of the heterochiral (Δ-Λ) complex which showed preference for $[Co(acac)_3]$ and was supported by circular dichroism measurements and by the decomposition rate of each optical isomer [80]. A new kind of photoelectrochemical cell has been constructed using Pt-nf-$[Ru(bpy)_3]^{2+}$ and Pt-bt-$[Ru(bpy)_3]^{2+}$ electrodes with cobalt(III) complexes and Fe^{3+} ion as electron relays (nf = Nafion and bt = bentonite clay). The origin of the photocurrent and the related quenching rate constant of the photoreaction were determined [81].

A density functional study on the MLCT states of $[Ru(bpy)_3]^{2+}$ in D_3 symmetry was presented [82]. Its resonance Raman and time-resolved resonance Raman spectra have been compared to those obtained for $[Ru(5\text{-mmb})_3]^{2+}$ (5-mmb = 5-methyl-2,2′-bipyridine) and its methyl-deuterated analogue $[Ru(5\text{-}d_3\text{-mmb})_3]^{2+}$. Evidence for the polarization of the ^{3}MLCT state electron density in the asymmetric ligand was also given [83]. Determination of excited-state redox potentials of $[Ru(bpy)_3]^{2+}$ by phase-modulated voltammetry was carried out and was consistent with the calculated value obtained by the Rehm-Weller equation [84].

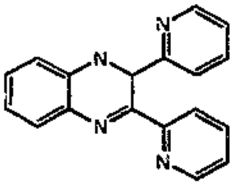
Reductive quenching of four mixed ligand tris(bipyridyl) ruthenium(II) complexes by anionic ascorbate and *N*-phenylglycine electron donors was performed in aqueous solution; the results were compared to that measured in a suspension of inert colloidal alumina-coated silica particles and also that of the parent $[Ru(bpy)_3]^{2+}$ [85]. The reductive quenching of the luminescent excited states of complexes of general formula $[Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z{}^{2+}]$ (bpm = 2,2′-bipyrimidine; bpz = 2,2′-bipyrazine, m and $z = 0,1,2,3$ and $m + z \leq 3$) by a number of electron donors and oxygen has likewise been examined by continuous and pulsed laser flash photolysis techniques [86,87]. The effect of a polymer based film plasticized with a trialkylphosphate ester on the quenching of the luminescence of $[Ru(bpy)_3]^{2+}$ by oxygen with regard to the film medium, the film thickness and the concentration of the metal complex within the film medium was reported [88].

Electron transfer quenching of the excited states of Ru(II) in the double complex salts $[Ru(bpy)_3]_2[M(CN)_6]Cl \cdot 8H_2O$ (M = Co and Fe) has also been reported [89]. Photoinduced energy transfer and the luminescence quenching behaviour from two surfactant Ru(II) diimine complexes of the type $[(bpy)_2Ru(L)]^{2+}$ [L = 4-methyl-4′-heptadecyl-2,2′-bipyridine (**29**) and 4,4′-diheptadecyl-2,2′-bipyridine (**30**)] towards anthracene-9-carboxylate (ANC) have also been described [90].



n = 0 ; n′ = 16 (**29**)
n = n′ = 16 (**30**)

Absorption and emission spectra of $[Ru(bpy)_3]^{2+}$ exchanged onto porous Vycor glass (PVG) were found to closely resemble the corresponding aqueous solution spectra. However, complementary measurements of emission lifetime and quantum yield (ϕ_{em}) revealed the temperature dependence of the "ϕ_{em}/T" parameter and was ascribed to intersystem crossing efficiency [91]. The absorption spectra of the charge transfer excited states and the related one-electron reduced states of $[Ru(dhp)_3]^{+*}$ [dhp = 2,3-bis(2-pyridyl-5,6-di-hydropyrazine], $Ru(dpp)_3^{+*}$ [dpp = 2,3-bis(2-pyridyl)pyrazine] and $[Ru(dbq)_3]^{+*}$ [dbq = 2,3-bis(2-pyridyl)quinoxaline (**31**)] were obtained using laser flash photolysis and pulse radiolysis techniques; the spectra of the first complex were assigned with reference to that of $[Ru(bpy)_3]^{+*}$ [92].



(**31**)

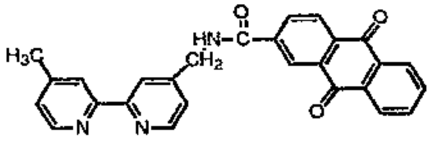
Upon visible light photolysis and in the presence of $[Ru(bpy)_3]^{2+}$, Se-phenyl-n-tolueneselenosulfonate (PhSeTos) reacted with olefins $CH_2 = CHOR$ (R = e.g. Et) to give $TosCH_2CH(OR)SePh$ in high yield [93]. Photo-oxidation of $[Ru(bpy)_2Cl_2]$ and the associated photo-reduction of $[Ru(bpy)_2Cl_2]^+$ in a number of aerated solvent systems have been studied under UV irradiation [94]. The binding characteristics of $[Ru(bpy)_3]^{2+}$ in regenerated bacteriorhodopsin (6R) were determined from Scotchard plots by conducting fluorescence measurements at varying pH. The difference between the binding properties of organic and metal cations was also explored [95]. Electronic dichroism studies on the adsorption of the complex $[Ru(dmbpy)_3]^{2+}$ (dmbpy = 5,5′-dimethyl-2,2′-bipyridyl) by a colloidally dispersed montmorillonite or sponite have been reported and the results for those of $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ were compared [96]. A number of Ru(II)-diimine photosensitizers containing bpy, 2,2′-bipyrazine and 2,2′-bipyrimidine have been compared with regard to their spectral, electrochemical, acid-base and kinetic properties in both of their excited and one-electron reduced states [97]. The chiral complex Δ-$[Ru(menbpy)_3]^{2+}$ (menbpy = 4,4′-dimethoxycarbonyl-2,2′-bipyridine) photocatalysed the oxidation of 1,1′-bi-2-naphthol by $[Co(acac)_3]$ enantioselectivity ($\leq 15.2\%$ e.e.) [98].

Heating a mixture of $[RuCl_2(p\text{-cymene})]_2$ and 6,6′-bis(oxazolinyl)-2,2′-bipyridine (L) (**34**) in MeOH produced $RuCl_2L$ which was active in catalysing the cyclopropanation of styrene and transformation of diazoacetates in dimerization [99]. A new class of asymmetric complexes including $[Ru(bpy)_2(dcbpy)]$ has been developed as luminescent probes to monitor and measure the rotational motions of proteins which were inaccessible by current luminescent methods [100].

The rates of intramolecular electron transfer between Ru(III) and Fe(II), and between Ru(I) and Fe(III) of three derivatives of cytochrome *c* labelled with $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)]^{2+}$ at lysines 86, 8 and 7 have been measured [101]. Preliminary analysis suggested that the observed rate constants were not consistent with the large free energy of reaction expected for Ru(I). In addition, the attachment of $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)]^{2+}$ to antimony-doped tin oxide (SnO_2:Sb), tin-doped indium oxide (In_2O_3:Sn), or glass surfaces was respectively described and was ascribed to the interaction between surface hydroxyls and carboxylic acid groups. Measurements with respect to the roughness, thickness, modes of binding, the corresponding binding constants of the metal oxide surfaces as well as the resulting photophysical properties were discussed [102].

The complex $[Ru(bpy)_2(bpy\text{-}AQ)]^{2+}$ [bpy-AQ = *N*-((4′-methyl-2,2′-bipyridyl)-4-methyl)-9,10-anthraquinone-2-carboxamide] (**32**) underwent intramolecular electron transfer quenching following MLCT excitation. In contrast, MLCT excitation of $[Ru(bpy\text{-}AQ)_2\text{-}(bpy\text{-}PTZ)]^{2+}$ [bpy-PTZ = {10-[(4′-methyl-2,2′-bipyridin-4-yl)-methyl]phenothiazine}] (**33**) led to formation of the redox-separated state $[Ru(bpy\text{-}AQ)(bpy\text{-}AQ^{\cdot-})(bpy\text{-}PTZ^{\cdot+})]^{2+}$. All results were obtained via transmission, emission and adsorption measurements [103]. The preparations and photophysical behaviours of $[Anq\text{-}Lys(Ru^{II}bpy_2m)^{2+}\text{-}NH\text{-}prPTZ](PF_6)_2$ [Anq = 9,10-anthraquinone-2-carbonyl; Lys = L-lysine, m = 4′-methyl-2,2′-bipyridine-4-carbonyl; prPTZ = 3-(10H-phenothiazine-10)propyl] were reported. All spectroscopic studies of electron transfer were measured by nanosecond transient absorption and time resolved resonance Raman techniques [104].

New supramolecular assemblies consisting of Ru(II) tris-{4,4′-bis[(metheneoxy)tris(etheneoxy)(4-methoxybenzene)]-2,2′-bipyridine} (**34**) and bipyridinium salts of *N*,*N*′-dimethyl-4,4′-bipyridinium, MV^{2+} (**35**) or cyclo-



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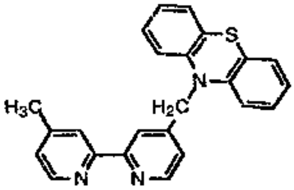

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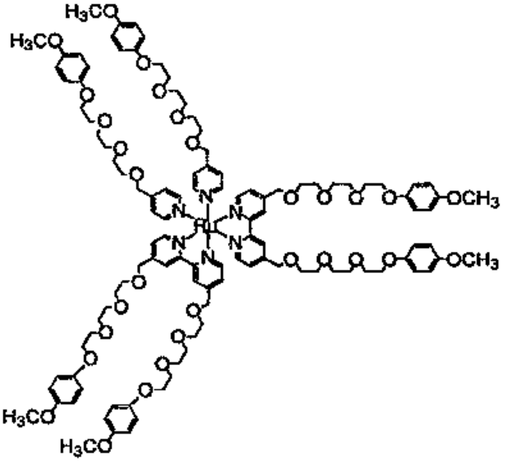
[bis(N,N'-p-xylylene-4,4'-bipyridinium)], BXV^{4+} (**36**) have been achieved. Formation of the supramolecular assemblies was supported by the intramolecular electron-transfer quenching of (**34**) and by the fact that the assemblies dissociated upon addition of β-cyclodextrin [105].

The syntheses of the 1,1'-biisoquinoline (BIQN) complexes, $[Ru(tpy)(BIQN)Cl](ClO_4)$ and $[Ru(tpy)(BIQN)(OH_2)](ClO_4)_2$, and the crystal structure of the latter have been reported. Related redox properties and its catalytic activity on the oxidation of alkene were also elucidated [106]. The complex $[Ru\text{-}\Delta/\Lambda\text{-}(\delta/\lambda\text{-}1,1'\text{-}BIQN)(bpy)_2](PF_6)_2$ existed in acetone as a ~3:1 mixture of two diastereomeric forms of which the major isomer has been characterized by single crystal X-ray analysis. Diastereomerically pure samples of the complex isomerized rapidly at room temperature to give a thermodynamic mixture of two diastereomers which was the result of an intramolecular process of C_2 symmetry. Nevertheless, this did not lead to the change of the *cis*/*trans* relationships between 1,1-BIQN and bpy ligands, as manifested by spin saturation transfer (SST), spin inversion transfer (SIT) and 2D-exchange spectroscopy (2D EXSY) NMR spectroscopic experiments [107].



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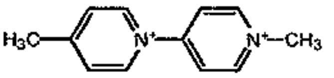

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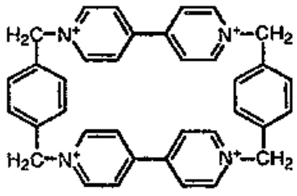

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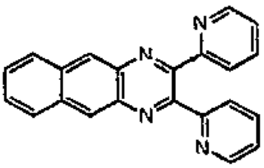
The syntheses and stereochemistries of $[Ru(dmbpy)(pmbpy)(CO)_2]^{2+}$ [dmbpy = 4,4′-dimethyl-2,2′-bipyridine; pmbpy = 4-(2,2-dimethylpropyl)-4′-methyl-2,2′-bipyridine] and $[Ru(pmbpy)_2(CO)_2]^{2+}$ were described. Both complexes decarbonylated to afford $[Ru(dmbpy)(pmbpy)_2]^{2+}$. All complexes were characterized by NMR spectroscopic techniques [108]. A reaction intermediate during the photosubstitution of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy = 3,3′-dimethyl-2,2′-bipyridine) bearing a monodentate dmbpy ligand has successfully been separated by HPLC and characterized by ^1H NMR spectroscopy [109].

The effect of decreasing π* energies in the series $[Ru(Me_2bpy)(Me_4bpy)(BL)]$ [Me_4bpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine; BL = 2,3-bis(2-pyridyl)pyrazine (dpp), 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (Me_2dpq), 2,3-bis(2-pyridyl)quinoxaline (dpq), or 2,3-bis(2-pyridyl)-1,4-diaza-anthracene (dpa)] (**37**) was disclosed and established the order of the acceptor ability to be dpa > dpq > Me_2dpq > dpp by electrochemical method [110]. Moreover, the syntheses and excited state properties of $[\textit{trans}\text{-}Ru(o\text{-}bpy)(CH_3CN)(Cl)]^+$ (**38**) and $\textit{trans}\text{-}[Ru(o\text{-}bpy)(CH_3CN)_2]^{2+}$ [*o*-bpy = 1,2-bis(2,2′-bipyridyl-6-yl)ethane] were established; both were synthons for *trans*-MLCT excited states and ideal precursors for the synthesis of *trans* oligomers [111].



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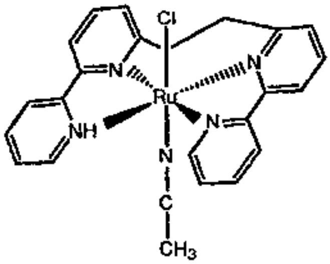


(38)

Exotic calix[4]arene mono- and ditopic anion receptors containing one and two Ru(II) bipyridyl moieties such as (**39**) have been prepared and shown by ^1H NMR spectroscopy and CV to bind to electrochemically recognized halide, dihydrogen phosphate and hydrogen sulfate anions [112]. A novel approach for creating film-based electrocatalytic arrays with spatial control of the film pattern has been achieved in film of poly-*cis*-$[Ru(vbpy)_2(py)_2]^{2+}$ [vbpy = 4-vinyl-4′-methyl-2,2′-bipyridine (**40**)], which upon photolysis converted to poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ as confirmed by cyclic voltammetry [113]. Complete assignments of the ^1H and ^{13}C NMR spectra of a family of complexes $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (Hdpa = di-2-pyridylamine; $n = 0$-2) have been carried out on the basis of proton-proton coupling constants, ^1H-^1H COSY spectra, ^{13}C-^1H COSY spectra and the aromatic ring-current effects of the ligand and were compared with the calculated results obtained from a current-loop model [114].

