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COORDINATION CHEMISTRY REVIEWS

Ruthenium 1995

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Contents

1. Introduction

This review covers the coordination chemistry of ruthenium for 1995 and is based upon a search of volumes 122, 123 and 124 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched separately for the calendar year 1995. The metal complexes are classified according to the ligand type. Most of the organometallic ruthenium complexes are not covered in this article.

2. Complexes with hydrogen or hydride ligands

A new 16-electron Ru complex $[RuHX(H_2)(P^iPr_3)_2]$ (**1**) was isolated from the reaction of [Ru(COD)(COT)] with P^iPr_3, MeX (X = Cl, I) and hydrogen. The

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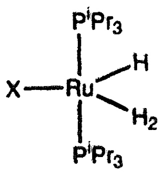
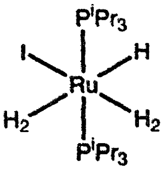
solution structures of the complexes were established by NMR spectroscopic analysis. Complex (**1**) (X = I) reacts with excess H_2 to give unstable $[RuHI(H_2)_2(P^iPr_3)_2]$ (**2**) [1].



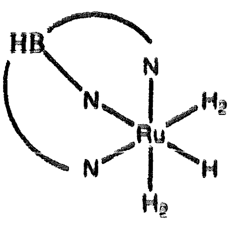
(**1**)



(**2**)

Hydrogenation of the cyclohexyl ring of $[RuH_2(H_2)_2(PCy_3)_2]$ with C_2H_4 generates a highly efficient catalyst for the selective dehydrogenative silylation of ethylene to vinylsilane $CH_2{=}CHSiEt_3$ [2].

Reaction of [RuHCl(COD)(bpm)] (bpm = bispyrazolylmethane) with various hydridotris(pyrazolyl)borate salts produces [RuLH(COD)] (**3**) (L = hydridotris-(3-isopropyl-4-bromopyrazolyl)borate or hydridotris(3,5-dimethylpyrazolyl)-borate). Hydrogenation of (**3**) in pentane yields $LRuH(H_2)_2$ (**4**) in high yield. Complex (**4**) was characterized by spectroscopic methods including T_1 measurements [3].



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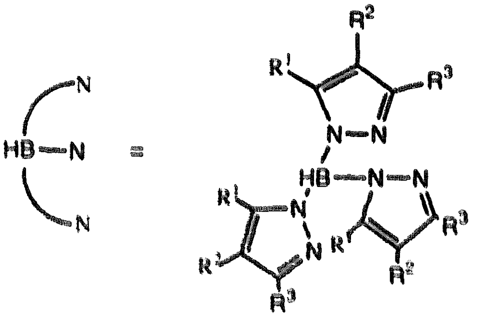


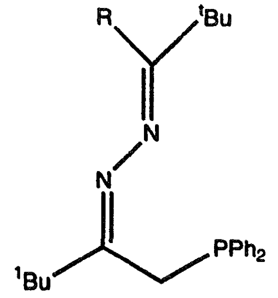
$R^1 = H$ $R^2 = Br$ $R^3 = {}^iPr$

$R^1 = Me$ $R^2 = H$ $R^3 = Me$

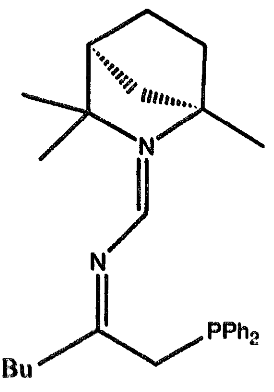
The catalytic activity of the system containing $[RuH_2(PPh_3)_4]$ and ferrocenylphosphines towards the cross coupling reaction of hydroxy allenes and 1-alkynes has been investigated [4]. The photochemical properties of the complexes $[RuL_2H_2]$ (L = depe, dppe or dfepe) have been studied by matrix isolation at 12 K and laser flash photolysis at ambient temperature. The kinetics of the reactions of the complexes with C_2H_4 were determined [5].

The geometries and relative stabilities of the classical and non-classical isomers of $M(PH_3)_3H_4$ (M = Fe, Ru, Os) have been studied using non-local, quasi-relativistic density functional methods and NL-SCF+QR calculations. According to energy calculations, the classical model is the isomer of lowest energy for Os whereas the nonclassical isomer is found to be more stable for Fe and Ru [6].

A general method of generating agostic interactions between Ru(II) and C–H bonds of *tert*-butyl, methyl, aryl, heterocyclic or alkenyl groups using azine phosphine ligands has been reported. The agostic interactions in the complexes $[RuL(PPh_3)Cl]$ (L = (5)-(9)) have been studied by ^1H, ^{13}C and ^{31}P NMR spectroscopies [7].



R = Me (5)
= H (6)
= CH_2PPh_2 (7)



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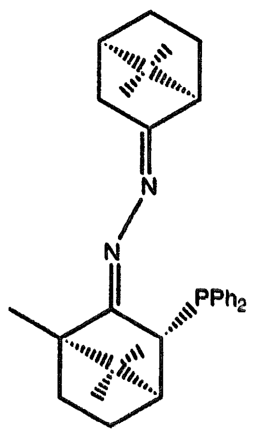


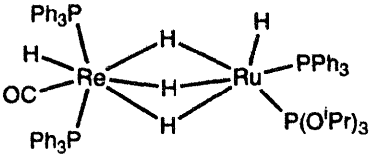
(9)

The reactions of $[Ru(acac)_3]$ with trioctylphosphine and phosphate esters give $[RuH(H_2)(PR_3)_3S]X$ or $[RuH(PR_3)_3S_2]X$ (S = Solvent). The complexes were used to catalyse the hydrogenation of succinic anhydride to butane-1,4-diol [8].

The complex $K[H_6ReL_2]$ reacts with $[RuHCl(CO)(PPh_3)_{3-x}\{P(O^iPr)_3\}_x]$ to give $[L_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_{2-y}\{P(O^iPr)_3\}_y]$ (10) (L_2 = $(PMePh_2)_2$, dppe, $(AsPh_3)_2$ or $(PPh_3)_2$; x = 0 or 1 y = 0, x = 2, y = 1). The molecular structure of $[(PMePh_2)_2(CO)Re(\mu\text{-}H)_3Ru(PPh_3)_3]$ was established by X-ray structure analysis [9]. The hydridoruthenium complexes $[RuH_2(PPh_3)_4]$ and $[RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)]$ were found to be effective in catalysing the Aldol condensation and Michael reactions of nitriles with carbonyl compounds and olefins respectively in high chemo- and stereoselectivities. Kinetic and mechanistic studies for the reactions have been described [10].

3. Complexes with halide or pseudo-halide ligands

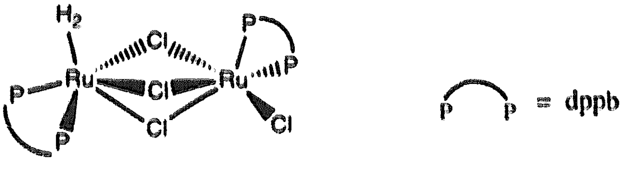
The dinuclear complexes $[RuCl(EPh_3)_2(\beta dk)]_2$ (E = P or As, βdk = β-diketonate) were prepared and characterized by elemental analyses, IR, ^1H NMR and electronic spectral data [11].



(10)

A simple catalytic system for the oxidation of nitrobenzene, chlorobenzenes and chlorophenols using $RuCl_3$, $[Ru(H_2O)_2L_4](BF_4)_2$ or $[RuCl_2L_4]$ (L = DMSO) and monopersulfate has been described. A kinetic and mechanistic study has been carried out. It was found that phenol and polychlorophenols were more sensitive to oxidation than substituted benzenes [12].

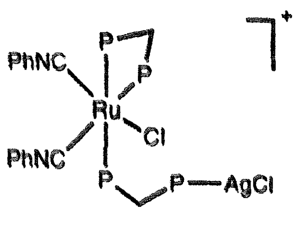
The kinetics and mechanism of H_2-hydrogenation of styrene catalysed by $[RuCl(dppb)(\mu\text{-}Cl)]_2$ (**11**) in DMF have been studied. Evidence for the formation of dinuclear molecular hydrogen complex $[Ru(\eta^2\text{-}H_2)(dppb)(\mu\text{-}Cl)_3RuCl(dppb)]$ (**12**) as intermediate was obtained from NMR spectroscopic and tensiometric analysis [13]. Reactions of benzylamine with (**11**) yielded $[Ru_2Cl_4(dppb)_2(NH_2CH_2Ph)]$ (**13**). Dehydrogenation of (**13**) gives a coordinated imine which readily hydrolyzed to give a coordinated dealkylated amine and a free aldehyde [14].



(12)

The synthesis and spectroscopic characterization of the neutral and cationic ruthenium(II) complexes *cis,cis,trans*-$[RuCl_2(CNPh)_2(dppm\text{-}P)_2]$ (**14**), *mer*-$[RuCl(CNR)_3(dppm)Cl$ (R = Ph, ^tBu) and $[RuCl(CNPh)_2(dppm)(dppm\text{-}P)]PF_6$ were reported. Treatment of (**14**) with $AgClO_4$ and $HgCl_2$ gives the heterodimetallic complexes $[(dppm)(PhNC)_2ClRu(\mu\text{-}dppm)AgCl]ClO_4$ (**15**) and $[\{(dppm)(PhNC)_2ClRu(\mu\text{-}dppm)HgCl_2\}_2]Cl_2$ (**16**), respectively [15].

The crystal structure of $[Ru_2Cl\{Me_2SO\}_5(\mu\text{-}Cl)_3]$ (**17**) and



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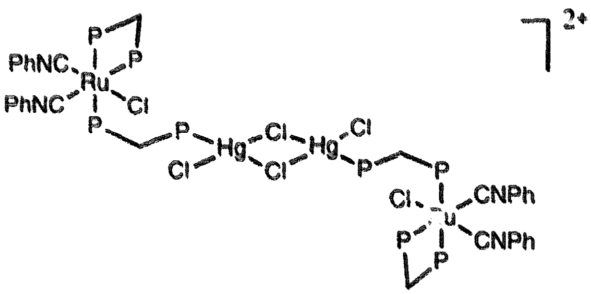
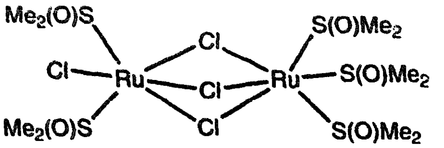


(16)

trans-$(Et_4N)[RuCl_4(MeCN)_2]$ (**18**) have been established by X-ray crystallographic studies [16,17].



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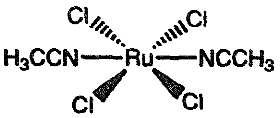
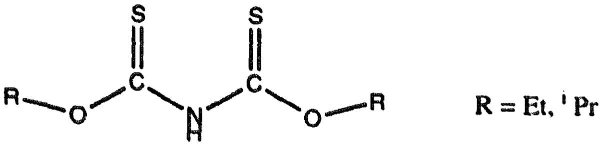


(18)

The synthesis and characterization of the complexes $[RuX_2(EPh_3)_2]_2Se(C_5H_6O_2)_2$ and $[RuX_2(EPh_3)_2L]$ ($X = Cl$ or Br; $E = P$ or As; $L =$ imidodi(thiocarbonic acid-*O*-alkyl ester, alkyl = Et, ^iPr (**19**)) have been described. An octahedral geometry was proposed for all complexes [18].

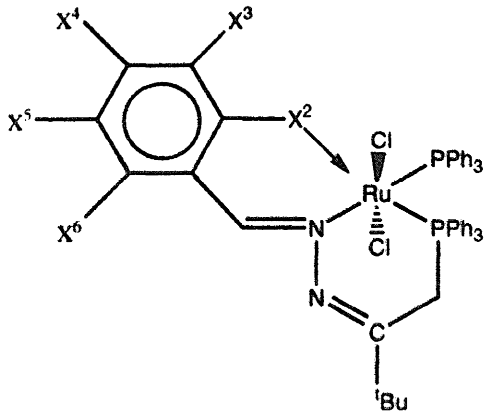


(19)

The reaction of F_2 with $AgMF_6$ (M = Ir, Ru, Sb, Bi) produces the salt $AgF^+MF_6^-$. Three structural form of $AgF^+MF_6^-$ have been identified. The fluoride coordination of Ag(II) in $AgF^+RuF_6^-$ is roughly square. It was found that the paramagnetism of the $AgF^+MF_6^-$ salt is temperature-independent whereas $Ag(MF_6^-)_2$ obeys the Curie–Weiss Law [19].

A systematic method of promoting aryl fluoride coordination to ruthenium(II) in complexes (**20**)–(**24**) was reported. The interaction has been studied by ^{19}F NMR and ^{31}P NMR spectroscopies [20]. Two novel complexes $[RuH_3(Si(OEt)_3(PPh_3)_2]$ and $[Ru\{Si(OEt)_3\}_2(PPh_3)_2]$ were found to be regioselective catalysts for the cyclopropanation of activated olefins in high yields [21]. Living radical polymerization of methyl methacrylate is achieved using an initiating system containing $[RuCl_2(PPh_3)_3]$, CCl_4 and methylaluminum bis(2,6-di-*tert*-butylphenoxide). The living nature of the polymerization was demonstrated by a monomer-addition experiment [22]. Highly selective redistribution and the desilanative condensation of disilylbenzene to poly(dihydrosilylene)phenylenes was catalysed by $[RuCl_2\{P(C_6H_4Me\text{-}p)_3\}_3]$ [23].

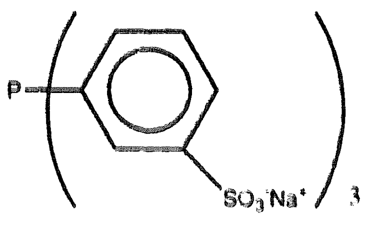
Catalytic hydrosilylation of C=C bonds in alkenes in the presence of $[RuCl_2(PPh_3)_3]$, oxygen and alkoxy-substituted silanes was reported. The characterization of the isolated intermediates from a $RuCl_2(PPh_3)_3\text{-}HSi(OEt)_3$ system was reported and a general mechanism for the hydrosilylation of alkenes was discussed [24]. A new method for the synthesis of lactones by liquid phase homogeneous catalytic hydrogenation of saturated or unsaturated dicarboxylic and anhydride in the presence of $[Ru(PPh_3)_3Cl_2]$ and diphosphine complexes such as 1,1′-bis(diphenyl-



X^2	X^3	X^4	X^5	X^6	
F	H	H	H	F	**(20)**
F	F	F	F	F	**(21)**
Cl	H	H	H	F	**(22)**
F	H	H	H	H	**(23)**
F	F	H	H	H	**(24)**

phosphino)ferrocene, BINAP or 1-[1,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate has been described [25,26].

The water soluble complex $[RuCl_2L_3]$ (**25**) has been synthesized from $RuCl_3$ and L (Na_3L = (**26**)). The formation of the complex in aqueous solution was followed by ^{31}P NMR spectroscopy [27]. The catalytic activity of (**25**) for selective hydrogenation of α,β-unsaturated aldehydes in the presence of surfactant has also been reported and was compared with that of $[RuCl_2(CO)_2L_2]$ [28].



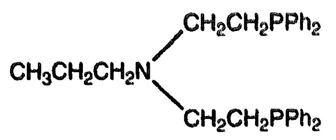
(26)

Time-resolved temperature-dependent laser-induced optoacoustic techniques were used to determine volume changes associated with the intramolecular electron transfer of the complexes $[Ru(bpy)(CN)_4]^{2-}$, $[Ru(bpy)(CN)_3(MeCN)]^-$ and $[Ru(bpy)(CN)_2(MeCN)_2]$. A correlation between the number of cyano ligands and the solvent effect on the MLCT energy of the complexes has been obtained [29]. The remote shielding effect of the cyano ligand in the ^1H NMR spectra of the complexes $[Ru(L)(CN)_4]^{2-}$, $[RuL_2(CN)_2]$ (L = bpy, 4,4′-dimethylbipyridine and 5,5′-dimethylbipyridine) was studied. It was shown that remote shielding by CN^- induces a downfield shift of the proton which is located above it [30]. The isocyanate bridged complexes $[Cp_2Ti(\mu\text{-NCS})_2RuCl(PPh_3)_2]Cl$ and $[Cp_2Ti(\mu\text{-NCS})_2RuCl(DMSO)_2]$ have been synthesized and characterized by spectroscopic methods [31].

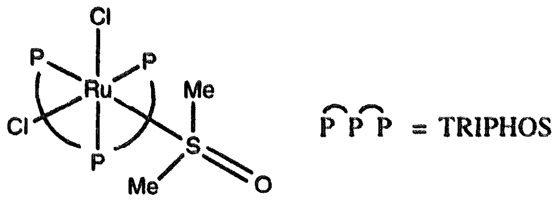
The reaction of $[MCl_6]^{2-}$ (M = Ru, Os) with $SnCl_2$ in HCl was studied by ESR spectroscopy. The ligand field parameters of the complex $[M(SnCl_3)_2Cl_4]^{3-}$ were determined from ESR spectroscopic data [32].

4. Complexes with phosphorus donor ligands

The structure of [$RuCl_2(PPh_3)L$] (L = (**27**)) has been determined by single crystal X-ray crystallography. The ruthenium metal centre is pseudo-octahedrally coordinated by a meridonal tridentate ligand (**27**) [33]. The complex [$RuCl_2$(TRIPHOS)(DMSO)] (**28**) has been synthesized and characterized. Its X-ray structure shows a slightly distorted octahedral geometry with a TRIPHOS ligand occupying three coordination positions in a facial arrangement [34]. In addition, X-ray powder diffraction data for (**28**) was obtained [35].



(**27**)

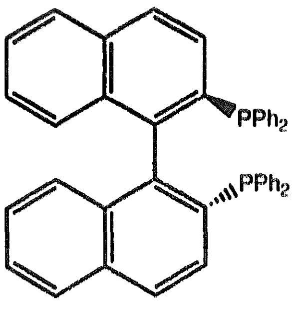


(**28**)

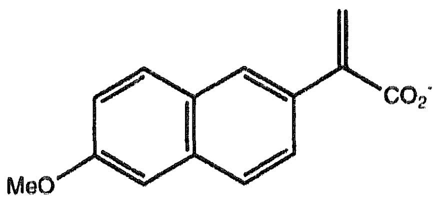
Two new chiral tripodal ligands $MeSi(CH_2PPh_2)_3$ and $BuSn(CH_2PPh_2)_3$ (generally abbrviated to tripod) and their Rh(I) complexes of the type [Ru(NBD)(tripod)][OTf] (NBD = norbornadiene) and Ru(II) complexes of the type [$Ru(O_2CCF_3)_2$(tripod)] were synthesized. The coordination chemistry of ruthenium(II) complexes indicated that the Sn-tripod ligand displays an enhanced steric bulk and is not able to stabilize the mononuclear five coordinate dichloro complexes [36].

The reduction of [$Ru(acac)_3$] with activated Zn in the presence of (*S*)-BINAP (**29**) gives [$Ru(acac)_2$(*S*-BINAP)] (**30**) in quantitatively yield. The solid state structure of (**30**) has been established by an X-ray diffraction study. Complex (**30**) was used to catalyse the asymmetric hydrogenation of 2-(6′-methoxy-2′-naphthyl)acrylic acid (**31**) to (*S*)-naproxen (**32**) in high optical purity [37]. The mechanism of (BINAP)Ru-catalysed asymmetric hydrogenation of vinyl carboxylic acid has been investigated via detailed deuterium labelling studies. The activation of H_2 by the catalyst was found to be via a heterolytic splitting route. A unified mechanism which was consistent with the experimental results was also proposed [38].

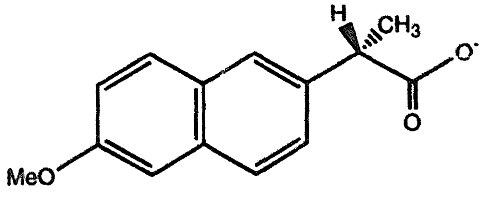
The preparations of optically active 4-methyl-2-oxetanone via the asymmetric



(**29**)

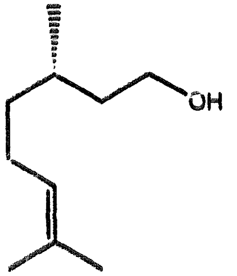


(**31**)



(32)

hydrogenation of 4-methylene-2-oxetanone by [Ru_2Cl_4{(+)-BINAP}$_2$] [39] and [Ru_2Cl_4{(−)-Tol-BINAP}$_2$(NEt_3)] (Tol-BINAP = 2,2′-bis[di(*p*-tolyl)phosphino-1,1′-binaphthyl]) have been reported [40]. A striking inversion in enantioselectivity from 85% ee in the formation of (*S*)-citronenol (**33**) and 40% ee in the formation of (*R*)-citronenol was observed from the asymmetric homogeneous hydrogenation of the allylic alcohol geraniol (**34**) with [$RuCl_2$((*S*)-(−)-Tol-BINAP)]$_2$ as catalyst. The factors in directing the ultimate enantioselectively achieved in the hydrogenation reaction have been discussed [41].



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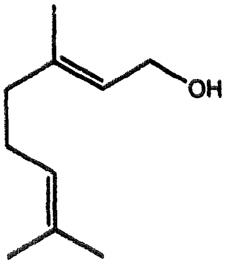
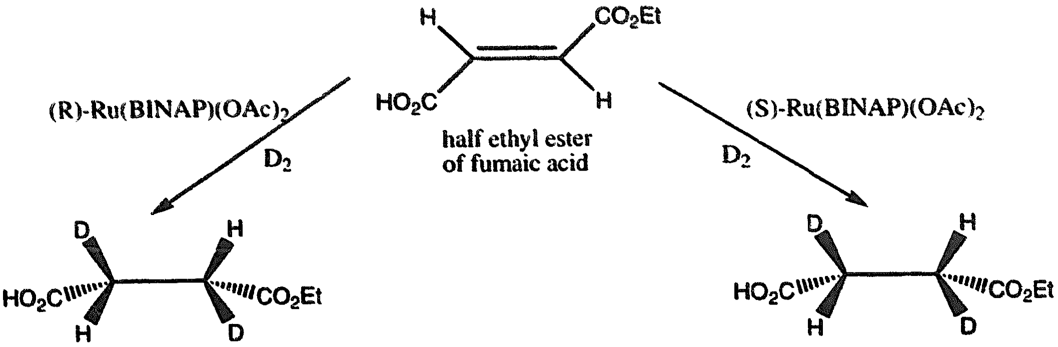


(34)

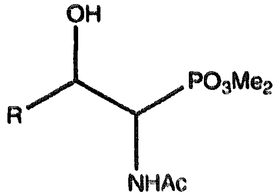
The compounds (2*R*, 3*R*) and (2*S*, 3*S*) dideuteriosuccinic acid were prepared in 63 ± 10% ee by the catalytic reduction of the half acid ester of fumaric acid by (*R*)- and (*S*)- BINAP ruthenium(II) acetate respectively (Scheme 1). The compounds were identified by ^1H and ^{13}C NMR and CD spectra [42]. The complexes [Ru(OAc)$_2${(*R*)-BINAP}] and [RhI(COD)$_2$] catalyse the hydrogenation of 1,1-disubstituted unfunctionalized olefins in 71–82% ee. The enantioselectivity of the ruthenium catalyst exhibited a remarkable dependence on solvents. The mechanistic aspects of the asymmetric hydrogenation have been discussed [43].

Cyclic α,β-unsaturated ketones, alkylidene, lactones and alkenyl ethers have been hydrogenated in high ee by use of [RuCl(BINAP)(benzene)]Cl, Ru_2Cl_4(BINAP)$_2$(NEt_3) or Ru(OAc)$_2$(BINAP) [44]. A new catalyst system consisting of RuCl[(*S*)-BINAP](DMF)$_n$ (*S*)-diamine and KOH effects facile hydrogenation of alkyl aryl ketones to give corresponding alcohols in near 100% yield and in 97% ee [45]. The ruthenium(II) complex of BINAP was proven to be an effective catalyst in the hydrogenation of configurationally labile α-acetamido β-keto phosphonic esters (**35**) in a highly enantio- and diastereoselective manner via dynamic kinetic resolution [46]. The reaction of the five-coordinate complex [$RuCl_2$(PPh_3){(*S*)-BINAP}] ((*S*)-BINAP = (**36**)) with pentane-2,4-dione has been



Scheme 1.

reported. The relevance of this reaction to the enantioselective hydrogenation of 2,6-diketone was studied [47].



