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2. RUTHENIUM

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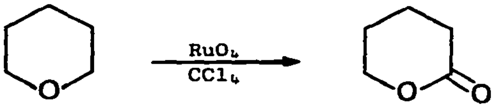
INTRODUCTION

The period of this review essentially coincides with the coverage of Vols. 92 and 93 of Chemical Abstracts. Thus, although the majority of the papers covered were published in 1980, many from 1979 are included. The review is a continuation of last year's [1], and no paper on the coordination chemistry of ruthenium has been deliberately omitted (although work of an essentially organometallic nature is not included). It is this essentially comprehensive approach which distinguishes these reviews from related reviews covering a similar period, produced by the Chemical Society [2]. The chemistries of ruthenium and osmium have now diverged to such an extent that it is no longer appropriate to consider them together. For this reason, separate reviews for these elements have been produced this year.

2.1 RUTHENIUM(VIII)

The use of RuO_4 for the oxidation of simple ethers has been further investigated. In homogeneous solution (*e.g.* in CCl_4), lactones are formed [3]:

e.g.



For two-phase (CCl_4/H_2O) catalytic reactions (the RuO_4 being regenerated with $Na[IO_4]$), oxidation to di-acids or ketones was typically observed [3]:

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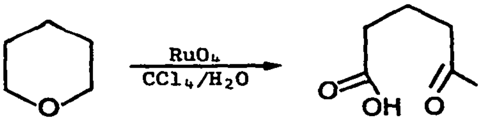
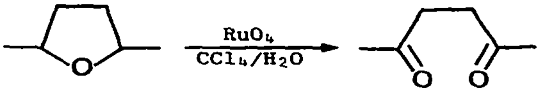




2.2 RUTHENIUM(VI)

A very useful compilation of the physical and chemical properties of RuF_6 and $RuOF_4$ has been published [4] and it has been reported that $RuOF_4$ can be converted into RuO_4 at room temperature by hydrolysis, followed by fluorination of the hydrosylate [5].

A correction to an earlier report [1; ref. 9] on the antiresonance Raman effect for $[RuO_4]^{2-}$ has been published [6].

2.3 RUTHENIUM(V)

2.3.1 Fluorides

The magnetic properties of $[Ru_4F_{20}]$ have been studied from 4.2-300 K. A maximum in the χ/T curve at 40 K does not correspond to T_N, however, and localised antiferromagnetic interactions within the tetrameric unit are responsible for the magnetic behaviour. This was confirmed by neutron diffraction measurements (4.2-77 K), as no long-range ordering was observed at 40 K [7]. A compilation of the chemical and physical properties of $[Ru_4F_{20}]$ has appeared [4] and its hydrolysis has been further studied [5].

Treatment of $[RuF_6]$ with NO, or a large excess of NOF, at room temperature yields $[NO][RuF_6]$, which has been characterised by Raman spectroscopy [8].

2.3.2 Oxides

Na_3RuO_4 has been studied by ^{99}Ru Mössbauer spectroscopy between 4.2 and 30 K, and the results are believed to contradict the published interpretation of its magnetic behaviour in terms of tetranuclear intracluster antiferromagnetism. Instead, it is proposed that Na_3RuO_4 shows antiferromagnetic three-dimensional long-range order, with T_N = 30 K [9]. ^{99}Ru Mössbauer studies and VT magnetic susceptibility measurements have also been reported for $BaLaM^{II}Ru^{V}O_6$ (M^{II} = Mg, Co, Ni or Zn): they show long-range antiferromagnetic order, with T_N ~20-40 K [10]. The preparations and characterisation of the novel cubic $Ba_2M^{III}Ru^{V}O_5$ (M^{III} = La, Nd, Sm, Eu, Gd, Dy or Y) and rhombically distorted $Sr_2M^{III}Ru^{V}O_6$ (M^{III} = Eu, Gd, Dy or Y) perovskites have been described; Ba_2ScRuO_6 has a hexagonal 6L structure [11].

2.4 RUTHENIUM(IV)

2.4.1 Fluorides

$[NO]_2[RuF_6]$ has been prepared by the prolonged reaction between $[NO][RuF_6]$ and an excess of NOF at 150 °C, and characterised by Raman spectroscopy [8]. The hydrolysis of RuF_4 has been studied [5] and a short review of $[RuF_6]^{2-}$ salts has been published [4].

2.4.2 Chlorides and oxochlorides

$[RuCl_6]^{2-}$ is reduced to $[RuCl_6]^{3-}$ by H• (generated by pulse radiolysis), whereas $[RuCl_6]^{3-}$ is oxidised to $[RuCl_6]^{2-}$ by $[Cl_2]^{\bar{\cdot}}$: both these hexachlororuthenate complexes have been characterised by electronic spectroscopy [12]. The reduction of $[RuCl_6]^{2-}$ by H_2 has also been studied in 6 *M* hydrochloric acid [13].

The syntheses of $[Ru_2OCl_6(NCR)_4]$ (R = Me, Ph, C_6H_4-2-Me or $CH_2{=}CHCH_2$), from "$RuCl_3.xH_2O$" and RCN, have been described [14]. These air-stable, violet dimers are diamagnetic and probably have a structure analogous to that of $[Ru_2OCl_{10}]^{4-}$. They are potentially very valuable synthetic reagents [15]:

e.g.

$$\begin{tikzcd} {[Ru_2OCl_6(NCR)_4] + 4[NEt_4]Cl} \arrow[r, "CH_2Cl_2"] & {[NEt_4][RuCl_5(NCR)]} \arrow[d, "dmf"] \\ & {[NEt_4][RuCl_5(dmf)]} \end{tikzcd}$$

(R = Me or Ph)

These reactions can be performed conveniently by generating $[Ru_2OCl_6(NCR)_4]$ *in situ*, and then treating the reaction mixture with the desired reagent (*e.g.* $[NEt_4]Cl$) [15].

Treatment of "$RuCl_3.xH_2O$" in 12 *M* hydrochloric acid (aged at 90 °C) with $[NEt_4]Cl$ in the presence of a few drops of mercury, followed by filtration and heating, leads to the isolation of a complex described as "$[NEt_4]_2[Ru_2Cl_7(OH)_3]$", which is stable in nitromethane solution but unstable in aqueous or MeCN solution. An analogous $[AsPh_4]^+$ salt has been isolated, and these complexes may well contain an Ru-O-Ru linkage [15].

2.4.3 Oxides and related mixed-valence compounds

The chemical diffusion coefficient for protons in crystalline RuO_2 powders (with varying chloride content) has been measured and correlated with data obtained for thin films [16]. Studies of the anodic evolution of O_2 on RuO_2 single crystals have led to the conclusion that its catalytic activity is not as great as that of poorly crystalline hydrous RuO_x. Nevertheless, the former is still a good stable electrode material for O_2 evolution, at potentials upto 1.6 V [17]. The reaction of $RuO_2.xH_2O$ with sulphuric acid at high temperatures has been studied [18]. The use of RuO_2 as a catalyst for the photodecomposition of water is discussed in Section 2.16.

The preparations and properties of RuO_2 and RuO_2/TiO_2 films have been described

[19], as has a method for determining their surface area [20]. Dichlorine evolution at RuO_2 coated Ti electrodes has been further studied [21] and these electrodes have also been used for the electro-oxidation of methanol [22]. The electrochemistry of RuO_2 and RuO_2/TiO_2 films in basic conditions has been investigated; redox reactions involving Ru(VI) and Ru(VII) species were observed [23].

The magnetic behaviour of $BaRuO_3$ has been reexamined in the light of its crystal structure and Mössbauer data: the absence of long-range magnetic ordering at low temperature is explained by spin-orbit coupling effects giving rise to a non-magnetic ground state ($J = 0$) for each site, when exchange is neglected. The exchange contribution between excited states was expressed in terms of isotropic coupling within the $\{Ru_3O_{12}\}^{12-}$ entity and the analysis agreed well with both the Mössbauer results and the magnetic susceptibility data [24]. As well as $BaRuO_3$, the compounds Ba_2RuO_4(tetragonal) and Ba_3RuO_5(rhombic) have been isolated from the BaO/RuO_2 system [25].

Bi_2O_3 reacts with RuO_2 to give the cubic phase $Bi_2Ru_2O_{7+x}$ ($x<0.2$; $a = 0.9300$ nm), which irreversibly gives the pyrochlore $Bi_2Ru_2O_7$ at temperatures above 975 °C [26]. The Bi_2O_3/RuO_2 system also yields $Bi_3Ru_3O_{11}$ (b.c.c.) and Bi_8RuO_{14} (monoclinic) under appropriate conditions [27], and preparations of $PbBi_2Ru_3O_{10}$, $Pb_2Bi_2Ru_4O_{13}$ and $Pb_3Bi_2Ru_4O_{14}$ have been reported [28]. A new and facile route to $A_2Ru_2O_{7-y}$ (A = Pb or Bi) and to $(Pb,Bi)_2Ru_2O_{7-y}$ has been developed, based on precipitation from aqueous solution of mixtures of the nitrate salts with base at 75 °C, followed by prolonged digestion [29]. The powders which have X-ray diffraction characteristics identical to those of conventionally prepared materials have a high surface area and are useful for the construction of *catalytic* oxygen electrodes (*cf.* [1; p. 44]). The preparation of $Pb_2(Ru_{2-x}Pb_x)O_{7-y}$ has also been described and its use in oxygen reduction illustrated [30]. The specific heats of the pyrochlores $Cd_2Ru_2O_7$ [31] and $Y_2Ru_2O_7$ [32] have been measured below 20 K, and the formation of solid solutions $Nd_2(M,M')_2O_7$ (M,M' = Ru, Sn, Sb, Ti), with the pyrochlore structure, have been studied from 1300 to 1350 °C [33]. The temperature and concentration dependence of the electrical conductivity of $Nd_2(Ru_xSn_{1-x})O_7$ ($0<x<0.5$) were also investigated in this study: the *n*-type semiconductivity increases smoothly with an increasing proportion of $Nd_2Ru_2O_7$, upto 30 mol%, and then abruptly increases more rapidly [33].

Magnetic studies of Li_xRuO_2 (x ~1.3) indicate that its susceptibility behaviour with temperature is not very different from that of RuO_2, suggesting that the insertion of lithium does not produce localised electron density on the ruthenium [34]. In contrast, for the perovskites $(ACu_3^{II})(Ru_4)O_{12}$ (A = Na, Ca, Sr, Cd, La, Pr or Nd), a change in the charge on A is balanced by the introduction of a Ru^{III} or Ru^{V} ion: these compounds were characterised by X-ray powder crystallography and χ/T plots [35]. The new, mixed-valence, oxides

$Ba_4NbRu_3O_{12}$ and $Ba_4TaRu_3O_{12}$ have been prepared and structurally characterised: they contain the trinuclear unit $\{Ru_3O_{12}\}^{13-}$; their low temperature magnetic properties have been determined and rationalised [36].

The magnetic and structural properties of the K_2NiF_4 phases, $Sr_2(Fe_xRu_{1-x})O_4$ ($0 \le x \le 0.5$), have been studied by ^{57}Fe and ^{99}Ru Mössbauer spectroscopy and magnetic susceptibility measurements. For $x \le 0.4$, the iron is present as Fe^{III} and the ruthenium as Ru^{IV} and Ru^{V}; at $x = 0.5$, partial oxidation of Fe^{III} to Fe^{IV} has occurred; even at $x = 0.1$, the Pauli paramagnetism of Sr_2RuO_4 has given way to long-range antiferromagnetic ordering and localised-electron behaviour [37]. ^{99}Ru Mössbauer spectra and VT magnetic susceptibility measurements upon $La_2MRu^{IV}O_6$ (M = Mg, Co, Ni or Zn) and $BaLaFe^{III}Ru^{IV}O_6$ have been reported; the La_2MRuO_6 phases are not magnetically ordered at 4.2 K [10].

Heating a mixture of La_2O_3, Ru and RuO_2 yields the unusual phase $La_{3.5}Ru_4O_{13}$. Its crystal structure has been determined and its lattice is composed of perovskite-type slabs, three-octahedra thick {parallel to (100)}, linked together by La atoms or $\{RuO_6\}$ octahedra (the latter being joined together by opposite edges to form one-dimensional infinite chains parallel to the *b* axis) [38].

2.4.4 *Sulphides*

Amorphous, low-spin, RuS_2 has been prepared by treating anhydrous $RuCl_3$ with $[NH_4][HS]$ in an ethereal solution at room temperature, followed by heating the isolated product in a stream of H_2S at 250 °C [39]. The high temperature (374–1480 K) enthalpy of $RuS_2(s)$ has been measured and decomposition pressures have been determined for the reaction:

$$RuS_2(s) \longrightarrow Ru(s) + S_2(g)$$

This yielded [40]:

$$Ru(s) + 2S(rh) \longrightarrow RuS_2(s);\ \Delta H_f^\circ(298\text{ K}) = -199\text{ kJ mol}^{-1}$$

2.4.5 *Other complexes*

$[Ru(bipy)_2(py)(OH_2)]^{2+}$ or $[Ru(terpy)(bipy)(OH_2)]^{2+}$ can be electrochemically oxidised to $[O{=}Ru(bipy)_2(py)]^{2+}$ or $[O{=}Ru(terpy)(bipy)]^{2+}$ at potentials of 0.6–0.8 V (*vs.* SCE). These ruthenium(IV) species are active oxo-transfer agents and can induce the following chemically catalysed electrochemical oxidations [41]:

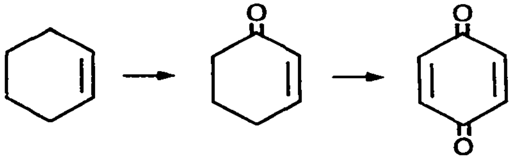
$$Me_2CH(OH) \longrightarrow Me_2C{=}O$$

$$C_2H_5OH \longrightarrow [CH_3CO_2]^-$$

$$CH_3CHO \longrightarrow [CH_3CO_2]^-$$

$$C_6H_5CH_3 \longrightarrow [C_6H_5CO_2]^-$$

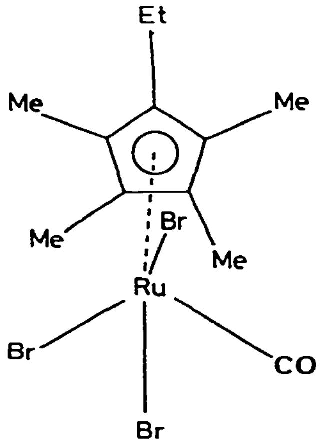
$$1,4\text{-}Me_2C_6H_4 \longrightarrow [C_6H_4\text{-}1,4\text{-}(CO_2)_2]^{2-}$$



Ethene was unreactive under these conditions [41].

The ruthenium(IV) complexes, $[RuH_3(SiR_3)L_n]$ (R_3 = F_3, MeF_2, Cl_2Me, $(OEt)_3$, $ClMe_2$, HPh_2, $MePh_2$ or Ph_3; L = PPh_3, $AsPh_3$ or $P(C_6H_4\text{-}4\text{-}Me)_3$; n = 2 or 3) have been prepared by the reaction of an excess of $HSiR_3$ with $[RuH_2L_4]$, $[RuHClL_3]$, $[RuCl_2L_3]$ or $[RuCl_3(AsPh_3)_3]$. The corresponding $[RuH_2Cl(SiCl_3)L_3]$ compounds were prepared by the reaction of $[RuHClL_3]$ with $HSiCl_3$. $[RuH_2X\{Si(OEt)_3\}L_3]$ (X = Cl or I) have been obtained by the treatment of $[RuH_3\{Si(OEt)_3\}(PPh_3)_3]$ with $CDCl_3$ or I_2. The complexes $[RuH_3(SiR_3)L_3]$ undergo silyl exchange or H-D exchange with $HSiR'_3$ or D_2, respectively [42].

Halogenation of $[Ru_2(C_5Me_4Et)_2(CO)_4]$ has been reported to give, initially, $[(C_5Me_4Et)Ru(CO)_2(\mu\text{-}X)Ru(CO)_2(C_5Me_4Et)]^+$ (X = Cl, Br or I), and then, for the bromide, an unusual ruthenium(IV) organometallic derivative $[Ru(C_5Me_4Et)(CO)Br_3]$ (1) is formed. (1) is air-stable, and has been characterised crystallographically.

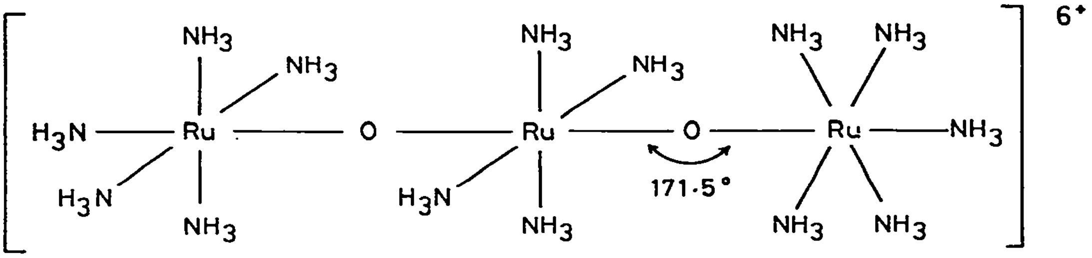


(1)

It shows a displacement of the alkyl carbon atoms *ca.* 0.014 nm away from the Ru atom, with r(CO) = 0.187 nm and $\bar{r}$(RuBr) = 0.2547 nm [43].

2.5 Ru(IV/III), MIXED-VALENCE COMPLEXES

An X-ray crystal structure determination of a ruthenium red salt, $[Ru_3O_2(NH_3)_{14}][S_2O_3]_3.4H_2O$ has revealed a surprising structure for the cation $[Ru_3O_2(NH_3)_{14}]^{6+}$ (2). Although it possesses the expected essentially linear Ru-O-Ru-O-Ru backbone, the ion does not possess a centre of symmetry. One of the terminal $\{Ru(NH_3)_5\}$ groups is twisted through 31°, with respect to the two, essentially eclipsed (dihedral angle = 4°), $\{Ru(NH_3)_5\}$ and $\{Ru(NH_3)_4\}$ groups. r(RuO) lies in the range 0.1845–0.1857 nm but individual bonds are not significantly different in length [44]. The resonance Raman spectra of ruthenium red, ruthenium brown, $[Ru_3O_2(NH_3)_{10}(en)_2]^{6+}$ and $[Ru_3O_2(NH_3)_{10}(en)_2]^{7+}$ have been reported: their excitation profiles have maxima close to the intense visible absorption bands and it was found that *all* of the a_{1g} modes (and some of the a_{2u} modes) were enhanced (and *not* just those associated with the Ru–O stretching frequencies) [45]. The use of ruthenium red as a staining reagent in optical and electron microscopy has been reviewed [46].



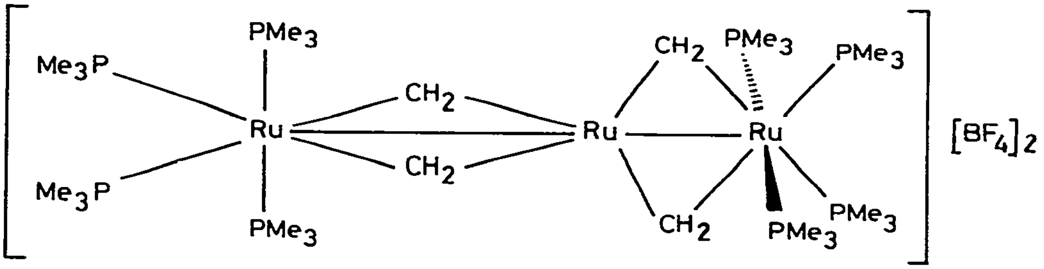
(2)

Treatment of $[Ru(NH_3)_5(Me_2CO)]^{2+}$ with O_2 (under anhydrous conditions) generates the novel, red, dimeric complex $[(NH_3)_5RuORu(NH_3)_5]^{4+}$, clearly related to ruthenium red. Oxidation of this complex with bromine generates the mixed-valence species $[(NH_3)_5RuORu(NH_3)_5]^{5+}$. The tetrapositive cation is unstable in solutions over long periods (>1 h) but the pentapositive cation is significantly more stable. In MeCN, the following CV behaviour (L = NH_3) was observed [47]:

$$[L_5RuORuL_5]^{6+} \xleftarrow[+1.67\ V]{-e^-} [L_5RuORuL_5]^{5+} \underset{+0.32\ V}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} [L_5RuORuL_5]^{4+} \xrightarrow[-1.98\ V]{+e^-} [L_5RuORuL_5]^{3+}$$

Thus, the ruthenium(IV) analogue of $[Ru_2OCl_{10}]^{4-}$, with all ammine ligands, is unstable. Salts of $[(NH_3)_5RuORu(NH_3)_5]^{4+}$ and $[(NH_3)_5RuORu(NH_3)_5]^{5+}$ (and their perdeuterated analogues) have been characterised by XPES, UV-VIS and IR spectroscopy. The Ru-O-Ru bridge appears to be bent, and μ_{eff} (per Ru atom) is *ca.* 1.15 μ_B at room temperature and 0.38 μ_B at 18.4 K [47].

The treatment of a red oil formed in the preparation of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ [1; p. 49] with aqueous $H[BF_4]$ gives $[(Me_3P)_4Ru^{III}(\mu\text{-}CH_2)_2Ru^{IV}(\mu\text{-}CH_2)_2Ru^{III}(PMe_3)_4][BF_4]_2$ (3) and a dimeric ruthenium(II) complex $[Ru_2(\mu\text{-}OH)_3(PMe_3)_6][BF_4]$. The molecular structure of (3) involves a metal-metal separation of 0.2637 nm [48]. The mixed-valence complex $[C_{12}H_{25}NH_3]_3[Ru_2O_2(SO_4)_3(H_2O)_2]$ has also been reported [49].



(3)

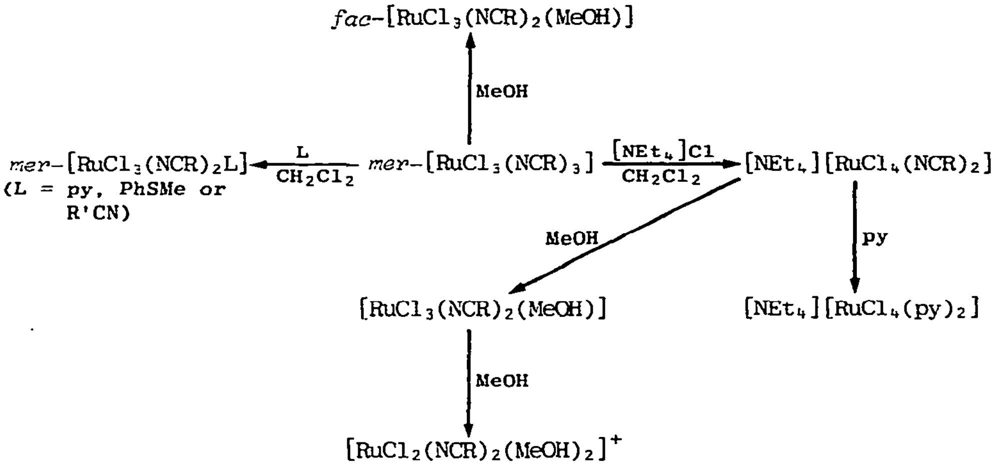
2.6 RUTHENIUM(III)

2.6.1 Halides and halide complexes

Further studies of "$RuCl_3.xH_2O$" or "$RuCl_3(OH)$" have been discussed in terms of the multicomponent and heterogeneous nature of these materials [50]. However, the fact that commercial "$RuCl_3.xH_2O$" is a mixture of, *inter alia*, chlororuthenium(III), chlororuthenium(IV) and chloronitrosylruthenium complexes cannot receive too much publicity, as many papers are still being published where this is clearly not appreciated. One report this year, which highlights this problem, is the formation of an ammine derivative of ruthenium(III), where the only source of nitrogen was "$RuCl_3.xH_2O$" (see Section 2.6.7) [51]. The ageing of solutions of "$RuCl_3.xH_2O$" in hydrochloric acid media has been studied by electronic absorption spectroscopy [50], and "$RuCl_3.xH_2O$" in sodium hydroxide solution has been used as a chirality transfer reagent, in the stereospecific isomerisation of chiral allyl alcohols to chiral acyclic ketones [52]. $RuCl_3$ (origin and nature unspecified) reacts with cyclopropane and CO in benzene solution to give a mixture of $PhCH_2CH_2CH_3$ and $PhCHMe_2$ (44:56), but no chlorobutanoates [53].

Crystals of KCl, or NaCl, doped with $RuCl_3$ have been studied by optical absorption spectroscopy; the bands observed at 43480, *ca.* 31000 and *ca.* 26800 cm^{-1} were assigned to $[RuCl_6]^{3-}$ and a band at *ca.* 40000 cm^{-1} was assigned to an $[RuCl_6]^{2-}$ impurity [54]. $[C_{12}H_{25}NH_3]_3[RuCl_6]$ has been isolated by solvent extraction and characterised by electronic absorption spectroscopy [55].

Treatment of "$RuCl_3.xH_2O$" with RCN in methanol at 70 °C produces *mer*-$[RuCl_3(NCR)_3]$ (R = Me, Ph, C_6H_4-2-Me, C_6H_4-3-Me or $CH_2{=}CHCH_2$), with the corresponding salt $[Ru^{II}Cl(NCR)_5][Ru^{III}Cl_4(NCR)_2]$ (R = Me, Ph, C_6H_4-2-Me, C_6H_4-3-Me, C_6H_4-4-Cl, $CH_2{=}CH$ or $CH_2{=}CHCH_2$) formed as a by-product [14]. $[RuCl_3(NCR)_3]$, like its vanadium(III) and titanium(III) analogues, promises to be a very useful synthetic reagent. In particular, the compound can be prepared *in situ* and used without isolation. Some of the reactions of this compound are given in Scheme I [14,15].



SCHEME I: The use of *mer*-$[RuCl_3(NCR)_3]$ for the synthesis of other ruthenium(III) complexes [14,15].

2.6.2 Complexes with oxygen donor ligands

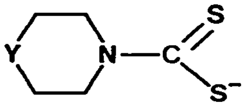
The electronic absorption spectrum of $[Ru(H_2O)_6]^{3+}$ has been measured, and fitted to Tanabe-Sugano matrices to yield values for the ligand-field parameters, 10 Dq = 28600 cm^{-1} and B = 640 cm^{-1} [56]. The pK_a value for the formation of $[Ru(H_2O)_5(OH)]^{2+}$, from the hexaaqua cation, has been measured as 2.4 at 20 °C and the CT bands of $[Ru(H_2O)_6]^{3+}$ and $[Ru(H_2O)_5(OH)]^{2+}$ interpreted in terms of the optical electronegativities of H_2O and $[OH]^-$ [56].

The temperature dependence of the CH_3 isotropic shifts in $[Ru(acac)_3]$ has been studied [57], its ^{13}C relaxation times (T_1 and T_2) have been calculated and compared with the experimental value [58], and the kinetics of ligand exchange between $[Ru(acac[2-{}^{14}C])_3]$ and acacH have been investigated [59]. Treatment of $[RuCl_3(PPh_3)_3]$ with $MeC(O)CH_2C(O)CH_2(CO)Ph$ yields $[Ru(acac)(CO)(PPh_3)Cl_2]$ [60].

$[Ru_3O(O_2CMe)_6(OH_2)_3]^+$ has been shown to be an active catalyst, in a two-liquid phase system, for the isomerisation of allyl alcohols to saturated ketones [61].

2.6.3 *Complexes with sulphur donor ligands*

The complexes $[Ru(S_2CNR_2)_3]$ {R = Me, Et, Pr, $CHMe_2$ or $(CH_2)_2$} and $[RuL_3]$ {L = (4; CH_2 or O)} have been studied by a variety of electrochemical methods [62].



(4)

The complexes $A[RuCl_4(MeSCH_2CH_2SMe)]$ (A = $[NMe_4]$ or $[PPh_4]$) have been prepared by treatment of "$RuCl_3.xH_2O$" with $MeSCH_2CH_2SMe$ in EtOH or Me_2CO, in the presence of ACl [63]. Ruthenium(III) complexes with the following ligands have also been reported: 4-quinolinedithiocarboxylic acid [64], 3,4,5-pyridazinetrithiol [65], *N*-phenylcarbamoylpyrrole-2-thiocarboxamide [66], piperazine(dithiocarboxylic acid) [67], piperazinebis(dithiocarboxylic acid) [67], 1,2,4-triazoline-5-thione derivatives [68], bis(4-ethylphenyl)dithiophosphinic acid [69] and 1-imino-3-thioisoindoline [70].