The reaction of the newly synthesized ligand 1,4,7-tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane (L) (**41**) with ruthenium(II) salts produced $[Ru(LH)][PF_6]_3$. The complex was characterized by X-ray analysis. In aqueous solution a single proton was trapped in the cavity between the macrocycle and the Ru^{II} centre which cannot be removed even at high pH [115]. The syntheses and characterization of $[Ru((Et_2N)_2bpy)_2Cl_2]Cl$ [$(Et_2N)_2$bpy = 4,4′-bis(*N*,*N*′-diethylamino)-2,2′-bipyridine], $[Ru((Et_2N)_2bpy)_2(bpy)](PF_6)_2$ and $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)](PF_6)_2$ [py-bzimH = 2-(2-pyridyl)benzimidazole] and their exceptionally low Ru(III/II) potentials have been outlined [116].

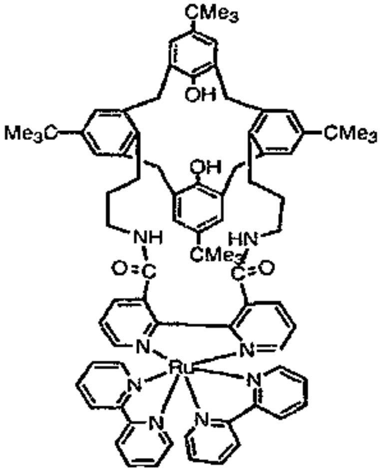
6.2. Complexes with phenanthroline ligands

The sterically hindered complex *cis*-$[Ru(dmp)_2(S)_2](PF_6)_2$ [S = H_2O or CH_3CN; dmp = 2,9-dimethyl-1,10-phenanthroline] catalysed the oxidation of alkenes with dioxygen and also of alkanes with hydrogen peroxide under mild conditions [117]. A number of $[RuL_2(pdphen)]^{2+}$ salts (pdphen = planar pyrido[3,2-f]-[1,7]phenanthroline; L = 2,2′-bipyridine, 2,9-dimethylphenanthroline and 5-nitrophenanthroline) have also been prepared and characterized by elemental analyses, spectroscopic techniques and cyclic voltammetry [118].

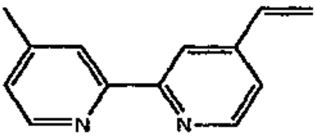
Stereochemical effects on formation of monolayers of racemic and enantiomeric $[Ru(dpp)_3]^{2+}$ (dpp = 4,7-diphenyl-1,10-phenanthroline) at an air-water interface were investigated and led to the conclusion that the racemic mixture forms a more compact monolayer than that due solely to the enantiomers [119]. The monomeric triacrylate complex RuAAP (Ru-phenanthroline chromophore) (**42**) has been utilized in microstructural photopolymer films, displaying interesting and electrochemically suitable phase gratings which can be electrochemically modulated. The preparation and factors affecting the quality of the photopolymer films and the underlying free radical chain mechanism were described [120].

Several new but different models of photosensitive chemically modified electrodes were proposed and all of them were examined as prospective objects for developing electro- and photo-sensors, as well as photogalvanic systems. A number of experiments focusing on the electropolymerization of $[Ru(5\text{-}Clphen)_3](ClO_4)_2$ and $[Fe(5\text{-}Clphen)_3](ClO_4)_2$ were carried out which shed light on the construction of photogalvanic cells [121].

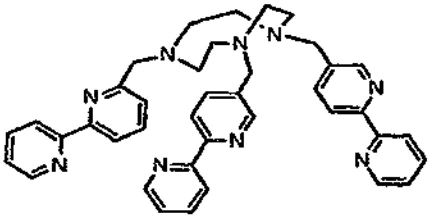
A novel crystal semiconductor $[Ru(binap\text{-}2)_3](PF_6)$ (binap-2 = 6,7-dihydrodipyrido[2,3-b:3′,2′-j][1,10-phenanthroline]) with well-defined organic cationic binding centres was reported along with a review focusing on the redox


CMe3
OH
Me3C
CMe3
OH
NH
HN
CMe3
O=C
C=O
N
N
Ru
N
N
N
N

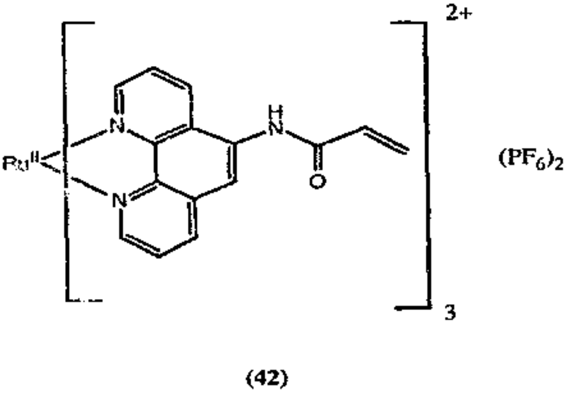
(39)


N
N

(40)


N
N
N
N
N
N
N
N
N

(41)


2+
Ru^II
N
N
H
N
O
3
(PF6)2

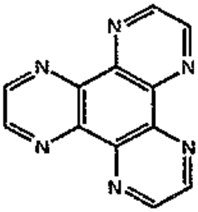
(42)

chemistry of fullerenes, tris-bpy cryptates and tris-bpy transition metal complexes [122].

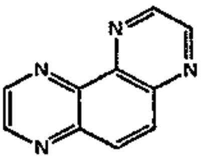
The effects of the interactions of a number of complexes, $[Ru(bpy/phen)_2(hat)]^{2+}$ (hat = 1,4,5,8,9,12-hexaazatriphenylene) (**43**), $[Ru(tap)_2(hat)]^{2+}$ (tap = 1,4,5,8-tetraazaphenanthrene) (**44**) and $[Ru(phen)_3]^{2+}$ with DNA and hence their photophysics have been investigated. The data presented provided evidence that DNA affected both k_{nr} and the luminescence decays from the ^{3}MLCT state to the ^{3}MC (metal centred) state. Detailed discussion of the luminescence decays and lifetimes of the complexes was presented [123].

6.3. Complexes with other N-heterocyclic ligands

The electronic structure of $[Ru(NH_3)_5(pz)]^{2+}$ (pz = pyrazine) or $[Ru(NH_3)_5(pz)]^{3+}$ was assessed by transition operator calculations; metal-ligand π conjugation and its implications in electronic delocalization were discussed. Identities and symmetry designations of the six $\bar{\omega}$ states of the free ligand's were also illustrated [124]. Studies with regard to the spectrophotometric, electrochemical and ^{1}H NMR spectroscopic properties of 18-crown-6 ether adducts with $[Ru(NH_3)_5(pz)](PF_6)_2$, $[Ru(NH_3)_5(dmapy)](PF_6)_2$ [dmapy = 4-(dimethylamino) pyridine] and $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ have been conducted. The last complex formed the adduct in stepwise manner with the ether having 1:2, 1:3 and 1:4 stoichiometries [125].



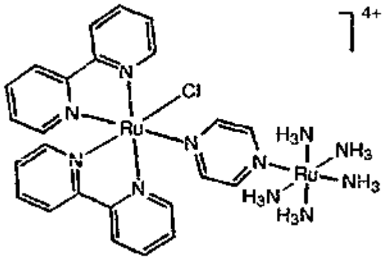
(**43**)



(**44**)

The intervalence charge transfer absorbance energy changes in $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ (**45**) have been employed as a measure of the solvent dependence of $Ru^{III}(NH_3)$ association with various macrocyclic ether species such as DCH-24-C-8 (**46**), DB30-C-10 (**47**), DB36-C-12 (**48**) and DB42-C-14 (**49**). The association constant was found to vary by as much as four orders of magnitude depending on the basicity of the solvents [126].

A discussion on the optical conductivity spectra of the $[Ru(pz\text{-}Ru)_3]^{m+}$ mixed-valence chains has been accomplished by a two-band Hubbard Hamiltonian. The spectra for different values of the relevant parameters were analysed in terms of various quantities obtained from the many-particle eigenvalues to give a realistic assignment of the observed peaks and their dependence on the values of the parameters [127].



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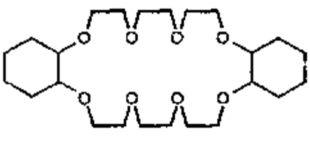

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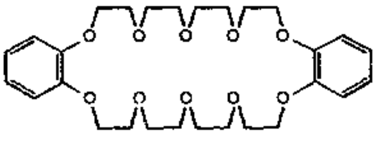

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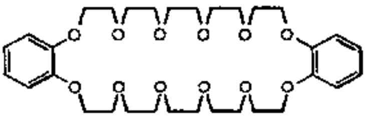

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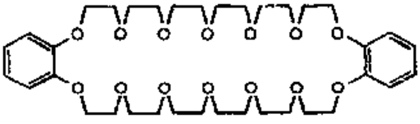
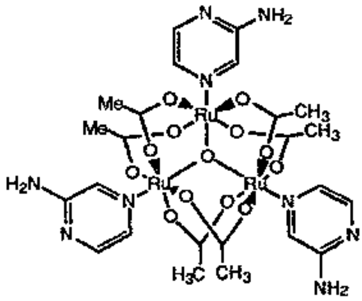


(49)

The triruthenium cluster $[Ru^{III}Ru^{III}Ru^{II}O(Ac)_6(ampz)_3]$ **(50)** (ampz = 2-aminopyrazine) has been investigated using spectroelectrochemical and cyclic voltammetry techniques. The binding of $[Ru^{II}edta]$ to the ampz ligands in complex **50** proceeded rapidly and led to multibridged complexes, exhibiting strong MLCT bands [128]. Similar studies on $[Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})PtMe_2]^{2+}$ **(51)**, $[Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})PtCl_2]^{2+}$ **(52)** and $[Ru(bpy)_2(\mu\text{-}2,3\text{-dpp})PdCl_2]^{2+}$ **(53)** [2,3-dpp = 2,3-bis(2-pyridyl)pyrazine **(54)**] have also been reported [129]. Moreover, the electrochemical, photophysical and photochemical properties of a hexanuclear ruthenium(II) bis(2,2′-bipyridyl) complex containing 1,3,5-tris(5-(pyrazin-2-yl)-1,2,4-triazol-3-yl)benzene (H_3tpzb) **(55)** were depicted. The complex $[\{Ru(bpy)_2\}_3(tpzb)]^{3+}$ and also the protonated species $[\{Ru(bpy)_2\}_3(H_3tpzb)]^{6+}$ were isolated upon photolysis [130]. The electrochemical and photochemical properties of a related system $[((NH_3)_4Ru)_n(dpop)]^{2n+}$ ($n = 1,2$) [dpop = dipyrido(2,3-a;-2′,3′-h)phenazine] **(56)** were also reported [131].

A series of mixed-tris complexes of general formula $[ML'L_2](ClO_4)_2 \cdot H_2O$ [M = Ru or Os; L′ = 2,2′-bipyrazine (bpz), 2,2′-bipyrimidine (bpm) and L = 2-(phenylazo)pyridine (papy) **(57)** or 2-(*m*-tolylazo)pyridine (tapy) **(58)**] has been prepared and characterized by spectroscopic and physicochemical methods [132]. Selective deuteration together with 1- and 2-dimensional ^1H NMR spectroscopies



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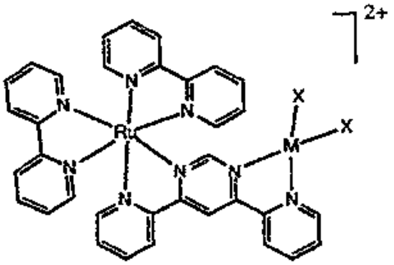
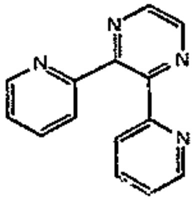


M = Pt ; X = Me (**51**)
M = Pt ; X = Cl (**52**)
M = Pd ; X = Cl (**53**)



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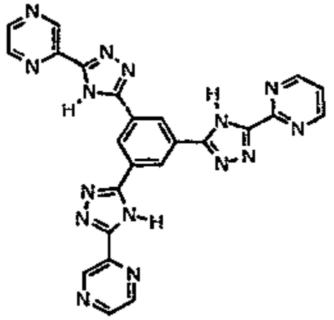


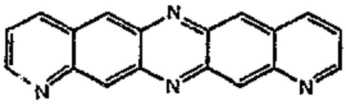
(55)

has been shown to be useful in demonstrating the major groove binding of Δ-$[Ru(phen)_2dppz]^{2+}$ (**59**) (dppz = dipyridophenazine) to the hexamer oligonucleotide $d(GTCGAC)_2$ and the notion that (**59**) is intercalated selectively into duplex DNA through the dppz ligand has gained support [133]. In contrast, the complexes $[Ru(bpy)_2dppz]^{2+}$ and $[Ru(bpz)_2dppz]^{2+}$ [bpz = 2,2′-bipyrazine(**60**)] have been selected as photosensitive DNA breakers, owing to the high affinity of the dppz ligand to the major groove of DNA and the results were compared with $[Ru(bpy)_3]^{2+}$ [134].

A single crystal X-ray structure of one of the diastereomers of the PF_6 salt of bis[bpy(6,11-dimethoxy-1,4-di(2′pyridyl)-5,12-dihydro-5,12-methanonaphtho[2,3-g]-phthalazine)ruthenium(II)] (**61**) has been established and revealed unambiguously the absolute configuration of the ligand moiety [135].

Aquation of the anti-cancer complex *trans*-$[H_2im][RuCl_4(Him)_2]$ (**62**) (Him = imidazole) has been studied in D_2O at different pH values by ^1H NMR spectroscopy, conductivity measurement as well as EPR spectroscopy after separating the products on a reversed-phase column of HPLC [136].