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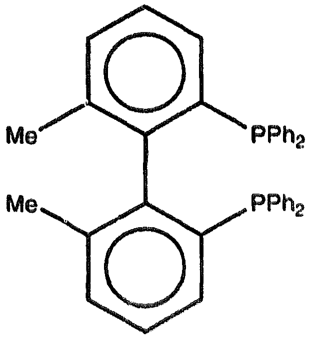
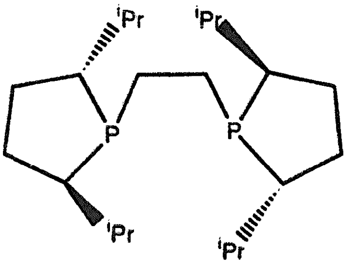


(36)

The preparation of $[Ru(PP)(RCN)_4]^{2+}$ (PP=dppb, R=Me, Ph) (37) from the ruthenium (II) precursors $Ru_2Cl_4(PP)_2$ and $RuCl_2(PP)(PPh_3)$ has been reported. The molecular structure of (37) suggested that the nitrile ligands function solely as σ-donors in these complexes [48]. The complexes $[Ru(OAc)_2(PPh_3)_nL_{2-n}]$ (n=1,0, L=dppe, dppm) have been prepared from $[Ru(OAc)_2(PPh_3)_2]$ and the corresponding diphosphine. The solution dynamics of these complexes have been studied by variable temperature ^{31}P NMR spectroscopy. The catalytic activity of these complexes for the selective hydrogenation of acrylic acid and styrene has been investigated [49,50].

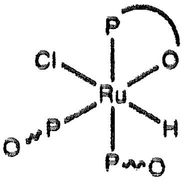
Asymmetric hydrogenation of β-keto esters was catalysed by $RuBr_2L$ (L=(38)) to give a variety of β-hydroxy esters with enantioselectivities of 98–99% ee. Enantiomerically pure β-hydroxy esters are the key intermediates in the synthesis of chiral phospholane ligands [51]. Nucleophilic addition of $RuCl_2(PPh_3)_3$ to dppen in the presence of NH_2R afforded the diphosphine complex $[RuCl_2\{(Ph_2P)_2CHCH_2NHR\}_2]$ (39) (R=n-octyl, $PhCH_2$, *R*-PhCHMe, $H_2N(CH_2)_3$) suitable for surface anchoring. A novel method for oxide surface modification using the electrochemistry of a coordinated phosphine was developed.

The extent of coverage of (**39**) anchored to In-doped tin oxide (ITO) was determined by using cyclic voltammetry [52].

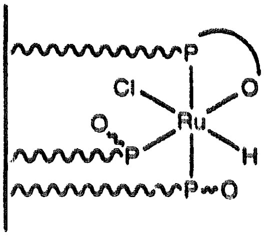


(**38**)

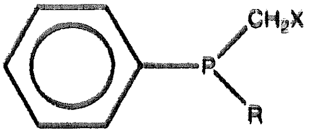
The monomeric ruthenium complex $[RuHCl(P{\sim}O)_2(PO)]$ (**40**) ($P{\sim}O = \eta^1$-P coordinated; $PO = \eta^2$-P coordinated) has been isolated from the reaction of $HRuCl(PPh_3)_3$ and ether-phosphine ligands. The polysiloxane bound ruthenium complexes (**41**) were prepared according the 'sol-gel' process in the presence of water and NEt_3. Solid state ^{29}Si CP-MAS NMR spectroscopy was used to establish a highly cross-linked polysiloxane matrix in the complex [53].



(**40**)



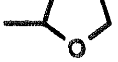
(**41**)



R = Ph, $CH_2CH_2CH_2Si(Si(OMe)_3$,

$CH_2CH_2CH_2SiO_{n/2}(OH)_{3-n}$

X = $-CH_2OCH_3$

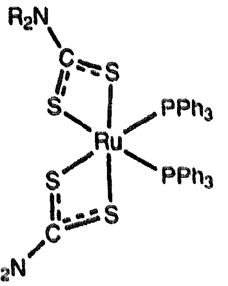


The chemical behaviour of the octahedrally coordinated bis(chelate)ruthenium(II) complexes $[Cl_2Ru(PO)_2]$ ($PO = Ph_2PCH_2CH_2OCH_3$, $Ph_2PCH_2C_4H_7O_2$, $PCy_2CH_2CH_2OCH_3$) having two pseudo-vacant coordination sites toward a wide variety of small molecules have been studied. A facile cleavage of one or both ruthenium-oxygen bonds is achieved by reaction with small molecules such as sulfur dioxide, carbon disulfide, acetonitrile, phenylacetylene and isocyanide. The fluxional behaviour of a variety of substrate complexes in solution was investigated by temperature-dependent ^{31}P NMR spectroscopy. All exchange phenomena are coupled with the 'opening and closing' mechanism of the ether-phosphines employed [54].

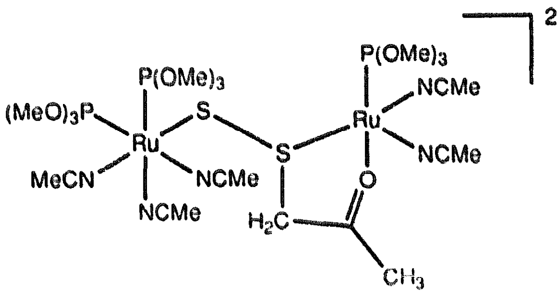
Reactions of $RuCl_2(PPh_3)_3$ with 1, 2 or 3 equivalents of $Ph_2PCH_2C(O)Ph$, (L), afforded selectively *trans,trans*-$[RuCl_2L(PPh_3)_3]$ (**42**) *trans,cis,cis*-$[RuCl_2L_2]$ (**43**) or *trans,mer*-$[RuCl_2L_3]$ (**44**). The products obtained from further reactions of (**44**) under various conditions included *trans,cis,cis*-[$RuL_2(NCMe_2)](PF_6)_2$ (**45**) or *mer*-[$RuClL_3]PF_6$ (**46**), *fac* and *mer*-isomers of Na[Ru{$Ph_2PCHC(O)PPh_3$}] (**47a, 47b**) [Na(15-crown-5)(H_2O)[*mer*-Ru{$PhP_2CHC(O)Ph$}$_3$]·THF (**48**), *mer*-[Ru{$Ph_2PCHC(O)Ph$}$_2$L] (**49**), *mer*-[$RuL_3][BF_4]_2$ (**50**) and *mer,trans*-[$RuCl_3L_2$] (**51**). The solid state structures of (**43**), (**45**) and (**48**) have been established by single-crystal X-ray analysis. The fluxional behaviour of (**44**) in solution was studied by ^1H NMR spectroscopy at various temperatures [55].

5. Complexes with sulfur donor ligands

The complex [$Ru(PPh_3)_2L_2$] (**52**) ($L = S_2CNEt_2$) has been isolated from the reaction of *cis*-[$RuCl_2(PPh_3)_2$] with Na[S_2CNEt_2]. Oxidation of (**52**) by Ce(IV) furnished paramagnetic *trans*-[$RuL_2(PPh_3)_2]^+$ (**53**). Variable temperature voltammetric studies have been employed to study the electrode reactions of (**52**) and (**53**) [56]



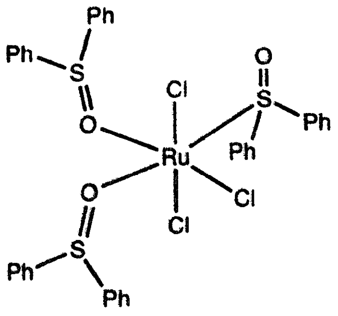
(**52**)



(**55**)

A novel C-S bond formation was observed in the reaction of [{Ru(NCMe)$_3${P(OMe)$_3$}$_2$}$_2$(μ_1-S_2)]$^{4+}$ (**54**) with acetone which leads to the formation of [{Ru(NCMe)$_2$(P(OMe)$_3$)$_2$}(μ-S_2CH_2COMe){Ru(NCMe)$_2$(P(OMe)$_3$)$_2$}]-$(CF_3SO_3)_3 \cdot 0.5Me_2CO$ containing cation (**55**). The crystal structure of (**55**) was established by single-crystal X-ray diffraction studies. The carbonyl oxygen atom in (**55**) coordinated to one of the ruthenium atom to form a RuOCCS five-membered ring [57]. The complex [$RuCl_3(dpso)_3$] (dpso = Ph_2SO) (**56**) was synthesized and structurally characterized. Two of the sulfoxides are O-bonded and the remaining one is S-bonded. The bond distances are consistent with the order of *trans*-influence. The strain energies and conformational entropies of the three isomers of (**56**) have been investigated using molecular mechanics calculations [58].

The 16-electron complex [Ru(NO)'$^{Bu}S_5'$] (**57**) ($^{Bu}S_5^{2-}$ = 2,2′-bis(2-mercapto-3,5-di-*tert*-butylphenylthio)diethylsulfide) has been isolated from the reaction of [$RuCl_3(NO)(PPh_3)_2$] with $^{Bu}S_5^{2-}$. Alkylation of (**57**) with bis(β-bromoethyl)-sulfide afforded *meso*-[Ru(NO)($^{Bu}S_5$)]Br (**58**) stereoselectively. Compound (**58**) reacts with $LiBEt_3H$ to yield (**59**) with Ru($^{Bu}S_5$)-Ru(NO)($^{Bu}S_2$)($^{Bu}S_2$-C_2H_4SH) as a byproduct. Reaction of (**59**) with σ–π- and σ-ligands such as CO, PMe_3, PPh_3, PCy_3, py, CN^-, NH_2NHPh, NH_2NHMe, NH_2NMe, NH_2Ph and $NHEt_2$ leads to the mononuclear complexes (**60**). However, insoluble polymeric complexes [RuL($^{Bu}S_5$)]$_x$ were isolated from the reactions of (**59**) with NH_3 and N_2H_4 [59].



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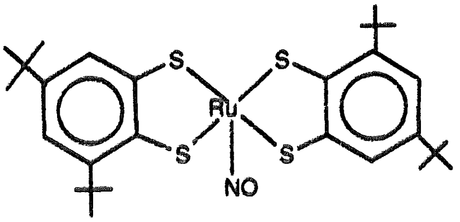

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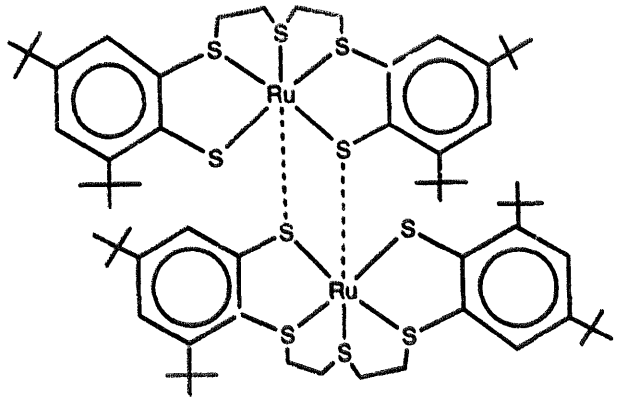

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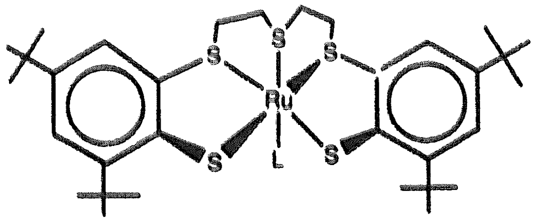
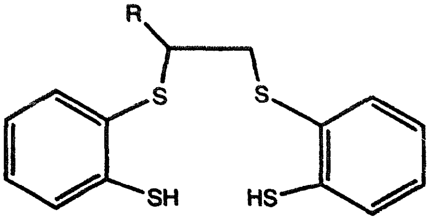


L = CO, PMe_3, PCy_3, py, CN^-
NH_2NHPh, NH_2NHMe, NH_2NMe
NH_2Ph, $NHEt_2$

(60)

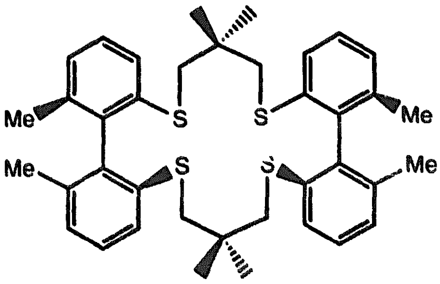
A series of ruthenium(II) complexes with chiral thioether thiolate ligands RS_2-H_4 (**61**) have been prepared and structurally characterized by X-ray crystallography. The metal centres are surrounded pseudo-octahedrally by four S donors and two other ligands in a *cis*-configuration. The reactivities of the complexes towards the achiral substrates CO and PMe_3 and the optically pure diphosphine (+)2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane have been studied [60]. A new optically active doubly helical 18-membered quadridentate crown thioethers (**62**) was prepared. The reaction of $K_2[RuCl_5(H_2O)]$ with (**62**) gives *trans*-$RuCl_2L$ (L = (**62**)). The asymmetric hydrosilylation of PhCOMe in the presence of a catalyst prepared from $[RuCl(C_8H_{12})_2]_2$ and (**62**) was achieved [61].

A series of ruthenium complexes with a $RuPS_2N_2$ core, *viz* $[Ru(PPr_3)_2(S_2N_2H_2)]$ (**63**) ($S_2N_2H_2$ = 1,2-ethanediamine-*N*,*N'*-bis(2-benzenethiolate), $[Ru(CO)(PPr)_3$-



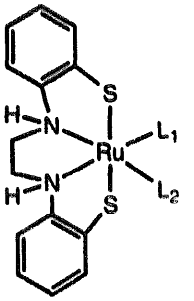
R = Me, $CH_3(CH_2)_2$, $(CH_2)_9OH$, CH_2Ph

(61)



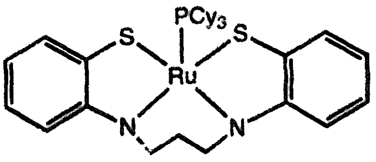
(62)

$(S_2N_2H_2)]$ (**64**), $[Ru(CO)(PCy_3)(S_2N_2H_2)]$ (**65**), $[Ru(PCy_3)(S_2N_2)]$ (**66**) (S_2N_2 = 1,2-ethanediamide-*N*,*N'*-bis(2-benzenethiolate), $[RuBr(PPh_3)(Et_2S_2N_2H_2)]$-Br (**67**) ($Et_2S_2N_2H_2$ = 1,10-diethyl-2,3,8,9-dibenzo-1,10-dithia-4,7-diazadecane) and $[RuBr(PPh_3)(PhCH_2)_3(S_2N_2H_2)]Br$ (**68**) ($(PhCH_2)_3S_2N_2H_2$ = 1,10-dibenzyl-2,3,8,9-dibenzo-1,10,dithia-4,7-diazadecane), have been prepared. The conversions of the coordinatively unsaturated Ru(IV) complex, (**66**), to (**65**) by reaction with formic acid or to $[Ru(PMe_3)_2(gma)]$ by reaction with PMe_3 have also been discussed (gma = (**69**)) [62].



$L_1 = L_2 = PPr_3$ (**63**)
$L_1 = PPr_3$; $L_2 = CO$ (**64**)
$L_1 = PCy_3$, $L_2 = CO$ (**65**)

Treatment of $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ and $[RuHCl(CS)(PPh_3)_3]$ with 1,4,7-triazacyclononane yields $[RuX(CS)(PPh_3)([9]aneS_3)]$ (**70**) (X = H, Cl). Reaction of (**70**) with $K[4\text{-}SC_6H_4Me]$ and KSCN replaced H or Cl by thiolate or SCN^- respectively but reaction with NaN_3 yields $[RuCl(NCS)(PPh_3)([9]aneS_3)]$ [63]. It has been shown that *cis*-$RuCl_2L$ (L = $Me_8[16]aneS_4$, $Me_6[15]aneS_4$) reacts with an excess of $NaBH_4$ to give *trans*-$RuH(\eta^1\text{-}BH_4)L$. (L = $Me_8[16]aneS_4$ (**71**),



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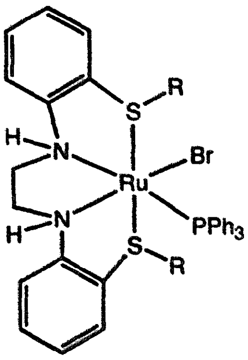
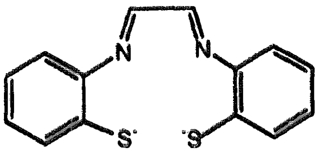


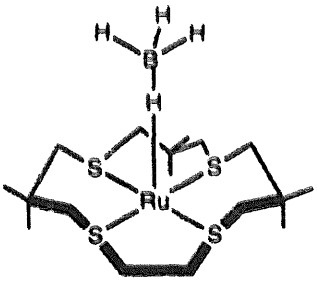
R = Et **(67)**

R = PhCH$_2$ **(68)**



(69)

L = Me$_6$[15]aneS$_4$ (**72**). Reaction of (**71**) with oxygen in the presence of MeOH and EtOH yielded *trans*-[Ru(OR)$_2$(anti-Me$_8$[16]aneS$_4$)]$^+$ (R = Me, Et) (**73**). The structures of (**72**) and (**73**) were obtained by X-ray crystallographic studies [64].



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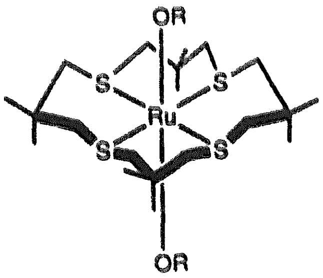


(73)

The ruthenium(II) mixed ligand complexes [RuL(2-Spy)$_2$] and [RuL(2-SpyO)$_2$] (L = dppm, dppe, dppp, dppb, triphos; Spy = 2-pyridinethione, SpyO = 1-oxopyridine-2-thione) have been prepared either from RuL$_2$Cl$_2$ and Spy or RuCl$_2$(PPh$_3$)$_3$ and SpyO. The complexes were characterized using IR, UV–VIS, ^{1}H and ^{13}C NMR spectroscopies, cyclic voltammetry and microanalysis [65].

A new method for the preparation of RuS$_2$ nanocrystallites has been reported. Optical measurements suggested the suitability of this material for semiconductor sensitization experiments [66]. The interaction of ammonia with the surface of RuS$_2$ catalyst has been investigated using conventional absorption measurements and inelastic neutron scattering [67].

6. Complexes with nitrogen donor ligands

6.1. Complexes with 2,2'-bipyridine ligands

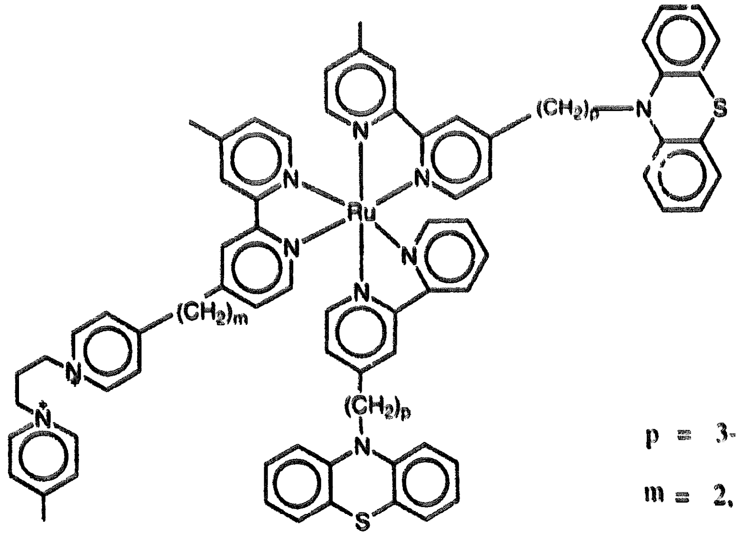
The luminescence quenching of $[Ru(bpy)_3]^{2+}$ by $[Co(phen)_3]^{2+}$ in various locations in and on Bentolite-H clay has been discussed [68]. The quenching of the excited states of $[Ru(bpy)_3]^{2+}$ in a series of aqueous solutions with different proton concentrations has been investigated by laser flash photolysis and time-resolved near IR-emission spectrophotometry. The quantum yield of the oxidized complex was shown to be dependent on the proton concentration in the solution [69].

Two different spectroscopic sites (A and B) of $[Ru(bpy)_3]^{2+}$ were identified in the emission of near single crystals $[Ru(bpy)_3](PF_6)_2$. The emission lifetime of site B is shorter than that of A by a factor of about 4000 and is determined by the radiationless energy transfer to the lower energy site A [70]. The bimolecular oxidative quenching of excited $[Ru(bpy)_3]^{2+}$ by methylviologen and the electron transfer recombination reaction of the redox products in aqueous solution have been studied. The relationship between the rate constant, ionic strength and temperature has been discussed [71]. The magnetic field dependence of the cage escape yield of radicals generated by the photoelectron transfer between $[Ru(bpy)_3]^{2+}$ and methylviologen for a series of solvent mixtures of increasing viscosity has been investigated. The absolute values of the rate parameters characterizing the primary radical ion pair have also been obtained [72].

Lattice energy minimization techniques were used to study the 2-dimensional molecular organization of a monolayer of $[Ru(bpy)_3]^{2+}$ confined into a smectite clay. The reported effect of chirality on the adsorption capacity was rationalized [73]. The photophysics of the complex $[Ru(bpy)_3]^{2+}$ bound to hydrophobically modified α-zirconium phosphate has been examined. The excited state lifetime and the emission yield observed were much longer/larger than that observed with $[Ru(bpy)_3]^{2+}$ in other heterogeneous media [74]. The oxidation luminescence quenching of $[Ru(bpy)_3]^{2+}$ by various quenchers was investigated in homogeneous solutions and in sodium dodecylsulfate (SDS) micelles. The intramicellar quenching rate constants were obtained and were compared with those in homogeneous solutions [75].

The mechanisms of the radiative ^{3}MLCT-based transition of $[Ru(bpy)_3]^{2+}$ produced by alkali halide in water have been discussed [76]. The mass transport processes in the redox reactions of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ in a clay modified electrode were studied by the quartz crystal microbalance method [77]. A series of polymer-immobilized luminescent transition metal complex systems with $[Ru(bpy)_3]^{2+}$ as chromophore, and gels made of different molar ratios of poly-2-hydroxyethylmethacrylate and its monomer were prepared [78]. The oxidation of water to dioxygen by $[Ru(bpy)_3]^{2+}$ entrapped within supercages of zeolite Y has been reported. The mechanism of the reaction was investigated using diffuse reflectance, resonance Raman and ESR spectroscopies [79].

The charge transfer between $Ru(bpy)_3^{2+}$ complexes incorporated into a Nafion membrane was studied using *in situ* spectrocyclic voltammetry and statistical calculations [80]. The effects on the properties of the adsorbed [Ru(bpy$_3$)]$^{2+}$ and methylviologen ions in Nafion layers were studied by exposure of the thin Nafion layers to 300 kV electron-beam irradiation. Irradiation both in the presence and in the absence of the adsorbents showed a pronounced effect on slowing charge migration rates and induces a red shift in the [Ru(bpy)$_3$]$^{2+}$ emission band [81]. The oscillatory behaviour of a [Ru(bpy)$_3$]$^{2+}$ catalysed bromomalonic acid/bromate Belousov–Zhabotinskii system has been studied. Two different negative feedback loops are involved [82]. Fluorescence microscopic studies of the cerium-catalysed Belousov–Zhabotinskii reaction involving [Ru(bpy)$_3$]$^{2+}$ monolayers have been performed. Spatial patterns are found to evolve with time as propagating dark waves in response to oscillatory chemical reactions [83]. In addition, the phase relationship between oscillatory fluorescence radiation of the [Ru(bpy)$_3$]$^{2+}$ catalysed Belousov–Zhabotinoskii reaction was investigated [84]. The first observation of a proton-coupled photoinduced electron transfer within a donor-acceptor pair [Ru(bpy)$_3$]$^{2+}$-3,5-dinitrobenzene juxtaposed by a salt bridged was presented. The influence of proton motion on the rate of electrons transfer through the salt bridge was revealed by deuterium isotope effect of $k_H/k_D = 1.34$ [85]. A series of donor chromophore-acceptor molecules (74) was prepared and the intramolecular electron transfer rates were obtained by time resolved absorption studies. It was found that the back electron transfer rate is independent of the methylene chain length. The results suggested the formation of an association complex during the oxidative quenching of the MLCT state [86].



p = 3-8

m = 2, 3 or 4

(74)

The catalytic hydrogenation of CO$_2$ to HCO$_2$H by the complex *cis*-[Ru(6,6′-Clbpy)$_2$(H$_2$O)$_2$] in the presence of NEt$_3$ has been investigated. It was found that the turnover number is much lower in the absence of NEt$_3$ [87]. The kinetics and mechanism of the photo-oxidation and the photoreduction of [Ru(bpy)$_2$Cl$_2$]$^{0/+}$ have been examined [88]. The photophysical properties of

$[Ru(bpy)_3]Cl_2$ entrapped within monoliteric SiO_2 gels in the presence or absence of methylviologen have been reported. The kinetics and cage escape efficiencies are similar to those observed in fluid solution [89].