2.6.4 *Ammine and amine complexes*

NMR studies of aqueous solutions containing $[Ru(NH_3)_6]^{3+}$ have been used to probe the second coordination sphere of this complex; it was deduced that the distance of closest approach of the water to the cation is 0.39 nm and the structure of the second coordination sphere has been discussed [71]. Contact and *pseudo*contact shifts for $[Ru(NH_3)_6]^{3+}$ have also been calculated [72]. $[Ru(NH_3)_6]^{3+}$ has been studied in the salts $[Ru^{III}(NH_3)_6][Fe^{II}(CN)_5L].xH_2O$ (L = CO, CN, dmso, pz, py or imidH), which show intervalence transitions in their visible spectra, of an energy very dependent upon L, whereas $[Ru^{III}(NH_3)_6][Fe^{III}(CN)_6]$ shows no similar phenomenon [73].

$[Ru(NH_3)_6]^{3+}$ has been used to load a NaY zeolite with ruthenium metal [74]. Indeed, Fischer-Tropsch catalysts on Faujasite-type zeolites normally involve the degradation of a metal complex to its metallic state before activity is observed [75,76]. However, when $[Ru(NH_3)_6]^{3+}$ is supported on a Faujasite-type zeolite (X or Y) and thermally activated at 240-280 °C, a complex (postulated as $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$) is formed which is very active for the water gas shift reaction ($H_2O + CO \rightleftharpoons CO_2 + H_2$); this complex is stable upto 280 °C, whence it loses activity irreversibly [77].

Raman and far IR spectra of $[Ru(NH_3)_5X]Y_2$ ($X \neq Y$; X = Cl, Br or I; Y = Cl, Br, I, $[ClO_4]$ or $[NO_3]$) and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ have been recorded and analysed [78]. The aquation of $[Ru(NH_3)_5Cl]^{2+}$ in acidic aqueous solution at 60 °C has been reinvestigated: the volume of activation is $-30\ cm^3\ mol^{-1}$ at zero pressure and shows a high pressure dependence. For the reverse anation process, $\Delta V^* = -20\ cm^3\ mol^{-1}$. These results provide strong evidence that, for this reaction and other simple substitution reactions of ruthenium(III) complexes, the mechanism is associative (A, or S_N2 limiting) in acid conditions [79]. The equilibrium constants for:

$$[Ru(NH_3)_5(H_2O)]^{n+} + NH_{3-x}R_x \rightleftharpoons [Ru(NH_3)_5(NH_{3-x}R_x)]^{n+} + H_2O$$
$$(n = 2 \text{ or } 3) \quad (x = 2,\ 1 \text{ or } 0)$$

have been measured for various amino acid esters ($NH_{3-x}R_x$): affinity of these ligands for both ruthenium(III) and ruthenium(II) was found to decrease as x increased [80]. The acid hydrolysis of $[Ru(NH_3)_5(NH_2CH_2CO_2Et)]^{3+}$ gives a mixture of $[Ru(NH_3)_5(OH_2)]^{3+}$ and $[EtO_2CCH_2NH_3]^+$ and of $[Ru(NH_3)_5(O_2CCH_2NH_3)]^{3+}$ and and EtOH. The reaction proceeds *via* an initial isomerisation of the ethyl glycinate complex to $[Ru(NH_3)_5\{OC(OEt)CH_2NH_2\}]^{3+}$; the protonation of the amine function prevents reversal to the *N*-bonded isomer, followed by competing ester hydrolysis and aquation reactions [81].

The complexes $[Ru(NH_3)_5(O_2CR)]^{2+}$ (R = CCl_3, $CHCl_2$, CH_2X, CH_3, Et, $CHMe_2$ or H; X = F, Cl, Br, I, OH or NH_2) have been studied by polarography and electronic absorption spectroscopy [82]. The reduction of $[Ru(NH_3)_6]^{3+}$, $[Ru(NH_3)_5(py)]^{3+}$, $[Ru(NH_3)_4(py)_2]^{3+}$ or $[Ru(NH_3)_4(bipy)]^{3+}$ by H_2S has been demonstrated to occur efficiently at pH 4, producing elemental sulphur [83]. The kinetics for the $[Ru(NH_3)_5(py)]^{3+}/[Ru(NH_3)_5(py)]^{2+}$ couple has been estimated by studying the rates of electron-transfer reactions between $[Ru(NH_3)_5(isonic)]^{3+}$ and $[Ru(NH_3)_5(nic)]^{2+}$, and between $[Ru(NH_3)_5(nic)]^{3+}$ and $[Ru(NH_3)_5(isonic)]^{2+}$ [84]. The kinetics of the reactions between $[Ru(NH_3)_5(isonic)]^{n+}$ (n = 2 or 3) and superoxide, $[O_2]^{\dot{-}}$, have been determined [85]:

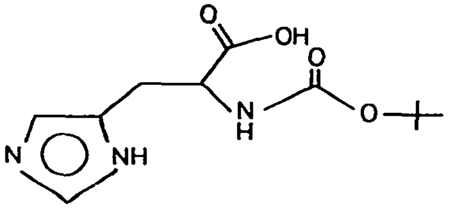
$$Ru(III) + [O_2]^{\dot{-}} \longrightarrow Ru(II)$$

$$Ru(II) + [HO_2]^{\bullet} \longrightarrow Ru(III)$$

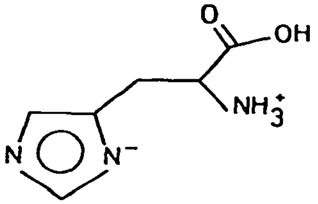
The rates of reduction of $[Ru(NH_3)_5(isonic)]^{3+}$ by $\cdot OH$, $H\cdot$, e^-, $[CO_2]^{\dot{-}}$ and $H\dot{C}(OH)_2$ were also derived, as was the rate of oxidation of $[Ru(NH_3)_5(isonic)]^{2+}$ by $\cdot OH$ [85]. The kinetics of the electron-transfer reaction between $[Ru(NH_3)_5L]^{3+}$

(L = py or 4,4'-bipy) and $[\mathrm{Co(edta)}]^{2-}$ have been reported [86].

Work on binuclear imidazole complexes [1; p. 48] has now been extended to encompass histidine derivatives. The complex *trans*-$[\mathrm{Ru(NH_3)_4(SO_4)(bochisH)}][\mathrm{BF_4}]$ (5) was prepared by treatment of *trans*-$[\mathrm{Ru(NH_3)_4(SO_4)(H_2O)}]$ with (6) in the presence of $\mathrm{H[BF_4]}$, followed by oxidation with $\mathrm{H_2O_2}$. Reaction of (5) with *trans*-$[\mathrm{Ru(NH_3)_4(SO_3)(H_2O)}]$, in the presence of $\mathrm{Li[OH]}$, followed by treatment with $\mathrm{H[BF_4]}$ and $\mathrm{H_2O_2}$, results in the dimerisation and hydrolysis of the protecting butoxycarbonyl group, to yield *trans*-$[\mathrm{(SO_4)(H_3N)_4Ru(his)Ru(NH_3)_4(SO_4)}][\mathrm{BF_4}]$. Reduction of this dimeric species with $[\mathrm{Ru(NH_3)_5(hisH)}]^{2+}$ results in the formation of a mixed-valence neutral dimer (IT = 8600 $\mathrm{cm^{-1}}$) [87].



(6; bochisH)



(7; hisH)

Photolysis of *cis*- or *trans*-$[\mathrm{Ru(en)_2Cl_2}]^+$ in aqueous solution at energies corresponding to ligand field transitions result in aquation and isomerisation, yielding mixtures of *cis*- and *trans*-$[\mathrm{Ru(en)_2(H_2O)Cl}]^{2+}$ (ϕ ~0.003-0.005): *cis*- or *trans*-$[\mathrm{Ru(en)_2(H_2O)Cl}]^{2+}$ are photoconverted into each other (ϕ ~0.04) [88]. The complexes *trans*-$[\mathrm{Ru(LL)_2X_2}]^+$ (LL = en, 1,3-pn or dmen; X = Cl, Br or I) and *trans*-$[\mathrm{Ru(L_4)X_2}]^+$ ($\mathrm{L_4}$ = 2,3,2-tet, 3,2,3-tet, 3,3,3-tet, cyclam or $[14]\mathrm{aneS_4}$; X = Cl, Br or I) have been prepared by a modification of the conventional route and characterised by IR and UV-VIS spectroscopy and μ_{eff} measurements [89]. The complexes *cis*- or *trans*-$[\mathrm{Ru(L_4)X_2}]^+$ and *cis*- or *trans*-$[\mathrm{Ru(L_4)(H_2O)X}]^{2+}$ ($\mathrm{L_4}$ = $\mathrm{(NH_3)_4}$, $\mathrm{(en)_2}$, 2,3,2-tet or cyclam; X = Cl or Br) have been studied by CV and the kinetics of aquation of their ruthenium(II) analogues have been determined [90]. Treatment of $\mathrm{K_2[RuCl_5(H_2O)]}$ with cyclam results in the formation of a mixture of *cis*- and *trans*-$[\mathrm{Ru(cyclam)Cl_2}]\mathrm{Cl}$; the isomers can be separated by ion-exchange and gel-filtration chromatography [91].

The complexes $[\mathrm{Ru(H_3ATP)(H_2O)_4}]\mathrm{Cl_2}$ ($\mathrm{H_4ATP}$ = adenosine triphosphate) [92] and $[\mathrm{RuCl_3L_2}]$ (L = 3,3'-dimethoxy- or 3,3'-dimethylbenzidine) [93] have been reported.

2.6.5 *Diimine complexes*

The rates of oxidation of $[\mathrm{Co(LL)_3}]^{2+}$ (LL = bipy or phen) by $[\mathrm{Ru(bipy)_3}]^{3+}$ have been determined using flash photolysis techniques [94], and a detailed study of the oxidation of cyclohexanone by $[\mathrm{Ru(bipy)_3}]^{3+}$ has been reported [95,96].

The oxidation of water by $[Ru(bipy)_3]^{3+}$ has been investigated in a further and independent study and "covalent hydration" of the coordinated ligand again postulated (with very little supporting evidence) [97].

Although claims for the existence of such complexes as *trans*-$[Ru(bipy)_2Cl_2]$ [98] and *trans*-$[Ru(bipy)_2(py)_2]^{2+}$ [99] have been made recently, they were unconfirmed and poorly supported by experimental evidence (although, nevertheless, probably correct). Now, convincing proof that such isomers exist has been published. $[Ru(bipy)_2(H_2O)_2]^{2+}$, as produced by the acid hydrolysis of *cis*-$[Ru(bipy)_2(CO_3)]$ has a *cis* configuration and it has been demonstrated that this complex will undergo photoisomerisation in aqueous solution, according to:

$$\textit{cis}\text{-}[Ru(bipy)_2(H_2O)_2]^{2+} \overset{h\nu}{\rightleftharpoons} \textit{trans}\text{-}[Ru(bipy)_2(H_2O)_2]^{2+}$$

In the presence of $[ClO_4]^-$, photochemical oxidation to $[Ru(bipy)_2(OH_2)(OH)]^{2+}$ occurs, and the *trans* isomer of $[Ru(bipy)_2(OH_2)(OH)][ClO_4]_2$ has been structurally characterised $\{\bar{r}(RuN) = 0.2095$ nm; $\bar{r}(RuO) = 0.2007$ nm$\}$ [100].

Electrochemical oxidation of $[Ru(bipy)_2L(NO_2)]^+$ ($L = NH_3$, py, pz, MeCN or PPh_3) or $[Ru(bipy)_2Cl(NO_2)]$ proceeds according to:

$$\begin{tikzcd}
2[Ru(bipy)_2L(NO_2)]^+ \arrow[r, "-2e^-"] & 2[Ru(bipy)_2L(NO_2)]^{2+} \arrow[d] \\
& {[Ru(bipy)_2L(NO)]^{3+} + [Ru(bipy)_2L(NO_3)]^+} \arrow[d, "-e^-"] \\
& {[Ru(bipy)_2L(NO_3)]^{2+}}
\end{tikzcd}$$

The oxidation of the coordinated nitro group proceeds *via* isomerisation of the Ru^{III}-*N*O_2 linkage to Ru^{III}-*O*NO, followed by reaction with $[Ru^{III}(bipy)_2L(NO_2)]^{2+}$ [101].

The complexes $[Ru(terpy)Cl_3]$ [102] and $[Ru(biquin)Cl_3]$ [93] have been prepared by treatment of "$RuCl_3.xH_2O$" with the diimine ligand.

2.6.6 *Porphyrin and phthalocyanine complexes*

The discussion of ruthenium(III) porphyrin and phthalocyanine complexes is reserved until Section 2.8.5.

2.6.7 Phosphine and arsine complexes

As a by-product of the reaction between "$RuCl_3.xH_2O$" and $P(OMe)_3$ in refluxing methanol, the complex *mer,trans*-$[RuCl_3\{P(OMe)_3\}_2(NH_3)]$ was isolated as red crystals and structurally characterised [51]. The source of the NH_3 was the "$RuCl_3.xH_2O$" (see Section 2.6.1) in which, as long ago as 1966 [103], nitrosyl impurities have been reported.

An electrochemical study of a wide range of $[RuCl_3L_3]$ (L = phosphines or arsines), $[RuCl_4L_2]^-$ (L = phosphines or arsines), and $[RuCl_3LL'_n]$ (L = phosphines or arsines; L' = amines or nitriles; *n* = 1 or 2) complexes has been reported. Most of the neutral complexes show a reversible one-electron reduction but an irreversible one-electron oxidation, whereas the anionic complexes show irreversible reduction and *quasi*-reversible oxidation behaviour [104]. Studies of solutions of $[RuCl_3(AsPh_3)_2(MeOH)]$ in CH_2Cl_2 have indicated that the expected dimerisation

$$2[RuCl_3(AsPh_3)_2(MeOH)] \longrightarrow [Cl_2(Ph_3As)_2Ru(\mu\text{-}Cl)_2Ru(AsPh_3)_2Cl_2]$$

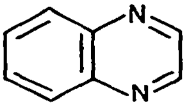
occurs within a few minutes of dissolution. *No* evidence was obtained for the existence of the purported [105] five-coordinate $[RuCl_3(AsPh_3)_2]$ complex [104]. EPR measurements on a similar range of complexes, $[RuX_3L_3]$, $[RuX_3L_2]$, $[RuX_4L_2]^-$, $[RuX_3L_2(solvent)]$ and $[RuX_2(dik)L_2]$ (L = PPh_3 or $AsPh_3$; X = Cl or Br), have also been reported [106], as have UV-VIS and EPR spectra and μ_{eff} measurements for $[RuX_3L_n]$,$[RuX_3L_2(MeOH)]$ and $[RuX_3L(CNC_6H_4\text{-}4\text{-}Me)_2]$ (X = Cl or Br; L = PPh_3 or $AsPh_3$; *n* = 2 or 3) [107,108].

2.7 Ru(III/II), MIXED-VALENCE COMPLEXES

$\{Ru_2(O_2CMe)_4Cl\}_n$ must be one of the most popular molecules with crystallographers, as the results of two more independent X-ray studies have been published for the anhydrous material this year [109,110] {*r*(RuRu) = 0.2287 nm; *r*(RuCl) = 0.2577 nm; *cf.* [1; p.46, Table 1]}. The results of SCF-Xα-SW calculations upon $[Ru_2(O_2CH)_4Cl_2]^-$, $[Ru_2(O_2CH)_4]^+$ and $[Ru_2(O_2CH)_4]$ have been reported; the mixed-valence complexes are predicted to have a $\sigma^2\pi^4\delta^2(\pi^*)^2(\delta^*)^1$ configuration, corresponding to the experimentally verified three unpaired electrons per dimeric unit. The band in the electronic spectrum of $\{Ru_2(O_2CR)_4\}^+$ at *ca.* 20000 cm^{-1} is assigned to an $O\pi \rightarrow \pi^*$ transition (where $O\pi$ is principally a Ru–O orbital but contains a significant amount of Ru–Ru π character), and the band at *ca.* 10000 cm^{-1} is assigned to the $\delta\rightarrow\delta^*$ transition [111]. The previous assignments of the $\delta\rightarrow\delta^*$ transition to the band at *ca.* 20000 cm^{-1} is a consequence of the mistaken assignment of the lowest observed band in the electronic spectrum of a complex to the expected lowest energy electronic transition, even though the whole spectral region (particularly the NIR) had not been examined. Norman and coworkers' calculations [111] predict a $\delta\rightarrow\delta^*$ transition energy at 8800 cm^{-1}, close to a weak band (doublet) observed in the solution spectrum of $\{Ru_2(O_2CMe)_4Cl\}_n$ in water; this doublet was explained in terms of a forbidden $\delta\rightarrow\pi^*$ transition (predicted at 8600 cm^{-1}) contributing to the observed intensity. However, the solid-state spectrum of $\{Ru_2(O_2CMe)_4Cl\}_n$ in this region has not been reported previously; it is illustrated in Fig. 1 [112] and clearly confirms the presence of a doublet in this region, in support of Norman's assignments. Independently, polarised absorption spectra (12500–30000 cm^{-1}) were recorded at 300 K and 5 K [110]. The results fit reasonably well with Norman's SW-Xα calculations [111] but there are some significant discrepancies, possibly explained by the fact that the calculation was for a dimer and not the polymeric array of $Ru_2{}^{5+}$ centres.

For trimeric systems, the rate constants for electron exchange between $[Ru_3O(O_2CMe)_6(py)_3]^+$ and $[Ru_3O(O_2CMe)_6(py)_3]$ have been determined by VT ^{1}H NMR line broadening experiments [113].

Interest in the Creutz-Taube ion shows no sign of waning. Single-crystal VT EPR measurements [114] upon $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]Br_4Cl$ apparently favour a delocalised ground state, rather than the valence-trapped ground state argued for following previous work [115] on powdered samples. EHMO calculations upon this ion and the related $[(H_3N)_5Ru(L\text{-}L)Ru(NH_3)_5]^{5+}$ (L-L = 4,4'-bipy or N≡C-C≡N) systems has confirmed that valence-trapping exists for the μ-4,4'-bipy complex, and that valence delocalisation occurs for the μ-cyanogen complex, but the results were inconclusive with regard to the μ-pyrazine species [116]. A novel μ-quinoxaline (8) analogue, $[(H_3N)_5Ru(\mu\text{-quinoxaline})Ru(NH_3)_5]^{5+}$, has now been



(8)

reported and possesses an absorption in the NIR at 5900 cm^{-1} {*cf*. 6300 cm^{-1} for $[(H_3N)_5Ru(\mu\text{-pz})Ru(NH_3)_5]^{5+}$}: this has been taken as evidence for valence trapping in both molecules, as the π^* levels of (8) are considerably lower than those in pz [117].

The salts $[(bipy)_2ClRu(\mu\text{-dppm})RuCl(bipy)_2]X_2$ (X = $[ClO_4]$ or $[PF_6]$) have been isolated, following the treatment of $[Ru(bipy)_2Cl_2]$ with dppm in ethanol; subsequent stoicheiometric oxidation with $[Fe(bipy)_3]^{3+}$ generates the mixed-valence tripositive cation, which is a valence-trapped species with $\tilde{\nu}_{IT}$ at 8020 cm^{-1}. Oxidation of this with a further equivalent of $[Fe(bipy)_3]^{3+}$ yields the ruthenium(III) tetrapositive dimeric cation [118]. The related mixed-valence

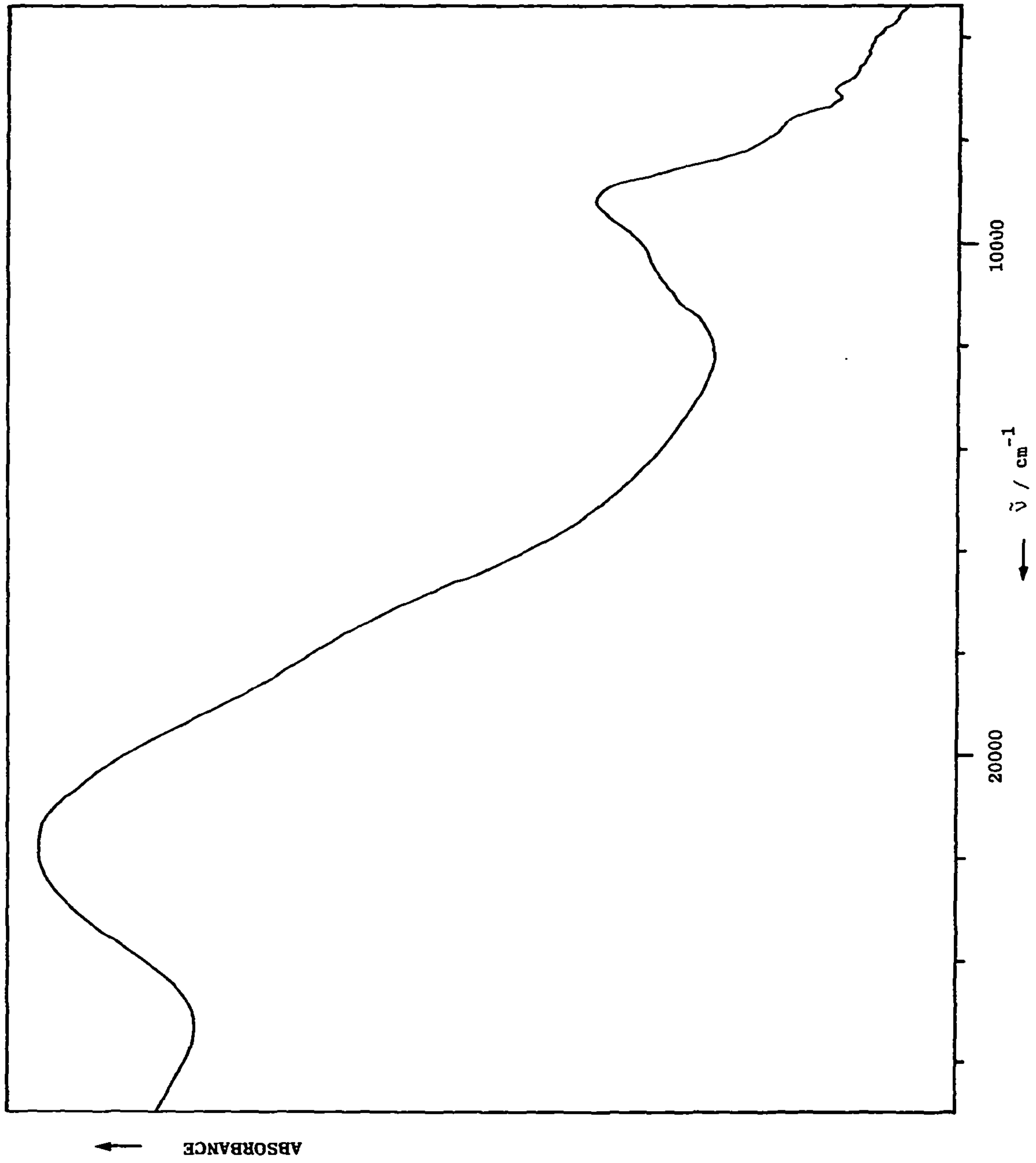
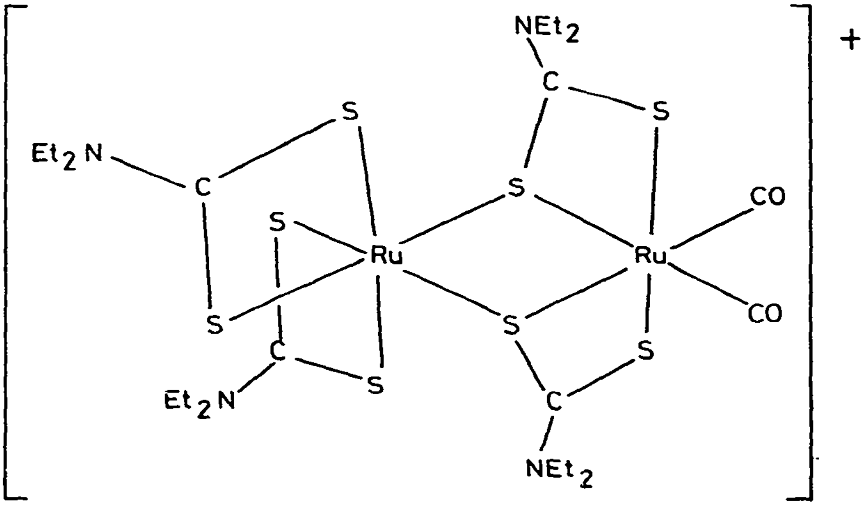


Fig. 1: The reflectance spectrum of $\{Ru_2(O_2CMe)_4Cl\}_n$ [112].

complexes $[(bipy)_2ClRu(L\text{-}L)RuCl(bipy)_2]^{3+}$ (L-L = pz, 4,4'-bipy, pyrimidine, *trans*-1,2-bis(4-pyridyl)ethene or 1,2-bis(4-pyridyl)ethane) have been prepared in a similar manner by the oxidation of their diruthenium(II) analogues, and characterised by CV and UV-VIS-NIR spectroscopy (with particular emphasis being given to the solvent dependence of the NIR band). The results have been discussed in terms of the effects of solvation and the Ru...Ru separation upon optical and thermal electron-transfer [119].

Slow electrochemical oxidation of $[Ru_2(S_2CNEt_2)_4(CO)_2]$ in CH_2Cl_2 has yielded the novel mixed-valence complex $[Ru_2(S_2CNEt_2)_4(CO)_2]^+$ (9), which has been crystallographically characterised as its $[BF_4]^-$ salt. The Ru...Ru separation is 0.3614 nm, suggesting that there is no significant metal-metal interaction [120]. The formation of the cation involves an unusual CO transfer, from the starting material which contains one CO on each Ru atom, to the product which has two CO's bound to one Ru atom and none to the other. The question of localised or delocalised valence states in (9) is still to be answered.



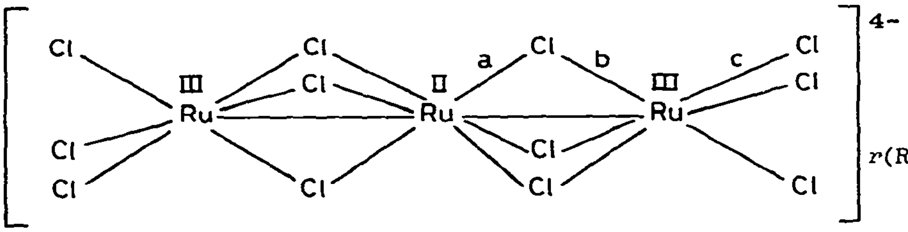
(9)

Studies upon $[Ru_2Cl_5L_4]$ (L = phosphines or arsines) are reported in Section 2.8.6.1.

2.8 RUTHENIUM(II)

2.8.1 *Chlorides and cyanides*

Dissolution of $\{Ru_2(O_2CMe)_4Cl\}_n$ in 12 *M* hydrochloric acid, under argon, results in the formation of a deep blue solution. Addition of $[NEt_4]Cl$ to this solution has resulted in the isolation of a compound $[H_7O_3]_2[NEt_4]_2[Ru_3Cl_{12}]$, which has been characterised crystallographically, and shown to contain the mixed-valence $[Ru_3Cl_{12}]^{4-}$ anion (10) [121]. The complex is *not* believed to be the chromophore in the well-known but little-understood "ruthenium blue" solution, but rather is derived from it by trace amounts of aerial oxidation. Unfortunately, electronic spectral data for this complex were not published but, nevertheless, this constitutes the first complex to be unambiguously identified from the ruthenium blue system. In the introduction to his paper, Cotton [121] highlighted the almost total disagreement amongst all publications dealing with the "ruthenium blue" species, or (more generally) any other ruthenium(II) chloride species. This situation has been exacerbated by a publication from my own laboratory [122], in which we claimed (based upon total elemental analyses of ≥99.8%) the isolation of brown trimeric complexes of the general formulation $A_3[Ru_3Cl_9]$ (A = a monopositive cation). We now know that the analysis figures for the metal (supplied by a commercial Analytical Laboratory in West Germany) were inaccurate and that the complexes should have been formulated as $A_3[Ru_2^{IV}OCl_9(OH_2)].xH_2O$. We thus retract these observations, and apologise to any workers who have attempted to repeat the reported preparations.



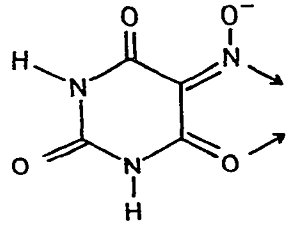
a = 0.237 nm
b = 0.238 nm
c = 0.237 nm
r(RuRu) = 0.2805 nm

(10)

^{1}H NMR studies and a mechanism for the spontaneous polarisation of the ferroelectric material $K_4[Ru(CN)_6].3H_2O$ have been reported [123] and the kinetics of the oxidation of $[Ru(CN)_6]^{4-}$ by $[MnO_4]^-$ has been studied [124]. An aqueous solution containing $[Ru(CN)_6]^{4-}$ and the histidine (7) complex $[Co(his)_2]^+$ was observed, upon irradiation with visible light, to develop a red-orange colour. This colouration was ascribed to the formation of $[(his)_2Co(\mu\text{-}NC)Ru(CN)_5]^{3-}$ [125]. In a similar manner, $[Ru(CN)_6]^{4-}$ in the presence of $[Fe(H_2O)_6]^{3+}$ generates an intense violet-blue colour, but no explanation of this phenomenon has been offered [126].