The nature of the head-to-head conformation of an untethered lopsided ligand,



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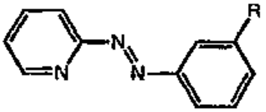
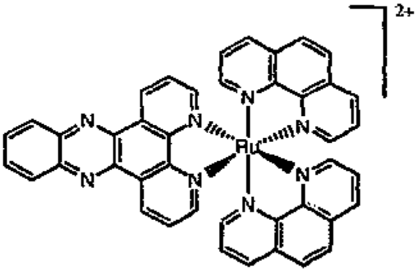


R = H **(57)**
R = Me **(58)**



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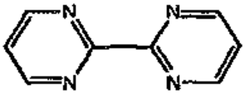

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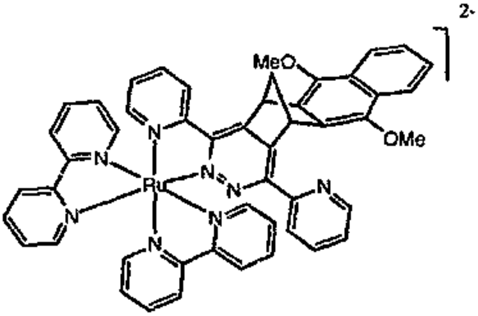

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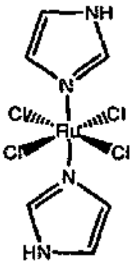
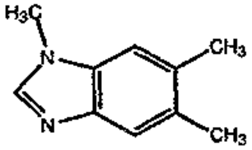


(62)

1,5,6-trimethylbenzimidazole (Me_3Bzm) (**63**), has been elucidated in *cis,cis,cis*-[$RuCl_2(Me_2SO)_2(Me_3Bzm)_2$] (**64**) which has also been characterized by X-ray diffraction studies. Detailed fluxional analysis of the two atropisomers of complex **64** by ^1H NMR ROESY and EXSY was presented [137].

The synthesis and characterization of [*cis*-Ru(bpy)$_2$(9mhyp-KN^7)L]$^{+/2+}$ and [*cis*-Ru(bpy)$_2$(9egua-KN^7)L]$^{+/2+}$ (9mhyp = 9-methylhypoxanthine (**65**); 9egua = 9-ethylguanine (**66**); L = Cl^- or H_2O) were reported. Inter-ligand interaction between the lone pairs on the keto group and the π systems of the pyridyl groups could be deduced from ^1H NMR spectroscopic data and solid state structural analysis [138].

Vibrational studies by IR and Raman spectroscopies and normal coordinate analysis of [Ru(tpy)$_2$]$^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) (**67**) were presented and, to do



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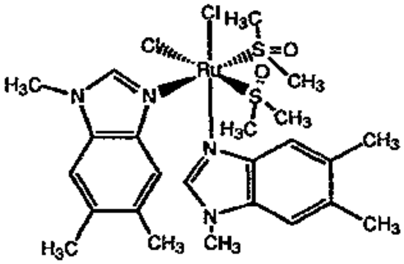

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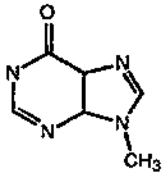

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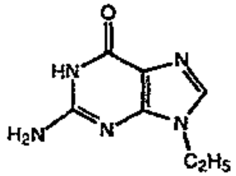

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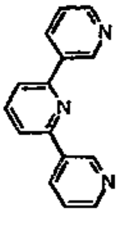
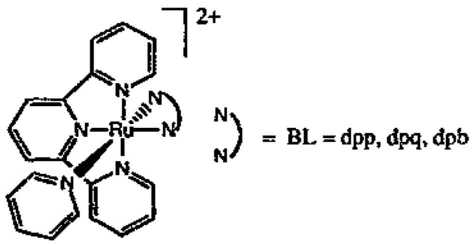


(67)

so, two specific deuterated analogues of the complex were synthesized [139]. Moreover, six ruthenium monometallic complexes of $[Ru(tpy)(BL)Cl]^+$ and $[Ru(tpy)(BL)(py)]^{2+}$ (**68**) (BL = bridging ligand like 2,3-bis(2-pyridyl)pyrazine (2,3dpp) (**69**), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb)] emitted light in fluid solution at room temperature. These complexes were of interest as starting materials for the preparation of multimetallic systems capable of intramolecular electron transfer [140]



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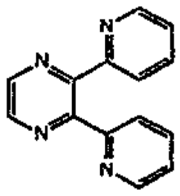
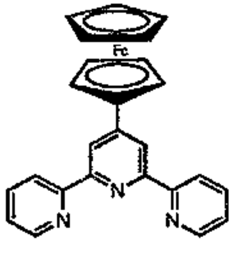


(69)

The new ligand, 4'-ferrocenyl-2,2':6',2''-terpyridine (**70**), was synthesized and structurally characterized. The homoleptic complexes $[ML_2][PF_6]_2$ (M = Co, Fe or Ru) as well as the related homoleptic complexes $[RuL(tpy)][PF_6]_2$ have been prepared [141]. The electrochemical behaviours of $[Ru(pytpy)Cl_3]$ [pytpy = 4'-

(4-pyridyl)-2,2′:6′,2″-terpyridine] (**71**) and its osmium analogue were studied and compared. Correlation between the redox potentials and the Hammett σ^+ parameter was justified [142]. The photophysics of $[Ru(tpy)(L)(H_2O)]^{2+}$ (L = bpy, phen and dppz = dipyridophenazine) both in solution and upon binding to DNA covalently via displacement of the aqua ligand have been compared [143].



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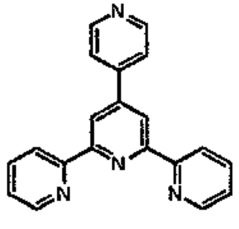

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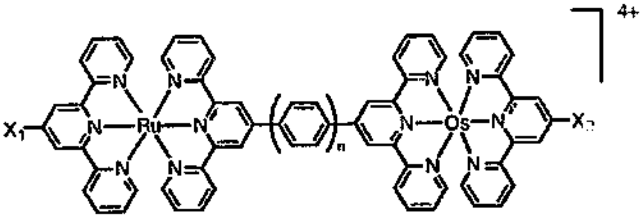
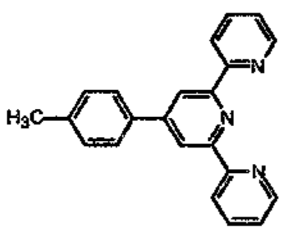


(72)

Under different conditions, the luminescence properties of another family of heterometallic dinuclear complexes of general formula $[(X_1tpy)Ru(tpy(Ph)_ntpy)Os(tpyX_2)]^{4+}$ ($n = 0$-2) (**72**) were investigated with the metal-to-metal distance varying from 11 to 20 Å [144]. Similar studies have also been carried out on Ru(II)- and Os(II)-based mononuclear and dinuclear complexes containing ttp (4-*p*-tolyl-2,2′:6′,2″-terpyridine) (**73**), dpbH (di-*o*-pyridyl-1,3-benzene) (**74**), $tpbpH_2$ (3,3′,5,5′-tetrapyridylbiphenyl) (**75**) with special attention paid on $[(ttp)Ru(tpbp)Os(ttp)]^{2+}$ in which the two metal centers were held at a fixed distance of 11 Å [145].

Three electroactive ligands [3-(2,2′:6′,2″-terpyridin-4′-yl)aniline (**76**), 2-(2,2′:6′,2″-terpyridin-4′-yl)phenol (**77**), 4-(2,2′:6′,2″-terpyridinyl)styrene (**78**)] and their Ru(II) as well as Fe(II) complexes were synthesized. In particular, the electropolymerization of bis[3-(aminophenyl)-2,2′:6′,2″-terpyridine]M(II) and bis[2-(hydroxyphenyl)-2,2′:6′,2″-terpyridine]M(II) (M = Fe and Ru) on Pt or In-SnO_2 (ITO) electrodes in acetonitrile has been explored [146].

Attempts to synthesize $[Ru(N,N',N''\text{-}Xtpy)_2][PF_6]$ (Xtpy = 4′-substituted 2,2′:6′,2″-terpyridine; X = H, Cl, MeO_2S) led to the isolation of the novel $[Ru(N,N',N''\text{-}Xtpy)(N,N'\text{-}Xtpy)Cl][PF_6]$ (**79**) [147]. Photocatalysed regiocontrolled



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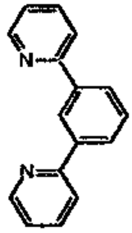

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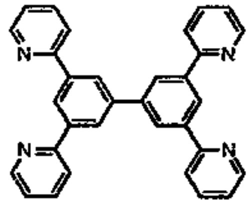

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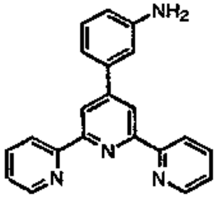

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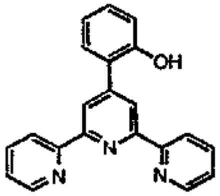

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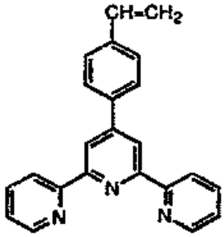
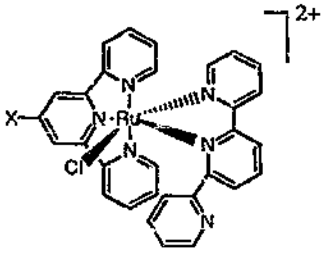


(78)

reduction of the 1-benzyl-4-carbamoylpyridinum cation to the dihydrido form by $[Ru(tpy)(bpy)(py)]^{2+}$ (**80**) and $[Ru(LL)_2(py)_2]^{2+}$ (LL = a didentate ligand) has also been achieved without the formation of the half-reduced dimers [148].

Bridging ligands containing two spatially separated 2,2′:6′,2″-terpyridinyl metal-binding domains were prepared and used for the controlled assembly of coordination oligomers incorporating Ru(II) and other metal ions. Two such bridging ligands were structurally characterized [149]. A related ligand 4′-(9-anthryl)-2,2′:6′2″-terpyridine (**81**) was also prepared. The photochemical properties of complex (**81**) and its ruthenium and iron complexes were also described [150].

Photoaddition of $[Ru(tap)_3]^{2+}$ to DNA and mononucleotides has also been monitored by gel electrophoresis, UV-VIS spectroscopy, and dialysis methods [151]. Moreover, with hydroquinone as reductant, spectroelectrochemical and photoreductions of $[Ru(tap)_3]^{2+}$, $[Ru(bpy)_2(tap)]^{2+}$ and $[\{Ru(phen)_2\}_2(hat)]^{4+}$ (**82**) (hat =



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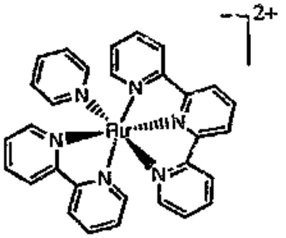

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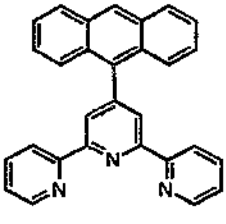


(81)

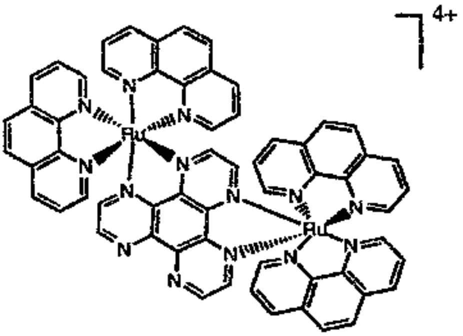
1,4,5,8,9,12-hexaazatriphenylene) were examined and compared. Laser flash photolysis of the complexes led to corresponding transient at ≈500 nm as $[\mathrm{Ru(tap)_2(tap^{\bullet -})}]^+$, $[\mathrm{Ru(bpy)_2(tap^{\bullet -})}]^+$ and $[\{\mathrm{Ru(phen)_2}\}_2\mathrm{(hat^{\bullet -})}]^{2+}$ respectively and was confirmed by the kinetic changes during their decays in the presence of oxidants such as benzoquinone and O_2 [152].

Combined applications of scanning electron microscope (SEM), quasi-elastic light scattering and UV-VIS titrations as well as some specially designed bis-heteroleptic sensors such as $[\mathrm{Ru(bpy)_2(MS\text{-}R)}]^{2+}$, $[\mathrm{Ru(bpy)_2(DS\text{-}R)}]^{2+}$, $[\mathrm{Ru(tap)_2(MS\text{-}R)}]^{2+}$ $[\mathrm{Ru(tap)_2(DS\text{-}R)}]^{2+}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$, have been employed to characterize four colloids which were useful in model systems employed for artificial photosynthesis: Ru, RuO_2, IrO_2 and MnO_2 [153].

The luminescence quenching rate constant K_Q by oxygen for a series of polyazaaromatic complexes with tap, bpy and hat as ancillary ligand was re-examined by a photoelectrochemical (PEC) method and was correlated with the oxidation potentials in the excited state of the complexes [154].

6.4. Complexes with macrocyclic ligands

The dimeric complex $[\mathrm{Ru(pc)}]_2$, obtained from $[\mathrm{Ru(pc)(dmso)_2}]\cdot 2\mathrm{dmso}$, has been examined structurally by the large-angle X-ray scattering (LAXS) technique which revealed a short intradimer Ru(II)···Ru(II) contact (2.40 Å). Electrical conductivity and magnetic properties of the complex and its role in dioxygen activation and

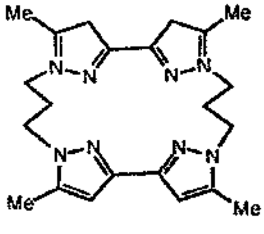


(82)

thereby the oxygen atom transfer towards 1-octene to form 2-octanone have also been investigated in great detail [155].

