ELSEVIER
Coordination Chemistry Reviews
172 (1998) 389–436
COORDINATION CHEMISTRY REVIEWS

# Ruthenium 1996

Janesse Wing-Sze Hui, Wing-Tak Wong *

*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China*

**Contents**

## 1. Introduction

This review covers work on the coordination chemistry of ruthenium for 1996 and is based upon a search of volumes 124, 125 and 126 of Chemical Abstracts. In addition, major inorganic chemistry journals have been searched independently, covering the period January to December 1996. The metal complexes are classified according to ligand type. Most of the organometallic ruthenium complexes are not covered in this article.

## 2. Complexes with hydrogen or hydride ligands

Reaction of *cis*-$Ru(dmpe)_2H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) with $CO_2$ at 293 K gave two formate complexes: the major product, *trans*-$Ru(dmpe)_2(OCHO)H$; and

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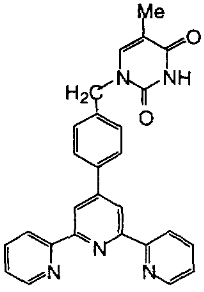
* Corresponding author. E-mail: wtwong@hkucc.hku.hk

0010-8545/98/$32.00
*PII* S0010-8545(98)00096-4

the minor species, *cis*-Ru(dmpe)$_2$(OCHO)$_2$ (**1**). When the reaction was performed at 195 K, both the bis(formate) and the *cis*-formate hydride complex *cis*-Ru(dmpe)$_2$(OCHO)H are obtained in higher yields. All these complexes were characterized by NMR spectroscopy while (**1**) was isolated and characterized by X-ray crystallography. The symmetric and antisymmetric OCO stretching modes in the IR spectrum of (**1**) were identified by $^{13}$CO isotope labelling [1].

The compound (**2**) was formed by the covalent attachment of a thymine residue to a 2,2′:6′,2″-terpyridine metal-bonding domain. The compound (**2**) and its Ru(II) complex show specific H-bonding interactions with 2′,3′-isopropylideneadenosine in CHCl$_3$ or MeCN solution [2].



(2)

A series of new hydrotris(1-pyrazolyl)borate complexes of ruthenium was synthesized. The reaction rates of catalytic hydrogenations with tris(1-pyrazolyl)borato complexes [Ru(HB(pz)$_3$)(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ and [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)$_2$]BF$_4$ were enhanced in the presence of water or Et$_3$N. Further study revealed that the enhanced catalytic activity could be best explained by the involvement of the molecular dihydrogen complexes [Ru(HB(pz)$_3$)(PPh$_3$)$_2$(H$_2$)]BF$_4$ and [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(H$_2$)]BF$_4$, which do not have the M–H functional group. The synthesis and characterization of these molecular dihydrogen complexes, and their roles in catalytic hydrogen reactions, are discussed [3].

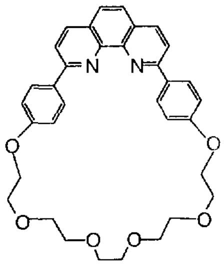
## 3. Complexes with halide or pseudo-halide ligands

The reduction of [RuCl$_3$(NO)(PPh$_3$)$_2$] with Zn/Cu generates [RuCl(NO)(PPh$_3$)$_2$], which by ligand exchange with PR$_3$ (R$_3$ = $^i$Pr$_3$, $^i$Pr$_2$Ph) affords the stable 16-electron ruthenium(0) complex *trans*-[RuCl(NO)(PR$_3$)$_2$]. When treated with CO, TCNE (tetracyanoethene), CH$_2$N$_2$ and O$_2$, five coordinate 1:1 adducts [RuCl(NO)(L)(PR$_3$)$_2$] were formed [4].

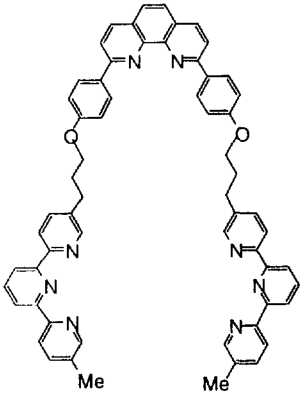
The complexes [RuBr$_2$(PPhH$_2$)$_4$] and [RuBr$_2$(PPh$_2$H)$_4$] were obtained upon reaction of RuBr$_3$ with an excess of the appropriate primary or secondary phosphine in refluxing deoxygenated EtOH. $^{31}$P{$^1$H} and $^{31}$P NMR spectroscopies confirmed the retention of the P-bound protons and indicated that a *trans*-dibromo arrangement occurred in the former, whereas both the *cis* and *trans* forms were seen in the latter [5].

The preparation of $[RuCl_2(MeCN)_4]$ (**3**) by photolytic displacement of *o*-di-*n*-butylbenzene from $[RuCl_2(\eta^6\text{-}o\text{-}{}^nBu_2C_6H_4)]_2$ in MeCN has been reported. The latter compound was prepared in a similar manner to its *p*-cymene analogue, as a poorly soluble solid in 66% yield by reaction of $RuCl_3 \cdot 3H_2O$ with 1,2-di-*n*-butyl-1,4-cyclohexadiene in refluxing ethanol. Complex (**3**) has been characterized by X-ray analysis [6].

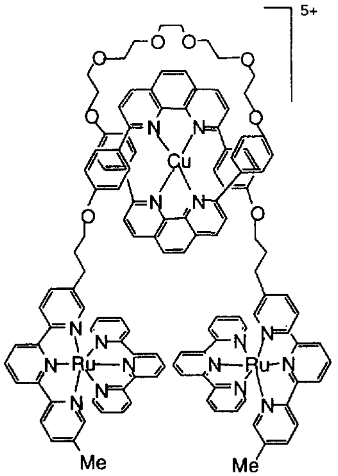
The reaction between $[Cu(MeCN)_4]BF_4$ and (**4**) followed by addition of (**5**) gave a threaded complex; and the subsequent reaction with $[Ru(terpy)(Me_2CO)_3][BF_4]_2$ at 70 °C gave the trimetallic complex (**6**). This approach has opened a new route for the preparation of multicomponent species with interesting photochemical properties [7].



(**4**)



(**5**)



(**6**)

A new method for the synthesis of *cis*-$[Ru^{III}Cl_2(cyclam)]Cl$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), using *cis*-$Ru^{II}Cl_2(dmso)_4$ as a starting complex, has been reported. The reaction between $K_3[Ru^{III}(ox)_3]$ (ox = oxalate) and tren [tren = tris(2-aminoethyl)amine] afforded *fac*-$[Ru^{III}Cl_3(trenH)]Cl \cdot 0.5H_2O$ (**7**) and $(H_5O_2)_2[K(tren)]\,[Ru^{III}Cl_6]$ as major products. The reaction between (**7**) and bpy afforded $[Ru^{II}(baia)(bpy)](BF_4)_2$ [baia = bis(2-aminoethyl)(iminomethyl)amine], in which tren underwent selective dehydrogenation into baia. The crystal structures of the complexes have been determined by X-ray analysis and their structural features were discussed in detail [8].

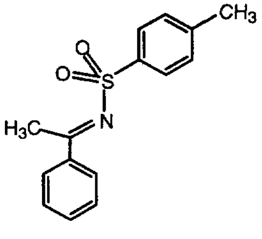
## 4. Complexes with phosphorus donor ligands

Reaction of $H_2$ with $RuCl_2(CO)L_2$ ($L = P^tBu_2Me$) in benzene forms $RuHCl(CO)L_2$ and HCl. The latter reacts with $RuCl_2(CO)L_2$ to give

$[LH][Ru_2Cl_5(CO)_2L_2]$ and [LH]Cl. The $[Ru_2Cl_5(CO)_2L_2]^-$ ion was detected by NMR spectroscopy as several isomers, and was shown by X-ray diffraction to have a face-shared bioctahedral structure with three bridging chlorides. It was also shown that HCl reacts with $RuHCl(CO)L_2$ to give $RuCl_2(H_2)(CO)L_2$, in which $H_2$ is *trans* to Cl [9].

The complex $Ru(PMe_3)_4(GeMe_3)_2$ has been found to be an effective catalyst for the preparation of high molecular weight polygermanes from trimethylgermane in high yields (80–90%). The coupling of the tertiary germane, $HGeMe_3$, proceeded with loss of $CH_4$ and concurrent formation of Ge–Ge bonds [10].

The asymmetric hydrogenation of *N*-tosylimines (**8**) was accomplished with a catalytic amount of Ru[(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] $(O_2CCH_3)_2$ to afford the corresponding amine in high enantiomeric excess. Compound (**8**) can easily be converted into the corresponding free amines in high yields and optical purities [11].



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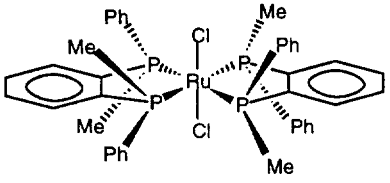


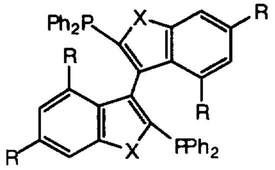
**(9)**

The complex *trans*-dichlorobis[(*R*,*R*)-1,2-phenylenebis(methylphenylphosphine)]ruthenium(II) (**9**) is a convenient precursor for the synthesis of symmetrical or asymmetrical optically active ruthenium σ-acetylide complexes. X-ray analysis showed complex (**9**) has a *trans* geometry about the octahedral Ru atom [12].

The synthesis and application of a new class of chiral ($C_2$) atropisomeric diphosphines characterized by two interconnected five-membered heteroaromatic rings with hindered rotation around the interanular bond have been described. Optically pure (+)- and (−)-2,2′-bis(diphenylphosphino)-4,4′,6,6′-tetramethyl-3,3′-bibenzo[*b*]thiophene (tetraMe-bitianp) (**10**) and the parent unsubstituted system (+)- and (−)-bitianp (**11**) were synthesized. The optical and chemical yields were comparable with those reported for the same Ru(II)-binap-catalyzed reactions carried out under the same experimental conditions. The advantages of these biheteroaromatic ligands over the classical biaryl systems were discussed [13].

Treatment of $[RuCl_2(COD)]_n$ with (*R*)-*p*-MeO-BINAP [*p*-MeO-BINAP = 2,2′-bis(bis(*p*-methoxyphenyl)phosphino)-1,1′-binaphthyl] in toluene in the presence of triethylamine afforded the anionic dinuclear complex $[NH_2Et_2][\{RuCl((R)\text{-}p\text{-}MeO\text{-}BINAP)\}_2(\mu\text{-}Cl)_3]$ (**12**), whose structure has been determined by an X-ray crystallographic study. Complex (**12**) is found to be an efficient catalyst for asymmetric hydrogenation of functionalized olefins and ketones [14].

Complexes of the form $[Ru(C{\equiv}CR')_2(L\text{–}L)_2]$ [L–L = $R_2PCH_2CH_2PR_2$; R = Me (dmpe) or Et (depe); R′ = $^t$Bu, Ph, 4-HC≡$CC_6H_4$, 4-$MeOC_6H_4$ or 3,5-$(CF_3)_2C_6H_3$]



(**10**) X=S; R=$CH_3$
(**11**) X=S; R=H

were prepared by reaction of $[RuCl_2(L–L)_2]$ or $[RuH_2(L–L)_2]$ with terminal acetylenes in methanol solution. The spectroscopic data indicates that the acetylide groups adopt a *trans* stereochemistry across the metal centre. The crystal structure of $[Ru(C{\equiv}CPh)_2(dmpe)_2]$ was determined [15].

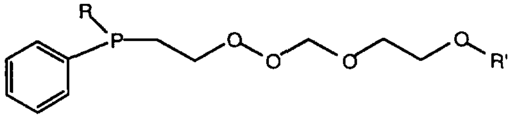
The hydration of phenylacetylene in the presence of *mer,trans*-$(PNP)RuCl_2(PPh_3)$ in THF at 60 °C leads to the cleavage of the C–C triple bond with formation of the carbonyl complex *fac,cis*-$(PNP)$-$RuCl_2(CO)$ and toluene $[PNP = PrN(CH_2CH_2PPh_2)_2]$. It has been shown that the C–C bond cleavage reaction comprises a number of steps [16].

Mononuclear iodoruthenium(II) complexes *trans*-$[Ru(L–L)_2I_2]$ [L–L= $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, *o*-$C_6H_4(AsMe_2)_2$], *trans*-$[Ru(SbPh_3)_4I_2]$ and $[Ru(PPh_3)_3I_2]$ were isolated from reaction of $[Ru(H_2O)_6](BF_4)_2$ with the respective ligand and NaI in aqueous EtOH. Oxidation with concentrated $HNO_3$–$HBF_4$ yielded *trans*-$[Ru(L–L)_2I_2]BF_4$. The complexes were characterized by spectroscopy (IR, UV–vis, $^{31}P$ NMR) and cyclic voltammetry, and their properties compared with chloro and bromo analogues. The crystal structure of $[Ru(Ph_2AsCH_2CH_2AsPh_2)_2I_2]BF_4$ is also reported [17]. The structure of *cis*-$[Ru(bpy)_2\{PPh_2(o\text{-tol})\}Cl][ClO_4]$ has been established by X-ray crystallography with the Ru(II) cation adopting an octahedral geometry [18].

The molecular structure determination of the ruthenatetraborane $[Ru(B_3H_8)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]$, obtained from $[RuCl(PPh_3)_2\{\kappa^3\text{-}HB(pz)_3\}]$ and $[NMe_4][B_3H_8]$, revealed *exo* borate and *endo* phosphine coordination about the central *arachno* $RuB_3$ skeleton [19]. The complex *cis*-$[Ru(bpy)_2\{PPh(o\text{-tolyl})_2\}Cl](ClO_4)$ has been structurally characterized by X-ray diffraction. The structure is stabilized by a hydrogen-bonded $CH_2Cl_2 \cdots ClO_4^- \cdots H_2O$ channel which incorporates adventitious water of crystallization [20].

New polydentate amphiphilic phosphines containing polyether chains $L_1$ or $L_2$ [$L_1$=(**13**); $L_2$=(**14**)] were prepared. The reaction between two equivalents of (**13**) and $[RuCl_2(PPh_3)_3]$ leads to the formation of $[RuCl_2(L_1)(PPh_3)]$; the unprecedented coordination and reactivity of the hemilabile ligand $PPh[(CH_2)_3CHMe_2][(CH_2CH_2O)_3Me]$ were also reported, and the $\eta^3$ mode of bonding of this ligand on Ru was established by X-ray analysis [21].

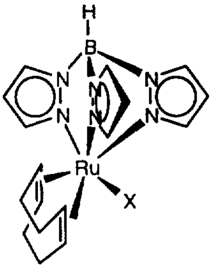
The mixed-phosphine complexes *trans*-$[Ru(NO_2)(terpy)(PMe_3)(PR_3)](ClO_4)$ (R = Et, Pr, Bz or Ph) were synthesized in high yields by a stepwise addition of each phosphine. In addition, a single crystal structural analysis of *trans*-



(**13**) R=isopentyl; R'=H
(**14**) R=*n*-octyl, R'=H

$[Ru(NO_2)(terpy)(PMe_3)(PPh_3)](ClO_4)$ was obtained. These syntheses demonstrate the utility of ruthenium(II) in the preparation of mixed-phosphine complexes. Their cyclic voltammetric behaviour has been reported [22].

The synthesis and catalytic reactivity of a variety of new ruthenium complexes of the tris(pyrazolyl)borate ligand ($HB(pz)_3$) were reported. From the parent complex $[Ru(HB(pz)_3)(COD)X]$ (**15**) (X=Cl, Br), the cationic derivatives $[Ru(HB(pz)_3)(COD)L]^+$ (L=$H_2O$, MeCN, pyridine, dmso) have been obtained by treatment with one equivalent of $AgCF_3SO_3$ in $CH_2Cl_2$ solutions of L. The catalytic properties of some of these complexes have been reported [23].