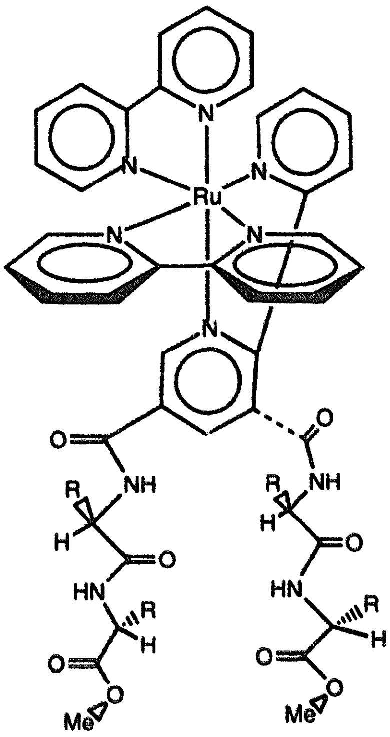
The solvent coordinated Ru(II) complex ions created by photodissociation of $[Ru(bpy)_3]X_2$ (X = Cl, ClO_4) and $[Ru(bpz)_3]Cl_2$ in acetonitrile solution were directly detected by online electrospray mass spectrometry [90]. In addition, the use of the online electrospray mass spectrometry to detect the reaction intermediate of the photosubstitution of $[Ru(bpy)_2LX_2]$ (L = 3,3′-dimethyl-2,2′-bipyridine (dmbpy), 2-(aminomethyl)pyridine (ampy); X = ClO_4^- or PF_6^-) was also reported [91].

Electrochemically reduced $[RuL(CN)_4]^{2+}$ has been characterized by ESR spectroscopy (L = bpy, 2,2′-bipyrimidine 2,2′-bipyrazine). Resolved hyperfine structure was observed in all complexes. Emission spectra, solvatochromic absorption spectra and cyclic voltammetry were also presented and discussed [92]. Moreover, the photophysical and photochemical properties of $[RuL(CN)_4]^{2-}$ (L = bpy, 4,4′-dimethyl-2,2′-bipyridine) were investigated in aqueous solution and in $CHCl_3$ at ambient temperature. Photolysis of $[Ru(bpy)(CN)_4]^{2-}$ was compared with that of $[Fe(bpy)(CN)_4]^{2-}$ [93].

The solvent effect on the photoinduced electron-transfer reaction between $RuL_2(CN)_2$ (L = bpy, phen) and Ru(β-diketonato)$_3$ has been discussed. Luminescence of $RuL_2(CN)_2$ was quenched by Ru(β-diketonato)$_3$ *via* an oxidative electron-transfer reaction. The activation enthalpy and the activation entropy of the electron transfer reaction were determined [94]. Studies of the pH dependence of the photoluminescent properties and the emission quenching of $Ru(dhcb)_3$ (dhcb = 4,4′-dicarboxy-2,2′-bipyridine) by $[Fe(CN)_6]^{3-}$, methylviologen, cupric ion, *N*,*N*′-bis(3-sulforopyl)-4,4-bipyridinium salt, nitrobenzene and oxygen were carried out [95]. The Hubbard-Hamiltonian formalism including the solvation contribution was used for the enumeration of the energies of all possible configurations in the redox sites of the heteroleptic ruthenium complexes of the form $[Ru(bpy)_{3-m}L_m]^{2+}$ (L = bpy, 5,5′-bis(ethylcarboxy)-2,2′-bipyridine (5dceb), 4,4′-bis(ethylcarboxy-2,2′-bipyridine (4dceb), 4,4′-bipyrimidine (bpym), 2,2′-bipyrimidine (bpm), 2,2′-biquinoline (bq)). It was shown that the assignment of electron localization along the redox series can be performed by detailed analysis of spectra of reduction products [96].

A novel water soluble metallopeptide (**75**) that consists of two divalinyl peptides attached to carboxylate group of $[Ru(bpy)_2L]^{2+}$ (L = 3,5-dicarboxy-2,2′-bipyridine) has been synthesized. The complex display many features reminiscent of a small, parallel β-pleated sheet structure as supported by circular dichroism measurements [97].

The ruthenium complexes $[Ru(bpy)_2L](ClO_4)_2$ (L = phen, 5-methyl-1,10-phenanthroline) were synthesized and characterized by IR, MS and NMR spectroscopies. Their solid state structures were determined by single crystal X-ray diffraction techniques. It was found that the coordination sphere was distorted to relieve the ligand interaction by forming specific angles between the polypyridyl ligand planes and coordination planes [98]. The formation of a novel class of supramolecular complexes $[RuL_2L']^{2+}$ (L = 4,4′-dimethyl-2,2′-bipyridine; L′ = (**76**)) and the determination of electron transfer rates between the sensitizers and electron



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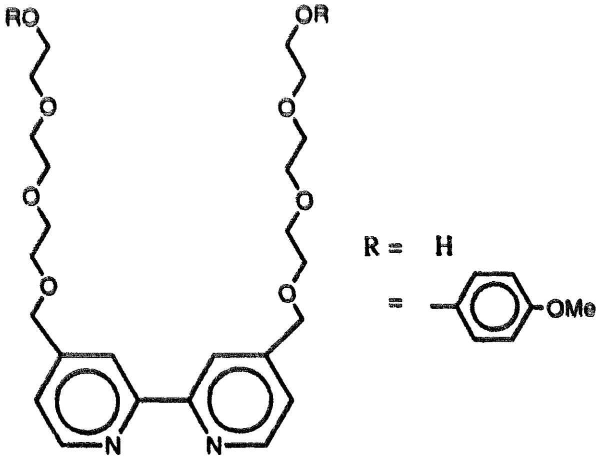
acceptors have been reported. Evidence for the supramolecular sensitizer in sacrificial mode systems for artificial photosynthesis was obtained [99].



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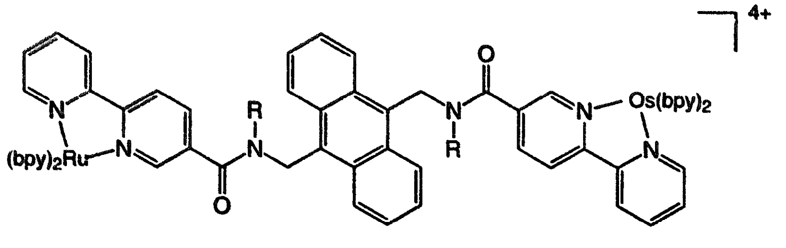
A very efficient and fast energy transfer ($k_e = 4.7 \times 10^8$ s^{-1}) was observed from the Ru to Os base moiety in the supramolecular complex (**77**). In the presence of oxygen, a self-photosensitized oxidation occurs and leads to a strong decrease in the rate and efficiency of the energy transfer process [100]. The photochemical behaviour of the ruthenium complex $[Ru(bpy)_2(dcbpy)]^{2+}$ (**78**) (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) on the surface of Al_2O_3 and TiO_2 particles has been investigated using



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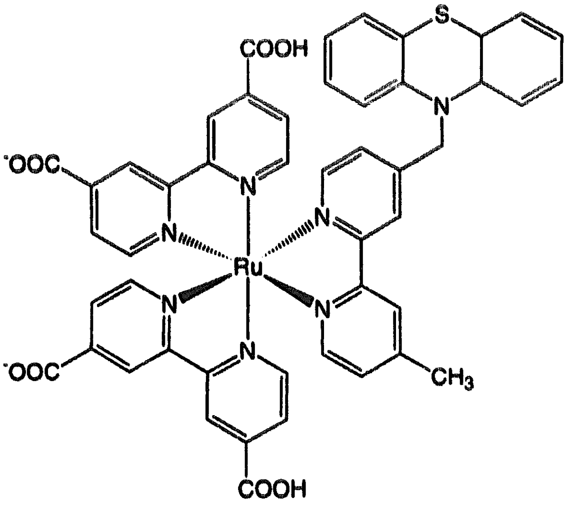
diffuse reflectance absorption studies. Steady state photolysis demonstrated trapping of electrons ejected from the excited sensitizer at the semiconductor surface [101]. Microwave absorption and luminescence measurements have been carried out to monitor the charge injection from excited complex (**78**) into SnO_2, ZnO and TiO_2 nanocrystallites. The appearance of microwave conductivity at rates corresponding with that of the luminescence decay directly confirms heterogeneous electron transfer from the excited dye to the semiconductor particle [102]. The preparation, characterization and electrochemical properties of two novel sensitizers [Ru(dcbH)$_2$(bpy-PTZ)] (**79**) and [Ru(dcbH)$_2$(dmb)] (**80**) were reported. The photoinduced charge separation processes for (**79**) and (**80**) across a nanocrystallite TiO_2 interface were also explored. For surface attached (**79**), rapid intramolecular electron transfer form PTZ to the ruthenium metal efficiently translated the hole away from the chromophoric unit to the pendant PTZ group and generated a long-lived charge separated pair. The general strategy of vectorial translation of photogenerated holes has been discussed [103].



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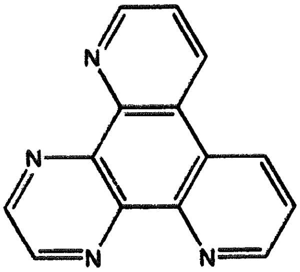
The binding of Cu(II) salts with the complex $[Ru(bpy)_2(ppz)]^{2+}$ (ppz=4′7′-phenanthrolino-5′,6′,5,6-pyrazine, (**81**)) has been investigated and characterized by ESR and visible spectroscopies. Evidence that the Cu(I) species binds to a hydrophobic region of calf thymus DNA was also presented. The cleavage of *E. coli* pBR322 DNA by the individual enantiomers is reassessed using sodium ascorbate as the reducing agent [104]. The interactions of enantiomers of $[Ru(bpy)_2(phi)]Cl_2$ and $[Ru(phen)_2((phi)]Cl_2$ (phi = 9,10-phenanthrenequinonedimine (**82**)) with calf thymus DNA, B-poly$[d(G\text{-}C)]_2$, B- and Z-poly$[d(G\text{-}m^5C)]_2$, B-poly$[d(A\text{-}T)]_2$ and B-[poly(dA).poly(dT)] have been investigated using spectroscopic titrations, CD, electric linear dichroism (LD) and emission measurements [105].



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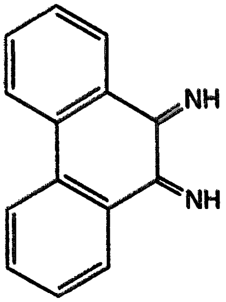


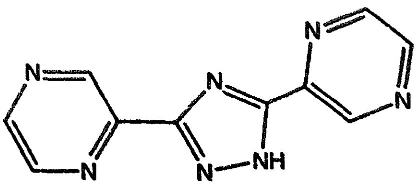
(82)

A theoretical study of photoinduced long-distance electron-transfer reactions in Ru modified proteins $Ru(bpy)_2$i.m.-(His X)-Cyt.C (X = 33, 39, 58, 62, 66, 72, 79) was performed. The method used include a detailed description of the donor and acceptor wavefunction in terms of ligand field theory [106].

The photochemical properties of the dinuclear complex $[\{Ru(bpy)_2\}_2(bpzt)]^{3+}$ (bpzt = 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (**83**)) have been reported. Photolysis of this complex, studied using HPLC and UV-VIS spectroscopy, indicated a unique labilization of the metal moiety bound to the triazole N4 site. The results were compared with that for the analogous compound $[\{Ru(bpy)_2\}_2(bpt)]$ (bpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole (**84**)) [107]. The novel dinuclear species $[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_3]^{4+}$ (dpt-cy-dpt = (**85**)) has been synthesized. Its absorption spectrum, luminescence properties and electrochemical behaviour have been investigated and compared to those of the parent homometallic dinuclear compounds [108]. The rate constants for the photoinduced electron transfer and the thermal charge recombination of a series of Ru complexes of the type $[RuL_2L']$ (L = 4,4'-R_2-2,2'-bipyridine, L' = 4'-Me-2,2'-bipyridine-4-CONHR'; R = H, CH_3, -COO, COOH, $CONH(CH)(CH_3)_2$, $R' = (CH_2)_xMV^{2+}$) were measured. The effects of the number of intervening methylene unit and the nature of substituents on the chromophore and electronic properties of the compound have been discussed [109].

The electrochemical properties of the complex $[Ru(bpy)_2(tpt)]^{2+}$ (tpt = 2,4,6-tris(2-pyridyl)triazine (**86**)) have been studied in both DMF and acetonitrile. UV–VIS spectroelectrochemical measurements was used to characterize the reduction products of the complex [110].

The use of the chiral $[RuL_2(CO)_2]^{2+}$ species, (L = bpy, phen, 4,4'-dimethylbipyridine) in the stereoselective synthesis of $[RuL_3]^{2+}$ and the ligand bridged dinuclear



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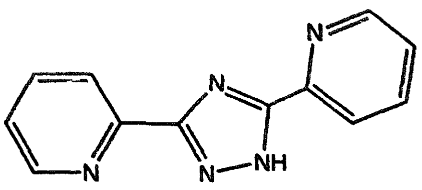

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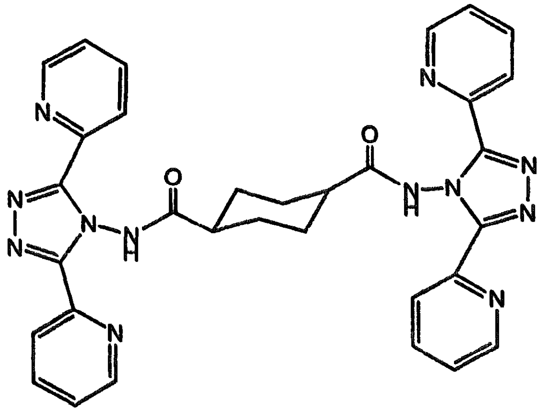

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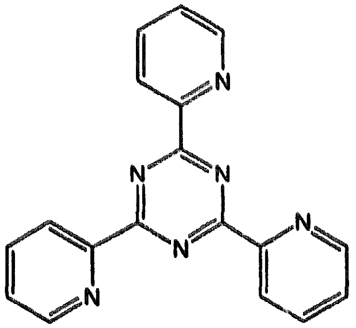
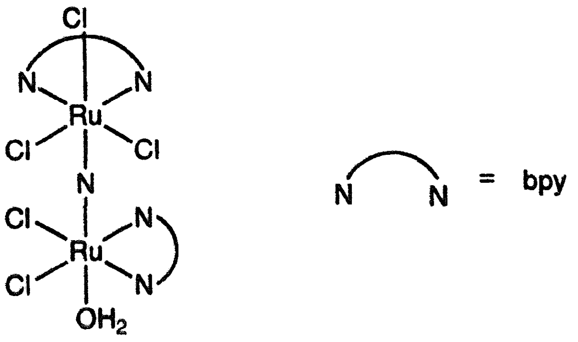


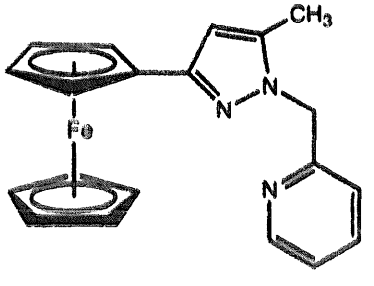
(86)

complexes of the type $[RuL_2BLRuL_2]^{4+}$ (BL = 2,2′-bipyrimidine) was explored [111]. The formation of *fac*- and *mer*-$[Ru(bpy)Cl_3(NO)]$ (**87**) and the nitrido-bridged dimeric complexes $[Ru_2N(bpy)_2Cl_5(H_2O)]$ (**88**) from the reaction of $[Ru(bpy)(CO)_2Cl_2]$ in conc. HCl/HNO_3 have been studied. It was shown that the distribution of the products is basically time-dependent. The X-ray structure of (**87**) has been determined [112]. A general synthetic method has been developed for the synthesis of tris-heteroleptic complexes of ruthenium(II) containing didentate polypyridyl ligands [113]. Two new pyridinopyrazole ligands (**89**) and (**90**) bearing electroactive ferrocenyl subunits were prepared. The corresponding Ru(II) $[Ru(bpy)_2L](PF_6)_2$ (L = (**89**), (**90**)) were prepared and characterized by ^1H and



(88)

^{13}C NMR spectroscopies. Electrochemical and UV–VIS studies suggested that an intramolecular interaction occurs between Ru(II) and Fe(II) [114]. A novel macrocyclic ruthenium-ferrocene polynuclear complex (**91**), had been synthesized. It was shown by fluorescence emission spectroscopy that complex (**91**) exhibited remarkable selectively for the chloride anion in preference to dihydrogen phosphate [115].



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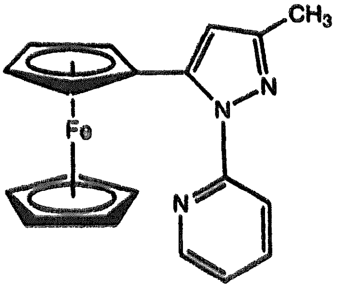
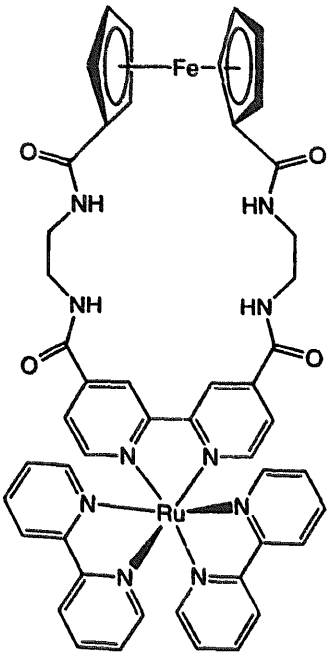


(90)

A new approach to fabrication of electropolymerized films of [poly-(bpy)$_2$Ru(vpy)$_2$]$^{2+}$ (vpy = vinylpyridine) on an electrode was explored. The resulting films display excellent stability and were characterized electrochemically. The application of these films as electrochemical switches and diffraction gratings have been demonstrated [116]. Homogeneous electrochemical reactions with the immobilized hydrogen of the metallopolymer [Ru(bpy)$_2$(PVP)$_{10}$(H$_2$O)]$^{2+}$ (**92**) (PVP = poly(4-vinylpyridine)) were studied using the electrochemical quartz crystal microbalance. Studies on pH-dependent mass transfer processes through a thin-film of (**92**) have been presented [117]. The asymmetric light-induced electron transfer in the system containing (**93**) and (**94**) in water at pH ≥ 5 has been investigated. From the experimental results, chiral recognition in the diastereomeric exciplex was inferred [118].

A new pendant-arm derivative of cyclam (**95**) has been isolated and characterized. Reaction of (**95**) with *cis*-[Ru(bpy)$_2$Cl$_2$] in a 1:4 ratio gives the highly fluorescent [{Ru(bpy)$_2$}$_4$L] (**96**) (L = (**95**)). The formation of complex (**96**) has been investigated by molecular mechanics and molecular dynamic calculations. The p*K*a values of (**96**) in the ground and excited states have also been determined [119].



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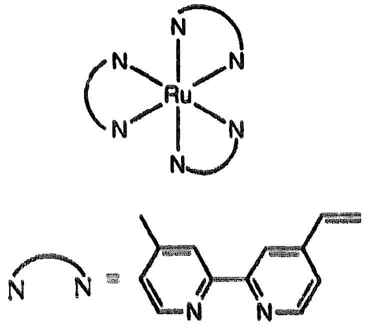

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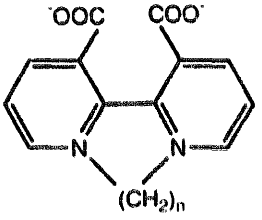
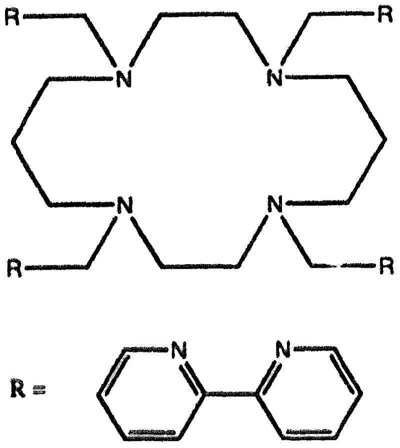


n = 1, 2, 3, 4, 5

(94)

The solid state structures of the major diastereomers of the complexes Δ/λ-$[M(bpy)_2L]$ (M = Os, Ru; L = δ/λ-1,1'-diisoquinoline) have been determined by X-ray crystallographic studies. The interconversion of the diastereomers for both complexes were studied by spin perturbation NMR spectroscopic experiments. The kinetics, thermodynamics and the mechanism of such interconversions have also been examined [120]. Two pairs of enantiomers Δ- and Λ-$[RuL_2(py)_2]^{2+}$ (L = phen, bpy) have been resolved. The use of these enantiomerically pure Δ and Λ complexes as building blocks for the synthesis of the dinuclear complexes $[RuL_2(BL)RuL_2]^{2+}$ (BL = 2,2'-bipyrimidine (**97**) or 2,4-di-2-pyridylpyrimidine (**98**)) with defined stereochemistry have been reported. The dinuclear complexes were characterized by CD and NMR spectroscopies [121].

The formation of $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ from the conproportionation reaction between $[Ru^{IV}(bpy)_2(py)O]^{2+}$ and $[Ru^{II}(bpy)_2(py)(OH)_2]^{2+}$ was investigated by



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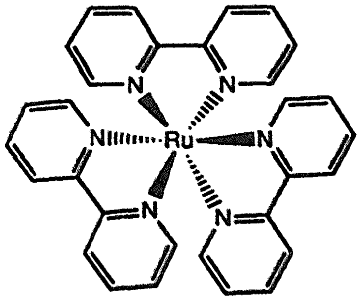

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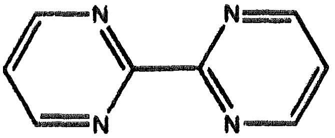

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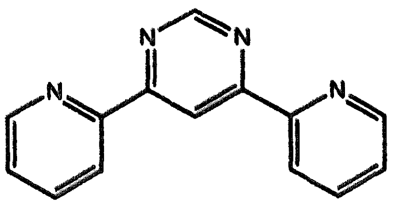


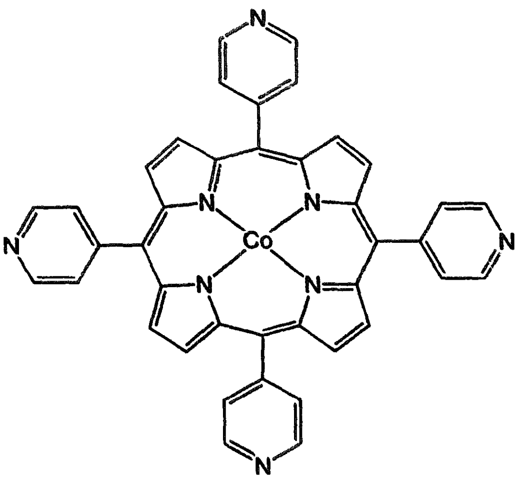
(98)

means of rapid scan, stopped-flow kinetics. The observed large solvent isotope effect, kH_2O/D_2O, of 14.6 suggested the reaction is *via* a proton-coupled electron transfer [122]. The photochemical behaviours of $[Ru^{II}L_2(BL)X]^+$ (**99**) and $[L_2XRu^{II}(BL)Ru^{II}XL_2]^{2+}$ (**100**) (L = bpy, phen; BL = 4,4′-bpy, pyrazine or (*E*)-1,2-bis(diphenylphosphino)ethene (dppene); X = Cl, NO_2) in methanol and acetonitrile have been studied. Complexes (**99**) and (**100**) with dppene ligand were found to be photochemically inert [123].