The new macrocycle L (**83**) has two bipyrazole subunits which reacted readily with Ru(dmso)$_4$Cl$_2$ to give *trans*-[RuL(dmso)Cl]Cl. Attempts to establish the nature of the axial ligands were achieved by ^{1}H and ^{13}C NMR, IR, and UV spectroscopic experiments [156]. Another macrocyclic multidentate ligand, [4′,4″″-bis(ferrocenyl)-2,2′:6′,2″:6″,2‴:6‴,2″″-quinquepyridine] (L) (**84**), has been prepared; coordination of L with [RuCl$_3$L′] (L′ = tpy or its 4′-dimethylamino, -methylsulfonyl or -ferrocenyl derivatives) produced the heteroleptic complex [RuL(L′)][PF$_6$]$_2$ (**85**) in which L behaved as a tridentate hypodentate ligand. In addition, the tetranuclear complex [L′RuLRuCl(L′)][PF$_6$]$_3$ (**86**) bearing a N$_6$ and a N$_5$Cl donor environment has also been synthesized [157].

Preparation of three ruthenium(II) porphyrins, [Ru(TBP)(CO)(EtOH)], [Ru(TBP)(pz)$_2$] and [Ru(TBP)(pz)]$_n$ [TBP = tetrakis-(1,3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin], and their photophysical properties were reported [158].



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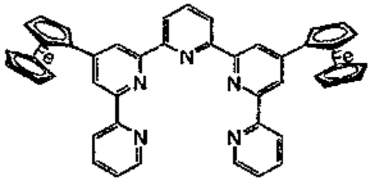
A group of ruthenium(II) complexes bearing the tetraazaporphyrinogen moiety (**87**) with heteroaromatic axial ligands (**88a-j**) has been prepared so as to study their dynamic conformational behaviour by variable temperature NMR spectroscopy [159].



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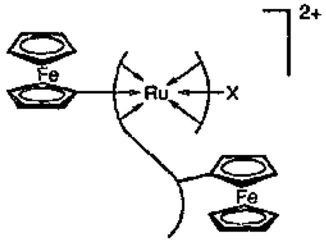

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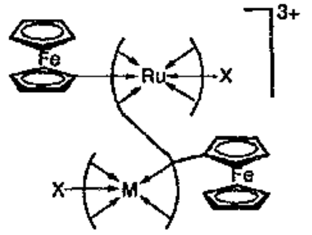

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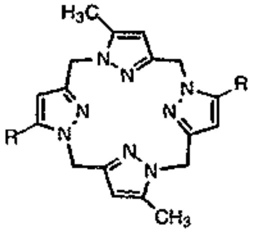
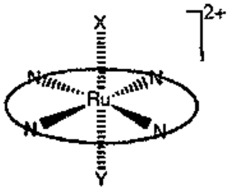


R = CH_3 or C_6H_5

(87)

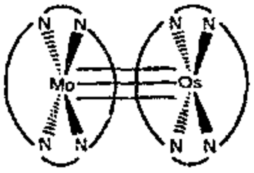


(88)

a X = dmso, Y = H_2O
b X = Y = CH_3CN
c X = Y = C_6H_5CN
d X = dmso, Y = py
e X = CH_3CN, Y = py
f X = Y = Py
g X = Y = 4-OMepy
h X = Y = 3-Mepyz
i X = Y = pz
j X = Y = 3,5-diMePz

The first definitive examples of a number of heterometallic porphyrin dimers containing multiple bonds between two metals from different triads like [(OEP)MoOs(OEP)] (**89**) and [(OEP)MoRu(TOEP)] (**90**) [$OEPH_2$ = octaethylporphyrin (**91**); $TOEPH_2$ = 5-(4-methylphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (**92**)] were reported. Factors affecting the observed paramagnetism of the dimers were discussed [160]. Moreover, multicomponent systems consisting of two different porphyrin moieties and a central Ru(II) complex were prepared by following a new strategy based on the coordination of two differently substituted tpy ligands at the ruthenium centre [161].

The mononuclear complexes [Mo(NO){$HB(dmpz)_3$}Cl(L)] (**93**) [dmpz = 3,5-dimethylpyrazol-1-yl; L = a potential bridging ligand of which one terminus e.g.: (**94a-d**) is attached to the Mo centre and the second terminal (pyridyl) is pendant] were coordinated to the axial positions of the Ru(ttp) core



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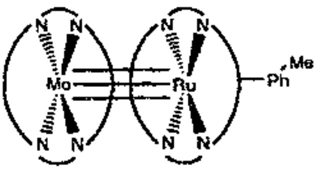

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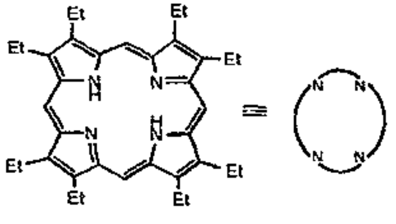

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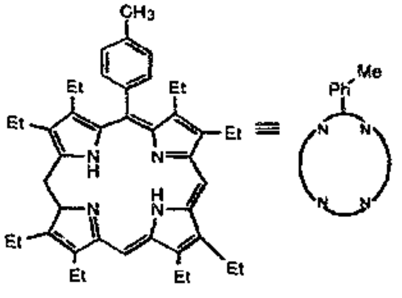


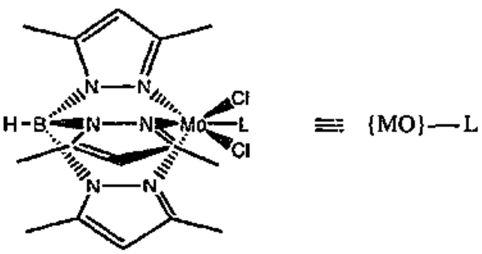
(92)

(tpp = *meso*-5,10,15,20-tetraphenylporphyrinate) **(95)** to produce [{(OC)(tpp)Ru}(μ-L){Mo(NO)[HB(dmpz)$_3$]Cl}] **(96)** and [{Cl[HB(dmpz)$_3$](ON)Mo}(μ-L){Ru(tpp)}(μ-L){Mo(NO)[HB(dmpz)$_3$]Cl}] **(97)** respectively on reacting with [Ru(tpp)(CO)(EtOH)] and [Ru(tpp)(thf)$_2$]. All new complexes have been thoroughly characterized by ^{1}H NMR, IR, UV-VIS and EPR spectroscopies and FAB MS, as well as electrochemistry [162].

6.5. *Complexes with ammonia or amine ligands*

Single-crystal X-ray diffraction analyses for $[Ru(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$, $[Ru(NH_3)_6]CdCl_5$, $[Ru(NH_3)_6]ZnCl_5$, $[Ru(NH_3)_6]Cl_2SCN$, $[Ru(NH_3)_6]_2(S_2O_5)_3 \cdot H_2O$ and a salt of approximate formula $[Ru(NH_3)_6]_2[POF_5]_3 \cdot 4H_2O$ were presented. Analysis of the intramolecular N-Ru-N-H dihedral angles and their correlations strongly suggested that the conformations were random, given the crystallographic site symmetry [163]. The charge density distribution in $[Ru(ND_3)_6](SCN)_3$ has been analysed by X-ray diffraction at 92 K using the multipole and valence-orbital population model [164]. Moreover, the crystal structures of $[M^{III}(NH_3)_6]Cl(SO_4) \cdot 3H_2O$ for M = Ru at 295 K and M = Ru and Co at 92 K were established. Single crystal ESR experiments on a Ru doped cobalt crystal at 77 K were also conducted and the results were compared with those of pure ruthenium salt [165].

The rate of substitution of $[M(NH_3)_5(H_2O)]^{3+}$ **(98)** (M = Ru and Os) by $[Fe(CN)_6]^{3-}$, $[Ru(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ was measured and compared. In particular, reaction of $[Ru(NH_3)_5(H_2O)]^{3+}$ and $[Fe(CN)_6]^{3-}$ afforded $[Ru^{III}(NH_3)_5Fe^{III}(CN)_6]$ and $[Ru^{IV}Fe^{II}(CN)_6]$; the former complex was unstable and



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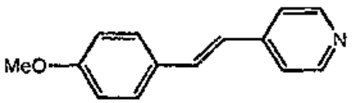
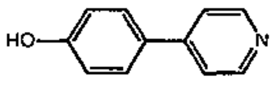
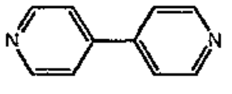


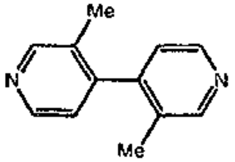
(94a)



(94b)



(94c)

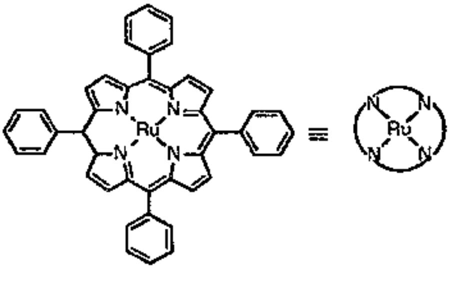


(94d)

ultimately converted to the latter complex slowly [166]. Furthermore, treatment of $[Ru(NH_3)_5(H_2O)]^{3+}$ with $[Os(CN)_6]^{4-}$ generated the mixed valence ion $[(NH_3)_5Ru^{III}\text{-}NC\text{-}Os^{III}(CN)_5]^{-}$. IR and Raman as well as kinetic studies of the dinuclear complex were depicted [167]. On the other hand, the ion exchange from aqueous solution of $[Ru(NH_3)_6]^{3+}$, ruthenium red cation $[Ru_3O_2(NH_3)_{14}]^{6+}$ and the ruthenium nitrosyl species by α-Sn(IV) bismonohydrogenphosphate (SnP) has been examined [168].

The preparations of a number of complexes of formula $[LM(CNRu(NH_3)_5)_2]^{n+}$ {$n=5$, M = Co, Cr, L = $(bpy)_2$; M = Rh, L = $(phen)_2$; M = Co, L = Me_4[14]tetraene-N_4 or $n=6$, M = Fe, L = $(bpy)_2$, $(phen)_2$] were documented. Their metal-to-metal charge transfer spectroscopy was compared with the variation in $[Ru(NH_3)_5]^{3+,2+}$ half-wave potentials for the complexes $[LM(CN)Ru(NH_3)_5]$ [M = Ru, Fe, Co, Rh or Cr; L = polypyridyl or tetraazamacrocyclic ligand] [169].

Monolayers created by co-adsorbing the thiols $[HS(CH_2)_nCONHCH_{2py}Ru(NH_3)_5](PF_6)_2$ (**99**) and $[HS(CH_2)_nCOOH]$ ($n=10$ or 15) on gold electrolytes have been characterized electrochemically and their electron transfer kinetics in a range of non-aqueous solvents such as methanol, ethanol, propanol, butanol, MeCN, dmso, dmf, propylene carbonate, acetone and thf have been studied; associated cyclic voltammetry and chronoamperometry of the complex in non-aqueous and aqueous electrolyte were also examined. The reversible CVs ($n=10$) indicated the



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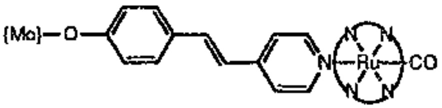
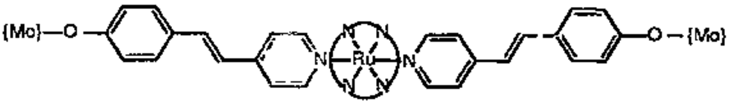


L = 105a

(96)



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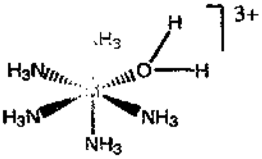
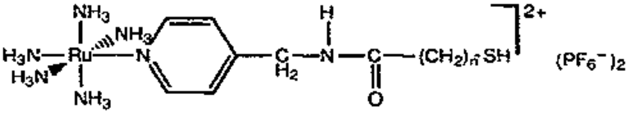


M = Ru or Os

(98)

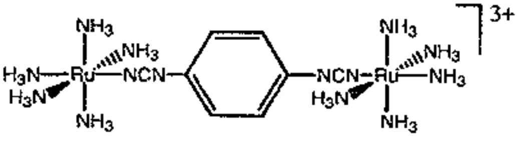


(99)

presence of strong ion-pairing and the relatively disordered structure of the monolayers in aqueous solvents [170]. Electrochemical studies of some NH_2-, OH- and COOH- terminally substituted alkanethiol monolayers formed on a gold electrode through the thiol head have been carried out. The effects of the terminal group on the redox responses of $[Fe(CN)_6]^{3-}$, $[Ru(NH_3)_6]^{3+}$ and ferrocene dimethanol were attributed to the shift of the potential drop across the diffuse layer as well as the change of the concentration of redox species around the electrode surface [171]. Prolonged exposure of graphite electrodes coated with cobalt tetrapyridylporphyrin in *fac*-$[Ru(NH_3)_3(OH_2)_3]^{2+}$ solution produced polymeric complexes in which the porphyrins were linked by bridging Ru centres. Electrochemical evidence in support of this assertion and the ability of the complex to catalyse the four-electron reduction of O_2 at unusual positive potential were presented [172].

An unprecedented solvent dependence of metal-metal coupling observed in

$[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ (**100**) (dicyd = 1,4-dicyanamidobenzene dianion) has been measured by cyclic voltammetry and the resulting conproportionation constant was determined [173]. The synthesis, characterization and reactivity of a comparable complex $[\{Ru(NH_3)_5\}_2DTDP](PF_6)_4$ [DTDP = 4,4′-dithiopyridine (**101**)] were also described in addition to those of $[Ru(NH_3)_5DTDP](PF_6)_2$, $K_3[Ru(CN)_5DTDP]\cdot 3H_2O$, $Na_3[Fe(CN)_5DTDP]\cdot 4H_2O$ and $Na_6[\{Fe(CN)_5\}_2\text{-}DTDP]\cdot 6H_2O$ [174].



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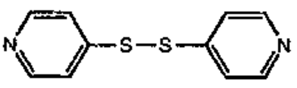

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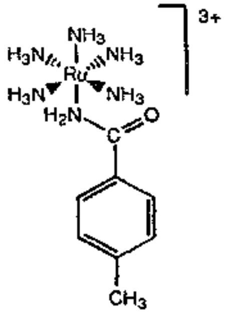
Laser activation of carbon fibre microdisk electrodes and the surface oxide effects on the electron transfer kinetics of $[Ru(NH_3)_6]^{2+/3+}$ were reported [175]. Steady state and fast scan voltammetry of a Pt microdisk electrode was used to study the kinetics of the $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$ couple at different electrolyte concentrations. Associated thermodynamic and kinetic parameters were estimated and were contrasted with those obtained for the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple [176].

