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3. RUTHENIUM

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CONTENTS

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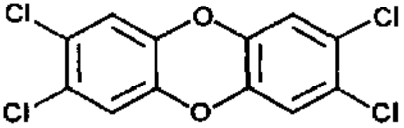
INTRODUCTION

The period of this review essentially coincides with the coverage of Vols. 94 and 95 of Chemical Abstracts. Thus, although the majority of the papers covered were published in 1981, many from 1980 are included. The review is a direct continuation of the two earlier reviews in this series [1,2], and no paper dealing with the coordination chemistry of ruthenium has been deliberately omitted (although work of an essentially organometallic nature is not included). The sections normally included on clusters, photophysics, surface modification and photocatalytic decomposition of water have been omitted this year, to allow a more comprehensive overview to be presented next year.

3.1 RUTHENIUM(VIII)

A new method for the preparation of anhydrous [RuO_4] has been described, involving the reaction of ruthenium metal with ozone at room temperature [3], and the [RuO_4]/[OsO_4] system has been shown to form continuous solid solutions, with a nearly linear liquidus curve [4].



(1; TCDD)

The tragedy at Seveso, in which 2,4,5-trichlorophenol containing 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (1; **TCDD**) was released, highlighted the environmental hazard presented by polychlorodibenzo-*p*-dioxins, due not only to their high toxicity but also to the remarkable stability of the dibenzodioxin nucleus to chemical attack. It has now been reported [5] that the polychlorodibenzo-*p*-dioxins, in particnlar TCDD, will undergo oxidative degradation with [RuO_4]; the kinetics of that process have been studied, although the oxidation products were not identified. It was suggested [5] that [RuO_4] might be used both for the detoxification of glassware and for the periodic purging of industrial reactors to counteract the accumulation of polychlorodibenzo-*p*-dioxin residues.

Two new applications of [RuO_4] in polymer chemistry have been reported. Isobutene-piperylene copolymer and 2,3-dimethylbutadiene-isobutene copolymer are both oxidatively cleaved by [RuO_4] in ethanoic acid to give bifunctional oligomers [6]. A 1% aqueous solution of [RuO_4] has been used as a staining agent in the transmission electron microscopy of *cis*-1,4-polybutadiene latex, ABS polymer containing 18% rubber, and ASA resin: the first two polymers revealed similar effects as staining with [OsO_4], but the ASA resin (which could not be stained with [OsO_4]) was hardened and stained by [RuO_4] [7].

3.2 RUTHENIUM(VI)

A new simpler procedure for the preparation of [RuF_6] from its elements has been described, and its reactions with EF_3 (E = P, As, Sb, Bi or Cl), CS_2, dihydrogen and ruthenium metal have been studied [8]. With PF_3, in anhydrous hydrogen fluoride, the polymeric adduct $\{RuF_4(PF_3)\}_n$ was formed, but with AsF_3 an adduct of stoicheiometry $RuF_4.AsF_5$ was isolated (see also Section 3.4.1). With EF_3 (E = Sb or Bi), only the free fluorides EF_5 and RuF_5 were identified, whereas the reaction of [RuF_6] with ClF_3 produces a mixture of [ClF_2][RuF_6] and [ClF_4][RuF_6]. Treatment of [RuF_6] with carbon disulphide produced a mixture of tetrafluoromethane and sulphur(IV) fluoride, whereas reduction of [RuF_6] with dihydrogen in anhydrous HF gave ruthenium(V) fluoride, which was then further reduced to ruthenium(IV) fluoride upon standing. The reaction between [RuF_6] and ruthenium metal in anhydrous HF also produces RuF_5; in the presence of KF, K[RuF_6] is formed [8]. The order of oxidising strength for the hexafluorides of the second row transition metals appears to be [8]:

$$Rh > Ru > Tc > Mo$$

The structure of [$AsPh_4$][$RuNBr_4$], prepared by boiling [$AsPh_4$][$RuNCl_4$] in an ethanenitrile/bromoethane mixture for eight days, has been determined by X-ray crystallography: the anion has the expected C_{4v} symmetry, with r(RuN) = 0.158 nm, $\bar{r}$(RuBr) = 0.2453 nm and N-Ru-Br = 104.25° [9]. The polarised single-crystal electronic absorption spectra of [$AsPh_4$][$RuNX_4$] (X = Cl or Br) in the range 40000-10000 cm^{-1} have been measured both at room temperature and at 5 K, and interpreted using experimental polarisation data and a parameterised ligand-field model [9].

3.3 RUTHENIUM(V)

3.3.1 Fluorides

Convenient new preparative routes to RuF_5 and K[RuF_6] by the reduction of ruthenium(VI) fluoride in anhydrous hydrogen fluoride, in the absence or presence of KF respectively, have been developed [8]. The reduction of [RuF_6] by ClF_3 gives a mixture of [ClF_4][RuF_6] and [ClF_2][RuF_6], but the novel [ClF_2][RuF_6] can be prepared pure by treating ruthenium metal with ClF_3 [8].

3.3.2 Oxides

A number of papers describing quaternary ruthenium(V) oxides and mixed-valence ruthenium(V/IV) oxides have appeared this year. Neutron diffraction experiments have resulted in the determination of the structures of Ba_2LaRuO_6 (Fig. 1) and Ca_2LaRuO_6 (Fig. 2). Both are ordered, distorted perovskites: Ba_2LaRuO_6 (monoclinic) has the A sites occupied by barium, whilst the B sites show an ordered arrangement of lanthanum and ruthenium; Ca_2LaRuO_6 (triclinic) has the A sites occupied by a disordered arrangement of calcium and lanthanum and the B sites occupied by an ordered arrangement of calcium and ruthenium [10]. These results contradict those of previous workers [11], and force a reinterpretation of the earlier Mossbauer data. The magnetic interactions in M_2EuRuO_6 (M = Ca, Sr or Ba) have been studied by ^{151}Eu Mossbauer spectroscopy; the Curie temperatures are approximately 18, 31 and 42 K, respectively [12].

^{99}Ru Mossbauer spectroscopy has been used at 4.2 K to study the compounds $Ba_3Ru_2MO_9$ (M = Mg, Ca, Sr, Co, Ni, Cu, Zn and Cd), all of which exhibit the hexagonal barium titanate(IV) structure. The calcium, strontium and cadmium compounds show no magnetic hyperfine splitting (consistent with the accepted model of binuclear intracluster spin pairing, with an $S = 0$ ground state), but the magnesium, zinc, cobalt(II), nickel(II) and copper(II) compounds do show magnetic hyperfine splitting, which can only be explained in terms of long-range magnetic order and the absence of an $S = 0$ ground state [13].

The black perovskites Ba_2InRuO_6 {containing Ru(V)} and $Ba_3InRu_2O_9$ {containing Ru(V/IV)} adopt the hexagonal $BaTiO_3$ structure, and form a continuous series of mixed crystals, whereas black Ba_2RhRuO_6 and $Ba_3RhRu_2O_9$ adopt a rhombohedral 9L structure {cf. $BaRuO_3$} [14]. The black compounds $Ba_3SmRu_2O_9$ and $Ba_3MIrRuO_9$ (M = La, Nd, Sm, Gd, Dy, Er, Yb, and Sc) also are perovskites, crystallising with the hexagonal $BaTiO_3$ structure [15,16]. The compounds $A_2(Ru_{2-x}A_x)O_{7-x}$ (A = Bi or Pb) are discussed in Section 3.4.3.

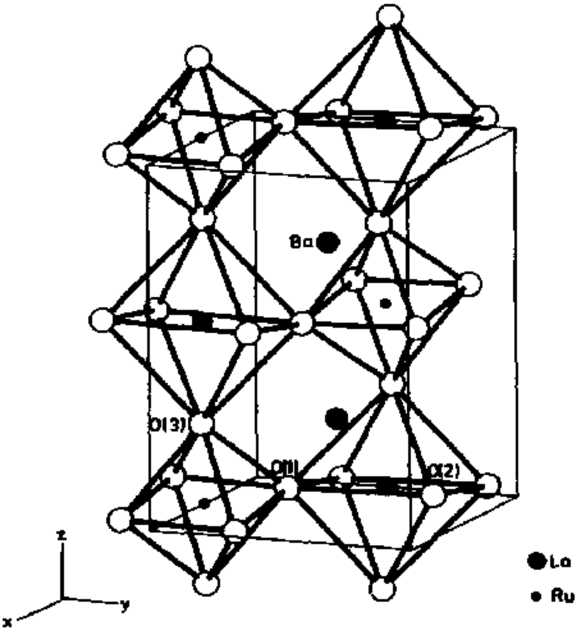


Fig. 1: The crystal structure of Ba_2LaRuO_6 [10].

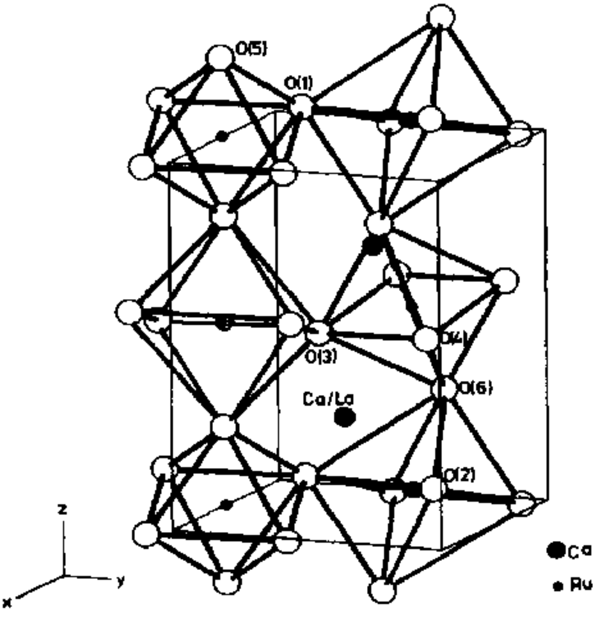


Fig. 2: The crystal structure of Ca_2LaRuO_6 [10].

3.4 RUTHENIUM(IV)

3.4.1 Halide and oxohalide complexes

A new convenient method for the preparation of ruthenium(IV) fluoride, by the reduction of ruthenium(VI) fluoride in anhydrous hydrogen fluoride with dihydrogen for several hours, was reported [8].

The novel complex $\{RuF_4(PF_3)\}_n$ was formed in the reduction of ruthenium(VI) fluoride by PF_3, whereas a similar reaction with AsF_3 (in the absence of HF) gave a complex of stoicheiometry $RuF_4.AsF_5$, believed to be best formulated as $[\{RuF_3\}_n]^{n+}([AsF_6]^-)_n$ [8].

The hydrolytic stability of the hexafluororuthenate(IV) anion has been investigated. $K_2[RuF_6]$ in acidic and alkaline solution, as in neutral solution, undergoes hydrolysis extremely slowly (if at all). The catalysed acid hydrolysis of $K_2[RuF_6]$ requires the presence of oxozirconium(IV) or oxohafnium(IV) salts, salts of aluminium(III), lanthanide(III) or thorium(IV) being ineffective [17]. A new estimate of the ion hydration energy for $[RuF_6]^{2-}$ of -990 kJ mol^{-1} has been calculated [17].

Salts of $[RuF_6]^{2-}$ and $[RuCl_6]^{2-}$ have been examined by XPES, and their electronic structure discussed; the 4d ionisation energy for $[RuF_6]^{2-}$ is reported at 9.3 eV, whereas that for $[RuCl_6]^{2-}$ is at 9.1 eV [18]. The resonance Raman spectra of salts of $[Ru_2OCl_{10}]^{4-}$ [19] and $[Ru_2NCl_8(OH_2)_2]^{3-}$ [20] have been reported. The former ion had previously been studied in some detail [1; p.43], but this new report supplements the experimental data with force constant calculations, and compares the results with other $[M_2OX_{10}]^{n-}$ (M = W, Os or Re, X = Cl, $n = 4$; M = W, X = Br, $n = 4$; M = Re, X = Cl, $n = 3$) ions: it confirms the assignment of the intense visible resonant electronic transition as being the $e_g \rightarrow e_u^*$ transition [19]. The only clearly defined bands in the resonance Raman spectrum (334.5 nm excitation) of $K_3[Ru_2NCl_8(OH_2)_2]$ are $\nu_1(a_{1g})$ $\{\nu_{sym}(RuNRu)$; 329 $cm^{-1}\}$, $\nu_2(a_{1g})$ $\{\nu_{sym}(RuO)$;

413 cm$^{-1}\}$, and $\nu_3(a_{1g})$ $\{\nu_{sym}$(RuCl); 301 cm$^{-1}\}$, and consideration of the excitation profiles of these bands led to the assignment of the band at 31200 cm^{-1} in the electronic absorption spectrum of the complex to $e_g \rightarrow e_u^*$ $({}^1A_{1g} \rightarrow {}^1A_{2u})$ [20]. SCCC-MO calculations have been applied to $[Ru_2OCl_{10}]^{4-}$ and $[Ru_2NCl_8(OH_2)_2]^{3-}$, and predict the presence of a band in the former ion at about 8000 cm^{-1}, due to $(b_{2g}, b_{1u}, e_g) \rightarrow e_u^*$ [21], significantly lower in energy than that found in the resonance Raman study [19].

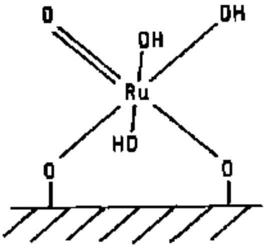
3.4.2 Ruthenium(IV) oxide

Interest in RuO_2 has dramatically increased over the past few years, both due to its use in forming dimensionally stable anodes (titanium metal coated with RuO_2/TiO_2) for the chlor-alkali industry and its more recently discovered property of being an extremely active redox catalyst (especially in systems designed for the photocatalytic decomposition of water).

The unit cell parameters and crystal structures of single crystals of RuO_2 at pressures up to 30 kbar have been measured at 20 °C, enabling its bulk moduli and linear compressibilities to be determined. The *a* axis is approximately twice as compressible as the *c* axis; *r*(RuO) changes from the values of 0.1984 and 0.1941 nm at 0.001 kbar to 0.1979 and 0.1943 nm at 11.1 kbar, *r*(RuRu) changes from 0.31065 nm to 0.31044 nm over the same pressure range [22]. The point of zero charge has been measured for RuO_2, prepared by the thermal decomposition of $RuCl_3.xH_2O$ in air: it occurs at pH 5.1 for samples prepared at 400 °C, but at pH 6.1 for samples prepared at 700 °C [23].

The large number of papers which have been published this year concerning redox catalysis at RuO_2 (not just oxidation of water, but also chloride and bromide ions) will be discussed next year. Relevant to the observed redox activity is an interesting report discussing the importance of reactive surface groups with regard to the electrocatalytic activity of RuO_2

anodes [24]. RuO_2/Ti electrodes were examined electrochemically (in acidic and basic conditions) in the presence and absence of both benzaldehyde and benzyl alcohol (N.B. ruthenate(VI) will oxidise benzaldehyde but not benzyl alcohol, ruthenate(VII) will oxidise both): evidence for the formation of surface oxoruthenium species in oxidation states (VI) and (VII), which may be represented schematically by **(2)** and **(3)** respectively, was presented [24]. Active ruthenium(IV) sites may be represented by **(4)**.



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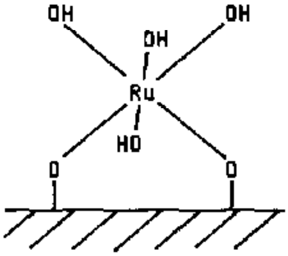

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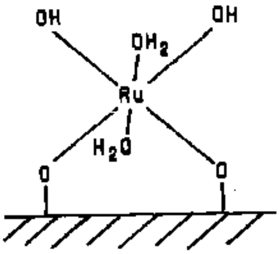

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The presence of the surface hydroxyl groups in RuO_2 is also demonstrated by the ease with which RuO_2 electrodes can be silanised with monolayers of trialkoxyalkylaminesilanes [25]. In further support of the intermediacy of higher oxidation states of ruthenium in reactions in which RuO_2 is believed to behave as a redox catalyst, $[RuO_4]$ has been detected in the gas phase when solutions of $RuO_2.xH_2O$ in dilute sulphuric acid were added to an aqueous solution of cerium(IV) [26]. No $[RuO_4]$ was detected when RuO_2 was bound to TiO_2, however [26].

In a very different type of catalytic reaction, $RuO_2.xH_2O$ (in the presence of RI (R = H, Me or Et) as promoter) acts as a catalyst precursor in the homologation of aliphatic carboxylic acids using synthesis gas (CO/H_2): the catalytically active species generated under the reaction conditions (220 °C, 270 atm) is based upon $[Ru(CO)_3I_3]^-$, which was detected spectroscopically [27,28].

Significant effort has been invested in studying both coprecipitated and supported RuO_2 with other metal oxides, and also solid solutions of RuO_2. Thus, the solid solutions formed by the RuO_2/IrO_2 system appear to be present over the entire composition range $(Ru_{1-x},Ir_x)O_2$ [29], and a series of coprecipitated RuO_2/Al_2O_3 samples have been characterised by X-ray diffraction, XPES, and Auger spectroscopy: the existence of a substitutional solid solution of Al^{3+} ions in RuO_2 was indicated [30]. A RuO_2/Al_2O_3 support has also been used for immobilising amino acid oxidase enzymes [31]. Reports continue to appear concerning the use of RuO_2/TiO_2 electrodes for the production of chlorine [32], but their use both for the electrolytic reduction of carbon dioxide [33] and as photoanodes [34] has also been described. The reason for the loss of activity of RuO_2/TiO_2 anodes in acidic media during the evolution of dioxygen has now been ascribed to the formation of a non-conducting (probably TiO_2) film [35,36].

3.4.3 Metal ruthenates(IV)

$BaRuO_3$ has been reinvestigated by X-ray diffraction techniques [37a], the semiconductor-metal transition in the $LaRhO_3/SrRuO_3$ system has been studied [37b], and some hydroxyruthenates(IV) have been reported [38]. The centre of attention this year, however, has been ruthenium pyrochlores. The vibrational spectra of $A_2Ru_2O_7$ (A = Pr, Gd, Lu or Y) have been analysed [39], and patents have been lodged for the use of $Bi_2Ru_2O_7$ as a thick-film resistor material [40] and for the use of $A_2(Ru_{2-x}A_x)O_{7-y}$ (A = Pb or Bi; x = 0-1; y = 0-1) as oxygen electrodes [41]. These last pyrochlore phases have also been described in the open literature [42], and the conduction mechanisms in $Pb_2Ru_2O_7$ (?) have been investigated [43]. The Bi_2O_3/RuO_2 system is reported to give rise not only to the well known $Bi_2Ru_2O_7$ and $Bi_3Ru_3O_{11}$, but also to a new phase $Bi_{12}RuO_{20}$ [44,45].

3.4.4 Ruthenium(IV) sulphide

It should be noted that, although the oxidation state formalism classifies RuS_2 as ruthenium(IV), it is in fact a ruthenium(II) compound with the pyrites structure, $Ru^{2+}[S_2]^{2-}$.