(**15**) X=Cl, Br

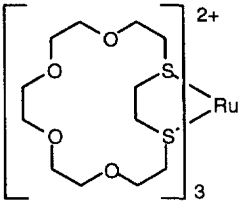
The interaction of $RuCl_2(dmso)_4$ with 1 equiv. 1*R*,2*R*-cyclohexyl-$P_2N_2$ (*N*,*N'*-bis[*o*-(diphenylphosphino)benzylidene]-1*R*,2*R*-diiminocyclohexane) and the diamino analog 1*R*,2*R*-cyclohexyl-$P_2N_2H_4$ in refluxing toluene gave *trans*-$RuCl_2$(1*R*,2*R*-cyclohexyl-$P_2N_2$) (**16**) and *trans*-$RuCl_2$(1*R*,2*R*-cyclohexyl-$P_2N_2H_4$) (**17**) in 80% and 75% yields, respectively. Compounds (**16**) and (**17**) were fully characterized by analytical and spectroscopic methods and are believed to be active hydrogenation catalysts [24].

## 5. Complexes with sulfur donor ligands

The diruthenium(II) complex $[Ru_2(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}Me_2SO)Cl_2(Me_2SO)_4]$ was prepared from $[RuCl_2(Me_2SO)_4]$ in methanol in the presence of $Na_2(xdk)$ [$H_2xdk$=*m*-xylenediamine bis(Kemp's triacid imide)] and characterized by X-ray crystallography which revealed an unprecedented S,O-bidentate bridging $Me_2SO$ ligand coordinating to one ruthenium via S and to the other via O resulting in a four-membered ring [25].

Ruthenium trichloride reacted with thiocyanate to form a complex, which has extracted into the surfactant phase with Zephiramine (Z) by heating. The structure of this ion-pair was estimated to be $[RuX_2(SCN)_2]^- \cdot Z^+$, X = Cl, and was observed to cause an increasing absorbance and a blue shift of the spectrum. The determination of ruthenium(III) was investigated by the surfactant extraction–spectrophotometric method using a non-ionic surfactant of Triton X-100 as an extraction solvent [26].

The crystal structure of $[Ru([18]aneS_2O_4)_3](PF_6)_2 \cdot 2H_2O \cdot CH_3OH$ (**18**) showed that the $Ru^{II}$ ion lay on a crystallographic three-fold axis and was coordinated to three symmetry-equivalent macrocyclic ligands via their S donor atoms. The macrocycle adopted a typical bidentate chelating coordination mode with S donors in *exo* and O donors in *endo* orientations [27].



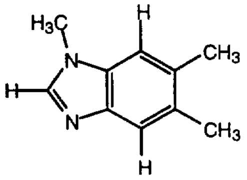
(**18**)

The reaction of ctc-$[RuL_2Cl_2]$ [L = 2-(phenylazo)pyridine, ctc = *cis–trans–cis* with respect to chlorides, pyridine and azo nitrogens, respectively] with K salt of *o*-ethyldithiocarbonate in boiling DMF produced the diamagnetic $Ru^{II}(SC_6H_4N{=}NC_6H_4N)_2$ (**19**). The ortho-C atom of the pendant Ph ring of each L was selectively thiolated. The X-ray structure of (**19**) was reported. Their spectroscopic and photophysical properties have been discussed [28].

The syntheses, crystal structures and spectroscopic properties of several diruthenium compounds with novel *cis*- and *trans*-$Ru_2S_2$ core structures: $[\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$, $[\{RuCl(P(OMe)_3)_2\}(\mu\text{-}Cl)_2(\mu\text{-}S_2)\{Ru(CH_3CN)(P(OMe)_3)_2\}](CF_3SO_3)$, $[\{Ru(CH_3CN)(P(OMe)_3)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)](CF_3SO_3)_2$ and $[\{Ru(CH_3CN)_3(P(OMe)_3)_2\}_2(\mu\text{-}S_2)]^{n+}$ [$n = 3$ (**20**), 4] have been described. Complex (**20**) is the first paramagnetic ruthenium compound with a mixed-valent $Ru^{II}SSRu^{III}$ core, whose crystal structure and detailed spectroscopic properties have also been reported [29].

The complexes *cis,cis,cis*-$RuCl_2(Me_2SO\text{–}S)_2(py)(Me_3Bzm)$ (**21**) [$Me_3Bzm$ = 1,5,6-trimethylbenzimidazole (**22**)], *cis,cis,cis*-$RuCl_2(Me_2SO\text{–}S)_2(Me_3Bzm)_2$ (**23**), *cis,cis,cis*-$RuBr_2(Me_2SO\text{–}S)_2(Me_3Bzm)_2$, *cis,fac*-$RuCl_2(Me_2SO\text{–}S)_3(Me_3Bzm)$ and *cis,fac*-$RuCl_2(Me_2SO\text{–}S)_3(py)$ have been prepared. The solution and solid state structures of (**21**) and (**23**) were compared and discussed [30].

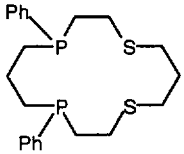
Reaction of $[RuCl_2(py)_4]$ with a one molar equivalent of the tetradentate acyclic phosphathia compound $RSC_2H_4SR$ (**24**) or the macrocycle *meso*-$Ph_2[14]aneP_2S_2$ [4,8-diphenyl-1,11-dithia-4,18-diphosphacyclotetradecane (**25**)] in refluxing toluene



**(22)**

afforded the ruthenium(II) complexes [$RuCl_2(RSC_2H_4SR)$] (**26**) and [$RuCl_2(Ph_2$[14]ane$P_2S_2$)], respectively as yellow solids. All complexes were fully characterized and the X-ray structure of (**26**)·$0.75Et_2O$ was determined [31].

**(24)**

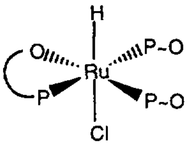


**(25)**

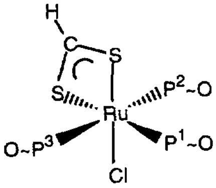
The synthesis of the Ru(II) crown thioether complex, bis(1,4,7-trithiacyclodecane)ruthenium(II) perchlorate, [Ru(10S3)$_2$]($ClO_4$)$_2$, and a study of its properties using single crystal X-ray diffraction, electronic spectroscopy, $^{13}C$ NMR spectroscopy and cyclic voltammetry has been reported. The crystal structure shows the two 10S3 ligands are arranged in a *trans* or *anti* fashion around the Ru(II) centre in nearly octahedral fashion to yield the *meso* stereoisomer [32].

The dithioformato complexes RuCl(P~O)$_3$($\eta^2$-$S_2CH$) (**28a,b**) and RuCl(P∩O)(P~O)($\eta^2$-$S_2CH$) (**29a,b**) were accessible by insertion of $CS_2$ into the Ru–H bond of the (ether-phosphine)(hydrido)ruthenium complexes RuClH(P∩O)(P~O)$_2$ (**27a,b**) [P~O = $\eta^1$(P)-coordinated, P∩O = $\eta^2$(O,P)-chelated; O,P = diphenyl(2-methoxyethyl)phosphine (**a**), (1,3-dioxan-2-ylmethyl)diphenylphosphine (**b**)]. Treatment of (**28a**), (**29a**) and (**28b**), (**29b**) with carbon monoxide in $CH_2Cl_2$ results in the formation of the carbonyl complexes Ru(CO)Cl(P~O)$_2$($\eta^2$-$S_2CH$) (**30a,b**) [33].

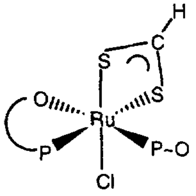
Reaction of [Ru(MeCN)$_3$([9]ane$S_3$-$\kappa^3$S)][$CF_3SO_3$]$_2$ ([9]ane$S_3$ = 1,4,7-trithiacyclononane) with 1,3-benzothiazole-2-thione (Hbtt) and pyridine-2-thione (Hpyt) in MeOH in a 1:1 molar ratio afforded dinuclear complexes [{Ru[9]ane$S_3$-$\kappa^3$S)}$_2$($\mu$-L)$_2$][$CF_3SO_3$]$_2$ [L = btt (**31**) or pyt (**32**)] in which the ligands exhibit a tridentate $\mu$-1$\kappa$S:2$\kappa^2$N,S bridging mode. A triply $\mu$-S bridged complex [{Ru[9]ane$S_3$-$\kappa^3$S)}$_2$($\mu$-btt)$_3$][$CF_3SO_3$] was also obtained from [Ru(MeCN)$_3$([9]ane$S_3$-$\kappa^3$S)][$CF_3SO_3$]$_2$ and btt$^-$ in 2:3 molar ratio. Fragments ($Ph_3P$)([9]ane$S_3$-$\kappa^3$S)Ru$^{II}$ can be bridged with tetra- or tridentate dtuc$^{2-}$ ($H_2$dtuc = 2,4-dithiouracil) anions in [{Ru($PPh_3$)([9]ane$S_3$-$\kappa^3$S)}$_2$($\mu$-dtuc)]$^{2+}$ and [{RuCl($PPh_3$)([9]ane$S_3$-$\kappa^3$S)}($\mu$-dtuc){Ru($PPh_3$)([9]ane$S_3$-$\kappa^3$S)}]$^+$ (**33**). The structures of all four complexes were determined by X-ray crystallography [34].



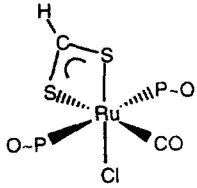
**(27 a,b)**



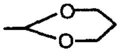
**(28 a,b)**



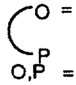
**(29 a,b)**



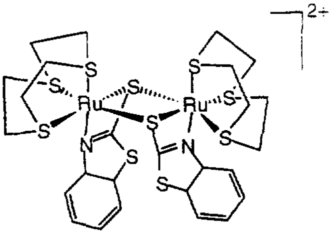
**(30 a,b)**

| | O,P |
|---|---|
| a | $Ph_2PCH_2CH_2OCH_3$ |
| b | $Ph_2PCH_2$  |

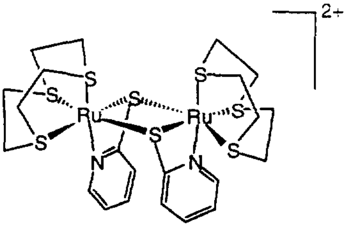
P~O = $h^1$-P-coordinated

 = $h^2$-O,P-coordinated

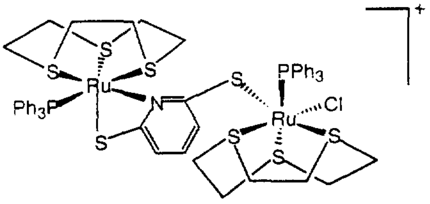
O,P = Ether-phosphine ligand



**(31)**



**(32)**



**(33)**

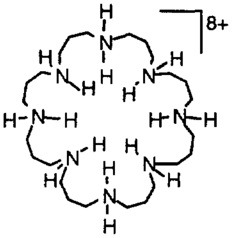
The complexes *mer*-trichloro-*cis*-bis(1-methylimidazole)(dmso)ruthenium(III) and 4-ethylpyridinium *trans*-(4-ethylpyridine)(dmso)tetrachlororuthenate(III) were synthesized and structurally characterized. The conformation of the planar N-ligand observed in the X-ray structures was discussed in terms of an interaction between the ligands [35].

## 6. Complexes with nitrogen donor ligands

### 6.1. Complexes with 2,2′-bipyridine ligands

Reaction of *cis*(CO),*trans*(Cl)-[Ru(bpy)(CO)$_2$Cl$_2$] with HBr and HI produced the corresponding compounds *cis*(CO),*trans*(Br)-[Ru(bpy)(CO)$_2$Br$_2$] and *cis*(CO),*trans*(I)-[Ru(bpy)(CO)$_2$I$_2$]. By using HBr–HNO$_3$ solutions and extended reaction times, nitrido-bridged [(H$_2$O)Br$_2$(bpy)Ru–N–Ru(bpy)Br$_3$] was formed at 240 °C. The complexes were characterized by IR, NMR spectroscopies and single crystal X-ray crystallography [36].

The formation of a "supercomplex" between the Ru(bpy)(CN)$_4^{2-}$ complex and the [32]ane-N$_8$H$_8^{8+}$ macrocycle (**34**) has been studied in water and in acetonitrile. Its redox, spectroscopic and photophysical properties have been studied [37].

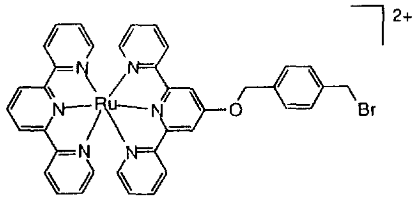


(**34**)

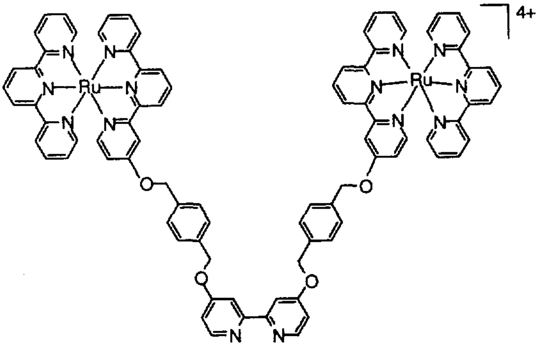
The oxidized form of the blue dimer water oxidation catalyst [(bpy)$_2$(H$_2$O)Ru$^{III}$ORu$^{IV}$(OH)(bpy)$_2$](ClO$_4$)$_4$ has been characterized by X-ray crystallography. A resonance-Raman spectroscopic study focused mainly on the frequency of the symmetrical Ru–O–Ru stretch and the effect of $^{18}$O isotopic substitution was reported [38]. The syntheses, electrochemical and spectroscopic properties of mono- and dinuclear ruthenium complexes based on the ambidentate bridging ligand 3,3′-dihydroxy-2,2′-bipyridine (H$_2$L) were studied [39].

The complex [(terpy)Ru(HOterpy)](PF$_6$)$_2$ was treated with 1,4-bis(bromomethyl) benzene in MeCN in the presence of K$_2$CO$_3$, to give (**35**); subsequent reaction with HO$_2$bpy in refluxing MeCN in the presence of K$_2$CO$_3$ gave (**36**). The compound (**36**) is the building block for the heptanuclear species (**37**) and (**38**) as it is a dinuclear complex which contains a vacant bidentate metal-binding domain [40].