2.8.2 Complexes with Group VIB donor ligands

The crystal structure of $Ba[Ru(H_2vi)_3]_2.9H_2O$ has been determined; the anion has *facial* geometry and the ligand is bonded to the metal *via* the atoms indicated



(11; $[H_2vi]^-$)

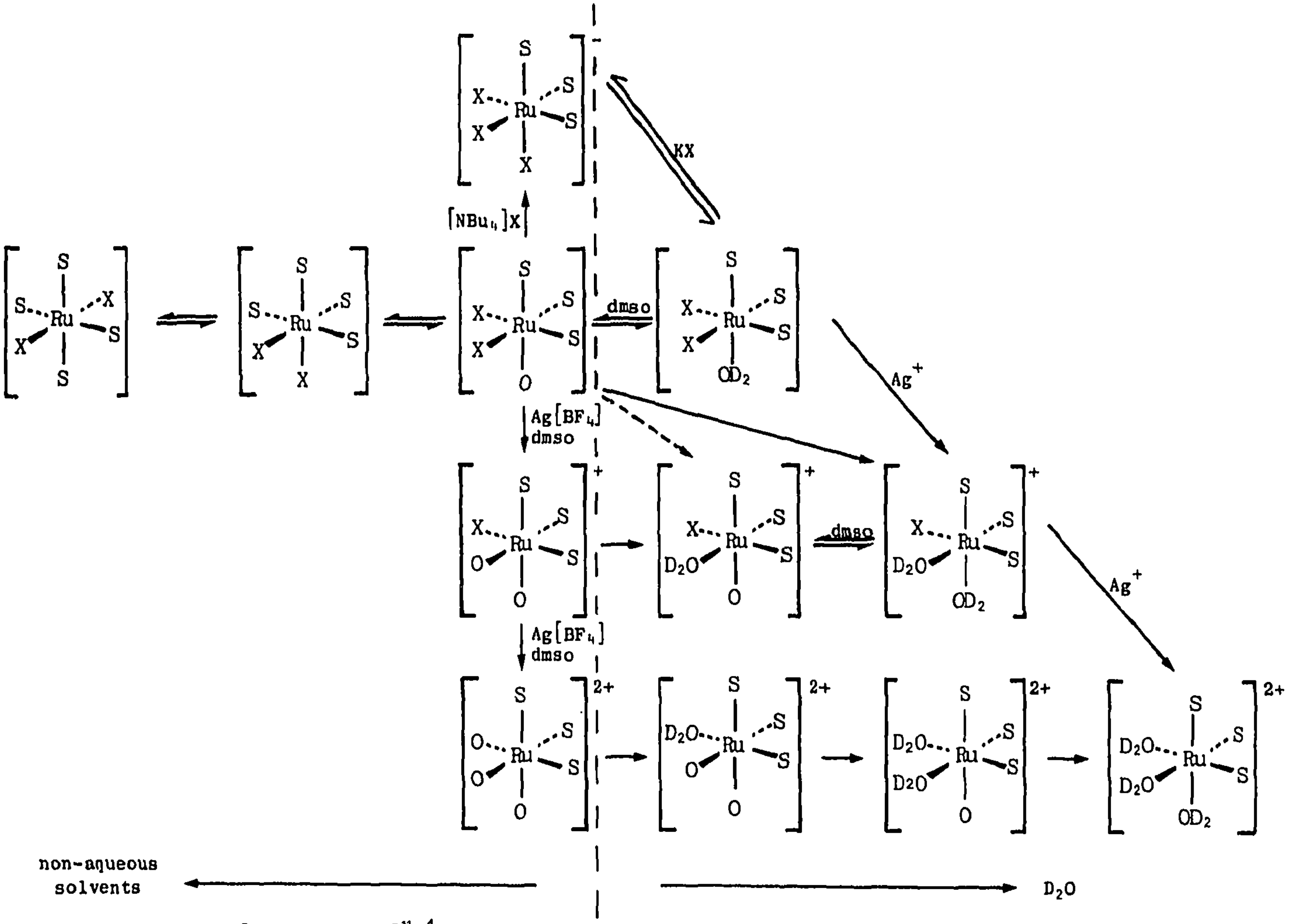
in (11) [127]. A ^{1}H NMR and IR spectroscopic study has led to the characterisation of the species $[RuX_{6-n}(dmso)_n]^{n-4}$ (n = 3,4,5 or 6; X = Cl or Br) and their hydrolysis products; Scheme II shows their interrelationships [128]. *O*-bonded dmso is labile in D_2O, whereas *S*-bonded dmso appears not to be. New assignments for ν(Ru-Cl) stretching modes have been suggested for $[RuCl_3(dmso)_3]^-$ (at 265 and 241 cm^{-1}), $[RuCl_2(dmso)_4]$ (at 258 and 248 cm^{-1}) and $[RuCl(dmso)_5]^+$ (at 246 cm^{-1}), bringing them into line with the frequencies for many other ruthenium(II) complexes. Bands at 1100 and 425 cm^{-1} were found to be characteristic of *S*-bonded dmso, whereas bands at 925 and 480 cm^{-1} were found when *O*-bonded dmso was present [128]. A paper, submitted after [128] was published, but not referring to it, contains a limited study of the same hydrolysis phenomenon [129].

The macrocyclic complexes $[Ru(L_4)X_2]$ (L_4 = [14]aneS$_4$ or bzo[15]eneS$_4$) [89] and some dithiocarbamate complexes of formulae $[RuL_2(H_2O)_2]$ and $[RuL_2]$ {L = (4; Y = CH_2, NH, NMe, O or S)} have been reported [130]. Ruthenium(II) complexes have also been reported with the ligands 3,4,5-pyridazinetrithiol [65], *N*-phenylcarbamoylpyrrole-2-thiocarboxamide [66], and a number of substituted thiosemicarbazides and thiosemicarbazones [131].

2.8.3 *Ammine and amine complexes*

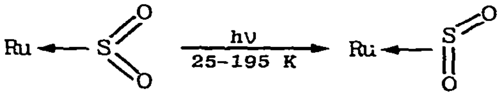
The IR spectra of $[Ru(NH_3)_6]X_2$ (X = Cl, Br, I, $[PF_6]$ or $[BF_4]$) and $[Ru(ND_3)_6]Br_2$ have been reported and the ν(Ru-N) stretching modes have been identified as occurring at *ca.* 400–420 cm^{-1} [132]. *Ab initio* SCF calculations have been performed upon $[Ru(NH_3)_5L]^{2+}$ (L = N_2, CO or H_2O) and upon the $\{Ru(NH_3)_5\}^{2+}$ fragment of these ions [133].

Ligand substituent effects on the photochemistry of $[Ru(NH_3)_5L]^{2+}$ (L = py or a substituted derivative) complexes have been the subject of an excellent review [134]. The preparations of *trans*-$[Ru(NH_3)_4(py)L]^{2+}$ (L = pz, pzH^+ or py-4-C(O)Me) and *trans*-$[Ru(NH_3)_4L_2]$ (L = pz or pzH^+) have been reported, and their basicities



SCHEME II: Structures of $[RuX_{6-n}(dmso)_n]^{n-4}$ (n = 3, 4, 5 or 6; X = Cl or Br) and their hydrolysis products [128]. S = *S*-bonded dmso; O = *O*-bonded dmso.

in aqueous solution, and their electronic spectra have been studied. Visible light photolyses of these complexes lead to the predominant photoaquation of one coordinated ammonia molecule [135]. A novel, photochemically induced, linkage isomerism has been observed for $[Ru(NH_3)_4Cl(SO_2)]Cl$ in a KBr pellet, involving a change in the bonding mode of the SO_2 [136]:

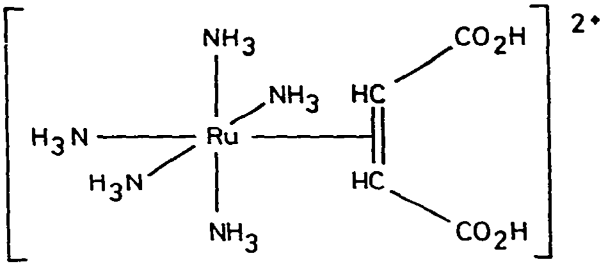


Full details of the structure and some chemical properties of the interesting metalloflavin complex $[Ru(NH_3)_4(10\text{-Meialo})][PF_6]_2$ (10-Meialo = 10-methyliso-alloxazine), which was discussed last year [1; p. 51], have now been published: NMR and electronic absorption measurements, along with CV and OTTLE studies, are described in an excellent paper [137]. Novel alkene and alkyne derivatives of the pentaammineruthenium(II) moiety have been prepared by an extremely facile route [138]:

$$[Ru(NH_3)_5(H_2O)]^{2+} + \text{alk} \longrightarrow [Ru(NH_3)_5(\text{alk})]^{2+} + H_2O$$

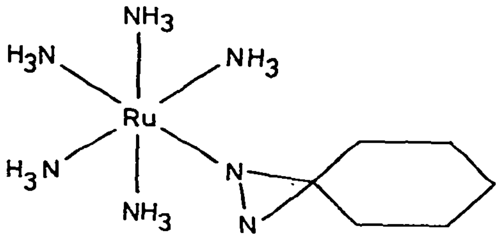
(alk = ethene, isobutene, 1,4-cyclohexadiene, fumaric acid, ethyne, phenylethyne or hex-3-yne)

The bonding in these complexes is comparable with that in Zeise's salt, with 'edge-on' bonded alkenes and alkynes. The complexes were characterised by UV-VIS, IR and ^1H NMR spectroscopy, and by cyclic voltammetry, all of which indicate the presence of strong $d_\pi \rightarrow p_{\pi^*}$ back-bonding. The molecular structure of one of these complexes, $[(H_3N)_5Ru(HO_2CH{=}CHCO_2H)]^{2+}$, (12), was determined [138].



(12)

In an analogous reaction, treatment of $[Ru(NH_3)_5(H_2O)]^{2+}$ with an excess of 3,3-pentamethylenediazirine yields $[Ru(NH_3)_5(N_2C_6H_{10})]^{2+}$, (13), which has been isolated and structurally characterised as its $[PF_6]^-$ salt. (13) is oxidised



(13)

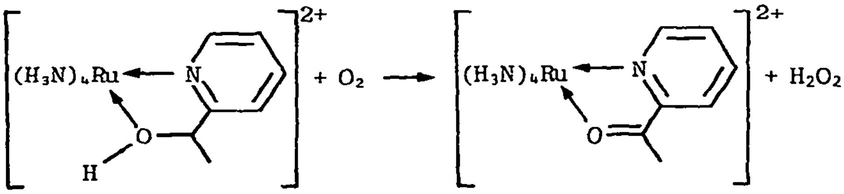
in acidic solution, by O_2 or H_2O_2, to give $[Ru(NH_3)_5(N_2)]^{2+}$ and cyclohexanone; (13) can also undergo the following fascinating dimerisation reaction [139]:

$$[Ru(NH_3)_5(N_2C_6H_{10})]^{2+} \underset{NH_3 \text{ or } N_2C_6H_{10}}{\overset{[Ru(NH_3)_5(H_2O)]^{2+}}{\rightleftharpoons}} \underset{(14)}{[(H_3N)_5Ru(\mu\text{-}N_2C_6H_{10})Ru(NH_3)_5]^{4+}}$$

(14) can also be prepared by treating $N_2C_6H_{10}$ with an excess of $[Ru(NH_3)_5(H_2O)]^{2+}$ [139].

The kinetics of the anaerobic reduction of beef heart mitochondrial cytochrome *c* oxidase [140] and of various platinum(IV) complexes (*e.g.* *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ or $[PtCl_6]^{2-}$) [141] by $[Ru(NH_3)_6]^{2+}$ have been reported. The reduction of O_2 to H_2O_2 by $[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_5(isonic)]^{2+}$, *cis*- or *trans*-$[Ru(NH_3)_4(isonic)(H_2O)]^{2+}$ or $[Ru(NH_3)_4(phen)]^{2+}$ has also been investigated: the mechanism involves outer-sphere electron-transfer, generating $[O_2]^{\dot{-}}$ [142]. In a related study, the kinetics of the reduction of H_2O_2 by $[Ru(NH_3)_6]^{2+}$ or $[Ru(NH_3)_5L]^{2+}$ (L = H_2O or 1-Meimid) were determined; a common mechanism for all three reactions was postulated, involving the formation of a seven-coordinate ruthenium(II) intermediate [143]. The difference in the mechanisms postulated for the respective reductions of O_2 and H_2O_2 is striking.

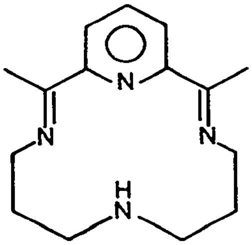
The oxidation of alcohols coordinated to ruthenium, by dioxygen, to yield ketones and hydrogen peroxide, has been observed. Thus, for the 2-(1'-hydroxyethyl)pyridine complex (15), oxidation to the 2-ethanoylpyridine complex (16) occurs [144]:



(15) (16)

The reaction involves the formation of a ruthenium(IV) alkoxide intermediate, which then undergoes a metal-ligand redox reaction to yield the ruthenium(II) ketone complex [144]. A complex $[Ru(NH_3)_5(H_4ATP)]Cl_2$ (H_4ATP = adenosine triphosphate) has been reported [92].

The complex $[Ru(py)_6]^{2+}$ will be considered in Section 2.8.4. The complexes *cis*- or *trans*-$[Ru(cyclam)Cl_2]Cl$ can be reduced by zinc amalgam to yield their ruthenium(II) analogues, which react with an excess of isonicotinamide to give *cis*- or *trans*-$[Ru(cyclam)(isonic)_2]^{2+}$. Similarly, *cis*-$[Ru(cyclam)Cl_2]$ reacts with bipy to give *cis*-$[Ru(cyclam)(bipy)]^{2+}$ but *trans*-$[Ru(cyclam)Cl_2]$ reacts with bipy to yield a product with different spectral properties, and the latter has been postulated to contain the elusive monodentate bipy ligand [91]. Treatment of *mer*-$[RuCl_3\{NH_2(CH_2)_3NH(CH_2)_3NH_2\}]$ in aqueous ethanol with 2,6-diethanoylpyridine yields a violet, diamagnetic macrocyclic complex of L, (17) [145].



(17)

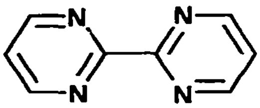
This complex, $[Ru(L)(H_2O)]^{2+}$, has been postulated to exist as either a five-coordinate monomer or a Ru-Ru bonded dimer; the possibility of a μ-oxo bridged dimer does not appear to have been considered. Thirty new oxime complexes of ruthenium(II) have been prepared by the treatment of $[RuCl_2(PPh_3)_3]$ with chelating or simple oximes, in both the presence or absence of base. These complexes were characterised by ^1H and ^{31}P NMR spectroscopy [146].

2.8.4 *Diimine complexes*

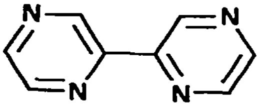
Interest in $[Ru(bipy)_3]^{2+}$ and its derivatives continues unabated. Two extremely important structural studies have been published this year: $[Ru(py)_6][BF_4]_2$ [147] and $[Ru(bipy)_3][PF_6]_2$ [148] have been characterised by X-ray crystallography. Although the cation of the former salt is not a diimine complex, $[Ru(py)_6]^{2+}$ has particular relevance to the studies of $[Ru(bipy)_3]^{2+}$. $[Ru(py)_6][BF_4]_2$ was prepared by the prolonged reaction of $[RuHL_3(PPh_3)_2][BF_4]$ (L = MeOH or H_2O) with pyridine in methanol, and characterised structurally $\{\bar{r}(RuN) = 0.212\ nm\}$, spectroscopically (UV-VIS, IR, ^1H and ^{13}C NMR) and electrochemically (CV) [147]. This is an excellent and interesting paper, not least because it details the remarkable similarity of the properties of $[Ru(py)_6]^{2+}$

and $[Ru(bipy)_3]^{2+}$, which have essentially identical, reversible, oxidation potentials, and similar Ru-N bond lengths. $[Ru(bipy)_3][PF_6]_2$ shows the expected D_3 ground state point symmetry $\{\bar{r}(RuN) = 0.2056$ nm$\}$ [148]. However, the structure determined for this latter compound was of an anhydrous salt and a good deal of interest lies in the hydrated $[Ru(bipy)_3]Cl_2.6H_2O$ complex, particularly in the dispositions of the water molecules. Therefore it is hoped that the appearance of this paper will not discourage a future X-ray crystallographic determinations upon a hydrated $[Ru(bipy)_3]^{2+}$ salt.

An interesting series of complexes, involving ligands which would be conventionally considered to be sterically hindered towards coordination, has been prepared. The complexes, $[Ru(LL)_3]Cl_2$ (LL = 6-Mebipy, 6,6'-Me$_2$bipy, 2-Mephen or 2,9-Me$_2$phen) were prepared by the interaction of LL with a blue ruthenium(II) chloride solution and characterised by electronic absorption and emission spectroscopy (including ϕ and τ measurements). Despite the steric hindrance, the energies of the observed MLCT absorption bands and the emission bands of these complexes are remarkably similar to those of $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, but the magnitude of ε, ϕ and τ are all much smaller than those of the parent complexes [149]. In a superb example of synthetic chemistry, a vast series of complexes with seventeen different bidentate ligands, LL (see Fig. 2), of formulation $[Ru(LL)_3]^{2+}$, $[Ru(LL)_2(bipy)]^{2+}$, and $[Ru(LL)(bipy)_2]^{2+}$ have been prepared, isolated as $[PF_6]^-$ salts, and characterised by ^1H NMR, IR, electronic absorption and emission spectroscopy, and cyclic voltammetry [150]. $[Ru(4\text{-}NO_2\text{-}bipy)_3]^{2+}$, included in the above study [150], and $[Ru^{II}(4\text{-}Et_3P\text{-}bipy)_3]^{5+}$ have been independently prepared and isolated as perchlorate salts [151]. Also, in a variant on a well-known theme {*cf.* $[Ru(bipym)_3]^{2+}$ [152]; bipym = (18)},



(18; bipym)



(19; bpz)

the complex $[Ru(bpz)_3]Cl_2.4.5H_2O$ {bpz = (19)} has been prepared by treatment of $[RuCl_2(dmso)_4]$ with (18) and, perhaps not surprisingly, shows similar photophysical and photochemical properties to $[Ru(bipy)_3]^{2+}$ and $[Ru(bipym)_3]^{2+}$ [153].

Meyer's excellent synthetic work, based upon the $\{Ru(bipy)_2\}^{2+}$ moiety, continues. The *cis* $\rightleftharpoons$ *trans* photoisomerisation of $[Ru(bipy)_2(H_2O)_2]^{2+}$ [100] has already been discussed (see Section 2.6.5) and novel, high yield routes for the photochemical syntheses of $[Ru(bipy)_2LX]^+$ (L = py, 4-Me$_3$C-py or MeCN; X = Br, NO$_2$, [NCS], [NO$_3$], [ClO$_4$], [CF$_3$CO$_2$] or [MeC$_6$H$_4$-4-SO$_3$]) and $[Ru(bipy)_2X_2]$ have now been published [154]:

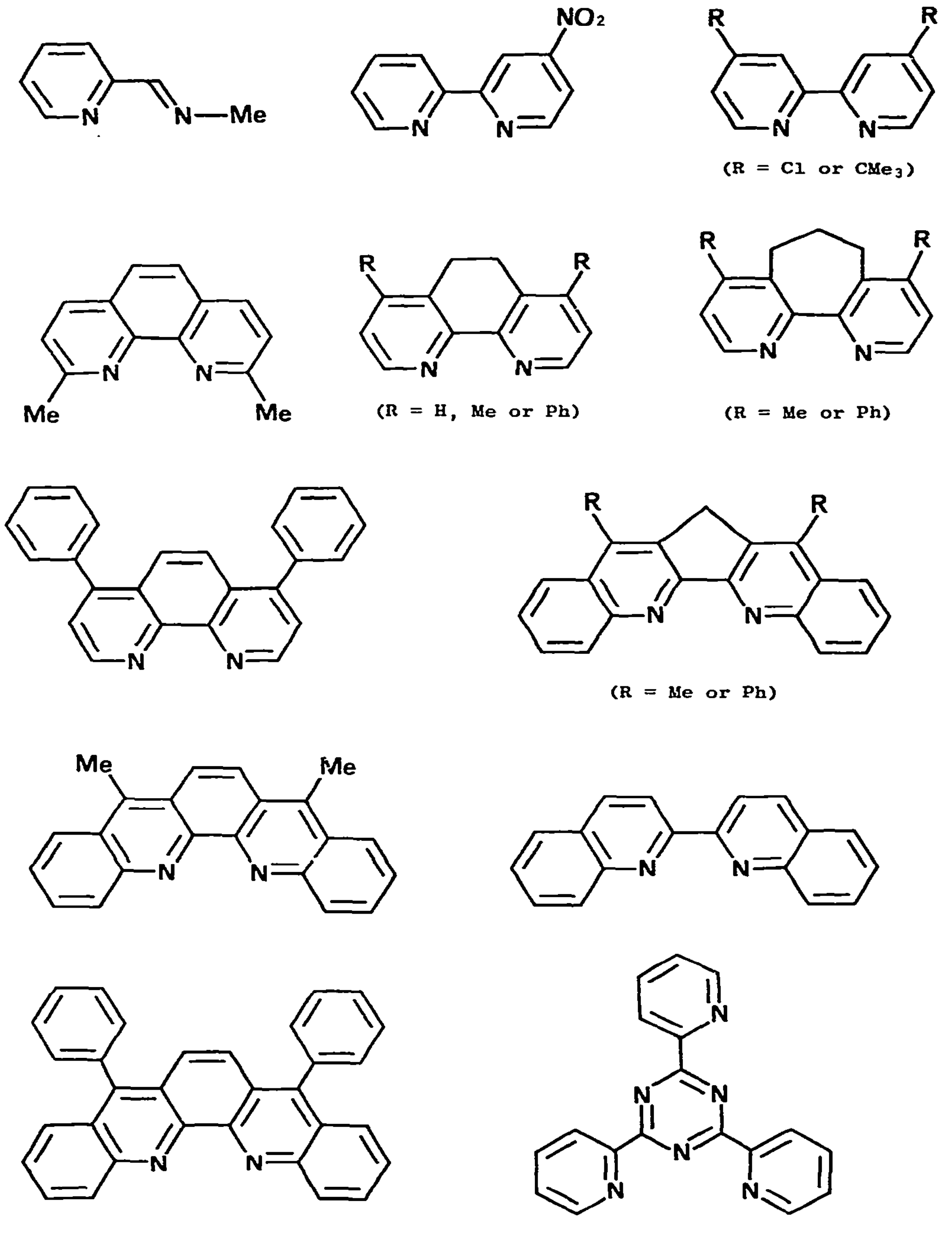


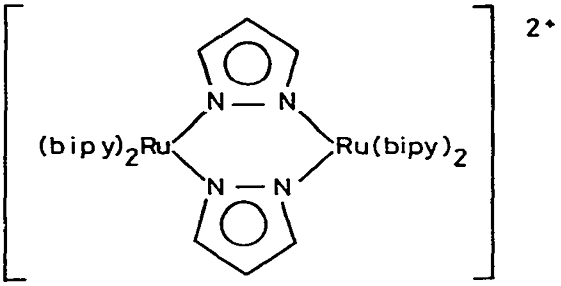
Fig. 2: The ligands used in the synthetic study of $[Ru(LL)_3]^{2+}$ complexes by Belser and von Zelewsky [150]. Many of these ligands are conventionally considered as sterically hindered towards coordination.

e.g.

$$[\mathrm{Ru(bipy)_2(py)_2}]^{2+} + \mathrm{X}^- \xrightarrow[\mathrm{CH_2Cl_2}]{h\nu} [\mathrm{Ru(bipy)_2(py)X}]^+ + \mathrm{py}$$

$$[\mathrm{Ru(bipy)_2(py)X}]^+ + \mathrm{X}^- \longrightarrow [\mathrm{Ru(bipy)_2X_2}] + \mathrm{py}$$

The complexes were characterised by CV, and UV-VIS and IR spectroscopy. In the photochemical reaction between $[\mathrm{Ru(bipy)_3}]^{2+}$ and $[\mathrm{NCS}]^-$, an intermediate was observed which was postulated as $[\mathrm{Ru(bipy)_2(\eta^1\text{-}bipy)(NCS)}]^+$, containing the elusive (but oft sought after) monodentate 2,2'-bipyridine ligand (*cf.* the product of the reaction of *trans*-$[\mathrm{Ru(cyclam)Cl_2}]$ with bipy; Section 2.8.3) [154]. The first well-defined complexes of pyrazole (pzlH) in this system have now been prepared by conventional routes: $[\mathrm{Ru(bipy)_2(pzlH)_2}][\mathrm{PF_6}]_2$, $[\mathrm{Ru(bipy)_2(pzlH)(pzl)}][\mathrm{PF_6}]$ and $[\mathrm{Ru(bipy)_2(pzl)_2}]$ were characterised by CV and UV-VIS spectroscopy [155]. Of more interest, $[\mathrm{Ru(bipy)_2(pzl)_2}]$ reacts with $[\mathrm{Ru(bipy)_2(Me_2CO)_2}]^{2+}$ to yield the doubly bridged dimer, $[(\mathrm{bipy})_2\mathrm{Ru}(\mu\text{-pzl})_2\mathrm{Ru(bipy)_2}]^{2+}$ (20). Although stable on the CV time-scale, the mixed-valence tripositive form of (20) is unstable towards electrochemical synthesis, decomposing in MeCN (*cf.* $[(\mathrm{bipy})_2\mathrm{Ru}(\mu\text{-Cl})_2\mathrm{Ru(bipy)_2}]^{3+}$ [156]) to give $[\mathrm{Ru(bipy)_2(MeCN)_2}]^{2+}$ and $[\mathrm{Ru(bipy)_2(pzl)_2}]^+$ [155]. A novel series of alkyl nitrite complexes, $[\mathrm{Ru(bipy)_2(py)\{N(O)OR\}}]^{2+}$ (R = Me, Et, Bu or $\mathrm{CMe_2H}$), has been prepared by treatment of $[\mathrm{Ru(bipy)_2(py)(NO)}]^{3+}$ with $[\mathrm{OR}]^-$ in MeCN. These complexes, which were characterised by CV and by UV-VIS, IR and ^{1}H NMR spectroscopy, react with acid to regenerate the parent nitrosyl species and ROH. The complexes $[\mathrm{Ru(bipy)_2Cl\{N(O)OR\}}]^+$ were prepared in a similar manner from $[\mathrm{Ru(bipy)_2Cl(NO)}]^{2+}$ [157].



(20)

The molecular structure of *cis*-$[\mathrm{Ru(bipy)_2(CO)Cl}][\mathrm{ClO_4}]$ has been reported, and some of its reactions (*e.g.* with monodentate ligands to give thermal displacement of Cl^-, or photochemical displacement of CO) have been investigated. The Ru-N bond *trans* to CO, at 0.218 nm, is longer than the mutually *trans* Ru-N bonds $\{\bar{r}(\mathrm{RuN}) = 0.210\ \mathrm{nm}\}$, which are in turn longer than the Ru-N bond *trans* to Cl (at 0.207 nm) [158]. Aqueous solutions of $[\mathrm{Ru(bipy)_2(CO)Cl}]^+$ produce $\mathrm{H_2}$, CO and $\mathrm{CO_2}$

upon visible-light photolysis; under an atmosphere of CO, the reaction is catalytic and represents the first report of the photocatalysis of the water-gas shift reaction [159]. The complexes $[Ru\{4,4'\text{-}(NO_2)_2\text{-bipy}\}_2Cl_2]$ and $[Ru^{II}\{4,4'\text{-}(Et_3P)_2\text{-bipy}\}_2Cl_2][ClO_4]_4$ have also been prepared and characterised by UV-VIS spectroscopy and CV [151].