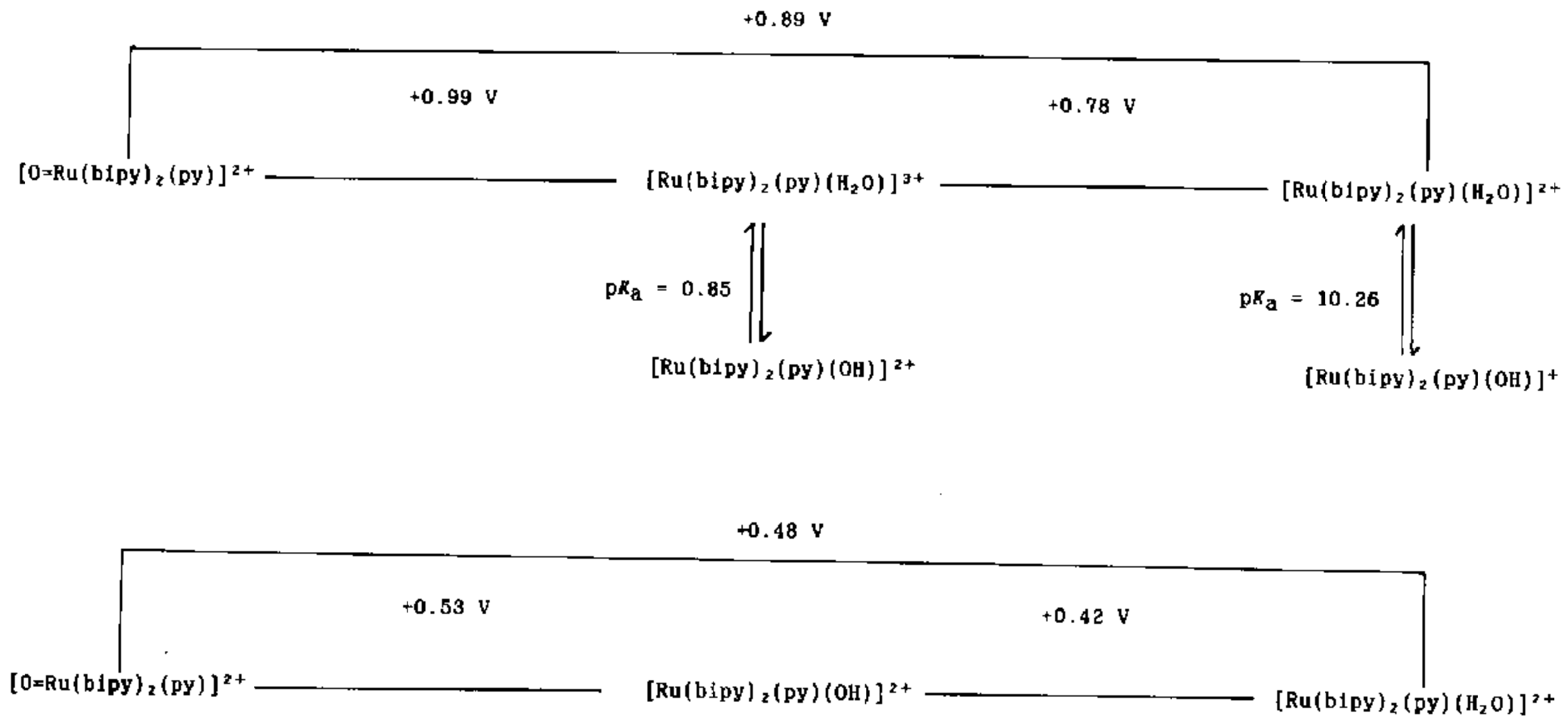
Heating ammonium hexachlororuthenate(IV) in a stream of hydrogen sulphide at 180 °C for four hours gives a new form of RuS_2, which is described as "poorly crystallised" (meaning that the X-ray diffraction pattern might be classified as almost amorphous, but that there is some evidence for short-range order): annealing this material at 800 °C for four days produces the normal crystalline pyrite form [46]. Both the poorly crystallised and the crystalline RuS_2 are diamagnetic [46]. The average crystallite size for the poorly crystallised form is 2.6 nm, compared with >200 nm for the crystalline phase [47].

3.4.5 Other complexes

Further details have emerged [48-50] concerning Meyer's exciting oxoruthenium(IV) complex, $[O{=}Ru(bipy)_2(py)]^{2+}$, which was introduced last year [2; p.84]. The Latimer diagrams for the system are shown in Scheme I, both in 1 *M* acid and at pH 7; the ruthenium(III) hydroxo complex $[Ru(bipy)_2(py)(OH)]^{2+}$ has been isolated and characterised as its perchlorate salt [48]. $[^{18}O{=}Ru(bipy)_2(py)]^{2+}$ has been prepared, and this showed the Ru=O stretching frequency shifted from 792 cm^{-1} in the unlabeled complex to 752 cm^{-1} in the ^{18}O derivative [48]. The comproportionation reaction between the ruthenium(IV) and the ruthenium(II) complex shows a very high solvent isotope effect (16.4) [49]:

$$[O{=}Ru(bipy)_2(py)]^{2+} + [Ru(bipy)_2(py)(OH_2)]^{2+} \longrightarrow 2[Ru(bipy)_2(py)(OH)]^{2+}$$

A kinetic study of the oxidation of triphenylphosphine to triphenylphosphine oxide by $[O{=}Ru(bipy)_2(py)]^{2+}$ in MeCN demonstrated that the reaction proceeds *via* an initial fast redox step, the product of which was



SCHEME I: Latimer diagrams for the [O=Ru(bipy)$_2$(py)]$^{2+}$ system in 1 *M* acid (upper) and at pH 7 (lower). Potentials are quoted *vs.* SCE [48].

observed spectroscopically [50]:

$$[O{=}Ru(bipy)_2(py)]^{2+} + PPh_3 \longrightarrow [Ru(bipy)_2(py)(OPPh_3)]^{2+} \ ; \quad k$$

$$k = 1.75 \times 10^5 \ M^{-1} \ s^{-1} \ (26.6 \ ^\circ C)$$

The second step is a much slower solvation process:

$$[Ru(bipy)_2(py)(OPPh_3)]^{2+} + MeCN \longrightarrow [Ru(bipy)_2(py)(MeCN)]^{2+} + OPPh_3; \quad k'$$

$$k' = 1.15 \times 10^{-4} \ s^{-1} \ (25 \ ^\circ C)$$

^{18}O labelling experiments showed that the transfer of the oxygen from the ruthenium to the phosphorus was essentially quantitative [50].

The novel imido complex $[HN{=}Ru(terpy)(bipy)]^{2+}$, analogous to the oxo complex $[O{=}Ru(bipy)_2(py)]^{2+}$, has been postulated as an intermediate in the electrochemical oxidation of coordinated ammonia in the complex $[Ru(terpy)(bipy)(NH_3)]^{2+}$ [52]; this reaction is discussed in Section 3.8.4.

The fascinating oxo-bridged ruthenium(IV) porphyrin complex, $[\{Ru(OEP)(OH)\}_2O]$, has been characterised by X-ray crystallography. The important bond distances in $[\{Ru(OEP)(OH)\}_2O]$ are $r(RuO)_b$ = 0.1847 nm, r(Ru–OH) = 0.2195 nm and r(RuN) = 0.2067 nm; the Ru–O–Ru skeleton is strictly linear, and the torsion angle between the OEP rings is 22.7° [53]. Its structure (Fig. 3) might be compared with that of $[Ru_2OCl_{10}]^{4-}$ (see Section 3.4.1 and [1; p.43]). For related chemistry, see Section 3.8.5 (Scheme VII).

The reactions of $[Ru(PPh_3)_3H_4]$ with some diazadienes have been studied [54], and are discussed in Section 3.8.6.6. An eccentric discussion of the formation of $[Ru(PPh_3)_4H_3]^+$ in the reaction between $[Ru(PPh_3)_4H_2]$ and 1,4-dichlorooctaphenyltetrasilane has been published [55]: this paper describes the cation as ruthenium(II), treats the species as being novel, and ignores an earlier report [56] of the same complex.

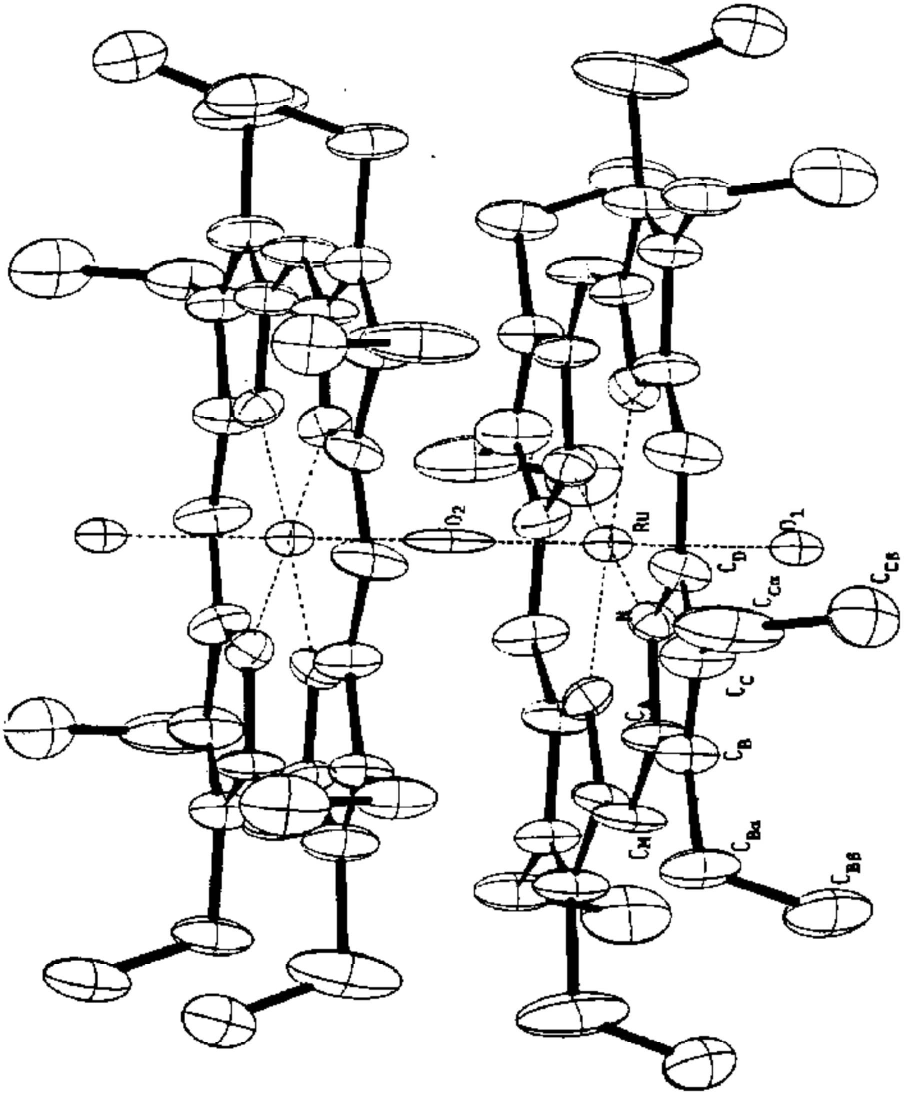


Fig. 3: The molecular structure of $[(Ru(OEP)(OH))_2O]$ [53].

Dynamic ^1H and ^{31}P NMR studies of the ruthenium(IV) carborane complex, 2,1,7-[Ru(PPh$_3$)$_2$H$_2$(C$_2$B$_9$H$_{11}$)], show that the metal vertex undergoes hindered, but rapid (even at -90 °C), rotation with respect to the carborane cage [57]. Organometallic complexes of ruthenium(IV) are still a rarity, and so the report [58] of a new complex type, $[Ru(cp)(PMe_3)_2(Cl)(X)]^+$ (X = H or Cl), formed by the oxidation of $[Ru(cp)(PMe_3)_2Cl]$ with HCl or Cl_2, respectively, is welcomed.

Finally, a new method for determining ruthenium(IV) by the indicator reaction of *N*-methyldiphenylamine-4-sulphonic acid with ammonium vanadate(V) has been reported [59].

3.5 RUTHENIUM(IV/III), MIXED-VALENCE COMPLEXES

All of the papers in this Section deal with aspects of the chemistry of ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{6+}$, or ruthenium brown, $[Ru_3O_2(NH_3)_{14}]^{7+}$. A new theory for the calculation of *A*-term resonance Raman excitation profiles has been applied [60] to the results of an earlier experimental study [2; p.86] of ruthenium red and ruthenium brown (and their 1,2-diaminoethane derivatives), and relative values for the a_{1g} displacement parameters were reported. A dependence of the excitation wavelength upon the metal in the SERS from ruthenium red adsorbed on silver and copper has been observed, suggesting that the excitation is primarily of the metal surface, and not of the complex [61].

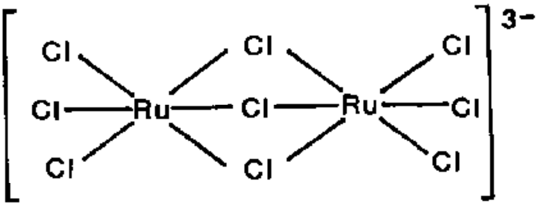
The reduction of ruthenium brown by the hydroxide ion has been reexamined [62], and (contrary to earlier reports) little evidence could be found to support the significant involvement (*i.e.* >5% of the total reaction) of ruthenium(VI). Furthermore, nitrosyl stretching frequencies were detected in the IR spectrum of the "ruthenium red" product, indicating that this complex reaction involves oxidation of at least one coordinated ammine ligand to NO, with the possible intermediacy of coordinated hydroxylamine [62]. The kinetics of the reduction of ruthenium brown by hydrogen peroxide in basic solution, and the oxidation of ruthenium red by hydrogen peroxide in acid solution, have also been investigated [63].

The electron-transfer activity towards cytochrome *c* which had previously been ascribed to ruthenium red [64] has now been shown to be due to impurities of a hexaammineruthenium(III) salt [65]. In contrast, $[Ru(NH_3)_6]^{3+}$, adsorbed in zeolites X and Y, reacts with zeolite-absorbed water to give ruthenium red, and in air gives a mixture of ruthenium red and ruthenium brown; these complexes are thermally unstable at temperatures >373 K [66].

3.6 RUTHENIUM(III)

3.6.1 Chlorides and chloride complexes

The complex $Cs_3[Ru_2Cl_9]$ has been prepared from the stoicheiometric reaction between CsCl and $RuCl_3$ at 700 °C, *in vacuo*: single crystals were sublimed from the product by heating at 850 °C for three days [67]. However, this salt, in contrast to the claim in the paper, had been reported previously [68]. The structure of the anion, **(5)**, is similar to those of $Cs_3[M_2Cl_9]$ (M = Cr, Fe or Mo), and shows $r(RuCl)_t$ = 0.2332 nm, $r(RuCl)_b$ = 0.2391 nm and $r(RuRu)$ = 0.2725 nm. The presence of a strong metal-metal bond is suggested not only by the geometry of the anion, but also by its magnetic properties. $Cs_3[Ru_2Cl_9]$ shows a temperature-independent paramagnetism between 50 and 300 K (corresponding to μ_{eff} = 0.51 μ_B at 300 K). Below 50 K, the paramagnetism starts to rise, possibly due to the presence of some monomeric ruthenium(III) impurity [67].



(5)

The dissolution of ruthenium(III) chloride in molten lithium nitrite - potassium nitrite eutectics at >250 °C is said to produce a yellow precipitate of $K_4[Ru(NO_2)_6]$, according to [69]:

$$RuCl_3 + 7K[NO_2] \longrightarrow K_4[Ru(NO_2)_6] + 3KCl + NO_2$$

At 350 °C, this ruthenium(II) complex decomposes to give ruthenium(IV) oxide [69]:

$$K_4[Ru(NO_2)_6] \longrightarrow RuO_2 + 4K[NO_2] + 2NO$$

Commercial ruthenium(III) chloride has been used to impregnate Al_2O_3 pellets [70] and to modify the surface of GaP [71].

Commercial $RuCl_3.xH_2O$ has been shown to be an efficient intramolecular hydrogen transfer catalyst from primary or secondary alcohol functions to adjacent C=C double bonds [72]:

$$R^1R^2C{=}CR^3CH(OH)R^4 \longrightarrow R^1R^2CHCHR^3C(O)R^4$$

This reaction proved a useful synthetic route to β-diketones [72]. Also, commercial $RuCl_3.xH_2O$ in glacial ethanoic acid, in the presence of quaternary phosphonium or ammonium salts, has been used as a catalyst for the synthesis of vicinal glycol esters from synthesis gas [73]:

$$2CO + 3H_2 + 2RCOOH \longrightarrow RCO_2CH_2CH_2O_2CR + 2H_2O$$

3.6.2 Oxides and hydroxides

Ruthenium(III) hydroxide is, and remains, a poorly defined and poorly characterised solid. The DTA of a material described as $Ru(OH)_3.H_2O$ has been reported this year: the material appears to undergo a disproportionation reaction in nitrogen between 100 and 150 °C, yielding ruthenium metal and hydrated ruthenium(IV) oxide [74,75]. The magnetic anisotropy of single crystals of $Ba(Fe_{12-x}Ru_x)O_{19}$ has also been investigated [76].

3.6.3 Complexes with oxygen donor ligands

Tris(pentane-2,4-dionato)ruthenium(III), $[Ru(acac)_3]$, has been partially resolved (molecular rotations at 490 nm of −9200 and +6700 for the Λ- and Δ-isomers, respectively) by liquid chromatography on a Δ-tris(phenanthroline)-nickel(II) montmorillonite column, a novel application for modified colloidal clays [77]. The reduction of $[Ru(acac)_3]$ by aqueous titanium(III) is an outer-sphere reaction; the reduction of $[Ru(acac)_2\{MeC(O)C(CHO)C(O)Me\}]$ proceeds by an inner-sphere mechanism [78]. $[Ru(acac)_3]$ is reported to be a catalyst for the homologation of methanol to ethanol [79], but similar reactions with propanol produced only propyl methanoate and propyl ethanoate [80]. The preparation of a fascinating new mixed-metal compound, $[\{[(C_5H_5)Fe(C_5H_4)]C(O)CHC(O)CR_3\}_3Ru]$ (R = H or F), by treatment of $RuCl_3.xH_2O$ with the parent diketones in the presence of aqueous ammonia or potassium hydrogencarbonate, has been described, along with a TGA/DTA study of their thermal decomposition [81].

The complexes $[Ru(3\text{-bromotropolonato})(EPh_3)_2X_2]$ (E = P or As; X = Cl or Br) have also been reported [82].

Mond's early work [83] with ruthenium methanoates has been repeated, and the principal product demonstrated spectroscopically to be $[Ru_3O(O_2CH)_6(OH_2)_3][O_2CH]$ [84]. Treatment of this trimeric complex with CO gives the mixed-valence compound $[Ru_3O(O_2CH)_6(OH_2)_2(CO)]$, but with pyridine gives either $[Ru(O_2CH)_2(py)_2]$ or $[Ru(O_2CH)_2(py)_4]$, according to the reaction conditions [84]. The reactions of the longer-established ethanoate analogue, $[Ru_3O(O_2CMe)_6(MeOH)_3][O_2CMe]$, and its mixed-valence reduction product, $[Ru_3O(O_2CMe)_6(MeOH)_3]$, with both dppm and dppe (LL) give the novel dimeric ruthenium(III) species $[Ru_2(O_2CMe)_4(LL)_2][ClO_4]_2$; the neutral species $[Ru_2(O_2CMe)_4(dppm)_2]$, $[Ru(O_2CMe)_2(dppm)_2]$, and $[Ru_6O_2(O_2CMe)_{12}(dppe)_3]$ were also reported [84]. The reduction of $[Ru_3O(O_2CMe)_6(H_2O)_3]^+$ by titanium(III) has also been briefly reported [78].

The hydrothermal preparations of edta and pdta complexes of ruthenium(III) have been reported [85], as have the more routine preparations of ruthenium(III) complexes of diethylenetriaminepentaacetic acid [86] and *N*-2-aminoethylimino-*N*,*N*-diacetic acid [87].

3.6.4 Complexes with sulphur donor ligands

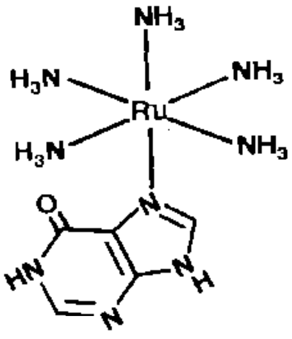
Complexes of ruthenium(III) with *N*-ethoxycarbonylpyrrole-2-thiocarboxamide have been reported [88], and the thermal decomposition of some ruthenium(III) dithiocarbamate derivatives has been studied [89]. Complexes with macrocyclic quadridentate thioethers are described in Section 3.8.2, and $[Ru_2(CO)_4Br_2(SMe)_4]$ is discussed in Section 3.6.8.