Pretreated edge-plane pyrolytic graphite electrodes were found to facilitate the oxidation of Ru ammine to Ru nitrosyl in aqueous media. Different intermediates during the interconversion between the $Ru\text{-}NH_3$, Ru-NO and $Ru\text{-}NO_2$ species were observed in the cyclic voltammograms recorded and hence provided a convenient means of obtaining mechanistic information about the multielectron transfer reactions [177]. The pH dependence of the spectral and electrochemical properties of $[(NH_3)_5RuNHC(O)R]$ (R = Ph, 4-py-*N*-Me$^+$, 4-py-*N*-H$^+$) and $[(NH_3)_5RuOC(O)R]$ (R = 4-py-*N*-Me$^+$) complexes in aqueous solution has been examined. Rate and equilibrium constants for the formation of the protonated Ru(II) amide and Ru(II) carboxylate complexes were measured and the solid state structures of $[(NH_3)_5Ru(C_7N_2H_8O)](ClO_4)_3$ (**102**) and $(NH_4)[Ru(NH_3)_5(C_6N_2H_6O)](PF_6)_3$ (**103**) were also reported [178]. The electrochemical behaviour of *N*-R-4-cyanopyridinium (4-rcp; R = Me, decyl, dodecyl or benzyl) derivatives of $Ru(NH_3)_5$ were examined in aqueous CF_3COOH/CF_3COONa medium by cyclic voltammetry and constant potential electrolysis [179].

Coordination of $[Ru(NH_3)_5]^{2+}$ centres to the nitrile sites in (5,10,15-tris(4-cyanophenyl)-20-(1-methylpyridinium-4-yl)porphyrinato)cobalt(II) (**104**) immobilized on pyrolytic graphite electrodes produced the triruthenated complex which acted as an active electrocatalyst for the four-electron reduction of dioxygen to water. Along with this, the syntheses and the electrocatalytic behaviour of a set of structurally related porphyrins were also described. The ruthenated porphyrins were believed to achieve their catalytic activity by back-bonding inter-



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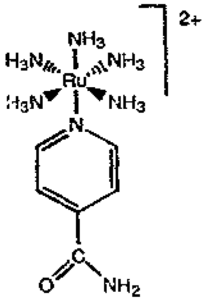


(103)

actions between the $[Ru(NH_3)_5]^{2+}$ groups and the cobalt centre of the porphyrin ring [180].

Synthesis of the mixed-valence complex **(105)** was achieved in which the two ruthenium atoms were found to be valence averaged ($Ru^{2.5+}$, $Ru^{2.5+}$) by XPS examination [181].

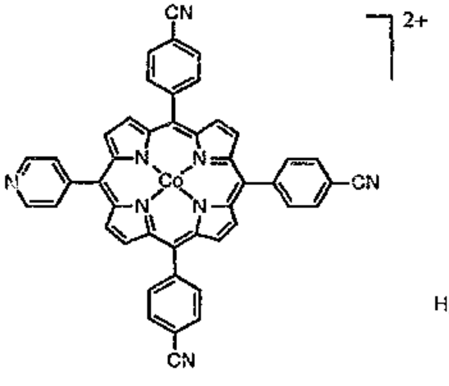
A family of dimetallic complexes containing $Re^IL(CO)_3$ chromophores [L = bpy, Me_4bpy, 4,4′-di(isopropylcarboxylate)-2,2′-bipyridine (DCObpy) **(106)**] and a covalently attached $Ru(NH_3)_5$ moiety via a bridging ligand BL [BL = 1,2-bis(4-pyridyl)ethane (bpa) and 1,3-bis(4-pyridyl)propane (bpp)] has been prepared and characterized. Related photoinduced intramolecular electron transfer processes in the complexes were also investigated [182].

6.6. Complexes with nitrosyl, nitrate and cyanide ligands

The nitrosyl complexes *trans,mer*-$[RuCl_2(dien)NO](PF_6)$ and *mer*-$[RuBr_3(Hdien)NO]Br$ (dien = diethylenetriamine) have been prepared and structurally characterized [183]. Moreover, the molecular structures of *trans*-$[RuX(en)_2NO]X'_2$ (X = OH, Cl or NCS, X′ = Br, Cl or NCS), *trans*-$[Ru(H_2O)(en)_2NO]Cl_3$, *cis*-$[RuX(en)_2NO]XPF_6$ (X = Cl or Br), and *cis*-$[Ru(NCS)(en)_2NO]I_2 \cdot H_2O$ have also been determined by X-ray diffraction [184].

Studies on the MLCT charge transfer of $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$, $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$, $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$, $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(bpy)_2(NC)Ru^{II}(bpy)_2(CN)]^{2+}$ and $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(dcb)_2(NC)Ru(bpy)_2(CN)]^{2-}$ (dcb = 4,4′-dimethoxy-2,2′-bipyridine) and a model mononuclear complex by time-resolved resonance Raman and transient UV-VIS absorption spectroscopies have been conducted and the results discussed [185].

The molecular structure of *cis*-$[Ru(bpy)_2\{$*trans*-$Cr(cyclam)(CN)_2\}_2]^{4+}$ **(107)** (cyclam = 1,4,8,11-tetraazacyclotetradecane) revealed a staggered conformation



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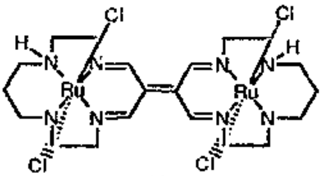

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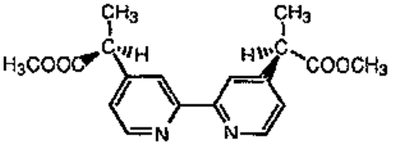
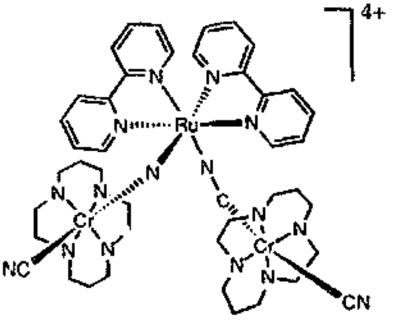


(106)

between the Ru(II) and Cr(II) units. Solid state linkage isomerism of the complex was also demonstrated [186].



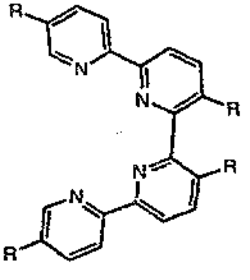
(107)

Under ambient conditions, the trinuclear complex $[(NH_3)_5Ru^{III}(\mu\text{-NC})Ru^{II}(CN)_4(\mu\text{-CN})Co^{III}(NH_3)_5]Cl_2 \cdot 2H_2O$ was prepared and characterized spectroscopically; it exhibited two long-wavelength absorptions at $\lambda_{max} = 647$ and 327 nm. The electronic spectrum as well as the photoreactivity were discussed on the basis of a Hush diagram [187]. Syntheses of two new mixed valence compounds $[(CO)_5M^0(\mu\text{-CN})Ru^{III}(NH_3)_5](CF_3SO_3)_2$ (M = Mo, W) were also reported along with the related intervalence characteristics and electrochemistry [188].

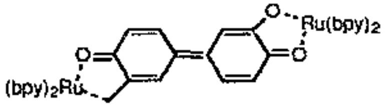
The complex $[\{(NH_3)_5Ru\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ [Me_2dicyd = 1,4-dicyanoamido-2,5-dimethylbenzene dianion] was studied with regard to its magnetic properties and ^1H NMR spectroscopic chemical shifts. The origin of solvent dependence of the metal-metal coupling and stability of the complex were also examined [189].

6.7. Complexes with other N- and mixed donor ligands

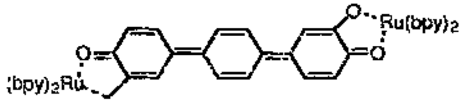
Synthesis, electrochemical oxidation and crystal structures of $[RuL^1(OH_2)_2]^{2+}(ClO_4)_2$ and $[RuL^2(OH_2)_2]^{2+}(ClO_4)_2$ where L^1 = 2,2′: 6′,2″: 6″,2‴-quaterpyridine, (**108**), and L^2 = 3″,5,5′,5‴-tetramethyl-2,2′: 6′,2″: 6″,2‴-quaterpyridine, (**109**), were reported [190]. The complex $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ reacted with 3,3′,4,4′-tetrahydroxybiphenyl (H_4L^3) or 3,3″,4,4″-tetrahydroxy-*p*-terphenyl (H_4L^4) to produce the respective dinuclear $[\{Ru(bpy)_2\}(\mu\text{-}L)\{Ru(bpy)_2\}]^{2+}$ ($L = L^3$, L^4) (**110**) and (**111**). Five redox series of cat-cat, cat-sq, sq-sq, sq-q and q-q for the bridging ligands were established (cat = catecholate fragment; sq = semiquinone; q = quinone) to account for the electrochemistry of the complexes [191].



R = H (**108**)
R = Me (**109**)



(**110**)



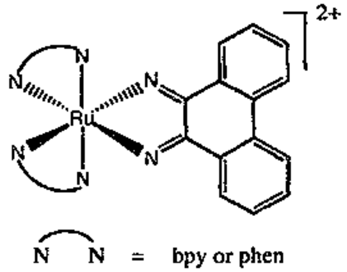
(**111**)

The complexes $[Ru^{II}(bpy)_2(N\text{-ph-bqdi})]^{2+}$ (*N*-ph-bqdi = *N*-phenyl-*o*-benzoquinonediimine) were synthesized and structurally characterized. Infrared, ^1H and ^{15}N NMR and electronic absorption spectra, elemental analyses, and magnetic as well as cyclic voltammetric data were obtained [192]. The interactions of the enantiomers of $[Ru(L)_2(phi)]Cl_2$ (**112**) (L = bpy, phen, phi; phi = 9,10-phenanthrenequinonediimine) with thymus DNA have also been studied by spectroscopic titration, CD and electric linear dichroism methods [193].

The preparations of [2,3-NcRu(II)], $[2,3\text{-NcRu}(L)_2]$ ($2,3\text{-NcH}_2$ = 2,3-naphthalocyanine; L = quinoline, pyridine, pyrazine, 2-ethylhexylamine, *tert*-butylisocyanide, 3-chloropyridine) and $[2,3\text{-NcRu}(L)]_n$ (L = pyrazine, tetrazine) were achieved and characterized by IR, UV and ^1H and ^{13}C NMR spectroscopies, ^{13}C-CP/MANMR and cyclic voltammetry [194].

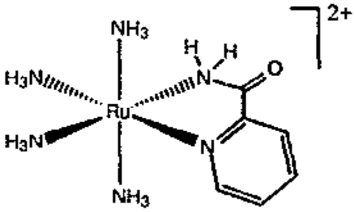
A series of new polypyrazolylborate complexes $[RuCl(\eta^3\text{-Bpz}_4)(L^1)(L^2)]$ (pz = 1-pyrazolyl) ($L^1 = L^2$ = 4-picoline, PEt_3, $P(OCHMe_2)_3$, $NCCH_3$; L^1 = NCPh, L^2 = 2,4-lutidine, PPh_3), $[Ru(\eta^3\text{-Bpz}_4)(L)_3]PF_6$ (L = $NCCH_3$, CO), $[Ru(\eta^3\text{-BR}^1pz_3)(\eta^3\text{-BR}^2pz_3)]$ (R^1, R^2 = pz, H) and $Ru(\eta^3\text{-BRpz}_3)(\eta^2\text{-BHpz}_3)(NCPh)]$ (R = pz, H) was prepared from $[RuCl(\eta^3\text{-BRpz}_3)(NCPh)_2]$ and the complexes were characterized by spectroscopic techniques [195].

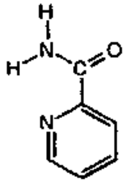
Reduction of $[Ru^{III}(NH_3)_5(NHC(O)\text{-2-py})]$ led to $[Ru^{II}(NH_3)_5(NH_2C(O)\text{-2-py})]$ which further underwent a chelation reaction to produce



(112)

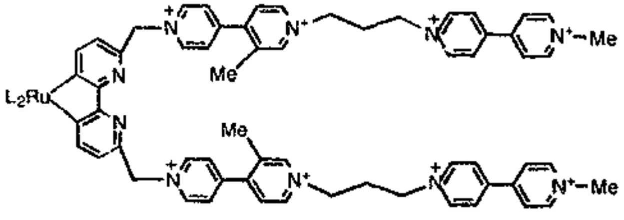
cis-[Ru^{II}(NH$_3$)$_4$(NH$_2$C(O)-2-py)] (**113**), along with an aquation reaction to afford [Ru^{II}(NH$_3$)$_5$(OH)$_2$] and free picolinamide (**114**) [196]. A general route leading to [RuL$_3$](ClO$_4$)$_2$ · H$_2$O [L = *N*-phenyl- and *N*-*p*-tolyl(2-pyridylmethylene)amines, L^1 and L^2] and [RuL$_n$^{2}(bpy)$_{3-n}$][ClO$_4$]$_2$ · 2H$_2$O (n = 1, 2) and related optical spectral and electrochemical properties of the complexes were described [197].





(113) **(114)**

A facile synthetic method leading to Ru(II) polypyridine complexes by microwave irradiation was developed and may be used for the synthesis of a variety of metal polypyridine complexes [198]. The synthesis of a new type of supramolecular Ru(II)-polypyridine based sensitizer (S)-relay(A$_1$)-relay(A$_2$) triads (**115**) and its spectroscopic properties were also achieved [199].



(115)

The complexes *cis*-[4,4′-(CO$_2$H)-2,2′-bipyridine]$_2$RuX$_2$ and *cis*-[5,5′-(CO$_2$H)$_2$-2,2′-bipyridine]$_2$RuX$_2$ (X = Cl$^-$, CN$^-$ and SCN$^-$) were prepared and spectroscopically characterized. They have been employed for the conversion of visible light into electricity when anchored to high surface area TiO_2 electrodes [200].