The reaction of $[Ru(terpy)Cl_3]$ with an excess of L $\{L = PPh_3, P(C_6H_4\text{-}4\text{-}Me)_3$ or py$\}$, in the presence of NEt_3, yields violet *trans*-$[Ru(terpy)LCl_2]$. This complex can be converted to pink *cis*-$[Ru(terpy)LCl_2]$ by boiling in 1,2-dichloroethane and the *cis*-isomer can also be prepared by treatment of $[Ru(PPh_3)_3Cl_2]$ with terpy. The chloride in the *cis*-isomer is significantly more labile than that in the *trans*-isomer. Thus:

$$\textit{trans}\text{-}[Ru(terpy)(PPh_3)Cl_2] \xrightarrow[Me_2CO;\ 25\ ^\circ C]{PPh_3} \text{no reaction}$$

$$\textit{cis}\text{-}[Ru(terpy)(PPh_3)Cl_2] \xrightarrow[Me_2CO;\ 25\ ^\circ C]{PPh_3} \textit{trans}\text{-}[Ru(terpy)(PPh_3)_2Cl]^+$$

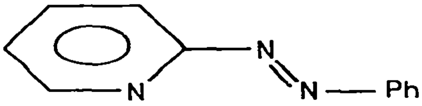
This represents a good example of the *trans*-labilising effect of phosphines bound to ruthenium(II). With CO, the *cis*- and *trans*-isomers give different isomeric products [102]:

$$\textit{trans}\text{-}[Ru(terpy)(PPh_3)Cl_2] \xrightarrow[1,2\text{-}C_2H_4Cl_2;\ \text{reflux}]{CO} \textit{trans}\text{-}[Ru(terpy)(CO)Cl_2]$$

$$\textit{cis}\text{-}[Ru(terpy)(PPh_3)Cl_2] \xrightarrow[1,2\text{-}C_2H_4Cl_2;\ \text{reflux}]{CO} \textit{cis}\text{-}[Ru(terpy)(CO)Cl_2]$$

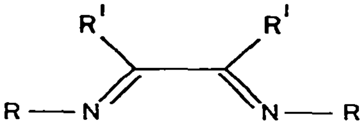
The monothiobenzoate complex $[Ru(OSCPh)_2(PMe_2Ph)_2]$ reacts with LL (LL = bipy or phen) to give *cis,cis,cis*-$[Ru(LL)\{SC(O)Ph\}_2(PMe_2Ph)_2]$. When LL = phen, a minor by-product *cis,cis,trans*-$[Ru(phen)\{SC(O)Ph\}_2(PMe_2Ph)_2]$, was also isolated. Both *cis,cis,cis*- and *cis,cis,trans*-$[Ru(phen)\{SC(O)Ph\}_2(PMe_2Ph)_2]$ were structurally characterised and have $\bar{r}$(RuN) values of 0.212 and 0.209 nm, respectively [160]. In contrast, the analogous reaction with 1,2-diaminoethane yielded *cis,trans,cis*-$[Ru(en)\{SC(O)Ph\}_2(PMe_2Ph)_2]$ [160]. Treatment of $[(bipy)(Ph_3P)_2Ru(\mu\text{-}Cl)_2Ru(PPh_3)_2(bipy)]Cl_2$ with $[C_6F_5S]^-$ gives an isomeric mixture of products (as judged by ^{19}F NMR spectroscopy) of formula $[(bipy)(Ph_3P)_2Ru(\mu\text{-}SC_6F_5)_2Ru(PPh_3)_2(bipy)]Cl_2$ [161].

2-(phenylazo)pyridine (21; azpy) is structurally analogous to a diimine, and indeed acts as a bidentate ligand. Thus, the reaction of (21) with an ethanolic solution of "$RuCl_3.xH_2O$" at reflux yields the dark blue complex *cis*-$[Ru(azpy)_2Cl_2]$, whereas treatment of $[Ru(dmso)_4Cl_2]$ with (21) in Me_2CO produces the green complex,



(21; azpy)

trans-$[Ru(azpy)_2Cl_2]$; the latter, upon heating in xylene, produces a different blue *cis*-isomer to that already described. The characterisation does not give unambiguous structural assignments, however [162]. Further details of the interesting diazadiene complexes described last year [1; p. 54] have appeared. Treatment of $[RuCl_2(PPh_3)_3]$ with (22) or (23) yielded $[Ru_2Cl_3(PPh_3)_2(dad)_2]X$



(22; R = $CHMe_2$, R' = H)
(23; R = Ph, R' = Me)

{dad = (22) or (23), X = Cl or $[BPh_4]$}, whereas using only half an equivalent of (23) produced $[Ru_2Cl_4(PPh_3)_3(dad)]$. The reaction of $[RuHCl(PPh_3)_3]$ with (22) in Et_2O produces $[RuHCl(PPh_3)_2(dad)]$, which reproportionates in MeOH to give a mixture of $[RuH_2(PPh_3)_2(dad)]$ (and $[RuH_2(CO)(PPh_3)_3]$) and $[Ru_2Cl_3(PPh_3)_2(dad)_2]Cl$. $[RuH_2(PPh_3)_2(dad)]$ has also been prepared by treating $[RuH_4(PPh_3)_3]$ with (22). $[RuHCl(PPh_3)_2(dad)]$ {dad = (22)} reacts with water in toluene to eventually yield $[Ru_2H(\mu\text{-}Cl)(\mu\text{-}OH)_2(PPh_3)_3(dad)]$ [163].

Three more papers claiming "pseudo-base" formation for a series of complexes related to $[Ru(5\text{-}NO_2\text{-}phen)_3]^{2+}$ have appeared [164-166].

Good progress is also being made in gaining an understanding of the reduction products of $[Ru(bipy)_3]^{2+}$. Although formally ruthenium(I) and ruthenium(0), $[Ru(bipy)_3]^+$ and $[Ru(bipy)_3]$ are much more usefully considered as $[Ru^{II}(bipy)_2(bipy^-)]^+$ and $[Ru^{II}(bipy)(bipy^-)_2]$, and so their chemistry will be discussed in this section. Electrochemically generated $[Ru(bipy)_3]^+$ is quantitatively oxidised to $[Ru(bipy)_3]^{2+}$ in deaerated acidic aqueous solutions, but there is little or no production of dihydrogen. Similar treatment of $[Ru(bipy)_3]$ (produced electrolytically, precipitating from MeCN solutions as a dark solid), in contrast, results in the rapid, stoicheiometric evolution of dihydrogen at pH 1, pH 7 or pH 12, with the concomitant generation of $[Ru(bipy)_3]^{2+}$ [167]:

$$[Ru(bipy)_3] + 2H_3O^+ \longrightarrow [Ru(bipy)_3]^{2+} + H_2 + 2H_2O$$

$$[Ru(bipy)_3] + 2H_2O \longrightarrow [Ru(bipy)_3]^{2+} + H_2 + 2[OH]^-$$

Experiments in D_2O resulted in the evolution of D_2, confirming that the evolved dihydrogen originates from the solvent and not the ligand. Similar results were obtained for $[Ru(terpy)_2]$ and $[Ru(terpy)_2]^+$ (H_2 evolution being observed for the former, but not the latter), but no H_2 evolution was observed with either $[Ru(phen)_3]$ or $[Ru(bipy)_2(4,4'\text{-bipy-}N\text{-Me})_2]^{2+}$ [167]. The CV of $[Ru\{bipy\text{-}4,4'\text{-}(CO_2Et)_2\}_3]^{2+}$ has been reported and the reduction monitored by the OTTLE technique: intense NIR absorption bands were observed, progressing to lower energy as the reduction proceeded [168]. It should be noted, however, that similar multireduction waves to those observed in this paper had been observed as early as 1976 [169]. Cathodic voltammograms have also been reported for $[Ru(4,7\text{-}Ph_2phen)_3]^{2+}$ and $[Ru(tpt)_2]^{2+}$ in dmf [170]. The reactions of radiolytically generated radicals $R_1R_2\dot{C}OH$ (R_1=R_2 = H or Me; R_1 = H, R_2 = Me) with $[Ru(bipy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ have been investigated, radical attack appearing to occur at the coordinated ligand [171].

A remarkably tenuous correlation has been drawn between the oxidation potentials of the complexes $[Ru(bipy)_2(LL)]^{2+}$ (LL = bipy, en, $(py)_2$, $(NH_3)_2$ or $[CN^-]_2$) and the ionisation energies of their 3*d* (??) electrons [172]. It is remarkable that such a paper can be published in a reputable journal - to refer to the 3d electrons of ruthenium as the valence level is unbelievable, to draw a correlation between five points of a total spread of 0.4 eV which have been measured only to ±0.1 eV defies sensible comment!

The reduction and oxidation of $[Ru(bipy_3]^{2+}$ at illuminated semiconducting electrodes has been studied. The complex is reduced at a potential *ca.* 0.5 V more positive than its thermodynamic reversible reduction potential at illuminated *p*-type silicon [173], and is oxidised at a potential *ca.* 0.5 V more negative than its thermodynamic reversible oxidation potential at illuminated MoS_2 [174].

The many developments in the photochemistry and photophysics of $[Ru(bipy)_3]^{2+}$ and related complexes are considered separately in Section 2.15. The use of these complexes for the photocatalytic decomposition of water is also considered separately, in Section 2.16, and their attachment to modified surfaces is discussed in Section 2.17.

2.8.5 Porphyrin and phthalocyanine complexes

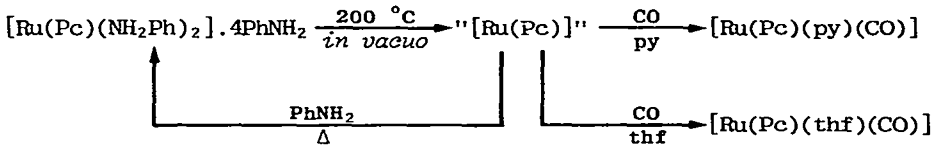
The complexes $[Ru(TPP)L_2]$ (L = PEt_3, PMe_2Ph, PPh_3, $P(OMe)_3$ or $CNCMe_3$) have been prepared from $[Ru(TPP)(CO)]$ and characterised by UV-VIS, IR and ^1H NMR spectroscopy, as well as by CV; the complexes show reversible oxidation and reduction waves [175]. In what is probably this year's most important paper on ruthenium chemistry, it has been observed that $[Ru(TPP)(PPh_3)_2]$, in the presence of free phosphine, is an extremely efficient decarbonylation reagent for aromatic and aliphatic aldehydes *under ambient conditions*. Moreover, the decarbonylation is catalytic, with (for the decarbonylation of $PhCH_2CHO$ to $PhCH_3$) a turnover number of $>10^4$ in 30 min at 50 °C (10^3 at room temperature) [176].

The complexes [Ru(MPIXDME)(CO)L] and [Ru(TIPPP)(CO)L] (L = one of a variety of imidazoles, pyridines, pyrazoles or benzylamines) have been studied by ^1H NMR spectroscopy, and the resonances due to L were all found to be markedly shifted upfield; these shifts have been used to determine the ring currents in the porphyrin rings [177]. Two similar, but independent, reports of the preparation of ruthenium myoglobin complexes have appeared this year. [Ru(MPIX)(CO)] interacts with apomyoglobin in neutral pH solution to give a 1:1 protein complex, [Ru(Mb)(CO)], with a normal Soret band; the pH dependence of the electronic spectrum was determined [178]. Independently, ruthenium(II) myoglobin, [Ru(Mb)], has been prepared by the reconstitution of horse heart apomyoglobin with $[Ru(MPIX)(dmf)_2]$; it contains one ruthenium porphyrin per heme binding site, and is readily oxidised to the ruthenium(III) complex, $[Ru(Mb)]^+$ [179]:

$$[Ru(Mb)] \underset{[S_2O_6]^{2-}}{\overset{Br_2}{\rightleftharpoons}} [Ru(Mb)]^+$$

[Ru(Mb)] reacts with CO [179] to form the known complex [Ru(Mb)(CO)] [178,180]; the reaction with dioxygen is interesting because, although reversible oxygenation of protein-free $[Ru(MPIX)(dmf)_2]$ occurs readily, irreversible oxidation to yield $[Ru(Mb)]^+$ occurs *via* an outer-sphere electron-transfer mechanism [179].

In the chemistry of ruthenium(II) phthalocyanine complexes, we again find the work of independent groups proceeding in parallel. The complexes $[Ru(Pc)L_2]$ (L = py, 4-Me-py, $4\text{-}Me_3C\text{-}py$, imidH, MeCN, dmf or dmso) and [Ru(Pc)L(CO)] (L = py, 4-Me-py, $4\text{-}Me_3C\text{-}py$, dmf or dmso) have been prepared in solution by the photolysis of [Ru(Pc)L′(CO)] in the presence of an excess of L (where L may, or may not, be the same as L′), or by extraction of "[Ru(Pc)]" with L. Alternatively, "[Ru(Pc)(CO)]" (formed from $[Ru_3(CO)_{12}]$ and PcH_2) reacts with L to give [Ru(Pc)L(CO)], which can also be formed by treatment of $[Ru(Pc)L_2]$ with CO. The complexes were characterised by electronic absorption spectroscopy and CV. Chemical or electrochemical oxidation generates $[Ru^{II}(Pc^+)L_2]$ and *not* $[Ru^{III}(Pc)L_2]^+$, as evidenced by EPR and electronic absorption spectroscopy [181]. Treatment of $RuCl_3.xH_2O$ with 1,2-dicyanobenzene or 2-cyanobenzamide has been found to yield mixtures of "[Ru(Pc)]", "[Ru(Pc)Cl]" and [Ru(Pc)L(CO)] (L = solvent used for extraction) in *ca.* 5% yield [182]. However, when the reaction was performed under CO, the CO complex was obtained in good yield, and (for example) extraction of the reaction mixture with pyridine yielded [Ru(Pc)(py)(CO)]. This latter complex has also been prepared from $[Ru_3(CO)_{12}]$ and 1,2-dicyanobenzene, followed by an extraction of the products with pyridine. Other related reactions which have been investigated include:



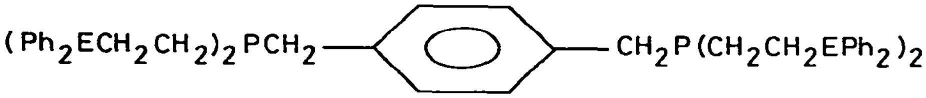
These carbonyl complexes all showed a high solubility in organic solvents [182]. Boucher and Rivera [183] have recently claimed that conventional methods for the preparation of ruthenium(III) phthalocyanine complexes (*e.g.* those discussed in the above paper [182]) do not, in fact, yield phthalocyanine complexes, but give derivatives of a monochlorinated phthalocyanine ring, represented hereinafter by (ClPc), in which the chlorine is a substituent of the ring and *not* attached to a metal. Thus, these authors have found that they can achieve yields of 60–70% of $[Ru(ClPc)(py)_2].4py$ and $[Ru(ClPc)(PPh_3)_2]$ with no evidence being obtained for the complexes of ruthenium(III) claimed in the literature [*e.g.* [182] and references therein]. Their evidence relies heavily on ^1H NMR spectroscopy, however, and work from my own laboratory [184] would strongly suggest that this has been misinterpreted: the spectra reported are much more consistent with a mixture of $[Ru(Pc)(py)_2]$ and [Ru(Pc)(py)(solvent)], and (as described) do not resemble the spectra of genuinely ring-substituted derivatives of ruthenium(II) such as $[Ru\{Pc\text{-}(SO_3)_4\}]^{4-}$ $\{H_2Pc\text{-}(SO_3H)_4$ = phthalocyanine tetrasulphonic acid}. We also cannot support Boucher and Rivera's suggestion that "$[Ru^{III}(Pc)Cl]$" (or, in the light of James' results above [181], "$[Ru^{II}(Pc^+)Cl]$" – no distinction between these formulations will be made in this discussion) cannot be prepared by conventional literature methods; in our hands [184], good yields of a paramagnetic "[Ru(Pc)Cl]" compound were obtained. It is, perhaps, worthy of note that many of the "discrepancies" in the literature can be ascribed to the variable, heterogeneous composition of "$RuCl_3.xH_2O$" (see Section 2.6.1) – we find that the use of pure ruthenium(III) or ruthenium(IV) starting materials can result in very different products or product distributions, but, even so, we have found no evidence for the formation of "[Ru(PcCl)]" [184].

The complexes "[Ru(Pc)]", $[Ru(Pc)(dmso)_2].4dmso$ and $[Ru(Pc)\{(CD_3)_2SO\}_2].4(CD_3)_2SO$ have been demonstrated (like their porphyrin analogues, *vide supra*) to be effective NMR shift reagents for a wide range of imidazoles, pyridines, primary aliphatic amines and primary aromatic amines, for a substantial range of secondary aliphatic amines, secondary aromatic amines and hydrazines, and for a narrow range of tertiary aliphatic amines [185].

2.8.6 *Phosphine, phosphite and arsine complexes*

2.8.6.1 *Halo, carbonylhalo and hydroxo complexes*

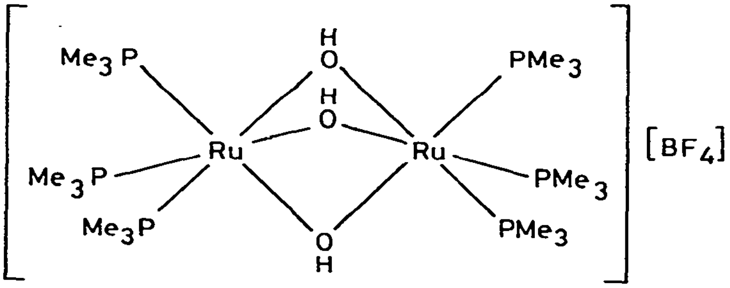
New preparations of $[RuCl_2\{P(OMe)_3\}_4]$ (from "$RuCl_3.xH_2O$" and $P(OMe)_3$ in methanol at reflux) [51] and *trans*-$[RuCl_2(PMe_3)_4]$ (from "$RuCl_3.xH_2O$" and PMe_3 in methanol, or by treatment of $[RuCl_2(PPh_3)_4]$ with PMe_3 in hexane) [186] have been reported, as have the complexes of (24), [Ru(L)Cl]Cl [187]. Some of the reactions of



(24; E = P or As)

[Ru(L)Cl]Cl {L = (24)} with H_2, CO or NO were also investigated in this latter study. It has been reported independently that, although *trans*-$[RuCl_2(PMe_3)_4]$ can be made from $[RuCl_2(PPh_3)_3]$ and an excess of PMe_3, it is better prepared by treating $\{Ru_2(O_2CMe)_4Cl\}_n$ with Na/Hg in thf, in the presence of PMe_3 and lithium chloride [188,189]. Benzene solutions of *trans*-$[RuCl_2(PMe_3)_4]$, upon ageing, produce $[(Me_3P)_4Ru(\mu\text{-}Cl)_2Ru(PMe_3)_4]Cl_2$ and, upon treatment with Na/Hg in thf, yield *cis*-$[RuHCl(PMe_3)_4]$ [189]. $[RuCl(PMe_3)_4][BF_4]$ has also been isolated, as a by-product in the preparation of $[(Me_3P)_2ClRu\text{-}RuCl(PMe_3)_2]$ (see Section 2.9) [189].

The complex $[Ru_2(OH)_3(PMe_3)_6][BF_4]$ (25) was formed as a by-product in the



(25)

preparation of (3) (see Section 2.5) and was characterised by X-ray crystallography: (25) has an Ru...Ru separation of 0.3004 nm [48]. The complex $[Ru_2(OH)_2(\mu\text{-}OH)_2(PMe_3)_6]$ is discussed in Section 2.8.6.5.

CV studies for solutions of $[Ru_2Cl_4(PR_3)_5]$ (R_3 = $ClPh_2$, $MePh_2$ or Et_2Ph) and $[Ru_2Cl_4(PPh_3)_4(CO)]$ show reversible *one-electron* oxidation waves, corresponding to the formation of the mixed valence monopositive cations. Similarly, the stable compounds $[Ru_2Cl_5(PR_3)_3L]$ (R = Ph or C_6H_4-4-Me; L = CO or CS) show a corresponding one-electron reduction wave, corresponding to the formation of $[Ru_2Cl_5(PR_3)_3L]^-$. Intriguingly, the complexes $[Ru_2Cl_5L_4]$ {L = PEt_2Ph or $As(C_6H_4\text{-}4\text{-}Me)_3$} and $[Ru_2Cl_6(AsPh_3)_3]$ show both reversible one-electron oxidation waves *and* reversible one-electron reduction waves [190]. An electrochemical study of $[RuCl_2(CO)_2L_2]$ (L = one of a variety of phosphines, arsines, diimines, or amines) has revealed that these complexes also undergo a one-electron oxidation [104].

$[RuCl_2(PPh_3)_3]$ has been shown to catalyse the following reactions of secondary alcohols, R_2CHOH (R = aryl) [191]:

$$R_2CHOH \longrightarrow R_2CO + H_2 \qquad \text{(dehydrogenation)}$$

$$2R_2CHOH \longrightarrow R_2CHOCHR_2 + H_2O \qquad \text{(dehydration)}$$

$$3R_2CHOH \longrightarrow R_2CHCHR_2 + R_2CO + 2H_2O \qquad \text{(reductive coupling)}$$

$$2R_2CHOH \longrightarrow R_2CH_2 + R_2CO + H_2O \qquad \text{(disproportionation)}$$

$$R_2CHOH + R'_2CHOH \longrightarrow R_2CH_2 + R'_2CO + H_2O \qquad \text{(hydrogenolysis)}$$

The conditions for the promotion of each of the above reactions have been optimised and defined, and hydrido and alkoxy complexes of ruthenium have been shown to be involved as intermediates [191]. $[RuCl_2(PPh_3)_3]$ will also catalyse the reduction of azobenzene to aniline by Me_2CHOH [192], the selective hydrogenation of α,β-unsaturated ketones to saturated ketones under mild homogeneous conditions [193], and the hydrogenation of aldehydes or ketones [194], and will decarbonylate $[(cp)Fe(CO)_2\{C(O)R\}]$ (R = Me or Ph) to give $[Ru(PPh_3)_2(CO)_2Cl_2]$ [195]. This last reaction occurs only slowly, even in benzene at reflux, and so is of little synthetic utility. Studies with $[Ru_2Cl_4\{(+)\text{-diop}\}_3]$ and $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ continue and these complexes have been found to be catalysts for the asymmetric transfer hydrogenation of prochiral unsaturated acids or esters by alcohols, giving typical values of *ca.* 15% optical purity for the acids and *ca.* 5% for the esters [196]:

$$RR'CHOH + R''CH{=}C(R''')CO_2R'''' \longrightarrow RR'C{=}O + R''CH_2\overset{*}{C}H(R''')CO_2R''''$$

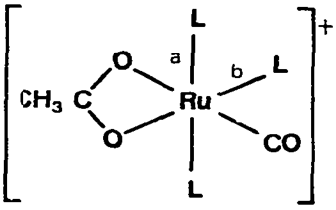
The complexes $[RuCl_2(PMe_3)_4]$ and $[Ru(PMe_3)_2(CO)_2Cl_2]$ are both catalysts for the hydrogenation of dec-1-ene in the presence of $Me_2NH.BH_3$ and alcohol; the latter complex is the better catalyst [197].

In an interesting series of papers [198-200], water-soluble analogues of several triphenylphosphine complexes of ruthenium(II) (see also Section 2.8.6.5) have been prepared using the salt Na[(SO_3-3-C_6H_4)PPh_2] (Na[L]), including $Na_2[RuL_2(CO)_2Cl_2]$ and $Na_2[RuL_2Cl_2]$: the latter complex was shown to catalyse the aqueous phase hydrogenation of *trans*-MeCH=CH(CO_2H) and of MeC(O)CO_2H.

The complex $[(CO)_3ClRu(\mu\text{-}AsMe_2)_2RuCl(CO)_3]$ has been prepared by treating $[Ru_3(CO)_{12}]$ with $AsMe_2Cl$ in petroleum ether [201].

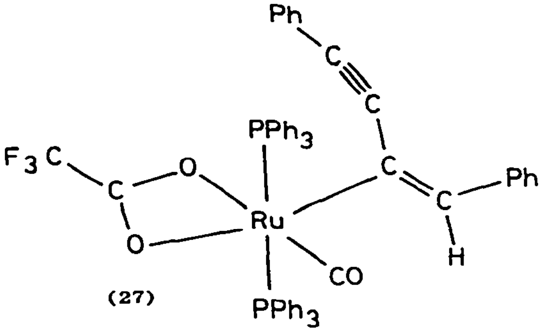
2.8.6.2 *Complexes containing oxygen donor ligands*

The molecular structure of $[Ru(O_2CMe)(CO)(PMePh_2)_3][PF_6]$ **(26)** has been reported [202]. Treatment of $[RuH(PMe_2Ph)_5][PF_6]$ with CO_2 in an ethanolic solution of $NHMe_2$ yields $[Ru(O_2CNMe_2)(PMe_2Ph)_4][PF_6]$, which was also structurally characterised and, like **(26)**, shown to possess Ru-P bonds *trans* to oxygen which are significantly shorter (at 0.228 nm) than those of the mutually *trans* phosphines (at 0.241 nm) [203].



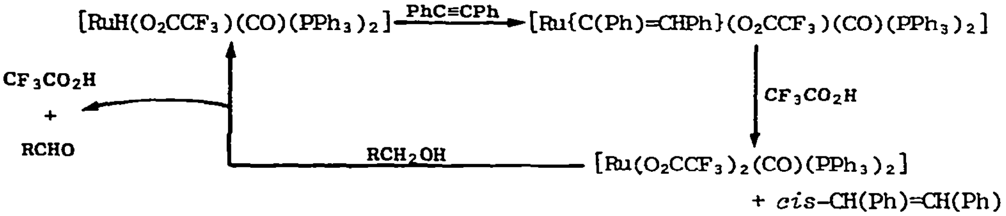
a = 0.241 nm
b = 0.231 nm

(26; L = PMe_2Ph)



(27)

The complexes $[RuH(O_2CCF_3)(CO)(PPh_3)_2]$ and $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ react with alkynes, with terminal or internal C≡C linkages, to give oligomerisation or hydrogenation products, respectively, along with vinyl complexes. Thus:



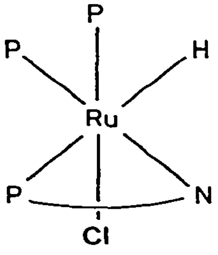
With phenylethyne, the initial product is $[Ru(C{\equiv}CPh)(O_2CCF_3)(CO)(PPh_3)_2]$, which reacts with a further mole of PhC≡CH to give $[Ru(C_4HPh_2)(O_2CCF_3)(CO)(PPh_3)_2]$ **(27)** [204].

2.8.6.3 *Complexes with nitrogen donor ligands*

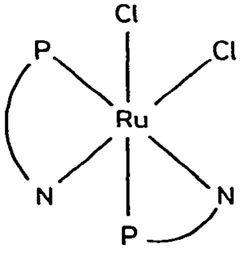
Treatment of $[NEt_4][RuCl_4(NCR)_2]$ (R = C_6H_4-2-Me) with $PMePh_2$ yields

$[RuCl_2(NCR)_2(PMePh_2)_2]$ [15], whereas $[RuHCl(PPh_3)_3]$ reacts with $Li[N(SiMe_3)_2]$ in thf to yield the red, monomeric and diamagnetic compound, $[RuH\{N(SiMe_3)_2\}(PPh_3)_2]$, which is air-stable and soluble in hydrocarbons. On heating, however, this latter complex eliminates $NH(SiMe_3)_2$ [205].

Two complexes of tris(2-pyridyl)phosphine, $[Ru\{P(py)_3\}_3HCl]$ (28) or



(28)

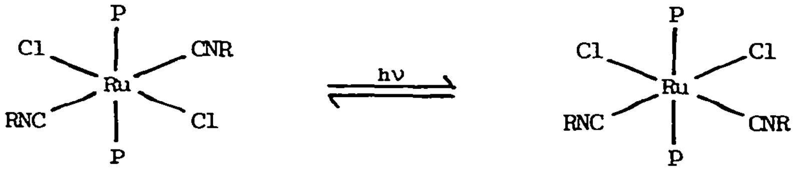


(29)

$[Ru\{P(py)_3\}_2Cl_2]$ (29), have been prepared by treating $[Ru(PPh_3)_3HCl]$ or $[Ru(PPh_3)_3Cl_2]$ with $P(py)_3$ in C_6H_6, respectively. Their structures have been postulated although (29) is thought to have been obtained as a mixture of isomers [206].

2.8.6.4 Isonitrile and dithiomethylester complexes

The complexes $[RuX_2(CNC_6H_4\text{-}4\text{-}Me)_2L_2]$ (X = Cl or Br; L = $AsPh_2R$, $AsPh_3$ or $SbPh_3$; R = Me, Et or Pr) have been reported [108,207]. UV irradiation of $[RuCl_2(CNCMe_3)_2(PPh_3)_2]$ brings about an isomerisation reaction; the composition of the photo-stationary state was found to be wavelength dependent [208]:

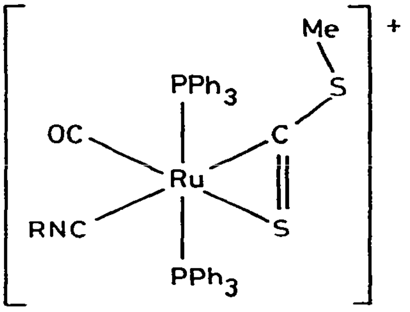


The molecular structures of the interesting η^2-dithiomethylester complexes $[Ru(\eta^2\text{-}CS_2Me)(CO)\{CNC_6H_4\text{-}4\text{-}Me\}(PPh_3)_2][ClO_4]$ (30) and $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2][ClO_4]$ (31) have been determined [209].