3.6.5 Ammine and amine complexes

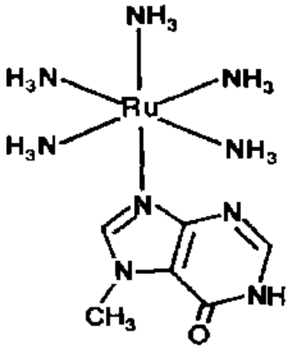
Much of the interest in $[Ru(NH_3)_6]^{3+}$ lies in its redox activity, and Marcus [90] has used the $[Ru(NH_3)_6]^{3+/2+}$ system to study quantum effects in outer-sphere electron-transfer reactions in polar solvents; it was concluded that the Frank-Condon factors can be well approximated by classical expressions for a non-adiabatic model. The problem of non-adiabaticity in the outer-sphere electron-transfer reactions of $[Ru(NH_3)_6]^{3+}$ has been studied, and the reactions shown to be essentially adiabatic [91]. DVM Hartree-Fock-Slater (HFS) calculations for $[Ru(NH_3)_6]^{3+}$ give very good agreement between observed and calculated electronic spectral bands [92]. From a more practical viewpoint, $[Ru(NH_3)_6]Cl_3$ is an excellent accelerator of the photographic development process, acting as an electron-transfer agent from the developer (*e.g.* hydroquinone or ascorbic acid) to the silver halide [93]. The decomposition of $[Ru(NH_3)_6]^{3+}$ salts in zeolites under dioxygen has been studied, and nitrosyl intermediates were detected; ruthenium(IV) oxide was the final product [94]. *In vacuo*, ruthenium red (see Section 3.5) was formed [66].

The outer-sphere interaction of $[Ru(NH_3)_5Cl]^{2+}$ with dianions (*e.g.* sulphate, sulphite and thiosulphate) and the thermodynamics of that interaction have been reported [95,96], as have the kinetics of the outer-sphere reduction of $[Ru(NH_3)_5(O_2CMe)]^{2+}$, $[Ru(NH_3)_5(C_2O_4)]^{+}$ and *cis*-$[Ru(NH_3)_4(C_2O_4)]^{2+}$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ [97]. The reductions of $[Ru(NH_3)_5(NCS)]^{2+}$ by $[Ti(H_2O)_6]^{3+}$ and [Ti(hedta)] (H_3hedta = *N*-(hydroxyethyl)ethylenediaminetriethanoic acid) and of $[Ru(NH_3)_5(sal)]^{+}$ by $[Ti(H_2O)_6]^{3+}$ proceed by an inner-sphere mechanism [78,98,99].

An excellent review of substitution reactions for ruthenium(III) ammine complexes, at a level suitable for undergraduates, has been published by Taube [100]. The complex $[Ru(NH_3)_5(py)]^{3+}$ has been used to study the oxidation of horse heart ferrocytochrome *c* [101], and $[Ru(NH_3)_5(py\text{-}4\text{-}NMe_2)]^{3+}$ has been investigated by electronic, infrared and resonance Raman spectroscopy [102]. $[Ru(NH_3)_5(py\text{-}4\text{-}NH_2)]^{3+}$ was shown to contain the pyridine ligand bound via the heterocyclic nitrogen atom, but the lone-pair of the amine nitrogen interacts with the pyridine ring to significantly modify its ligand properties [103]. The crystal and molecular structure of $[Ru(NH_3)_5(pz)][CF_3SO_3]_3.H_2O$ has been determined, and the cation shows $r(RuN)_{ammine}$ = 0.210-0.213 nm and $r(RuN)_{pz}$ = 0.2076 nm (*cf.* Section 3.8.3) [104]. The structures of $[Ru(NH_3)_5(hyp)]Cl_3.3H_2O$ and $[Ru(NH_3)_5(7\text{-}Mehyp)]Cl_3$ have also been determined by X-ray crystallography [105], and the bonding modes of the purine ligands (through the 7- and 9- *N* atoms, respectively) are indicated in (6) and (7). The equatorial $Ru\text{-}NH_3$ bond lengths are unexceptional at an average of 0.210 nm, the axial $Ru\text{-}NH_3$ bond lengths are 0.2081 and 0.2097 nm in (6) and (7) respectively, and the $Ru\text{-}N_{pur}$ bond lengths are 0.2087 and 0.2094 nm in (6) and (7) respectively.

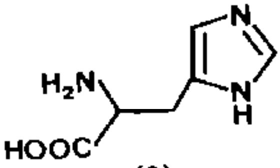


(6)



(7)

A kinetic study of the previously reported [106] linkage isomerism of *N*(3)-bonded $[Ru(NH_3)_5(7\text{-Mehyp})]^{3+}$ to *N*(9)-bonded $[Ru(NH_3)_5(7\text{-Mehyp})]^{3+}$ was also described [105].



(8)

The pentaammineruthenium(III) moiety has been shown to form stable complexes with three of the four histidine, (8), residues of ribonuclease A, and this interaction can be used as an optical probe for conformational change [107], and also to aid the assignment of histidine proton resonances in the ^{1}H NMR spectrum of the parent protein [108]. Interactions of $\{Ru(NH_3)_5\}^{3+}$ with other nucleosides have also been investigated [109]. Finally, a number of complexes of general formulae $[Ru(NH_3)_5L]^{3+}$ and $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{6+}$ have been prepared in work related to mixed-valence compounds, and these are discussed in Section 3.7.

The reduction of $[Ru(en)_3]^{3+}$ by titanium(III) in hydrochloric acid proceeds by an outer-sphere electron-transfer reaction from $[Ti(OH)(H_2O)_5]^{2+}$ rather than from $[Ti(H_2O)_6]^{3+}$ [110]. In contrast, the reduction of *trans*-$[Ru(en)_2Cl_2]^+$ or *trans*-$[Ru(L_4)Cl_2]^+$ (L_4 = 1,9-diamino-3,7-diazanonane or 1,4,8,11-tetraazacyclotetradecane) by $[Cr(H_2O)_6]^{2+}$ proceeds by an inner-sphere mechanism [111]. The preparations and spectral characterisation of a series of macrocyclic complexes, *trans*-$[Ru(cyclam)X_2]^+$ (X = Cl, Br, I, [NCS] or $[MeCO_2]$) and *trans*-$[Ru(L_4)X_2]^+$ (X = Cl or Br; L_4 = 1,4,8,12-tetraazacyclopentadecane, $[15]aneN_4$, or 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $Me_6[14]aneN_4$), have been reported [112a]; the aerial oxidative dehydrogenation of *trans*-$[Ru(Me_6[14]aneN_4)Cl_2]^+$ to its 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene analogue has also been described [112b]. A related series of macrocyclic complexes *trans*-$[Ru(L_4)Cl_2]^+$ (L_4 = 1,4,8,11-tetraazacyclotetradecane (cyclam), 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane, $[15]aneN_4$ or 1,5,9,13-tetraazacyclohexadecane ($[16]aneN_4$)) containing 14-, 15- and 16-membered rings have also been prepared, independently [113]. Changes in ring size have little effect upon the electronic absorption spectrum or the Ru–Cl stretching frequency (321–331 cm^{-1}) of these complexes, but a small cathodic shift in the reduction potential of *trans*-$[Ru(L_4)Cl_2]^{+/0}$ and a decrease in affinity of the reduced species for chloride is observed as the ring size is increased [113]. The molecular structure of *trans*-$[Ru(cyclam)Cl_2]Br$ revealed $r(RuCl)$ = 0.2343 nm and $r(RuN)$ = 0.2083 nm, and a significant non-bonded interaction within the cation between the chloride ligands and the *N*-bonded hydrogen atoms of the cyclam was detected [113]. The related *cis*-macrocyclic complexes *cis*-$[Ru(cyclam)X_2]^+$ (X = Cl, Br, I, [NCS] or $\frac{1}{2}[C_2O_4]$) and *cis*-$[Ru([15]aneN_4)Br_2]^+$ were prepared by treating $[Ru(C_2O_4)_3]^{3-}$ with the appropriate macrocycle in the presence of HX (X = Cl or Br), followed by a metathetical exchange, if necessary; similar reactions of the open chain L_4 ligands, 2,3,2-tet and 3,2,3-tet, produced only the *trans* complexes, *trans*-$[Ru(L_4)X_2]^+$ [112c].

Ruthenium(III) complexes of (arylazo)oximes {LL'H; ArN=NC(=NOH)R; Ar = Ph, R = Me, Ph or Me-4-C_6H_4; Ar = Me-4-C_6H_4, R = Ph} [114a] and α-benzil oxime {LL'H; PhC(=O)C(=NOH)Ph} [114b] of the general formula *trans*-$[Ru(LL')(LL'H)X_2]$ (X = Cl or Br) have been prepared, and characterised spectroscopically and electrochemically; the *trans* structure appears to be stabilised by a strong intramolecular O--H--O hydrogen bond between the oxime groups. Finally, ruthenium(III) complexes with 2-pyridyl thiosemicarbazide [114c], 1-benzilidene-4-(2-pyridyl) thiosemicarbazone [114c] and 3-methylrhodanine [115] have also been reported.

3.6.6 Diimine complexes

Quantum effects in the reduction of $[Ru(bipy)_3]^{3+}$ by $[Fe(H_2O)_6]^{2+}$ were concluded to be negligible [90], but similar calculations [116] for the reduction of $[Ru(bipy)_3]^{3+}$ in the "inverted" region, by electronically excited reductants, suggest that quantum effects may be significant. The reduction of $[Ru(bipy)_3]^{3+}$ by a series of peroxocobalt(III) complexes, $[(H_3N)_5Co(O_2)Co(NH_3)_5]^{4+}$, $[(H_3N)_4Co(O_2)(NH_2)Co(NH_3)_4]^{3+}$ and $[(LL)_2Co(O_2)(NH_2)Co(LL)_2]^{3+}$ (LL = en, bipy or phen), has been investigated; the reactants were generated by the flash photolysis of a mixture of $[Ru(bipy)_3]^{2+}$ and the analogous superoxocobalt complexes [117]. The chemiluminescent reduction of $[Ru(bipy)_3]^{3+}$ by dilute sulphuric acid has been observed, but reduction of $[Ru(bipy)_3]^{3+}$ by $[Cr(bipy)_3]^{2+}$ produced chemiluminescence from $\{[Cr(bipy)_3]^{3+}\}^*$ and not from $\{[Ru(bipy)_3]^{2+}\}^*$ [118].

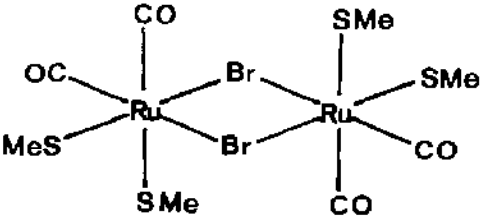
A fast equilibrium has been demonstrated between $[Ru(bipy)_2Cl_2]^+$ and $[Ru(bipy)_2Cl(H_2O)]^{2+}$ in aqueous solution, leading to the isolation of salts of either cation, depending upon the reaction conditions [119]. This reaction mixture can be partially resolved, by asymmetric induction using (+)-tartrate, to give the first genuine examples of the resolution of these ions; earlier reports by Wajda and coworkers [120-122] of the resolution of these ions (and related thiocyanato complexes) were convincingly demonstrated to be erroneous [119]. The chemistry surrounding $[Ru(bipy)_2(py)(H_2O)]^{3+}$ is discussed in Section 3.4.5 (Scheme I).

3.6.7 Porphyrin complexes

These complexes are discussed in Section 3.8.5.

3.6.8 Carbonyl complexes

The polymeric ruthenium(II) complex $\{Ru(CO)_2(SMe)_2\}_n$ reacts with bromine to give $[Ru_2(CO)_4Br_2(SMe)_4]$, **(9)**, which is proposed to contain two bridging bromide ligands (and, presumably, a metal-metal bond, as the complex is diamagnetic) [123].



(9)

3.6.9 Cyanide complexes

The absorption and emission spectra of $[NEt_4]_3[Ru(CN)_6]$ in ethanol (see Fig. 4) have been reported [124]. The emission band at 19050 cm^{-1} has a very short lifetime (0.5 ns), and is independent of the exciting frequency between 33112 and 22935 cm^{-1}. It is assigned as originating with the LMCT excited state: $a^2T_{1u} \longrightarrow {}^2T_{2g}$; the corresponding absorption, ${}^2T_{2g} \longrightarrow a^2T_{1u}$, occurs at 21050 cm^{-1} [124].

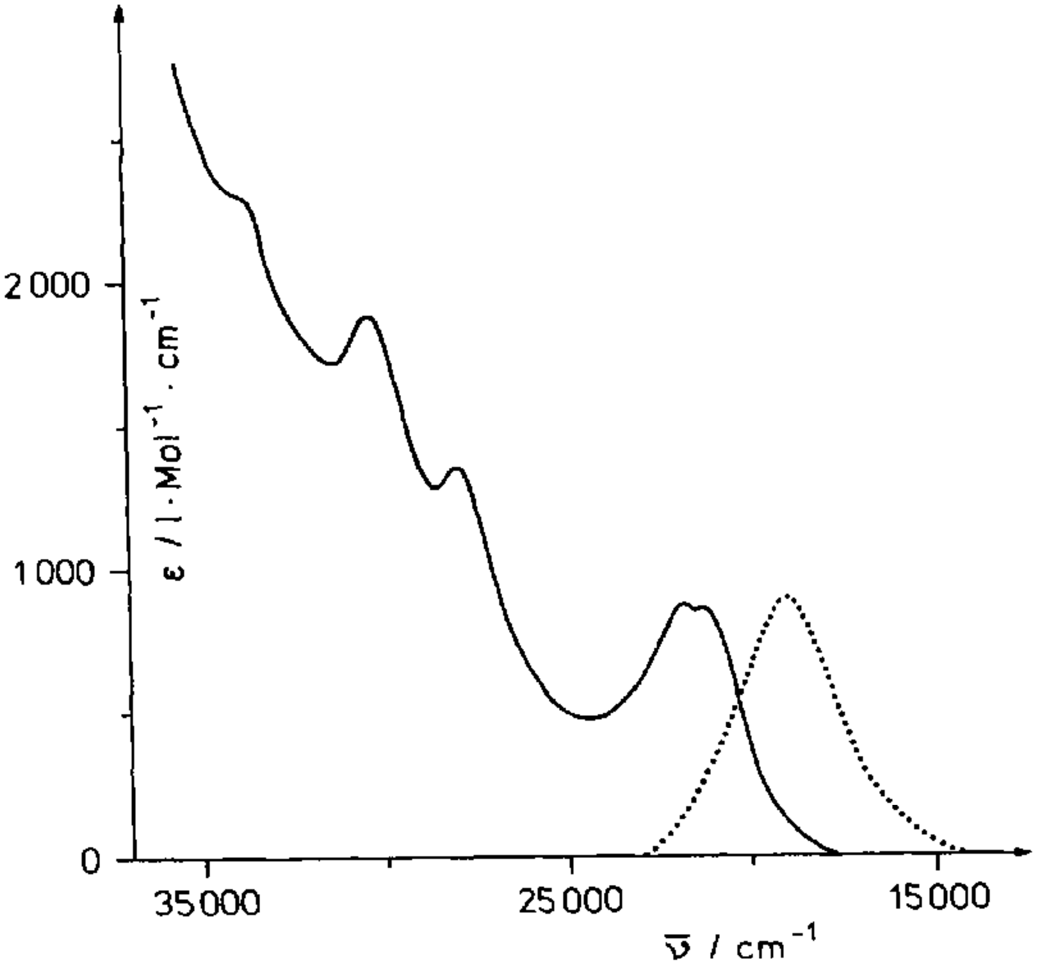


Fig. 4: The electronic absorption (solid line; 298 K) and emission (dashed line; 77 K; exciting line, 27322 cm^{-1}) spectra of $[NEt_4]_3[Ru(CN)_6]$ in ethanol [124].

3.6.10 Organometallic compounds

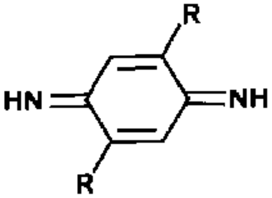
A new claim [125] that $[Ru(cp)_2][RuCl_4]$ is formed by the UV irradiation of ruthenocene in tetrachloromethane/ethanol should be treated with caution, as neither the formation of $[Ru(cp)_2]^+$ nor $[RuCl_4]^-$ was established convincingly, and both of these ions are unknown.

3.7 RUTHENIUM(III/II), MIXED-VALENCE COMPLEXES

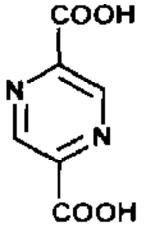
The new assignments of the electronic absorption spectra of $\{Ru_2(O_2CMe)_4Cl\}_n$, which were described last year [2; pp.93–95], have now led to a reexamination of the resonance Raman spectra of this complex, along with those of $\{Ru_2(O_2CR)_4Cl\}_n$ (R = H, Et or Pr) and $[Ru_2(O_2CMe)_4(H_2O)_2][BF_4]$ [126]. The complexes were excited at *ca.* 21000 cm^{-1} (into the $O(\pi) \longrightarrow \delta^*$, $6e_u \longrightarrow 6e_g$ band); ν(RuRu) was observed in the range 326–340 cm^{-1} and ν(RuO) at 369–432 cm^{-1}. These new studies [26] support the assignment proposed last year [2; pp.93-95], in which the $\delta \longrightarrow \delta^*$ band is now located at *ca.* 10000 cm^{-1}, and suggest that earlier assignments based on the $\delta \longrightarrow \delta^*$ transition being at *ca.* 21000 cm^{-1} are in error. The reduction of $\{Ru_2(O_2CMe)_4Cl\}_n$ by aqueous titanium(III) has also been reported [78]. Other mixed-valence carboxylate complexes of ruthenium are discussed in Section 3.6.3.

A short review of mixed-valence ruthenium complexes has been published [127], and the rest of the papers described in this Section concern the Creutz-Taube ion, $[(H_3N)_5Ru(pz)Ru(NH_3)_5]^{5+}$, and related complexes (see also Sections 3.6.5 and 3.8.3 [104]). The XPES of $[(H_3N)_5Ru(pz)Ru(NH_3)_5]X_5$ (X = Br or Me-4-$C_6H_4SO_3$) show two ruthenium core ionisations, from both the 3d and 3p levels, in an intensity ratio of 1:1 [128]. Although this is obviously consistent with a valence-trapped model (Class II), the same result is also predicted for a delocalised ground state (Class III), when account is taken of the high polarisability of the delocalised electrons and the expected large decrease in the electron coupling integral in the photoionised state. Thus, despite the excellent quality of the experimental data, it was concluded that XPES measurements cannot be used to distinguish Class II and Class III behaviour in the Creutz-Taube ion (or, indeed, any other related mixed-valence system) [128]. The far IR FT spectra of $[(H_3N)_5Ru(pz)Ru(NH_3)_5]Br_5$ at 6 K and at room temperature were recorded [129], but no evidence for the intervalence tunnelling transition predicted by the vibronic coupling model [130] was found: it was thus suggested [129] that the complex has an essentially delocalised ground state, and that the asymmetric electronic absorption profile *cannot* be wholly vibronic in origin (as originally proposed [130]). The same vibronic coupling model was applied [131] to the absorption spectra of sixteen complexes of the type $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{5+}$ and two of the type $[(bipy)_2ClRu(LL)Ru(bipy)_2Cl]^{3+}$, and encouraging results were obtained (which may need to be reexamined in the light of the results discussed above). Complexes of the type $[(phen)_2ClRu(pz)Ru(phen)_2Cl]^{3+}$ are discussed in Section 3.8.4.

Pulse and cyclic voltammetry have been used in an elegant manner to determine $E_2^\circ - E_1^\circ$ for two-step electrochemical charge transfer processes, and the methods tested on the complexes $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{n+}$ (LL = 4,4'-bipy, pyrimidine, 1,2-dicyanobenzene, 1,4-dicyanobenzene or 1,5-dicyanonaphthalene; n = 4 or 6), for which the separation of the 4+/5+ and 5+/6+ couples is between 50 and 150 mV: results agreed to within 10% for the measurement of comproportionation constants, as compared with spectrophotometric methods [132]. The ruthenium(III) complexes $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{6+}$ (LL = 4,4'-bipy, 3,3'-dimethyl-4,4'-bipyridine, bis(4-pyridyl)amine, bis(4-pyridyl)methane, *trans*-1,2-bis(4-pyridyl)ethene, or bis(4-pyridyl)ethyne) were prepared by new routes, and the comproportionation constants for the formation of the weakly coupled mixed-valence pentapositive ions were found to be 20, 9.8, 26, 6.7, 14 and 13.8, respectively [133].