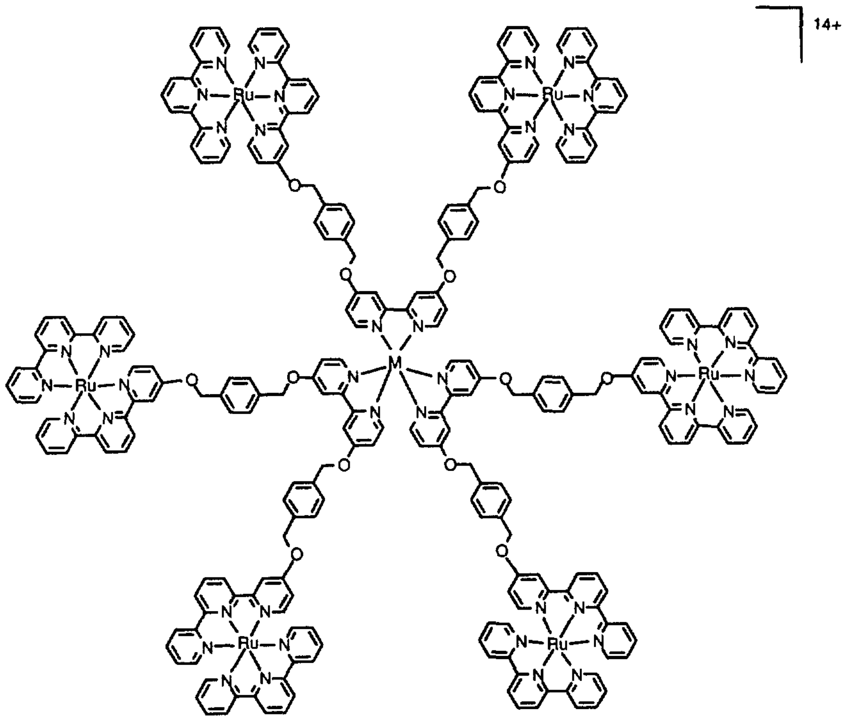
The hexafluorophosphate salts of the dinuclear complexes [(bpy)$_2$Ru(PAP)Ru(bpy)$_2$]$^{4+}$ (Ru$^{II}$PAPRu$^{II}$), [(bpy)$_2$Os(PAP)Os(bpy)$_2$]$^{4+}$ (Os$^{II}$PAPOs$^{II}$) and [(bpy)$_2$Ru(PAP)Os(bpy)$_2$]$^{4+}$ (Ru$^{II}$PAPOs$^{II}$) have been prepared where PAP was a rod-like bridging ligand made of an adamantane-based spacer collinear with the coordination axis of two 1,10-phenanthroline units. Their luminescence properties and the results of intercomponent energy-transfer and electron-transfer processes have been reported [41]. The ruthenium μ-oxo dimer *cis*-[{Ru$^{III}$L$_2$(OH$_2$)}$_2$O]$^{4+}$ [L$^1$=4-(4-pyrrol-1-ylbutyl)-4′-methyl-2,2′-bipyridine (**39**); L$^2$=4,4′-di-*tert*-butyl-2,2′-bipyridine] complexes were synthesized and studied



**(35)**

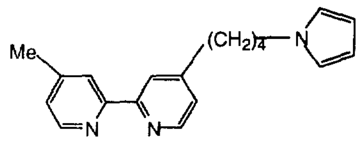


**(36)**



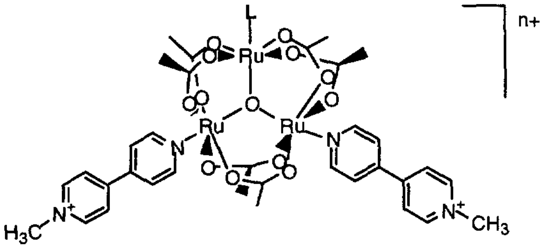
**(37)** M=Fe
**(38)** M=Co

in a non-conducting $CH_2Cl_2$ electrolyte in order to elaborate by electropolymerization corresponding polypyrrole functionalized films. Their cyclic voltammograms were recorded and discussed [42].



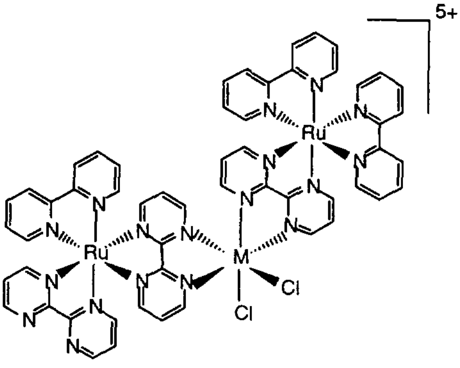
**(39)**

A new series of oxo-centred acetate-bridged triruthenium complexes having two redox-active *N*-methyl-4,4′-bipyridinium ions (mbpy$^+$) has been prepared, and their reversible multistep and multielectron electrochemical properties were reported. These include $[\mathrm{Ru_2^{III}Ru^{II}(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(mbpy^+)_2(CO)}]^{2+}$ and $[\mathrm{Ru_3^{III}(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(mbpy^+)_2(L)}]^{3+}$ [(**40**)–(**45**)] [L = $H_2O$, pyrazine (pz), pyridine (py), imidazole (Him), and 4-(dimethylamino)pyridine (dmap)]. Among this series, the CO complex $[\mathrm{Ru_2^{III}Ru^{II}(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(mbpy^+)_2(CO)}](\mathrm{ClO_4})_2\cdot$ 2DMF was structurally characterized by X-ray crystallography. The ligand–ligand interactions were discussed in terms of the extent of splitting of the ligand-based redox potentials in the cyclic and differential-pulse voltammograms [43].



| | $PF_6^-$ salt | $ClO_4^-$ salt |
|---|---|---|
| $[\mathrm{Ru^{III}_2RU^{II}(O)(CH_3CO_2)_6(mbpy)_2^+(CO)}]^{2+}$ | **(40b)** | |
| $[\mathrm{Ru^{III}_3(O)(CH_3CO_2)_6(mbpy^+)(_2H_2O)}]^{3+}$ | **(41a)** | |
| $[\mathrm{Ru^{III}_3(O)(CH_3CO_2)_6(mbpy^+)(_2pz)}]^{3+}$ | **(42a)** | |
| $[\mathrm{Ru^{III}_3(O)(CH_3CO_2)_6(mbpy^+)(_2py)}]^{3+}$ | **(43a)** | **(43b)** |
| $[\mathrm{Ru^{III}_3(O)(CH_3CO_2)_6(mbpy^+)(_2Him)}]^{3+}$ | **(44a)** | |
| $[\mathrm{Ru^{III}_3(O)(CH_3CO_2)_6(mbpy^+)(_2dmap)}]^{3+}$ | **(45a)** | **(45b)** |

Bipyrimidine-bridged trimetallic complexes of the form $\{[(\mathrm{bpy})_2\mathrm{Ru(bpm)}]_2\mathrm{MCl_2}\}^{5+}$ (**46**), where M = Rh$^{III}$ or Ir$^{III}$ and bpm = 2,2′-bipyrimidine, have been synthesized and characterized. The ability of the bipyrimidine to function as a bridging ligand within these metal frameworks and how the properties of these complexes varied as the central metal changed from Ir$^{III}$ to Rh$^{III}$ have been explored [44].



**(46)**

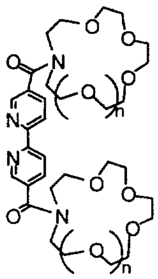
Photolysis of $Ru(bpy)_2(en)^{2+}$ and $Ru(bpy)_2(tn)^{2+}$, where en = ethylenediamine and tn = 1,3-propylenediamine, was studied in acetonitrile using on-line electrospray mass spectrometry (ES-MS). These complexes are known to undergo a four-electron oxidation photochemistry, giving the α,α′-diimine complexes [45].

A number of star-burst type tetranuclear complexes $[Ru^{II}L_2B]_3RuX_8$ were examined by positive ES-MS, where L is bpy or btfmb [4,4′-bis(trifluoromethyl)-2,2′-bipyridine], bridging ligand B is 1,1′-dimethyl-2,2′-bis(2″-pyridyl)-6,6′-bibenzimidazole (dmbbbim), 2,2′-bis(benzimidazole-2-yl)-4,4′-bipyridine ($bbbpyH_2$) and X is $ClO_4^-$. The advantage of using ES-MS was demonstrated for these multinuclear compounds and the collision-induced dissociation (CID) chemistry of the ions studied was discussed [46].

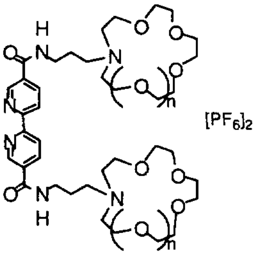
Novel aza crown and dibenzo crown ether mono- and bis-ruthenium(II) bipyridyl amide-containing receptors L [L = (**47**)–(**52**)] have been synthesized and their preliminary Group 1 metal cation and halide anion complexing properties investigated. The electrochemical and photochemical studies of the complexes have been reported [47].

A new series of soluble metallopolymers based on amide-derivatized, styrene-*p*-(aminomethyl)styrene, containing on average 16 repeat units, has been synthesized by reaction with a stoichiometric amount of the acid-functionalized metal complexes, $(Ru^{II}L_2^1L^2)(PF_6)_2$ ($L^1$ = bpy, $L^2$ = 4′-methyl-2,2′-bipyridine-4-carboxylic acid), in the presence of a coupling reagent. Their photophysical properties have been studied. They all exhibit characteristic MLCT absorption and emission which were only slightly solvent dependent [48].

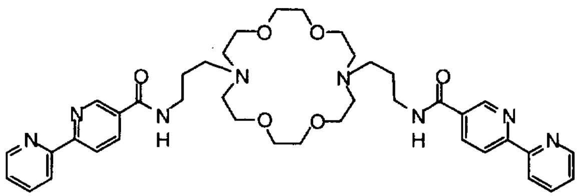
Coordination compounds of the type $Ru(dmb)_2(LL)(PF_6)_2$ [dmb = 4,4′-$(CH_3)_2$-2,2′-bpy; LL = 4-$(CH_3)$-4′-(COOH)-2,2′-bpy, 4-$(CH_3)$-4′-($(CH_2)_3COOH$)-2,2′-bpy or 4-$(CH_3)$-4′-($(CH_2)_3COCH_2COOC_2H_5$)-2,2′-bpy] were prepared for attachment to semiconductor metal oxide surfaces. The spectroscopic, surface attachment, optical and redox properties of these compounds in $CH_2Cl_2$ solution were reported. Binding to porous nanostructured $TiO_2$ films was analysed with the



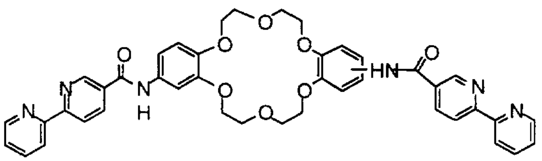
**(47)** n=1
**(48)** n=2



**(49)** n=1
**(50)** n=2



**(51)**



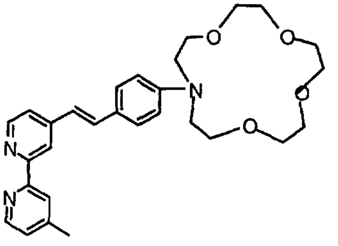
**(52)**

Langmuir adsorption isotherm model. Photochemical measurements of the modified $TiO_2$ electrodes in regenerative solar cells were also reported [49].

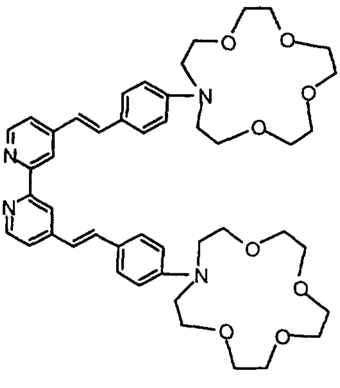
The electrochemical polymerization of the mono(ligand) and tris(ligand) ruthenium(II) complexes, $[RuL^{1,2}(bpy)_2]^{2+}$ and $[RuL_3^{1,2}]^{2+}$ [$L^1$=4-methyl-4′-(*N*-styryl-aza-15-crown-5)-2,2′-bipyridine (**53**), $L^2$=4,4′-bis(*N*-styryl-aza-15-crown-5)-2,2′-bipyridine (**54**)], was studied in acetonitrile. A technique for the preparation of electroactive polymer films was established on reductive electropolymerization of the tris(ligand) ruthenium(II) complexes [50].

Hydrated ruthenium(III) chloride reacted with $[Os(bpy)_2(bbbpyH_2)](ClO_4)_2$ [$bbbpyH_2$=2,2′-bis(benzimidazol-2-yl)-4,4′-bipyridine] to give $[\{Os(bpy)_2(bbbpyH_2)\}_3Ru](ClO_4)_8$ (**55**). Deprotonation of (**55**) gave $[\{Os(bpy)_2(bbbpy)\}_3Ru](ClO_4)_2$. The cyclic voltammetry of the complexes has been investigated [51].

Photoinduced electron transfer in photosystems consisting of complexes (**56**)–(**59**) with bis(*N*,*N*′-*p*-xylylene-4,4′-bipyridinium) [$BMV^{4+}$, (**60**)] was examined. The series of photosensitizers includes alkoxyanisyl donor components tethered to the photosensitizer sites, capable of generating donor–acceptor supramolecular complexes

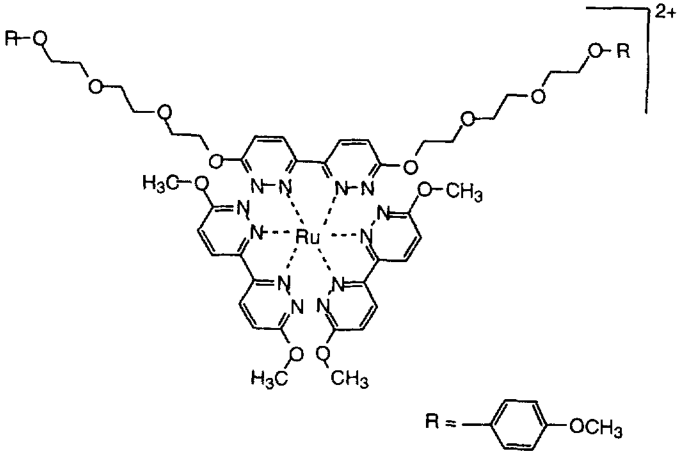


**(53)**



**(54)**

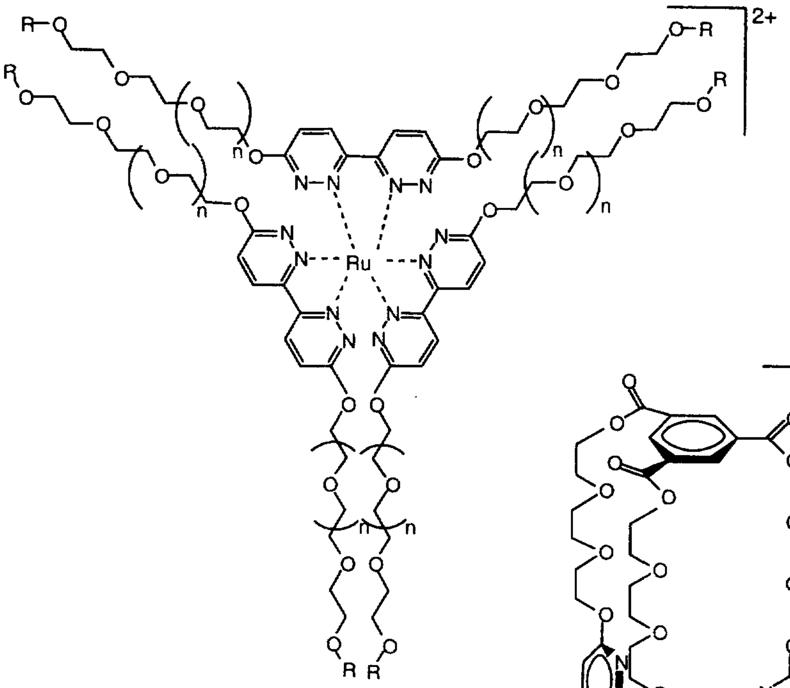
with $BMV^{4+}$. Detailed analyses of the steady state and time-resolved electron-transfer quenching reactions were reported [52].



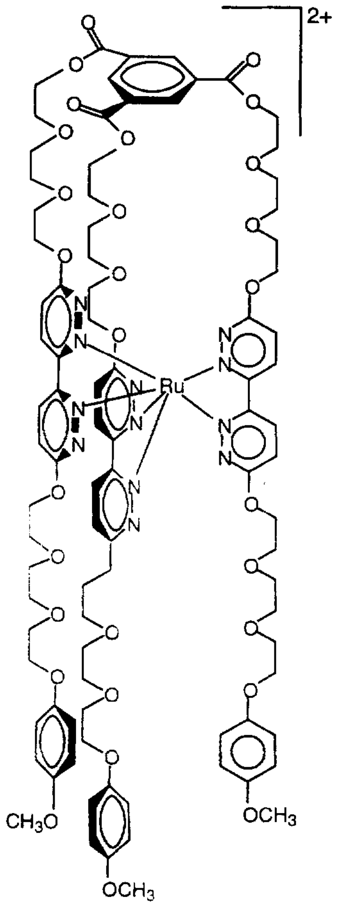
**(56)**

The electropolymerization of the ligands 3-{ω-[4-(2,2′-bipyridylyl)]alkyl} thiophene [B(*n*)T; $n=2$, 5, 7, 9, 11] and their tris(ligand) ruthenium(II) complexes, $[Ru\{B(n)T\}_3]^{2+}$, has been reported. The electrochemical properties of the polymers were studied using cyclic voltammetry, chronoamperometry and a.c. impedance spectroscopy. The mechanism of charge transfer in the polymer-modified electrodes was evaluated, and interpreted [53].