Treatment of the *meso*-tetra(pyridyl) substituted Co(III) porphyrin L = (**101**) with an excess of $[RuCl_2(bpy)_2]$ gives $[\{Ru(bpy)_2Cl\}_4L](CF_3SO_3)_5$ (**102**). The electrochemistry of complex (**102**) has been examined. The preparation of stable homogeneous films of complex (**102**) on conventional glassy carbon electrodes has also been reported. The modified electrode has been successfully employed for analytical purposes in the determination of reducing analytes such as nitrite and sulfite ions at ppb levels [124].

The redox interaction of the tetraruthenium complex (**103**) with the simplest starburst configuration has been investigated on a thermodynamic basis. Correlation between the electrode potential and the interaction energies has been sought. The experimental findings were compared with that of the tetraruthenium complex coordinated by pyridines [125].

Oxidation of $[Ru^{II}(bpy)_2(NH_2CMe_2CMe_2NH_2)]^{2+}$ by Ce(IV) in water generates the highly reactive *cis*-bis(imido)ruthenium(VI) intermediate which was found to



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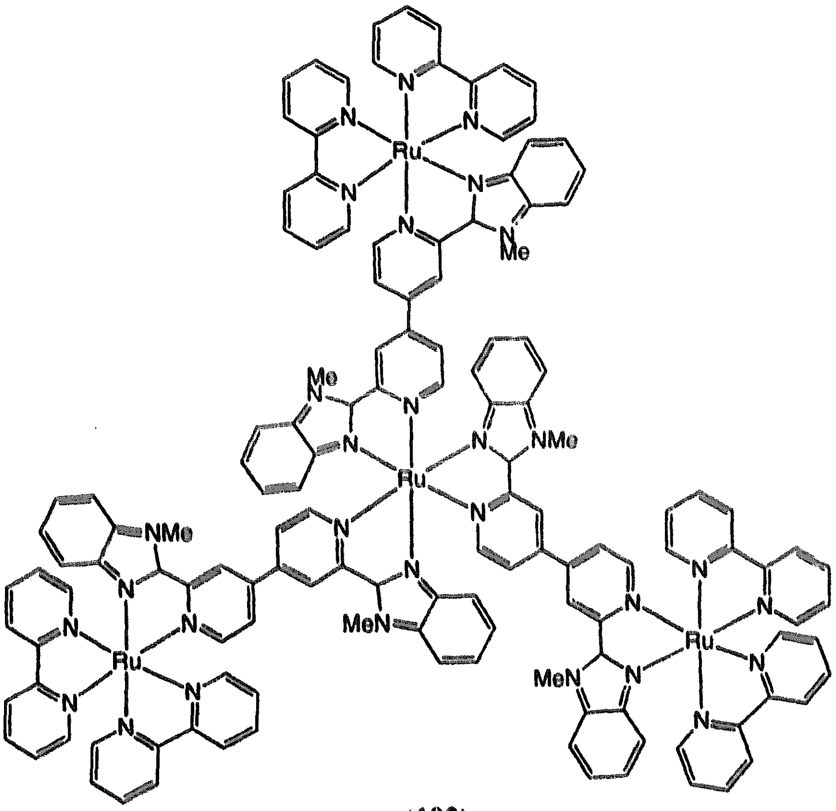
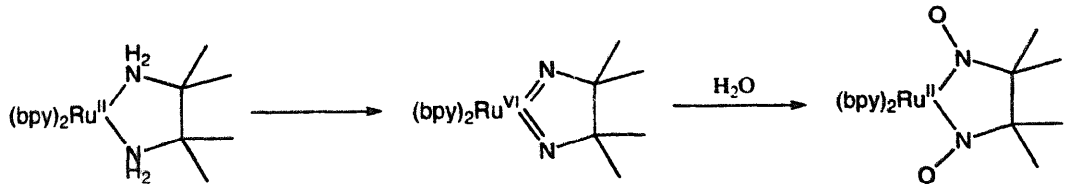


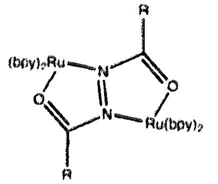
(103)

react with water to give $[Ru^{II}(bpy)_2(ONCMe_2CMe_2NO)]^{2+}$ (Scheme 2). The single crystal structure of the latter has been determined [126]. A comprehensive study of electronic structures of the complex $[Ru(bpy)_2]_2(Adc\text{-}R)$ (**104**) (Adc-R = azodicarbonyl ligand) was conducted using cyclic voltammetry, UV–VIS, IR and XPS spectroscopies of the neighbouring 2+ and 3+ oxidation states as well as EPR spectroscopy and magnetic susceptibility studies of the paramagnetic 3+ intermediate. The results



Scheme 2.

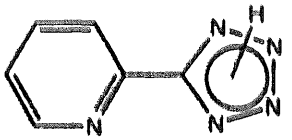
were compared to those of complexes with Ru(III)/Ru(II) mixed valent character and interpreted according to the hole as electron transfer mechanistic scheme [127].



R = NR'$_2$, OEt, OCH$_2$Ph, Me, Ph, 4-C$_6$H$_4$COOH, 4-C$_6$H$_4$COOMe

(104)

A series of chelating tetrazole-containing ligands (**105**)–(**117**) and their bis(bipyridyl) ruthenium(II) complexes have been synthesized. The natures of the metal–ligand interactions in these complexes were studied by ^{1}H NMR and electronic absorption spectroscopies and cyclic voltammetry. It was shown that the negatively charged tetrazolate group is a strong electron donor whereas the protonated or alkylated tetrazoles demonstrated a significant lowering in the energy of the metal-based HOMOs and raising in the energy of the ligand-based LUMOs [128].



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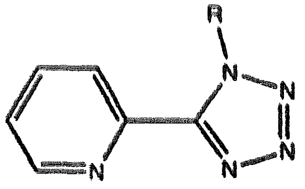
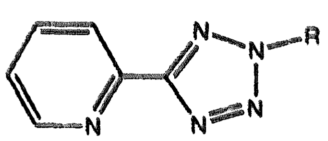


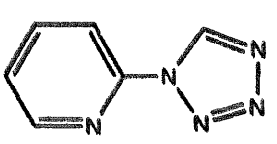
R = Me **(106)**

R = ^{t}Bu **(107)**



R = Me **(108)**

R = ^{t}Bu **(109)**



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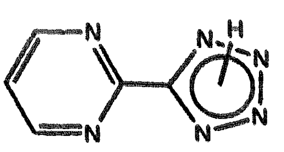
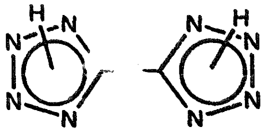


(111)

The association of the molecular-based magnet $[Cu(opba)_3]^{2-}$ (**118**) with the photophysically active chromophore $[Ru(bpy)_3]^{2+}$ has been discussed. The luminescence of the $[Ru(bpy)_3]^{2+}$ cation is quenched by the $[Cu(opba)_3]^{2-}$ anion and an intramolecular energy transfer from Ru(II) to Cu(II) occurs [129].

The reaction of $[Ru(bpy)_2Cl_2]$ with $Na_2S_2C_2(CN)_2$ or $(C_6H_5CH_2)_2S_2C_2(CN)_2$



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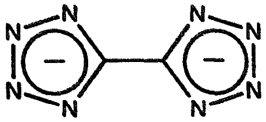

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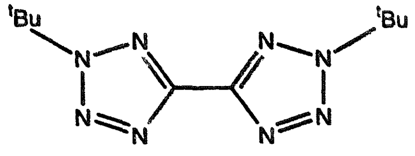

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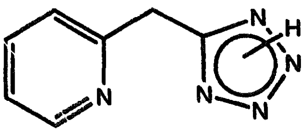

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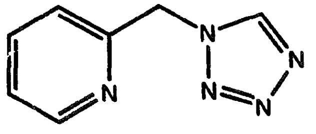

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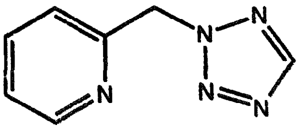

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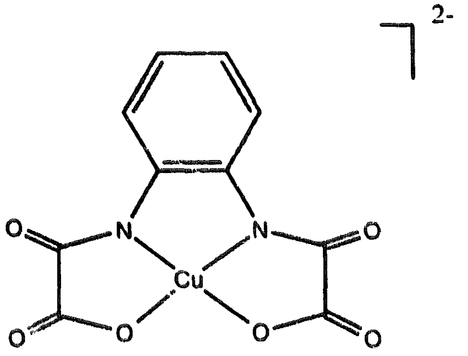

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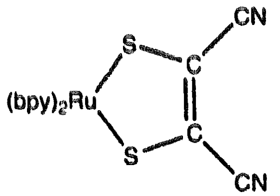

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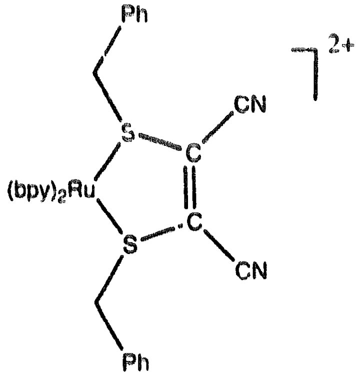
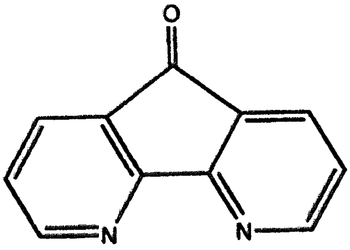


(120)

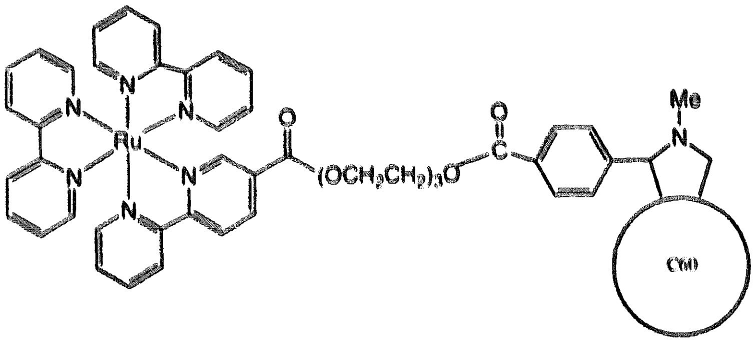
gives [Ru(bpy)$_2${S$_2$C$_2$(CN)$_2$}] (**119**) and [Ru(bpy)$_2${(C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$}]$^{2+}$ (**120**). The corresponding dinuclear complexes were also isolated by binding Cp(PPh$_3$)Ru^{II} or (bpy)$_2$ClRu^{II} moieties onto the CN sites. The spectral and electrochemical properties of all complexes were studied [130]. The preparation and photophysical properties of the monomeric complex [Ru(bpy)$_2$(dafo)](PF$_6$)$_2$ (dafo = diazafluorenone (**121**)) have been reported. The complex displays absorption at

438 nm, 285 nm and 249 nm and a broad emission centred at 626 nm in H_2O. The X-ray structure of the complex has been established [131].



(121)

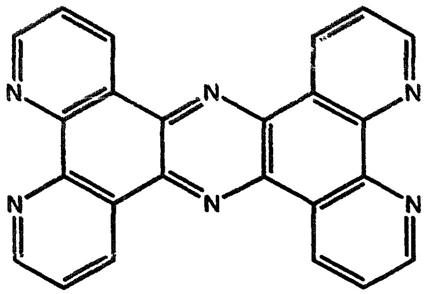
The synthesis of a C_{60}-fullerene derivative covalently bound to a $[Ru(bpy)_3]^{2+}$ unit in complex (**122**) and its characterization using ^1H and ^{13}C NMR, FTIR, MACDI-MS and UV-VIS spectroscopies were described. The UV-VIS spectrum shows an absorption typical of two independent chromophores [132]. In addition, photoluminescence from the triplet state of $[Ru(bpy)_3]^{2+}$ was quenched by C_{60} in (**122**) and a well defined photo-excited absorption spectrum was observed. Light-induced ESR signals confirm the existence of radicals generated by a charge transfer reaction. Evidence for reversible, photoinduced electron transfer from $[Ru(bpy)_3]^{2+}$ to C_{60}, and for a long-lived charge separated state in the donor-bridge-acceptor supramolecule (**122**) have been reported [133].



(122)

The mononuclear complex $[Ru(bpy)_2L]^{2+}$ (L = tetrapyrido(3,2-a: 2′,3′,-3″,2″-h:2″,3″j]phenazine (**123**)) was obtained from the reaction of $[(bpy)_2Ru(L')]^{2+}$ (L′ = (**124**)) and 5,6-diamino-1,10-phenanthroline. The dinuclear complex $[Ru(bpy)_2LRu(bpy)_2]^{4+}$ (**125**) has also been prepared. The crystal structure of (**125**) has been determined and both complexes have been characterized by UV–VIS spectroscopy and electrochemical oxidation [134]. Resonance Raman spectroscopy has been used to study the electronic structure in the excited states of $[Ru(dmb)_2(dppz)]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine dppz = dipyrido(3,2-a:2′,3′-c)phenanzine (**126**)]. Excited state measurements showed that the excited electron was delocalized over the entire ligand framework [135].

Elastic and quasi-elastic light scattering and conductivity experiments have been performed on the supramolecular species $[M\{(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,3\text{-dpp})\text{-}Ru(bpy)_2]_2\}_2](PF_6)_{20}$ (M = Ru, Os, 2,3-ddp = 2,3-bis(2-bipyridyl)pyrazine (**127**)) in



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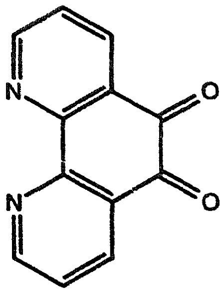

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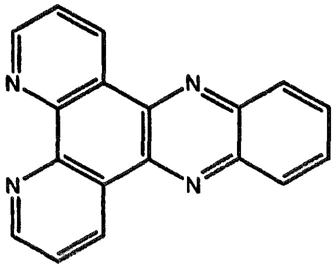

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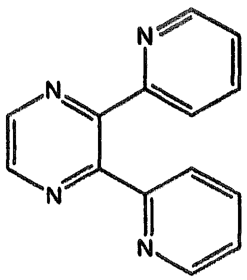
dilute solution. The effect of ionic strength and solvent polarity on the aggregation properties of the complex have been investigated [136]. A comparative study of the spectroscopic and oxidative spectroelectrochemistry of a series of homo- and heterodimetallic complexes of the form [(bpy)$_2$Ru(BL)Os(bpy)$_2$]$^{4+}$, [(bpy)$_2$Ru(BL)Ru(bpy)$_2$]$^{4+}$ and [(bpy)$_2$Os(BL) Os(bpy)$_2$]$^{4+}$ (BL = 2,3-dpp, 2,3-bis(2-pyridyl-quinoxaline (dpq) (**128**) and 2,3-bis(2′-pyridyl)benzoquinoxaline (dpb) (**129**)) have been carried out. It was found that the spectroscopy of the mixed-metal dimetallic complexes bridged by polyazine bridging ligands can be interpreted by comparison with the homometallic analogues [137].



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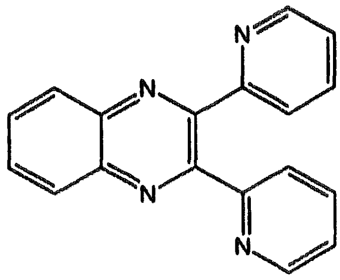

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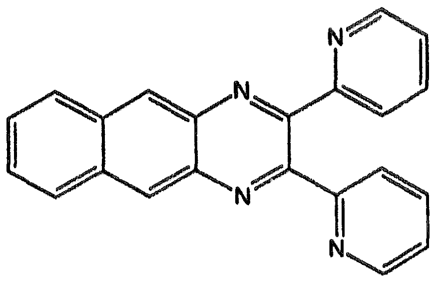

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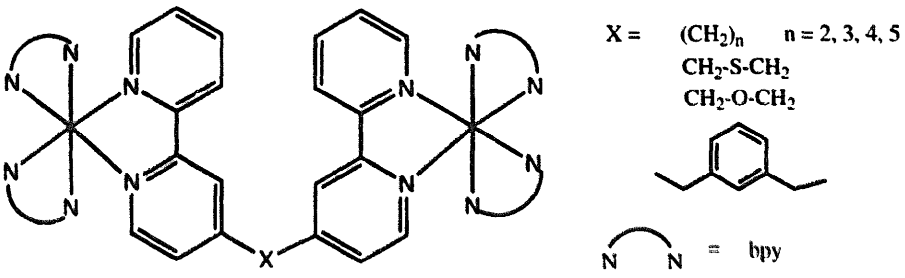
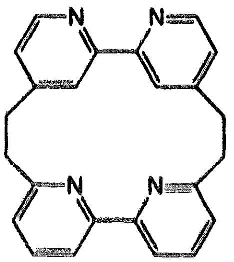
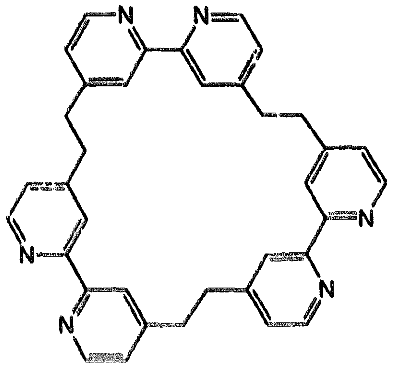
A series of rigidly-linked heterodinuclear ruthenium(II)/iron(II) complexes (**130**) have been prepared. Photo-excitation of the RuL$_3^{2+}$ moiety yields the emissive MLCT state and is quenched by energy transfer to the FeL$_3^{2+}$ unit. The emission decay rates were found to be essentially independent of the nature of the bridge. An exchange mechanism which does not involve super-exchange through the σ-bonding framework has been suggested for the energy transfer quenching [138]. Three new cyclic oligobipyridine ligands (**131**)–(**133**) have been synthesized and characterized. The X-ray structure of $[\{Ru(bpy)_2\}_2L]$ (L=(**131**)) showed that the metal centres were held in close proximity [139].



(**130**)



(**131**)



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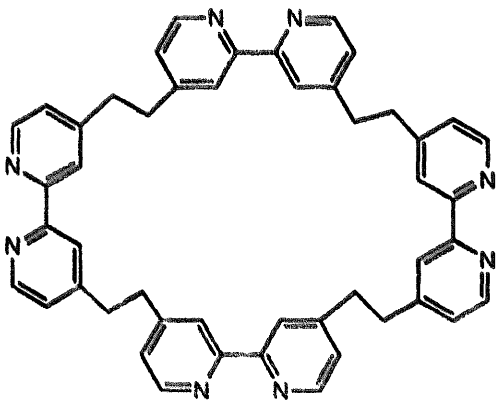
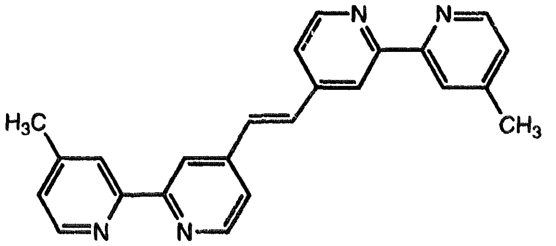


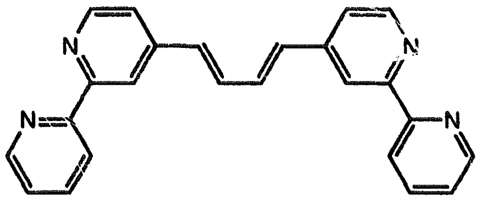
(**133**)

Transient UV–VIS and resonance Raman spectroscopy were used to study the MLCT excited states of the ligand bridged complexes $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2](PF_6)_4$ and $[(bpy)_2Os(\mu\text{-bbpe})Os(bpy)_2](PF_6)_4$ (dmb=4,4′-dimethyl-2,2′-bipyridine, bbpe=(*E*)-1,2-bis(4-(4′-methyl)-2,2′-bipyridyl)-

ethene (**134**)). It was shown that the excited electron in the Ru complex was delocalized over the molecular framework of the bbpe ligand and that the lifetime of the excited state were unusually long when compared with related systems [140]. The redox and photophysical properties of a series of dimetallic complexes of the type $[(dmb)_2Ru(BL)](PF_6)_2$ and $[\{(dmb)_2Ru\}_2(BL)](PF6)_4$ (BL = 1,4-bis(4′-methyl-2,2′-bipyridine-4-yl)buta-1,3-diene (**135**), 1,4-bis(4′-methyl-2,2′-bipyridine-4-yl)-2-cyclohexene-5,6-dicarboxylic acid diethyl ester (**136**) and 1,4-bis(4′-methyl-2,2′-bipyridine-4-yl)benzene (**137**)) were reported. Excited states of complexes of the butadiene-containing ligand have low-lying triplet intraligand excited states which are formed competitively with the luminescent MLCT states [141].



(**134**)



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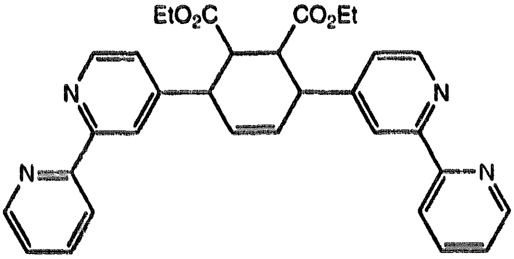

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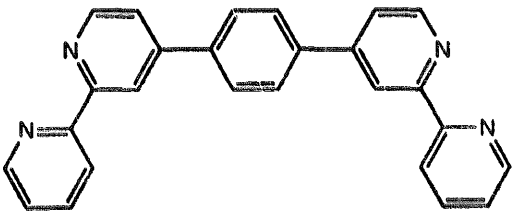
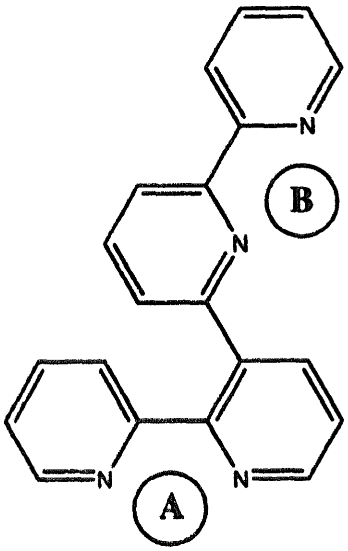


(**137**)

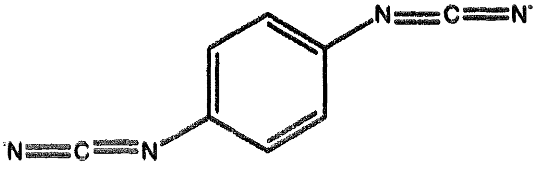
A series of homo- and heterodinuclear complexes of the asymmetric bridging ligand 2,2′:3′,2″:6″,2‴-quaterpyridine have been prepared and fully characterized by mass spectroscopic, electrochemical, UV–VIS spectroscopic and luminescence spectral data (**138**)-(**143**). From the electrochemical and spectroscopic properties of the complexes, it was shown that the chromophore which occupies the A site is easier to oxidize and possesses a lower energy MLCT excited state than the same chromophore which is linked to B site. The crystal structure of (**143**) has been established [142]. The preparation of the mononuclear and dinuclear complexes (**144**)–(**147**) have been described. The electrochemical properties, absorption spectra, excited-state lifetime, intercomponent energy transfer and emission spectra were reported and discussed. The electronic energy transfer from the higher energy to the lower energy moiety in the heterodinuclear complexes is 100% efficient [143].

The complex $[\{Ru(tpy)(bpy)_2\}_2(\mu\text{-dicyd})](PF_6)_2$ was synthesized and characterized by cyclic voltammetry and spectroelectrochemical methods (dicyd = (**148**)).