(10; R = H or Me)



(11; H_2dcpz)

Ludi and coworkers have reported some interesting new types of mixed-valence compounds. The benzoquinone diimine complex $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{5+}$ (LL = (10; R = H)), with an intense MLCT transition at 15800 cm^{-1} (molar extinction coefficient = 88000 l mol^{-1} cm^{-1}), shows three intervalence transitions (not present in the tetrapositive or hexapositive ions) at 10530, 7380 and 5850 cm^{-1}: the possibility that this complex was a ruthenium(II) dimer bridged by a semiquinone anion radical was ruled out by EPR measurements [134]. A complex with similar properties was also formed with (10; R = Me) [134]. Complexes of the dinegative anion of 2,5-pyrazine dicarboxylic acid, (11; H_2dcpz), $[(H_3N)_4Ru(dcpz)Ru(NH_3)_4]^{n+}$ (*n* = 2, 3 or 4), $[(H_3N)_4Ru(dcpz)Ru(bipy)_2]^{n+}$ (*n* = 3 or 4) and $[(bipy)_2Ru(dcpz)Ru(bipy)_2]^{2+}$, have also been prepared; the mixed valence complexes are stable towards disproportionation in all cases [135].

(12)

Finally, two types of complex of 2,6-dithiospiro[3.3]heptane, *trans*-$[(isonic)(H_3N)_4Ru(LL)Ru(NH_3)_4(isonic)]^{4+}$ and $[(H_3N)_5Ru(LL)Ru(NH_3)_5]^{4+}$ (LL = (12)), have been oxidised to their pentapositive mixed-valence analogues, with comproportionation constants of *ca.* 10: the presence of through-bond interactions was strongly indicated [136].

Heteronuclear mixed-valence ions containing Ru/Fe and Ru/Co are discussed in Section 3.8.3.

3.8 RUTHENIUM(II)

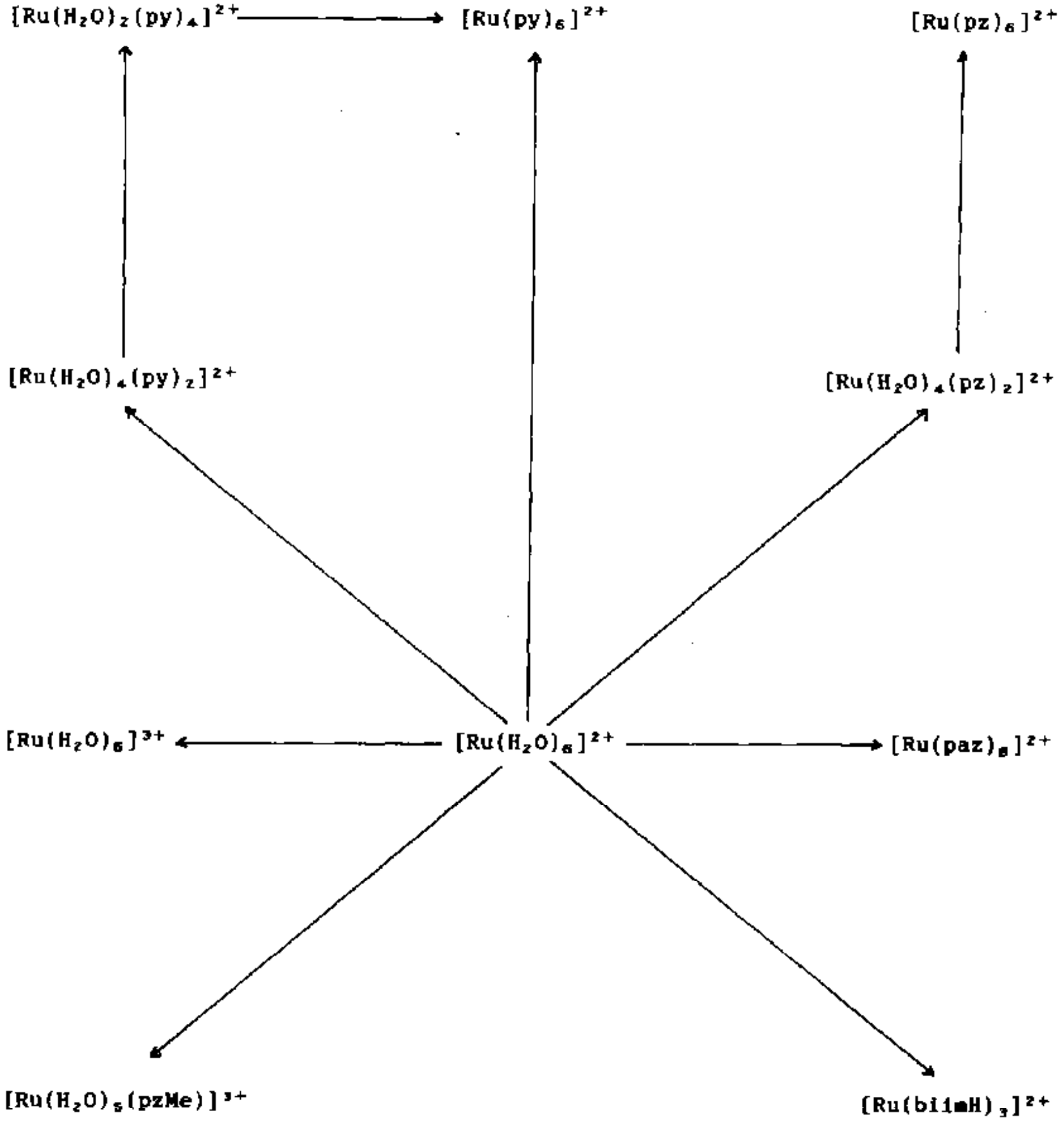
3.8.1 Chloride complexes

Multiple-scattering $X_{\alpha\beta}$ spin-polarised calculations on the hypothetical linear {Cl-Ru-Cl} and bridged {ClRu(μ-Cl_2)RuCl} species have been reported: the ground states for both species are predicted to be high-spin [137].

3.8.2 Complexes with Group VIB donor ligands

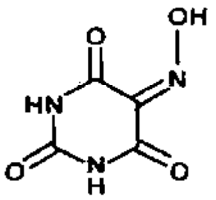
The ionic radius of Ru^{2+} in a titanium(IV) oxide solid solution has been estimated at 0.073 nm by the elastic matrix approach [138].

The prize for the most exciting paper published this year in ruthenium chemistry goes to Ludi and coworkers [139], who have developed a facile new synthesis of the hexaaquaruthenium(II) cation, $[Ru(H_2O)_6]^{2+}$, isolated pink crystals of $[Ru(H_2O)_6][Me\text{-}4\text{-}C_6H_4SO_3]_2$, and examined its uses as a versatile synthetic reagent. A summary of the reactions of $[Ru(H_2O)_6]^{2+}$ reported [139] is given in Scheme II: most of the reaction products in the Scheme are new compounds.



SCHEME II: The syntheses of $[Ru(H_2O)_nL_{6-n}]^{2+}$ from $[Ru(H_2O)_6]^{2+}$ and L under argon at 50 °C [139].

A separable mixture (TLC; SiO_2) of $[RuH(hfacac)(PPh_3)_2(CO)]$ and $[Ru(hfacac)_2(PPh_3)(CO)]$ was prepared by treating $[RuH_2(PPh_3)_3(CO)]$ with $[Pd(hfacac)_2]$ [140]. Similarly, treatment of $[Ru(H)Cl(PPh_3)_3(CO)]$ with $[Pd(hfacac)_2]$ yields the complex $[RuCl(hfacac)(PPh_3)_2(CO)]$ [140]. Treatment of $\{Ru_2(O_2CMe)_4Cl\}_n$ with Na[mhp] (mhpH = 6-methyl-2-hydroxypyridine) yields yellow crystals of $[Ru_2(hmp)_4]$ [141]. This complex was characterised crystallographically [141,142], and shown to have the classic lantern structure (Fig. 5A), with $r(RuRu) = 0.2238$ nm, $\bar{r}(RuN) = 0.2089$ nm and $\bar{r}(RuO) = 0.2044$ nm. This complex thus contains the shortest recorded Ru-Ru bond distance, corresponding to a formal bond order of two $\{\nu(RuRu) = 281\ cm^{-1}\}$. $[Ru_2(hmp)_4]$ was also studied by UVPES (He I), and ionisations from the π^* (5.8 eV), δ^* (6.3 eV), δ (6.8 eV), and σ (8.2 eV) levels of the Ru=Ru bond were identified [141]. The molecular structure of a related, but simpler, complex *trans*-$[Ru(hmp)_2(PPh_3)_2]$ has also been reported (Fig. 5B) [143]; it exhibits $\bar{r}(RuN) = 0.2092$ nm, $\bar{r}(RuO) = 0.2051$ nm and $\bar{r}(RuP) = 0.2367$ nm.



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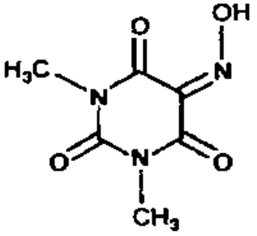


(14)

Further details of the ruthenium(II) complexes of violuric acid (13; H_3viol) and 1,3-dimethylvioluric acid (14; Me_2violH) have appeared this year. The known red salts $Na[Ru(H_2viol)_3]$ and $Na[Ru(Me_2viol)_3]$ have been characterised by IR, UV-VIS and ^1H NMR spectroscopy, and the new salts violet $K_4[Ru(Hviol)_3]$ and blue $Ba_5[Ru(Hviol)_2(viol)]_2$ have been described [144]. The first four pK_a values for $[Ru(H_2viol)_3]^-$ were measured as 5.96, 7.05, 7.93 and *ca.* 13.3 [144].

A welcome report of a series of complexes formed by the much under-studied ruthenium(II)-edta system has appeared. Thus, the complexes

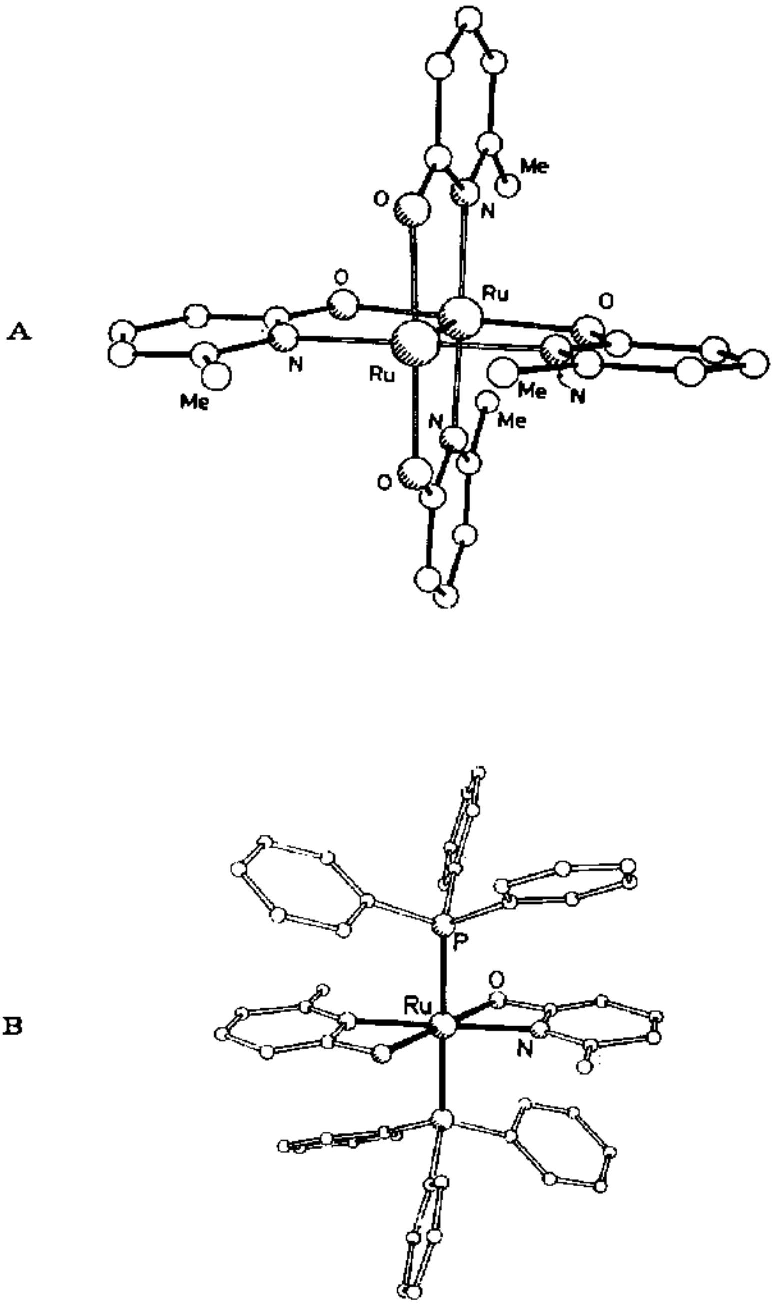


Fig. 5: The molecular structures of (A) $[Ru_2(mhp)_4]$ [141,142] and (B) *trans*-$[Ru(mhp)_2(PPh_3)_2]$ [143].

$[Ru(H_2edta)L_2]$ (L = MeCN, PhCN or 1,2-$C_6H_4(CN)_2$), $[Ru(H_2edta)(NO)Cl]$, $K[Ru(Hedta)(CO)]$, $[NH_4]_2[Ru(edta)(N_2)]$ and $Mg_2[\{Ru(edta)\}_2(N_2)]$ were prepared by treating $[Ru(Hedta)(H_2O)]^-$ (formed by reducing $[Ru(Hedta)(H_2O)]$ with dihydrogen in the presence of platinum black) with the appropriate ligand [145]. All the complexes were characterised by ^1H and ^{13}C NMR, IR and UV-VIS spectroscopy, as well as conductivity measurements.

Following last year's detailed report [2; pp.98-99] of the ruthenium(II)-dmso-water system, a further account has appeared [146]. Further details have also appeared concerning ruthenium(II) complexes with the macrocyclic quadridentate thioethers 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4) and 1,4,7,10-tetrathiacyclotridecane ([13]aneS_4). Thus full synthetic details and IR and UV-VIS spectroscopic characterisation have been reported for the complexes *trans*-$[Ru([14]aneS_4)X_2]$ (X = Cl, Br, I, [NCS], $[N_3]$ or $[NO_2]$), *trans*-$[Ru([14]aneS_4)X(H_2O)]^+$ (X = Cl or Br), *cis*-$[Ru([13]aneS_4)X_2]$ (X = Cl, Br, I, [NCS], $[N_3]$ or $[NO_2]$) and *cis*-$[Ru([13]aneS_4)Cl(H_2O)]^+$ [147]. The ruthenium(III) complexes *trans*-$[Ru([14]aneS_4)X_2]^+$ (X = Cl or Br) and *cis*-$[Ru([13]aneS_4)Cl_2]^+$ were prepared by oxidising their ruthenium(II) analogues with hot perchloric acid [147].

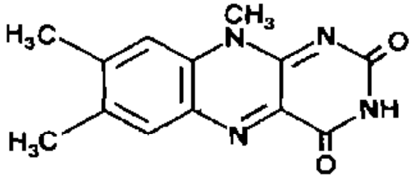
The known polymeric ruthenium(II) complex $\{Ru(CO)_2(SMe)_2\}_n$ has been prepared by treating $[Ru_3(CO)_{12}]$ with S_2Me_2 [123], a route originally used to prepare the ethyl and phenyl analogues in 1968 [148]: *n* was estimated to be 242. The oxidation of $\{Ru(CO)_2(SMe)_2\}_n$ with bromine is described in Section 3.6.8. Finally, complexes of ruthenium(II) with *N*-ethoxycarbonylpyrrole--2-thiocarboxamide have been reported [88].

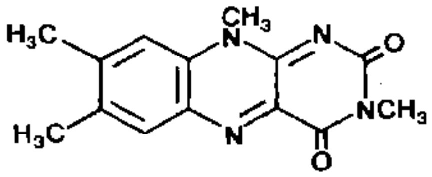
3.8.3 Ammine and amine complexes

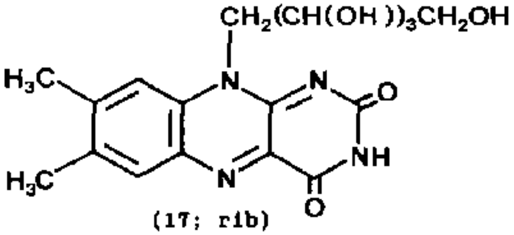
DVM-HFS calculations for $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(N_2)]^{2+}$ give very good agreement between observed and calculated electronic spectral bands [92]. Moreover, $[Ru(NH_3)_6]^{2+}$ appears to undergo essentially pure adiabatic electron transfer reactions [91]. As usual, the principal interest in $[Ru(NH_3)_6]^{2+}$ has centred upon its redox activity, and it is of interest to note that the electron-transfer activity towards cytochrome *c* which had previously been ascribed to ruthenium red [64] has now been shown to be due to impurities of a hexaammineruthenium(III) salt [65]. Indeed, $[Ru(NH_3)_6]^{2+}$ has now been shown to be an efficient electron donor directly to cytochrome oxidase, without the mediation of cytochrome *c* [65]. Moreover, cytochrome *c* acts as a competitive inhibitor of $[Ru(NH_3)_6]^{2+}$, indicating that the two electron donors interact with cytochrome oxidase at the same site(s) [65]. The kinetics of the outer-sphere reduction of $[Ru(NH_3)_5(O_2CMe)]^{2+}$, $[Ru(NH_3)_5(C_2O_4)]^{+}$ and *cis*-$[Ru(NH_3)_4(C_2O_4)]^{2+}$ by $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{2+}$ have been reported [97], as has the reduction of a related series of cobalt(III) macrocycles, *trans*-$[Co(L_4)(OH_2)_2]^{3+}$, by $[Ru(NH_3)_6]^{2+}$ [149].

The molecular structure of $[Ru(NH_3)_5(pz)][BF_4]_2$ has been determined, and the cation shows $r(RuN)_{ammine} = 0.215\text{–}0.217$ nm and $r(RuN)_{pz} = 0.2006$ nm [104]. The Ru-pz bond is 0.007 nm shorter for the ruthenium(II) complex than for its ruthenium(III) analogue (cf. Section 3.6.5), and this is attributed to significant π-backbonding from ruthenium(II) to the pyrazine in the former case: the relevance of this to the problem of delocalisation in the Creutz-Taube ion (see Section 3.7) was also discussed. The electronic, IR, Raman and resonance Raman spectra of $[Ru(NH_3)_5(L)]^{3+}$ (L = 4-cyano-1-methylpyridinium or 1-methyl-4,4'-bipyridinium) have been reported, and the strong visible bands at 18350 and 16950 cm^{-1}, respectively, assigned to the *z*-polarised MLCT band, $b_2(dyz) \longrightarrow b_2(\pi^*)$ [102]. The complex $[Ru(NH_3)_5(py\text{-}4\text{-}NH_2)]^{2+}$ has been generated in solution by the europium(II) reduction of an aqueous acidic solution of $[Ru(NH_3)_5(py\text{-}4\text{-}NH_2)]^{3+}$, and its kinetics of aquation determined [103]. The kinetics of aquation for the complexes *trans*-$[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$ and *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}\{P(OR)_3\}]^{2+}$ (R = Me, $CHMe_2$ or Bu) have also been reported [150].

The affinity of *trans*-$[Ru(NH_3)_4(SO_3)(H_2O)]$ for nitrogen donor ligands has been found to decrease with the degree of alkylation of the donor atom (cf. [2; p.90]) for a series (including a number of amino acid esters) of ligands: ammonia (K = 1500), methylamine (K = 540), ethyl glycinate (K = 470), methyl sarcosinate (K = 3.1) and the prolinato anion (K = 5) [151].