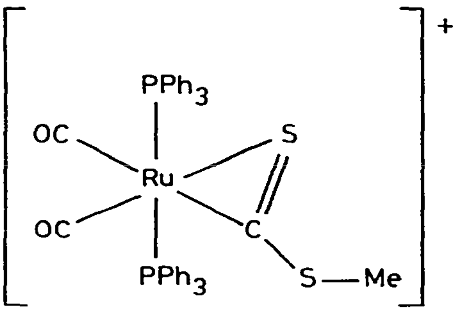
2.8.6.5 Hydride complexes

The molecular structure of *cis*-$[RuH_2(dppe)_2].C_6H_6$ has been determined $\{\bar{r}(RuH) = 0.158(15)\ nm\}$ and a novel synthetic route to $[RuH_2L_4]$ (L = PPh_3, PPh_2Me, $PPhMe_2$ or ½dppe) reported [210]:

$$[Ru(\eta^4\text{-}cod)(\eta^6\text{-}cotr)] \xrightarrow[L;\ thf]{H_2} [RuH_2L_4]$$



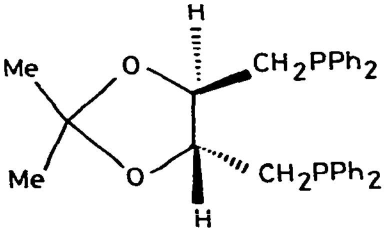
(30)



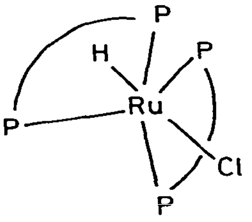
(31)

$[RuH_2(PPh_3)_4]$ reacts with a variety of *N*-, *S*- or *O*- donor ligands {*e.g.* bipy, 1,2-$C_6H_4(CN)_2$, py-2-OH, quin-8-OH, py-2-NH_2, py-2-SH, 1,2-$C_6H_4(NH_2)_2$, NH_2-2-C_6H_4SH, NH_2-2-C_6H_4OH, 1,2-$C_6H_4(OH)_2$, 1,3-$C_6H_4(OH)_2$ or 1,4-$C_6H_4(OH)_2$} to give, *inter alia*, $[RuH_2(PPh_3)_2(bipy)]$, $[RuH_2(PPh_3)_3\{1,2\text{-}C_6H_4(CN)_2\}]$, $[RuH(PPh_3)_3(L\text{-}L')]$ (L-L'H = quin-8-OH, py-2-OH or py-2-NH_2), $[Ru(PPh_3)_3(L\text{-}L')_2]$ (L-L'H = quin-8-OH, py-2-OH or NH_2-2-C_6H_4OH), $[Ru(PPh_3)_3(L\text{-}L)]$ or $[Ru(PPh_3)_2(CO)(L\text{-}L)]$ (HL-LH = 1,2-$C_6H_4(NH_2)_2$), $[RuH(PPh_3)_2(L\text{-}L')]$ (L-L'H = HO-3-C_6H_4OH or HO-2-C_6H_4OH) or $[Ru_2H_2(PPh_3)_4(1,4\text{-}C_6H_4O_2)_3]$ [211]. Moreover, the full details of the reactions of RNCO (R = C_6H_4-4-Me) with $[RuHX(CO)(PPh_3)_3]$ (X = Cl or Br), $[RuH_2(CO)(PPh_3)_3]$ or $[RuH_2(PPh_3)_4]$ to give the formamide, ureylene or formamidinate complexes reported last year [1; p. 58] have now appeared [212].

The exciting work with diop (32) continues, with a clarification of the structure of $[RuHCl(diop)_2]$ (33), which has now been crystallographically demonstrated to possess a *trans* configuration [213]. (33) was originally assigned a *cis* geometry on the basis of ^{31}P and ^1H NMR spectroscopic studies; this assignment was incorrect as the doublet of triplets observed arose, not from the *cis* configuration, but from the deceptively simple AA'BB'X spin system of the *trans* isomer [213]. (33) will catalytically hydrogenate activated alkenes (including prochiral alkenes in high optical yields) under mild conditions. Studies on acrylamide and α-phenylacrylic acid have indicated a mechanism



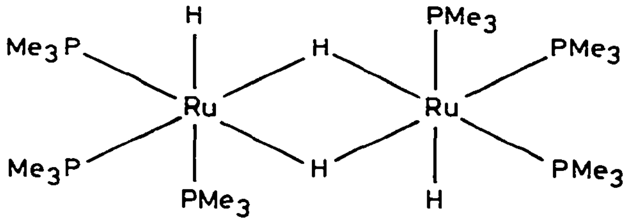
{32; (4R,5R)-(-)-diop}



{33; P-P = (32)}

involving the coordination of the alkene to give an alkyl intermediate that, in the rate-determining step, subsequently reacts with H_2 to give the saturated product and regenerate the compound (33): a diop ligand dissociates to allow the initial alkene coordination [214,215].

Some interesting dimeric complexes have been reported this year. Thus, treatment of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ with H_2 (3 atm) in petroleum ether gives $[Ru_2H_2(\mu\text{-}H)_2(PMe_3)_6]$ (34) quantitatively. This complex will react with one equivalent of $H[BF_4]$ in thf to give $[Ru_2(\mu\text{-}H)_3(PMe_3)_6][BF_4]$ {r(RuRu) = 0.2540 nm} (*cf.* (25); Section 2.8.6.1) [216]. $\{Ru_2(O_2CMe)_4Cl\}_n$ reacts with Na/Hg in thf, in the presence of PMe_3 and H_2 (3 atm), to give *cis*-$[RuH_2(PMe_3)_4]$; the latter complex reacts with an excess of water in thf at 60 °C to give $[Ru_2(OH)_2(\mu\text{-}OH)_2(PMe_3)_6]$, which is presumed to have a structure analogous to (34) [216]. $[Ru_2H_2(\mu\text{-}Cl)_2(PPh_3)_6]$, which also is presumed to have a structure similar to (34), has been prepared by the unusual method of treating $[RuH_2(PPh_3)_4]$ with $Si_4Cl_2Ph_8$ in benzene, in the presence of NEt_3. $[Ru_2H_2(\mu\text{-}Cl)_2(PPh_3)_6]$ is different, chemically and spectroscopically, from $[Ru(PPh_3)_3HCl]$.solvate, and undergoes spontaneous decomposition in benzene or thf to give H_2 and a compound analysing as $\{Ru(PPh_3)_3Cl\}_x$ (*cf.* Section 2.9) [217]. It is notable that the last occasion when $\{Ru(PPh_3)_3Cl\}_x$ was claimed [218], the material turned out to be $[Ru(PPh_3)_3HCl]$.



r(RuRu) = 0.2811 nm

(34)

In an interesting insertion reaction, $[RuHCl(CO)(PPh_3)_3]$ reacts with RCH=CHR' {= CH(CO$_2$Me)=CH(CO$_2$Me) or CH_2=CH-2-py} to give the compounds $[RuCl(CO)(RCH\text{-}CH_2R')(PPh_3)_2]$, in which the alkyl residue is bidentate, coordinated through the σ-alkyl bond and also *via* R' [219]. With CH_2=CH(CN), however, $[(Ph_3P)_2(OC)Ru\{CH(Me)(CN)\}(\mu\text{-}Cl)_2Ru\{CH(Me)(CN)\}(CO)(PPh_3)_2]$ is formed, with a more normal monodentate alkyl group present [219].

The preparation, properties and catalytic activity of $[RuH_2(PPh_3)_4]$ have been reviewed briefly [220], and $[RuHCl(PPh_3)_3]$ reported to induce the isomerisation of *N*-allylamides to give aliphatic enamides [221]:

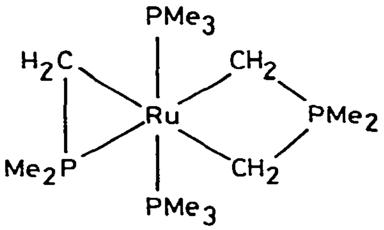
e.g.

$[RuHCl(CO)(PPh_3)_3]$ is a good homogeneous catalyst for the selective hydrogenation of α,β-unsaturated ketones, forming saturated ketones under mild conditions [193]; both $[RuHCl(CO)(PPh_3)_3]$ and $[RuHCl(PPh_3)_3]$ are effective catalysts for the hydrogenation of various aldehydes and ketones [194]. Water soluble analogues of several of these PPh_3 complexes have been prepared using the salt $Na[(SO_3\text{-}3\text{-}C_6H_4)PPh_2]$, Na[L], including $Na_2[RuHCl(CO)_2L_2]$, $Na_3[RuHCl(CO)L_3]$, $Na_3[RuH(O_2CMe)L_3]$ and $Na_3[RuHClL_3]$ [198]; $[RuH(O_2CMe)L_3]^{3-}$ has been demonstrated to catalyse the aqueous phase hydrogenation of *trans*-$MeCH{=}CH(CO_2H)$ [199] and of $MeC(O)CO_2H$ [200].

2.8.6.6 *Cycloruthenated complexes*

The novel complexes $K[Ru\{(C_6H_4)PPh_2\}(PPh_3)_2H_2].Et_2O.C_{10}H_8$ and $K_2[Ru_2(PPh_2)_2(PPh_3)_2H_4]$.2diglyme are active catalysts for the mild, homogeneous catalytic hydrogenation of aliphatic carboxylic acid esters to alcohols [222] or of polycyclic aromatics (*e.g.* anthracene → 1,2,3,4-tetrahydroanthracene) [223].

Treatment of *trans*-$[RuCl_2(PMe_3)_4]$ with $Li[(CH_2)_2PMe_2]$ yields the novel complex (35) and the interesting by-product (36) [186]. Full details of the *chemical* reduction of $[Ru(PPh_3)_3Cl_2]$ with Na or Mg amalgam, to give $[RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2]$, have now been published [224] {*cf.* the product claimed from the *electrochemical* reduction, $[Ru(MeCN)(PPh_3)_4(\pi\text{-}MeCN)]$ [225]}. Cole-Hamilton and Wilkinson contend that the products from the chemical and electrochemical reduction are identical and should be formulated as $[RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2]$ [224], whereas the original workers maintain that the products are not the same, and that the product of the electrochemical reduction is correctly formulated as a ruthenium(0) complex [226]. The complexes $[RuH(C_6H_4PPh_2)(py)(PPh_3)_2]$ and $[RuH(C_6H_4PPh_2)(bipy)(PPh_3)]$ have also been reported and characterised [224].



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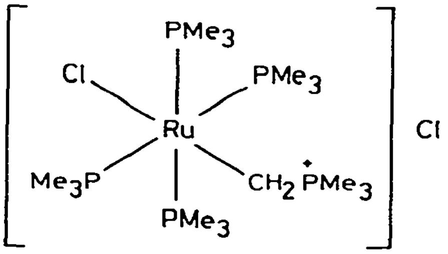
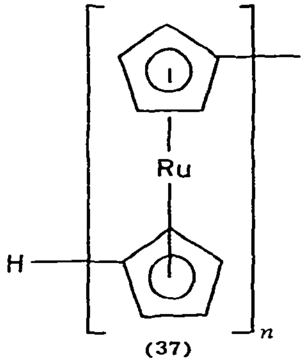


(36)

2.8.7 *Organometallic compounds*

Whilst organometallic chemistry is strictly outside the scope of this review, note is made here of a few papers of particular relevance to coordination chemists.

A new facile route to [Ru(cp)$_2$] has been described [227], and oligomers of ruthenocene (37; n = 2, 3 or 4) have been prepared in low yield [228]. The complex [(η^6-C_6Me_6)Ru(μ-H)$_2$(μ-Cl)Ru(η^6-C_6Me_6)]Cl has been shown to be an efficient homogeneous hydrogenation catalyst under mild conditions, converting alkenes to alkanes, arenes to cyclohexanes, styrene to ethylcyclohexane and aryl ketones to cyclohexyl ketones [229], whereas [(η^6-C_6Me_6)Ru(μ-OH)$_3$Ru(η^6-C_6Me_6)]$^+$ catalyses the disproportionation of ethanal to ethanoic acid and ethanol [230]. The crystal structure of [Ru(cp)(CO)$_2$(CONH$_2$)] has been reported [231]. Treatment of [Ru(CO)$_2$X(Me)L$_2$] (X = Cl, Br or I; L = PMe$_2$Ph or AsMe$_2$Ph) with L' (L' = CO, various phosphines or AsMe$_2$Ph) has been shown to yield [Ru(CO)X(COMe)L$_2$L']; the formation of the acetyl group involves an intramolecular rearrangement [232]. [Ru(CO)$_2$(PPh$_3$)$_3$] reacts with MeHgI to give [Ru(CO)(PPh$_3$)$_2$I{η^2-C(O)CH$_3$}] (38) which, in solution, is predominantly in the form [Ru(CO)$_2$(PPh$_3$)$_2$I(Me)] [233]. (38) has been structurally characterised, together with its analogue [Ru(CO)(PPh$_3$)$_2$I{η^2-C(O)C$_6$H$_4$-4-Me}] [233].



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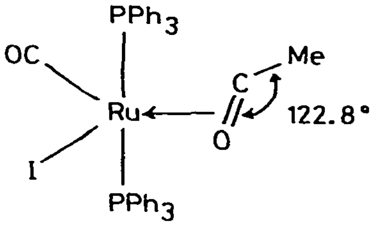


(38)

The compounds [Ru(cp)(dppe)L][PF$_6$] (L = alkene, CO, py or MeCN) have been prepared by the treatment of [Ru(cp)(dppe)Cl] with L and [NH$_4$][PF$_6$] in MeOH at 20 °C; treatment of [Ru(cp)(dppe)Cl] with Li[AlH$_4$] or LiMe gave [Ru(cp)(dppe)H] or [Ru(cp)(dppe)Me], respectively [234]. Some reactions of [Ru(cp)(PPh$_3$)$_2$Cl] and [Ru(cp)(CO)$_2$Cl] are summarised in Scheme III [235].

2.8.8 Trichlorosilyl derivatives

A new preparation of [Ru(CO)$_4$(SiCl$_3$)$_2$], from the photochemical reaction between [Ru$_3$(CO)$_{12}$] and SiCl$_3$H in hexane under CO (2 atm), results in the almost quantitative formation of the *cis*-isomer (which is extremely difficult to prepare pure by any other route). At 70 °C, this complex isomerises to give a mixture of 70% *trans* and 30% *cis* isomers; it reacts with PPh$_3$ at ambient temperatures to give *mer*-[Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$], and with 1,3,5-C$_6$H$_3$Me$_3$ at reflux to give [Ru(C$_6$H$_3$Me$_3$)(CO)(SiCl$_3$)$_2$] in good yield. *Mer*-[Ru(CO)$_3$(PPh$_3$)(SiCl$_3$)$_2$]

SCHEME III: Some reactions of $[Ru(cp)(PR_3)_2Cl]$ and $[Ru(cp)(CO)_2Cl]$ [235].

will not react with further quantities of PPh_3, even at 80 °C, but will react with $P(OMe)_3$ to yield $[Ru(CO)_2(PPh_3)\{P(OMe)_3\}(SiCl_3)_2]$ [236]. If, during the synthesis of *cis*-$[Ru(CO)_4(SiCl_3)_2]$, a shorter irradiation time is used, *cis*-$[Ru(CO)_4H(SiCl_3)]$ (air-sensitive; m.p. 22-23 °C) is formed, which will also react with PPh_3 to give *mer*-$[Ru(CO)_3(PPh_3)H(SiCl_3)]$ [236]. Substitution reactions of these complexes occurs *trans* to $SiCl_3$ in all cases, as this ligand has a greater *trans* labilising effect than either CO or hydride. This property has been used to prepare a wide range of $[Ru(CO)_3(PR_3)(SiCl_3)_2]$ and $[Ru(CO)_2(PR_3)_2(SiCl_3)_2]$ phosphine complexes [237]. *Cis*-$[Ru(CO)_4(SiCl_3)_2]$ will also react with bidentate ligands, L-L {L-L = $MeS(CH_2)_2SMe$, $R_2P(=S)P(=S)R_2$ (R = Me or Et), dppm, dppe, diars, dpae, bipy, nbd, cod or cot} to give specific substitution of the CO groups *trans* to the two $SiCl_3$ groups, yielding *trans*,*cis*,*cis*-$[Ru(CO)_2(L\text{-}L)(SiCl_3)_2]$: the complexes $[(Cl_3Si)_2(OC)_3Ru(\mu\text{-}L\text{-}L)Ru(CO)_3(SiCl_3)_2]$

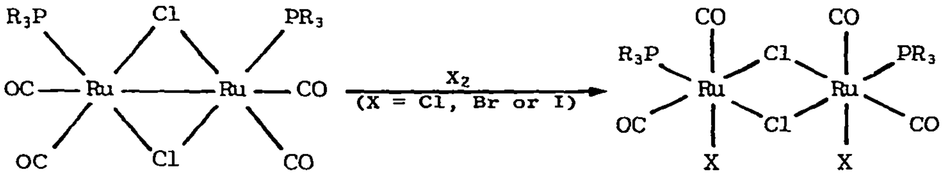
(L-L = dppm, dppe or dpae) were also isolated in this study [238].

2.8.9 *Hydrides*

The salts A_2RuH_6 (A = Ca, Sr, Eu or Yb) have been characterised by ^{99}Ru Mössbauer spectroscopy at 4.2 K and shown to contain low-spin ruthenium(II) [239].

2.9 RUTHENIUM(I)

The well known reaction [240]:



has been reinvestigated [241], using $P(CMe_3)_3$ instead of the $P(CMe_3)_2(Ar)$ (Ar = various aryl groups, *e.g.* C_6H_4-4-Me) ligands used originally, giving (not surprisingly) similar products. The complexes $[Ru_2(CO)_4(\mu\text{-}X)_2\{P(CMe_3)_3\}_2]$ (X = Cl, Br or I) have also been prepared [242] by conventional methods [240]; the bromide complex was crystallographically characterised and the molecules shown to possess the expected structure. Complexes of the well-established class $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(PR_3)_2]$ (*e.g.* $[Ru_2(CO)_4(O_2CMe)_2\{P(CMe_3)_2(C_6H_4Me)\}_2]$ [240]) have also been prepared by treating $[Ru_3(CO)_{12}]$ with $P(CMe_3)_3$ and RCO_2H (R = H, Me, Et, Pr or $C_{17}H_{35}$) [243]. The complex $[Ru_2(CO)_4(\mu\text{-}I)_2\{P(CMe_3)_2H\}_2]$ has been prepared by the reaction of $[Ru_2(CO)_6I_2(\mu\text{-}I)_2]$ with $P(CMe_3)_3$ in 2-methoxyethanol [244]; treatment of "$RuCl_3.xH_2O$" with CO, NaI and $P(CMe_3)_3$ in 2-methoxyethanol yielded only the ruthenium(II) complex $[(Me_3C)_3PH]_2[Ru_2I_4(\mu\text{-}I)_2(CO)_2\{P(CMe_3)_2H\}_2]$ [244].

Some interesting new chemistry has been reported by Wilkinson and coworkers. Thus, treatment of $\{Ru_2(O_2CMe)_4Cl\}_n$ with $Mg(C_6H_4\text{-}2\text{-}OMe)_2$ in the presence of PMe_3, followed by treatment with $[CPh_3][BF_4]$ in thf, yields $[(Me_3P)_2ClRuRuCl(PMe_3)_2]$ [189]. Treatment of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ with water in thf yields the unusual complex $[(Me_3P)_3Ru(\mu\text{-}OH)(\mu\text{-}H)Ru(PMe_3)_3]$ [216]. Each of these compounds represents a new type of complex.

The VT UV-VIS and IR spectra of $[Ru_2(cp)_2(CO)_4]$ have been reported [245], and the details are in accord with the temperature dependent equilibria established by Manning [246]:

$$[(cp)(CO)Ru(\mu\text{-}CO)_2Ru(CO)(cp)] \rightleftharpoons [(cp)(CO)_2Ru\text{-}Ru(CO)_2(cp)]$$

(bridged isomers) **(non-bridged isomers)**

The $\sigma \rightarrow \sigma^*$ transition associated with the Ru-Ru bond was identified at 37735 cm^{-1} in the bridged isomers, and at 30305 cm^{-1} in the non-bridged isomers. Irradiation of the isomeric mixture in CCl_4 yielded $[Ru(cp)(CO)_2Cl]$ as the sole carbonyl-containing product, illustrating the efficient cleavage of the Ru-Ru bond (even in the presence of bridging carbonyl groups) [245]. $[Ru_2(cp)_2(CO)_4]$ reacts with $P(OR)_3$ (R = Me, Et or Bu) to give $[Ru(cp)(CO)_2R]$, whereas with PPr_3 it yields a mixture of $[Ru_2(cp)_2(CO)_3(PPr_3)]$ and $[Ru(cp)(CO)(PPr_3)Cl]$. The chloride in this last complex is derived from CH_2Cl_2, and the precursor is believed to be $[Ru(cp)(CO)(PPr_3)H]$ [247]. Treatment of $[Ru_3(CO)_{12}]$ with $AsMe_2R$ (R = H or NMe_2) in C_6H_6 yields $[(CO)_3Ru(\mu\text{-}AsMe_2)_2Ru(CO)_3]$ [201].

2.10 RUTHENIUM(0)

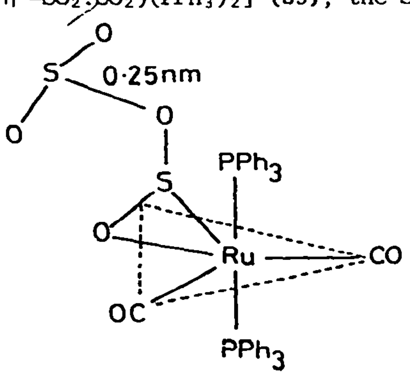
The kinetics of the following reaction have been studied [248]:

$$[Ru(CO)_5] + PR_3 \longrightarrow [Ru(CO)_4(PR_3)] + CO$$

(R = Ph, Bu or OMe)

The rate determining step involves the dissociation of CO to generate $[Ru(CO)_4]$. The oxidation of $[Ru(CO)_5]$ by I_2, to give *cis*-$[Ru(CO)_4I_2]$ and CO, proceeds by straightforward oxidative elimination reaction [248]. A report on the photoactivation of $[Ru(CO)_n(PPh_3)_{5-n}]$ (n = 5, 4 or 3) towards the isomerisation, hydrogenation and hydrosilylation of pent-1-ene has appeared [249]. $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ reacts with CO (5 atm) at 60 °C to give *trans*-$[Ru(CO)_3(PMe_3)_2]$, and this product has been characterised crystallographically [48].

Trans-$[Ru(CO)_3(PPh_3)_2]$ reacts with a saturated solution of SO_2 in benzene/heptane to give $[Ru(CO)_2(\eta^2\text{-}SO_2.SO_2)(PPh_3)_2]$ (39); the structure of (39) was

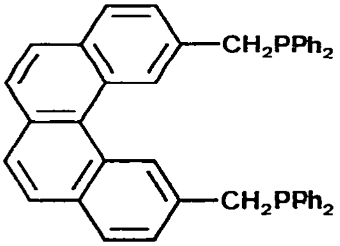


(39)

determined at -60 °C [250].

Full details are now available of the preparation and isolation of the red paramagnetic ruthenium(0) complex $[Ru(MeCN)_2(PPh_3)_2]$, as well as of $[Ru(MeCN)_3(PPh_3)_2]$ and $[Ru(MeCN)(PPh_3)_3]$ [224]. $[Ru\{P(OMe)_3\}_5]$ has been shown to undergo an interesting isomerisation at 150 °C to give $[\{(MeO)_3P\}_4Ru(Me)\{P(O)(OMe)_2\}]$: both isomers react with MeI to yield $[Ru\{P(OMe)_3\}_5Me]I$ [251].

Complexes of the *trans*-spanning bidentate phosphine ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (40), of formulation $[Ru(CO)_3(L\text{-}L)]$, have



(40)

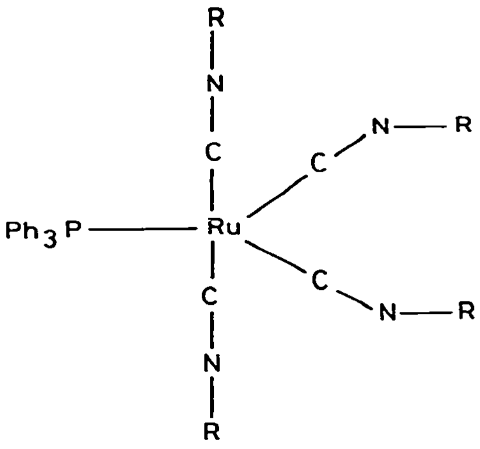
been prepared by the photochemical reaction of (40) with $[Ru(CO)_3(cot)]$: the complex $[Ru(CO)_3(Ph_2PCH_2Ph)_2]$ was also prepared by treating $\{RuCl_2(C_7H_8)\}_n$ with hydrazine hydrate and Ph_2PCH_2Ph in ethanol under CO. Both complexes $[Ru(CO)_3(L\text{-}L)]$ $\{L\text{-}L = (40)\}$ and $[Ru(CO)_3(Ph_2PCH_2Ph)_2]$ were characterised by ^1H and ^{31}P NMR and IR spectroscopy [252].

Ruthenium(0) isonitrile complexes have been prepared according to [253]:

$$trans\text{-}[RuCl_2(CNCMe_3)_4] \xrightarrow[CNCMe_3]{Na/Hg;\ thf} \underset{(41)}{[Ru(CNCMe_3)_5]} \xrightarrow{PPh_3} \underset{(42)}{[Ru(CNCMe_3)_4(PPh_3)]}$$

(42), and the iron analogue of (41), have been crystallographically characterised; (42) has a structure based on a trigonal bipyramid, with linear axial CNR ligands but with the equatorial isonitrile group being bent ($C\hat{N}R$ = 130°) [253].

$[Ru(CO)_2(PPh_3)_2(N_2R)]$ $\{R = C_5Cl_4$, C_5Br_4, -9-fluorene or -9-(2,7-Br_2-fluorene)$\}$ were prepared by treatment of $[Ru(CO)_2(PPh_3)_2(C_2H_4)]$ with the appropriate diazo derivative; $[Ru(CO)_2(PPh_3)_2(N_2C_5Cl_4)].CH_2Cl_2$ (43) was structurally characterised. All of these complexes show a $\nu(NN)$ stretching frequency at *ca*. 1500 cm^{-1}, strongly suggesting that they all involve η^2-coordination of the diazo group [254]. The 1,4-diazabutadiene ligands, R-N=CHCH=N-R (dad; R = CMe_3, $CHMe_2$ or cych), react with $[Ru_3(CO)_{12}]$ to yield $[Ru_2(CO)_6(dad)]$; these complexes were characterised by IR and NMR spectroscopy, and are believed to have the structure



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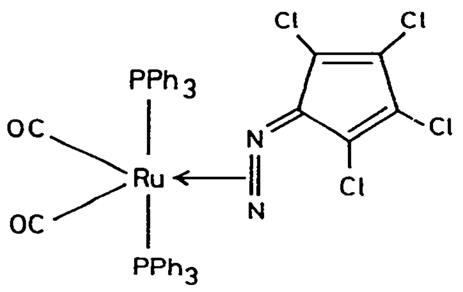
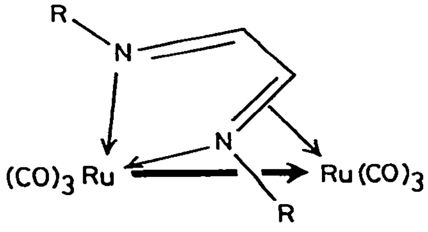


(43)

(44). Treatment of [$Fe(CO)_3$(dad)] with [$Ru_3(CO)_{12}$] yields an isomeric mixture of [$RuFe(CO)_6$(dad)]; one complex with the Ru receiving the π-donation from the dad ligand, the other with the iron accepting it. [$Ru_2(CO)_6$(dad)] reacts with



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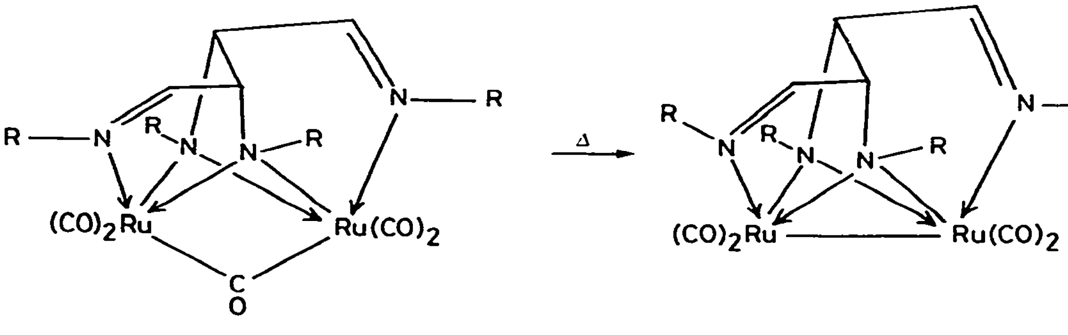
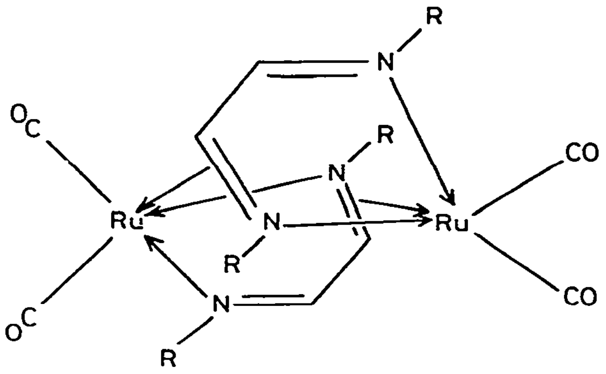


(45)

(46)

a further mole of dad to give (45), which involves a dimerised dad ligand; upon heating, (45) gives (46). Prolonged heating of (46) at 150 °C causes cleavage of the C–C bond, forming [$Ru_2(CO)_4(dad)_2$] (47); the dad (R = $CHMe_2$) complex has been crystallographically characterised [255,256].