Fragment at A	Fragment at B	
$[Ru(bpy)_2]^{2+}$		**(138)**
$[Ru(bpy)_2]^{2+}$	$[Ru(bpy)_2]^{2+}$	**(139)**
$[Re(CO)_3Cl]$		**(140)**
$[Re(CO)_3Cl]$	$[Re(CO)_3Cl]$	**(141)**
$[Ru(bpy)_2]^{2+}$	$[Re(CO)_3Cl]$	**(142)**
$[Re(CO)_3Cl]$	$[Ru(bpy)_2]^{2+}$	**(143)**
$[Ru(bpy)_2]^{2+}$	$[Os(bpy)_2]^{2+}$	**(144)**
$[Os(bpy)_2]^{2+}$	$[Ru(bpy)_2]^{2+}$	**(145)**
$[Os(bpy)_2]^{2+}$	$[Os(bpy)_2]^{2+}$	**(146)**
$[Os(bpy)_2]^{2+}$		**(147)**

The magnitude of the metal-metal coupling in these systems was shown to be dependent on the interaction of the ruthenium ions with the dicyd groups [144].



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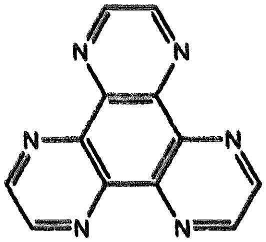

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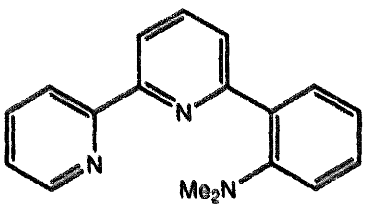

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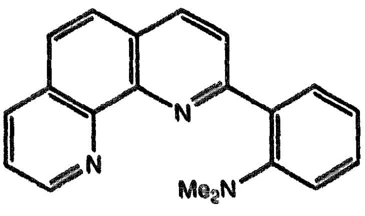
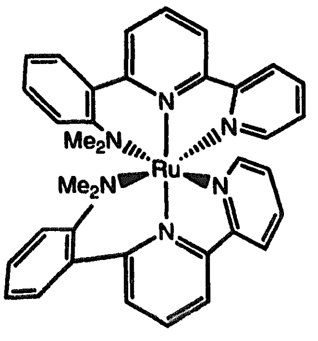


(151)

The synthesis and characterization of di- and trinuclear complexes with the building blocks $Rh(bpy)^{2+}$, $Ir(bpy)^{2+}$ and $Ru((bpy)^{2+}$ bridged by the HAT ligand (HAT = (149)) were reported. The methods of FAB and electrospray MS and HPLC were used to the characterize the complexes. The electrochemical and photophysical properties of the dinuclear complex have been studied [145]. The preparation of a series of polypyridyl ruthenium(II) complexes of the type $[Ru(tpy)(bpy)L]^{2+}$ (L = py, pyridylacetylene, phenylpyridyl acetylene, dipyridylacetylene, cyanoacetylene and cyanophenylacetylene) has been reported. The excited lifetimes of the complexes lie between those of $[Ru(bpy)_3]^{2+}$ and $[Ru(tpy)_2]^{2+}$ ions and the acetylenic function does little to change the electronic and structural properties of the metal complexes [146]. The potentially terdentate ligands 6-(2-dimethylaminophenyl)-2,2′-bipyridine (**150**) and 2-(2-dimethylaminophenyl)-1,10-phenanthroline (**151**) have been prepared. Treatment of these ligands with $RuCl_3 \cdot xH_2O$ yields conventional meridional N_3 chelate complexes (**152**)-(**153**) and the cyclometalled complexes (**154**)–(**155**). The characterization of the new complexes by conventional spectroscopic techniques and electrochemical measurements have been discussed [147].



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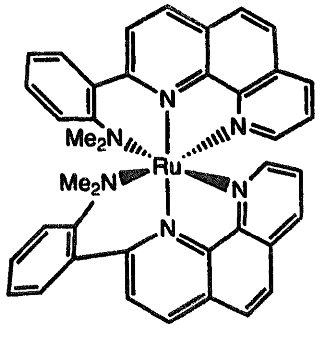

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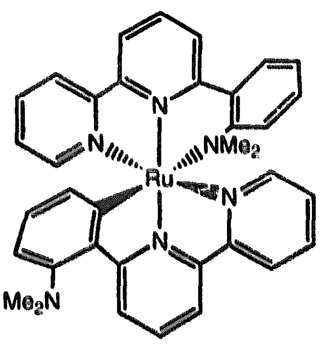

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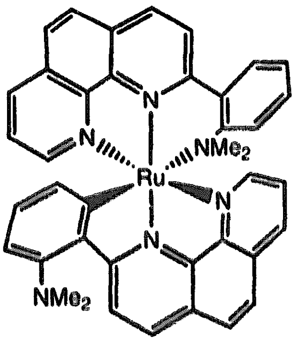

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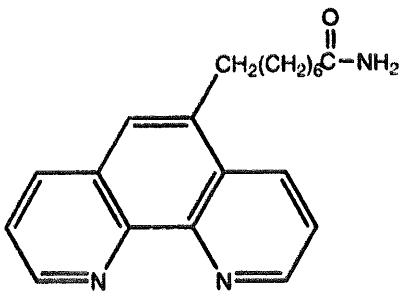
Relationships between charge transfer emission energies and redox potentials for a large diverse set of ruthenium diimine complexes of the type $[Ru(bpy)_2L]^{n+}$, $[Ru(bpy)L_2]^{n+}$ and $[RuL_3]^{n+}$ were reported. An alternative derivation of the excited state and corresponding ground state redox potentials was developed. The difference between the excited state and ground state potential was shown to be approximately constant for complexes in which the emission and reduction processes involve bipyridine-type ligands [148].

6.2. Complexes with phenanthroline ligands

A study was made on the effect of oxalate concentration on the intensity of chemiluminescence emission produced by the reaction between $[Ru(phen)_3]^{2+}$

(phen = phenanthroline) and Ce(IV). A novel chemiluminescence method for the determination of oxalate was thus proposed [149]. The binding constant for the association of $[Ru(phen)_3]^{2+}$ with starburst dendrimers and its quenching by $[Co(phen)_3]^{3+}$ has been studied. The quenching rate constant was shown to be independent of quencher concentration indicating that the quenching is intra-starburst in nature [150]. The spectroscopic features and photochemistry of an array of silicon membranes containing $[RuL_3]^{2+}$ (L = 5-octadecanamide-1,10-phenanthroline (**156**)) have been studied with regard to its application to the measurement of oxygen [151].



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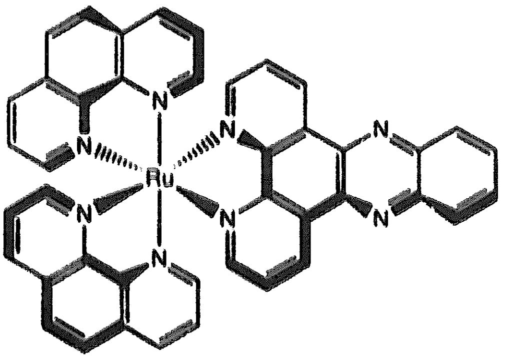

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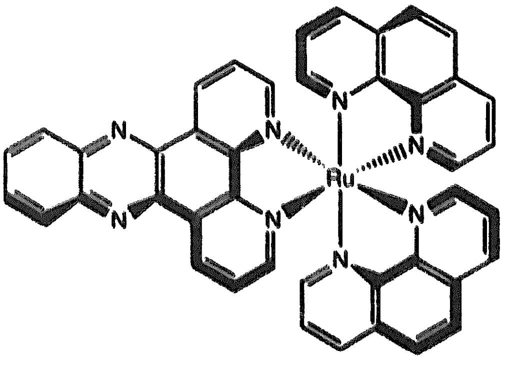

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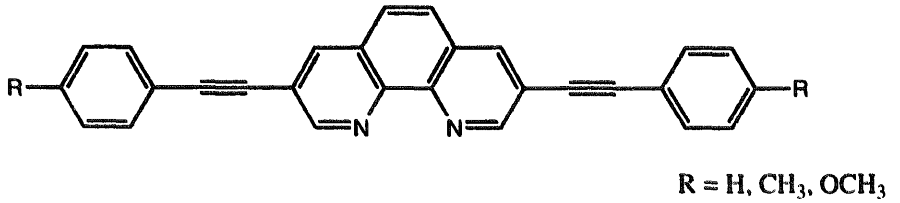
The syntheses of two new polypyridine ligands imidazo[f]1,10-phenanthroline (IP) and 2-phenyl-imidazo[f]1,10-phenanthroline (PIP) and their Ru(II) complexes have been reported. The complexes were characterized by elemental analysis, electronic absorption, IR and emission spectra and cyclic voltammetry [152]. The binding of $[Ru(bpy)_2(IP)]^{2+}$, $[Ru(bpy)_2PIP]^{2+}$, $Ru(phen)_2(PIP)]^{2+}$, $[Ru(phen)_2IP]^{2+}$ to calf thymus DNA has been investigated by electronic absorption, CD and fluorescence emission spectroscopies. Experimental results suggested the total binding affinities were consistent with the ligand planarity and hydrophobicity [153]. Fluorescence and absorption spectroscopy, isothermal titration calorimetry and viscosity measurements have been used to characterized the interaction of Δ- and Λ-$[Ru(phen)_2DPPZ]^{2+}$ (**157**) and (**158**) with calf thymus DNA [154]. The bimolecular quenching of the MLCT excited state of $[Ru(phen)_2(DPPZ)]^{2+}$ by proton transfer has been investigated in homogeneous acetonitrile solution and in the presence of calf thymus DNA. The biexponential decay of the emission is quenched more slowly in the presence of DNA. The difference in emission lifetimes in DNA and in acetonitrile has been discussed [155]. The binding of the complex $[RuL_2(pdphen)]^{2+}$ (pdphen = pyrido[3,2-f][1.7]phenanthroline, L = bpy, phen, 2,9-dimethylphenanthroline) to calf thymus DNA was investigated using absorption fluorescence and CD spectroscopies. The interaction with calf thymus DNA increases the fluorescence intensity and the excited state lifetime of this compound [156].

A novel family of highly conjugated ligands L = (**159**) has been synthesized by Pd-catalysed cross-coupling reactions between 3,8-dibromo-1,10-phenanthroline and substituted phenylacetylenes. The corresponding Ru(II) complexes could then be prepared. It was shown that the electronic transition in free ligands and Ru(II) complexes can be tuned by changing the substituent of the phenyl ring [157].

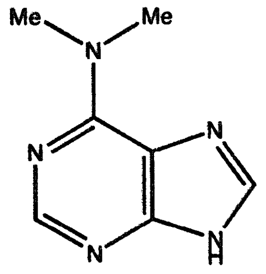


(**159**)

6.3. *Complexes with other N-heterocyclic ligands*

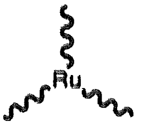
The spontaneous aquation reaction of the tumour inhibitor *trans*-$[RuCl_4Im_2]^-$ was studied as a function of pH, chloride concentration, imidazole buffer and temperature using spectrophotometric and chromatographic techniques. Evidence for the formation of $[RuCl_3(Im)_2(H_2O)]$ depending on the pH and free chloride concentration was found. The results have been discussed in respect to the tumour inhibiting properties of the complex [158]. In addition, the solvolysis of the $[RuCl_4(Im)_2]^-$ anion in water, methanol and dimethylsulfoxide was followed by ^1H NMR spectroscopy. The structure of the complex $[RuCl_2(DMSO)_2Im_2]$ was established by single crystal X-ray diffraction studies. The metal atom was found adopt a *trans,trans,trans*-coordination and the DMSO ligand is *S*-bonded [159]. The reactions of $[RuImCl_5]^{2-}$ and $[RuImCl_4]^-$ with water, imidazole and *N*6,*N*6-dimethyladenine (DMAD (**160**)) have been thoroughly examined using ^1H NMR spectroscopy. The subsequent substitution of the complex takes place at a much faster rate when non-protonated imidazole was added. Such unusual kinetic patterns were not observed with the less basic DMAD ligand [160].

Preparation, electrochemical and photochemical properties of the complexes $[RuL_{3-n}(bpy)_n]^{(5-n)+}$ (n = 0, 1, 2) and $RuL_2(\mu\text{-}2,3\text{-dpp})RuL_2$ (L = monomethylated 2,3-bis(2-pyridyl)pyrazine, 2,3-dpp = 2,3-bis(2-pyridyl)pyrazine (**127**)) were reported and compared to those of the mononuclear $[Ru(bpy)_3]^{2+}$ complexes [161]. The temperature dependence of the lifetimes of the lowest lying ^{3}MLCT state of a series of ruthenium heteroleptic complexes $[Ru(bpz)_2L]^{2+}$ (bpz = 2,2′-bipyrazine, L = bpy, 4,5-diazafluorene (daf), 5-methyl-2,2′-bipyridine (mmb), 4,4′-dimethyl-2,2′-



(160)

bipyridine (dmb)) has been discussed. The results were analysed by kinetic equations incorporating one or two thermal terms. It has been shown that one (^{3}MLCT) or other (^{3}dd) thermally activated decay pathway becomes dominant within the temperature range studied [162]. A general strategy for preparation of the ruthenium complexes (**161**)–(**169**) with dendrimers of nanometer size was described. Their photo- and electrochemical properties have been explored [163].



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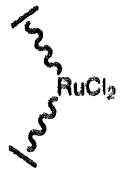

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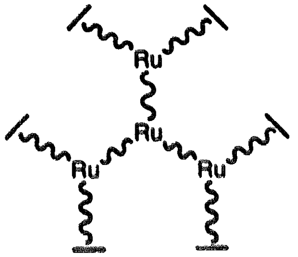

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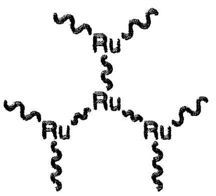

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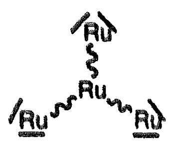

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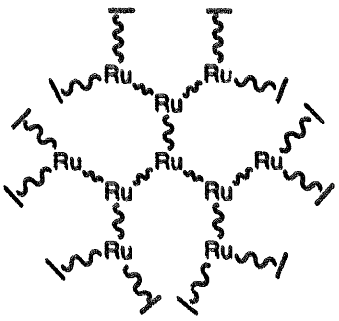

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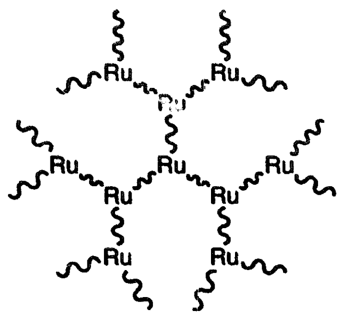
The complexes [(bpz)M(CN)$_4$]$^{2-}$ (M = Fe, Ru) and [(abpy)Fe(CN)$_4$]$^{2-}$ (abpy = 2,2'-azobis(pyridine)) were prepared and characterized by IR and UV-VIS absorption spectroscopies and cyclic voltammetry. EPR spectroscopic studies were employed to evaluate the radical anion formed from the low-lying MLCT [164]. The spectral (UV–VIS, IR), electrochemical and photophysical properties of the [Ru(bpz)(CN)$_2$]$^{2-}$ and [Os(bpy)(CN)$_4$]$^{2-}$ complexes in aqueous and organic solution were reported. The role of cyanide and the chromophoric ligand are discussed



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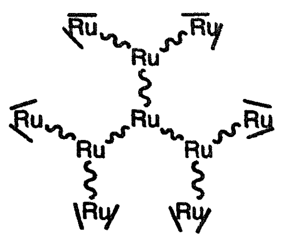

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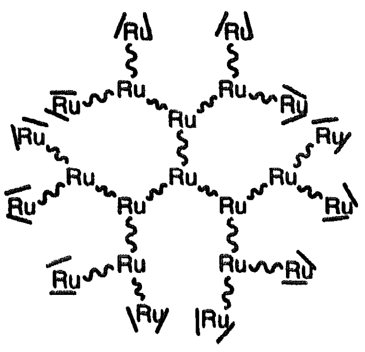

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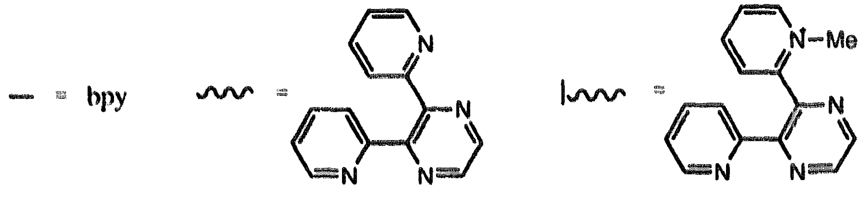
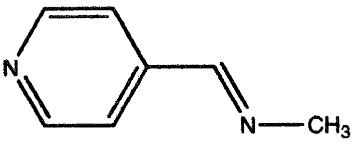


with emphasis on the assessment of the back-bonding ability of the metals towards a particular ligand [165]. A simple synthetic method to prepare mono- or dinuclear complexes containing dibasic ligands such as pyrazine or 4,4′-bipyridine from robust [Ru(dps)$_2$Cl] (dps = di-2-pyridylsulfide) was developed. The complexes were characterized by IR, UV–VIS, ^{1}H and ^{13}C NMR spectroscopies [166]. A new luminescent complexes [Ru(imin)$_2$(CN)$_2$] (imin = (**170**)) was synthesized and characterized. The correlation of MLCT absorption and Stokes Shift in protic and aprotic solvents with the solvent acceptor number and solvent dielectric parameter has been sought. The results were interpreted by means of DV-X$_\alpha$ molecular orbital calculations [167]. The role of the inner-sphere reorganization in the photoinduced oxidative and reductive electron transfer reaction of the excited complexes [Ru(imin)$_3$]$^{2+}$, [Ru(imin)$_2$(CN)$_2$] and [Ru(azpy)$_3$]$^{2+}$ (azpy = 2-(phenylazo)pyridine) in acetonitrile solution has been investigated. The factors which govern the electron transfer reaction were discussed and compared with other donor-acceptor systems [168].

The complex *trans*-[Ru(CN)$_2$(py)$_4$] has been used as a starting point for the stepwise construction of non-chromophoric Ru(II) *trans*-assemblies by addition of



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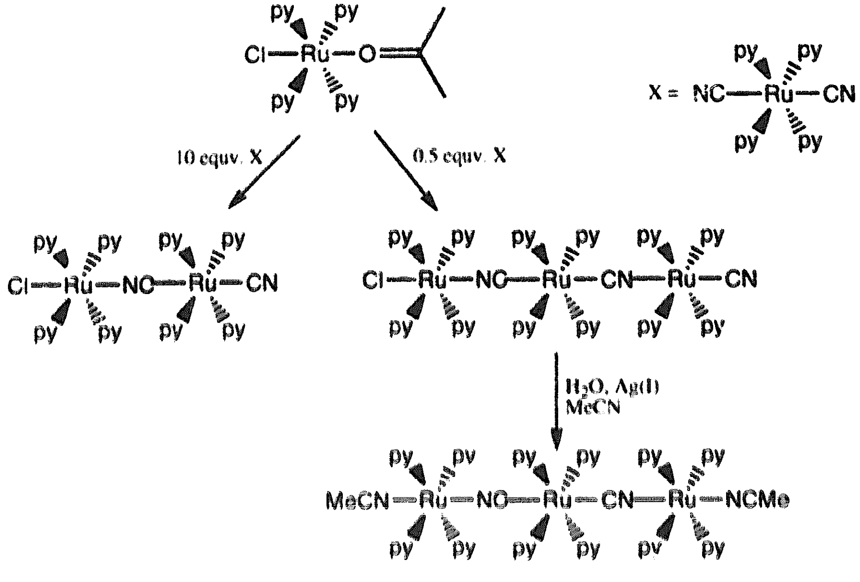
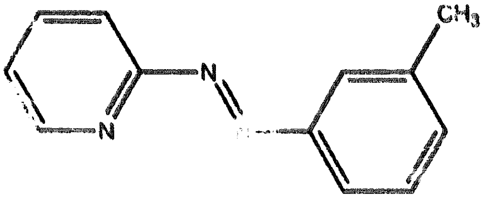
the *trans*-$[RuCl(py)_4]^+$ unit as shown in Scheme 3. The terminal chloride ligand can be selectively substituted showing promise for rational extension in one dimension to polynuclear structures. Evidence for electronic coupling between the Ru(II) centres was obtained from electrochemical and absorption studies [169].



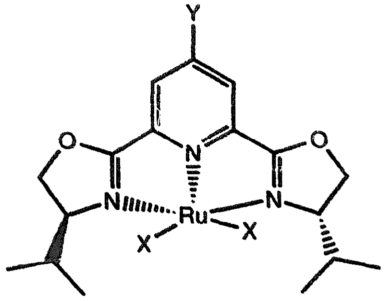
Scheme 3.

The kinetics and mechanism of the substitution of $[RuL_2(H_2O)_2]^{2+}$ (L = (**171**)) with thiourea have been investigated spectrophotometrically as a function of ionic strength, pH, temperature, medium dielectric constant and the concentration of the reactant. The activation parameters measured have been compared to those of related systems [170].



(171)

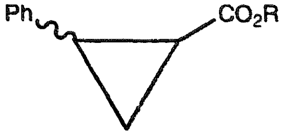
A chiral catalyst (**172**) was prepared *in situ* from the optically active ligand bis(2-oxazolin-2-yl)pyridine and $[RuCl_2(p\text{-cymene})]_2$. Complex (**172**) exhibited high activity for the asymmetric cyclopropanation of styrene and diazoacetates to give



X = Cl

Y = NMe_2, MeO, H, Cl, MeO_2C

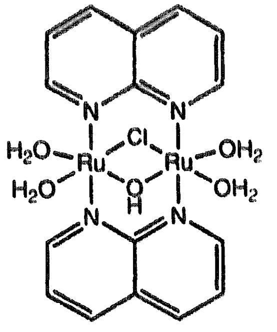
(172)



(173)

corresponding *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates (**173**) in good yields. A concerted mechanism for the reaction was postulated from the stereospecificity with deuterated styrene [171]. Electronic control by remote substituents in asymmetric cyclopropanation reactions with (**172**) has also been investigated. It was found that an electron-withdrawing group increases the catalyst activity and the *cis*/*trans* ratio of the products is not affected by these substituents [172].

A novel dinuclear ruthenium complex containing the didentate ligand 1,8-naphthyridine (**174**) was prepared and structurally characterized. Complex (**174**) was shown to be an active and stable catalyst in the oxidation of alcoholic substrates and in the epoxidation of *trans*- and *cis*-stilbene and cyclooctene [173]. NMR spectroscopic and ESMS studies indicated that the photolysis of $[Ru(tap)_3]^{2+}$ (tap = (**175**)) in the presence of 5-guanosine monophosphate yields a photoadduct (**176**) in which guanine is covalently bonded to the heterocyclic ligand by the nitrogen atom of the ligand tap [174].



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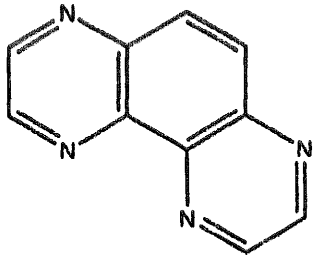
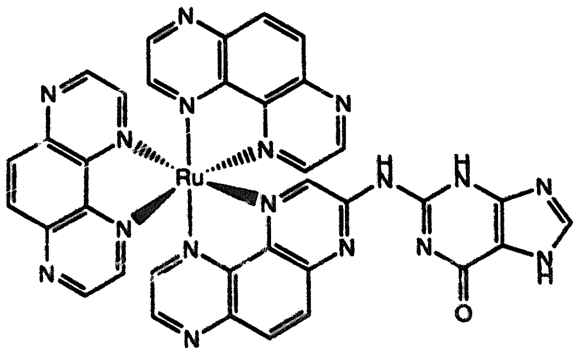


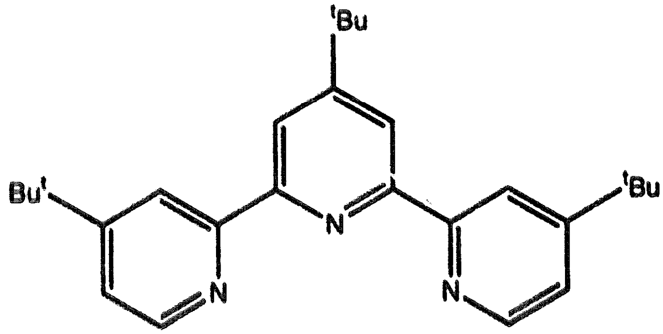
(175)

The preparation, characterization and a preliminary study of the *trans* to *cis* thermal and photochemical isomerization of $(trpy^*)RuCl_2L$ ($trpy^* = 4,4',4''$-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (**177**); L = CO, PPh_3, PMe_3, PMe_2Ph, $P(OPh)_3$, $P(OMe)_3$) have been described [175]. A systematic investigation on the effect of varying substituents on the luminescence properties of (**178**) has been carried out. A correlation between excited state energies and electrochemical redox potential has



(176)

been sought. The role played by various deactivation processes to determine the excited state lifetime in solution and in a rigid matrix was also discussed [176].