The reduction potentials of a series of polypyridine-Ru^{II} complexes have also been parameterized with the $\Sigma E_L(L)$ parameter. The slope S_L, and intercept, I_L, of the linear correlations were shown to relate to metal-ligand coupling and interligand coupling through the metal centre [201]. Oxidative homolysis of the superoxo complexes $[Cr(H_2O)_5O_2]^{2+}$ by polypyridine complexes of Ru^{III} and Fe^{III} produced $[Cr(H_2O)_6]^{3+}$ and O_2 in good yield, which constituted the first reported case of reaction of its type [202].

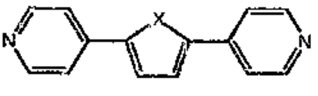
Intervalence transitions and the conproportionation constants have been measured in $[(NH_3)_5Ru(py)\text{-}X\text{-}(py)Ru(NH_3)_5]^{5+}$ [X = dipyridylpolyenes, dipyridylthiophene (**116a**) and dipyridylfuran (**116b**)] [203]. The same studies have been undertaken for nine mixed-valence ruthenium ammine dimers including $[(NH_3)_5Ru(4,4'\text{-bipyridine})Ru(NH_3)_5]^{5+}$ in 14 different solvents. The importance of both dielectric continuum effects and specific solvent-solute interactions were addressed [204]. The effect on the visible and near IR electronic absorption spectra for $[(NH_3)_5Ru\text{-pz-}Ru(NH_3)_5]^{5+}$ upon double crown encapsulation has also been recorded. The former absorption shifted systematically to lower energy with increasing crown size whereas the latter shifted to higher energy [205].

Synthesis, electron delocalization and electronic coupling of a class of polyene-bridged dinuclear Ru complexes, in particular complex (**117**), were reported. Significant electronic coupling between the terminal subunits was observed both in the mixed valence complex and in the triplet state of the ruthenium(II) complex. The effect on replacing one of the Ru(II) complex moieties by ferrocene was discussed [206]. Photoexcited state properties of a comparable ruthenium complex but bridged by 2,6′-bis(2-pyridyl)-2,2′:6′,2″-thiazolo[4,5-d]-benzothiazole (bptb) (**118**) were investigated. Comparison of HOMO/LUMO energies and the degree of electronic coupling between the Ru metal centre was made when 2,6-bis(2-pyridyl)benzodiimidazole ($dpimbH_2$) (**119**) was employed as bridging ligand [207].

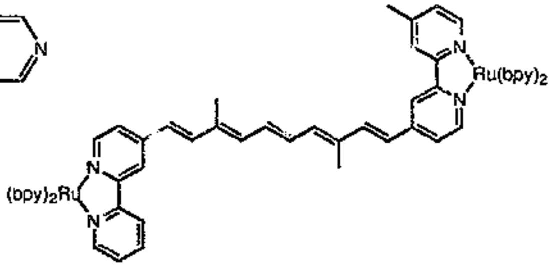
Treatment of 2,2′:3′,2″:6″,2‴-quaterpyridine (HL) (**120**) with 2 equivalents of $[Ru(tpy)Cl_3]$ afforded another dinuclear complex $[Cl(tpy)Ru(\mu\text{-}L)Ru(tpy)][PF_6]_2$ (**121**) which has been fully characterized by elemental analysis, ^1H NMR spectroscopy and fast atom bombardment mass spectrometry as well as cyclic and square-wave voltammetry [208].

The mixed metal complex $[Ru^{II}(Me_2phen)_2(Mebpy\text{-}CH_2\text{-}CH_2\text{-}Mebpy)\text{-}Rh^{III}(Me_2bpy)_2]^{5+}$ (Me_2phen = 4,8-dimethyl-1,10-phenanthroline; Mebpy = 4-methyl-2,2′-bipyridine; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) was synthesized and studied from several points of views: electron transfer from excited donor, electron transfer to excited acceptor, charge recombination and electronic energy transfer [209].

The ditopic ligand (**122**), bpy-cyclam, and its heterometallo-dinuclear complex $[Ru(bpy)_2(bpy\text{-cyclam-}Ni)]^{4+}$ (**123**), and the intermediate involved $[Ru(bpy)_2(bpy\text{-cyclam-}2H)]^{4+}$ have been isolated and characterized. Their spectroscopic and redox properties were reported [210]. A different but comparable super-



(116) a: X = S
b: X = O



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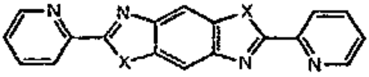
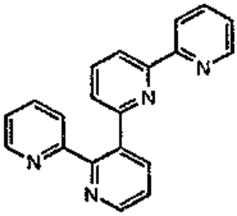
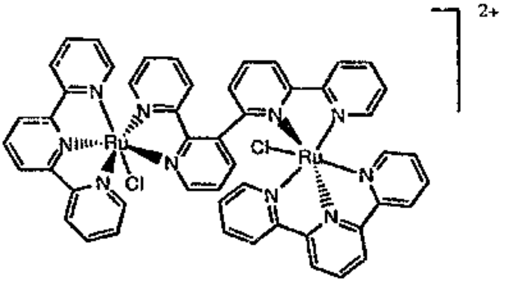


X = S (**118**)
= NH (**119**)





(120) **(121)**

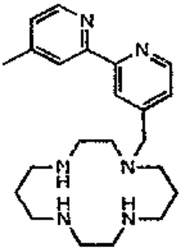
molecule [Ru(bpy)$_2$(bpy-py-cyclam-Ni^{II})] (**124**) has also been synthesized. Applications for the photoreduction of CO$_2$ were described [211].

Treatment of [Fe(CN)$_5$OH$_2$]$^{3-}$ with [Ru(NH$_3$)$_5$pym]$^{2+}$ generated the pyrimidine bridged complex [(NC)$_5$Fe(pym)Ru(NH$_3$)$_5$]$^-$ which was oxidized to [(NC)$_5$Fe(pym)Ru(NH$_3$)$_5$] by the peroxydisulfate ion. Rate constants for the formation and dissociation of both complexes have also been measured [212].

An unprecedented example of photoinitiated electron collection was demonstrated in the complex [{(bpy)$_2$Ru(dpb)]$_2$IrCl$_2$}]]$^{5+}$ (**125**) [dpb = 2,3-bis(2-pyridyl)benzoquinoxaline] which upon photolysis and in the presence of dimethylaniline led to [{(bpy)$_2$Ru(dpb$^-$)]$_2$IrCl$_2$}]]$^{3+}$. Details concerning the photoinitiated electron collection process were presented [213].

6.8. Complexes with biological activity

Derivatization of yeast cytochrome c peroxidase (CCP) using aquopentaamine ruthenium(II) [Ru(NH$_3$)$_5$(H$_2$O)] produced the stable, covalently-linked derivatives



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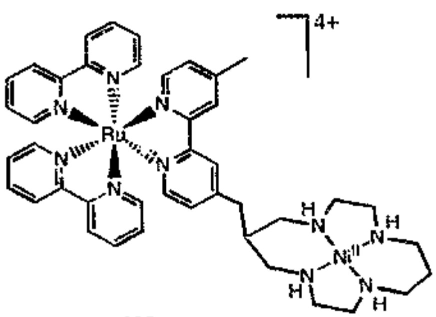

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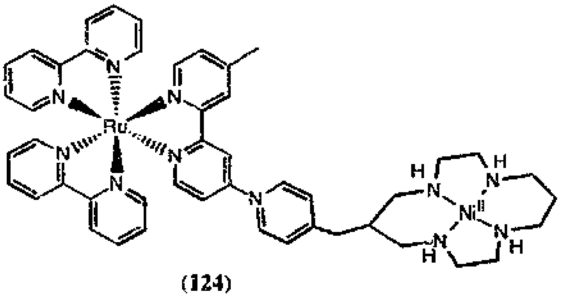

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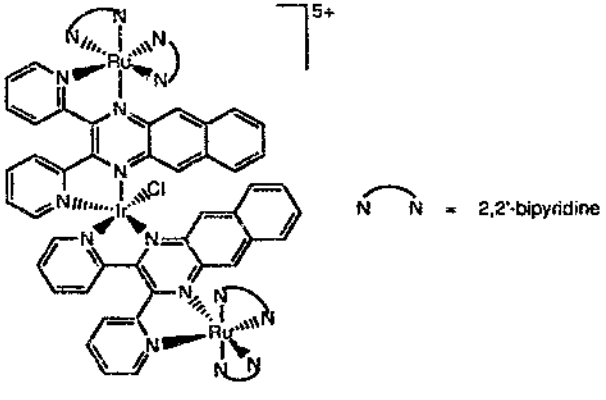


(125)

that were then purified by cation-exchange fast-protein liquid chromatography (FPLC). Activity measurements on the stability of enzyme intermediates, mass spectrometric analysis of the nature CCP and differential pulse voltammetry have shown that the derivatives possessed similar properties to that of native CCP [214]. In addition, the pressure effects on the rates of intramolecular electron transfer in

$[(bpy)_2(im)Ru(HisX)Fe\text{-}cyt\ c]$ (X = 33 and 72) and the role of the intervening medium in tuning the distant Fe^{2+}:Ru^{3+} electronic coupling were documented [215]. In addition, mechanistic studies on pentaamine(isonicotinamide)ruthenium(II/III) and horse-heart cytochrome *c* iron(III/II) have been carried out. An excellent agreement was observed between the respective predicted rate and equilibrium constants, which have been obtained by theoretical calculations by using Marcus-Hush theory [216].

The binding properties of two anti-tumour complexes, *trans*-indazolium(bisindazole) tetrachlororuthenate(III) and *trans*-imidazolium(bisimidazole) tetrachlororuthenate(III), with human serum apotransferrin have been investigated through spectroscopic and chromatographic techniques with the ultimate goal of preparing adducts with good selectivity for cancer cells. Their anti-cancer action was compared with that of cisplatin which suggested that the two ruthenium complexes could utilize transferrin as a drug delivery system [217]. The binding mode of the Ru(III) complexes around the iron(III) sites was disclosed by preliminary X-ray diffraction data [218]. On the other hand, the interactions of the Δ and Λ enantiomers of $[Ru(phen)_3]^{2+}$ with the oligonucleotide duplex $[d(CGCGATCGCG)]_2$ have been studied by NMR and CD spectroscopies. The observed NOEs also provided evidence that the metal complexes preferentially bind to the central AT region. A comparison study of the analogue $[Ru(phen)_2DPPZ]^{2+}$ (DPPZ = dipyrido[3,2-a:2′,3′-c]phenazine) was also performed [219].

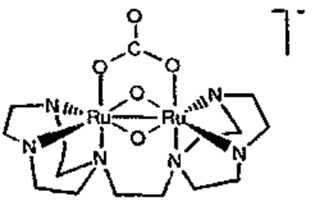
7. Complexes with oxygen donor ligands

7.1. Complexes with oxo ligands

The complexes $[Ru^{III}(tacn)Cl_3]$, $[Ru^{III}(dtne)Cl_6]$ and $[Ru_2^{III}(dtne)Br_6]$ have been synthesized from $[Ru^{II}(dmso)_4Cl_2]$ with the respective amine: tacn = 1,4,7-triazacyclononane; dtne = 1,2-bis(1,4,7-triazacyclonon-1-yl ethane) in concentrated HCl or HBr and were proven to be useful starting materials for the hydrolytic generation of hydroxy/oxo-bridged dinuclear Ru_2^{III} and $Ru^{III}Ru^{IV}$ species containing carboxylates or sodium carbonate. The related complexes $[Ru_2^{III}(dtne)(\mu\text{-}OH)_2(\mu\text{-}PhCO_2)](PF_6)_3$ and $[Ru_2^{III}(tacn)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]Br_2 \cdot 3.75\ H_2O$ and $[Ru_2^{3.5}(dtne)(\mu\text{-}O)_2(\mu\text{-}CO_3)]PF_6 \cdot 5H_2O$ (**126**) and the Ru_2^{IV} analogues of the latter two complexes were generated chemically and electrochemically [220].

The oxo-bridged dinuclear cation $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ (**127**) catalysed the oxidation of a series of sugars in its $Ru^{IV}Ru^{V}$ oxidation state and has been investigated electrochemically and confirmed by HPLC analyses. Kinetic studies revealed the first order dependence of the reaction on the catalyst and the substrate [221].

The first ruthenium analogues of the hemerythrin models with μ-alkoxo bridging groups, $Na[Ru(dhpta)(\mu\text{-}O_2CR)_2]$ ($dhptaH_5$ = 1,3-diamino-2-hydroxypropane-



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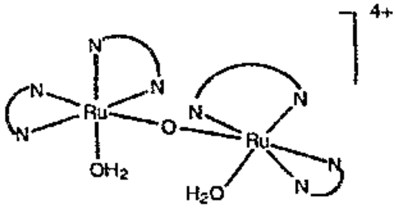
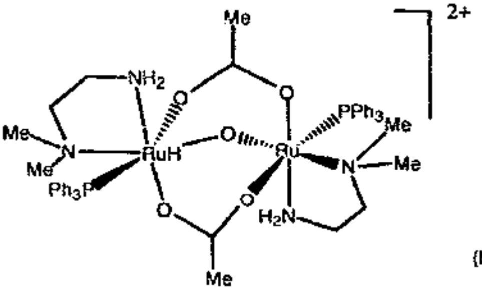


(127)

tetraacetic acid; R = Me, C_6H_4-*p*-OH and C_6H_4-*p*-NH_2), were prepared and structurally characterized. They underwent two successive one-electron reductions to its $Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{II}$ states with a large separation of ~0.6 V between the successive redox potentials, resulting in the formation of stable mixed-valence species [222]. The synthesis, molecular structure and redox properties of $[Ru_2(\mu\text{-}O)(\mu\text{-}OOCMe)_2(Me_2NCH_2CH_2NH_2)(PPh_3)_2](ClO_4)_2$ (**128**) have been reported. The complex underwent a nearly reversible one-electron oxidation as well as an irreversible reduction at 1.02 V and -0.52 V (vs SCE) respectively [223].

Spectroscopic and electrochemical studies on $[Ru(bpy)_2(HpicOH)]^+$ and $[\mu\text{-picO-}\{Ru(bpy)_2\}]^{2+}$ (picOH = 3-hydroxypicolinic acid (**129**); Hpic = picolinic acid) were recorded; the latter dinuclear complex was shown to be a Robin-Day class II mixed valence complex [224].