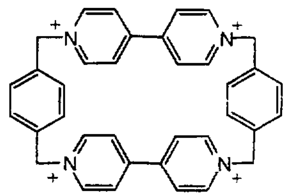
A systematic survey of zeolites Y containing tris(2,2′-bipyridine)ruthenium(II) with various levels of loading was undertaken. Almost pure $Ru(bpy)_3^{2+}$ was obtained whenever the loading was less than approximately one complex per two supercages. At higher loading an increasing amount of by-products corresponding formally to $[Ru(bpy)_n(NH_3)_{6-2n}]^{2+}$, $n<3$, was observed [54]. In an acidic aqueous solution,



**(57)** n=1
**(58)** n=1

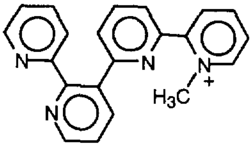


**(59)**



**(60)**

the $[Ru(bpy)_3]^{2+}$ photosensitized reduction of a macrocyclic $Co^{III}$ complex $Co(N_4)(OH_2)_2^{3+}$ ($N_4$=5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been found to proceed in the presence of phenol. The present results revealed that phenol was an excellent sacrificial donor, preferential to the usual ones such as triethanolamine (TEOA) and EDTA for the photosensitized reaction in an acidic aqueous solution [55]. The preparation and the electrochemical and spectroscopic properties of the $[Ru(bpy)_2(ABMe)]^{3+}$ complexes [ABMe=(**61**); Me indicates methylation at a pyridyl N] were described. The electrochemical and photophysical properties (luminescence spectra, emission lifetimes, quantum yields) of the complexes have been compared with those of the parent species $[Ru(bpy)_2(AB)]^{2+}$ [56].



**(61)**

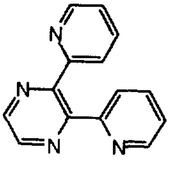
The stabilization of $[Ru(bpy)_3]^{3+}$ from $[Ru(bpy)_3]^{2+}$ at both 77 K and room temperature in silica gel by chemical oxidation with chlorine gas and by photoinduced electron transfer to suitable electron acceptors has been reported. Paramagnetic $[Ru(bpy)_3]^{3+}$ was characterized by ESR spectroscopy [57].

Surface-enhanced (resonance) Raman scattering [SE(R)RS] spectra of five mixed-ligand $Ru^{II}$ complexes were recorded and analysed in detail by comparison with the spectrum of $Ru(bpy)_3$ and the results of a normal-mode calculation for the ligands bpy and terpy. The interaction between terpy and the other ligands is reflected not only in the intensity distribution of the SE(R)RS spectra, but also in the excited state lifetimes [58].

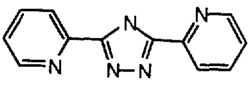
A new mixed-ligand polypyridylruthenium(II) complex, $[Ru(bpy)_2L]Cl_2$ (L=3,5-dicarboxy-2,2′-bipyridine), was prepared. Its photophysical properties in MeCN were recorded. Thermochromic emission data and temperature-induced energy-gap law behaviour indicate that the unique photophysical properties of this compound were due to specific interactions involving the protic solvent [59].

The first luminescent and redox active multinuclear Ru(II) compound $[(bpy)_2Ru(\mu\text{-bpt})Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]^{7+}$ (**62**) containing both electron-poor 2,3-dpp (**63**) and electron-rich Hbpt (**64**) ligands has been synthesized. Its absorption spectrum, luminescence properties and redox behaviour have been studied and compared with the properties of the parent complexes. A two-step energy-transfer mechanism is proposed to explain the photophysical properties of (**62**) [60].

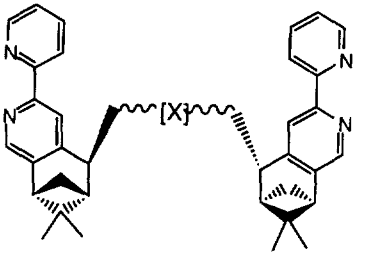
Tetradentate ligands (**65**) are obtained by joining two optically active [4,5]-pineno-2,2′-bipyridine molecules in a stereoselective reaction, whereby two new stereogenic centres are created. Ru(II) complexes with 4,4′-dimethyl-2,2′-bipyridine occupying the remaining coordination sites have been synthesized with all three new



**(63)**



**(64)**

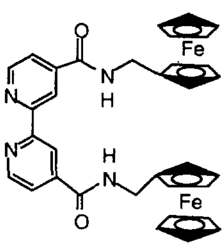


**(65)**

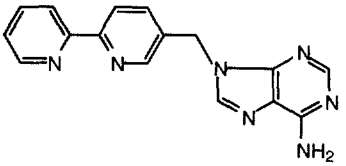
[X]=$(CH_2)_n$ n=2-4
[X]=*O*-xylene, *m*-xylene, *p*-xylene

ligands. Characterization of these ruthenium complexes by NMR spectroscopy confirmed $C_2$-symmetric structures in solution [61].

Condensation of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine with two equivalents of ferrocene methylamine afforded the bis-amide (**66**) which was reacted with $Ru(bpy)_2Cl_2$ to give the novel ruthenium(II) bipyridyl-bis(ferrocene) receptor (**67**). Relative to the $[Ru(bpy)_3]^{2+}$ prototype, the emission of (**67**) was almost completely quenched by the appended ferrocene moieties via an intramolecular mechanism [62].



**(66)**



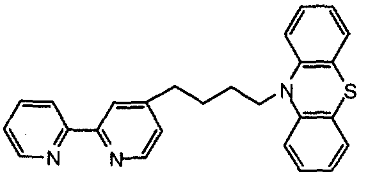
**(68)**

Reaction of 5-bromomethyl-2,2′-bipyridine with adenine afforded mixtures of *N*-alkylated products, from which the ligand L (**68**) was isolated. $[Ru(bpy)_2(L)](PF_6)_2$ was prepared and crystallographically characterized in which the adenine fragment is pendant from the $\{Ru(bpy)_3\}^{2+}$ core [63].

The complex $[Ru(terpy)L(H_2O)](ClO_4)_2$ [L=4,4′-$(OMe)_2$bpy and

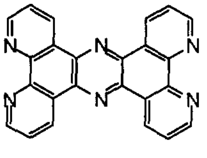
4,4′-$(NO_2)_2$bpy] was prepared and its spectral and redox properties in aqueous solution studied. These complexes are stable both in the solid state and in various solutions. Anomalous spectral and redox behaviour of [Ru(terpy){4,4′-$(NO_2)_2$bpy}$(H_2O)](ClO_4)_2$ is attributed to the existence of a deprotonated species in solution and interpreted from semi-empirical calculations [64].

Time-resolved emission studies have been performed on a series of covalently linked Ru$(bipyridine)_3$-phenothiazine complexes. The emissive Ru$(bipyridine)_3$ MLCT excited state is quenched by electron donation from a phenothiazine [PTZ; (**69**)] donor. The rates of electron transfer (ET) to the MLCT states from the PTZ donor have been analysed in terms of Marcus theory, in which each phenothiazine acts independently of other phenothiazines in the complex. The results are compared to those obtained for the analogous electron transfer in a related donor–chromophore–acceptor system [65].

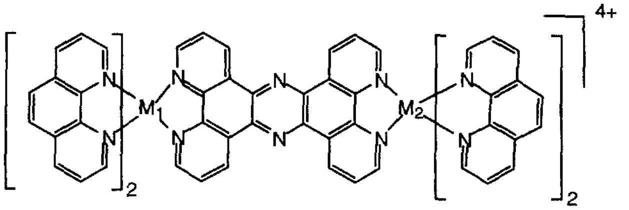


**(69)**

The complex $[(bpy)_2Ru^{II}(tpphz)]^{2+}$ (**70**) [tpphz = (**71**)] has been obtained by reaction of 5,6-diamino-1,10-phenanthroline with $[(bpy)_2Ru(phendione)]^{2+}$. The reaction of (**70**) with metallic precursors yielded the dimetallic complexes (**72**)–(**74**). Their synthesis, electrochemical and spectrophotometric characterization have been reported [66].



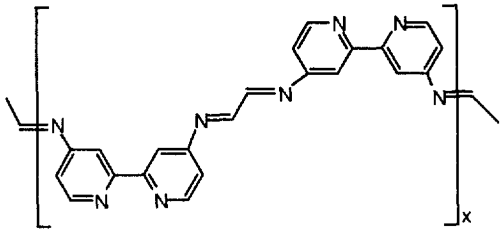
**(71)**



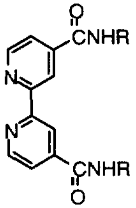
**(72)** $M_1$=Ru, $M_2$=Ru
**(73)** $M_1$=Os, $M_2$=Os
**(74)** $M_1$=Ru, $M_2$=Os

The synthesis, electrochemical, spectroscopic, emission lifetime and quantum yield data of a new bipyridine-containing conjugated polymer system, poly[1-(2,2′-bipyridine-4-yl)-1,4-diazabutadiene-4,4′-diyl)] (**75**), and its polymetallated ruthenium complex have been presented [67].

The binding of ruthenium polypyridyl complexes to DNA was investigated. In contrast to $[Ru(bpy)_3]^{2+}$, the dimetallic ruthenium bipyridyl complexes $[(bpy)_2Ru^{II}\{Mebpy(CH_2)_nbpyMe\}Ru^{II}(bpy)_2]^{4+}$ ($n = 5$, 7) bind more strongly to



**(75)**



**(76)**

DNA and can photosensitize a DNA strand which breaks even at high ionic strengths [68].

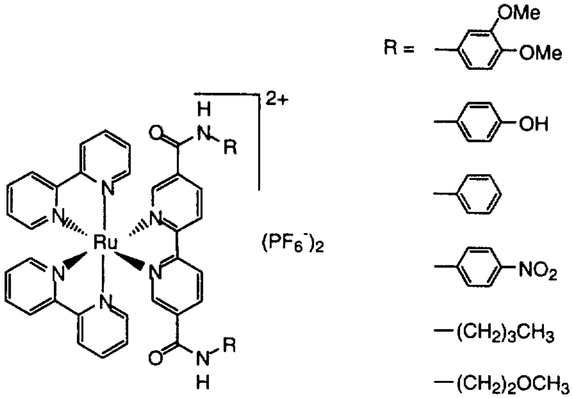
New acyclic mononuclear $[Ru(bpy)_2L]^{2+}$ [L = (**76**); R = Ph, *o*-, *m*-, *p*-$C_6H_4O$, $Me_3C$, *p*-$Me_3CC_6H_4$] complexes were prepared and characterized. Spectroscopic and electrochemical anion-coordination studies showed that these receptors bind chloride, bromide and iodide anions via a combination of electrostatic attraction and favourable amide CONH and phenolic ROH hydrogen-bonding interactions. The fluorescence-emission spectroscopic studies of the complexes have been discussed [69]. Intramolecular triplet energy transfer from a ruthenium(II) centre to an osmium(II) centre in a heteropolynuclear polypyridine complex at room temperature in MeCN have been studied. Their synthesis, characterization and electrochemical studies were reviewed [70].

The ruthenium complexes of 1,2,7,8-tetrahydrodipyrido[4,3-*b*;5,6-*b*]acridine, 1,2-dihydrodipyrido[4,3-*b*;5,6-*b*]acridine and dipyrido[4,3-*b*;5,6-*b*]acridine were prepared by heating two equivalents of ligand with $RuCl_3 \cdot 3H_2O$ in aqueous ethanol. These complexes were unambiguously identified by $^1H$ and $^{13}C$ NMR spectroscopies. The electronic absorption and luminescence data for the ligands and their Ru(II) complexes were recorded [71].

New acyclic Ru(II) 5,5′-bis-amide substituted 2,2′-bipyridyl receptor molecules (**77**)–(**82**) have been synthesized. $^1H$ NMR spectroscopy, cyclic and square-wave voltammetry, electronic absorption and fluorescence-emission spectroscopic measurements demonstrated the spectral and electrochemical recognition of chloride, and spectral recognition of the bromide anion in polar solvents [72].

The redox-active and photoactive ruthenium(II) bipyridyl moiety together with amide (CO–NH) groups has been incorporated into acyclic, macrocyclic, and lower rim calix[4]arene structural frameworks to produce a new class of anion receptor with the dual capacity of sensing anionic guest species via electrochemical and optical methodologies. The preparation of these receptor molecules was described, together with extensive anionic coordination investigations using NMR spectroscopy, X-ray crystallography, fluorimetry, and cyclic and square-wave voltammetry [73].

The synthesis, characterization, and redox and excited state properties of the three complexes $[Ru(bpy)_2(bpbtH_2)]^{2+}$, $\{[Ru(bpy)_2]_2(bpbtH_2)\}^{4+}$ and $\{[Ru(bpy)_2]_3(bpbt)\}^{4+}$ derived from the ligand [(**83**), bpbt-$H_2$] have been reported.



(77)

(78)

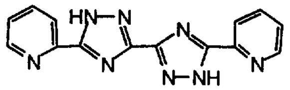
(79)

(80)

(81)

(82)

The coordination of the Ru(bpy)$_2$ unit is believed to occur via N$^1$ of the triazole and the pyridine nitrogen in the mononuclear and dinuclear complexes. All three complexes show emission in solution at ambient temperature. The absorption and emission properties were studied [74].



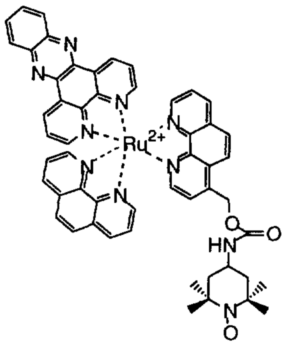
**(83)**

## 6.2. *Complexes with phenanthroline ligands*

Several new TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide) labelled ruthenium complexes were prepared. They can be divided into two different classes. The bis(heteroleptic) complexes were synthesized from [Ru(L)$_2$]Cl$_2$ (L = bpy or phen) and newly prepared phenanthroline-TEMPO ligands. Also, the tris(heteroleptic), spin labelled Ru complex (**84**) has been prepared from [Ru(dmso)$_4$]Cl$_2$, dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), phen and a phen-TEMPO ligand with a rigid linker [75].

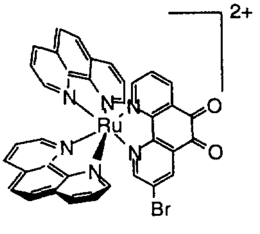
A convenient general method was described for the isolation of optically active Ru(II) complexes, *cis*-[Ru(phen)$_2$X$_2$]$^{n+}$. The resolution strategy involves the initial preparation of the Δ and Λ isomers of *cis*-[Ru(phen)$_2$(MeCN)$_2$](PF$_6$)$_2$. These precursor compounds were characterized by UV–vis, $^1$H NMR spectroscopy and CD spectral analysis, while enantiomeric purity was verified by conversion to optically active [Ru(phen)]$^{2+}$. The availability of authentic samples of resolved *cis*-[Ru(phen)$_2$Cl$_2$] is important for quantitative assessment of stereoselectivity in the covalent binding of such racemic complexes with DNA [76].

The condensation of Δ-[Ru(phen)$_2$(1,10-phenanthroline-5,6-dione)]$^{2+}$ [Δ-(**85**)] with Δ-[Ru(phen)$_2$(1,10-phenanthroline-5,6-diamine)]$^{2+}$ [Δ-(**86**)] in refluxing 1:1



**(84)**

MeCN/$H_2O$ yields the dinuclear complex Δ,Δ-$[(phen)_2Ru(tpphz)Ru(phen)_2]^{4+}$ [Δ,Δ-(**87**)] (tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2″,3″-*j*]phenazine). Formation of the phenazine ring has been optimized and occurs in nearly quantitative yield, which is essential for the practical synthesis of higher nuclearity species. The complexes have been characterized by $^1H$ and $^{13}C$ NMR spectroscopy and CD spectral analyses [77].