(15; Meialo)

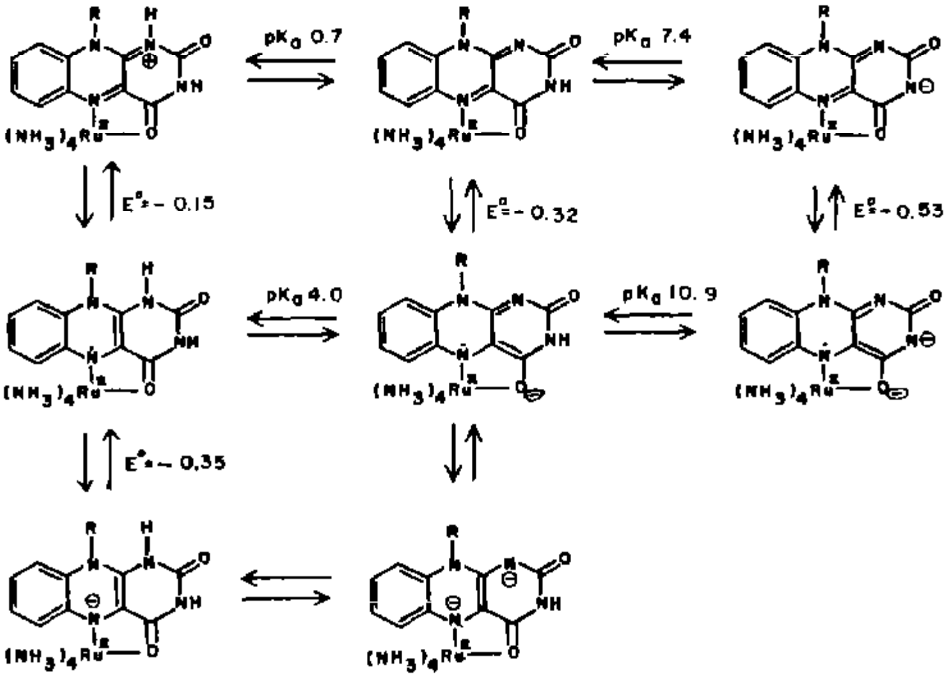

(16; Me$_2$ialo)


(17; rib)

Metalloflavin complexes have attracted significant interest this year. The complexes $[Ru(NH_3)_4(LL')]^{2+}$ {LL' = 10-methylisoalloxazine **(15; Meialo)**, 3,10-dimethylisoalloxazine **(16; Me$_2$ialo)** and riboflavin (17; rib)} have been studied electrochemically in aqueous solution, and whilst approximating metal-stabilised flavosemiquinones in some of their properties, these complexes are best formulated as $Ru^{II}-Fl_{ox}$ rather than $Ru^{III}-Fl\cdot$ [152]. The interrelationships of the structures, pK_a, and redox potentials of the various Ru(II)-flavin complexes are summarised in Scheme III [152]. The same complex has also been studied by resonance Raman spectroscopy [153,154].

The complexes $[Ru(NH_3)_5\{py\text{-}n\text{-}C(O)R\}]^{2+}$ {n = 4, R = $(CH_2)_3CH_3$, $CH_2CH(CH_3)_2$ or $(CH_2)_2CH(CH_3)_2$; n = 3, R = $(CH_2)_3CH_3$ or $CH_2CH(CH_3)_2$} undergo a photochemical degradation (quantum yield of *ca.* 0.02) upon irradiation into the intraligand $n \longrightarrow \pi^*$ band. For example [155]:

$$[Ru(NH_3)_5\{py\text{-}4\text{-}C(O)(CH_2)_3Me\}]^{2+} \longrightarrow [Ru(NH_3)_5\{py\text{-}4\text{-}C(O)Me\}]^{2+} + CH_2{=}CHMe$$



SCHEME III: The interelationships of the structures, pK_a, and redox potentials of the various Ru(II)-flavin complexes in aqueous solution [152].

The complexes $[(NH_3)_5Ru^{III}((NCC(H)=C(H)C_5H_4)Fe^{II}(cp))]^{3+}$ and $[(NH_3)_5Ru^{III}((NCC_5H_4)Fe^{II}(cp))]^{3+}$ are novel examples of heteronuclear mixed-valence compounds, and were prepared by the controlled potential electrochemical oxidation of their dipositive ruthenium(II)-iron(II) analogues [156]. Both mixed-valence complexes show NIR IT bands, at 8750 and 9090 cm^{-1} respectively, and the compounds are unambiguously Class II [156]. A wide range of mixed-valence ruthenium(II)-cobalt(III) complexes of the general formula $[(H_2O)(H_3N)_4Ru^{II}(LL')Co^{III}(NH_3)_5]^{4+}$ (LL' = 3-pyridylethanoate, 4-pyridylethanoate, nicotinate, isonicotinate, 3-cinchomeronate, 4-cinchomeronate or pyrazinecarboxylate) have been prepared by reducing either

$[(SO_4)(H_3N)_4Ru^{III}(LL')Co^{III}(NH_3)_5]^{3+}$ or $[X(H_3N)_4Ru^{III}(LL')Co^{III}(NH_3)_5]^{4+}$ (X = Cl or I) with either ascorbate or $[Ru(NH_3)_6]^{2+}$, and the rates of intramolecular electron-transfer (k = 0.00013-0.042 s^{-1} at 25 °C) have been measured [157]. For the related complexes $[(SO_3)(H_3N)_4Ru^{II}(LL)Co^{III}(NH_3)_5]^{3+}$ (LL = pz or 4,4'-bipy) the rate constants for intramolecular electron-transfer are 0.128 and 0.0004 s^{-1}, respectively [157].

The crystal and molecular structure of racemic $[Ru(en)_3][ZnCl_4]$ has been determined [158]; the cation shows a mean RuN distance of 0.2132 nm, essentially identical to that found in $[Ru(en)_3]^{3+}$ (0.211 nm [159]), meaning that there is no significant inner-sphere reorganisational energy barrier to electron transfer between the complex in its two oxidation states. The absolute configuration and axial rotational strength of $[(Zn,Ru)(en)_3][NO_3]_2$ single crystals have also been briefly reported [160].

The macrocyclic complexes $[Ru(L_4)Cl_2]$ (L_4 = [15]aneN_4 or [16]aneN_4), $[Ru([15]aneN_4)(PPh_3)_2Cl_2]$ and $[Ru([14]aneN_4)(PPh_3)Cl_2]$ have been prepared by treating $[Ru(PPh_3)_3Cl_2]$ with the appropriate macrocycle [113], whereas *trans*-$[Ru(L_4)X_2]$ (L_4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; X = I, $[NO_2]$ or [NCS]) [112b] and *trans*-$[Ru(L_4)(NCS)_2]$ (L_4 = cyclam) [112c] were formed by the reduction of *trans*-$[Ru(L_4)Cl_2]^+$ (see Section 3.6.5) with NaX.

3.8.4 Diimine complexes

A convenient route to $[Ru(bipy)_3]^{2+}$, by heating $RuCl_3.xH_2O$ with an excess of bipy in dmf, has been described [161], and the solubilities of $[Ru(phen)_3][BPh_4]_2$ in thf, diisobutyl ketone, ethyl ethanoate, propan-2-ol, diisopropyl ether, 3-methylbutan-1-ol, benzyl alcohol, 3-methylbutyl ethanoate, butan-2-one, butan-2-ol, butyl ethanoate, chlorobenzene, bis(2-chloroethyl) ether, trichloromethane, 1,2-dichloroethane, methyl 2-methylpropyl ether, 2-methylpropyl ethanoate, 1-nitropropane, methanol,

ethanol, propanone and propyl ethanoate have been documented [162]. The new synthetic routes summarised in Scheme II (Section 3.8.2) are also clearly applicable to the synthesis of tris(diimine)ruthenium(II) complexes (*e.g.* $[Ru(biimH)_3]^{2+}$). $[Ru(bipy)_3]^{2+}$ has also been synthesised within the large cavities of dehydrated Y-type zeolites, by treating zeolite Y loaded with $[Ru(NH_3)_6]^{3+}$ with an excess of bipy; the electronic absorption and emission spectra of this complex were determined as a function of concentration, and the effects of added water and dioxygen were investigated [163].

It has been a perpetuated myth, particularly in the world of the photocatalytic decomposition of water, that $[Ru(bipy)_3]^{2+}$ is indefinitely stable under irradiation with visible light for prolonged periods. Of course, many workers in the field realised that this was not the case [*e.g.* 164], but it is a pleasure to see further studies of this important phenomenon appearing. Giro and coworkers [165] observed that $[Ru(bipy)_3]Cl_2$, in oxygen-free aqueous room-temperature solution, slowly decomposes upon irradiation at 400 nm (over a wide pH range), albeit with a low quantum yield. The decomposition route increases with decreasing pH, and an association between $[Ru(bipy)_3]^{2+}$ and H^+, both in the ground and excited states, has been postulated. The change in absorption spectrum as a function of time is shown in Fig. 6 [165], and dissociation of one mole of bipy is clearly occurring: the final products were thought to be either $[Ru(bipy)_2(H_2O)_2]^{2+}$ or $[Ru(bipy)_2(H_2O)Cl]^+$ [165]. A further study of the of the photoanation of $[Ru(bipy)_3]Cl_2$, in both dichloromethane and ethanenitrile, has also appeared [161]: in the former solvent the product is $[Ru(bipy)_2Cl_2]$ (*n.b.* the chloride is derived from the counter-ion and *NOT* from the solvent), in the latter case the product is $[Ru(bipy)_2(MeCN)Cl]Cl$. The photoanation process is supressed by the presence of dissolved dioxygen in the solvent [161].

The presence of an impurity, showing an IR absorption at 1970 cm^{-1}, in samples of $[Ru(bipy)_2Cl_2]$ prepared by treating $RuCl_3.xH_2O$ in dmf at reflux with bipy, has been detected, and this has been postulated to be a hydrido

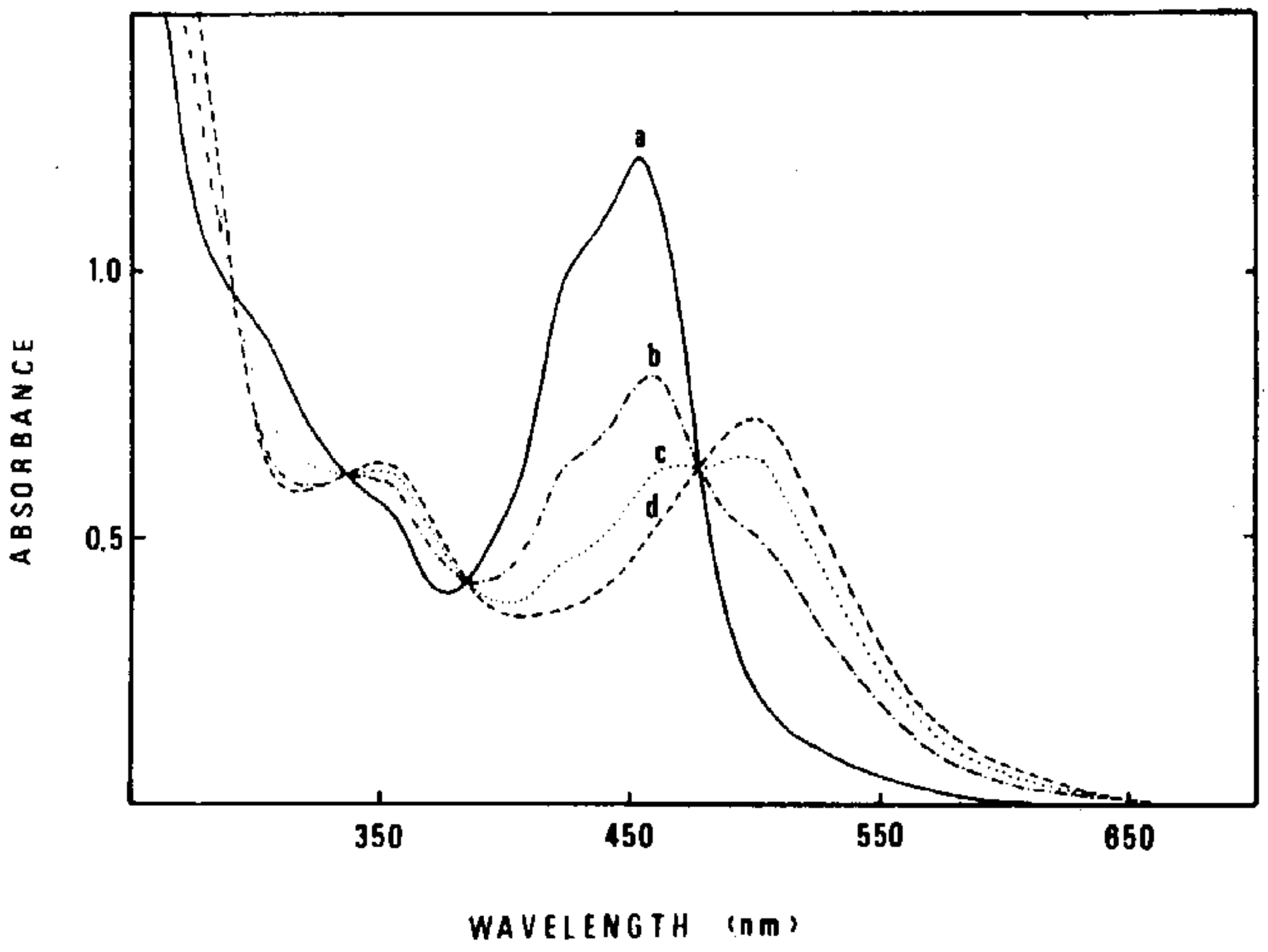
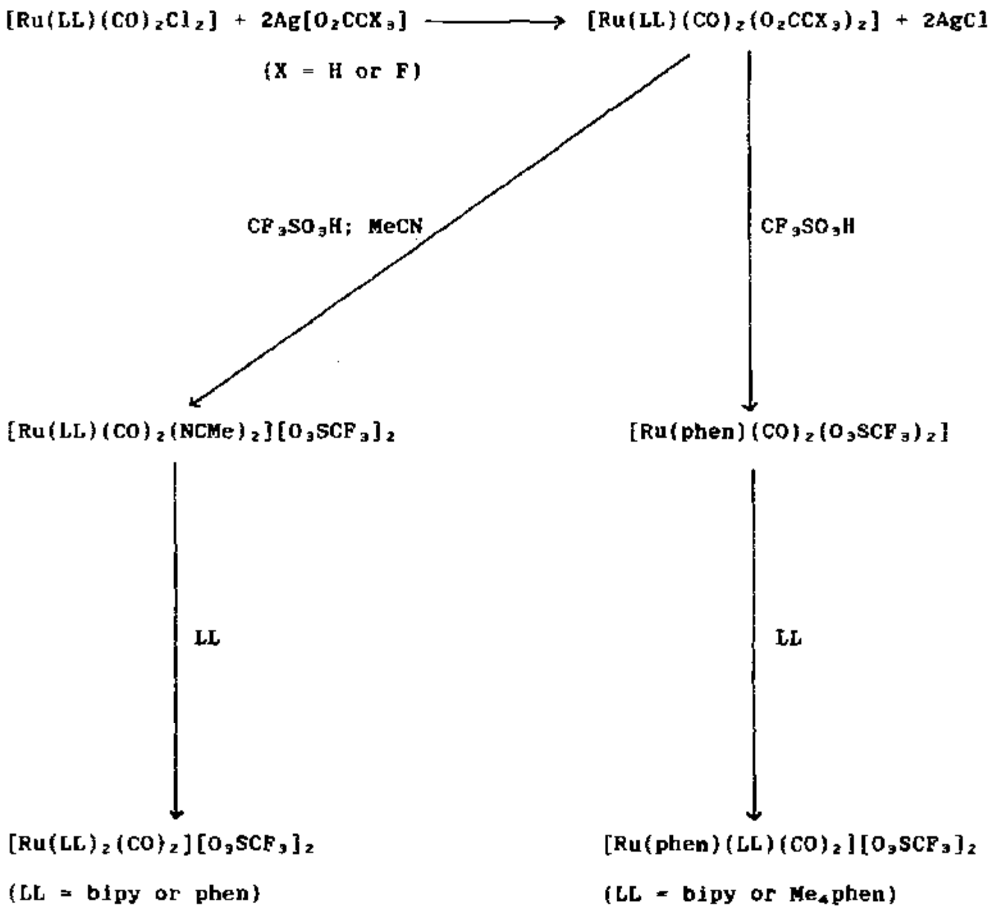
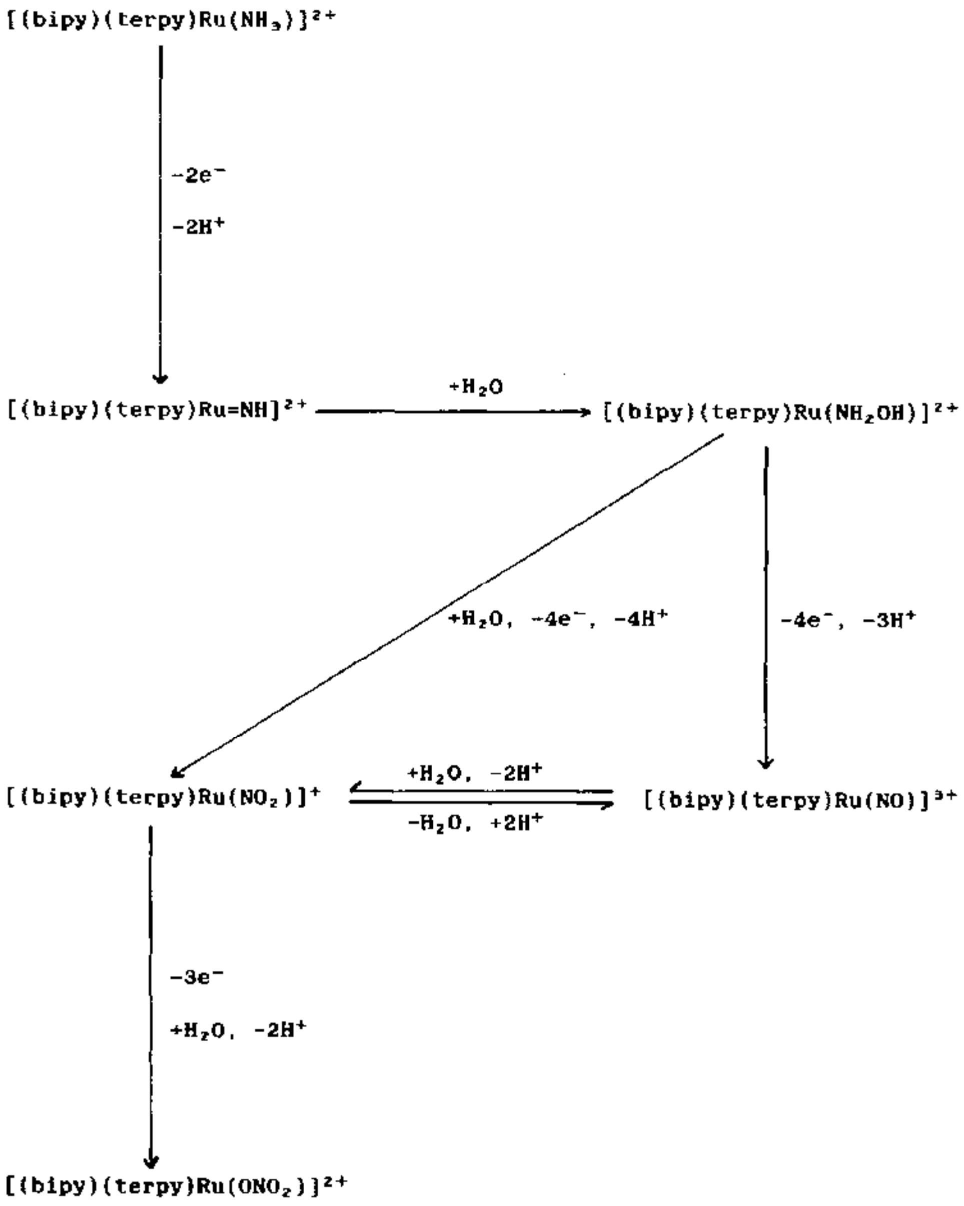


Fig. 6: The absorption spectra of $[Ru(bipy)_3]Cl_2$ ($8x10^{-5}$ *M* in 2 *M* aqueous hydrochloric acid) as a function of photolysis (400 nm; 10^{17} photons s^{-1}) time: (a) 0 min, (b) 10 min, (c) 20 min, and (d) 30 min [165].

species [161]. Partial resolution of a mixture of $[Ru(bipy)_2(H_2O)Cl]^+$ and $[Ru(bipy)_2Cl_2]$ has been achieved for the first time [119]. The IR and NMR spectra of $[Ru(bipy)_2(NCS)_2]$ have been reported [166], as has the extraction of ruthenium from other platinum group metals with 1,10-phenanthroline and thiocyanate [167]. Some new routes to $[Ru(LL)_2(CO)_2]^{2+}$ (LL = phen or bipy) and $[Ru(phen)(LL)(CO)_2]^{2+}$ (LL = bipy or 3,4,7,8-Me_4phen) are summarised in Scheme IV [168].