Electrophilic addition of *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ to camphor or alternatively the reaction of *cis*-$[RuCl_2(bpy)_2]$ with HA (A = anion of camphorquinone monoxime) afforded $[Ru(A)(bpy)_2]^+$ (**130**). An intense MLCT transition, the observed reversible Ru^{III}-Ru^{II} couple and two diimine reductions have also been described [225].



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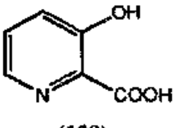

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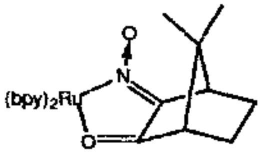


(130)

The oxo complex $[(C_2H_5COO)_6Ru_3(\mu_3\text{-}O)(H_2O)_3^+(C_2H_5COO^-)]$ underwent carboxyl exchange with silica-supported poly(maleic acid-co-styrene) to yield the supported poly(maleic acid-co-styrene)-triruthenium clusters which actively catalysed the oxidation of styrene to PhCHO under very mild conditions. A mechanism for the styrene cleavage was also proposed [226].

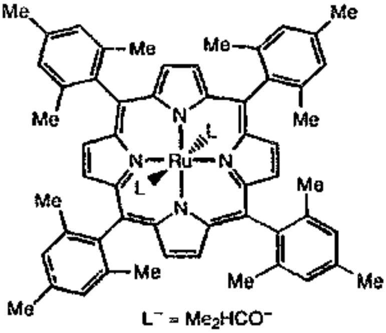
In the presence of Ce^{4+} ions, $[\{(bpy)_2Ru(OH_2)\}_2O]^{4+}$ catalysed the oxidation of water in acidic solutions; the underlying component species involved in the mechanism have been studied by ESR and Raman spectroscopies [227]. Alcohols were found to be oxidized readily by *trans*-$[Ru(tmp)(O)_2]$ (tmp = dianion of 5,10,15,20-tetramesitylporphyrin) via bis(alkoxy) species, of which the bis(isopropoxy) complex $[Ru(tmp)(OCHMe_2)_2]$ (**131**) has been characterized crystallographically [228].

7.2. Complexes with carboxylate ligands

Isolation of $[Ru_2(O_2CCPh_3)_4(H_2O)(EtOH)]\cdot 2EtOH$ (**132**) from the reaction of $Ru_2[O_2CCH(OH)Ph]_4(H_2O)_2$ and HO_2CCPh_3 has also been reported along with its X-ray crystal structure [229]. A number of edge-sharing bioctahedral complexes $[Ru_2(OMe)(O_2CC_6H_4\text{-}p\text{-}X)_3(1\text{-}MeIm)_4](ClO_4)_2$ (X = OMe, Me) (**133**) and $[Ru_2(O_2CC_6H_4\text{-}p\text{-}X)_4(1\text{-}MeIm)_4](ClO_4)_2$ (X = OMe, Me) have been successfully prepared by treating $[Ru_2Cl(O_2CR)_4]$ with 1-methylimidazole (1-MeIm) in methanol. Some of them have been characterized structurally [230]. The carboxylato complex *cis*-[bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)Ru(II)] has been utilized to prepare transparent non-crystalline ZnO films by the sol-gel method which was useful to produce light-harvesting units in a regenerative photoelectrochemical cell [231].

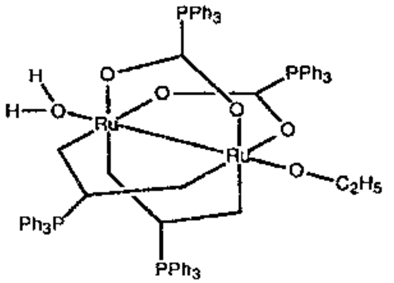
The first non-polymeric $[Ru_2Cl(\mu\text{-}L)_4(thf)\cdot thf\cdot H_2O]$ complex has been prepared by the reaction of $[Ru_2Cl(\mu\text{-}OAc)_4]$ with pyrrole-2-carboxylic acid (HL) and characterization by analytical, spectroscopic, magnetic techniques as well as X-ray crystallography have been performed. Single crystal X-ray analysis showed a non-polymeric nature with the two ruthenium atoms linked by four bridging pyrrole-2-carboxylate ligands [232]. Two mixed-valent diruthenium tetracarboxylates, $[Ru_2(OAc)_4(H_2O)_2]BPh_4$ and $[Ru_2(OAc)_4(pz)]BPh_4$ (**134**) were reported. Their magnetic behaviours were described in terms of intermolecular antiferromagnetic interaction and zero-field splitting [233].

The complex $[Ru(OAc)_2(PPh_3)_2]$ interacted with one or two equivalents of L



$L^- = Me_2HCO^-$

(**131**)



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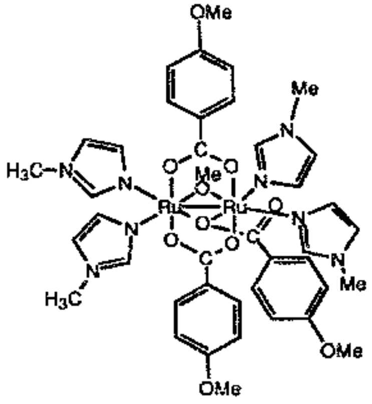

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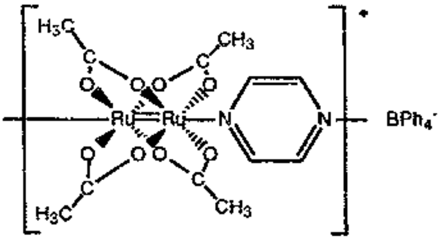

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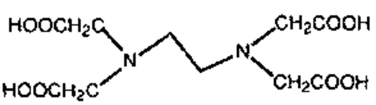
[L = $Ph_2P(CH_2)_nPPh_2$; $n = 1$-3] to give [$Ru(OAc)_2(Ph_3P)L$] and [$Ru(OAc)_2L_2$] respectively. The solution dynamics of complexes with n = 1 and 2 were established by variable temperature ^1H and ^{31}P {^1H} NMR spectroscopy [234]. The kinetics of the oxidation of formic acid by cerium(IV) in the presence of [$Ru^{III}(HCO_2^-)$], [$Ru^{III}(HCO_2^-)(HCO_2H)$] and in aqueous sulfuric acid has been followed at different temperatures; a possible mechanism was proposed [235].

7.3. Complexes with edta ligands

The reaction of the hydrazinium ion ($N_2H_5^+$) with [$Ru(edta)(H_2O)$], edtaH_4 = (**135**), was studied in aqueous solution in the pH range 1.0–4.5 by spectrophotometry and voltammetry. The reaction products, [$Ru^{III}(Hedta)(N_2H_5)$]$^+$ and [$Ru^{III}(edta)(N_2H_5)$], the mechanism of the catalytic electroreduction of hydrazine to ammonia and the related kinetic investigations were outlined [236]. Members of a family of dinuclear complexes of formula [$(edta)Ru^{III}LCo^{III}(NH_3)_5$]$^{2+}$ [L = pyrazine, 4,4′-bipyridine, 3,3′-dimethyl-4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,4-bis(4-pyridyl)butadyne] were prepared by the reaction of [$Ru^{III}(edta)OH_2^-$]

with $[Co^{III}(NH_3)_5L]^{3+}$. Reduction with ascorbic acid or dithionite led to $[(edta)Ru^{II}LCo^{III}(NH_3)_5]^+$ which simultaneously underwent intramolecular electron transfer from Ru(II) to Co(III). The results were compared with that obtained for $[(NC)_5Fe^{II}LCo^{III}L(NH_3)_5]$ [237]. Interaction of $[Ru^{III}(Hedtra)(H_2O)]$ with iodide ion afforded $[Ru^{III}(Hedtra)I]^-$ which has been investigated by spectrophotometry, electrochemistry and stopped-flow techniques. Rate and activation parameters indicated that the reaction proceeded via an associative interchange mechanism [238]. The synthesis and temperature dependence of the intervalence transfer in $K_4[Ru^{III}(Hedtra)NCFe^{II}(CN)_5]$ were reported and the results compared with those observed in the complexes $[Ru^{III}(edtra)NCFe^{II}(CN)_5]^{5-}$ and $[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$. The charge on the Ru centre of the dinuclear complexes was found to affect the intervalence thermochroism [239]. A number of experiments have been conducted aimed at the reduction of the coordinated nitrogen atom in $[Ru(Hedta)N_2]^-$ and also that in the associated dinuclear bridged complex $[\{Ru(Hedta)\}_2N_2]^{2-}$ using the conduction band electrons of an illuminated Pt/CdS ($\lambda_{ex} = 505$ nm). The dinitrogen in the mononuclear end-on complex was found to be more easily reduced to ammonia [240].



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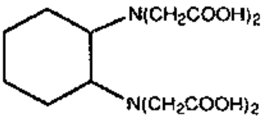

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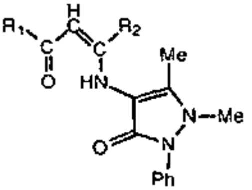
The first isolated anti-neoplasmic Ru^{4+} compound, $[Ru(H_2cdta)Cl_2]\cdot 2H_2O$, displacing cytostatic activity, was obtained by the reaction of $RuCl_3$ with H_4cdta ($cdtaH_4$ = 1,2-cyclohexanediaminetetraacetic acid) (**136**). The crystal structure, electronic spectroscopy and magnetic studies of the complex were reported [241].

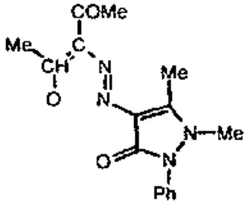
7.4. Complexes with acac type or ketone ligands

Reaction of 3-functionalized propenes (L) in the presence of Δ-(+)-Ru(acac)$_3$ afforded $[Ru(acac)_2L_2]$ whose configuration and formation mechanism have been examined [242]. Photoinduced electron-transfer (ET) reactions of $Ru(CN)_2L_2$ (L = bpy and phen derivatives) with a series of $Ru^{III}(dike)_3$ (dike = β-diketonate) have been investigated in MeCN and the results were compared with a number of organic quencher systems such as 7,7′,8,8′-tetracyanoquinanodimethane (tcnq), benzoquinone and nitrobenzene [243]. A number of β-diketones (HL) including acetylacetonylidene-4-aminoantipyrine (**137**), monobenzoylacetylacetonylidene-4-aminoantipyrine (**138**), dibenzoylmethanylidene-4-aminoantipyrine (**139**) and antipyrine-4-azo-β-ethylacetoacetate (**140**) reacted with $RuCl_3$ to give the corresponding Ru(HL)Cl_3. All complexes were characterized and studied using spectral, magnetic, thermal measurements as well as cyclic voltammetry [244].

The paramagnetic mixed ligand complex, [Ru(tpy)(DBQ)Cl] (**141**) (DBQ =



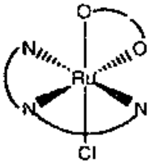
$R_1 = R_2 = Me$ **(137)**
$R_1 = Ph, R_2 = Me$ **(138)**
$R_1 = R_2 = Ph$ **(139)**



(140)

3,5-di-*tert*-butyl-*o*-benzoquinone), has been prepared and exhibited intense charge-transfer transitions in visible and near IR regions. The reactions of [Ru(tpy)(DBSQ)Cl] [BDSQ = semiquinone form of DBQ (**142**)] with Ag^+ also gave $[Ru(tpy)(DBSQ)(H_2O)]^+$ as the perchlorate salt. This complex was easily converted back to the parent chloro complex by reacting with the chloride ion [245]. The complex $Ru(dmso)_2Cl_2$ reacted with sodium salts of L (L = 5-hydroxyflavone, 5-hydroxy-4′-methoxyflavone and 5-hydroxy-3′,4′,5′,7′-tetramethoxyflavone) to generate the respective substitution products $[RuL_2(dmso)_2]$ via the intermediates $[RuLCl(dmso)_3]$ with the former complexes comprised two intramolecular non-equivalent intramolecular dmso ligands. All complexes isolated were well characterized spectroscopically so that detailed stereochemical analysis could be conducted [246].

Interconversion of linkage isomers of $[Ru(bpy)_2(alizarin)]$ (**143**) (alizarin =



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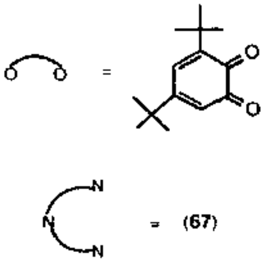

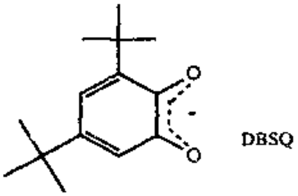

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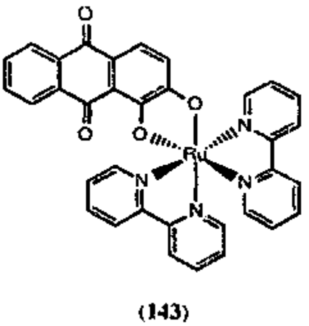
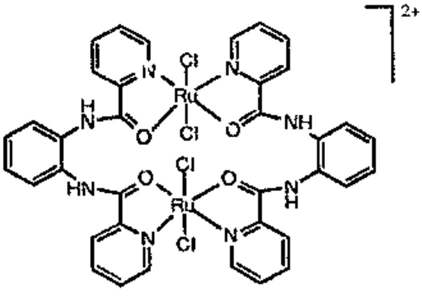


(143)

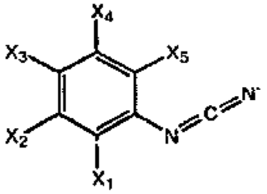
1,2-dihydroxy-9,10-anthraquinone) has been monitored by electronic and electrochemical techniques. Comparison with $[Ru(bpy)_2(QOH)]$ (QOH = 1-hydroxyanthraquinone) has been made to elucidate the bonding nature of the isomers [247].