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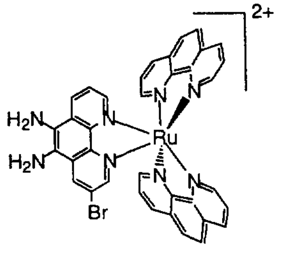
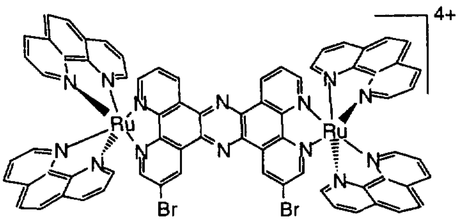
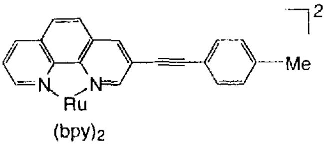


**(86)**

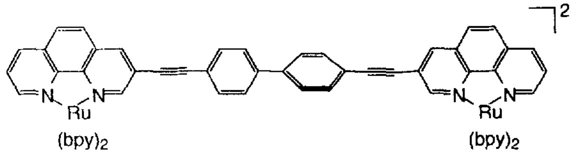


**(87)**

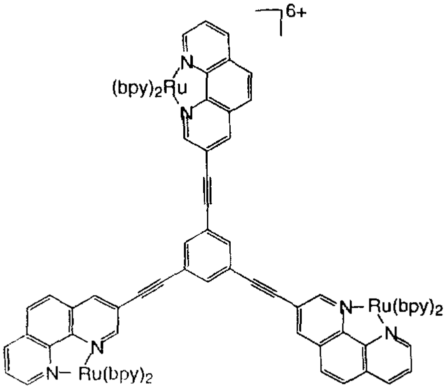
The complex $[(bpy)_2Ru(3\text{-bromo-}1,10\text{-phenanthroline})](PF_6)_2$ (**88**) is an attractive building block for the synthesis of multimetallic $Ru^{II}$ arrays using cross-coupling methodology. Palladium-mediated cross-coupling reactions of (**88**) with various aromatic acetylenes 1,4-diethynylbenzene, 4,4′-diethynyl-1,1′-biphenyl or 1,3,5-triethynylbenzene give mono- (**89**), di- (**90**), and trinuclear (**91**) complexes in high yields and under mild conditions [78].



**(89)**

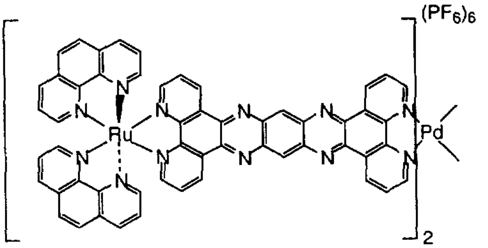


**(90)**

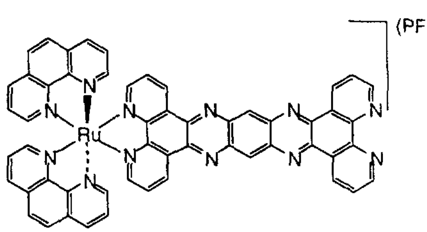


**(91)**

The construction of nanometre scale Ru$^{II}$Pd$^{II}$Ru$^{II}$ π-conjugated molecular rods, Λ,Λ-(**92**) and Δ,Δ-(**92**), from enantiomerically pure building blocks Λ-(**93**) and Δ-(**93**) respectively connected through a Pd$^{II}$ linkage, provides a method for obtaining enantio- and diastereomerically pure Ru$^{II}$-based molecular architectures. The compounds Λ,Λ-(**92**) and Δ,Δ-(**92**) were promising candidates for molecular wires due to their nanometre scale dimensions, rigid linear structure and extended π-system possessing redox-active Ru$^{II}$ centres [79].



**(92)**



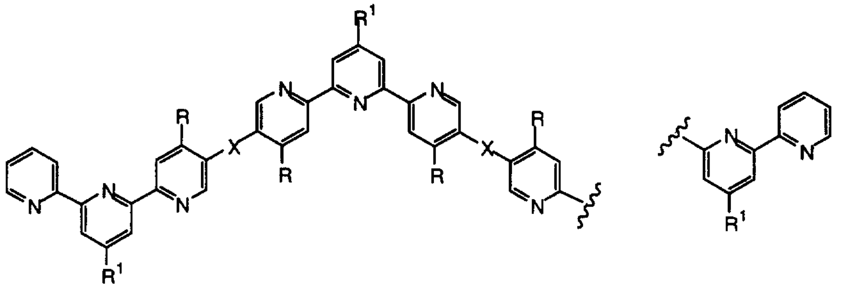
**(93)**

The photochemical (PEC) behaviour of mono- and dinuclear complexes, $[Ru(tap)_3]^{2+}$ (tap = 1,4,5,8-tetraazaphenanthrene) and $[Ru(phen)_2]_2(hat)^{4+}$ (hat = 1,4,5,8,9,12-hexaazatriphenylene), incorporated in recast Nafion on an $SnO_2$ electrode, in contact with an aqueous solution containing a reducing agent such as hydroquinone ($H_2Q$) was examined by continuous and pulsed laser excitation technique [80].

### 6.3. *Complexes with terpyridine ligands*

Monomethylation of 2,2′:6′,2″-terpyridine (terpy) afforded the *N*-methyl-2,2′:6′,2″-terpyridinium cation, $[\mathrm{Hmterpy}]^+$. With one of the terminal pyridine ring N atoms thus protected, this cation coordinates to Ru(II) either as a bidentate *N*,*N*′-donor giving [Ru(terpy)(Hmterpy-*N*,*N*′)Cl]$(PF_6)_2$, or as a cyclometallating tridentate ligand giving [Ru(terpy)(mterpy-*N*,*N*′,*C*)]$(PF_6)_2$, depending upon the reaction conditions. Both complexes were fully characterized by spectroscopic and electrochemical methods, and the crystal structures of [Ru(terpy)(mterpy-*N*,*N*′,*C*)]$(BF_4)_2$·2MeCN and [Ru(terpy)(Hmterpy-*N*,*N*′)Cl]$(PF_6)_2$·2MeCN were reported [81].

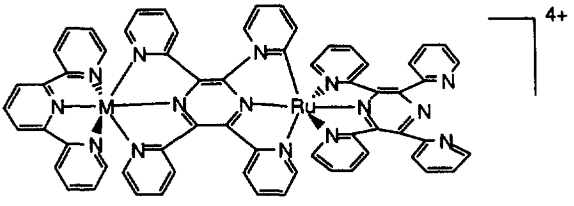
The absorption and luminescence spectra and lifetimes (at room temp and 77 K) of the linear tris-terpyridine bridging ligands [(**94**), (**95**)] and of their trinuclear Ru(II) complexes with terpy as terminal ligands were studied. The complexes $[Ru_3L(terpy)_3](PF_6)_6$ [L = (**94**) or (**95**) with $R' = CH_2CH_2OH$] were prepared and characterized by $^1H$ NMR and mass spectroscopy. The luminescence behaviours of the complexes were also discussed [82].



(**94**) $R=R'=H$, $X=-CH_2CH_2-$
(**95**) $R=CH_3$, $R'=CH_2CH_2OTBS$, $X=-CH=CH-$

Mono-, di-, and heterotrinuclear Ru(II) bis(terpy) complexes bearing a 4′-alkyne substituent are susceptible to reductive polymerization, in marked contrast to the corresponding tris(bpy) complexes. Efficient polymerization requires addition of at least two electrons to the complex, these being added to the alkyne-substituted ligand, while selectivity is most probably related to the severe steric crowding around the polymerizing function that is inherent in these systems [83].

Two classes of dimetallic complexes [(terpy)M(tpp)$RuCl_3$]$(PF_6)$ and [(terpy)M(tpp)Ru(tpp)]$(PF_6)_4$ (**96**) were prepared and their spectroscopic and electrochemical properties studied ($M = Ru^{II}$ or $Os^{II}$). Synthetic methods were developed for the stepwise construction of tpp-bridged systems using a building block approach [84].



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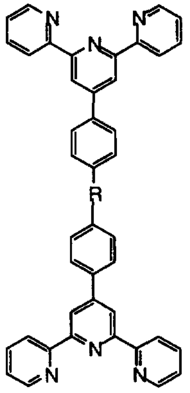

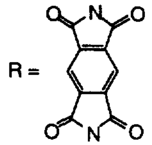

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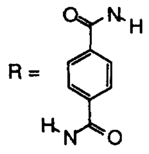

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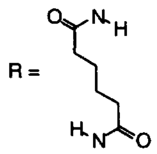
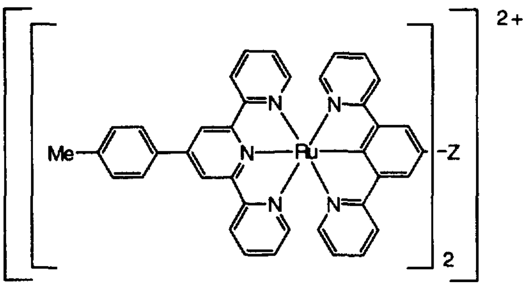


(99)

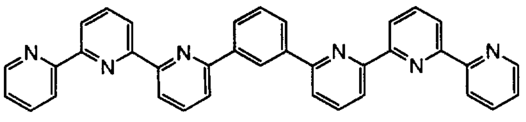
Transition metal complexes of 4′(4-anilino)-terpyridine have been prepared and used to construct coordination dimers and polymers linked by new binucleating terpyridine ligands (**97**)–(**99**) [85].

Two dinuclear Ru complexes (**100**) ($Z = m\text{-}C_6H_4$; *p*-terphenyl-1,4″-diyl) were prepared using functionalized mononuclear complexes as building blocks in a classical aromatic cross-coupling reaction (Suzuki's procedure) with diboronic derivatives of the aromatic spacers [86].

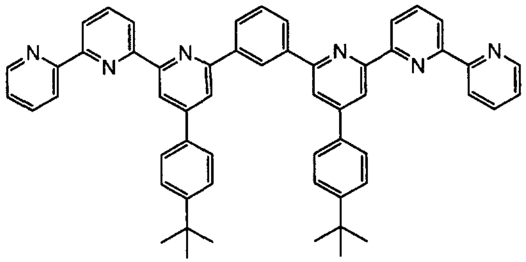


(100)

New polypyridines $L^1$ (**101**) and $L^2$ (**102**) were prepared. Their reaction with copper(II) acetate and silver(I) acetate gave $[Cu_2L^1_2]^{4+}$, $[Cu_2L^2_2]^{4+}$, $[Ag_2L^1_2]^{2+}$ and $[Ag_2L^2_2]^{2+}$ while $[Ru_2L_2(terpy)_2]^{4+}$ was obtained from $[Ru(terpy)Cl_3]$ with $L^2$. ES-MS showed that the double helical $[Cu_2L^2_2]^{4+}$ and $[Ag_2L^1_2]^{2+}$ complexes and the single helical $[RuL^2(terpy)_2]^{4+}$ complexes are the only species present in solution. All five complexes undergo reversible oxidations or reductions [87].



**(101)**



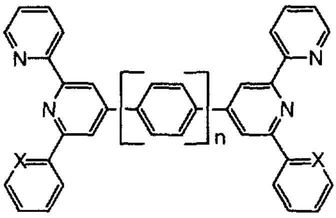
**(102)**

The resonance-Raman spectroscopic technique is an effective probe of the interaction between dipyridophenazine (dppz) complexes of ruthenium(II) and calf-thymus DNA, and provides evidence that DNA addition results in changes to electronic transitions of the intercalating dppz ligand in both ground and excited states [88].

The synthesis and characterization of the complex $[Ru(tpp)(4,4'\text{-}(CH_3)_2bpy)Cl]^+$ has been reported. The ion was obtained in a one-pot synthesis by reduction of $Ru(4,4'\text{-}(CH_3)_2bpy)Cl_4$ with triethylamine in the presence of tpp [89].

Multinucleating ligands containing one or more potentially cyclometallating 6-phenyl-2,2′-bipyridine domains (**103**) (X = CH, N; $n = 0$, 1) have been prepared. These ligands are related to previously studied systems containing multiple 2,2′6′,2″-terpyridine metal-binding domains. The coordination chemistry of these new ligands was studied and Ru(II) complexes, such as $[(terpy)Ru(\mathbf{103})Ru(terpy)]_2$, were prepared from (**103**) and $[Ru(terpy)Cl_3]$. A variety of metallated and non-metallated products were isolated [90].

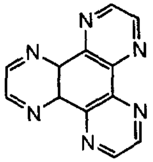
In a series of complexes $[(ttp)Ru\{(terpy)(C_6H_4)_n(terpy)\}]^{2+}$ [ttp = 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine]; the Ru-terpy type chromophore and the free terpy site are separated by a number of phenylene spacers ($n = 0$–2). For the complex with $n = 0$, modulation of the luminescence properties of the Ru-based chromophore can be performed by protonation at the free terpy site, suggesting a new approach for affording long-lived excited species of the basic Ru-terpy type unit [91].



**(103)**

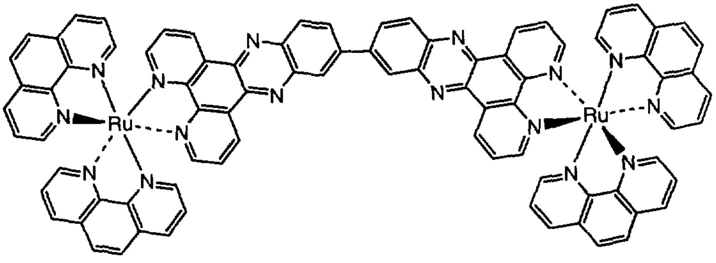
## 6.4. Complexes with other N-heterocyclic ligands

A new heptanuclear Ru(II) complex with dendritic characteristics, Ru(hat)$_3$[Ru(phen)$_2$]$_6$(PF$_6$)$_{14}$, was synthesized [hat = (**104**)]. This compound was characterized by ES-MS [92].



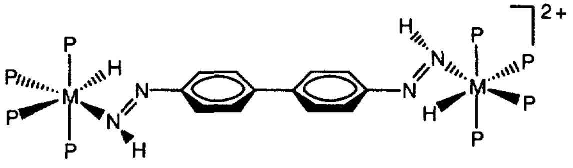
**(104)**

Dimeric homochiral ruthenium complexes [L$_2$Ru{dppz(11–11′)dppz}RuL$_2$]$^{4+}$ [L = phen (**105**), bpy, dppz] were prepared and bound extremely strongly to duplex DNA with different binding geometries for the ΔΔ and ΛΛ enantiomers of the phenanthroline complex but with similar geometries for the bipyridyl complex enantiomers [93].



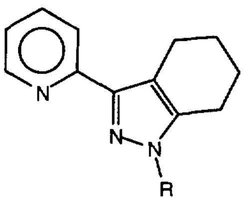
**(105)**

Dinuclear complexes [(MHP$_4$)$_2$(μ-HN=NAr–ArN=NH)](BPh$_4$)$_2$ (**106**) [M = Fe, Ru; P = P(OMe)$_3$, P(OEt)$_3$, PPh(OEt)$_2$; Ar–Ar = 4,4′-C$_6$H$_4$–C$_6$H$_4$, 4,4′-(2-CH$_3$)C$_6$H$_3$–C$_6$H$_3$(2-CH$_3$), 4,4′-C$_6$H$_4$–CH$_2$–C$_6$H$_4$] were prepared by reacting MH$_2$P$_4$ with bis(diazonium) salts (N$_2$Ar–ArN$_2$)(BF$_4$)$_2$ in a 2:1 ratio at low temperature. The compounds were characterized by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy (including $^{15}$N isotopic substitution) and an X-ray crystal structure determination [94].



**(106)**

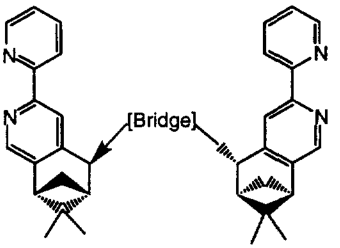
The synthesis of the hetero- and homoleptic ruthenium(II) complexes $Ru(bpy)_2L^{2+}$, $Ru(bpy)L_2^{2+}$ and $RuL_3^{2+}$ of six new bidentates L, and the substituted pyrazolylpyridines (**107**)–(**112**), has been reported and these compounds were fully characterized by $^1H$ and $^{13}C$ NMR spectroscopy and elemental analysis. The UV–vis spectra and redox properties of the complexes, some in the ruthenium(III) and reduced bipyridine oxidation states, were also discussed [95].