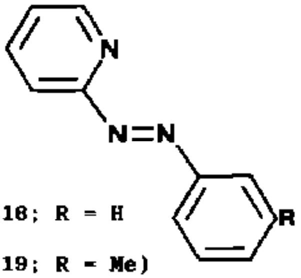


Scheme IV: The synthesis of some dicarbonyl(diimine)ruthenium(II) complexes [168].



Scheme V: The oxidation of ammonia coordinated to ruthenium(II) [52].

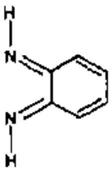
The chemistry of $[Ru(bipy)_2(py)(H_2O)]^{2+}$, and its relationship with $[O{=}Ru(bipy)_2(py)]^{2+}$, was summarised in Scheme I and Section 3.4.5. A reaction believed related to this is the six-electron electrochemical oxidation of $[Ru(terpy)(bipy)(NH_3)]^{2+}$ to $[Ru(terpy)(bipy)(NO_2)]^{+}$, which can be further oxidised in a three-electron step to give $[Ru(terpy)(bipy)(NO_3)]^{2+}$: the key steps in this process are summarised in Scheme V [52]. The oxidations of 2-(aminomethyl)pyridine (ampy) [169] and 2-aminopropane [170] coordinated to ruthenium(II) in $[Ru(bipy)_2(ampy)]^{2+}$ and $[Ru(bipy)(terpy)(H_2NCHMe_2)]^{2+}$ have also been studied. The formation of the product of the former oxidation, by cerium(IV), involves the oxidative dehydrogenation of coordinated (NH_2CH_2)-2-py to give coordinated $(NH{=}CH)$-2-py: the reaction is believed to proceed *via* a ruthenium(IV) intermediate (*cf.* Schemes I and V) [169]. The oxidation of $[Ru(bipy)(terpy)(H_2NCHMe_2)]^{2+}$ (either electrochemically or with cerium(IV)) yields firstly an isolable two-electron oxidation product $[Ru(bipy)(terpy)(HN{=}CMe_2)]^{2+}$ (containing a *monodentate* imine), and then proceeds further to give a four-electron oxidation product, $[Ru(bipy)(terpy)(NCMe_2)]^{3+}$ (possibly containing the coordinated *N*-isopropylideneamide anion) [170].

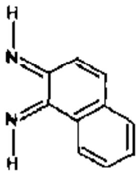


(**18**; R = H

19; R = Me)

A large number of papers dealing with complexes of the general type $[Ru(bipy)_2(LL')]^{2+}$ have been published this year. The red salts $[Ru(bipy)_2(LL')][ClO_4]_2$ (LL' = 2-(phenylazo)pyridine, **(18)**, or 2-(3-tolylazo)pyridine, **(19)**), and the green complexes *trans*-$[Ru(LL')_2X_2]$ (LL' = **(18)** or **(19)**; X = Cl, Br or I), have been prepared from the reaction between LL' and methanolic $[Ru(bipy)_2Cl_2]$ or $RuX_3.xH_2O$, respectively, and were spectroscopically and electrochemically characterised [171]. The results relating to [Ru(LL')$_2$Cl$_2$] (LL' = (18)) are very similar to those reported last year [2; pp. 106-107] by Krause [172]. Similar standard methods, starting with [Ru(bipy)$_2$(C$_2$O$_4$)] and a range of azophenols and azonaphthols, have been used to prepare [Ru(bipy)$_2$(LL')][ClO$_4$] (LL'H = 1-(phenylazo)-2-naphthol, 1-{(4-nitrophenyl)azo}-2-naphthol, 2-{(4-carboxyphenyl)azo}-4,5-dimethylphenol, 1-(2-pyridylazo)-2-naphthol, 2-(phenylazo)-4-cresol or 2-{(2,6-dimethylphenyl)azo}-4-cresol) or [Ru(bipy]$_2$(LL')] (LL'H$_2$ = 4-{(2-hydroxy-1-naphthyl)azo}benzene sulphonic acid), in the hope that they will model azotyrosines and azohistidines, present in some proteins [173].


(20)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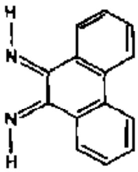

(22)

The 1,2-quinodiimine ligands (LL = (20), (21) or (22)) have been used to prepare [Ru(bipy)$_2$(LL)][PF$_6$]$_2$ and [Ru(bipy)(LL)$_2$][PF$_6$]$_2$ (LL = (20)) from [Ru(bipy)$_2$Cl$_2$] or Ru(bipy)Cl$_3$, respectively; the complexes were characterised spectroscopically and electrochemically [174]. The molecular structure of [Ru(bipy)$_2$(LL)][PF$_6$]$_2$ (LL = (20)) was determined; (20) retains its quinoid nature, but the average RuN bond length to (20) was shorter at 0.202 nm than the average RuN bond length to bipy at 0.206 nm [174]. The preparations of the complexes [Ru(bipy)$_2$(LL')][ClO$_4$] (LL'H = RC(=O)C(=NOH)R; R = Me or Ph) [175] and [Ru(bipy)$_2$(LL')]Cl (LL'H = diphenylthiocarbazone) [176] have also been described.

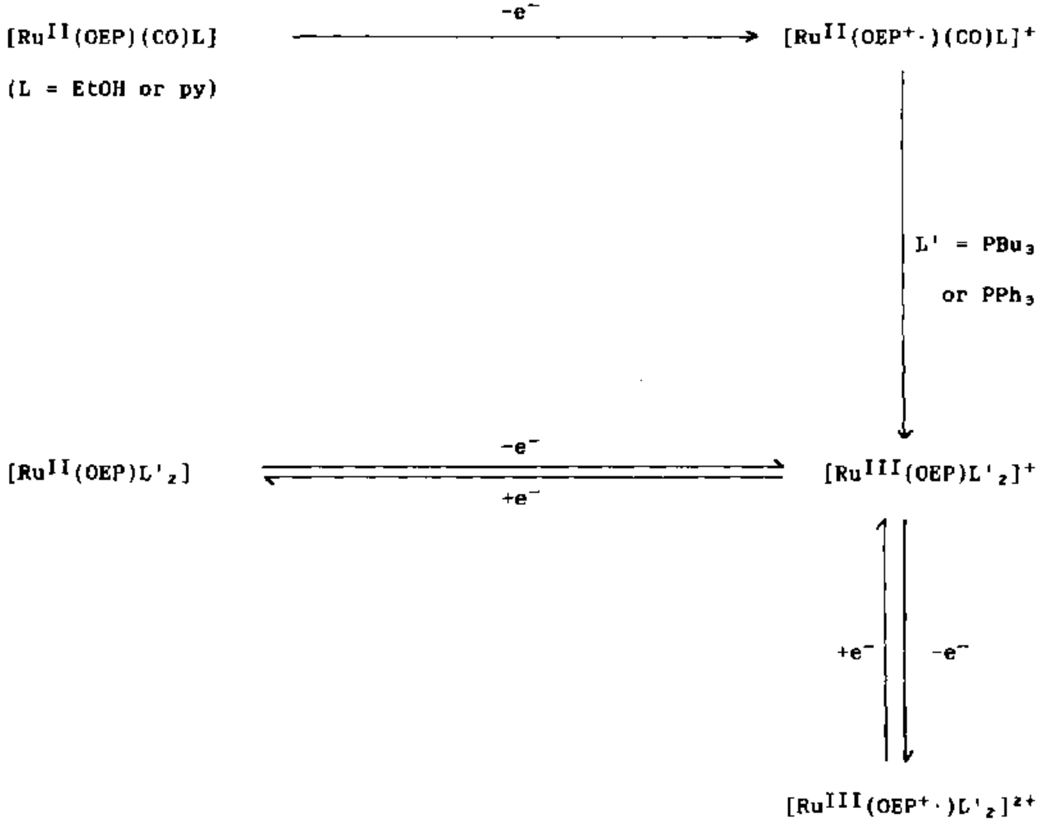
In an elegant synthetic programme, the ligands phen-2-R {R = OMe **(23)**, $O(CH_2CH_2O)_n$-2-phen (n = 2-4; **(24)**-**(26)**), $C(=O)NHC_3H_7$ **(27)**, $C(=O)NH(CH_2CH_2O)_nCH_2CH_2NHC(=O)$-2-phen ($n$ = 1 or 2; **(28)**-**(29)**), and $C(=O)NH(CH_2)_nNHC(=O)$-2-phen (n = 3 or 6; **(30)**-**(31)**)} and $(\text{phen-2-}OCH_2CH_2)_3N$ **(32)** have been prepared and used to form the following ruthenium(II) complexes: $[Ru(bipy)_2(LL')]^{2+}$ (LL' = **(23)** or **(27)**), $[(bipy)_2Ru(LL)Ru(bipy)_2]^{4+}$ (LL = **(24)**-**(26)**, **(28)**-**(31)**) and $[\{(bipy)_2Ru\}_3(L_3)]^{6+}$ (L_3 = **(32)**) [177]. Both the mononuclear and dinuclear complexes show only one oxidation wave, indicating the almost complete lack of coupling between the two ruthenium atoms in the dimers; the comproportionation constant for forming the mixed-valence pentapositive ions are *ca.* 4, the statistical limit [177]. $[Ru(LL)_2(pz)Cl]^+$ and $[(LL)_2ClRu(pz)RuCl(LL)_2]^{2+}$ (LL = phen, 5-NO_2phen, 4,7-Me_2phen or 3,4,7,8-Me_4phen) have been prepared by conventional routes [178]; the oxidation potentials of the monomers correlate well with the pK_a values of LL, the properties of the dimers are very similar to their well-known bipy analogues, and varying the substituent on the phenanthroline has little effect upon the stability of the mixed-valence analogue.

In a very interesting and important paper, Heath and coworkers [179] have performed a controlled *in situ* electrochemical reduction of $[Ru(bipy)_3]^{2+}$ in an OTTLE cell, generating each of the species $[Ru(bipy)_3]^+$, $[Ru(bipy)_3]$ and $[Ru(bipy)_3]^-$ and recording their electronic absorption spectra. The progressive growth of two bands (at *ca.* 29000 and *ca.* 12000 cm^{-1}) also found in Na[bipy], assignable to an intraligand $\pi \longrightarrow \pi^*$ band of $[bipy]^-$, argues strongly for all these complexes being treated as ruthenium(II) complexes, formulated as $[Ru^{II}(bipy)_2(bipy^-)]^+$, $[Ru^{II}(bipy)(bipy^-)_2]$ and $[Ru^{II}(bipy^-)_3]^-$, and containing ligand-localised molecular orbitals, in direct opposition to the Crosby delocalised ligand manifold model [2; pp. 138-140]. This work [179] represents a crucial piece of evidence in establishing the true extent of the intramolecular interligand interaction in $[Ru(bipy)_3]^{2+}$; the recent evidence is all pointing towards the traditionally accepted Crosby model of strong intramolecular interligand coupling as being incorrect [*cf.* 2; pp. 138-140]. Heath's work [179] also highlights errors present in two earlier spectral studies of reduced $[Ru(bipy)_3]^{2+}$ [180] and reduced $[Ru\{bipy\text{-}4,4'\text{-}(COOEt)_2\}_3]^{2+}$ [181]. Also published this year is a description of a new aqueous electrogenerated chemiluminescence system based on the reaction of electrogenerated $[Ru(bipy)_3]^{3+}$ with the strong reductants produced as intermediates in the oxidation of the oxalate ion (or other organic acids, including pyruvic, malonic and lactic) [182]. Quantum effects in the electron-transfer reactions of $[Ru(bipy)_3]^{2+}$ and its excited state have also been discussed in some detail [90,116], and the cyclic voltammetry of $[Ru(bipy)_2(CN)_2]$ has been reported [183].

Finally in this Section, treatment of $RuCl_3.xH_2O$ with a diazabutadiene derivative, $Me_2CHN{=}CHCH{=}NCHMe_2$ (dab; 2,7-dimethyl-3,6-diaza-3,5-octadiene), yields crystals of *cis*-$[Ru(dab)_2Cl_2]$, which were characterised by NMR and electronic absorption spectroscopy, as well as by X-ray crystallography $\{\bar{r}(RuCl) = 0.2426$ nm; $\bar{r}(RuN) = 0.2031$ nm$\}$ [184].

3.8.5 Porphyrin and phthalocyanine complexes

Treatment of $[Ru(L_4)(CO)(EtOH)]$ (L_4 = OEP or TPP) with dppm yields the complexes $[Ru(L_4)(dppm)_2]$; $[Ru(OEP)(dppe)_2]$ was prepared similarly [185]. The molecular structure of $[Ru(TPP)(dppm)_2]$ rather disappointingly reveals it to be a conventional six-coordinate complex $\{\bar{r}(RuN) = 0.2042$ nm, $\bar{r}(RuP) = 0.2398$ nm$\}$, containing two monodentate dppm ligands [185]: the dppe complex is believed to have a similar structure - the first dppe complex containing monodentate dppe. The complexes $\{Ru(L_4)(dppb)\}$ are believed to be polymeric, with bridging dppb ligands [185]. An NMR study of $[Ru(OEP)L_2]$ {L = PBu_3, dppe or $NEt_2(CH_2CH_2PPh_2)$}, $[Ru(OEP)(CO)L]$ {L = PBu_3, $P(CMe_3)_3$, dppe or $NEt_2(CH_2CH_2PPh_2)$} and $[Ru(TPP)\{NEt_2(CH_2CH_2PPh_2)\}_2]$ concludes that seven-coordination is feasible in solution, however [186]. An NMR study of the sterically hindered complexes $[Ru(R_nTPP)(CO)(Me_3C\text{-}4\text{-}py)]$ (R_nTPPH_2 = *meso*-tetrakis($R_n$phenyl)porphyrin; R_n = 3,5-dimethoxy-, 3,4,5-trimethoxy-, 3,5-di-*tert*-butyl-4-hydroxy- or 3,5-di-*tert*-butyl-4-hydroxy-) allowed the determination of both the activation energies for *tert*-butylpyridine exchange and for phenyl ring rotation [187].



Scheme VI: A summary of the redox chemistry of some ruthenium porphyrins, showing evidence for an internal electron transfer process induced by a change of axial ligation [188].

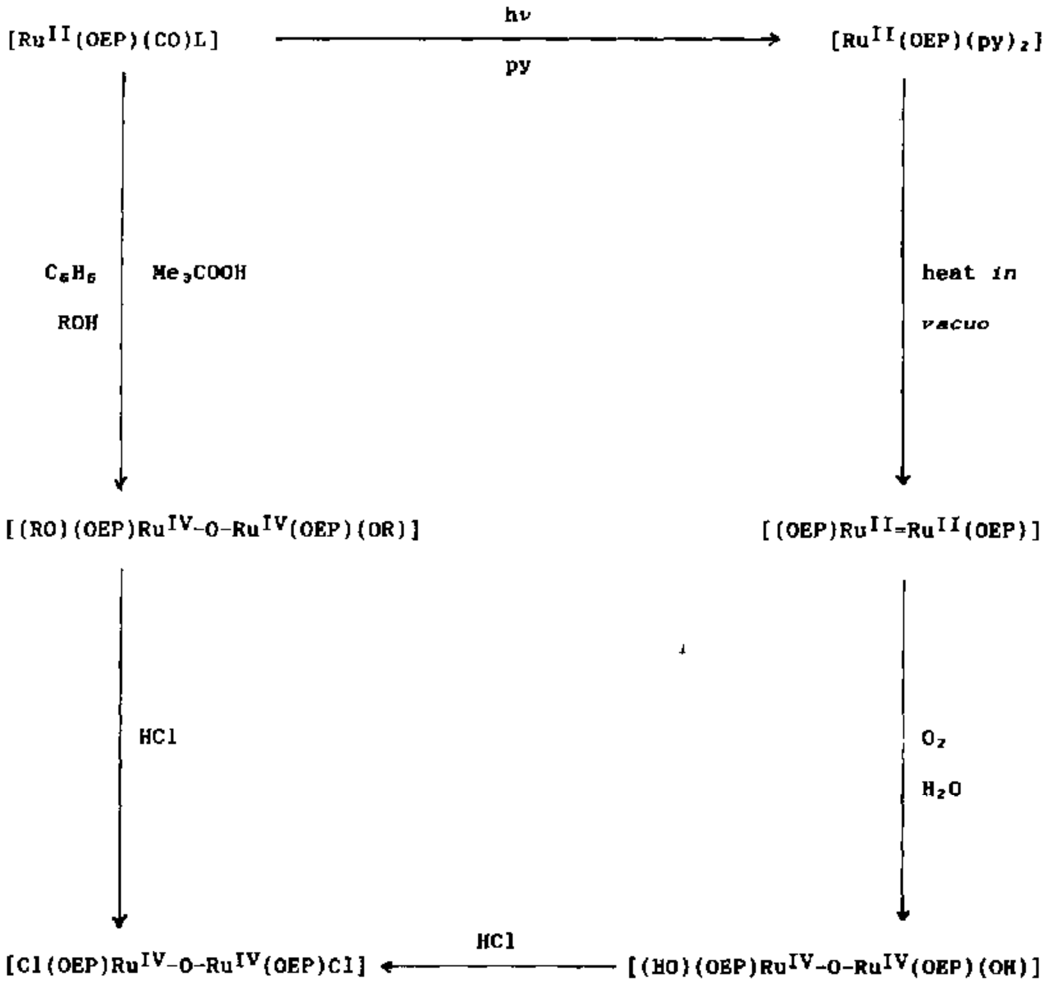
In a fascinating communication, James, Dolphin and coworkers have shown that an internal electron transfer process from ruthenium(II) to an OEP radical can be induced by changes in axial ligation (see Scheme VI) [188]. An example of a key step in this Scheme is:

$$[Ru^{II}(OEP^{+}\cdot)(CO)(py)]^{+} + 2PPh_3 \longrightarrow [Ru^{III}(OEP)(PPh_3)_2]^{+} + py + CO$$

The species in Scheme VI were characterised by EPR and electronic absorption spectroscopy [188]. The excited state and redox properties of [Ru(R-4-TPP)(CO)] (R-4-TPPH$_2$ = *meso*-tetrakis(R-4-phenyl)porphyrin; R = OMe, Me, H, F, Cl and Br) have also been measured; the first oxidation occurs at the porphyrin ligand, the second at the metal; the first reduction occurs at the porphyrin ligand [189]. The excited-state properties of $\{[Ru(R\text{-}4\text{-}TPP)(CO)]\}^{*}$, formed by a $\pi \longrightarrow \pi^{*}$ transition of the porphyrin ring, are comparable with those of $\{[Ru(bipy)_3]^{2+}\}^{*}$ (*i.e.* it is thermodynamically capable of reducing water) [189].

A splitting on the alpha band and broadening of the beta band of [Ru(Mb)(CO)] has been interpreted in terms of a lowering of the square planar symmetry of the complex, as a result of constraint of distal histidine on the linear RuCO moiety, forcing it off the axis normal to the porphyrin plane [190].

A remarkable chemistry is beginning to emerge around the formation of dimers, both metal-metal bonded and oxo-bridged, in the ruthenium porphyrin system, and this intriguing work is summarised in Scheme VII [191]. Space here does not permit justice to be done to the extensive chemistry reported in the communication, but the various aspects will be described in detail in future reviews when the full papers start to appear.



Scheme VII: The synthesis of a variety of ruthenium porphyrin dimers, containing both metal-metal bonds and oxo-bridges [191].

Problems with a recent report [192] of [Ru(ClPc)(py)$_2$] were highlighted in last year's review [2; p.110], and an excellent report from Sweigart's laboratory [193] confirms these doubts. The complexes [Ru(Pc)ClL$_2$] (L = P(OBu)$_3$, PBu$_3$, py or 1-Meimid) have now been prepared and spectroscopically characterised: no evidence for ring chlorination could be found [193], but the manner in which the chloride is bound to the complex still remains unexplained. The complexes [Ru(Pc)L$_2$] (L = P(OBu)$_3$ or PBu$_3$) were prepared and characterised, and the kinetics of their reactions with *N*-methylimidazole (*inter alia*) were measured; a dissociative mechanism involving a five-coordinate intermediate is indicated [193]. The doubling of the origin in low temperature electronic absorption spectra of [Ru(Pc)(CO)(py)] has been studied by optical hole burning at 5 K, and a non-degenerate singlet ground state of near C_{2v} symmetry has been proposed [194].