(47)

2.11 RUTHENIUM(-II)

IR evidence has been presented and interpreted as indicating that $[Ru(CO)_4]^{2-}$ is able to reduce CO_2 to CO, according to [257]:

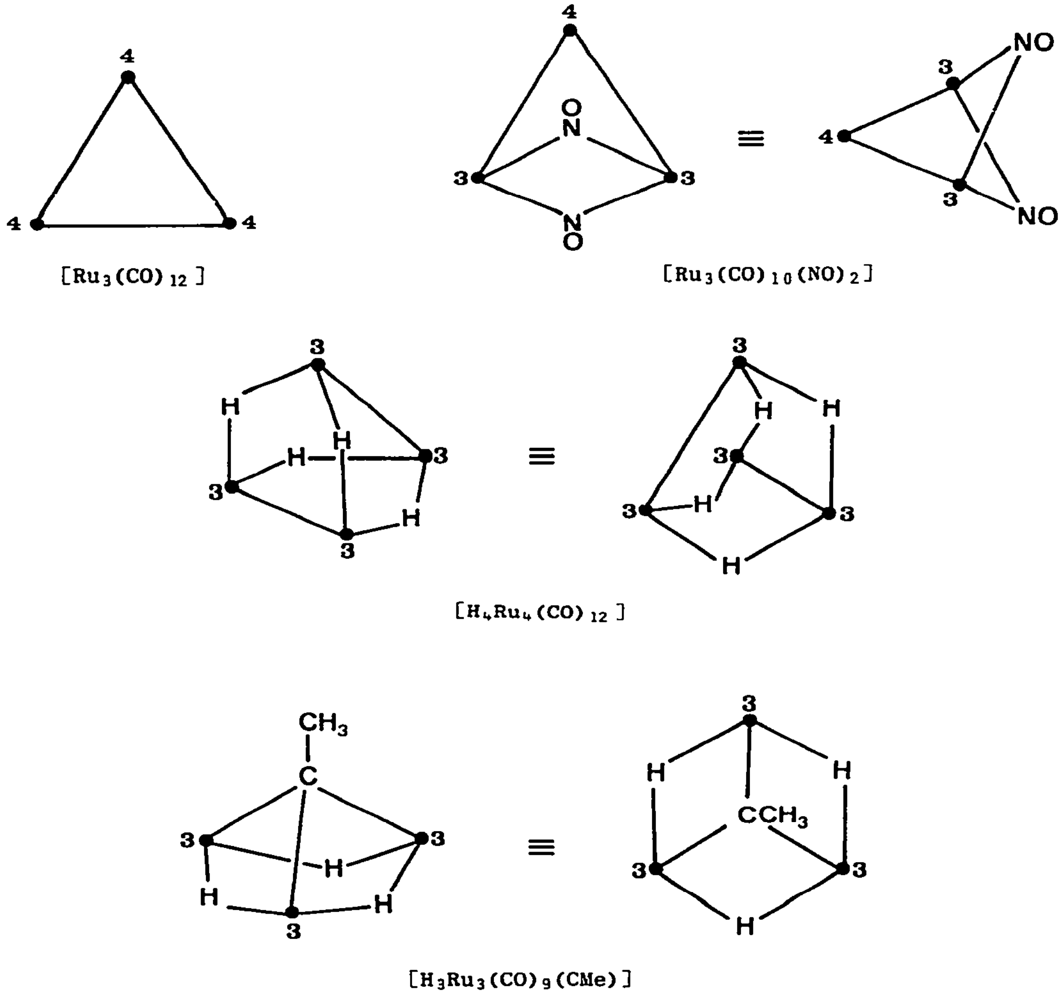
$$Na_2[Ru(CO)_4] + 2CO_2 \longrightarrow [Ru(CO)_5] + Na_2[CO_3]$$

2.12 BORIDES

The structure of Ru_7B_3 has been described in terms of the *stella quadrangula* building unit [258], and the magnetic behaviour of MRu_3B_2 (M = lanthanide) materials has been studied from 1.8-1100 K [259].

2.13 RUTHENIUM CARBONYL CLUSTERS

This year has seen many exciting advances in ruthenium cluster chemistry. High-yield synthetic routes have been developed for ruthenium and osmium clusters of nuclearity ≥6, and the chemistry of these species is now being developed. One problem this has created, however, is one of representation - it is very difficult to draw the structure of a high nuclearity cluster and see the chemically important features at a glance (or, indeed, after prolonged examination!) A system of representation is used in this section (and in Section 3.9 of the companion review on osmium) which, at least in part, circumvents some of the problems. Thus, all of the ruthenium atoms are represented by a solid circle (●) within a predominantly ruthenium cluster - only heteroatoms are marked by their chemical symbols. The number of terminal carbonyl groups on each metal atom is indicated numerically, rather than by inclusion of their geometric representation. All of the metal-metal bonds are marked, as are all of the bridging and interstitial ligands. Where a bridging hydride is found, no direct metal-metal bond is indicated (for the rationale of this, see Section 3.9.1). Some common structures are represented by the formalism in Fig. 3. This method may have some deficiencies (*e.g.* it shows nothing of the relative orientation of terminal ligands), but it does offer a clear view of the metal cluster core.



$[Ru_3(CO)_{12}]$

$[Ru_3(CO)_{10}(NO)_2]$

$[H_4Ru_4(CO)_{12}]$

$[H_3Ru_3(CO)_9(CMe)]$

Fig. 3: Some representations of well-known cluster complexes according to the abbreviated structural formalism described in Section 2.13.

A major feature of this year's publications has been the appearance of a book dedicated entirely to transition metal clusters [260]. It contains chapters dealing with the structure of metal cluster compounds [261], the bonding within clusters [262], cubane structures [263], thermochemical estimation of metal-metal bond enthalpy contributions in clusters [264], reactions of metal clusters [265], ligand mobility in clusters [266], the use of metal clusters in catalysis [267], and a physicist's view of the electron distribution within clusters [268]. This represents an invaluable addition to the documentation of metal cluster chemistry. Also of general interest, the second part [269] (for part I, see [270]) of Johnson's novel approach to structure and fluxional behaviour in binary carbonyl clusters has appeared. The model is based on the observation that carbonyl ligands pack in space so as to minimise non-bonded interactions, and the assumption that the structure of $[M_m(CO)_n]$ clusters is merely a reflection of the insertion of an M_m polyhedron within the $(CO)_n$ polyhedron. This model has come in for some criticism [*e.g.* 271], but this latest article [269] discusses most of these problems in detail. The recent advances in high nuclearity clusters will certainly prove to be a good testing ground for this theory.

Another important general article to appear this year describes a quantitative procedure for indirectly locating hydride ligands bound to transition metal clusters, and has been tested against a series of complexes in which the hydrides have been directly located by a combination of X-ray and neutron diffraction studies. The method was then applied to a number of structures where qualitative arguments had been unable to achieve an unambiguous location of the hydride ligands, and definite predictions made [272]. The rapid expansion in this area of chemistry will soon reveal the utility of the technique.

As last year, papers dealing solely with organometallic chemistry have been excluded from this Section.

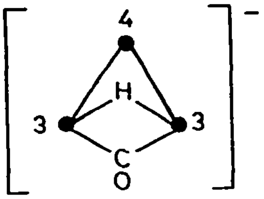
2.13.1 Trimeric clusters

Another autoclave synthesis for the preparation of $[Ru_3(CO)_{12}]$ has been reported [273]. ^{17}O NMR studies upon $[Ru_3(CO)_{12}]$ (enriched with 7% $C^{17}O$ by exchange) show a single resonance at room temperature: the narrow line-width observed (*ca.* 22 Hz) is very encouraging for further studies [274]. Two additional reports of the UVPES spectra of $[Ru_3(CO)_{12}]$ have appeared [275,276], which add little to results reported last year [1; pp. 60,71]. In particular, the utility of CNDO calculations [276] for molecules of this size must be open to question.

The adsorption of $[Ru_3(CO)_{12}]$ onto Al_2O_3 has been studied by inelastic electron-tunnelling spectroscopy; the cluster was found to retain its structure upon adsorption: heating of the material to 470 K (0.1τ of O_2) causes the desorption and possible oxidation of the cluster [277]. The high resolution IR and Raman spectra of $[Ru_nOs_{3-n}(CO)_{12}]$ (n = 0, 1, 2 or 3) have been reported [278], as have similar studies upon ^{13}CO enriched samples of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ [278,279]. The IR spectrum of $[Ru_3(CO)_{12}]$ has also been compared with data for CO adsorbed onto Ru(001) [280].

The activation energy for the thermal decomposition of $[Ru_3(CO)_{12}]$ at 130 °C is reported [281,282] to have the ludicrously low value of 41 kJ mol^{-1} {*cf.* $\Delta H^{\ddagger}$ for ^{14}CO exchange, with the rate-determining step of $[Ru_3(CO)_{12}] \rightleftharpoons [Ru_3(CO)_{11}] + CO$, is 133 kJ mol^{-1} [283]; ΔH_{decomp}(in argon) = 374 kJ mol^{-1} [284]}. The reported value is remarkably similar to the enthalpy of melting (43.5 kJ mol^{-1} at 155 °C [284]) of $[Ru_3(CO)_{12}]$, however! $[Ru_3(CO)_{12}]^{\bullet -}$ has been produced by electrochemical or alkali-metal reduction of the parent cluster, and characterised by EPR spectroscopy [285]. The catalytic properties of $[Ru_3(CO)_{12}]$ are discussed together with those of $[Os_3(CO)_{12}]$ in Section 3.9.1.

$[Ru_3(CO)_{12}]$, in basic conditions, catalyses the hydroformylation [286] and aminomethylation [287] of alkenes: species such as $[HRu(CO)_5]^-$, $[H_2Ru_2(CO)_8]^-$ and $[HRu_3(CO)_{11}]^-$ have been postulated as important catalytic intermediates. The last species, moreover, has seen an exciting development in its chemistry. Thus, $[HRu_3(CO)_{11}]^-$ (48) has been prepared in high yield by the treatment of $[Ru_3(CO)_{12}]$ with $Na[BH_4]$ in thf, and isolated as its $[Et_4N]^+$ or $[N(PPh_3)_2]^+$ salt. $[N(PPh_3)_2][HRu_3(CO)_{11}]$ has been crystallographically characterised, and VT ^{13}C NMR studies have shown the anion to be fluxional in solution at room temperature [288]. (48) is also generated by the treatment of $[Ru_3(CO)_{12}]$ with $Li[HBEt_3]$ in thf [289]. Protonation of $[HRu_3(CO)_{11}]^-$ with HSO_3CF_3 at −60 °C in CD_2Cl_2 yields the *O*-protonated complex (49), as indicated by ^1H NMR spectroscopy. Upon warming, (49) is irreversibly converted into the previously unobserved isomer, (50), which itself decomposes above −30 °C to give H_2 and $[Ru_3(CO)_{12}]$ (with small amounts of $[H_4Ru_4(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$) [290]. This behaviour is to be contrasted with the equally interesting behaviour of (48) towards room temperature protonation with concentrated H_2SO_4, which generates hexanuclear clusters (see Section 2.13.3). The catalytic activity of (48) has been demonstrated by the reports of the hydroformylation of ethene or propene in dmf at 100 °C [291]:



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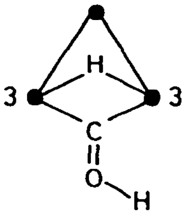

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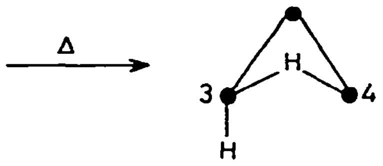


(50)

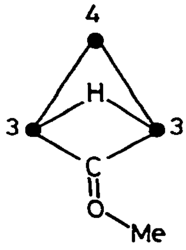
$$C_2H_4 + CO + H_2 \xrightarrow{(48)} CH_3CH_2CHO \quad (74\%)$$

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{(48)} CH_3CH_2CH_2CHO \quad (60\%)$$

$$+$$

$$(CH_3)_2CHCHO \quad (3\%)$$

In a related reaction, Na[$HRu_3(CO)_{11}$] was treated with [Me_3O][BF_4] in ethanenitrile, and shown to yield [$HRu_3(CO)_{10}(COCH_3)$] (51), which has been crystallographically characterised and its solution fluxionality studied by VT ^{13}C NMR spectroscopy [292]. (51) has also been prepared by methylation of (48) with $MeSO_3F$ and shown to undergo hydrogenation under mild conditions [293]:



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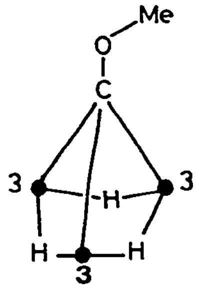

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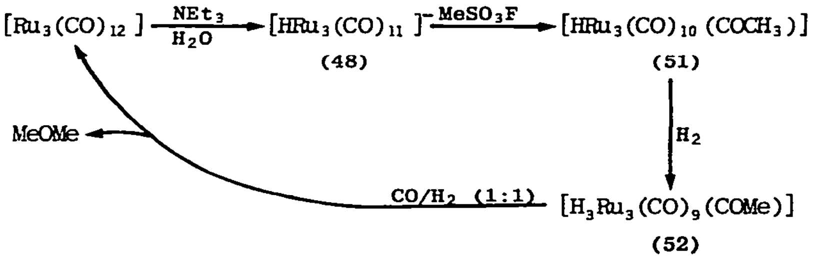
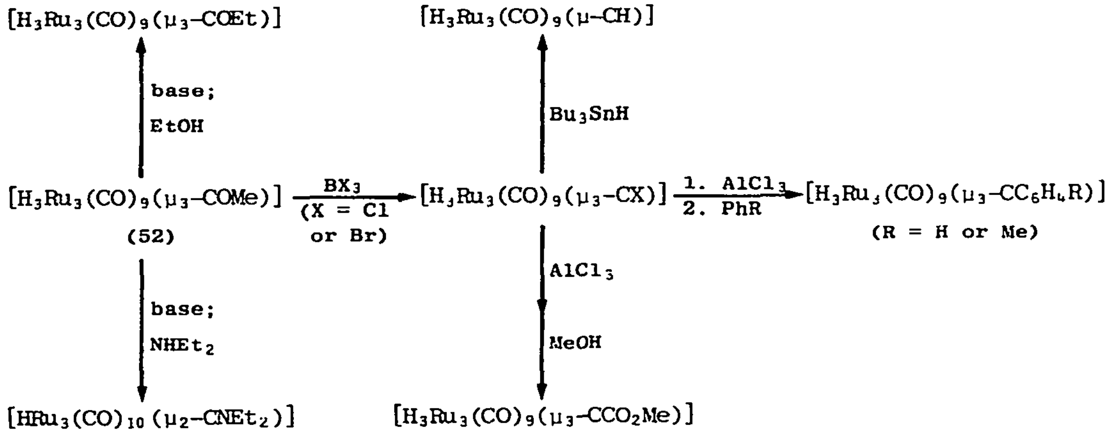


(52), itself, has an interesting chemistry and this is summarised in Scheme IV [294].

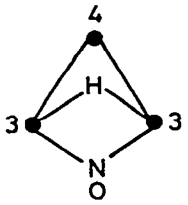
Treatment of Na[$HRu_3(CO)_{11}$] with [NO][PF_6] yields [$HRu_3(CO)_{10}(NO)$] (53), which reacts with $P(OMe)_3$ to give [$HRu_3(CO)_7(NO)\{P(OMe)_3\}_3$] (54). (53) is also formed in the reaction between [$H_2Ru_4(CO)_{13}$] and [NO][PF_6] in MeCN. Treatment of (53) with PPh_3 yields [$HRu_3(CO)_9(NO)(PPh_3)$], [$HRu_3(CO)_8(NO)(PPh_3)_2$] and [$HRu_3(CO)_7(NO)(PPh_3)_3$]. A determination of the molecular structure of (54) showed all the phosphite ligands to be essentially equatorial; the nature of this complex has been studied by VT ^{13}C NMR spectroscopy [295]. The crystal structure of [$Ru_3(CO)_{11}(PPh_3)$] has revealed the PPh_3 group to be in the expected equatorial



SCHEME IV: The synthesis and reactions of $[H_3Ru_3(CO)_9(\mu_3\text{-}CY)]$ (Y = OMe, OEt, Cl, Br, CO_2Me, H, Ph or C_6H_4-4-Me) [294].

position, but the arguments presented concerning possible isomerism are not definitive [296].

$[Ru_3(CO)_{12}]$ does not react with E_n (E = S, Se or Te) in propanone at reflux, but under CO/H_2 (35 atm; 1:1) $[Ru_3(CO)_9E_2]$ and $[H_2Ru_3(CO)_9E]$ are formed [297]. The structures of $[H_2Ru_3(CO)_9E]$ (55) are believed similar to that reported last



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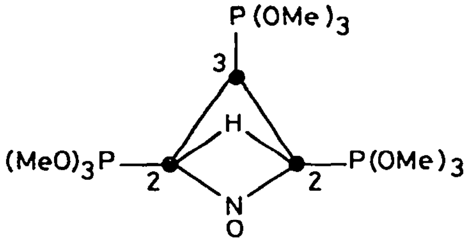

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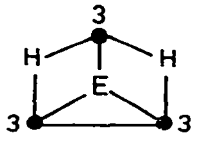

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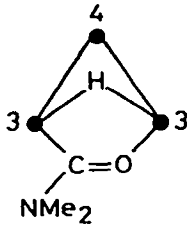
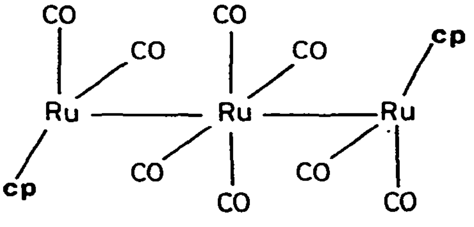


(56)

year for $[H_2Os_3(CO)_9S]$ [1; p.72]. Complexes described as $[(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}E)]$ (E = S, Se or Te) have been reported previously [298], but their IR spectra are not consistent (*i.e.* they have fewer bands) with the spectra reported in the recent paper [297]. Moreover, the earlier report [298] stated that $[H_2Ru_3(CO)_9S]$ is paramagnetic, containing two unpaired electrons per molecule - a very interesting phenomenon, if correct. $[H_2Ru_3(CO)_9S]$, (55; E = S), reacts with $K[BH(OCHMe_2)_3]$ at -60 °C to give a formyl derivative (*cf.* Section 3.9.1), which (upon warming) yields $[HRu_3(CO)_9S]^-$, which itself reacts with acid to regenerate $[H_2Ru_3(CO)_9S]$ [299].

$[Ru_3(CO)_{12}]$ reacts with Me_2NH to give $[HRu_3(CO)_{10}(O{=}CNMe_2)]$ (56), which has been structurally characterised, and the bridging hydride located [300]. In (56), the $\nu(Ru_2H)$ stretching mode occurs at 1400 cm^{-1} and for its deuterated analogue, $\nu(Ru_2D)$ is at 990 cm^{-1} [300]. $[Ru_3(CO)_{12}]$ reacts with $Me_2NCH_2SiMe_3$ or $Me_2NCH_2SnMe_3$ to yield $[HRu_3(CO)_{10}(C{=}NMe_2)]$ and, with the latter reagent, some $[Ru(CO)_4(SnMe_3)_2]$ was identified as a by-product [301].

In addition to the well-known product $[(cp)_2Ru_2(CO)_4]$ (*cf.* Section 2.9), the reaction of $[Ru_3(CO)_{12}]$ with cyclopentadiene has also been shown to yield the interesting eclipsed linear complex $[\{(cp)Ru(CO)_2\}Ru(CO)_4\{Ru(cp)(CO)_2\}]$ {*r*(RuRu) = 0.2889 nm}, containing mutually *trans* cyclopentadienyl rings, as illustrated in (57) [302].



(57)

2.13.2 Tetrameric clusters

A high yield synthetic route to $[Ru_4(CO)_{13}]^{2-}$ and $[Ru_4(CO)_{12}]^{4-}$, *via* the controlled reduction of $[Ru_3(CO)_{12}]$ with $K[Ph_2CO]$, has been developed [303]:

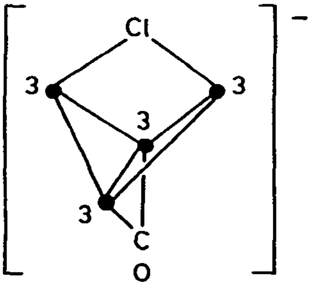
$$4[Ru_3(CO)_{12}] + 6K[Ph_2CO] \longrightarrow 3K_2[Ru_4(CO)_{13}] + 9CO + 6Ph_2CO$$

$$4[Ru_3(CO)_{12}] + 12K[Ph_2CO] \longrightarrow 3K_4[Ru_4(CO)_{12}] + 12CO + 12Ph_2CO$$

These anions were isolated as their $[N(PPh_3)_2]^+$ salts. The pK_a values for $[H_4Ru_4(CO)_{12}]$ (11.7) and $[H_2Ru_4(CO)_{13}]$ (14.7) have been measured for the first time [304].

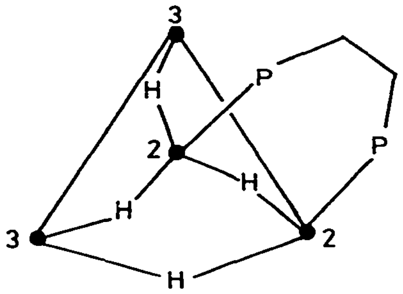
Treatment of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in thf at reflux has yielded crystals of $[N(PPh_3)_2][Ru_4(CO)_{13}Cl]$, suitable for crystallographic characterisation:

the Li^+ and $[NEt_3Bz]^+$ salts of $[Ru_4(CO)_{13}Cl]^-$ (58) were also prepared [305].



(58)

Treatment of $[H_4Ru_4(CO)_{12}]$ with dppe, in the presence of Me_3NO, leads to the formation of $[H_4Ru_4(CO)_{10}(dppe)]$ (59) in good yield; the compound was characterised crystallographically and all the hydride ligands were located. Upon heating, (59) rearranges to give the already known and crystallographically characterised isomer (60). (59) is fluxional in solution, and has been studied by VT ^1H NMR spectroscopy [306]. $[H_4Ru_4(CO)_{12}]$ also reacts with L (L = $P(OMe)_3$ or PPh_3) under UV irradiation to produce $[H_4Ru_4(CO)_{11}L]$, and with alkenes (depending on conditions) to cause photocatalytic hydrogenation or isomerisation [307]. The compounds $[H_4Ru_4(CO)_{12-n}\{P(OEt)_3\}_n]$ (n = 1, 2 or 4) catalyse the isomerisation and hydrogenation of dimethylfumarate [308], $[H_4Ru_4(CO)_{12-n}(PR_3)_n]$ (R = Ph, Bu, OEt or OPh; n = 1, 2 or 3) catalyse the hydrogenation of pent-1-yne and pent-2-yne [309], and $[H_4Ru_4(CO)_8(PBu_3)_4]$ catalyses the hydrogenation of RCO_2H $\{R = CH_3(CH_2)_n;\ n = 0\text{–}5\}$, $(R_2CO)_2O$ (R = Me or Pr) and several dicarboxylic acids to the corresponding alcohols, RCH_2OH, at 100–200 °C (100–200 atm of H_2) [310].



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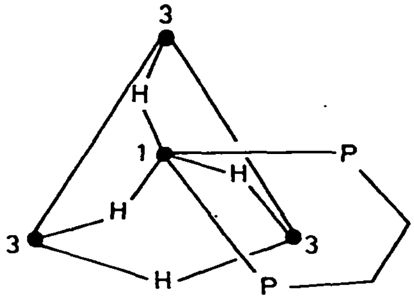
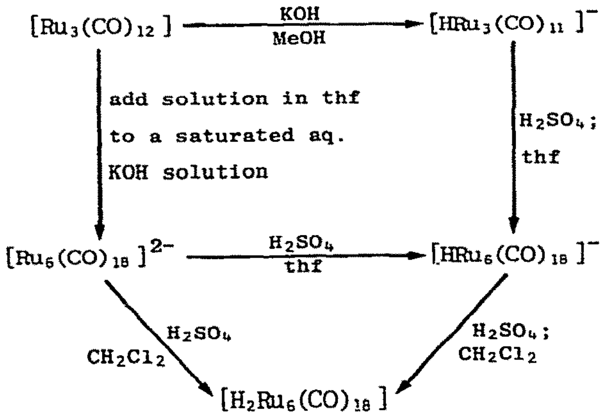


(60)

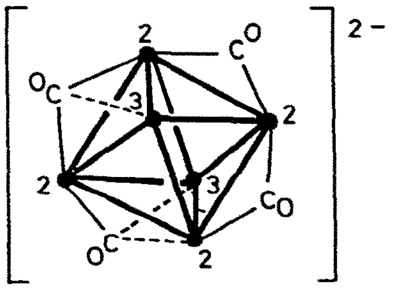
2.13.3 Hexameric clusters

This year's key development has been the discovery of new high yield synthetic routes to Ru_6 clusters, with the promise of exciting chemical developments in the near future. These new preparative routes are summarised in Scheme V [311,312].



SCHEME V: The syntheses of some Ru_6 clusters [311,312].

The anions $[Ru_6(CO)_{18}]^{2-}$ (61) [311] and $[HRu_6(CO)_{18}]^-$ (62) [312] were characterised crystallogaphically as their $[PPh_3Me]^+$ and $[N(PPh_3)_2]^+$ salts, respectively. It is of some interest to note that all the members of the series $[H_{2-n}M_6(CO)_{18}]^{n-}$ (M = Ru or Os; n = 0, 1 or 2) have been structurally characterised, and no ruthenium cluster has the same structure as its osmium analogue. The structure of $[AsPh_4][HRu_6(CO)_{18}]$ has also been determined, by a combination of X-ray and neutron analysis, and the position of the interstitial hydride was directly located {r(RuH) = 0.203-0.206 nm} [313]. This is an important result as, although this was the proposed structure for the complex [314], it had recently



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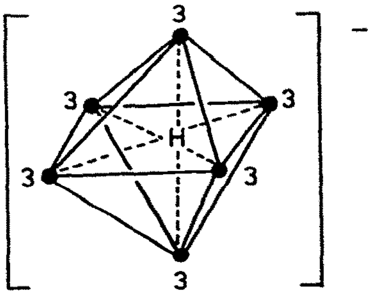
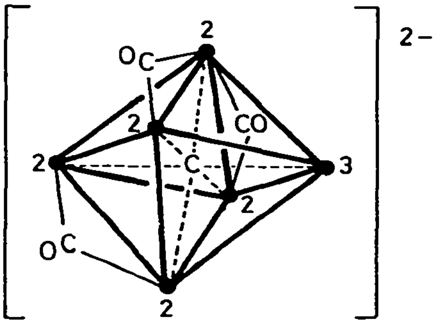


(62)

been questioned [315]. Moreover, the first observation of the ν(MH) stretching mode for an interstitial hydride has been reported for the $[NMe_4]^+$ and $[AsPh_4]^+$ salts of (62), at 825 cm^{-1}, and the ν(RuD) stretch in $[NMe_4][DRu_6(CO)_{18}]$ has been identified at 600 cm^{-1}. At 95 K, the ν(RuH) band in the $[NMe_4]^+$ salt splits into an equal intensity doublet at 845 and 806 cm^{-1} and a similar effect is found in the $[AsPh_4]^+$ salt (842 and 817 cm^{-1}): this phenomenon has been ascribed to Fermi resonance [316].