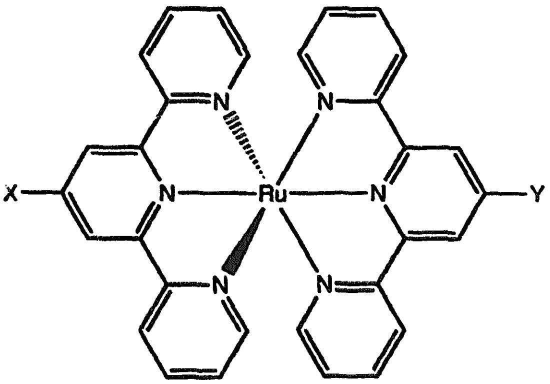


(177)

The surfactant terpyridine complexes $[Ru(tpy)L]^{2+}$ (L = 4′-alkyl-2,2′-6′,2″-terpyridine (**179**)) have been prepared from 4′-methyl-terpyridine and an appropriate 1-bromoalkene. These complexes are structurally related to surfactant $Ru(bpy)_3$ complexes and exhibit lyotropic mesomorphism in water [177].

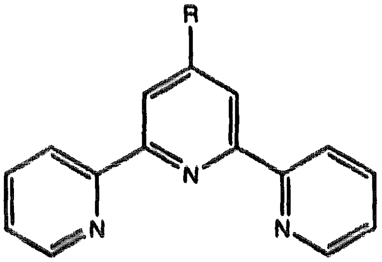
A new tridentate ligand (**180**) was prepared by Krohuke-type synthesis. The complexes $[Ru(tpy)L](PF_6)_2$ and $[RuL_2](PF_6)_2$ (L = (**180**)) have been isolated. It has been demonstrated that these ruthenium complexes can serve as building blocks for dinuclear and trinuclear complexes by attachment of additional metal fragments at the peripheral catecholate sites. The electrochemical, UV–VIS and ESR studies on the complexes have been reported [178]. The mononuclear complex ions $[Ru(tpy)(ML)Cl]^+$ (**181**) and $[Ru(tpy)(LH)]^{2+}$ (**182**) have been prepared by the reaction of $[Ru(tpy)Cl_3]$ with the potentially cyclometallating ligand L (2,2′:6′,4″-terpyridine (**183**)). Spectrochemical, electrochemical and photophysical properties of the complexes have been described [179].

The synthesis and electrochemical properties of complexes of the type $[Ru(tpy)(bpz)X]^{n+}$ ($X = Cl^-$, H_2O) as well as structural studies of the chloride derivative were reported. Oxidation of the aqua complex leads to the formation of



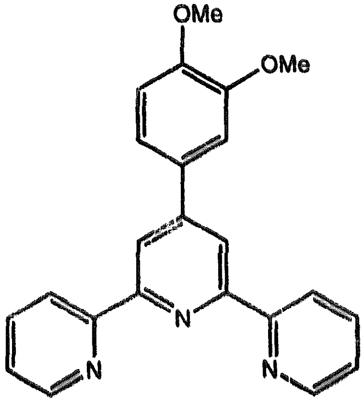
(178)

X	Y
$MeSO_2$	$MeSO_2$
Cl	Cl
H	H
EtO	EtO
OH	OH
Me_2N	Me_2N
H	$MeSO_2$
OH	$MeSO_2$
Cl	EtO
OH	Ph
$MeSO_2$	Me_2N
Cl	Me_2N
OH	Me_2N

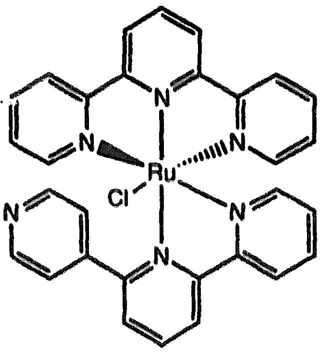


R = $C_{19}H_{39}$, $C_{31}H_{63}$

(179)



(180)



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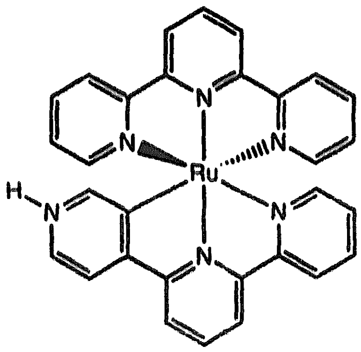

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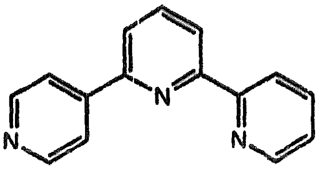
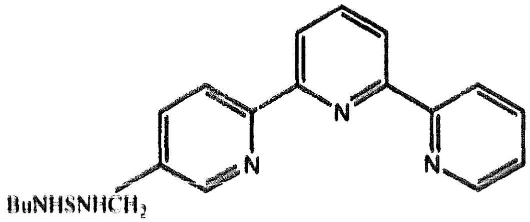
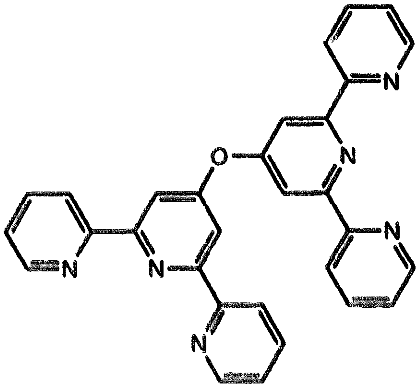


(183)

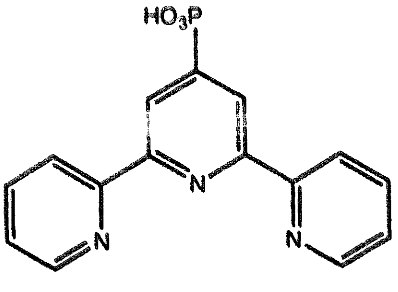
$[Ru^{IV}(tpy)(bpz)O]^{2+}$ (**184**) which has been found to be an active catalyst for the oxidation of benzyl alcohol. The rate constants for the oxidation by (**184**) and a related compound $[Ru^{IV}(tpy)(bpy)O]^{2+}$ were evaluated by cyclic voltammetry [180]. Systematic preparations of complexes containing hypodentate 2,2′:6′,2″-terpyridine ligands of the form $[RuL_2(terpy\text{-}N,N')]^{2+}$ have been presented (L = bpy, phen). The structural analyses and NMR spectroscopic studies of the complexes were described [181]. The new asymmetrical ligand L = (**185**) was prepared from 2-acetyl-5-picoline. The substitutionally inert Ru(II) template forms a well-ordered recognition site for dicarboxylate ions, as is evident from ^1H NMR spectroscopic studies [182]. A new type of ligand with two tpy metal-binding domains connected through an ether linkage (**186**) has been prepared *in situ* by reaction of 2,2′:6′,2″-terpyridine-4′(1′H)-one in the presence of K_2CO_3. This methodology was developed for the synthesis of a range of mono-, di- and hexanuclear complexes. Electrochemical studies and electronic spectra of the complexes suggested little electronic communication between linked metal centres [183].



(**185**)



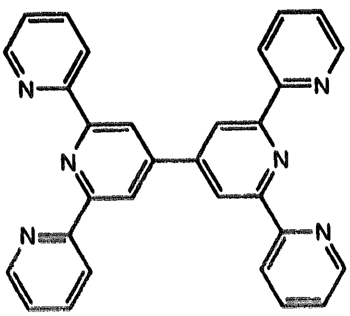
(**186**)



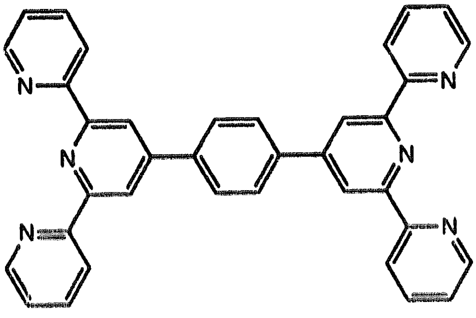
(**187**)

The complexes $[Ru(tpy)(X)(Y)(Z)]^{n+}$ ($X = PPh_3$, $Y = Z = CF_3CO_2$, n = 0; Y = Z = 4-ethylpyridine(4-Etpy), n = 2; Y = Z = 4-(dimethylamino)pyridine, n = 2; Y = 4-(Etpy), Z = Cl, n = 1; X = Cl, Y = Z = 4-Etpy, n = 1; X = Y = Z = 4-Etpy, n = 2) were prepared and characterized by UV–VIS spectroscopies and electrochemical studies. The effects of coordination geometry on the photophysical and photochemical properties of the complexes have been discussed [184]. The synthesis and characterization of the diethyl ester of the novel ligand 2,2′:6′,2″-terpyridine-4′-phosphoric acid (L=(**187**)) and the complex [Ru(4,4′-Me-2,2′-bpy)(L)(NCS)] have been reported. The phosphonate group enhances the adsorption onto TiO_2 surfaces and provides sufficient electronic coupling with the oxide to achieve efficient light-induced charge separation [185].

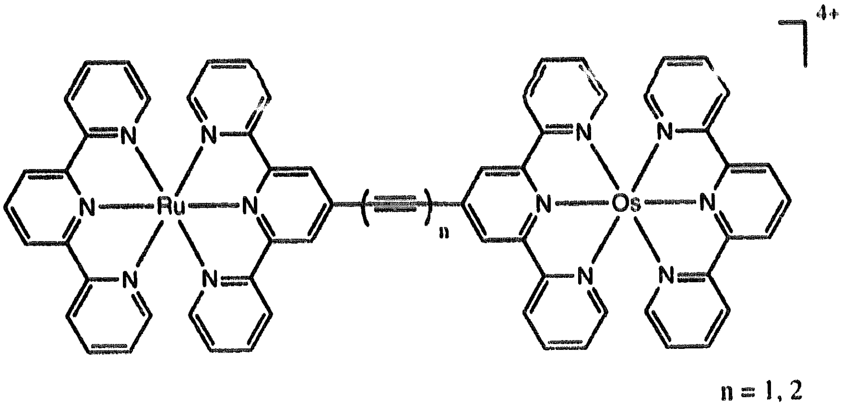
A new strategy for the assembly of homo- and hetero-metallic di- and tri-nuclear metallosupramolecular oligomers using complexes $[Ru(Xtpy)(dpqtpy)](PF_6)_2$ was described (dpqtpy=(**188**); X=H, EtO, MeO, Me_2N, Cl, MeO_2S, MeS, HO, Ph, Fe). All complexes were fully characterized and detailed spectroscopic, spectrometric and electrochemical studies were described [186]. Polymetallic complexes having well-defined geometries were prepared *via* attachment of an anchor ligand to a quartz surface followed by repeated sequential reactions with $[Fe(OH)_6]^{2+}$ and $[L_2RuCl_2]$ (L=(**189**)) [187]. A salt of t mixed-metal complex $[(tpy)RuLOs(tpy)]^{4+}$ (**190**) was prepared and characterized by FTIR, UV–VIS and FABMS spectroscopies and elementary analysis. The rate of intramolecular triplet energy transfer upon excitation of the Ru^{II} unit in the dinuclear complex decreased by one third when the alkyne spacer was extended by a second ethynyl group whilst the Ru-Os distance increased by 2.4 Å [188]



(**188**)



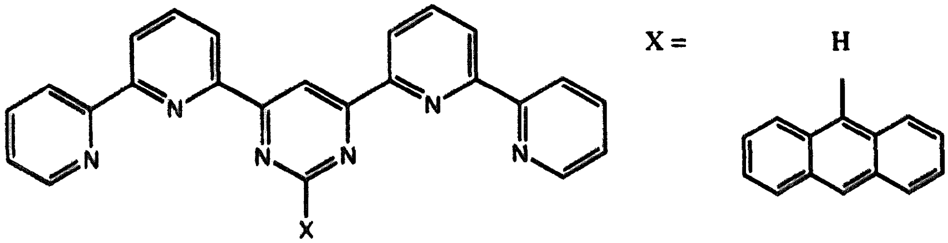
(**189**)



(**190**)

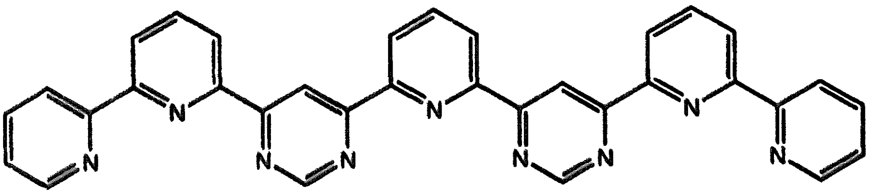
Two new pyrimidinyl ligands (**191**) and (**192**) were prepared from Pd catalysed cross-coupling of 2-substituted-4,6-dichloropyrimidines and 6-tributylstannyl-2,2′-

bipyridine. These ligands were found to form 'rack-type' homonuclear Ru(II) complexes $[Ru_3L(tpy)_3](PF_6)_6$ (L=(**191**)) and $[Ru_2L(tpy)_2](PF_6)_4$ (L=(**192**)). Electrochemical studies of the complexes have been presented [189]. In addition, the luminescence spectra and triplet-triplet transient absorption spectrum of the dinuclear rack-type complex containing L=(**193**) have been recorded [190].



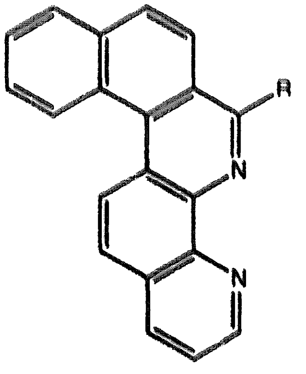
(191)

(192)



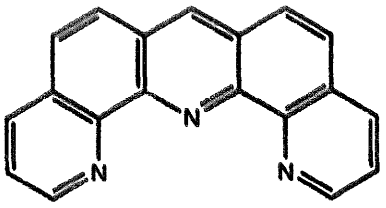
(193)

The syntheses of ruthenium complexes containing ligands (**194**) and (**195**) have been described. The complexes were characterized by ^{1}H NMR, IR, MS spectroscopies and cyclic voltammetry [191].



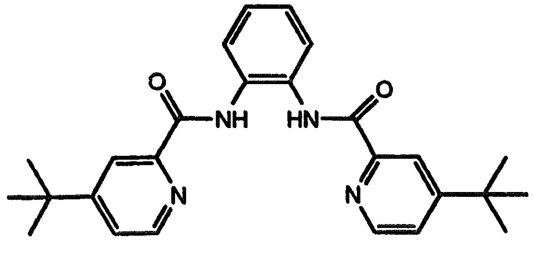
R = ^{i}Pr, Ph

(194)



(195)

The mononuclear ruthenium complex $[RuL(PPh_3)Cl]$ (L=(**196**)) was synthesized from the reaction of $[Ru(PPh_3)_3Cl_3]$ and the tetradentate amide. Its function as a catalyst for alkene epoxidation by PhIO, cyclopropanation of styrene by ethyl diazoacetate, and aziridiation of styrene by $PhINO_2SC_6H_4Me$ was described [192]. The complex $[RuL](PF_6)$ (L=(**197**)) was synthesized and characterized by spectral, electrochemical and crystallographic methods. Cyclic voltammetric studies of the complex show two reversible processes at +0.854 V and −0.056 V *vs* Fe/Fe$^+$ which have been assigned to Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples respectively [193].



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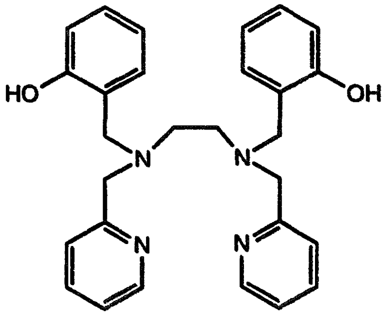
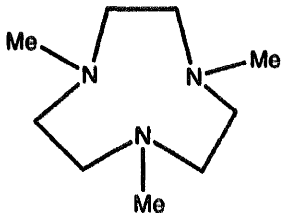


(197)

The interactions and photoreactions of $[Ru(hat)_3]^{2+}$, $[Ru(tap)_3]^{2+}$, $[Ru(tap)_2L]^{2+}$ or $[Ru(hat)_2L]^{2+}$ (hat = (**149**), tap = (**175**); L = bpy or phen) with nucleotides and DNA were studied. The complexes interact with DNA to produce a photo-electron transfer from a guanine base to the corresponding excited state of the complexes. Covalently-bound adducts were formed between the metal complexes and calf thymus DNA. The relation between rate constant of quenching and reduction potential of the metal complexes has been sought [194].

6.4. Complexes with macrocyclic ligands

The half-sandwich complex cations $[RuL(X)Y(Z)]^+$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane (**198**), X = Y = CO, Z = Cl; X, Y = dppe, Z = Cl, X, Y = dppe, Z = H; X = CO, Y = PPh_3, Z = H; X = Y = 2,6-$Me_2C_6H_3NC$, Z = O_2CCF_3) were synthesized and characterized by spectroscopic methods [195]. The structure of $[Ru(L)(DMF)_2](ClO_4)_2$ has been determined by single-crystal X-ray crystallography (L = tetrabenzo(b,f,j,n)[1,5,9,13]tetraaza-cyclohexadecane (**199**)) [196].



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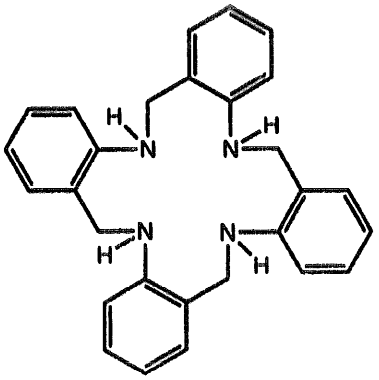
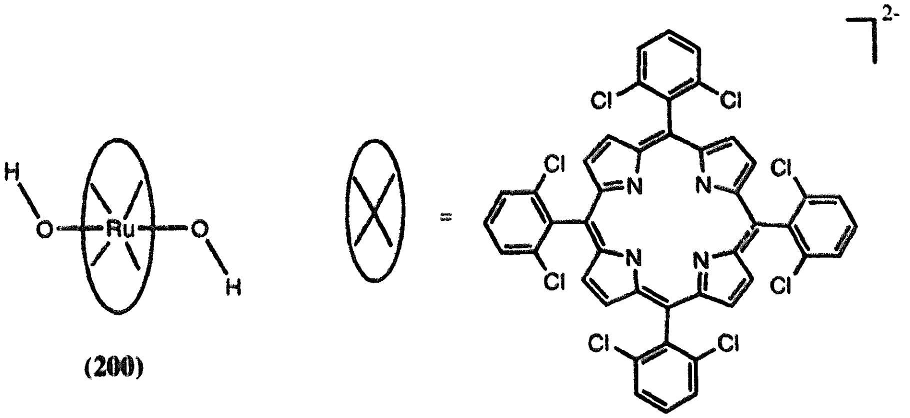


(199)

The complex *trans*-$[Ru(TDCPP)(OH)_2]$ (**200**) was isolated as air-stable crystals from the oxidation of [Ru(CO)(TDCPP)] (TDCPP = tetrakis-(2,6-dichlorophenyl)porphyrin) and was characterized by X-ray crystallography.

The short axial Ru-O bond distance (1.790(7) Å) is in the range expected for a Ru(IV)-O double bond [197]. The syntheses and characterizations of [Ru(TFPPX$_8$)(L$_n$)] (X = Br, Cl, L = CO, n = 1; py, n = 2) (TFPP = (**201**)) have been reported. The reduction potentials of these complexes are much more positive that those of the unhalogenated analogues. The electronic structures of the complexes were established based on electronic spectral data [198].



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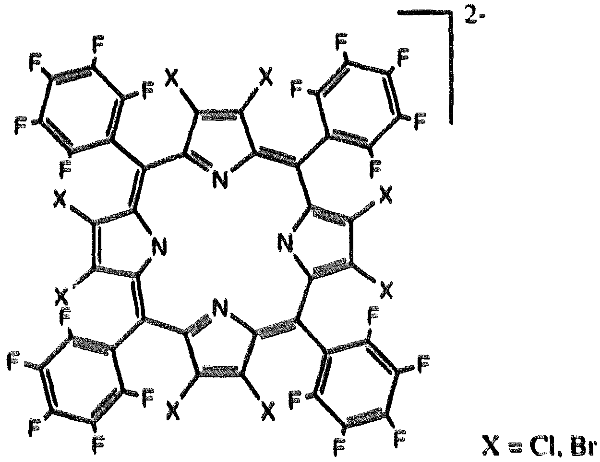
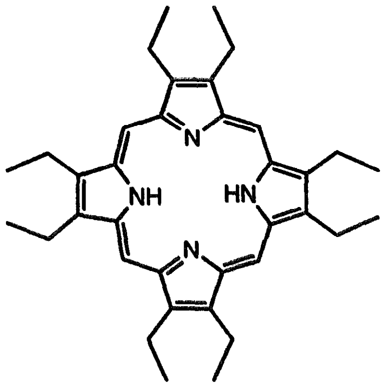


(201)

The complex [Ru^{VI}(TMP)(O)$_2$] was prepared by the oxidation of [Ru^{II}(TMP)(THF)$_2$] using nitrous oxide. The extent of oxidation was found to be dependent on porphyrin concentration. The mechanism of oxygen atom transfer form N$_2$O to ruthenium, and the use of N$_2$O as a potential oxidant in the ruthenium-promoted catalytic oxidation of organic substrates were also discussed [199]. The reactions of [Ru(OEP)]$_2$ with thioethers or sulfoxide ligands give [Ru(OEP)(L)$_2$] (L = RR′S or RR′SO) (H$_2$OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin (**202**)). All complexes were characterized using ^{1}H NMR, IR and UV–VIS spectroscopies, cyclic voltammetry and elemental analysis. The compound [Ru(OEP)L$_2$](BF$_4$) (L = *n*-decyl methyl sulfide) has been structurally characterized. Electrochemical studies suggested that rearrangement of *S*-bound to *O*-bound sulfoxide occurs in solution after a metal-centred oxidation [200]. Novel NMR spectroscopic aspects of the hexacoordinated ruthenium complexes [(EP)RuL$_2$] (L = tertiary phosphine) and the pentacoordinated complex [(EP)Ru(PPh$_3$)] have been reported (EP = (**203**)). The multiplicity observed in the ^{1}H NMR spectra was interpreted in terms of steric interactions between the axial ligands and the macrocycle [201].



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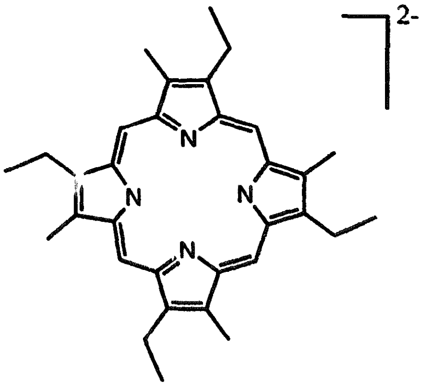
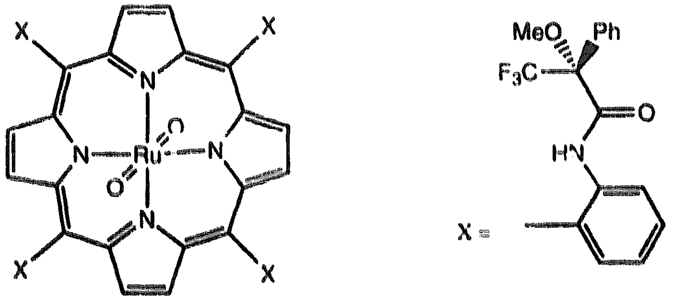


(203)

The synthesis of dioxoruthenium(VI) picket-fence porphyrins (**204**) bearing optically active α-methoxy-α(trifluoromethyl)phenylacetyl residues on both sides of the porphyrin plane, and the chiral induction in the oxygen-transfer to racemic benzylmethylphosphine from the α,β,α,β-isomer of (**204**) in high ee have been described [202].