3.8.6 Phosphine, phosphite and arsine complexes

3.8.6.1 Halo, carbonylhalo and nitro complexes

There has been very little published this year relating to the synthesis of new complexes in this category, but the spate of catalytic applications of known compound continues unabated. The only phosphine paper dealing with pure synthetic work relates to the preparation and characterisation of [Ru(Ph$_2$P-2-py)(CO)$_2$Cl$_2$], formed by the oxidation of [{Ru(CO)$_3$(Ph$_2$P-2-py)}$_3$] with chlorine [195]. The complex has been shown to have a *cis,cis,cis* configuration by X-ray crystallography, containing a chelating Ph$_2$P-2-py ligand {r(RuN) = 0.2119 nm, r(RuP) = 0.2322 nm, r(RuCl) = 0.2413 nm} [195]. [Ru(Ph$_2$P-2-py)(CO)$_2$Cl$_2$] reacts with an excess of Ph$_2$P-2-py in dichloromethane to form *trans,cis,cis*-[Ru(Ph$_2$P-2-py)$_2$(CO)$_2$Cl$_2$], in which the potentially ambidentate ligand is *P*-bonded [195].

mer,cis-[Ru(CO)(AsPh$_3$)$_3$Cl$_2$] has been prepared by adding RuCl$_3$.xH$_2$O and aqueous methanal to AsPh$_3$ in boiling 2-methoxyethanol; this complex eliminates a mole of $AsPh_3$ in boiling toluene to form the dimer $[Ru_2(CO)_2(AsPh_3)_4Cl_4]$, and carbonylates in boiling benzene to give $[Ru(CO)_2(AsPh_3)_2Cl_2]$ [196].

Included amongst the catalytic applications of $[Ru(PPh_3)_3Cl_2]$ reported this year are the following: a mechanistic study of the reductive coupling, dehydration, disproportionation and dehydrogenation of diarylcarbinols [197], the hydrosilylation of ethyne to give a wide range of vinylic silicon compounds {*e.g.* $SiCl_3(CH{=}CH_2)$} on a laboratory scale [198], the formation of secondary alcohols from ketones and methanoic acid [199], the selective oxidation of a primary alcohol in the presence of a secondary alcohol (*e.g.* 1,10-undecanediol to 10-hydroxyundecanal) [200], the oxidation of allyl alcohols to ketones by dioxygen [201], the hydrosilylation of carbon dioxide into silyl esters of methanoic acid [202], the catalytic reduction of the C=C bonds in α,β-unsaturated ketones by sodium methanoate [203], a mechanistic study of homogeneous hydrogen transfer from alcohols to $(PhCH{=}CH)_2C{=}O$ [204], the hydrosilylation of alkenes [205], the hydrogenation of cyclohexene [206], and hydrogen transfer from alcohols to cyclohexanone [207]. $[Ru(PPh_3)_4Cl_2]$, $[Ru(PPh_3)_3Cl_2]$ and $[Ru(PPh_3)_2(py)_2Cl_2]$ are reported, in the presence of small amounts of dioxygen, to catalyse olefin metathesis and ring-opening polymerisation reactions via the formation of metallaoxacyclobutanes [208]. In addition, $[Ru\{P(cych)_3\}_2(CO)_2Cl_2]$ catalyses the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols [209], fuller details of the water-soluble analogues of PPh_3 complexes, formed with $[(SO_3\text{-}3\text{-}C_6H_4)PPh_2]^-$, reported last year [2; pp. 112-113], have appeared [210], the asymmetric transfer hydrogenation of 2-methylcrotonic acid and its esters by alcohols has been catalysed by $[Ru_2\{(-)\text{-diop}\}_3Cl_4]$ [211], and the catalysis of the homogeneous hydrogenation of cyclohexene by $[Ru(EPh_3)_3Cl_2]$ (E = As or Sb), $[Ru(LL)_2Cl_2]$ (LL = dppe or dpae), $[Ru(SbPh_3)_3(dmso)Cl_2]$ and $[Ru(EPh_3)_3(SnCl_3)Cl]$ (E = P or As) has been studied [206].

The mechanism of the conversion of $[Ru(CO)_2(PPh_3)_2(NO_2)_2]$ to $[Ru(NO)_2(PPh_3)_2]$, carbon dioxide, carbon monoxide and triphenylphosphine oxide involves an intermolecular oxygen-atom transfer from coordinated nitrite to CO; the important intermediate [Ru(NO)(CO)$(PPh_3)_2$(ONO)] was also prepared [212a].

Complexes of stoicheiometry $\{Ru(NCS)_2(PPh_3)_2\}_n$ have been reported [212b].

3.8.6.2 Complexes containing oxygen donor ligands

[Ru(CO)$(PPh_3)_2(O_2CCF_3)_2$] has been shown to catalyse homogeneous bulk hydrogen transfer from secondary alcohols to ketones under mild conditions [213].

3.8.6.3 Complexes containing sulphur donor ligands

The kinetics and mechanism of the replacement of PMe_2Ph by $P(OMe)_3$ in $[Ru(S_2CH)(PMe_2Ph)_3\{P(OMe)_3\}]^+$ has been studied, and reveals that nucleophilic attack of the added PMe_2Ph on the dithiomethanoato carbon atom catalyses the substitution reaction [214]. Treatment of $[Ru(SOCPh)_2(PMe_2Ph)_2]$ with dppm gives the dppm-solvated complex *mer*-$[Ru(SOCPh)_2(PMe_2Ph)_3]$-dppm; in contrast, the reaction with dppe gives *mer*-$[Ru(SOCPh)_2(PMe_2Ph)(dppe)]$ [215]. This last complex exists in two different isomeric forms (S *trans* to S and S *trans* to O), and the molecular structure of the latter form has been determined crystallographically [215]. Similarly, the treatment of $[Ru(SOCPh)_2(PMe_2Ph)_2]$ with an excess of PMe_2Ph gives an isomeric mixture of *mer*-$[Ru(SOCPh)_2(PMe_2Ph)_3]$, but the reaction for short periods between *cis*-$[Ru(PMe_2Ph)_4Cl_2]$ and $[NH_4]$[SOCPh] gives *fac*-$[Ru(SOCPh)_2(PMe_2Ph)_3]$; the same reaction shaken for a prolonged period produces $[Ru(SOCPh)(PMe_2Ph)_4]^+$ [215].

3.8.6.4 Complexes containing nitrogen donor ligands

Treatment of $(Me_2HC)N{=}C{=}N(CHMe_2)$ with $[Ru(CO)(PPh_3)_3HX]$ (X = Cl or Br) gives $\{Ru(CO)(PPh_3)_2\{CH_2{=}C(Me)N{-}CH{-}NCHMe_2\}X]$, a complex of the

N-isopropenyl-*N'*-isopropylformamidinate anion; the molecular structure of the chloride complex revealed *trans* phosphine ligands [216]. Complexes of stoicheiometry $[Ru(PPh_3)_2(MeCN)_2(NCS)_2]$ and $[Ru(PPh_3)(py)_3(NCS)_2]$ have been reported [112b].

3.8.6.5 CSeS complexes

Nucleophilic attack upon the coordinated CS ligand in $[Ru(CS)(CO)(PPh_3)_2(CNC_6H_4\text{-}4\text{-}Me)Cl]^+$ by $[SeH]^-$ produces geometrical isomeric mixtures of $[Ru(\eta^2\text{-}CSeS)(CO)(PPh_3)_2(CNC_6H_4\text{-}4\text{-}Me)]$ and $[Ru(\eta^2\text{-}CSSe)(CO)(PPh_3)_2(CNC_6H_4\text{-}4\text{-}Me)]$ [217], whereas treatment of $[Ru(\eta^2\text{-}CSeS)(CO)(PPh_3)_2(CNC_6H_4\text{-}4\text{-}Me)]$ with MeI followed by HCl yields $[Ru(CSe)(PPh_3)_2(CNC_6H_4\text{-}4\text{-}Me)Cl_2]$ [217].

3.8.6.6 Hydride complexes

Full details of the structure of *trans*-$[Ru\{(+)\text{-diop}\}_2(H)Cl]$ {$r(RuCl)$ = 0.2549 nm, $r(RuH)$ = 0.165 nm, $r(RuP)$ = 0.2356, 0.2393 nm} have now appeared [218]. Treatment of $[Ru(PPh_3)_4H_2]$ with 1,4-$Cl_2Si_4Ph_8$ gives $[Ru_2(PPh_3)_6H_2Cl_2]$, H_2 and 1,8-$Cl_2Si_8Ph_{16}$ [55,219], and with dad {dad = RN=CH–CH=NR (R = $CHMe_2$ or C_6H_4-4-OMe) or PhN=C(Me)–C(Me)=NPh} gives *cis,cis,trans*-$[Ru(dad)(PPh_3)_2H_2]$ [55,219]. However, *cis,cis,trans*-$[Ru(PhN{=}C(Me)\text{–}C(Me){=}NPh)(PPh_3)_2H_2]$ is unstable towards isolation and yields the *cis*-dihydrido isomer and a pentacoordinate complex containing monodentate PhN=C(Me)–C(Me)=NPh [54].

The novel complexes $[Ru(PR_3)_4H_2]$ (R = Et or Bu) were prepared by reducing an ethanolic solution of $RuCl_3.xH_2O$ and PR_3, and were found to be catalysts for the selective linear codimerisation of terminal alkynes and buta-1,3-diene [220]. $[Ru(PPh_3)_3HCl]$ catalyses the isomerisation of acetylenic silyl ethers to dienol silyl ethers [221].

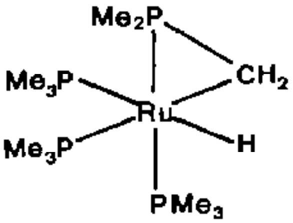
$[Ru(CO)(PPh_3)_3HCl]$ undergoes dehydrochlorination with diazabicycloundecene, in the presence of CO, to give $[Ru(CO)_3(PPh_3)_2]$ [222], whereas $[Ru(CO)_2(PPh_3)_2HCl]$ reacts with diazabicycloundecene and PPh_3 in boiling methanol to give $[Ru(CO)_2(PPh_3)_3]$ and $[Ru(CO)(PPh_3)_2(CN\text{-}4\text{-}C_6H_4)HCl]$ yields $[Ru(CO)(CN\text{-}4\text{-}C_6H_4)(PPh_3)_3]$ [222]. $[Ru(CO)\{P(cych)_3\}_3HCl]$ is reported to be an active catalyst for the hydrogen transfer reaction between cyclohexanol and acetophenone [223].

Treatment of $[Ru(CO)(PPh_3)_3H_2]$ with aqueous tetrafluoroboric acid gives $[Ru(CO)(PPh_3)_3(H_2O)H][BF_4]$, which carbonylates to give $[Ru(CO)_2(PPh_3)_2(H_2O)H][BF_4]$ [224]. The molecular structure of the latter salt reveals that the tetrafluoroborate anion is hydrogen-bonded to the coordinated water, that the phosphine ligands are mutually *trans*, but markedly unsymmetrical and non-linear $\{r(RuP) = 0.2329,\ 0.2416\ nm\}$, and that the carbonyl ligands are mutually *cis* $\{r(RuC)_{trans\ to\ H} = 0.197\ nm;\ r(RuC)_{trans\ to\ O} = 0.197\ nm\}$ [224]. Treatment of $[Ru(PPh_3)_3(O_2CMe)H]$ with a wide range of ligands, L (L = Me_3CNC, PF_2NMe_2, $P(OCH_2)_3CMe$, $P(OMe)_3$ or dppe), yields $[Ru(PPh_3)_{3-x}L_y(O_2CMe)H]$ (x = 1, 2 or 3), whereas L' (L' = PF_3, PF_2(piperidino) or PF_2NMe_2} caused reduction to a range of ruthenium(0) complexes, $[Ru(PPh_3)_{5-x}L'_x]$ (x = 3, 4 or 5) [225]. Treatment of $[Ru(PMe_3)_4Me_2]$ with $CNCMe_3$ in thf yields *cis,trans,cis*-$[Ru(CNCMe_3)_2(PMe_3)_2H_2]$ [226].

Treatment of a mixture of $RuCl_3.xH_2O$, methanal and $AsPh_3$ with NEt_3 in boiling 2-methoxyethanol gives $[Ru(CO)(AsPh_3)_3HCl]$, which carbonylates in boiling benzene to yield $[Ru(CO)_2(AsPh_3)_2HCl]$ [196]. Reduction of $[Ru(CO)(AsPh_3)_3Cl_2]$ with ethanolic $Na[BH_4]$ gives $[Ru(CO)(AsPh_3)_3H_2]$ [196].

3.8.6.7 Cycloruthenated complexes

The reduction of *trans*-$[Ru(PMe_3)_4Cl_2]$ with Na/Hg in benzene produces the cycloruthenated complex $[Ru(PMe_3)_3(CH_2PMe_2)H]$, (33) [227]. (33) reacts with MeI, CS_2 or $[NH_4][PF_6]$ to give $[Ru(PMe_3)_3(CH_2PMe_2)I]$, $[Ru(PMe_3)_3(S_2CHPMe_2CH_2)]$ or $[Ru(PMe_3)_5H][PF_6]$, respectively; it does not react with CO or $P(OMe)_3$ [227].



(33)

Fuller details of $K[Ru\{(C_6H_4)PPh_2\}(PPh_3)_2H_2].Et_2O.C_{10}H_8$ **(34)** and $K_2[Ru_2(PPh_2)_2(PPh_3)_2H_4].2(diglyme)$ **(35)**, both of which were briefly reported last year [2; p.117], have now appeared [228,229]. **(34)** and **(35)** were prepared by reducing $[Ru(PPh_3)_3HCl]$ or $[Ru_2(PPh_3)_4H_2Cl_2]$, respectively, with $K[C_{10}H_8]$ in thf at low temperature; **(34)** was characterised by X-ray crystallography, and the anion was shown to have a *cis,cis,cis* configuration (*n.b.* the hydrides were not directly located) [228]. Both **(34)** and **(35)** are active catalysts for the homogeneous hydrogenation of ketones, aldehydes, carboxylic acid esters and nitriles [229]. The cycloruthenated formazan complexes $[Ru\{(2-C_6H_4)N=NC(R)=NNPh\}(CO)(PPh_3)_2]$ **(36; R = H, Me or Ph)** and $[Ru\{(2-C_6H_4)N=NC(Ph)=NNPh\}(CO)(AsPh_3)_2]$ have been prepared by treating $[Ru(CO)(EPh_3)_3H_2]$ (E = P or As) with the appropriate 1,5-diphenylformazan [230]. The molecular structure of **(36; R = Ph)** has been determined by X-ray crystallography, and the compound shown to possess a *mer,trans* geometry [230].

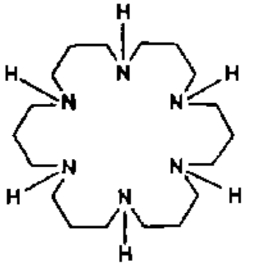
3.8.6.8 Alkene complexes

Treatment of $[Ru(CO)(C_2H_4)(PMe_2Ph)_2Cl_2]$ with PMe_2Ph at room temperature results in the anticipated ethene displacement product, $[Ru(CO)(PMe_2Ph)_3Cl_2]$; at lower temperatures, the important intermediate $[Ru(CO)(C_2H_4PMe_2Ph)(PMe_2Ph)_3Cl]^+$ was observed, and isolated as its chloride or perchlorate salt [231]. In related reactions, $[Ru(CO)(C_2H_4)(AsMe_2Ph)_2X_2]$ (X = Cl or Br) react with PMe_2Ph to give $[Ru(CO)(C_2H_4PMe_2Ph)(PMe_2Ph)(AsMe_2Ph)_2X]^+$, and $[Ru(CO)(C_2H_4)(PMe_2Ph)_2Cl_2]$ reacts with $PMePh_2$ to give $[Ru(CO)(C_2H_4PMePh_2)(PMePh_2)(PMe_2Ph)_2Cl]^+$ [231]. The first steps in these reactions appears to be nucleophilic attack upon the coordinated ethene, with subsequent displacement of the halide ion *trans* to the newly formed alkyl ligand; with the ligands L (L = $AsMe_2Ph$, NH_2Bz, $P(OMe)_2Ph$, 4-Mepy or SMe_2), no similar intermediate was observed, but the product of the room temperature reaction was still $[Ru(CO)L(PMe_2Ph)_2Cl_2]$ [231].

The crystal structure of $[Ru(bchd)(PPh_3)_2Cl_2]$ reveals that it possesses the *cis,trans,cis* structure {r(RuCl) = 0.2440 nm; r(RuP) = 0.2479 nm}, rather than the more common (for diene complexes of ruthenium(II)) *cis,cis,trans* arrangement [232].

3.8.7 Cyanide complexes

Mixtures of $K_2Fe[Ru(CN)_6]$, $K_2Fe[Os(CN)_6]$ and $K_2Fe[Fe(CN)_6]$ catalyse the formation of ammonia at low temperatures [233]. The absorption of $K_4[Ru(CN)_6]$ upon copper and silver has been studied by SERS; it is absorbed more strongly onto copper, *via* cyanide bridges to the surface [234]. The hexaprotonated form of (37) and the octaprotonated form of (38) form 1:1 complexes with $[Ru(CN)_6]^{4-}$; the redox potential of the $[Ru(CN)_6]^{3-/4-}$ couple is significantly shifted upon complexing with these macrocyclic receptors [235].



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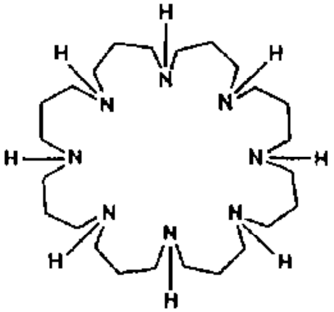

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3.8.8 Isonitrile and carbonyl complexes

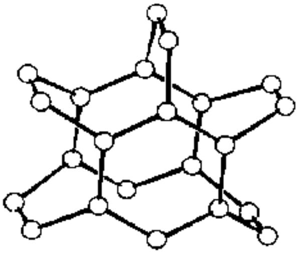
Treatment of $\{Ru_2(O_2CMe)_4Cl\}_n$ with Me_3CNC in methanolic diethyl ether yields white crystals of *trans*-$[Ru(Me_3CNC)_4(O_2CMe)_2]$ [236].

The cationic complexes $[Ru(CO)_5H]^+$ and *cis*-$[Ru(CO)_4(PPh_3)H]^+$ were prepared, in solution, by extracting hexane solutions of either $[Ru(CO)_5]$ or $[Ru(CO)_4(PPh_3)]$ with concentrated sulphuric acid; ^{13}C NMR spectroscopy revealed the complexes to be stereochemically rigid on the NMR time scale at room temperature [237]. The involvement of $[Ru(CO)_4H_2]$ in the $[Ru_3(CO)_{12}]$-catalysed water gas shift reaction has also been discussed [238].

3.8.9 Organometallic compounds

Whilst organometallic chemistry is strictly outside the scope of this review, this Section gives a brief summary of some of the papers which are of relevance to coordination chemists.

The molecular structure of ruthenocene has been redetermined both at room temperature and at 101 K: the molecule has an eclipsed D_{5h} structure with $r(RuC) = 0.2186$ nm [239]. The dynamics of ring rotation [240] and calculated IR frequencies [241] of ruthenocene were also reported. The electrochemistry of $[Ru(cp)_2]$ in the ionic liquid *N*-butylpyridinium chloride/aluminium chloride (in both 'acidic' and 'basic' conditions) has been investigated, and (as in other solvent systems) no evidence for the formation of stable $[Ru(cp)_2]^+$ was found [242]. This highlights the unlikely nature of the results reported by Sugimori and coworkers [125], in which the unsubstantiated formation of $[Ru(cp)_2][RuCl_4]$ by the photochemical irradiation of ruthenocene in chlorinated hydrocarbons is again reported (*cf.* Section 3.6.10). As reported last year [2; p.118], the oxidative coupling of tmen-solvated lithioruthenocene by $CuCl_2$ leads to low oligomers of ruthenocene [243]. Water-soluble $[Ru(cp)\{C_5(COOMe)_5\}]$ has also been prepared and crystallographically characterised [244].