**(107)** R=H
**(108)** R=$CH_3$
**(109)** R=Ph
**(110)** R=$C_6H_4$-4”-$COOCH_3$
**(111)** R=$C_6H_4$-4”-COOEt
**(112)** R=$C_6H_4$-4”-COOH

Photolysis of $Ru(bpy)_2(en)^{2+}$ and $Ru(bpy)_2(tn)^{2+}$ was studied in MeCN using on-line ES-MS. These complexes are known to undergo a four-electron oxidation photochemically, giving the α,α′-diimine complexes. Some mechanistic details of both oxidation and substitution reactions in photolysis of the diamine complexes have been presented [96].

The two enantiomers (Δ and Λ) of Ru(chiragen[X])$Cl_2$ (**113**), where chiragen is a tetradentate ligand with a chiral bridging unit between two bipyridine moieties, have been prepared in high yields. X is *m*-xylyl (*m*-xyl); other bridging groups [e.g. $-(CH_2)_5-$ or $-(CH_2)_6-$] behave similarly. All three isomers (ΔΔ, ΛΛ and ΔΛ) of [(chiragen[*m*-xyl]Ru(bpym)Ru(chiragen[*m*-xyl])]$(PF_6)_4$ were prepared and fully characterized by NMR spectroscopy and various other spectroscopic methods [97].

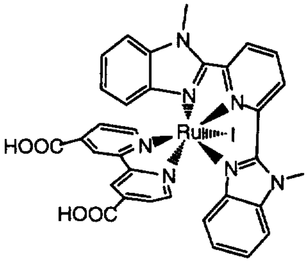


**(113)**

Laser dichroism (LD) has been used to probe the binding geometries of the diastereomeric adducts between DNA and the Δ and Λ enantiomers of $[Ru(phen)_2L]^{2+}$ (L = dppz or its benzologue benzodipyrido[*a*:3,2-*h*:2′,3′-*g*]phenazine (bdppz)). By combined use of LD and emission anisotropy an envelope of the MLCT region has been resolved for the first time in a complex of this type bound to DNA [98].

The complexes $[Ru^{IV}(terpy)(cxhn)O](ClO_4)_2$ (**114**) (cxhn = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminocyclohexane) and $[Ru^{IV}(Me_3tacn)(cbpy)O](ClO_4)_2$ [cbpy = (−)-3,3′-[(4*S*-*trans*)-1,3-dioxolane-4,5-dimethyl]-2,2′-bipyridine and $Me_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane] were prepared. Crystal structures of (**114**) and $[Ru^{II}(Me_3tacn)(3,3'\text{-}Me_2bpy)(OH_2)](ClO_4)_2$ were also determined [99].

The synthesis and properties of several complexes of Ru(II) containing 4,4′-dicarboxy-2,2′-bipyridine ($dcbpyH_2$), 2,6-bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine (ph-bmipy), and monodentate ligands ($X^- = Cl^-$, $I^-$, $NCS^-$, $NCSe^-$, $CN^-$) have been reported. The introduction of the ambidentate ligands $X^- = NCS^-$, $NCSe^-$, and $CN^-$ into the coordination sphere of $[Ru(bmipy)(dcbpy)I]^-$ (**115**) and $Ru(dcbpyH_2)Cl_2$ was studied in situ via $^1H$ and $^{13}C$ NMR spectroscopy using $^{13}C$-enriched ligands $X^-$. Possible strategies for the design of more efficient sensitizers were discussed [100].

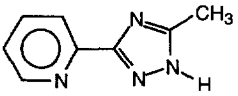


(**115**)

The compound 1,2-diamino-9,10-anthraquinone (daaq) binds to bis(2,2′-bipyridine)dichlororuthenium forming a complex containing the oxidized 1,2-diimino-9,10-anthraquinone (diaq). As inferred from theoretical calculations, electrochemical and spectroscopic data, there is an extensive π-backbonding interaction between the diaq ligand and the metal. The diaq is the best π-accepting neutral α,α′ diimine ligand known to date [101].

The synthesis and characterization of $[Ru(biq)_2(LL')]^{n+}$ compounds [LL′ = (**116**)–(**118**)] have been reported. NMR spectroscopy has been used to elucidate the coordination mode of the ligands. The complexes have been further characterized by electrochemical, UV–vis absorption and emission measurements [102].

The synthesis and X-ray crystal structures of the linear trinuclear metal complexes $[M_3^{II}(dpa)_4Cl_2]$ (M = Ru, Rh) with a *syn*,*syn* bis(2-pyridyl)amino (dpa) ligand were examined. These complexes possess a short M–M–M three-centred multiple bond [Ru–Ru 2.2537(5) Å, Rh–Rh 2.3920(5) Å] and are the first examples of three-centred multiple metal–metal bond complexes [103].



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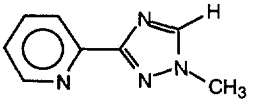

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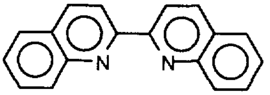
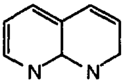
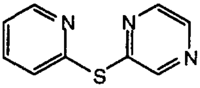


**(118)**

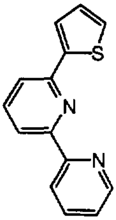
The complexes $[Ru(bpy)_2(napy\text{-}N)(MeCN)][PF_6]_2$ and $[Ru(bpy)_2(napy\text{-}N,N')][PF_6]_2$ [napy = 1,8-naphthyridine = (**119**)] were prepared, and their crystal structures determined by X-ray analysis. Napy is expected to be a suitable compound for the design of homogeneous catalysts having site-opening and -closing functions. The dynamic behaviour of napy in the complexes $[Ru(bpy)_2(napy\text{-}N)(solv)]^{n+}$ and $[Ru(bpy)(napy\text{-}N,N')]^{n+}$ ($n = 1$, 2; solv = solvent) in solution has been investigated [104].



**(119)**



**(120)**



**(121)**

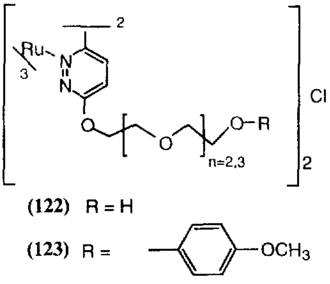
The Ru(II) complex *cis*-$[Ru(bpy)_2(npp)Cl]^+$ [npp = 4-(*N*-pyrrolyl)pyridine] was isolated from the reaction between *cis*-dichlorobis(bipyridine)ruthenium and 4-(*N*-pyrrolyl)pyridine. $^1H$ and $^{13}C$ NMR spectroscopic studies were used to characterize this novel complex together with IR and Raman data [105].

Pyrazin-2-yl 2-pyridyl sulphide [pzpys = (**120**)] was prepared by reaction of 2-sulphanylpyridine with chloropyrazine. By reaction of pzpys with $[RuL_2(NO)(NO_2)](PF_6)$ [L = bpy or di-2-pyridyl sulphide (dps)], mononuclear $[RuL_2(pzpys)(NO_2)](PF_6)$ was obtained in which pzpys is monodentate. The reactions of pzpys with *cis*-$[RuL_2Cl_2]$ (L = bpy, phen or dps) have been studied. The synthesis, IR, UV–vis, $^1H$ and $^{13}C$ NMR spectroscopic characterization of this series of mono- and binuclear Ru(II) complexes containing pzpys as mono- or bidentate mononucleating and tridentate binucleating ligand, respectively were reported [106].

The metallated complex $[Ru(tbp)(terpy)][PF_6]$ [Htbp = (**121**)] is converted to the non-metallated species $[Ru(Htbp)(terpy)][PF_6]$ containing an *N*,*N*,*S*-bonded Htbp ligand upon treatment with acid; this process is reversed upon reaction of $[Ru(Htbp)(terpy)][PF_6]$ with aqueous NaOH solution. This observation is the first example of a fully reversible cyclometallation system [107].

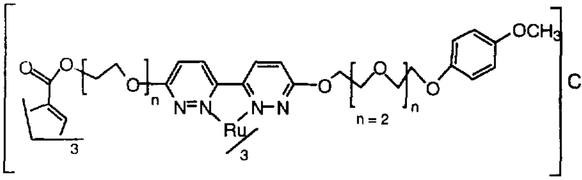
Absorption spectra, electrochemistry and MLCT properties were studied for the mixed ligand complexes $[Ru(imin)_n(bpy)_{3-n}](PF_6)_2$ ($n = 0$–3) [imin = 2-(*N*-methyl formimidoyl)pyridine]. The MLCT absorption maxima of the complexes were studied [108].

The preparation of (**122**)–(**124**) containing polyethylene glycol chains is described. The complexes are further functionalized by 4-oxyanisyl or by hydrophilic hydroxyl groups. These complexes may interact in supramolecular assemblies with suitable acceptors such as mono- and bis-viologens to form biomimetic models for photosynthesis [109].



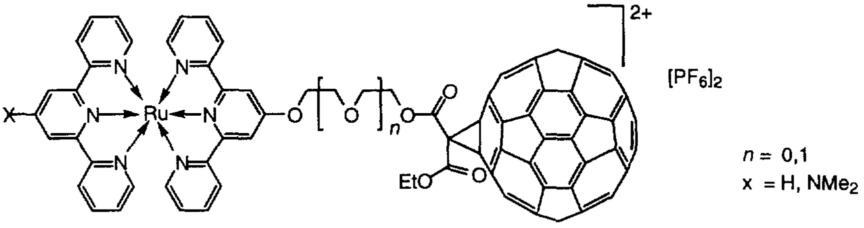
**(122)** R = H

**(123)** R =

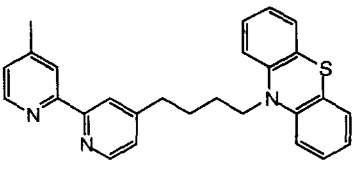


**(124)**

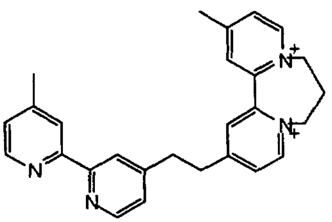
A new series of ligands was prepared in which $C_{60}$ units are attached to 2,2′:6′,2″-terpyridines; ruthenium(II) diads and triads (**125**) are prepared in which the pendant fullerene acts as an electron acceptor. The electrochemistry of these fullerene functionalized complexes has been investigated [110].



**(125)**



**(126)**



**(127)**

The kinetics of reduction of $[Ru^{III}(edta)(py)]^-$ (edta = ethylenedinitrilotetraacetate) with L-ascorbic acid ($H_2A$) and catechol ($H_2cat$) were studied spectrophotometrically as a function of $[H_2A]$ or $[H_2cat]$, pH, ionic strength and temperature (25–40 °C). Kinetic data and activation parameters are interpreted in terms of a mechanism involving outer-sphere electron transfer [111].

Under optimal conditions, the N7-coordinated complexes *trans*-$[L(py)(NH_3)_4Ru^{III}]$ (L = Guo, dGuo, 1MeGuo) disproportionate to give ~50% *trans*-$[Guo(py)(NH_3)_4Ru^{II}]$ and a putative $Ru^{IV}$ species that yields ~50% $[Guo(py)(NH_3)_4Ru^{III}]$. The first efficient hydrolytic mechanism for cleaving the *N*-glycosidic bond by a metal ion serving as a general acid catalyst at $G^7$ was reported [112].

Absorption spectra, electrochemistry and MLCT excited state properties were studied for $[Ru(imin)_n(bpy)_{3-n}](PF_6)_2$ ($n = 0$–3). They show systematic blue shifts with the replacement of the ligand imin by bpy. The oxidation and the reduction potentials also show a systematic shift to the negative with the replacement of imin by bpy [113].

A stepwise synthetic strategy has been developed by which 4-substituted pyridyl ligands (**126**), (**127**) are attached to the *trans*-$\{Ru(bpy)_2\}^{2+}$ core by using *trans*-$[Ru(bpy)_2(dmso)_2](CF_3SO_3)_2$ as a precursor. The application of this procedure to the preparation of chromophore-quencher complexes and the photophysical properties of the resulting complexes were reported [114].

The photosensitized aquation of pentaammine(pyridine)ruthenium(II) by several dyes has been studied under conditions where only the sensitizers absorb light. Sensitization was effective with singlet sensitizers Rhodamine-B (17 452 $cm^{-1}$) and Safranine-T (17 690 $cm^{-1}$) as well as the triplet sensitizer biacetyl (19 000 $cm^{-1}$). The results indicate that the excited state precursor, of the observed photosubstitution reaction in the complex, lies in the energy range between 17 000 and 17 700 $cm^{-1}$ [115].

Three geometric isomers of $[RuCl_2L_2](ClO_4)_2$ (L = *N*-phenyl-2-pyridine carboxaldimine) were isolated by stereoretentive oxidation of the corresponding isomeric Ru(II) complexes using $Cl_2(g)$ as an oxidant, followed by addition of aq. $NaClO_4$. Their synthesis, characterization and electron transfer were presented [116].

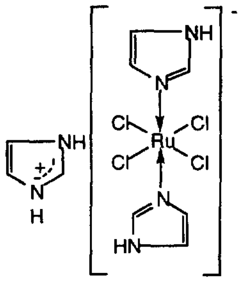
The modelling of solvent shifts in systems in which specific solute–solvent interactions such as H-bonding occur was studied. The interpretation was considered in terms of the MLCT absorption and electroabsorption spectra of $Ru^{2+}(NH_3)_5$-pyrazine-$H^+$ in dilute aqueous solution. The electroabsorption spectra of these complexes were reported [117].

The complexes $Ru(PPh_3)_2Cl_2L_2$ (L = 4-$^t$Bu-py, 4-vinyl-py, 4-CN-py, 4-Me-py, 3-Me-py) have been prepared by reaction of $RuCl_2(PPh_3)_3$ with the appropriate ligand under mild conditions and characterized by elemental analysis, IR, NMR ($^1H$ and $^{31}P$) and UV–vis spectra. The $Ru^{II}$ derivatives display a $RuP_2Cl_2N_2$ core with a *trans,cis,cis* arrangement of the donor atoms. $Ru(PPh_3)_2Cl_2(4\text{-}^tBu\text{-}py)_2$ is found to be an efficient catalyst precursor for the homogeneous hydrogenation of cyclohexene and benzaldehyde under moderate conditions [118].

The complex $[(Ru(bpy)_2)_2tpt](PF_6)_4$ [tpt = 2,4,6-tris(2-pyridyl)triazine] was prepared in good yield. Electrochemical characterization was carried out and the electrochemical properties were compared with its analogue, $[Ru(bpy)_2tpt](PF_6)_2$. Both complexes are emissive in a room temperature MeCN solution and their luminescence lifetimes and quantum yields were determined [119].

The crystal structure of $[Ru(terpy)(bpy)(pz)](PF_6)_2$ showed that the coordination geometry around the Ru(II) ion is a distorted octahedron, with the various Ru–N bond lengths indicative of considerable interligand steric strain. The Ru–N pyrazine bond is the longest within the structure, consistent with other evidence that π-backbonding to pyrazine is weak in this complex [120].

The aquation chemistry of the antitumour-active complexes *trans*-$Him[Ru^{III}Cl_4(im)_2]$ (**128**) (Him = imidazole) and *trans*-$Hind[Ru^{III}Cl_4(ind)_2]$ (**129**) (Hind = indazole) with plasma proteins has been investigated. For (**128**), the *trans* geometry was confirmed by X-ray crystallography [121].



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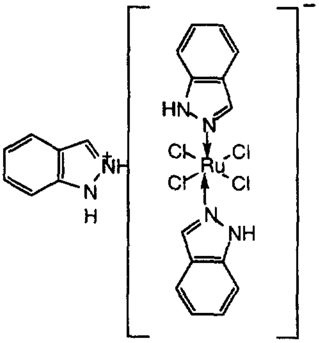
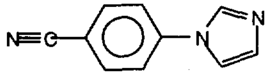


**(129)**

The complexes *cis*-$[Ru(bpy)_2(im)(OH_2)]^{2+}$, *cis*-$[Ru(bpy)_2(im)_2]^{2+}$, *cis*-$[Ru(bpy)_2(N\text{-}im)_2]^{2+}$, *cis*-$[Ru(dmbpy)_2(im)(OH_2)]^{2+}$ and *cis*-$[Ru(dmbpy)_2(N\text{-}im)(OH_2)]^{2+}$ were synthesized under ambient conditions in aqueous solution (pH 7). Their electrochemical and spectroscopic properties (absorption, emission and lifetimes) were determined and compared [122].