7.5. *Complexes with other O-donor ligands*

With iodosylbenzene as oxidant, the dinuclear amide complexes (**144**) and its isomers derived from *m*- or *p*-phenylenediamine were active catalysts for the epoxidation of norbornene, *cis*-cyclooctene and *trans*-4-octene. The underlying mechanism was established [248]. Six *cis*-$[Ru(bpy)_2(L)_2]$ complexes of chloro-substituted phenylcyanamide anion ligands [L = monoanions of phenylcyanamide(pcyd) (**145a**), (2-chlorophenyl)cyanamide (2-Cl-pcyd) (**145b**), (2,3-dichlorophenyl)cyanamide ($2,3\text{-}Cl_2pcyd$) (**145c**), (2,4,5-trichlorophenyl)cyanamide ($2,4,5\text{-}Cl_3pcyd$) (**145d**), (2,3,4,5-tetrachlorophenyl)cyanamide ($2,3,4,5\text{-}Cl_4pcyd$) (**145e**) and (pentachlorophenyl)cyanamide (Cl_5pcyd) (**145f**)] have been synthesized and characterized by elemental analysis, ^1H NMR, IR, UV-VIS, near IR spectroscopies and cyclic voltammetry. Oxidation of the complexes by controlled-potential electrolysis generated *cis*-$[Ru(bpy)_2(L)_2]^+$ whose photophysical properties were compared with their neutral counterparts [249].



(**144**)



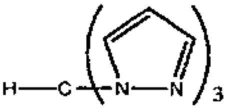
(**145**) a : $X_{1\text{-}5}$ = H
b : X_1 = Cl, $X_{2\text{-}5}$ = H
c : $X_{1\text{-}2}$ = Cl, $X_{3\text{-}5}$ = H
d : $X_{1\text{-}3}$ = Cl, $X_{4\text{-}5}$ = H
e : $X_{1\text{-}4}$ = Cl, X_5 = H
f : $X_{1\text{-}5}$ = Cl

The complexes $[Ru^{II}(L)(bpy)(H_2O)_2]^{2+}$ and $[Ru^{IV}(L)(bpy)O]^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) have been compared and their crystal structures determined. The latter compound was found to be an efficient oxidant for alkene epoxidation. Kinetic and the associated activation parameters were measured and interpreted [250]. Crystal structure data for $Pb[Ru(NO)(NO_2)_4OH]\cdot 0.5H_2O$ (including data that have already been established) were reported [251].

Members of a series of new Ru-aqua complexes $[(tpm)(4,4'\text{-}(X)_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$ [X = H, Me, NO_2, NH_2, COOEt; tpm = tris(1-pyrazolyl)methane] (**146**) have been synthesized and characterized. Their spectroscopic and electrochemical properties were studied by UV-VIS, cyclic voltammetry and coulometry [252].

Salts of the cations *trans*-$[Ru(OH)(en)_2NO]^{2+}$ and *trans*- and *cis*-$[RuX(en)_2NO]^{n+}$ (X = Cl, Br, I, OAc and NCS; $n = 2$; $X = H_2O$, $n = 3$) were synthesized. Although the magnitude of ν(NO) decreases as the π-donating ability of X increased in the *trans* isomers, the trend was not observed among the *cis*-isomers. Two kinds of isomerization reaction were involved during the formation of the complexes. One was accompanied by a substitution reaction from OH^- to X^-, and the other occurred after the substitution reaction [253].

Syntheses and detailed magnetic properties of $[Ru_2(tfac)_4(tempo)_2]$ (147) and $[Ru_2(pfbz)_4(tempo)_2]$ have been reported where tfac = tetrakis(trifluoroacetate), pfbz = tetrakis(perfluorobenzoate) and tempo = 2,2,6,6-tetramethylpiperidine-1-oxyl; relevant crystallographic parameters have also been presented [254].



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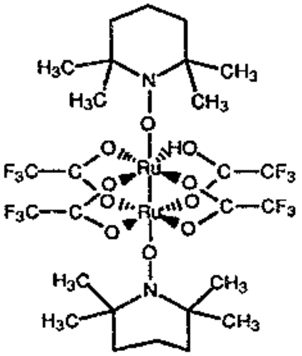
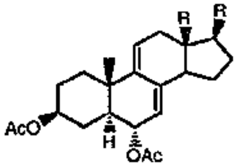


(147)

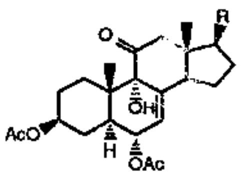
The complex $[Ru^{II}(H_2O)_2(dmso)_4](BF_4)_2$ catalysed the oxidation of a series of α-chloroalkenes to the appropriate carboxylic acid and/or carbon dioxide with rates in excess of almost 100 turnover min^{-1} at room temperature in the presence of a surfactant agent: cetyltrimethylammonium hydrogensulfate [255]. Reaction of either *cis*- or *trans*-$[Ru(dmso)_4X_2]$ with $[(dmso)_2H][Ru(dmso)_4X_4]$ (X = Cl, Br) in concentrated HBr led to the deoxygenation of dmso and the formation of $RuMe_2S$ and subsequently to $[RuBr_6]^{3-}$ [256].

A review focusing on the development of complexes with general formula Na[*trans*-$RuCl_4(R_1R_2SO)(L)$] (R_1R_2SO = dmso and tetramethylenesulfoxide (tmso); L = nitrogen donor ligand) possessing anti-tumour properties has appeared. The chemical behaviour of the complexes has been studied by spectroscopic means and the influence of some biological reductants on the chemical behaviour was also described [257]. Comparisons of the oxygen transfer reactions catalysed respectively by ruthenium tetraoxide, chromyl chloride and benzyltriethylammonium permanganate with thianthrene-5-oxide (SSO) have been made with special attention on the nature of the product. The underlying mechanisms of the reactions were investigated [258]. Structural information of the complex $(Bu_4N)[Ru(dmso)_2Cl_4]$ has been presented as well as the behaviour of the complex in different solvents. In particular, deoxygenation of dmso occurred with the formation of a di-Me sulfide complex in HBr solutions [259].

The oxidation of methyl- and octyl-α-D-glucopyranoside by $NaBrO_3$, as catalysed by three different high-valent ruthenium species, RuO_4, RuO_4^- and RuO_4^{2-}, has been compared at different pH values. Both kinetic and thermodynamic studies supported the fact that the oxidation proceeded via a hydride-transfer mechanism when catalysed by RuO_4 at pH 4.5, while at pH 10, $[RuO_4]^-$ appeared to catalyse the oxidation via a radical mechanism. However, no catalytic function was observed at pH 14 [260]. Oxidation of the 5α-cholesta-7,9(11)-diene-3β,6α-diol diacetate (**148**) by ruthenium tetraoxide produced 3β-6α-diacetoxy-9α-hydroxy-5α-cholest-7-en-11-one (**149**), 9α,11α-dihydroxysterol, 5α-cholest-7-ene-3β,6α,9α,11α-tetrol-3,6-diacetate (**150**) and 9,11-secosteroid (**151**). Special attention was paid to the product nature and overall yield which shed further light on the reactivities of the oxidizing agent. These results furnished a reliable route to Δ^7-9α,11β-dihydroxy sterols via $LiAlH_4$ reduction of the 11-keto group [261]. Further examples related to the oxidizing power of RuO_4 have also been demonstrated in the synthesis of ambraketal (**152**) and epiambraketal (**153**) from sclareol (**154**), which proceeded through the regioselective elimination of the ketoacetate (**155**) [262].



(**148**)



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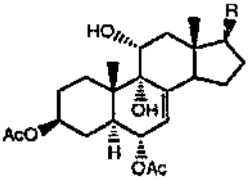
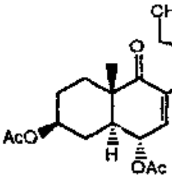


(**150**)

A highly efficient and mild synthetic pathway was developed for nitrones which involved the oxidation of N,N-disubstituted hydroxylamines by N-methylmorpholine-N-oxide and catalysed by $[^n\text{Pr}_4\text{N}][\text{RuO}_4]$. A competitive experiment in the presence of a primary alcohol gave a >50:1 nitrone to aldehyde ratio [263]. On the other hand, $RuO_2 \cdot 2H_2O$ in fluoro acidic medium has been used for the nonphenolic oxidative coupling of diarylbutanes. Along with the expected aryl-aryl coupling, an unusual aryl-benzyl coupling occurred, leading to a known class of ligands, the aryltetralins. Conformational studies of resultant *cis*- and *trans*-deoxyschizandrins were carried out using high resolution NMR spectroscopic techniques and molecular modelling [264].

A simple and convenient extractive spectrophotometric method for the determination of ruthenium was developed that was based on the oxidation of the different ruthenium(II, III or IV) species to perruthenate with potassium periodate at pH 7.8, followed by extraction with benzyltributylammonium chloride in chloroform [265].

Dioxoruthenium(VI) tetramesitylporphyrinate catalysed the epoxidation of (Z)-17-ethylideneandrostane (**156**) by dioxygen to give two isomeric 17,20-epoxides (**157**) and (**158**) as major products in a non-stereoselective process. The occurrence



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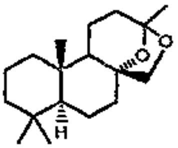

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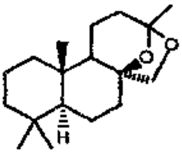

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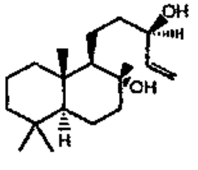

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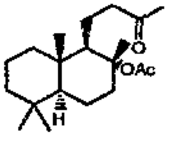
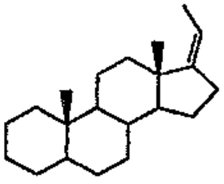


(155)

of a minor competitive pathway leading to isomeric olefins suggested the existence of a ruthenium(II) porphyrin intermediate during the oxidation [266].

The preparation and characterization of dioxoruthenium(VI) picket-fence complexes bearing optically active [α-methoxy-α-(trifluoromethyl)phenyl acetyl residues] (α,β,α,β (**159**) and α,α,β,β isomers) have been reported. Complex (**159**) oxidized racemic benzyl(methyl)(phenyl)phosphine to give optically active phosphine oxide (e.e. 41%) with retention of the configuration around the P atom [267].



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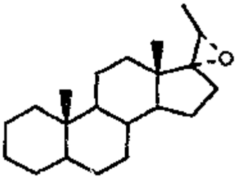

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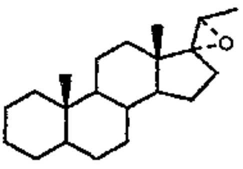
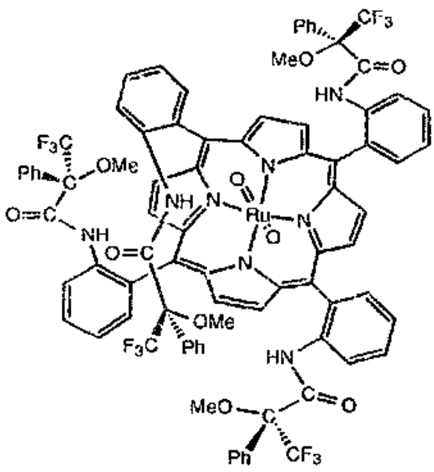


(158)

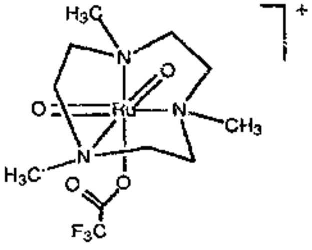
The electrooxidation of substituted benzyl alcohols by *trans*-$[Ru^V(tmc)(O)(NCO)]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) was studied in MeCN by rotating disk voltammetry. A mechanism involving hydrogen atom abstraction by the oxo ligand on the ruthenium complex was proposed on the basis of primary kinetic isotopic and Hammett plot analyses [268]. Furthermore, the kinetics of reduction of *trans*-$[Ru(TMC)O_2]^{2+}$ by iodide have been studied in aqueous acidic solution. The associated rate law was established and believed to proceed via a mechanism involving oxygen-atom transfer from Ru^{IV} to iodide [269]. Another tmc complex, $[Ru(tmc)O_2]^{2+}$, together with $[RuO_4]^-$, $[RuO_2Cl_3]^-$ and a number of oxometal species have been studied by electros-



(159)

pray tandem mass spectrometry; in each case the mass spectra obtained displayed the molecular ion as the base peak with a minimal degree of fragmentation [270].

The novel complex $[Ru(Me_3tacn)O_2(CF_3CO_2)]^+$ **(160)** has been synthesized by the reaction of $[Ru(Me_3tacn)Cl_3]$ with $AgCF_3SO_3$ in the presence of $(NH_4)_2[Ce(NO_3)_6]$ and was characterized by single crystal X-ray analysis. The complex catalysed alkene epoxidation and alkane hydroxylation by PhIO and Bu^tOOH respectively [271].



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The reduction of *trans*-$[Ru^{VI}(tpy)(O_2)(H_2O)]^{2+}$ or *trans*-$[Ru^{VI}(tpy)(O)_2(CH_3CN)]^{2+}$ by PPh_3, dppe or dppm occurred by successive Ru(VI)→Ru(IV) and Ru(IV)→Ru(II) oxygen atom transfer. The products subsequently underwent stepwise solvolysis to give the free diphosphine dioxides and $[Ru^{II}(tpy)(CH_3CN)_3]^{2+}$. Kinetics of the individual redox steps were studied by stopped flow/rapid scan spectroscopy [272].

Oxidation of water by Co^{3+} ion, as catalysed by $[(bpy)_2Ru(OH_2)]_2O^{4+}$, has been studied by the steady-state kinetic method. The results supported a mechanistic model in which a significant component of catalysis was activation of solvent water by hydrogen bonding to the bridging μ-oxo atom of the complex. Initial rates of O_2 evolution exhibited first-order dependence upon the catalyst concentration, indicating that the catalytic cyclic involved a single μ-oxo ion [273]. Comparisons have also been made between $[Ru_3O(O_2CCH_3)_3(py)_2(CO)]$, $[Ru_2O(O_2CCH_3)_2(py)_6](ClO_4)_2$, $[Fe_3O(O_2CCH_3)_6(py)_{3.5}]$ and $[Ru_3O(O_2CCH_3)_6(py)_3]$ on their catalytic properties towards cyclohexane oxygenation by O_2-zinc in pyridine-acetic acid solution. The former two complexes were more selective for alcohols whereas the latter two were more selective for ketones [274].

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