A high yield (~60%) synthesis of $A_2[Ru_6C(CO)_{16}]$ (A = $[NMe_4]$, $[NEt_4]$, $[AsPh_4]$ or $[N(PPh_3)_2]$) has been found; treatment of $[Ru_3(CO)_{12}]$ with $Na[Mn(CO)_5]$ in diglyme at reflux for several hours produces red solutions containing $[Ru_6C(CO)_{16}]^{2-}$. A ^{13}CO enriched sample of $[Ru_3(CO)_{12}]$ produced a product with a ^{13}C NMR spectrum confirming that the encapsulated carbide originates from a carbonyl group. $[Ru_6C(CO)_{16}]^{2-}$ can be protonated, in a stepwise manner, to give $[HRu_6C(CO)_{16}]^-$ and $[H_2Ru_6C(CO)_{16}]$; mild oxidation of this anion, in the presence of CO, yields $[Ru_6C(CO)_{17}]$ [317]. A determination of the crystal structure of $[NMe_4]_2[Ru_6C(CO)_{16}]$ has revealed the structure of the anion to be that illustrated in (63) [317,318].



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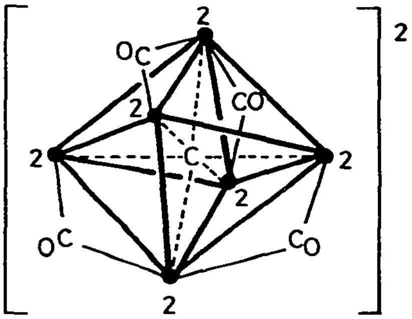


(64)

In an independent study, it was discovered that treatment of $[Ru_3(CO)_{12}]$ with ethene (30 atm; 150 °C) gives $[Ru_6C(CO)_{17}]$ in 70% yield. This latter complex reacts with $[OMe]^-$, *via* nucleophilic attack on a CO ligand, to give $[Ru_6C(CO)_{16}(CO_2Me)]^-$, which has been isolated as its $[N(PPh_3)_2]^+$ salt. This anion reacts with aqueous base to form $[Ru_6C(CO)_{16}]^{2-}$ which, in this study, was isolated as its $[AsPh_4]^+$ and $[N(PPh_3)_2]^+$ salts, and is protonated by sulphuric acid (−30 °C) to give $[H_2Ru_6C(CO)_{16}]$ [319]. A determination of the crystal structure of $[AsPh_4]_2[Ru_6C(CO)_{16}]$ has revealed the structure of the anion to be that illustrated in (64) [319]. (63) and (64) are the first examples of isomeric carbonyl cluster anions; (63) contains 3 bridging and 13 terminal groups, and (64) contains 4 bridging and 12 terminal carbonyl groups. The terminal CO group in (63), which becomes the bridging group in (64), is already in the correct plane and bent towards the appropriate Ru atom, exhibiting a RuC separation of 0.2615 nm [318]; the equivalent bond length in (64) is 0.2327 nm [319]. The two structures probably represent similar energy minima on a fluxionality profile.

2.13.4 Mixed-metal clusters

$[Fe_2Ru(CO)_{12}]^{\bullet-}$ and $[FeRu_2(CO)_{12}]^{\bullet-}$ have been generated by electrochemical or alkali-metal reduction of the neutral trimers and characterised by EPR spectroscopy [285]; $[Ru_nOs_{3-n}(CO)_{12}]$ (n = 1 or 2) have been characterised by high resolution vibrational spectroscopy [278]. The pK_a values for $[H_4FeRu_3(CO)_{12}]$ (13.4) and $[H_2FeRu_3(CO)_{13}]$ (14.3) have been measured [304], and VT ^1H and ^{13}C NMR studies upon $[H_2FeRu_3(CO)_{13}]$, $[H_2FeRu_2Os(CO)_{13}]$ and $[H_2FeRuOs_2(CO)_{13}]$ have been used to establish the fluxional behaviour of the carbonyl groups [320a].

The reactions of $[H_2FeRu_nOs_{3-n}(CO)_{13}]$ (n = 1, 2 or 3), $[HCoRu_3(CO)_{13}]$, $[H_2FeRu_3(CO)_{12}L]$ (L = PMe_2Ph), $[HFeRu_3(CO)_{13}]^-$ and $[CoRu_3(CO)_{13}]^-$ with CO (1 atm; 0–80 °C) result in cluster fragmentation to yield trimeric and monomeric products, but the fragmentation is selective [320b]:

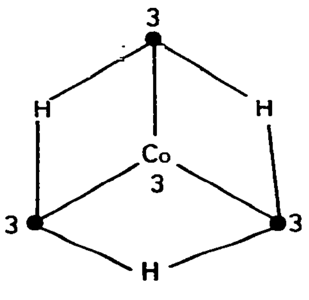
e.g.

$$[H_2FeRu_3(CO)_{13}] \xrightarrow{CO} [Ru_3(CO)_{12}] + [Fe(CO)_5] + H_2$$

$$[H_2FeRu_nOs_{3-n}(CO)_{13}] \xrightarrow{CO} [Ru_nOs_{3-n}(CO)_{12}] + [Fe(CO)_5] + H_2$$

$$[H_2FeRu_3(CO)_{12}(PMe_2Ph)] \xrightarrow{CO} [FeRu_2(CO)_{11}(PMe_2Ph)] + [Ru(CO)_5] + H_2$$

$[HCoRu_3(CO)_{13}]$ reacts with H_2 in hexane at reflux to give the new cluster $[H_3CoRu_3(CO)_{12}]$. In solution, $[H_3CoRu_3(CO)_{12}]$ shows two isomeric forms (as deduced by ^1H NMR and IR spectroscopy). One form, (65), has been crystallographically characterised whilst the structure of the other isomer, (66), has



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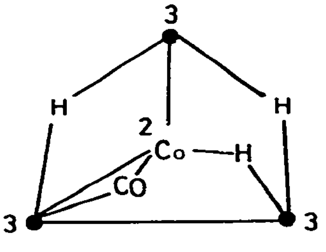
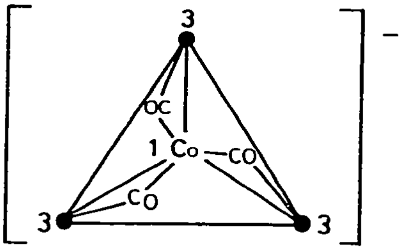


(66)

been deduced from its spectroscopic characteristics [321]. $[HCoRu_3(CO)_{13}]$, $[HCoRu_2Os(CO)_{13}]$, $[HCoRuOs_2(CO)_{13}]$ and $[HCoOs_3(CO)_{13}]$ (trace amounts) were prepared by treating $[Ru_nOs_{3-n}(CO)_{12}]$ (n = 3, 2, 1 or 0) with $K[Co(CO)_4]$, followed by protonation. The reaction between $[N(PPh_3)_2][Co(CO)_4]$ and $[Ru_3(CO)_{12}]$, *without* protonation, yielded $[N(PPh_3)_2][CoRu_3(CO)_{13}]$ and analogous reactions of $[Fe_nRu_{3-n}(CO)_{12}]$ (n = 2 or 1) gave $[N(PPh_3)_2][CoFe_nRu_{3-n}(CO)_{13}]$. $[N(PPh_3)_2][CoRu_3(CO)_{13}]$ was crystallographically characterised and the structure of the anion is illustrated in (67) [322].



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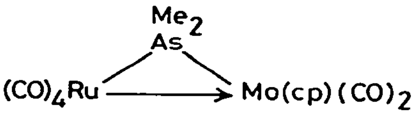
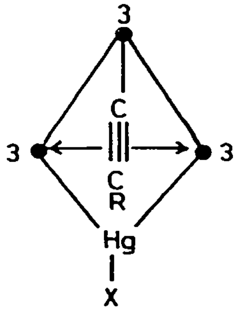
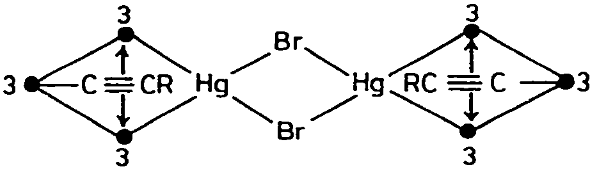


(68)

Treatment of $[Ru_3(CO)_{12}]$ with $[(Me_2As)M(cp)(CO)_3]$ (M = Mo or W) yields $[Ru_3(CO)_{11}\{(AsMe_2)M(cp)(CO)_3\}]$, together with (68) as by-product (M = Mo) [201]. It is of interest to note that (68) contains a donor-acceptor metal-metal bond (see Section 3.9.4). Similar treatment of $[Ru_3(CO)_{12}]$ with $[(Me_2As)Fe(cp)(CO)_2]$ yields $[Ru_3(CO)_{12-n}\{(AsMe_2)Fe(cp)(CO)_2\}_n]$ (n = 1, 2 or 3) [201]. Treatment of $[HRu_3(CO)_9\{C{\equiv}CCMe_3\}]$ with PhHgX (X = Br or I) gives $[Ru_3(CO)_9\{C{\equiv}CCMe_3\}(\mu\text{-}HgX)]$ (69) and benzene. (69) can also be prepared by the reaction between



(69; R = CMe₃)



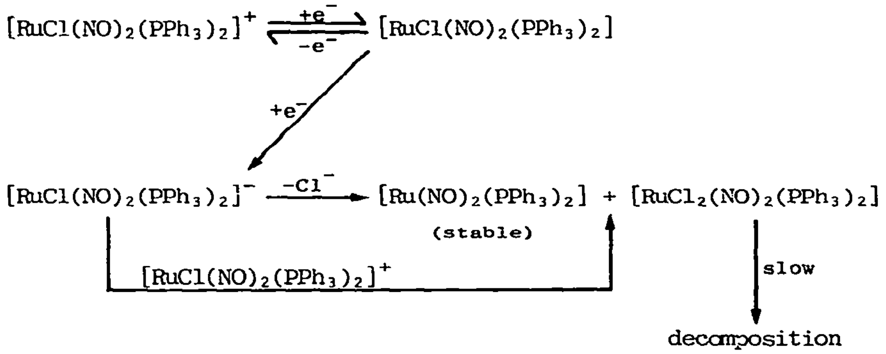
(70; R = CMe₃)

$[Ru_3(CO)_9\{C{\equiv}CCMe_3\}]^-$ and HgX_2. Although monomeric in solution, the crystal structure of $[Ru_3(CO)_9\{C{\equiv}CCMe_3\}(\mu\text{-}HgX)]$ (X = Br) reveals that it is dimeric in the solid state, with the structure (70) [323].

2.14 RUTHENIUM NITROSYLS AND THIONITROSYLS

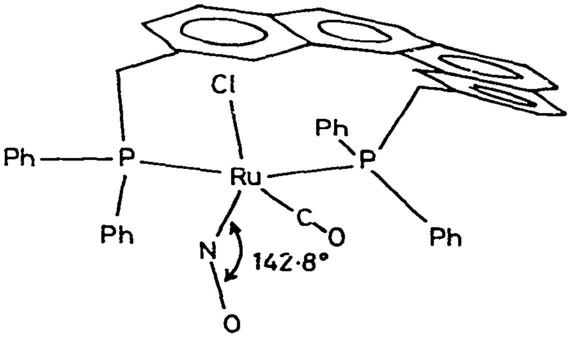
$K_2[Ru(NO)Cl_5]$ reacts with KHF_2 at 350 °C to give $K_2[Ru(NO)F_5].2H_2O$; $Ba[Ru(NO)F_5].H_2O$ was also prepared in this study [324]. $[Ru(CN)_6]^{4-}$ reacts with nitric acid to produce, as the final product, $[Ru(NO)(CN)_3(H_2O)_2]$; the intermediate $K_2[Ru(NO)(CN)_5]$ was also isolated [325]. The hydrolysis of $[Ru(NO)(NO_3)_3(H_2O)_2]$ in dilute nitric acid solution has been studied [326], and the absorption of $Na_2[Ru(NO)(NO_2)_4(OH)].2H_2O$ onto activated charcoal has been investigated with a view to elimination of ruthenium from fission products [327].

$[Ru(NO)_2(PPh_3)_2]$ reacts with SO_2 to give $[Ru(NO)_2(PPh_3)_2(SO_2)]$, which contains both a linear and a bent NO group, and is oxidised in air to give $[Ru(NO)_2(PPh_3)_2(SO_4)]$ [328]. The electrochemical reduction of $[RuCl(NO)_2(PPh_3)_2]$ has been investigated; the complex is reduced in two one-electron steps, the first of which is reversible, the second of which is not (see Scheme VI) [329].



SCHEME VI: Electrochemical reduction of $[RuCl(NO)_2(PPh_3)_2]^+$ [329].

The complexes *trans*-$[RuCl(NO)(L\text{-}L)]$, *trans*-$[RuCl(NO)(CO)(L\text{-}L)]$ and *trans*-$[RuCl(NO)\{P(OCH_2)_3CEt\}(L\text{-}L)]$ {L-L = (40)} and *trans*-$[RuCl(NO)(CO)(PPh_2CH_2Ph)_2]$ have been prepared; the crystal structure of *trans*-$[RuCl(NO)(CO)(L\text{-}L)]$ (71)



(71)

reveals the molecule to be a distorted trigonal bipyramid. The square-planar complex $[RuCl(NO)(L\text{-}L)]$ readily adds on a fifth ligand [330].

Either continuous or pulse radiolysis of solutions of $[Ru(NH_3)_5(NO)]^{3+}$ in the presence of RH yields the green alkylnitroso complexes $[Ru(NH_3)_5\{N(O)R\}]^{2+}$ (R = CH_2CMe_2OH, $[CH_2CMe_2NH_3]^+$, $[CH_2CMe_2CO_2]^-$, $[CH_2CMe(\overset{+}{N}H_3)(CO_2^-)]$, $[CH_2CMe(OH)CO_2]^-$ or $[CH_2(Me)NC(O)Me]$), which have been characterised by UV-VIS and IR spectroscopy [331]. Full details of the preparation and structure of the complexes $[H\{(R)(EtO)PO\}_2Cl(NO)Ru(\mu\text{-}Cl)_2Ru(NO)Cl\{OP(OEt)(R)\}_2H]$ (R = OEt or Ph), reported last year [1; p.61], have now been published [332], and the complexes *trans*-$[Ru(NO)(S_2CNR_2)_2Cl]$ (R_2 = Me_2, Et_2, MeEt or MePh), *trans*-$[Ru(NO)(S_2CNMe_2)_2(OH)]$, *trans*-$[Ru(NO)(S_2CNMe_2)_2L]^+$ (L = H_2O or MeOH), *cis*-$[Ru(NO)(S_2CNMe_2)_2X]$ (X = F, Br, I or NO_2), *cis*-$[Ru(NO)(S_2CNR_2)X]$ (R_2 = Et_2 or MeEt; X = Br or I) and *cis*- and *trans*-$[Ru(NO)(S_2CNMe_2)_2X]$ (X = $[N_3]$, [SCN] or [NCO]) have been prepared and characterised by UV-VIS, IR and ^1H and ^{13}C NMR spectroscopy [333]. The glycolic acid complex $K_2[Ru(NO)(OCH_2CO_2)_2(OH)]$ [334] and complexes of *N*-amidinothioureas (LLH), $[Ru(NO)(LL)Cl_2(H_2O)]$ [335] also have been described.

Two thionitrosyl complexes, $[Ru(NS)Cl_3L_2]$ (L = PPh_3 or $AsPh_3$) have been prepared this year, by treatment of "$RuCl_3.xH_2O$" with $N_3S_3Cl_3$ in thf in the presence of L [336].

2.15 PHOTOCHEMISTRY AND PHOTOPHYSICS OF THE TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) CATION, AND RELATED SYSTEMS

Interest in the photochemistry and photophysics of $[Ru(bipy)_3]^{2+}$ and its derivatives continues unabated and 1980 has seen some conventional views challenged. An excellent short review of the field upto 1979 has been published by Ford [134], and two summaries of the recent work of Crosby [337] and Valenty [338] have appeared.

The emission properties of $\{[Ru(bipy)_3]^{2+}\}^*$ and $\{[Ru(bipy\text{-}d_8)_3]^{2+}\}^*$ have been reinvestigated, between 2 and 77 K, in H_2O, D_2O, dmf and perdeutero-dmf [339], and the quantum yields for the emission from the complexes $\{[Ru(LL)_3]^{2+}\}^*$ (LL = bipy, 4,4'-Ph_2bipy, 4,4'-Me_2bipy, phen, 4,7-Ph_2phen, 5-Clphen, 5-Brphen or 2,3,5,6-(2-py)$_4$pyrazine) have been reexamined in aqueous solution at 25 °C [340]. A superb paper describing the preparation and photophysical properties of a wide range of surfactant derivatives of ruthenium(II) of the type $[Ru(LL)_2(L'L')]^{2+}$ (LL = bipy or phen; L'L' = bipy-4-Me-4'-$(CH_2)_6R$ or bipy-4,4'-$\{(CH_2)_6R\}_2$; R = C_2H_5, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$ or $C_{14}H_{29}$) has been published [341], but the space available in this review does not allow justice to be done to the excellent synthetic chemistry described. The absorption and emission spectra of $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(CO_2C_{18}H_{37})_2\}]^{2+}$, $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(C_{19}H_{39})_2\}]^{2+}$ and $[Ru(bipy)\{bipy\text{-}4,4'(C_{19}H_{39})_2\}(CN)_2]$ in aqueous micellar solution have also been the subject of a detailed investigation [342].

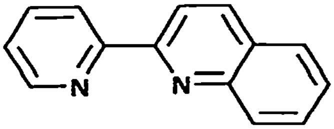
Although normally considered as unity, there have been several suggestions in the literature that the quantum yield, ϕ_T, for the production of the emitting state of $\{[Ru(bipy)_3]^{2+}\}^*$ or $\{[Ru(phen)_3]^{2+}\}^*$ might be as low as 0.5. It is timely, then, that new experiments based on the oxidative quenching of these species by $[S_2O_8]^{2-}$ confirm that ϕ_T is indeed unity [343].

For many years now, the Crosby model for the photophysical properties of $[Ru(bipy)_3]^{2+}$ [344] has remained essentially unchallenged: very briefly, it assumes that the lowest excited state of $\{[Ru(bipy)_3]^{2+}\}^*$ has D_3 symmetry (*i.e.* the ligand states are completely delocalised) and that spin-orbit coupling is so strong that the terms 'singlet' and 'triplet' are meaningless and that, therefore, there are no discrete singlet and triplet manifolds. The observed emissions, on the Crosby model, originate from individual ion-state manifolds, derived from an electron-ion coupling model. Evidence is now mounting, however, that this model is incorrect, and this is summarised in the following paragraphs.

Two papers by Ferguson and coworkers [345,346] have provided strong evidence for the existence of identifiable singlet and triplet manifolds (in complete contradiction to the Crosby model), whilst their assignments of their CD spectra are erroneous, leading them to some untenable conclusions concerning the bonding in $[Ru(bipy)_3]^{2+}$. Unfortunately, space limitations in this review do not allow all the vital arguments to be developed here (although they will be discussed at length, elsewhere [347]). The Ferguson model has been short-lived, as it has been very convincingly challenged by Daul and coworkers [348], who have pointed out an error in the published interpretation of the CD spectra of $[Ru(bipy)_3]^{2+}$ [345], and backed this up with $X\alpha$ and EHMO calculations [349]. The Daul model allows a conventional ordering of the bonding and anti-bonding levels of $[Ru(bipy)_3]^{2+}$, whilst only predicting a very weak intramolecular interligand interaction (significantly smaller than the Crosby model). It retains the convincing arguments of the Ferguson model for the existence of discrete singlet and triplet manifolds and offers (at least in my opinion) the best description so far achieved of the bonding and photophysical properties of $[Ru(bipy)_3]^{2+}$. Moreover, the spin-orbit coupling energy for $[(-)\text{-}Ru(phen)_3]^{2+}$ has been calculated to be much more important than the ligand-ligand interactions, which leads to an ordering sequence of lowest excited states of $^3A_2<^1A_2<^1E$ [350], in accord with the CD results, but again at variance with the conclusions of the Crosby model.

The other feature central to the Crosby model, the complete delocalisation of the excited state manifold with concomitant strong interligand coupling and overall D_3 symmetry, has also been challenged in several independent ways. Single-crystal polarised emission spectra of $[Ru(bipy)_3]^{2+}$ reveal that the symmetry of the excited state is lower than D_3, *independent of the choice of model* [351], and this is supported by the time-resolved resonance Raman spectra of $\{[Ru(bipy)_3]^{2+}\}^*$, which suggest that the excited electron is predominantly localised on one of the three bipy ligands [352]. In other words, the excited state appears to have C_{2v} symmetry and, to a zeroth approximation, may be thought of as $\{[Ru^{III}(bipy)_2(bipy^-)]^{2+}\}^*$. Luminescence photoselection spectra (77 K) have also been recorded for $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$: excitation polarisation rises to a maximum of 22% at 21000 cm^{-1} and decreases to 16% near the origin of the emission. The polarisation spectra of the complexes indicate an E-type emission (in contrast to the Crosby model), and so apparently verify the effective D_3 symmetry and delocalisation of the excited state (thus, supporting the Crosby model). However, a C_{2v} model with a 'hopping' mechanism would also explain the observed results [353].

The Crosby model was extended, in a paper with Elfring [354], to suggest that the excited states in mixed ligand complexes were also completely delocalised over all three ligands. However, in a paper to be published shortly [355], it has been shown that the NMR data, upon which some of these conclusions were (in part) based, are in error, and that the life-time measurements presented and interpreted in terms of a strong-coupling model [354] equally well support a model of *zero or minimal coupling* [355]. Moreover, absorption spectra of $[Ru(bipy)_2(bipy\text{-}4,4'\text{-}R,R')]^{2+}$ (R,R' = COOH, COOH; COOH, COO^-; COO^-, COO^-; or COOEt, COOEt) provide strong evidence for the localisation of charge in the excited states of the complexes, and emission from $\{[Ru(bipy)_2(bipy\text{-}4,4'\text{-}R_2)]^{2+}\}^*$ (R = COOH or COOEt) occurs from the substituted ligand, and *not* from the unsubstituted bipy [356]. The complexes $[Ru(bipy)_n(pq)_{3-n}]^{2+}$ {pq = (72);



(72; pq)

n = 0, 1, 2 or 3} have been prepared, and their room temperature absorption spectra and emission spectra (room temperature and 77 K) reported. The charge-transfer states initially populated by absorption of visible light are essentially localised on individual ligands (a similar phenomenon was noted in many of the complexes reported by Belser and von Zelewsky [150], see Section 2.8.4 and Fig. 2), and there is little coupling between the ligands. Emissions, however, were found to occur from a single state, localised and possessing the characteristics of the pq ligand alone [357]. Indeed, dual emission was briefly noted from the complexes $[Ru(phen)_n(pq)_{3-n}]^{2+}$ (n = 1 or 2) [357], and this phenomenon has been independently observed for the complex *cis*-$[Ru(bipy)_2(4,4'\text{-}bipy\text{-}N\text{-}Me)_2]^{4+}$ [358]. Thus, 1980 has seen a mounting body of new evidence that the excited states of $[Ru(bipy)_3]^{2+}$, and related species, should now be thought of as localised, rather than delocalised, and this should lead to a better understanding of the photochemistry of these complexes.

Full details of the excited-state acid-base reactions of $[Ru(LL)_2(CN)_2]$ (LL = bipy or phen) in acidic solution have now been published. The ground state equilibria may be represented as:

$$[Ru(LL)_2(CN)_2] + 2H^+ \rightleftharpoons [Ru(LL)_2(CN)(CNH)]^+ + H^+ \rightleftharpoons [Ru(LL)_2(CNH)_2]^{2+}$$

Irrespective of the degree of protonation in the ground state, room temperature emission is only observed from $\{[Ru(LL)_2(CN)_2]^{2+}\}^*$, indicating a very fast (with respect to emission decay rate constants) deprotonation reaction must occur in $\{[Ru(LL)_2(CN)(CNH)]^+\}^*$ and $\{[Ru(LL)_2(CNH)_2]^{2+}\}^*$. At 77 K, however, emission from the protonated forms has been observed [359]. A less detailed study of the emission from $\{[Ru(bipy)_2(CN)_2]\}^*$ has also appeared [360], and the absorption spectrum of $\{[Ru(bipy)_2(CN)_2]\}^*$ has been reported [361].

Many studies of the oxidative and reductive quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ and its derivatives have appeared this year, and an interesting treatment of the application of electron-transfer theory to excited-state redox processes has been published [362,369]. A brief review of some quenching reactions of $\{[Ru(bipy)_3]^{2+}\}^*$ has been presented [363]. Hydrophobic derivatives of $[Ru(bipy)_3]^{2+}$, such as $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(C_{20}H_{41})_2\}]^{2+}$, $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(COOC_{18}H_{37})_2\}]^{2+}$ and related species, in monolayer assemblies undergo rapid and efficient energy transfer at rates much greater than predicted by Förster theory: this suggests that the alkyl chains take part, in some way, in the transfer of excitation energy [364]. Abnormal decay kinetics for $\{[Ru(bipy)_3]^{2+}\}^*$ in surfactant solutions (containing sodium dodecyl sulphate) below critical micelle concentrations have been observed. $[Ru(bipy)_3]^{2+}$ appears to form complexes with the sodium dodecyl sulphate containing several $[Ru(bipy)_3]^{2+}$/SDS, and the abnormally fast decay is consistent with self-quenching within the same cluster [365]. $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}\{C(O)N(C_{12}H_{25})_2\}_2\}]^{2+}$ undergoes photoreduction by $PhNMe_2$ (under flash photolysis conditions) in micellar solutions of a cationic surfactant; catalytic reduction of a number of substrates (*e.g.* $[MV]^{2+}$) occurred subsequently at the micelle surface [366]. The same system has also been studied in synthetic bilayer membranes and phospholipid liposomes [367]. The quenching of $\{[Ru(bipy)_3]^{2+}\}^*$, $\{[Ru(bipy)_2(bipy\text{-}4,4'\text{-}R_2)]^{2+}\}^*$ (R = Me, COOH or COO^-) and $\{[Ru(bipy)_2(CN)_2]\}^*$ by $[MV]^{2+}$ has also been studied as a function of ionic strength [368].

Full details of the kinetic studies for the electron-transfer quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by a series of organic quenchers have now been reported. Both oxidative quenching (by nitroarenes) and reductive quenching (by aromatic amines) are detailed and experimental values of the redox potentials of the

$[Ru(bipy)_3]^{3+/2+*}$ and $[Ru(bipy)_3]^{2+*/+}$ couples of −0.81±0.07 V and +0.77±0.07 V (MeCN; *vs.* SCE), respectively, were determined [369]. These values are in excellent agreement with those calculated from spectroscopic and CV studies, at −0.84 V and +0.84 V, respectively. The full details of the reductive quenching of $\{[Ru(bipy)_3]^{2+}\}^*$, $\{[Ru\{bipy\text{-}4,4'\text{-}(CO_2CHMe_2)_2\}_3]^{2+}\}^*$ and $\{[Ru\{bipy\text{-}5,5'\text{-}(CO_2CHMe_2)_2\}_3]^{2+}\}^*$ by Et_3N and $PhNMe_2$ have also been reported this year. Spin-trapping experiments demonstrated the nature of some of the radicals generated, and point to a mechanism in which the amine radical cation is formed in the quenching step [370].

The quenching of a series of $\{[Ru(LL)_3]^{2+}\}^*$ by $[M(LL)_3]^{2+}$ (M = Fe, Ru or Os; LL = bipy, phen, 5-Clphen, 4,7-Me_2phen, *etc.*) has been reported in detail [371]. The oxidative quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by Hg^{2+} occurs to give $[Ru(bipy)_3]^{3+}$ and Hg^+, which rapidly dimerises to give $[Hg_2]^{2+}$ in competition with the thermal back reaction; this system has been used for the basis of a photogalvanic cell [372]. The kinetics of the oxidative quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by Fe^{3+}_{aq}, and the reverse thermal reaction, have been investigated as a function of pH and ionic media effects. The highest steady-state yield of $[Ru(bipy)_3]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ occurs in high concentrations of perchloric or trifluoromethylsulphonic acid, but the direct reaction of $\{[Ru(bipy)_3]^{2+}\}^*$ with $[ClO_4]^-$ eliminates perchloric acid as a useful medium. 2 *M* trifluoromethylsulphonic acid was thus proposed as a good candidate as a medium for a practical photogalvanic system [373]. An independent study of the quenching of $\{[Ru(LL)_3]^{2+}\}^*$ (LL = bipy, 5,5-Me_2bipy or 4,4'-Me_2bipy) and $\{[Ru(bipy)_2(CN)_2]\}^*$ by $[Fe(H_2O)_6]^{3+}$ by an elegant and novel electrochemical transient method has been described; the analysis yields both the quenching rate constant, k_q, and the rate constant for the reverse thermal reaction, and gives good agreement with previous conventional studies [374]. The oxidative quenching reactions of $\{[Ru(bipy)_2(CN)_2]\}^*$ by $[Fe(CN)_6]^{3-}$ in a polyelectrolyte solution [361], and of $\{[Ru(bipy)_3]^{2+}\}^*$ by $[Co(LL)_3]^{3+}$ (LL = bipy or phen) [94], or by a series of binuclear superoxide-bridged cobalt(III) complexes [375] have also been described. The reductive quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by Sb(III) in oxygenated hydrochloric acid results in the formation of hydrogen peroxide [376], whilst the reductive quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by a series of dithiocarbamate anions produces $[Ru(bipy)_3]^+$ [377]. Finally, the quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by $[Cu(H_2O)_6]^{2+}$ and $[CuCl(H_2O)_5]^+$ has been studied [378].