Comparisons of the spectroscopic properties of a number of $Ru^{III}$ complexes of imidazole ligands provide methods of distinguishing between various types of bonding that can occur in proteins and nucleic acids. In particular, EPR and $^1H$ NMR spectroscopic parameters arising from the paramagnetism of $Ru^{III}$ could aid in determining binding sites of $Ru^{III}$ drugs in macromolecules. Electrochemical studies on several imidazole complexes of Ru suggest that imidazole can serve as a significant π-acceptor ligand in the presence of anionic ligands [123].

A new bridging ligand CPI (**130**) has been prepared, as well as CPI–$Me^+$. The mononuclear complexes $[(NH_3)_5Ru\text{–}CPI\text{–}Me]^{3+}$ and $[(NH_3)_5Ru\text{–}CPI\text{–}Ru(NH_3)_5]^{4+}$ have been obtained. The spectral and electrochemical features of the two complexes are compared [124].



**(130)**

### 6.5. Complexes with macrocyclic ligands

A novel preparation of the useful synthon Ru(TTP)(NO)(OMe) is reported and this compound has been characterized by single crystal X-ray diffraction. Subsequent methoxide substitution reactions led to the preparation in high yield and purity of a wide variety of new complexes including a mercaptide complex which is the first reported analogue of the diamagnetic nitrosyl adducts of the P-450 monooxygenases [125].

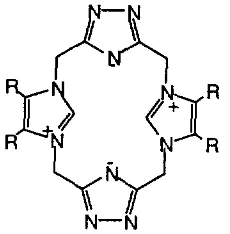
The synthesis and characterization of imino ester complexes of Ru(II) porphyrins from oxidation of racemic α-amino esters by the dioxoruthenium(VI) picket-fence complex $[Ru^{VI}(L)(O)_2)]$ (αβαβ isomer) (L = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3-trifluoropropanoylamino)phenyl]porphyrin) have been reported. They are the first examples of imine Ru porphyrin complexes which have been isolated and characterized [126].

Treatment of *trans*-$[Ru^{III}(16\text{-}TMC)Cl_2]Cl$ (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with zinc metal in aqueous solution under nitrogen resulted in the formation of *trans*-$[Ru^{II}(16\text{-}TMC)(N_2)Cl]PF_6$ which has been characterized by X-ray crystal analysis [127].

The $Ru_2$ and RuNi derivatives of 1,8-bis(10,15,20-trimesityl-5-porphyrinato)anthracene (a co-facial diporphyrin ligand comprising two hindered porphyrins spanned by an anthracene bridge) have been synthesized. Both $Ru_2$(DPAHM) and RuNi(DPAHM) are extremely reactive species that apparently contain 14-electron Ru(II) centres. In addition, these electron-deficient Ru(II) porphyrins all appear to bind aromatic solvents such as benzene and toluene, the weakest ligating solvents in which these Ru(II) porphyrins have been found to be soluble [128].

The Zn derivative of a new stable open-box shaped pentamer of vertically linked porphyrins $(TPyP)[Ru(TPP)(CO)]_4$ was formed quantitatively by treatment of tetrapyridylporphyrin (TPyP) with [Ru(TPP)CO]. Two trimers with different geometries, (*trans*-DPyDP)$[Ru(TPP)(CO)]_2$ and (*cis*-DPyDP)$[Ru(TPP)(CO)]_2$, and a dimer [Ru(TPP)(CO)(M-PyTP)] have been synthesized and characterized [129].

Mono-, di- and trinuclear complexes $Ru_aL_b(dmso)_cCl_d(PF_6)_e$ [$a = 1$–$3$, $b = 1$–$4$, $c = 3$–$7$, $d = 2$–$7$, $e = 0$–$3$; L = (**131**), R = H, $C_4H_9$; (**132**) R = H, $C_4H_9$, A = $CF_3SO_2^-$, $Cl^-$; (**133**) and (**134**) R = H, $C_4H_9$) were prepared by the reaction of *cis*-$Ru(dmso)_4Cl_2$ with (**131**)–(**134**). The complexes were characterized by elemental analyses, IR, $^1H$ NMR spectroscopy as well as mass spectroscopy [130].



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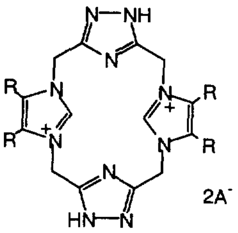

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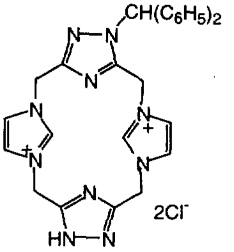

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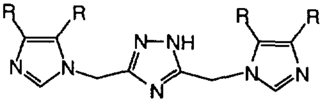
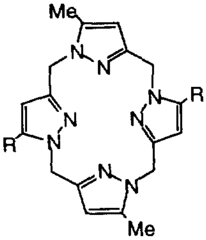


**(134)**

The complex *trans*-[Ru$^{VI}$(tmp)(O)$_2$] (tmp = dianion of 5,10,15,20-tetramesitylporphyrin), generated by in situ oxidation of [Ru$^{II}$(tmp)CO] by excess *m*-chloroperbenzoic acid in a benzene solution, catalytically dehydrogenates primary and secondary amines in the presence of air. During the process of an investigation of such a reaction employing benzylamine as the substrate, the bis(amine) complex [Ru$^{II}$(tmp)(PhCH$_2$NH$_2$)$_2$] was isolated and characterized crystallographically [131].

The synthesis and characterization of Ru(II) complexes with acyclic and macrocyclic ligands containing tautomerizable OH and fixed OCH$_3$ 5-pyrazolone heterocycles have been described. From the macrocycle with two CH$_3$ and two OCH$_3$ pyrazole subunits [L = (**135**); R = OMe), [Ru(L)XY(PF$_6$)$_2$] (X, Y = dmso, MeCN, py, pz, 3,5-dimethylpyrazole) were prepared. They show a behaviour close to that of the analogous tetrapyrazole complexes but with different complexing ability [132].



**(135)**

The charge-transfer excited states of $Ru^{II}OEP(py)_2$ and $Ru^{II}(tpp)(py)_2$ (OEP= octaethylporphyrin) have been investigated by nanosecond time-resolved resonance-Raman spectroscopy. The spectra reveal unexpected differences between the two species [133].

Reaction of ruthenium phthalocyanine $(PcRu)_2$ with dioxygen under a variety of conditions leads in all cases to a solid amorphous oxygen-containing aggregate formulated as $HO–[(Pc)RuO]_n–H$. Detailed structural information on this material was obtained by the large-crystal X-ray scattering technique. Additional information on the structure and electronic state of this ruthenoxane material was obtained by IR, resonance Raman, EPR, ESCA, and magnetic susceptibility studies [134].

Reaction of (OEP)Ru(CO) with $NO^+BF_4^-$ in $CH_2Cl_2$ generated $[(OEP)Ru(NO)]^+$ (**136**), which was recrystallized in air to give the aqua complex $[(OEP)Ru(NO)(H_2O)]^+$ (**137**). Reaction of (**137**) with diethylnitrosamine produces the air-stable $[(OEP)Ru(NO)(Et_2NNO)]^+$. Reaction of (**136**) with diethylnitrosamine gives the isoelectronic carbonyl analogue $(OEP)Ru(CO)(Et_2NNO)$ (**138**). The crystal and molecular structures of (**137**)$\cdot BF_4 \cdot H_2O$ and (**138**) were determined by X-ray crystallography [135].

The X-ray structural analysis of *trans*-[RuCl(cyclam)(4-acpy)]($BF_4$) showed that this complex adopts the trans geometry, with the macrocycle in the chair conformation. $^{13}C$ and $^1H$ NMR spectra in DMSO-$d_6$ and acetone-$d_6$ showed the same geometry and conformation of the macrocycle in solution [136].

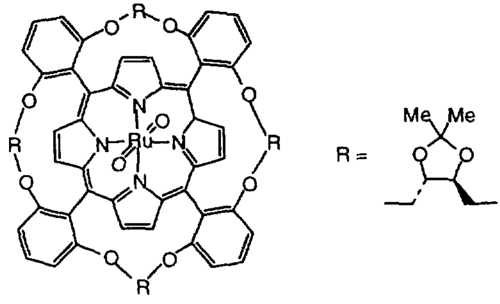
The photophysical properties of Ru(II) phthalocyanine [$(^tBu)_4Pc$ = tetra(*tert*-butyl)phthalocyocyanine] were studied at room temperature by steady state and time-resolved electronic absorption and emission spectroscopy. The important finding is that $(^tBu)_4PcRu(py)_2$ solutions show phosphorescence originating from a charge-transfer state [137]. The synthesis and characterization of new bridged phthalocyaninatoruthenium complexes $PcRuL_2$ and $[PcRu(L)]_n$ using 1,2,4-triazines as bridging ligand were reported. The preferred coordination of $N^1$ of the 1,2,4-triazines with the metal atom in $PcRuL_2$ was discussed based on NMR spectroscopy. $[PcRu(L)]_n$ exhibits good semiconducting properties without external doping [138].

Differences in the resonance-Raman spectra of the complexes $[Ru_2X_3(tacn)_2]^{2+}$ (X = Cl, Br, I) were explained in terms of variations in both Ru–Ru distances and the steric interactions between bridging and terminal ligands. X-ray crystal structure analyses were carried out to provide the Ru–Ru distances for these complexes and also the interatomic distances necessary for assessing ligand steric effects [139].

The enantioselectivity in the first catalytic conversion of styrene to its epoxide by a homochiral ruthenium porphyrin (**139**) displayed a remarkable sensitivity to the solvent and the identity of the oxidant. The latter phenomenon clearly indicates that several high valent intermediates with different selectivities participate in oxygen atom transfer from catalyst to substrate [140].

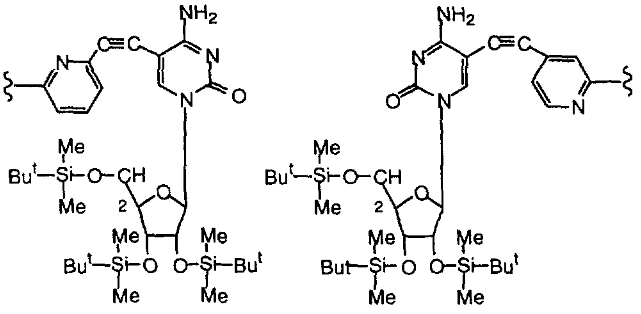
### *6.6. Complexes with other mixed-donor ligands*

The synthesis and characterization of the first cytidine-substituted Ru(II) trisbipyridine complex, $[Ru(bpy)_2L](PF_6)_2$ [L = (**140**)] has been reported. This complex,



**(139)**

which was characterized by UV–vis absorption bands at 484 and 368 nm, an emission band at 655 nm, and reduction/oxidation waves at 1.0, −1.4, −1.7 and 1.4V vs. Ag/AgCl, could serve as a new photodonor and/or acceptor for use in the construction of redox-active, non-covalent electron-transfer model systems [141].

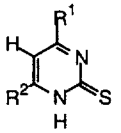


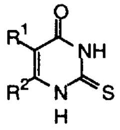
**(140)**

Mixed-ligand phenolato Schiff base complexes of Ru(II), $[Ru(pap)_2L]ClO_4$ [pap = 2-(phenylazo)pyridine; L = deprotonated form of HL ligand, 2-$HOC_6H_4CH{=}NC_6H_4R$-4, R = H, Me, OMe Cl, $NO_2$] and $[Ru(bpy)_2L^2]ClO_4 \cdot H_2O$ ($HL^2$ = 2-$HOC_6H_4CH{=}NC_6H_4Me$-4) were prepared and characterized. The complexes are diamagnetic and behave as 1:1 electrolytes in MeCN. All the complexes show strong MLCT transitions in the visible region. Their electrochemical redox properties were studied [142].

Ru(II) complexes containing pyrimidine-2-thione and related ligands were prepared, with formula $[Ru(L\text{-}N,S)(bpy)_2]ClO_4$ [$H_nL$ = (**141**)–(**149**)] and characterized by elemental analysis, UV–vis and $^1H$ and $^{13}C$ NMR spectra [143].

Some asymmetric Ru(III) chiral Schiff base complexes derived from 1*R*,2*R*-(−)-1,2-diaminocyclohexane with 3-acetyl-4-hydroxy-6-methyl-2-pyrone and salicylaldehyde, 5-chloro-5-methoxy- and 5-nitrosalicylaldehyde have been synthesized. The characterization of the complexes was accomplished by microanalysis, IR, UV–vis, CD spectroscopy, conductance measurements, magnetic susceptibility, optical rotation and electrochemical studies [144].



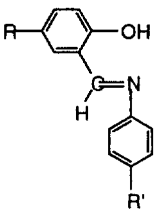


| **(141)** R¹ | R² | | R¹ | R² |
|---|---|---|---|---|
| **(142)** H | H | **(146)** | H | H |
| **(143)** CH₃ | H | **(147)** | CH₃ | H |
| **(144)** CH₃ | CH₃ | **(148)** | H | CH₃ |
| **(145)** NH₂ | H | **(149)** | H | *n*-C₃H₇ |

The complexes $[Ru(N,O\text{-hia})(bpy)_2]^+$ and $[Ru(N,O\text{-hia})(bpy)(py)_2]^+$ (hia = $CH_3COC(NO)COCH_3^-$) were prepared by reactions of *cis*-$[Ru(NO)(OH_2)(bpy)_2]^{3+}$ and *cis*-$[Ru(NO)(OH)(bpy)(py)_2]^{2+}$ with acetylacetone (Hacac), respectively. An X-ray structural analysis showed that the products have an identical nitroso ligand; however, the electrochemical properties of the complexes differ dramatically [145].

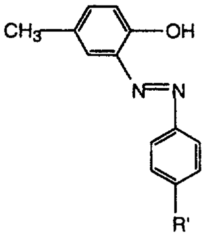
The complex [Ru(terpy)LCl] [L = salicylaldiminate and 2-(arylazo)phenolate anion] was synthesized and characterized. The complexes are diamagnetic and show intense MLCT transitions in the visible region. Cyclic voltammograms of these complexes were recorded. $[Ru^{III}(terpy)LCl]^+$ complexes were synthesized by chemical and electrochemical oxidations of their Ru(II) precursors and isolated as perchlorate salts [146].

The synthesis, characterization and electron-transfer properties of another series of the mixed-ligand Ru(II) complexes of general formula $[Ru(bpy)_2L]ClO_4$ [L = (**150**), (**151**)] have also been reported. The complexes are also diamagnetic and in solution show intense MLCT transitions in the visible region [147].



**(150)**

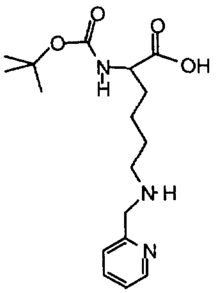
| R | R' |
|---|---|
| H | OMe |
| H | Me |
| H | H |
| H | Cl |
| H | NO₂ |
| Me | H |



**(151)**

| R' |
|---|
| OMe |
| Me |
| H |
| Cl |
| NO₂ |

(α-Imino acidato)ruthenium(II) complexes $[Ru^{II}\{N(R^1)=C(R^2)CO_2\}L_2]^+$ [$R^1=R^2=Me$ or $R^1=R^2=-(CH_2)_3-$] were obtained by anodic oxidation at a constant potential of the corresponding (α-amino acidato)ruthenium(II) complexes, *N*-methylalaninato or prolinato complexes, in good to excellent yields [148]. Synthetic amino acids suitable for the assembly of small, redox-active metallopeptides have been described. Ligands (**152**)–(**154**) have been synthesized by alkylation of the $N^{\alpha}$-protected amino acids. Ruthenium complexes containing these ligands have been prepared by reactions of the ligands with $[Ru(bpy)_2Cl_2]$. The ligand electrochemical properties and the luminescence properties of the complexes have been discussed [149].