(39)

The other area of significant interest to be developed this year is that of arene, cyclophane and ruthenocenophane derivatives. The ^{13}C NMR spectra of [4]ruthenocenophan-2-one and [3]ruthenocenophan-1-one have been recorded [245], and a remarkable synthesis of [25](1,2,3,4,5)cyclophane (39) has allowed the preparation of $[Ru\{[2_5](1,2,3,4,5)cyclophane\}(arene)][BF_4]_2$ (arene = C_6Me_6 or 1,4-$Me_2C_6H_4$) by reaction of the cyclophane with $[Ru_2(arene)_2Cl_4]$ [246]. Related derivatives of [2.2]paracyclophane have also been prepared similarly [247], and high yield syntheses of $[Ru_2(arene)_2X_3]^+$ (X = Cl, Br, I, OH or OR) have been developed [248,249].

3.8.10 Trichlorostannyl complexes

The salt $[NEt_4]_4[Ru(SnCl_3)_5Cl]$ has been crystallographically characterised {r(RuCl) = 0.2468 nm; $r(RuSn)_{trans}$ to Cl = 0.2553 nm; $\bar{r}(RuSn)_{tran}$ to Sn = 0.2579 nm}, and is the first complex for which ^{99}Ru spin-spin coupling constants {$1J(^{99}Ru^{119}Sn)$ = 846 Hz} have been measured [250]; this complex also possesses a huge $^{2}J(^{119}Sn^{117}Sn)$ coupling constant, at 21254 Hz [250,251]. $[Ru(PPh_3)_3(SnCl_3)Cl]$ has also been prepared, and shown to catalyse the hydrogenation of hex-1-ene, penta-1,3-diene and hex-1-yne, but not to catalyse their isomerisation [252].

The crystal and molecular structure of the optically active complex (−)-$[Ru(C_6H_6)(Ph_2PNHCH(Me)Ph)(SnCl_3)Me]$ has been determined {r(RuSn) = 0.2543 nm; $r(RuC_{Me})$ = 0.2155 nm; r(RuP) = 0.2295 nm} [253].

3.8.11 Carbaborane complexes

A new series of ten-vertex [254] and twelve-vertex [57] *closo*-phosphinoruthenacarbaboranes, of general types $[Ru(L_5)(PR_3)_n]$ (L_5 = dianion of a carbaborane; R = Et or Ph; *n* = 2 or 3) and $[Ru(L_5)(PEt_3)_2(CO)]$ have been prepared and characterised by dynamic FT NMR spectroscopy.

3.8.12 Hydrides

Low temperature (>7 K) magnetic susceptibility measurements upon Eu_2RuH_6 confirm ferromagnetic behaviour (T_C = 29 K) [255].

3.9 RUTHENIUM(I)

No true coordination chemistry of ruthenium(I) has been published this year. The nearest is a report of the electrochemical generation of $[Ru(bipy)_3]^+$ [179], which is discussed in Section 3.8.4 since the complex is best considered as a ruthenium(II) complex containing a localised $[bipy]^-$ ligand, $[Ru^{II}(bipy)_2(bipy^-)]^+$, not as a ruthenium(I) complex.

3.10 RUTHENIUM(0)

The protonation of $[Ru(CO)_5]$ with concentrated sulphuric acid yields $[Ru(CO)_5H]^+$, and a similar treatment of $[Ru(CO)_4(PPh_3)]$ gives $[Ru(CO)_4(PPh_3)H]^+$ (see also Section 3.8.8) [237].

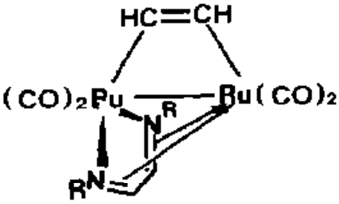
The preparation (from $[Ru_3(CO)_{12}]$ and $P(OMe)_3$) and molecular structure of $[Ru(CO)_4\{P(OMe)_3\}]$ have been reported [256]; the observed asymmetry of the methyl groups seems to be retained on the IR time-scale but lost upon the NMR time-scale. Treatment of $[Ru(PPh_3)_3(O_2CMe)H]$ with L {L = PF_3, PF_2(piperidino) or PF_2NMe_2} causes reduction to give a range of ruthenium(0) complexes, $[Ru(PPh_3)_{5-x}L_x]$ (x = 3, 4 or 5) [225]. In a similar manner, $[Ru(CO)(PPh_3)_3HCl]$ undergoes dehydrochlorination with diazabicycloundecene, in the presence of CO, to give $[Ru(CO)_3(PPh_3)_2]$ [222], whereas $[Ru(CO)_2(PPh_3)_2HCl]$ reacts with diazabicycloundecene and PPh_3 in boiling methanol to give $[Ru(CO)_2(PPh_3)_3]$ and $[Ru(CO)(PPh_3)_2(CN\text{-}4\text{-}C_6H_4)HCl]$ yields $[Ru(CO)(CN\text{-}4\text{-}C_6H_4)(PPh_3)_3]$ [222]. The photolysis of $[Ru_3(CO)_{12}]$ in the presence of an excess of a wide range of activated alkenes (*e.g.* methyl acrylate, dimethyl fumarate, dimethyl maleate, allyl acrylate, methyl vinyl ketone and acrylonitrile) yields $[Ru(CO)_4(alkene)]$, quantitatively [257].

Fuller details of the preparation of red $[Ru_2(CNCHMe_2)_9]$ from *trans*-$[Ru(CNCHMe_2)_4Cl_2]$, $CNCHMe_2$ and sodium amalgam in thf have now appeared [258]; the dimer is fluxional in solution, the process involving bridge-terminal exchange of ligands [258].

Some of the reactions of $[Ru(CO)_4H]^-$ (for example, its reaction with methanol to give $[HRu_3(CO)_{11}]^-$) have been explained in terms of a hydrogen migration mechanism involving formyl intermediates [238].

The remainder of the papers in this Section all deal with a growing range of complexes of diazabutadiene derivatives (see also [2; pp.122-124]. Thus, treatment of either $[Ru(PPh_3)_4H_2]$ or $[Ru(C_2H_4)(PPh_3)_2(C_6H_4PPh_2)H]$ with dab (dab = RN=CHCH=NR; R = C_6H_4-4-OMe) yields black diamagnetic crystals of $[Ru(dab)_3]$, which were characterised by X-ray crystallography {r(RuN) = 0.204-0.210 nm} [259]; this formally ruthenium(0) complex is unreactive towards dihydrogen or carbon monoxide, but is oxidised by $CHCl_3$, I_2, HCl or O_2 to give red $[Ru(dab)_3]^{2+}$ [259]. A ^{13}C VT NMR study of $[Ru_2(CO)_6(dab)]$ (dab = HN=CHCH=NH) has been published [260], the properties of $[M_2(CO)_6(dab)]$ (M = Fe, Ru or Os; dab = RN=CHCH=NR; R = CMe_2H or CMe_3) have been compared [261], and the use of HPLC in monitoring the formation of $[Ru_2(CO)_6(dab)]$ (dab = RN=CHCH=NR; R = CMe_2H or CMe_3) has been described [262]. $[Ru_2(CO)_6(dab)]$ (dab

= RN=CHCH=NR; R = CMe_2H or cych) reacts with ethyne to give $[Ru_2(CO)_4(dab)(HCCH)]$ **(40)**, and **(40**; R = $CHMe_2$) has been crystallographically characterised [263,264].



(40; R = $CHMe_2$)

Treatment of $[Ru_2(CO)_6(dab)]$ (dab = RN=CHCH=NR; R = CMe_3) with activated alkynes (such as MeO_2CCCCO_2Me) causes coupling of the dab and alkyne to form the 3-amino-4-imino-1-buten-1-yl (aib) ligand, resulting in complexes of the type $[Ru_2(CO)_5(aib)]$, $[Ru_2(CO)_5(aib)(alkyne)]$, and $[Ru_2(CO)_4(aib)(alkyne)]$, which are active catalysts for the cyclotrimerisation of alkynes [265]. The molecular structure of [2-phenyl-3-(tert-butylamino)-4-(tert-butylimino)--1-buten-1-yl]pentacarbonyldiruthenium was also reported [265]. Finally in this Section, a more detailed study of the reaction between $[Ru_3(CO)_{12}]$ and dab (dab = RN=CHCH=NR; R = CMe_2H, CHMeEt, CH_2CMe_3, $CH(CHMe_2)_2$, 2,4,6-$Me_3C_6H_2$ or cych) reveals products of stoicheiometry $[Ru(CO)_3(dab)]$, $[Ru_2(CO)_6(dab)]$, $[Ru_3(CO)_8(dab)]$ and $[Ru_4(CO)_8(dab)_2]$, the preferred product depending upon the reaction conditions used; the molecular structure of $[Ru_4(CO)_8(dab)_2]$ (R = $CHMe_2$) was determined by X-ray crystallography [266].

3.11 RUTHENIUM NITROSYLS

A review of the *trans* effect in ruthenium nitrosyl complexes has been published [267], along with yet another report of $[Ru(NO)Cl_3(PPh_3)_2]$ [268] and a further study of the reaction between $[Ru(NO)Cl_3(H_2O)_2]$ and glycine [269].

Aqueous solutions of $Na_2[^{106}Ru(NO)(NO_2)_4(OH)]$ have been studied by paper chromatography [270], their ageing to give dinitro and mononitro complexes investigated [270], and three more studies of the extraction of nitrosyl complexes from nitric acid using tributyl phosphate have appeared [271-273].

Related to the nitrosyl system, further details [2; p.122] of a number of diazocyclopentadiene complexes of ruthenium(0) have been published [274], and the complex $[Ru(NO_2)_6]^{4-}$ has been prepared (see Section 3.6.1) [69].

3.12 RADIONUCLIDES

The necessity for a rapid, simple preparation of "carrier-free" ^{97}Ru for the synthesis of complexes for medical use was emphasised in a recent and excellent review by Waters, published in this series [275], and details of such a preparation have now been published [276]. Alpha bombardment of natural molybdenum, followed by an ion-exchange separation using tin(IV) oxide, produces ^{97}Ru with an extraction efficiency of >95%. The gamma ray spectra of the target solution before and after separation are shown in Figs. 7 and 8. The level of ^{103}Ru, an undesirable long-lived contaminant, can be reduced by using enriched ^{94}Mo targets [276].

3.13 MISCELLANEOUS

The valence band structure of Ru_2P, RuP and RuP_2 has been determined [277], and the preparation of $ThRu_4P_{12}$ (from its elements) has been described [278]. ^{155}Gd Mössbauer spectra of $GdRuH_x$ (x = 0, 1 or 3) [279] and ^{99}Ru Mössbauer spectra of $(Ru,Pd)H_x$ (x<1) [280] have been reported, and the structure of $CeRu_2D_5$ has been determined by neutron diffraction [281].

Two reviews concerning absorption upon the basal plane of ruthenium have been published this year; one concentrates upon the absorption of water,

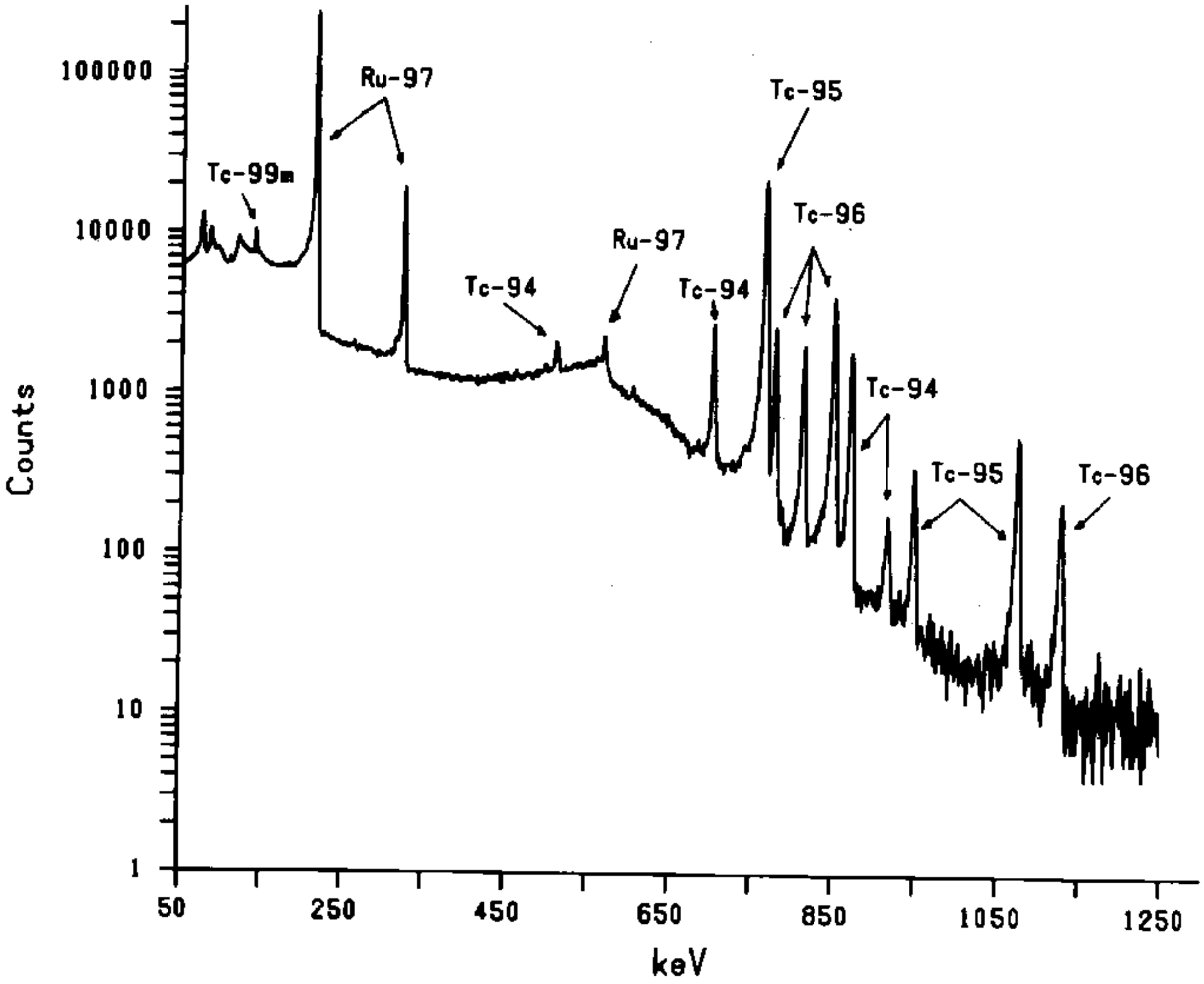


FIG. 7: The gamma-ray spectrum of the target solution at 34 h after the end of bombardment [276].

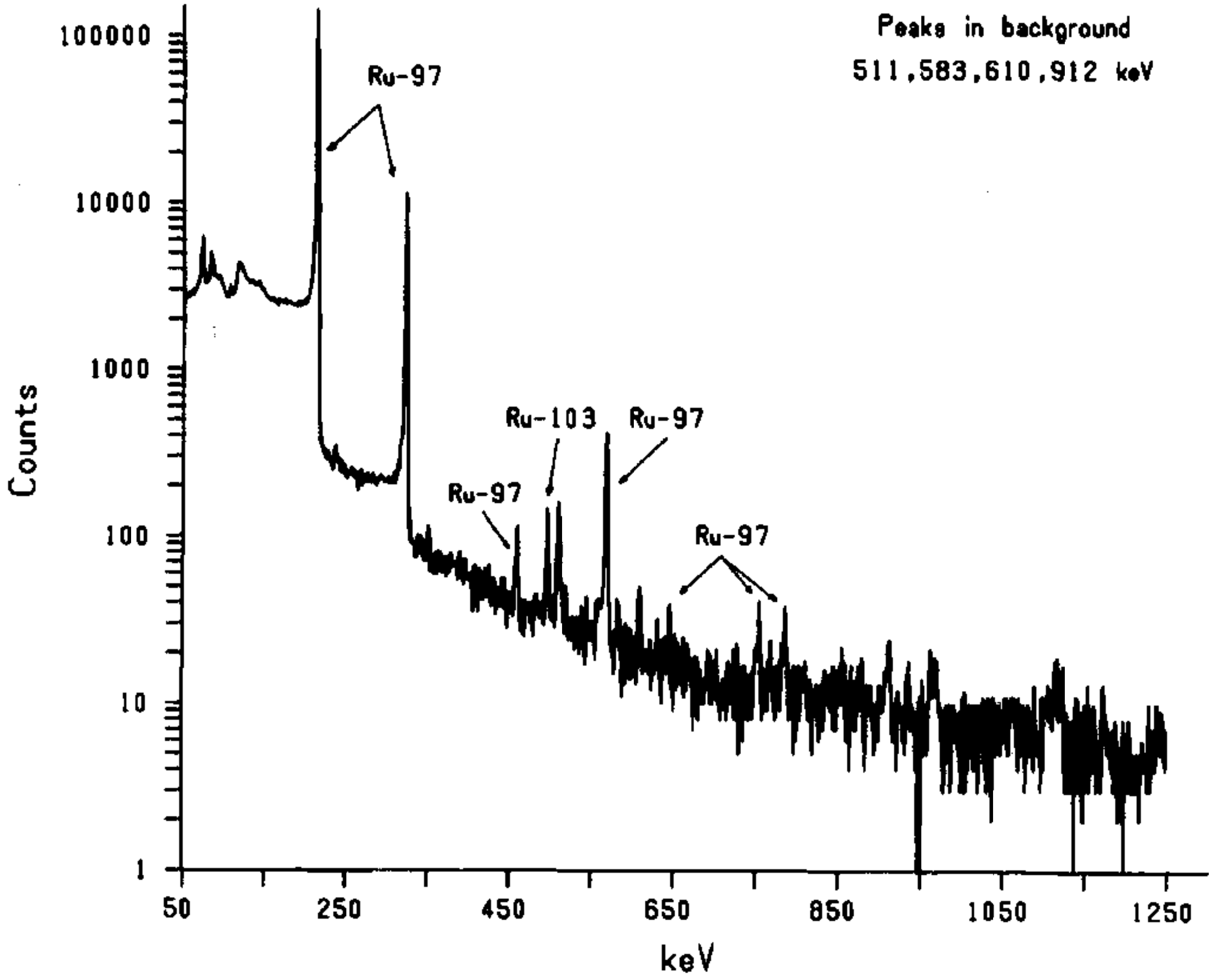


Fig. 8: Gamma-ray spectrum of separated ^{97}Ru [276].

carbon monoxide and dioxygen [282], whilst the other describes EELS studies of the absorption of nitrogen oxide, carbon monoxide and dihydrogen [283].

Ruthenium metal, prepared by reduction of RuO_2 with $Na[BH_4]$, will consistently catalyse deuterium exchange between organosilanes and perdeuteriobenzene, and this reaction may be utilised for tritium labelling of organosilanes [284]. Ruthenium metal supported on Al_2O_3 will catalyse the methanation of carbon dioxide [285,286], isotope exchange in CO [287] and the reduction of SO_2 [288]. A highly dispersed Ru/Al_2O_3 catalyst prepared from $[Ru_3(CO)_{12}]$ is much more active and selective for C_2-C_5 alkenes in the Fischer-Tropsch process than conventionally prepared catalyst, and this effect is promoted by the addition of potassium ions to the catalyst [289]. Dinitrogen has been detected (by IR spectroscopy) to adsorb to such catalysts [290]. A study of the H_2/D_2 isotope effects on Fischer-Tropsch syntheses over Ru/Al_2O_3 and Ru/SiO_2 reveals that CD_4 is formed some 1.4-1.6 times faster than CH_4 [291]; similar evidence for this inverse isotope effect was independently reported [292]. Ruthenium metal supported on SiO_2 has also been shown to catalyse carbon dioxide methanation [293], and the effects of using zeolite supports for ruthenium for the Fischer-Tropsch reaction have been investigated [294,295]. Finally, in this review, a 9.8% Ru/Pd alloy membrane will catalyse the selective hydrogenation of cyclopentadiene to cyclopentene in the presence of penta-1,3-diene and isoprene [296], although it will hydrogenate the last two dienes to alkenes in the absence of cyclopentadiene [297], and Ru/C will catalyse the hydrogenation of diphenylethyne [298].

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