(204)

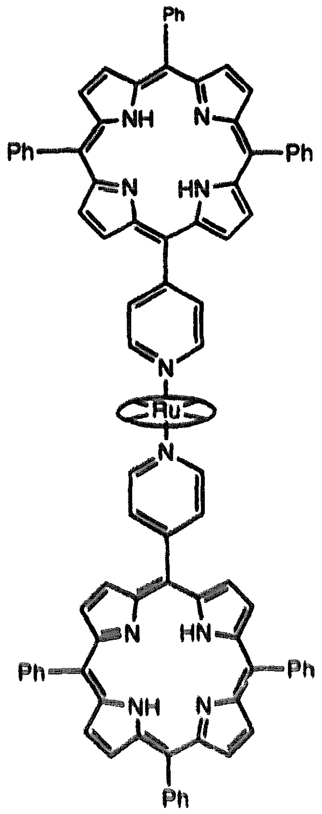
The decomposition of cyclohexyl hydroperoxide catalysed by ruthenium tetraarylporphyrins has been reported. During decomposition, hydroxylation of the solvent was observed. A mechanism consistent with the experimental results was proposed [203]. A novel facile synthesis of dihaloruthenium(IV) porphyrins which are versatile precursors to a unique organometallic chemistry of ruthenium porphyrins has been described and is shown in Scheme 4 [204].

$$\mathrm{Ru(TPP)(CO)} \xrightarrow[\text{vacuum, py}]{h\nu} \mathrm{RuTPP(py)_2} \xrightarrow[\text{vacuum}]{200^{\circ}\mathrm{C}} [\mathrm{Ru(TPP)}]_2 \xrightarrow{\mathrm{CX_4}} \mathrm{Ru(TPP)X_2}$$

X = Cl, Br

Scheme 4.

The novel vertically-linked porphyrin trimer (**205**) and ruthenium(II) oligomers (**206**) and (**207**) were synthesized and characterized. The trimer (**205**) exhibits intriguing electronic interactions [205]. Moreover, the synthesis of a vertically-linked cyclic ruthenium porphyrin tetramer (**208**) and its characterization by ^{1}H NMR, FAB MS, IR and UV–VIS spectroscopies were described. The reaction of (**208**) with pyridine in solution has also been investigated [206].



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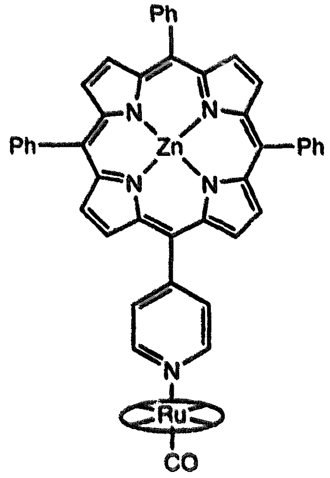

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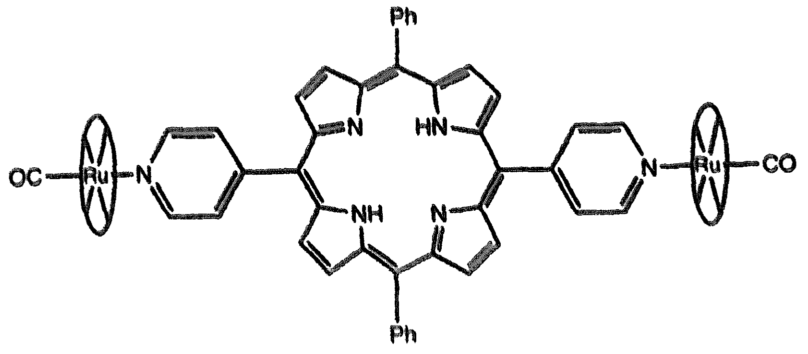
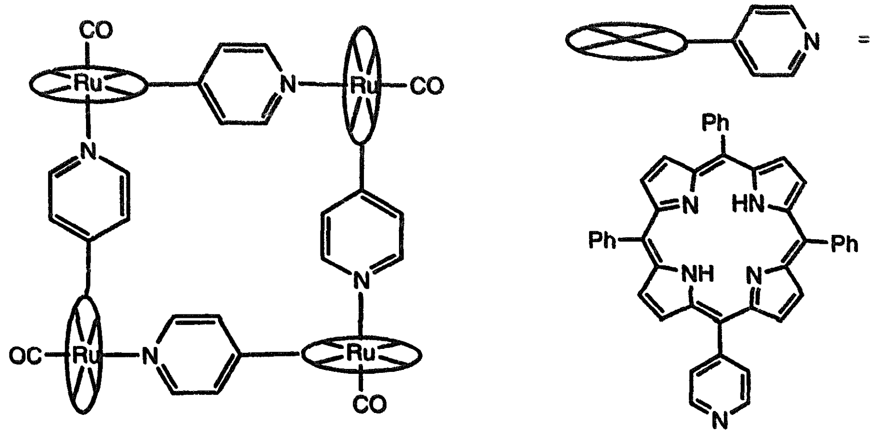


(207)

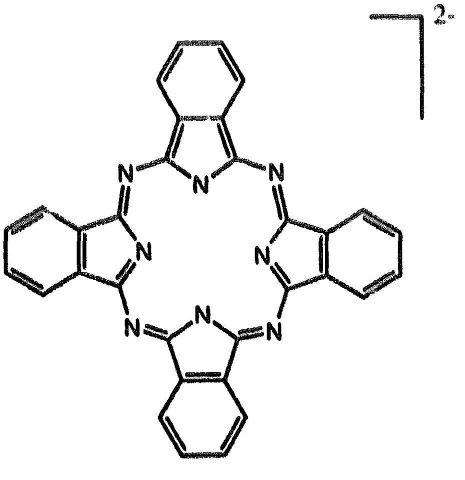
= (**202**)

The reaction of the complex [Ru(py)$_2$(Pc)] with molten [Bu$_4$N]X yielded the air stable complex (Bu$_4$N)$_2$[Ru^{II}(X)$_2$(Pc)] (**209**) (X = Cl, Br; Pc^{2-} = (**210**)). Complex (**209**) was characterized by UV, Raman, IR spectroscopies and electrochemical



(208)

techniques [207]. A simple high yielding synthesis of pure water soluble ruthenium phthalocyanine complexes [Ru(Pc)L_2] (L = 3-pyridine sulfonate, triphenylphosphine monosulfonate) has been described [208]. The preparation of the perfluorinated Ru phthalocyanine complex [Ru(F_{16}Pc)] (**211**) and the zeolite NaX-encapsulated [Ru(F_{16}Pc)] and their characterizations using FT–IR, UV–VIS and XRD spectroscopies have been reported. It was shown that complex (**211**) is an effective catalyst for the oxidation of cycloalkenes at room temperature. Encapsulation of (**211**) in zeolite NaX enhances its catalytic activity and selectivity [209]. In addition, preliminary mechanistic studies have been performed and suggested a P450 type pathway for the oxidation [210].



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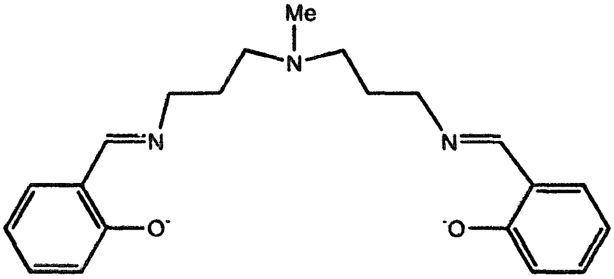
A series of heteronuclear oxo-bridged complexes [$LM^{III}ORu^{IV}(P)OM^{III}L$] have been synthesized by redox reactions involving [$Ru^{VI}(O)_2P$] and ML complexes (P = TPP, TMP or OEP; M = Fe(III), Cr(III), Mn(III); L = TPP, TMP OEP or dianion of salen, salmah (**212**)). Detailed studies of the temperature and field dependent magnetic properties and Mossbauer spectral measurements of [LMORu(P)OML] were made [211].



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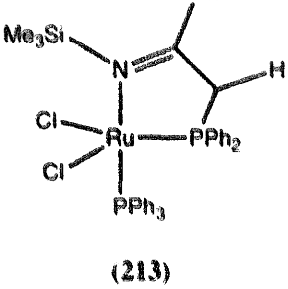
The syntheses of tetra-*tert*-butylphthalocyaninatoruthenium(II) and tetra-*tert*-butyl-2,3-naphthalocyaninatoruthenium(II) by thermal decomposition of the corresponding biaxially coordinated 3-chloropyridine and ammine complexes were described. These complexes were characterized by UV–VIS, IR and NMR spectroscopies and mass spectrometry. A dimeric structure was proposed for both complexes [212]. The preparation, characterization and electrical conductivity measurements of the stacked transition metal macrocycles $[\mathrm{MacM(L)}]_n$ (M = Fe, Ru, Os; H_2Mac = phthalocyanine or 2,3-naphthalocyanine; L = triazine, substituted tetrazines, tetrazines, dicyane, dicyanoacetylene, fumarodinitrile) have been described. The electrical and physical properties of these complexes (UV and Mossbauer spectra) have been discussed with respect to the intrinsic semiconducting properties of the compounds [213].

6.5. *Complexes with other mixed donor ligands*

Reaction of $[\mathrm{RuCl_2(PPh_3)_3}]$ with 1 equivalent of $\mathrm{(Ph_2P)NC(Ph)N(SiMe_3)_2}$ in THF yields $[\mathrm{RuCl_2(PPh_3)\{N(SiMe_3)C(Ph)NH(PPh_2)\}}]$ (**213**). The crystal structure was determined by X-ray crystallography. The $\mathrm{N(SiMe_3)C(Ph)NH(PPh_2)}$ moiety acts as a chelating ligand and a γ-agostic interaction occurs between Ru and one of the Me groups of the $\mathrm{N(SiMe_3)}$ imino group. A possible mechanism for the formation of (**213**) has been proposed [214].



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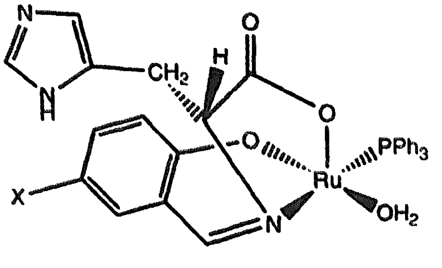
Mononuclear chiral ruthenium(II) Schiff base complexes $[\mathrm{RuL(PPh_3)(OH_2)}]$ (**214**) were synthesized and characterized. The asymmetric epoxidation of nonfunctionalized olefins with iodosylbenzene by these complexes has been reported; the mechanistic aspects of epoxidation were discussed [215]. The complex

$[RuL_2(PPh_3)_2]$ (HL = 8-hydroxyquinoline (**215**)) was isolated in the pure isomeric forms with the RuN_2O_2 coordination sphere having *cis,trans,cis*- and *trans,trans,trans*-configurations. Chemical or electrochemical oxidation of either isomer afforded the trivalent complex $[RuL_2(PPh_3)_2]^+$ in the *trans,trans,trans*-configuration [216]. The crystal structures of the three geometrical isomers of $[RuClL_2NO]$ (L = 2-methyl-8-quinolinol) and the kinetic analyses of reversible thermal isomerization among these isomers have been presented [217].



X = H, Cl, OMe

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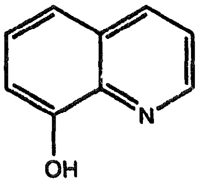

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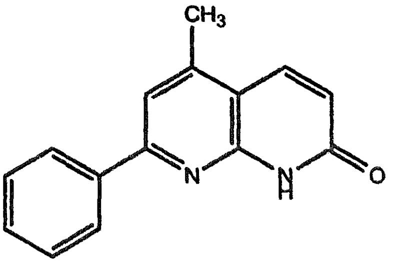

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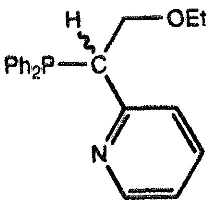
The preparation of the diruthenium complexes $[Ru_2ClL_2(OAc)_2]$ (**216**) and $[Ru_2L_2(OAc)_2]$ (**217**) (HL = 5-methyl-7-phenyl-1,8-naphthyridin-2-one (**218**)) have been described. The further reaction of (**216**) with L in refluxing methanol yielded $[Ru_2L_4]$ and its H_2O adduct $[Ru_2L_4(H_2O)]$ (**219**). All complexes were fully characterized. Complexes (**216**), (**217**) and (**219**) were also characterized by X-ray crystal structure analysis [218]. Three new compounds containing either a Ru_2^{4+} or Ru_2^{5+} core bridged by 2-hydroxy-6-chloro-pyridine ligands have been prepared and structurally characterized. The regioisomerism displayed by these complexes has been discussed [219]. Two stable ruthenium-picolinate complexes, $[Ru^{III}(pic)_3]$ and $[Ru(bpy)(pic)_2]$ (Hpic = picolinic acid), have been synthesized and characterized by ESR, UV, IR and NMR spectral data, and magnetic susceptibility and electrochemical measurements [220].

The amidato complexes $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)\{\mu\text{-}NH(CO)R_F\}_2(CO)_2(PPh_3)_4]$, $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)\{\mu\text{-}NHC(O)R_F\}_2(CO)(PPh_3)_2]$, $[Ru\{NHC(O)R_F\}_2(CO)(H_2O)(PPh_3)_2]$ ($R_F = CF_3$, C_2F_5, C_6F_5) were synthesized and characterized. The dinuclear amidato bridged complexes were obtained as a mixture of 'head-to-tail' and 'head-to-head' isomers. The crystal structure of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)\{\mu\text{-}NHC(O)C_2F_5\}_2(PPh_3)_4]$ was reported [221]. Transfer hydrogenation of ketones by propan-2-ol mediated by the complexes $[RuCl_2(PPh_3)L]$ (L = (**220**)-(**224**)) has been discussed. It was shown that no significant ee was observed [222].

6.6. Complexes with ammonia and amine ligands

Cation exchange between the NaY zeolite and $[Ru(NH_3)_6]Cl_3$ yields stable metallic Ru clusters incorporated in zeolite Y; these were active catalysts for ammonia synthesis. The influence of the precursor synthesis conditions on catalytic activity was studied by *in-situ* and *ex-situ* UV–VIS spectroscopy, AAS and XRD [223].



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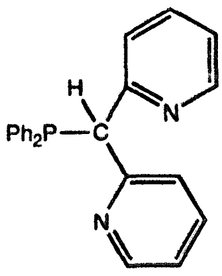

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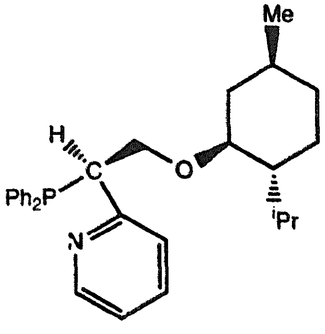

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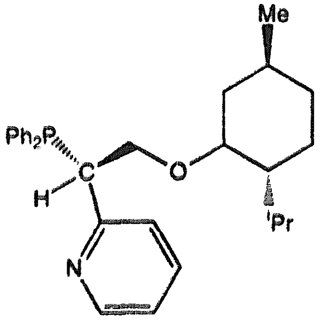

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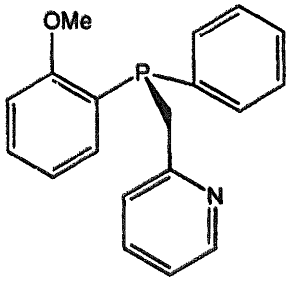

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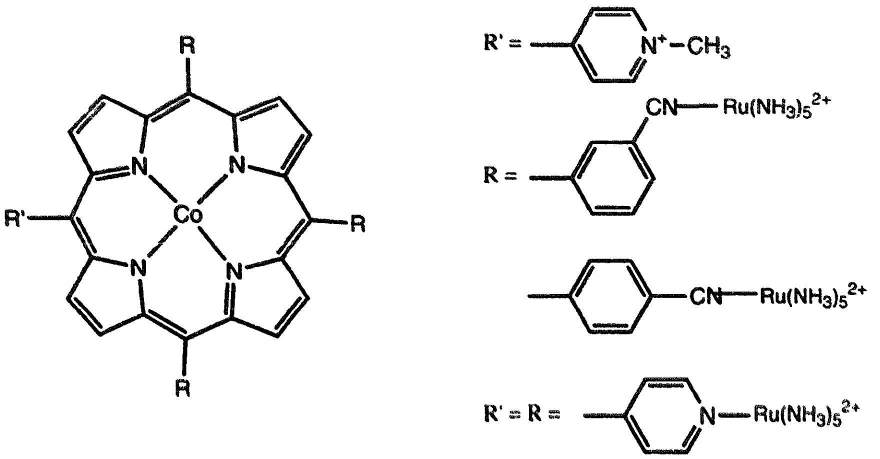
Investigations of the incorporation of $[Ru(NH_3)_6Cl_3]$, $[Fe(phen)_3]^{2+}$ and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21H,23H-porphyrin cations onto the poly(4-pyrrol-1-ylmethyl]benzoic acid film on indium tin oxide (ITO) electrodes were described [224].

The crystal and molecular structures of $[Ru(NH_3)_6]Cl_3$ have been determined. Four crystallographically independent $Ru(NH_3)_6$ fragments were observed in a unit cell of which only two were almost identical with respect to conformation and orientation. The ESR spectroscopic properties of the complex were also investigated [225]. The crystal structure of $[Ru(ND_3)_6](SCN)_3$ was determined at 20 K by time-of-flight neutron diffraction [226]. The tetraruthenated cobalt complexes (**225**)-(**226**) have been synthesized and adsorbed on a graphite electrode. The 3-cyanophenyl derivative catalyses the two-electron reduction of O_2 to H_2O_2 whereas the 4-cyanophenyl derivative catalyses the 4-electron reduction to H_2O. Evidence of the importance of back-bonding between $[Ru(NH_3)_5]^{2+}$ and the porphyrin rings was obtained [227]. It was found that tetraruthenated complex (**227**) adsorbed on a graphite electrode would act as a catalyst for the 4-electron reduction of O_2. In solution, only a 2-electron reduction of O_2 was obtained. The rate of intramolecular electron transfer from the $Ru(NH_3)_5$ site of the catalyst to the Co(II) centre in the porphyrin ring was shown to be slow and did not contribute to the catalytic reduction. The contrasting mechanistic behaviours of the catalyst in solution and on graphite electrodes was discussed [228].

The generation of singlet oxygen by a photochemical pathway involving the



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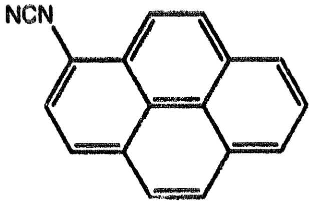
Ru(II) complexes $[\mathrm{Ru(NH_3)_5(NCPy\text{-}R)}]^{3+}$ ($\mathrm{R = CH_3, CH_2C_6H_5}$) was reported. The influence of the substituent on the stability of the complex in the presence of singlet oxygen was also studied. A kinetic treatment of this process showed that the quenching of singlet oxygen by the complex has diffusional character [229].

Complexes $[\mathrm{Ru(NH_3)_5L](ClO_4)_2}$ (L = **(228)**-**(232)**) have been prepared and characterized using cyclic voltammetry and electronic absorption spectroscopy. The extent of conjugation of the group attached to the cyanamide anion moiety has been found to have a significant effect on the oscillator strength of the $b_1 \rightarrow b_1^*$ LMCT transition of the Ru(III)-NCN chromophore. Extended Hückel MO calculations on the free anionic ligands were employed to estimate the transition dipole moment for the $b_1 \rightarrow b_1^*$ transition of the cyanide complexes [230]. The effects of dibenzo-30-crown-10, dibenzo-36-crown-12 or dibenzo-42-crown-14 towards the electron transfer reactivity of $[\mathrm{Ru(NH_3)_5(4\text{-}methylpyridine)}]^{3+/2+}$ have been examined using electrochemical and optical intervalence measurements. A sequential electron transfer/crown transfer mechanism was proposed based on the barrier analysis [231].



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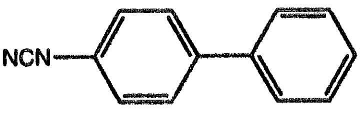

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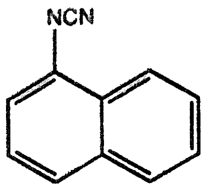
The air stable complexes $[(\mu_4\text{-TCNX})\{\mathrm{Ru(NH_3)_5}\}_4]^{8+}$ (TCNX = TCNE, TCNQ, TCNP, TCNB) have been prepared and studied. They show spectroscopic equivalence for the four nitrile and pentaamminemetal groups on the IR, UV–VIS and XPS spectroscopic time scales. The redox behaviour was studied using IR spectroelectrochemical techniques [232].

Theoretical studies of solvent effects on electronic spectra of $[\mathrm{Ru(NH_3)_5py}]^{2+}$ in aqueous solution were performed using *ab initio* MCSCF and INDO/S-CI methods.



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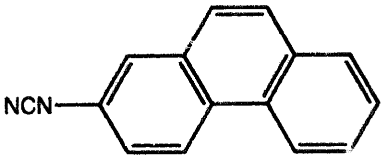

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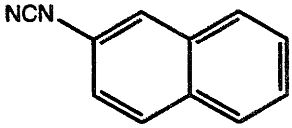

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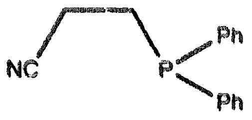
Intermolecular potential surfaces were used to investigate the relationships between the solvent shift and solvent structure [233]. The complex $[Ru(SB_{12}H_{11})(NH_3)_5]\cdot 2H_2O$ was prepared by reaction of $Cs_2[B_{12}H_{11}SH]$ with $[RuCl(NH_3)_5]Cl_2$. The structure of the complex was determined by single-crystal X-ray analysis [234].

The mechanism of the substitution reaction of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ (L = imidazole, pyrazine or isonicotinamide) in aqueous solution was studied by a volume-profile analysis. Based on the volume of activation data and the controlled volume profiles, a dissociative mechanism was proposed [235]. The spin-density distributions in heterocyclic ligands coordinated in *trans*-$[(L)ImRu^{III}(NH_3)_4]$ (L = isonicotinamide, py, Im, NH_3, Cl^-, SO_4^{2-}) have been investigated by EPR and NMR spectroscopies. X-Ray diffraction study of *trans*-$[(Im)_2Ru^{III}(NH_3)_4]Cl_3\cdot H_2O$ revealed that the imidazole rings adopt an eclipsed conformation [236].

The trinuclear Ru complex $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}Ru(NH_3)_5]^{6+}$ was adsorbed onto electrodeposited Pt-black; effective catalytic oxidation of water by this adsorbed complex has been reported [237]. A preference for *N*-coordination over *P*-coordination was observed in $[Ru(NH_3)_5(2\text{-}EDP)]^{2+}$ (2-EDP = 2-cyanoethyldiphenylphosphine (**233**)) by using FTIR, ^{31}P NMR spectroscopic and electrochemical techniques. The stability of $[Ru(NH_3)_5(2\text{-}EPD)]^{2+}$ in aqueous solution and the kinetics of the formation of the dinuclear complex ion $[(NH_3)_5Ru(2\text{-}EDP)Ru(NH_3)_5]^{2+}$ have been studied [238]. The thiocyanato-bridged dinuclear complex $[Ru_2(NH_3)_8(SCN)_3]^{3+}$ (**234**) has been prepared by the treatment of $[Ru(NH_3)_5Cl]^{2+}$ with SCN^-. Kinetic and mechanistic studies for the formation of (**234**) have also been carried out [239].