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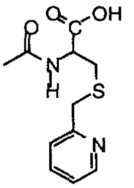

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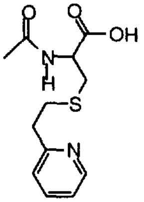
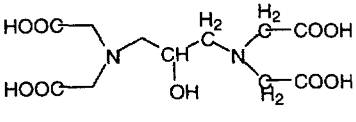


**(154)**

The kinetics of reduction of $[Ru^{III}(edta)(pz)]^-$ with L-ascorbic acid ($H_2A$) and catechol ($H_2cat$) were studied spectrophotometrically as a function of $[H_2A]$ or $[H_2cat]$, pH, ionic strength and temperature (25–45 °C). The reduction was found to be first order in both the complex and reductant concentrations. The pH dependence of the process (for $H_2A$) was ascribed to the deprotonation of $H_2A$. Kinetic data and activation parameters are interpreted in terms of a mechanism involving outer-sphere electron transfer [150]. The compound $[RuCl_2(dmso)_4]$ was treated with dhptaH$_5$ (**155**) and carboxylate ligands in the presence of NaOH or KOH and gave dinuclear Ru(III) complexes of dhpta with two bridging carboxylates, $M[Ru(dphta)(\mu\text{-}O_2CR)_2]$ (M = Na, K; R = alkyl), which were fully characterized [151].

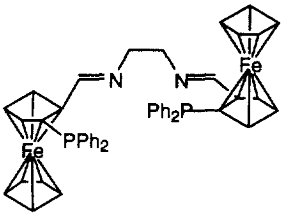


**(155)**

Mixed-metal polymers $[Os(bpy)_2(PVPS)_nClRu(edta)]$ ($n$ = 10, 15, 20) were prepared by reaction of $[Os(bpy)_2(PVPS)_nCl]Cl$-coated electrodes with $K[Ru(edta)(H_2O)]$ ($n$ = 10, 15, 20) in solutions of various electrolytes [PVPS = poly(vinylpyridine–styrene), 10% styrene]. Incorporation of the $[Ru(edta)]^-$ unit and binding to pyridine of PVPS take place with displacement of water from the coordination sphere of the Ru centre [152].

Low-spin Ru(III) complexes $[RuX(EPh_3)(LL')]$ (X = Cl, Br; E = P, As; LL' = Salen, Salpn and Saldien) were synthesized by reacting $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(AsPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ with tetradentate Schiff bases such as bis(salicylaldehyde)ethylenediimine($H_2$-Salen), bis(salicyladehyde)propylenediimine($H_2$-Salpn) and bis(salicylaldehyde)diethylenetriimine($H_2$-Saldien). All complexes were characterized by elemental analyses, IR and electronic spectra, EPR, magnetic moment and cyclic voltammetric data [153].

α-(Diphenylphosphino)ferrocenyl carboxaldehyde, 1,2-Fc($PPh_2$)CHO (Fc = ferrocenyl), prepared by asymmetric synthesis, was reacted with ethane diamine to give a bisimine bisphosphine complex (**156**). Ru(II) complex (**157**) was easily formed from (**156**) and $RuCl_2(dmso)_4$ and both their electrochemical properties have been studied [154].



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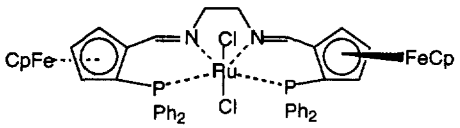


**(157)**

Detailed syntheses and characterization of ruthenium(II) diimino-, diamino- and diamidodiphosphine complexes have been reported. The catalytic hydrogenation activity of Ru(II) diimino- and diaminodiphosphine complexes was also presented [155].

### 6.7. Complexes with ammonia or amine ligands

The complexes $[Ru(NH_3)_5L](PF_6)_n$ ($n = 2$, 3), L = $NCCHCH_2$, $NCCH_2COOH$, have been isolated and characterized by elemental analysis, electronic and vibrational spectroscopies, and cyclic voltammetry. In aqueous medium, the $Ru^{II}$ species undergoes hydrolysis yielding the corresponding tetramine aquo complex; whereas the hydrolysis of the $Ru^{III}$ species occurs at the coordinated nitrile ligand with the formation of the corresponding amide ligand. The relative contributions of the σ- and π-components of the $Ru^{II}$-NCR bond were discussed in terms of spectroscopic and electrochemical data [156].

The absorption, luminescence, and transient-absorption spectra of $[(bpy)(terpy)Ru^{II}(CN)]^+$ and $[(bpy)(terpy)Ru^{II}CNRu^{II,III}(NH_3)_5]^{3+/4+}$ have been measured. Quantum mechanics descriptions of the nuclear reorganization accompanying electron transfer are required to explain the observed kinetics [157].

The activity of a water oxidation catalyst based on a trinuclear Ru complex, ruthenium Red (Ru-Red) $[(NH_3)_5Ru\text{–}O\text{–}Ru(NH_3)_4\text{–}O\text{–}Ru(NH_3)_5]^{6+}$, has been investigated both in homogeneous aqueous solution (AS) and in a heterogeneous Nafion membrane (HM) using $Ce^{IV}$ oxidant. The effect of intermolecular distance distribution of the catalyst in the membrane on the catalytic activity has been analysed based on statistical calculations of the distribution [158].

The novel trimethylphosphine azido Ru(II) complex *trans*-$Ru(N_3)_2(PMe_3)_4$ has been obtained and characterized by elemental analysis, IR and NMR spectroscopies and electrochemistry. Its structure has been determined by single crystal X-ray diffraction methods. Conversion into the *cis* isomer in $CH_2Cl_2$ has been followed by $^{31}P$ NMR spectroscopy and cyclic voltammetry [159].

Excellent catalytic activity was observed for the electroreduction of $H_2O_2$ by a nontronite (SWa-1, ferruginous smectite) clay coating on a glassy carbon electrode (GCE) with incorporated Me viologen ($MV^{2+}$) as mediator. The effect of pH on the electrochemistry of $MV^{2+}$ and $Ru(NH_3)_6^{3+}$ exchange cations in montmorillonite- and nontronite-modified GCEs provides an insight into the electrochemical accessibility of redox active species in the electrodes [160].

Second-sphere coordination was studied spectrophotometrically and electrochemically with various Ru–ammine complexes with crown ethers in MeCN solution. Spectrophotometric results revealed that the acidity of the ammine ligands of the complex, which depends on the valence of the metal centre, predominately affects the second-sphere coordination of the crown ether to the Ru–ammine complexes [161].

The mixed-valence dinuclear complexes $[(NC)_5Fe(pyCN)Ru(NH_3)_5]^n$ (4- and 3-cyanopyridine isomers with nitrile-*N* and pyridine-*N* binding to Ru and Fe, respectively) were prepared through stoichiometric oxidation of the fully reduced (II, II) dinuclear complexes, R, with peroxydisulphate. By analysis of IR spectra, the solids were observed to be a mixture of the predominant electronic isomers with an $Fe^{II}$, $Ru^{III}$ distribution, with minor amounts of the $Fe^{III}$, $Ru^{II}$ isomers [162].

The Ru(III) complexes $[(NH_3)_5Ru(LH)]^{2+}$ [LH = 1,4-dicyanamido-2,5-dimethylbenzene ($Me_2dicydH_2$), 1,4-dicyanamidobenzene and 1,4-dicyanamido-2,5-dichlorobenzene] and the deprotonated complex $[(NH_3)_5RuL]^+$ were prepared and characterized by electronic absorption spectroscopy and cyclic voltammetry. The Ru(IV) complex, $[(NH_3)_5Ru(Me_2dicyd)]^{2+}$, was also synthesized and permitted comparison with LMCT transitions of the Ru(III)-cyanamide and Ru(IV)-cyanamide chromophores [163].

The bis(pentaammineruthenium(II)) complex of dicyanonorbornadiene has been prepared and characterized. Its photochemical conversion into a dicyanoquadricyclane complex by irradiation in MeOH has been followed by UV–vis spectroscopy, IR and $^1H$ NMR spectroscopy, and cyclic voltammetry [164].

### 6.8. *Complexes with nitrosyl ligands*

The structure of the laser-light-induced metastable state of the $[Ru(NO_2)_4(OH)(NO)]^{2-}$ anion in $K_2[Ru(NO_2)_4(OH)(NO)]$ was determined by X-ray analysis at 50 K of a crystal with a 16% excited state population. Results of an independent determination of the ground state structure were used in the analysis. The most pronounced geometrical change upon excitation was an increase of the Ru–(NO) distance by 0.097(11) Å, significantly longer than the change of the corresponding distance in sodium nitroprusside [165].

An oxygen transfer between the NO and the ONO ligands occurs in *cis*-$[Ru(NO)(ONO)(bpy)_2]^{2+}$ (**158**) when the complex undergoes a redox-induced nitrito-to-nitro linkage isomerization. Such an oxygen transfer does not occur in the thermally-induced linkage isomerization reported previously. Complex (**158**) was characterized by cyclic voltammetry and controlled potential electrolysis and exhibits two one-electron reductions [166].

The first series of isolable (nitro)ruthenium(III) complexes was prepared by the chemical oxidation of *trans*-$[Ru(NO_2)(PR_3)_2(terpy)]^+$ (R = Me, Et, Pr) and *trans*-$[Ru(NO_2)(PMe_3)(PR_3)(terpy)]^+$ (R = Et, Pr). These complexes were characterized by elemental analysis, cyclic voltammetry, UV–vis spectroscopy and magnetic susceptibility. The mechanism of the decomposition reactions of these complexes in MeCN was studied using the electrochemical data and a $^{15}NO_2$ IR spectroscopic labelling study [167].

The complex *trans*-$[Ru(NO)(dmgH)_2Cl]$ (dmgH = dimethylglyoximate ion) reacts with $Me_2CO$ in the presence of $NH_3$ or substituted amines such as $MeNH_2$ and 4-$NH_2CH_2$py, to yield intermediate addition complex of the general formula *trans*-$[Ru(dmgH)_2Cl\{N(OH)CHC(NHR)Me\}]^-$. The kinetic, analytical and spectroscopic results are consistent with nucleophilic attack by enamines, e.g. $CH_2{=}C(NHR)Me$, on the coordinated $NO^+$ ligand [168].

Axial ligand substitutions in *trans*-$[RuCl(pdma)_2(NO)]^{2+}$ [pdma = 1,2-phenylene bis(dimethylarsine)] (**159**) were studied. Reaction of (**159**) with 1 equiv. $NaN_3$ in acetone at room temperature followed by reflux with an excess of L (L = MeCN, py, 1-methylimidazole, benzonitrile, 4-ethylpyridine, dmso, pz or $PPh_3$) yielded *trans*-$[RuCl(pdma)_2L]PF_6$ [169].

## 7. Complexes with oxygen donor ligands

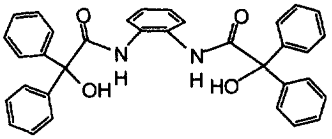
The synthesis, structure and electrochemical properties of three diruthenium(III) complexes $[\{Ru(bipy)L\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2][ClO_4]_2$ (L = imidazole, 1- or 4-methyl imidazole) have been described. The complexes show an intense charge-transfer band near 600 nm. They are redox-active and display reversible one-electron oxidation and reduction processes [170].

Treatment of the *cis*-dioxoruthenium(VI) complex, *cis*-$[Ru^{VI}(L)O_2](PF_6)_2$ (L = *N*,*N*,*N′*,*N′*,3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) with *tert*-butyl(trimethylsilyl) amine in benzene at room temperature gave *cis*-$[Ru^{III}(L)(OSiMe_3)_2][PF_6]$, which was characterized by X-ray diffraction crystal analysis [171].

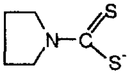
The synthesis, electrochemical and spectroscopic properties of $[\{(bipy)_2Ru\}_2(\mu\text{-}L)](PF_6)_2$, where $L^{2-}$ is the dianion of 2,5-dihydroxy-1,4-benzoquinone, were reported. Electrochemical studies and ESR spectroscopy of the complex were also described [172].

Direct reaction of $RuO_4^-$ with $H_4PHAB$ (**160**) gives the paramagnetic mono-oxoruthenium complex $Pr_4N[Ru(O)PHAB]$. Subsequent oxidation by $Ce^{IV}$ yields the diamagnetic mono-oxo complex [Ru(O)PHAB]. Both their crystal structures were determined [173].

Reaction of phenolic ligands with different functional groups at the 2-position with $[Ru(PPh_3)_3Cl_2]$ affords stable complexes of Ru(II) and Ru(III). The Ru(II)



**(160)**



**(161)**

complexes are diamagnetic and show intense absorption in the visible region due to MLCT transitions [174].

The first example of amplification of metal-to-metal communication in $Ru^{IV}$–$Ru^{III}$ mixed-valence state of the two new dinuclear β-diketonato $Ru^{III}$ complexes was reported, by inserting thiophene and anthracene into acetylene linkers. Both complexes exhibited two well-defined one-electron oxidation steps and two overlapping one-electron reduction steps in triangular wave voltammograms in a $CH_2Cl_2$ medium at 25 °C [175].

The influence of the O-donor ligands oxalate dianion ($C_2O_4^{2-}$) and acetylacetonate anion ($acac^-$) and of the phosphine chelate dppene ($Ph_2PCH{=}CHPPh_2$) on the Ru aqua/oxo chemistry and on the properties of the nitrosyl ligand is studied. The complexes [Ru(terpy)(acac)Cl], $[Ru(terpy)(acac)(H_2O)](PF_6)$, $[Ru(terpy)(C_2O_4)(H_2O)]$, $[Ru(terpy)(dppene)Cl](PF_6)$, $[Ru(terpy)(dppene)(H_2O)](PF_6)_2$, $[Ru(terpy)(C_2O_4)(py)]$, $[Ru(terpy)(acac)(py)](ClO_4)$, $[Ru(terpy)(acac)(NO_2)]$, $[Ru(terpy)(acac)(NO)](PF_6)_2$ and [Ru(terpy)(pscs)Cl] [pscs = 1-pyrrolidinedithiocarbamate anion (**161**)] have been prepared and characterized by cyclic voltammetry and UV–vis and FTIR spectroscopy [176].

The synthesis and characterization of some pentacoordinated Ru(II) complexes, viz. $[RuX_2(MPh_3)L_2]$ (X = Cl, Br; M = P, As; L = $o$-$HOC_6H_4CHO$ or $p$-$CH_3OC_6H_4CHO$), have been described. The compounds were characterized by physicochemical and spectroscopic methods. The catalytic oxidation of $PPh_3$ in the presence of molecular oxygen by $[RuBr_2(PPh_3)L_2]$ has also been studied [177].

The chain complex of Ru(II,III) cation dimer linked by a nitroxide radical, $[Ru_2(O_2CCMe_3)_4(nitph)]_n(BF_4)_n$ (nitph = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide), was prepared from the reaction of nitph with $[Ru_2(O_2CCMe_3)_4](BF_4)$ in benzene and characterized [178].

New $[(binap)Ru(carboxylate)_2]$ complexes such as $[((R)\text{-binap})Ru(O_2CPh)_2]$ (**162**) were prepared and used for the enantioselective hydrogenation of 2′-chloroacetophenone. Compound (**162**) catalyzed hydrogenation of 2′-chloroacetophenone in MeOH to give 97% (+)-2′-chlorophenylethanol in 87% enantiomeric excess, whereas similar hydrogenation in hexane gave (−)-2′-chlorophenylethanol in 68% enantiomeric excess [179].

The syntheses of $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ (L = py, 2-Mepy, 3-Mepy), *trans*-$[Ru(O_2CCF_3)_2L_4]$ (L = 2-Mepy or 3-Mepy), $[Ru(diimine)_3](CF_3CO_2)_2$ (diimine = bpy, phen), $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ and $[Ru(O_2CCF_3)_2(CO)(MPh_3)_3]$ (M = P, As) were described. These complexes were characterized by physical and electrochemical studies [180].

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