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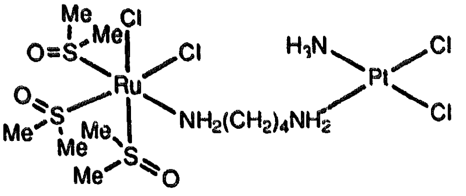
The natural dioxolene complex $[Ru(NH_3)_4(diox\text{-}COO)]$ (**235**) was prepared from the reaction of $[Ru(NH_3)_5Cl]Cl_2$ and 3,4-dihydroxybenzoic acid. The use of (**235**) as a precursor for synthesizing *cis*-$[Ru(NH_3)_4L_2]^{n+}$ (L = H_2O, acetone, n = 3; L = Cl, Br, n = 2) and their chemical and electrochemical behaviour were discussed [240]. The factors affected the solution phase recognition of the complexes $[Ru(NH_3)_x(bpy)_y]^{2+}$ (x = 4, y = 1; x = 2, y = 2; x = 0, y = 3), $[Ru(NH_3)_4(phen)]^{2+}$

and $[Ru(NH_3)_x(py)_y]^{2+}$ (x=5, y=1; x=4, y=2) by dibenzo crown ethers were examined. The preferred associated geometries in solution have been studied using NMR (NOE) spectroscopic measurements [241].

The synthesis and characterization of the heterodinuclear DNA-DNA and DNA-protein crosslinking agent [{*cis-fac*-$(RuCl_2(Me_2SO)_3$}μ-$NH_2(CH_2)_4NH_2$-{*cis*-$(Pt(NH_3)Cl_2)$}] (**236**) have been reported [242].



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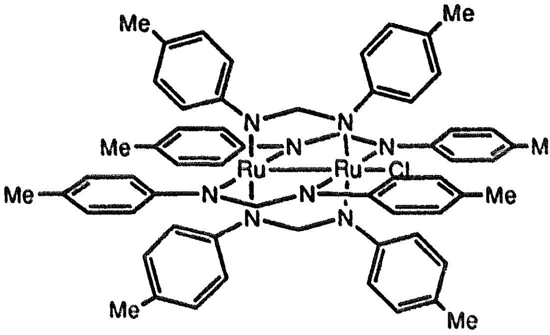

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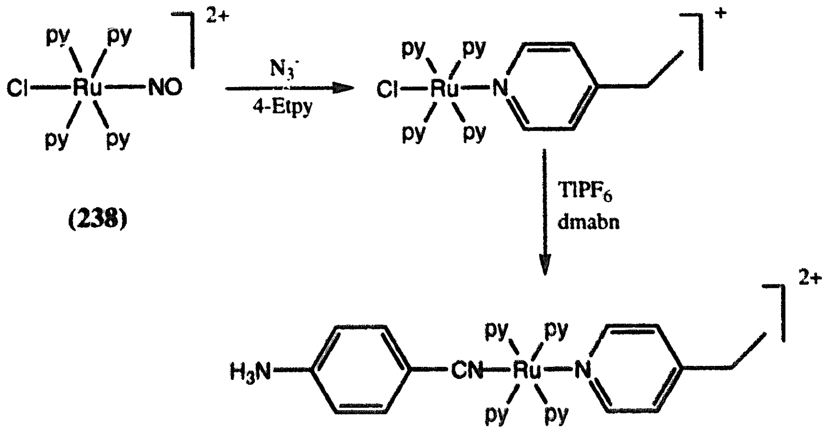
The dinuclear complex $[Ru_2(DtolF)_2Cl]$ (**237**) was isolated from the reaction of $[Ru(OAc)_4Cl]$ and molten HDtolF (di-*p*-tolylformanidine). The crystal structure of (**237**) was established and the Ru-Ru separation is 2.370(2) Å [243].

6.7. Complexes with nitrosyl ligands

The complexes *cis*-$[Ru(NO)(X)(bpy)(py)_2]^{n+}$ (X=OH, Cl, NO_2, n=2, X=py, n=3) have been synthesized and characterized by spectroscopic techniques. An X-ray analysis of the compound *cis*-$[Ru(NO)(OH)(bpy)(py)_2](PF_6)_2$ has been performed. Chemical oxidation and electrochemical reduction of the complexes were discussed [244]. The complex $[Ru(NO)Cl_3(AsPh_3)_2]$ was prepared from $[RuCl_3(NO)]$ and $AsPh_3$. The complex was fully characterized and the crystal structure was determined by X-ray diffraction. The central Ru atom is octahedrally coordinated with arsine ligands in a *trans*-configuration [245]. Three new nitro-nitrito isomeric complexes *cis*-$[Ru(NO)_x(2,2'\text{-bpy})_2]^{2+}$, *cis*-$[Ru(NO)X(pyca)_2]$ and *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (X=ONO, NO_2; pyca=pyridine-2-carboxylate) were prepared and characterized. A reversible redox-induced and thermally-induced nitro-nitrito linkage isomerization occurs in *cis*-$[Ru(NO)X(2,2'\text{-bpy})(py)_2]^{2+}$ (X=ONO, NO_2) [246].

The reaction of *trans*-$RuCl_2(py)_4$ with excess $[NO_2]^-$ in refluxing pyridine gives *trans*-$[Ru(NO_2)_2(py)_4]$ which transforms to *trans*-$[RuCl(py)_4(NO)](PF_6)_2$ (**238**) in refluxing concentrated HCl. A strategy for the synthesis of asymmetric *trans* complexes derived from (**238**) has been developed (Scheme 5). The asymmetric dimetallic complex [{*trans*-$RuCl(py)_4$}$_2$(μ-pyz)]$^{2+}$ has been structurally characterized and its reactivity has also been investigated [247].



(238)

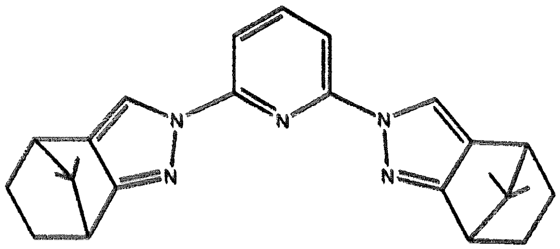
Scheme 5.

7. Complexes with oxygen donor ligands

7.1. Complexes with oxo ligands

The synthesis and characterization of $[Ru_2OCl_6(MeCN)_4]\cdot 2MeCN$ (**239**) have been reported. The reactions of (**239**) with alcohols, ethers and carbohydrates were presented. A single-crystal X-ray structure determination of (**239**) was carried out [248].

The optically active cation *cis*$[Ru(bpy_2(py)(O)](ClO_4)_2$ (**240**) has been prepared by the oxidation of the aqua precursor complex. Complex (**240**) catalysed the asymmetric oxidation of prochiral methyl *p*-tolyl sulfide to a chiral sulfoxide with 30% ee in water-acetonitrile mixture [249]. The mechanism of epoxidation of (**240**) has been investigated by GC–MS, ^1H NMR spectroscopic and global kinetic analytical techniques. The cation $[Ru(bpy)_2(py)(OH)]^{2+}$ was detected as the intermediate complex [250]. The synthesis and characterization of the new chiral complex $[RuL(bpy)O]^{2+}$ (L = (**241**)) have been reported. The X-ray crystal structure of the aqua precursor complex was determined. It has been shown that the oxo complex is a powerful oxidant for the epoxidation of unfunctionalized alkenes and exhibits promising enantioselectivity [251].



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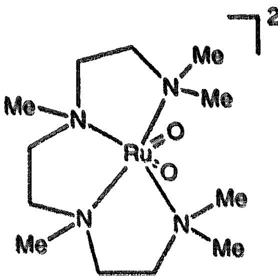

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A kinetic study of oxidation of alcohols, aromatic hydrocarbons and alkenes by *cis*-$[Ru^{VI}LO_2]^{2+}$ (**242**) (L = *N,N,N',N'*-tetramethyl-3,6-diazaoctane-1,8-diamine) has been reported. These oxidations are similar to those of *trans*-dioxoruthenium(VI) compounds [252]. The redox reactions of the 'isostructural' complexes $[Ru(tpy)(bpy)O]^{2+}$ and $[Ru(tpy)(py)OH]^{2+}$ (tpy = 2,2′:6′2″-terpyridine, bpy = 2,2′-bipyridine) with DNA have been investigated. The relative rates and potentials for the complexes of competing redox processes during DNA cleavage were studied [253]. The kinetics of the oxidation of ascorbic acid by $[\{Ru(H_2O)(bpy)_2\}_2O]$ (**243**) in aqueous $HClO_4$ were investigated. The rate law was determined and a feasible mechanism consistent with experimental results has been proposed [254]. In addition, *in situ* spectro-cyclic voltammetric investigations of the dimeric complex (**243**), used for water oxidation in homogeneous aqueous solution and in a Nafion membrane, were reported [255].

The stoichiometry, kinetics and mechanisms of the oxidation of $HSCH_2CH_2OH$ and $[HSCH_2CH_2NH_3]^+$ by (**243**) to the corresponding disulfides were studied in aqueous $HClO_4$. The results were rationalized in terms of plausible free radical mechanisms [256]. The Mg^{2+}-activated double-stranded DNA cleavage reaction by (**243**) has been examined. The formation of $[Ru(bpy)_2(OH)_2]^{2+}$ during the reaction was detected by absorption spectroscopy and cyclic voltammetry. A mechanism for the cleavage of DNA has been proposed [257].

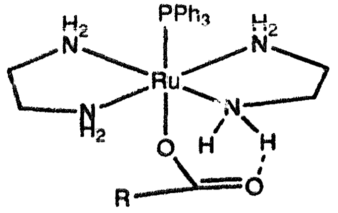
The synthesis and characterization of the complexes $[\{L_2(H_2O)Ru\}_2O]^{4+}$ (L = 4,4′-dichloro or 5,5′-dichloro-2,2′-bipyridine) have been described. The electrochemical properties and the catalytic properties of the complexes towards water oxidation were studied using cyclic voltammetry and spectroelectrochemical spectroscopy. Experimental results showed that the complexes are more stable towards reductive cleavage than (**243**) [258].

Barium ruthenate, $BaRuO_3(OH)_2$, when dissolved in trifluoroacetic acid-CH_2Cl_2 containing a few equivalents of 2,2′-bipyridine generates a very reactive ruthenium oxo system which is capable of oxidizing ethane and propane at room temperature in good yields [259].

7.2. *Complexes with carboxylate ligands*

The preparation of diamagnetic $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ and paramagnetic $[Ru(O_2CR)(en)(PPh_3)](BPh_4)_2$ (**244**) (R = Ph, C_6H_4-*p*-OMe, C_6H_4-*p*-Me) from $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)$ (**245**) have been reported [260]. The synthesis, spectroscopic characterization and crystal structure of the novel asymmetric triply-bridged diruthenium(III) complexes $[Ru_2(\mu\text{-}O)(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ (R = C_6H_4-*p*-OMe, C_6H_4-*p*-Me) (**246**) have been described. The X-ray structures of the complexes revealed that the metal centres have PO_5 and PO_2N_2 coordination environments. The electrochemical properties of (**246**) were also studied; the complexes display a reversible Ru_2(III,III) Ru_2(III,IV) couple near 0.8 V vs SCE in MeCN [261].

The dinuclear ruthenium(II,III) compounds $[Ru_2(O_2CCMe_3)_4L_2]$ and $[Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (L = (**247**)) have been prepared and characterized



R = Ph, C_6H_4-*p*-Me, C_6H_4-*p*-OMe

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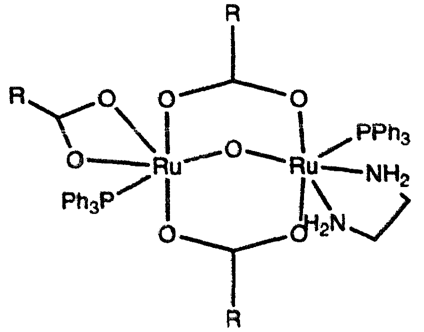
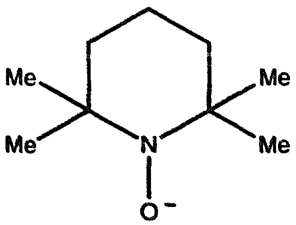


R = C_6H_4-*p*-OMe, C_6H_4-*p*-Me

(246)



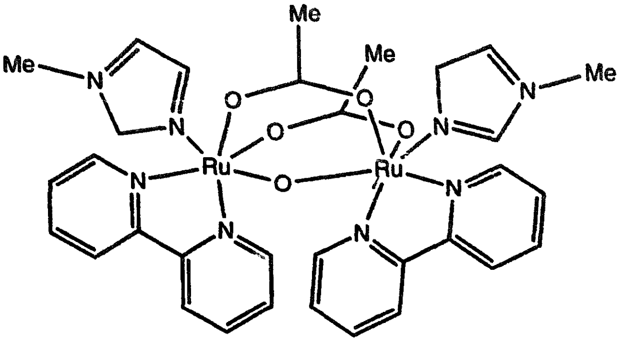
(247)

by elemental analysis, X-ray crystallography, variable temperature magnetic susceptibility and ESR spectroscopic measurements. A fairly large antiferromagnetic interaction ($J = -130\ \mathrm{cm}^{-1}$) between the diruthenium core and the nitroxide radical was observed [262].

Reactions of $[Ru_2Cl(\mu\text{-}O_2CCH_3)_4]$ with indole-2-carboxylic acid, *N*-methyl-pyrrole-2-carboxylic acid, furan-2-carboxylic acid, thiophene-2-carboxylic acid and benzofuran-2-carboxylic acid lead to the formation of $[Ru_2Cl(\mu\text{-}O_2CR)_4]$. Except for the indole-2-carboxylato derivative, all other complexes have polymeric structures with Cl atoms bridging Ru_2^{5+} units. The triphenylphosphine adducts of the complexes were also synthesized and characterized [263].

A new dinuclear complex $[Ru_2(\mu\text{-}O)(\mu\text{-}OAc)_2(bpy)(mim)_2]^{2+}$ (**248**) (mim = 1-methyl-imidazole) was prepared and characterized. The redox behaviour of (**248**) in acetonitrile in the presence of various proton donors with different pK_a values was investigated [264]. Detailed kinetic and mechanistic studies were conducted on the pulse radiolysis of $[Ru_2(\mu\text{-}O)(\mu\text{-}OAc)_2(py)_6](PF_6)_2$ in acetonitrile. In oxygen-containing solutions, Ru_2(III,III) was reduced by $MeC\dot{N}^{\cdot}$ and superoxide O^{2-} to Ru_2(III,II) [265]. The magnetic susceptibilities of $[Ru_2(\mu\text{-}O)(\mu\text{-}OAc)_2(py)_6](PF_6)_2$ and $[Ru_2(\mu\text{-}O)(\mu\text{-}OAc)_2(OAc)_2(H_2O)(CH_3OH)(PPh_3)_2]\cdot H_2O$ were measured. The complexes have a strong antiferromagnetic exchange interaction through the M–O bridge [266].

The magnetic behaviour of the trinuclear clusters $[Ru_2M(\mu\text{-}OAc)_6(\mu_3\text{-}O)(py)_3]^{n+}$ (M = Zn(II), Mg(II) and Ru(II), n = 0; Ru(III), n = 1) have been studied using magnetic susceptibility measurements and EPR spectroscopy. The super-exchange interaction between two Ru(III) ions was analysed using the Goodenough-Kanamori rule. A trinuclear cluster containing Ru(II) and Ru(III) showed a weak ferromagnetism [267]. The ruthenium (III,III,III) complex $[Ru_3(\mu\text{-}O)(\mu\text{-}OAc)_6(OH_2)_3](ClO_4)$ (**249**) was isolated from the 2.0 M $HClO_4$ eluate of an aqueous solution of $[Ru_3(\mu\text{-}O)(\mu\text{-}OAc)_6(OH_2)_3](OAc)$ and characterized by X-ray crystallography. Elution with 0.2 M $HClO_4$ solution lead to the isolation of the Ru(III,III,IV) complex only. The structural analysis of (**249**) provides further



(248)

support for the non-bonded character of the orbitals involved in electron transfer between Ru(III,III,III) and Ru(III,III,IV) forms of these complexes [268].

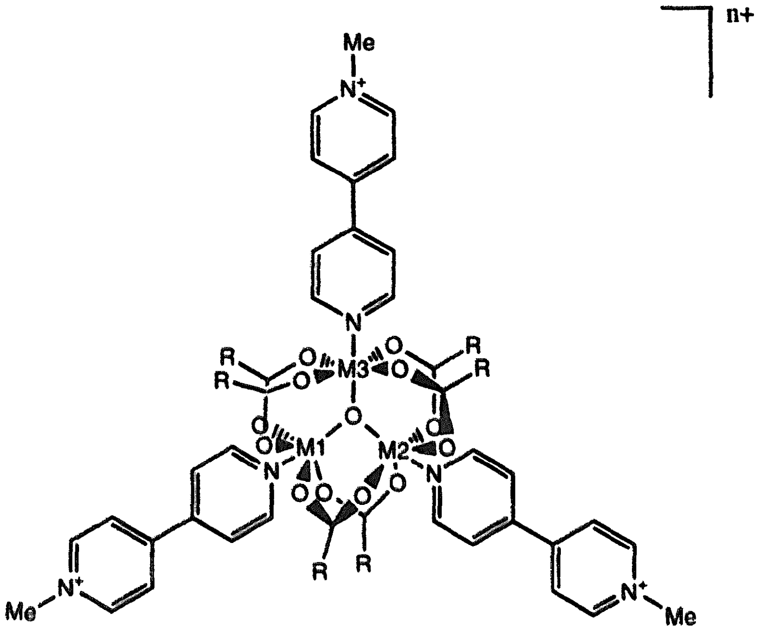
The oxo-bridged triacetate complexes $[Ru_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6L_3]_n$ ($L = H_2O$, AcO^-, $n = +1$, 0, -1 and -2) were detected by electronic spectroscopy and cyclic voltammetry as products from the reactions of $K_2[Ru(H_2O)Cl_5]$, $K_2[RuCl_6]$, $K_4[Ru_2OCl_{10}]$ and $RuOHCl_3$ with HOAc [269]. Oxo-centred carboxylate-bridged trinuclear Ru_3 and Ru_2Rh complexes having redox-active m-bpy$^+$ ligands (**250**) were prepared. Their versatile electrochemical properties were studied by cyclic voltammetry, differential-pulse voltammetry and controlled-potential absorption spectroscopy [270].

A novel dodecanuclear complex $[Ru_3(\mu_3\text{-}O)(OAc)_6\{Ru_3(\mu_3\text{-}O)(OAc)_6(py)_2\text{-}(4,4'\text{-}bpy)\}_3]^{4+}$ containing a central $[Ru_3(\mu_3\text{-}O(OAc)_6(4,4'\text{-}bpy)_3]^+$ unit attached to three $[Ru_3(\mu_3\text{-}O)(OAc)_6(py)_2]^+$ groups via the bridging 4,4′-bipyridine ligands was prepared and characterized by NMR spectroscopic and spectroelectrochemical techniques [271]. The complex cation $[Ru_3(\mu_3\text{-}O(OAc)_6\{(pz)Ru_3(\mu_3\text{-}O)\text{-}(OAc)_6(py)_2\}_3]^{4+}$ exhibiting four $[Ru_3O(OAc)_6L_3]^+$ units bridged by pyrazine ligands was also prepared. It was shown that the electronic interactions between the various units in the tetrameric species increase as the oxidation states decrease [272].

7.3. Complexes with ligands derived from edtaH$_4$

A novel complex $[Ru(H_2L)Cl_2]H \cdot H_2O$ (**251**) ($H_4L =$ (**252**)) was formed by reduction of a Ru(III) salt with the ligand. X-ray diffraction studies revealed an almost symmetric octahedral geometry around the metal ion with the two chlorine atoms in a *cis*-arrangement. The antitumour activity of (**251**) against a variety of murine and human cancers was reported [273].

The interaction of $[Ru^{III}(edta)(H_2O)]^-$ with azide ion in aqueous solution (pH = 5.3) was investigated using cyclic voltammetry and polography. The coordinated azide was reduced electrolytically to ammonia at a Hg-pool cathode. The turnover number with respect to the formation of ammonia was obtained from the constant potential electrolysis data. A probable mechanism for the electrocatalytic reduction of azide to ammonia has been proposed [274]. The mixed ligand complex $[Ru(H_2edta)(HL)]$ (**253**) ($H_2L =$ salicylaldehyde oxime) was synthesized and charac-



M1 = M2 = M3 = Rh(III) R = CH_3 n = 4

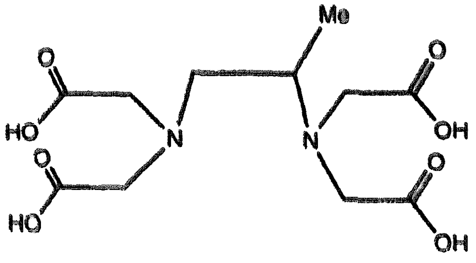
M1 = M2 = M3 = Ru(III) R = CH_3 n = 4

M1 = M2 = M3 = Ru(III) R = C_6H_5 n = 4

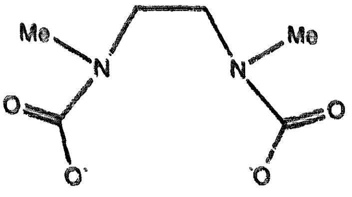
M1 = M2 = Ru(III) M3 = Ru(II) R = CH_3 n = 3

M1 = Rh(III) M2 = M3 = Ru(III) R = CH_3 n = 4

(250)



(252)

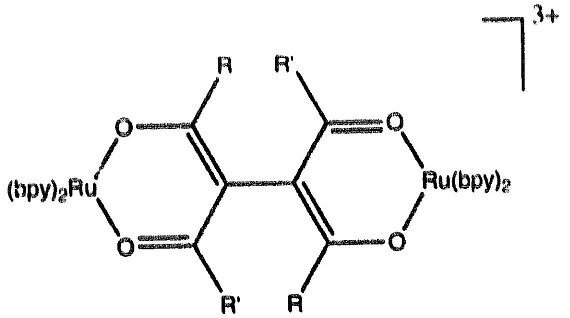


(254)

terized by elemental analysis, pH titration, IR spectroscopy and magnetic susceptibility. The rate of formation of **(253)** is first order with respect to [Ru(H_2O)(Hedta)] and salicylaldehyde oxime [275]. The electrochemical and spectroelectrochemical behaviour of the dinuclear and trinuclear complexes generated from the association of *cis* and *trans*-$[Ru(NH_3)_4(pz)]^{3+/2+}$ with $[Ru(edta)(H_2O)]^{2-/-}$ complexes in aqueous solution have been investigated.[276] The complexes $[\{Ru(LH)\}_2L']$ (H_4L=edta, L′=pyrazine, 4,4′-bipyridine, 3,3′-dimethyl-4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene)) were synthesized and characterized. All complexes exhibit a weak metal-metal interaction. The electrochemical and magnetic susceptibility measurements are consistent with weak interactions between ruthenium centres [277]. Stereochemically controlled molecular recognition in forming η^2 and η^4 olefin complexes by $[Ru^{II}(Me_2edda)(H_2O)_2]$ (Me_2edda=**(254)**) was established by ^1H NMR spectroscopic and electrochemical studies. An $\eta^2 \rightleftharpoons \eta^4$ equilibrium with an apparent value of $K=22$ at 25°C was observed [278].

7.4. Complexes with other O-donor ligands

A series of dinuclear complexes **(255)** were prepared in which the through-bond distance and driving force between donor and acceptor are constant. Molecular mechanics calculations showed that the complexes are oriented with parallel phenyl/methyl and phenyl/pyridyl rings. Through-space and inductive effects were employed in explaining the observed spectral, electrochemical, ZINDO and QSAR correlation in the electron transfer studies [279].



R = R′ = CH_3
R = CH_3, R′ = Ph
R = R′ = Ph

(255)

The preparation of conducting thin films on RuO_2 by metal–organic chemical vapour deposition using $[Ru(tfa)_3]$ (tfa = trifluoroacetylacetonate) as precursor has been reported. The films were investigated by spectroscopic ellipsometry in the energy range of 1.5 to 5.0 eV [280].

The reaction of $RuCl_3 \cdot xH_2O$ with DMF in the presence of a catalytic amount of Pt black gave $[Ru(DMF)_6]^{n+}$ **(256)** (n=2, 3). The single-crystal X-ray structure analysis revealed that the metal ions in both complexes adopt an octahedral geometry with coordination through the oxygen atom. The electrochemical properties of **(256)** were also presented [281].

The mechanism of the reversible acid-induced isomerization in [Ru(bpy)$_2$L] (L = 1,2-dihydroxy-9,10-anthraquinone) (**257**) has been studied using *ab initio* and semiempirical AM1 methods (Scheme 6). The theoretically determined mechanism suggested the possibility of creating a novel reversible photodriven molecular switch based on the isomerization [282].

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