An excellent example of photoinduced chiroselective electron-transfer has appeared this year. The quenching of $\{\Delta\text{-}[Ru(bipy)_3]^{2+}\}^*$ by racemic $[Co(acac)_3]$ leads to the decay of the isotropic absorbance of $[Co(acac)_3]$, and the appearance of the CD absorption of $\Delta\text{-}[Co(acac)_3]$ [379,380]. A photoracemisation of $\Delta\text{-}[Ru(bipy)_3]^{2+}$ occurs on irradiation with visible light in neutral aqueous solution, but with a low quantum yield; the racemisation was postulated to occur *via* a 'one-legged' bipy intermediate (*cf.* Sections 2.8.3 and 2.8.4) [380]. Finally, the photoanation of $[Ru(bipy)_3]Br_2$ (*cf.* Section 2.8.4) in dmf has been studied, and the quantum yields for the formation of $[Ru(bipy)_2(dmf)Br]^+$ and $[Ru(bipy)_2Br_2]$ determined; the mechanism was discussed in terms of an ion pair/ion triplet model (rather than the alternative involving 'one-legged' bipy) [381].

2.16 PHOTOCATALYTIC DECOMPOSITION OF WATER

The discussion in this section system draws heavily upon the discussion in last year's review [1; p.62-64]; in particular the Schemes referred to in the following discussion are those to be found in last year's article.

The "bouillabaisse" technique is as popular as ever. Another study of the system described in Scheme III [1; p.63] has appeared [382] and, in a new variation, [Ru(TPP)(CO)] has replaced $[Ru(bipy)_3]^{2+}$ and *Desulphovibrio vulgaris* has replaced PtO_2 [383]. In relation to Scheme III [1; p.63], the back reaction of $[Ru(bipy)_3]^{3+}$ with $[MV]^+$ can be retarded by ~10^2 by using an $[MV]^{2+}$ derivative in which one of the *N*-methyl groups has been replaced by a *N*-$C_{14}H_{19}$ linear chain, imparting amphiphilic properties (these derivatives form micelles at concentrations >7 x 10^{-3} *M*) but leaving the quenching rate of $\{[Ru(bipy)_3]^{2+}\}^*$ essentially unaffected [384]. Taking a slightly different approach, the quenching of $\{[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(C_{18}H_{37})_2\}]^{2+}\}^*$ by $[MV]^{2+}$ has been investigated in anionic and cationic micelles. Quenching in anionic micelles is far more effective than in homogeneous solution; in cationic micelles, in contrast, quenching is far less effective than under homogeneous conditions [385].

Irradiation of an aqueous solution containing Eu(II) or Pr(II) and $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(CO_2C_{18}H_{37})\}]^{2+}$ (on a glass slide) produced a very low yield of H_2 and gave substantial decomposition of the complex [386]. Research into the use of metal oxide catalysts continues and RuO_2 has been shown to catalyse Scheme III [1; p.63] at least as well as colloidal Pt [387]. MnO_2 [388a] or hydroxycobalt(III) complexes [388b] catalyse the oxidation of water by $[Ru(bipy)_3]^{3+}$, whilst RuO_2 deposited onto Y-zeolites has been demonstrated to be a far more efficient catalyst for mediating the oxidation of water than unsupported RuO_2. Thus RuO_2/Y-zeolite was used to catalyse Scheme V [1; p.63], and O_2 evolution was at an optimum at *ca.* pH 4 [389].

In a related system, UV irradiation of aqueous methanol in the presence of $TiO_2/RuO_2/Pt$ has been found to produce dihydrogen [390], whilst TiO_2/RuO_2 was also found to catalyse the following reactions [391]:

$$2H_2O(g) + C(s) \xrightarrow{h\nu;\ 80\ ^\circ C} 2H_2(g) + CO_2(g)$$

$$H_2O(g) + C(s) \xrightarrow{h\nu;\ 80\ ^\circ C} H_2(g) + CO(g)$$

A useful review dealing with the use of $[Ru(bipy)_3]^{2+}$ in photogalvanic systems has appeared [392], and an excellent and detailed study of transient processes in photogalvanic cells, focussing upon the $[Ru(bipy)_3]^{2+}/[Fe(H_2O)_6]^{3+}$ cell, has been reported [393,394]. An independent, and equally thorough, investigation of the $[Ru(bipy)_3]^{2+}/[Fe(H_2O)_6]^{3+}$ and $[Ru(3,4,7,8\text{-}Me_4phen)_3]^{2+}/[Fe(H_2O)_6]^{3+}$ systems, found that the overall quantum efficiency, ϕ, was close to its maximum value of unity, but that the rate constants for the back reactions are too large by an order of magnitude for the cell to be practically useful. Moreover, the system is limited by the relatively low solubilities of the ruthenium complexes, but increasing those concentrations would have a further deliterious effect upon the already unsatisfactory back reaction [395]. It was also discovered that the electroreduction of $[Ru(bipy)_3]^{3+}$ at a thionine-coated electrode is dramatically inhibited, the potential for reduction being depressed by *ca.* 0.6 V; the consequences of this observation upon the above photogalvanic systems were discussed [396,397].

An interesting new photoelectrochemical cell, based on the oxidative quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by $[Co(C_2O_4)_3]^{3-}$, results in the evolution of O_2 and the production of significant photocurrents (at the expense of consuming $[Co(C_2O_4)_3]^{3-}$) according to [398]:

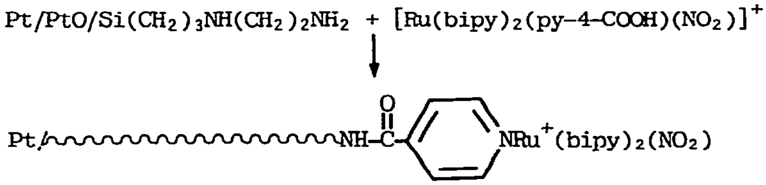
$$
\begin{array}{lrcl}
\text{CATHODE :} & [Ru(bipy)_3]^{2+} + h\nu & \longrightarrow & \{[Ru(bipy)_3]^{2+}\}^* \\
& \{[Ru(bipy)_3]^{2+}\}^* + [Co(C_2O_4)_3]^{3-} & \longrightarrow & [Ru(bipy)_3]^{3+} + [Co(H_2O)_6]^{2+} \\
& 6H_3O^+ & & + 3H_2C_2O_4 \\
& [Ru(bipy)_3]^{3+} + e^- & \xrightarrow{Pt} & [Ru(bipy)_3]^{2+} \\
\text{ANODE :} & [OH]^- & \xrightarrow{Pt} & e^- + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \\
\hline
\text{CELL REACTION :} & [Co(C_2O_4)_3]^{3-} + 5H_3O^+ + \tfrac{3}{2}H_2O & \xrightarrow{h\nu} & [Co(H_2O)_6]^{2+} + 3H_2C_2O_4 + \tfrac{1}{4}O_2 \\
\hline
\end{array}
$$

Finally, there has been disappointingly little progress with approaches aimed at the photoelectrolysis of water. The only paper to appear this year deals with the sensitisation of single crystals of TiO_2 and $SrTiO_3$ coated with thin films of $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(C_{19}H_{39})_2\}]^{2+}$ or $[Ru(bipy)_2\{bipy\text{-}4,4'\text{-}(CO_2C_{18}H_{37})_2\}]^{2+}$ [399].

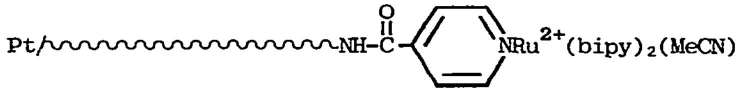
2.17 SURFACE MODIFICATION

This section, which last year dealt only with electrode modification, has been extended to cover the whole area of surface modification. Nevertheless, the highlight of the year is the appearance of a splendid review by Murray dealing solely with chemically modified electrodes [400].

In an excellent example of synthetic chemistry (see Scheme VII), an $[Ru(bipy)_3]^{2+}$ derivative has been covalently attached to *n*-SnO_2, and characterised by electronic absorption spectroscopy and CV. Thick coatings (*ca.* 1000 monolayers) were produced by this method (presumably *via* oligomerisation of hydrolysed $SiCl_3$ groups) which were stable to organic solvents, as well as aqueous acids and bases. Upon prolonged irradiation, the electrode coating undergoes extensive hydrolysis. The coated electrode produces significant photocurrents when irradiated with visible light [401]. A derivative of $[Ru(bipy)_2(py)(NO_2)]^+$ (see Section 2.6.5) has been attached, *via* a silylamine linkage, to a platinum electrode surface [402]:

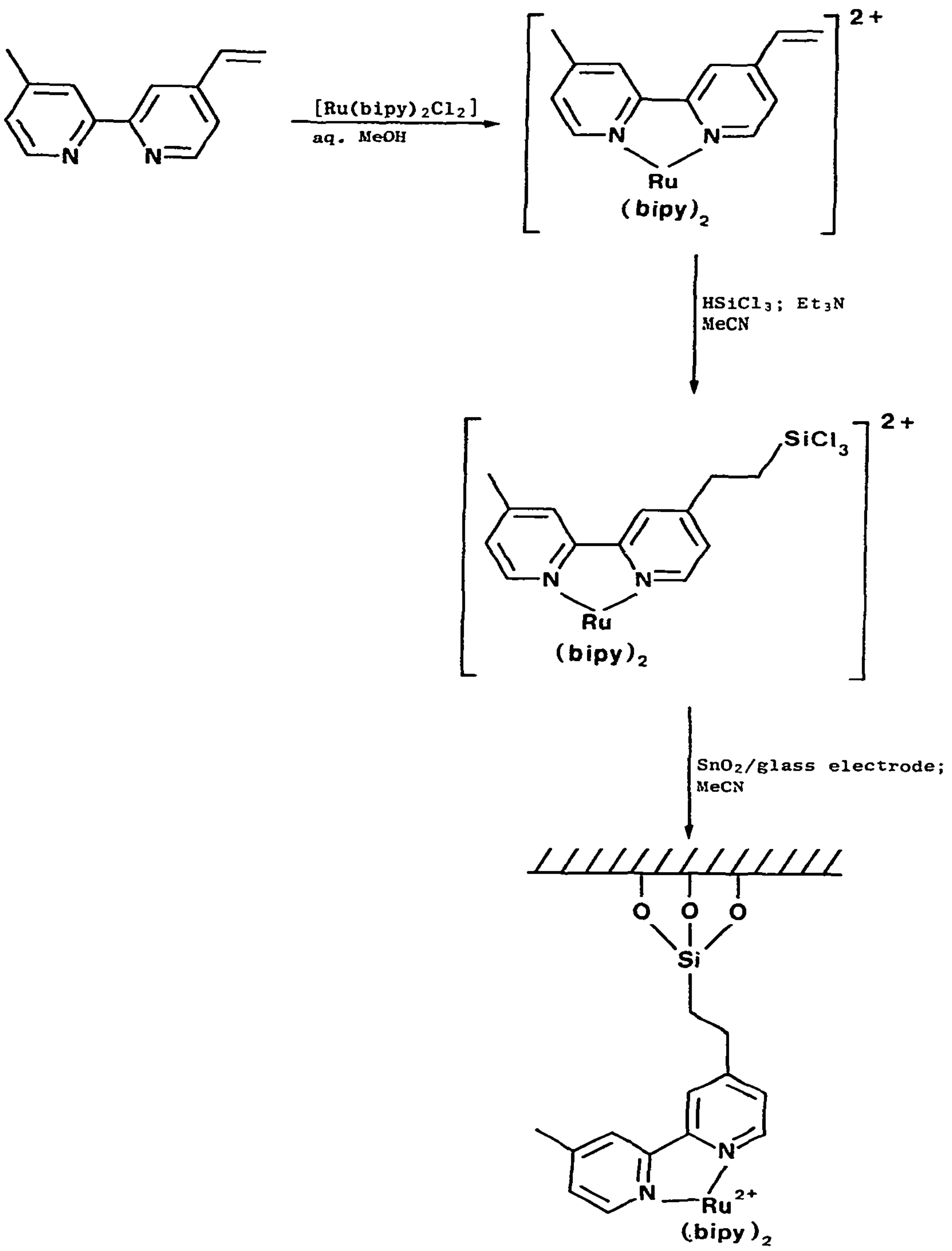


Electrochemical studies suggest that the general form of reactivity observed in homogeneous solution is retained upon electrode modification, but that reaction rates are substantially changed. This slows down the conversion of $[Ru(bipy)_2(py)(NO)]^{3+}$ (see Section 2.6.5) to $[Ru(bipy)_2(py)(NO_2)]^+$ in basic solution, a key step in any catalytic cycle designed for this electrode, and thus lowers the utility of such modified surfaces for oxo-transfer electrodes. Moreover, solvolysis of the surface-attached complex yields [402]:



which terminates any catalytic activity. However, development of systems of these sorts should lead, in the near future, to practical oxo-transfer catalytic electrodes.

p-type Si surfaces have been modified with an $[MV]^{2+}$ derivative, and used to bring about the photoreduction of $[Ru(NH_3)_6]^{3+}$ in aqueous solution (an endergonic reaction) [403], whilst *n*-type Si surfaces modified with ferrocene derivatives can achieve the photooxidation of $[Ru(NH_3)_6]^{2+}$, *via* a surface ferricenium cation [404].

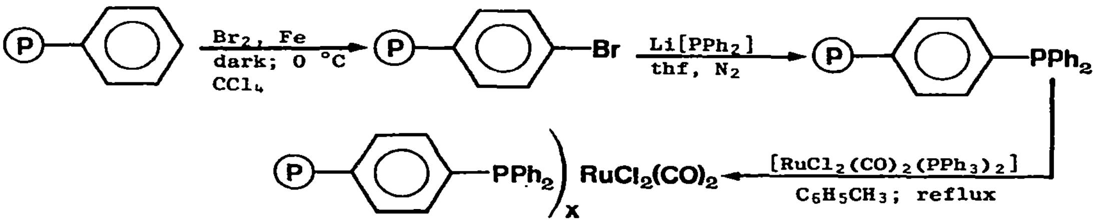


SCHEME VII: Covalent attachment of $[Ru(bipy)_3]^{2+}$ to an SnO_2 electrode [401].

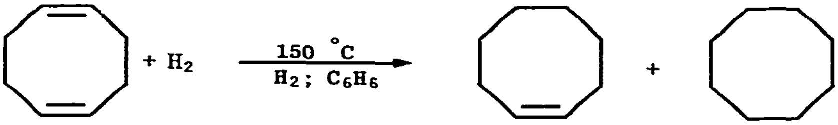
Full details of the electrochemical response of $[Ru^{III}(edta)]^-$ coordinated to films of high molecular weight poly(4-vinylpyridine) on pyrolytic graphite electrodes have now been published; the effects of film thickness, temperature, supporting electrolyte and solvent were investigated [405]. When attached in a similar manner to thin-film transparent graphite, $[Ru^{III}(edta)]^-$ has been studied by simultaneous electronic absorption spectroscopic and electrochemical measurements. Not all of the ruthenium(III) within the polymer coating was reduced to ruthenium(II) during a reductive voltammetric scan, but it could be all reduced if the potential was held negative for some minutes [406]. The reduction of $[Fe(CN)_6]^{3-}$ is impeded by unprotonated films of PVP, but is catalysed by a similar film modified with $[Ru^{II}(edta)]^{2-}$: the reaction was studied using a polymer-coated rotating disc electrode. The current is limited by the rate of reaction between $[Fe(CN)_6]^{3-}$ and $[Ru^{II}(edta)]^{2-}$, and *not* by the conductivity of the polymer coating [407].

As an alternative to covalent attachment, electrostatic binding may be used. Coating graphite electrodes with polymers bearing charged ionic groups produces centres which will strongly bind multiply-charged metal complexes bearing the opposite charge to that of the polymer. Thus, $[Ru(NH_3)_6]^{3+}$ is absorbed onto an electrode coated with polyacrylic acid, but the complex is rapidly released upon continuous cycling of the potential [408]. A pyrolytic graphite electrode coated with the perfluorinated ion-exchange polymer, Nafion, and containing $[Ru(bipy)_3]^{2+}$ incorporated by the electrostatic binding technique, has been shown to produce electrogenerated chemiluminescence upon oxidation of the $[Ru(bipy)_3]^{2+}$ in the presence of oxalate ions in aqueous solution. In MeCN, in the absence of $[C_2O_4]^{2-}$, rapid cycling of the potential (to generate sequentially $[Ru(bipy)_3]^{3+}$ and $[Ru(bipy)_3]^{+}$) also produces short-lived ECL, but the polymer film is unstable under such conditions [409].

In respect of polymer-bound catalysts *not* attached to electrodes, $[RuCl_2(CO)_2(PPh_3)_2]$ has been anchored to styrene-divinylbenzene resins by the following reaction scheme [410]:



This polymer-anchored catalyst was used to promote the hydrogenation of 1,5-cod [410]:



High selectivity for the formation of cyclooctene (compared to cyclooctane) was observed, particularly at high P/Ru ratios (which is comparable to the results found for $[RuCl_2(CO)_2(PPh_3)_2]$ in the presence of excess PPh_3 in homogeneous solution) [410]. The kinetics of attachment of $[RuCl_3(NO)(SbPh_3)_2]$ to the same polymer have been studied; the results suggest that the complexes are each anchored to the polymer at two sites [411].

$[Ru(bipy)_3]^{2+}$ has been attached to polystyrene by a series of reactions involving successive bromination, lithiation, treatment with bipy, and finally reaction with $[Ru(bipy)_2Cl_2]$. Preliminary experiments indicate that the anchored material is photochemically active for the reduction of $[MV]^{2+}$ in the presence of triethanolamine [412]. In a reverse approach, $[MV]^{2+}$ has been adsorbed onto cellulose and photoreduced, sensitised by $[Ru(bipy)_3]^{2+}$ in the presence of $[edtaH_4]$ [413].

REFERENCES

1 K.R. Seddon, *Coord. Chem. Rev.*, 35 (1981) 41.
2 P. Thornton, *Annu. Rep. Progr. Chem. Sect. A: Inorg. Chem.*, 76 (1979) 161.
3 A.B. Smith, III and R.M. Scarborough, Jr., *Synth. Commun.*, 10 (1980) 205.
4 V. Rak and F. Lisý, Ústav Jaderného Výzkumu, (Report), ÚJV 4502 (1979) [*Chem. Abstr.*, 92 (1980) 120882].
5 T. Sakurai and A. Takahashi, *J. Inorg. Nucl. Chem.*, 41 (1979) 681.
6 P.S. Santos, M.L.A. Temperini and O. Sala, *J. Mol. Struct.*, 56 (1979) 310.
7 J. Darriet, L. Lozano and A. Tressaud, *Solid State Commun.*, 32 (1979) 493.
8 W.A. Sunder, A.L. Wayda, D. Distefano, W.E. Falconer and J.E. Griffiths, *J. Fluorine Chem.*, 14 (1979) 299.
9 T.C. Gibb, R. Greatrex and N.N. Greenwood, *J. Solid State Chem.*, 31 (1980) 153.
10 I. Fernandez, R. Greatrex and N.N. Greenwood, *J. Solid State Chem.*, 32 (1980) 97.
11 H. Bader and S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*, 466 (1980) 97.
12 R.K. Broszkiewicz, *Radiat. Phys. Chem.*, 15 (1980) 133.
13 V.I. Maslov and A.V. Goncharov, *Zh. Neorg. Khim.*, 25 (1980) 484.
14 J. Dehand and J. Rosé, *J. Chem. Res.(S)*, (1979) 155, *J. Chem. Res.(M)*, (1979) 2167.
15 J. Dehand and J. Rosé, *Inorg. Chim. Acta*, 37 (1979) 249.
16 J.E. Weston and B.C.H. Steele, *J. Appl. Electrochem.*, 10 (1980) 49.
17 M.W. Shafer, R.A. Figat, R. Johnson and R.A. Pollack, *Ext. Abstr., Meet. Int. Soc. Electrochem., 30th*, (1979) 313 [*Chem. Abstr.*, 92 (1980) 118461].
18 N.N. Chalisova, M.I. Yuz'ko, T.A. Fomina, L.K. Shubochkin, Yu.S. Shorikov and A.M. Orlov, *Nauch. Tr. Gos. N.-i. i Proekt. In-t Redkomet. Prom-sti Gipedmet*, (1979) 18.
19 R. Landsberg, *Z. Chem.*, 20 (1980) 203.
20 L.D. Burke and O.J. Murphy, *J. Electroanal. Chem. Interfacial Electrochem.*, 112 (1980) 39.
21 L.D. Burke and J.F. O'Neill, *J. Electroanal. Chem. Interfacial Electrochem.*, 101 (1979) 341.
22 L.D. Burke and O.J. Murphy, *J. Electroanal. Chem. Interfacial Electrochem.*, 101 (1979) 351.
23 L.D. Burke and O.J. Murphy, *J. Electroanal. Chem. Interfacial Electrochem.*, 109 (1980) 199.
24 M. Drillon, L. Padel and J.C. Bernier, *J. Chem. Soc., Faraday Trans. 2*, 75 (1979) 1193.

25 I.I. Prosychev and I.S. Shaplygin, *Zh. Neorg. Khim.*, 25 (1980) 876.
26 I.I. Prosychev, I.S. Shaplygin, V.P. Komarov and V.B. Lazarev, *Zh. Neorg. Khim.*, 24 (1979) 2839.
27 T.L. Popova, N.G. Kisel, V.P. Karlov, V.I. Bezrukov and V.I. Krivobok, *Zh. Neorg. Khim.*, 25 (1980) 1617.
28 J. Dobrowolski, *Zesz. Nauk Politech. Slask., Chem.*, 639 (1980) 57.
29 H.S. Horowitz, J.M. Longo and J.T. Lewandowski, U.S. Patent 4176094 (27/11/1979).
30 H.S. Horowitz, J.T. Lewandowski and J.M. Longo, U.S. Patent 4203871 (20/5/1980).
31 K. Blacklock and H.W. White, *J. Chem. Phys.*, 71 (1979) 5287.
32 K. Blacklock, H.W. White and E. Gürmen, *J. Chem. Phys.*, 73 (1980) 1966.
33 S.A. Andryushenkova, I.D. Belova and Yu.E. Roginskaya, *Zh. Neorg. Khim.*, 24 (1979) 2777.
34 F.J. DiSalvo, D.W. Murphy and J.V. Waszczak, *Synthetic Metals*, 1 (1979/80) 29.
35 M. Labeau, B. Bochu, J.C. Joubert and J. Chenavas, *J. Solid State Chem.*, 33 (1980) 257.
36 M. Drillon, J. Darriet, P. Hagenmuller and R. Georges, *J. Phys. Chem. Solids*, 41 (1980) 507.
37 R. Greatrex, N.N. Greenwood and M. Lal, *Mater. Res. Bull.*, 15 (1980) 113.
38 F. Abraham, J. Trehoux and D. Thomas, *J. Solid State Chem.*, 32 (1980) 151.
39 J.D. Passaretti, R.C. Collins, A. Wold, R.R. Chianelli and T.A. Pecorara, *Mater. Res. Bull.*, 14 (1979) 1167.
40 S.R. Svendsen, *Acta Chem. Scand. Ser. A*, 33 (1979) 601.
41 B.A. Moyer, M.S. Thompson and T.J. Meyer, *J. Am. Chem. Soc.*, 102 (1980) 2310.
42 R.N. Haszeldine, L.S. Malkin and R.V. Parish, *J. Organomet. Chem.*, 182 (1979) 323.
43 I.W. Nowell, K. Tabatabaian and C. White, *J. Chem. Soc., Chem. Commun.*, (1979) 547.
44 M.A.A.F. de C.T. Carrondo, W.P. Griffith, J.P. Hall and A.C. Skapski, *Biochem. Biophys. Acta*, 627 (1980) 332.
45 J.R. Campbell, R.J.H. Clark, W.P. Griffith and J.P. Hall, *J. Chem. Soc., Dalton Trans.*, (1980) 2228.
46 P.R. Blanquet, *Histochemistry*, 47 (1976) 63.
47 J.A. Baumann and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 345.
48 R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 1771.
49 A.M. Orlov, Yu.S. Shorikov, I.V. Kuraeva, N.N. Chalisova and T.A. Fomina, *Zh. Neorg. Khim.*, 24 (1979) 2477.
50 A.V. Belikin, V.V. Borisov, N.M. Sinitsyn and A.S. Solomonova, *Russ. J. Inorg. Chem.*, 24 (1979) 1693.
51 M.I. Bruce, D.A. Kelly, G.M. McLaughlin, G.B. Robertson, I.B. Tomkins and R.C. Wallis, *Aust. J. Chem.*, 33 (1980) 195.
52 W. Smadja, G. Ville and C. Georgoulis, *J. Chem. Soc., Chem. Commun.*, (1980) 594.
53 T.H. Johnson and T.F. Baldwin, *J. Org. Chem.*, 45 (1980) 140.
54 P.C. Mehendru and N. Kumar, *Phys. Status Solidi B*, 77 (1976) K133.
55 K.A. Bol'shakov, N.M. Sinitsyn, T.M. Buslaeva and A.P. Ivchenko, *Dokl. Akad. Nauk S.S.S.R.*, 251 (1980) 1406.
56 Z. Harzion and G. Navon, *Inorg. Chem.*, 19 (1980) 2236.
57 A.K. Gregson, D.M. Doddrell and M.R. Bendall, *Aust. J. Chem.*, 32 (1979) 1407.
58 H.A. Bergen, R.M. Golding and L.C. Stubbs, *Mol. Phys.*, 37 (1979) 1371.
59 H. Kido, *Bull. Chem. Soc. Jpn.*, 53 (1980) 82.
60 M. Samiullah, U.C. Agarwala and S.K. Dikshit, *Indian J. Chem. Sect. A*, 17 (1979) 304.
61 Y. Sasson, A. Zoran and J. Blum, *J. Mol. Catal.*, 6 (1979) 289.
62 M. Ahmed and R.J. Magee, *Proc. Indian Acad. Sci. Sect. A*, 88 (1979) 401.
63 D.J. Gulliver, W. Levason, K.G. Smith, M.J. Selwood and S.G. Murray,

J. Chem. Soc., Dalton Trans., (1980) 1872.

64 Z. Usklinge, G. Mezaraups and E. Jansons, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, (1979) 435.

65 J. Dwivedi and U. Agarwala, *Indian J. Chem. Sect. A*, 17 (1979) 276.

66 T. Singh and U. Agarwala, *Transition Met. Chem. (Weinheim, Ger.)*, 4 (1979) 340.

67 K.S. Siddiqi, P. Khan, N. Singhal and S.A.A. Zaidi, *Indian J. Chem. Sect. A*, 19 (1980) 265.

68 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 269.

69 R.N. Mukherjee and P.K. Gogoi, *Indian J. Chem. Sect. A*, 19 (1980) 455.

70 A.K. Nigam and G.D. Tiwari, *J. Indian Chem. Soc.*, 57 (1980) 223.

71 D. Waysbort and G. Navon, *J. Phys. Chem.*, 84 (1980) 674.

72 D. Waysbort and G. Navon, *Chem. Phys.*, 49 (1980) 333.

73 H.E. Toma, *J. Chem. Soc., Dalton Trans.*, (1980) 471.

74 J.J. Verdonck, P.A. Jacobs, M. Genet and G. Poncelet, *J. Chem. Soc., Faraday Trans. 1*, 76 (1980) 403.

75 H.H. Nijs, P.A. Jacobs and J.B. Uytterhoeven, *J. Chem. Soc., Chem. Commun.*, (1979) 180.

76 H.H. Nijs, P.A. Jacobs and J.B. Uytterhoeven, *J. Chem. Soc., Chem. Commun.*, (1979) 1095.

77 H.J.J. Verdonck, P.A. Jacobs and J.B. Uytterhoeven, *J. Chem. Soc., Chem. Commun.*, (1979) 181.

78 N. Itoh, S. Kohata and A. Ohyoshi, *Spectrochim. Acta Part A*, 36 (1980) 433.

79 M.T. Fairhurst and T.W. Swaddle, *Inorg. Chem.*, 18 (1979) 3241.

80 A. Yeh and H. Taube, *Inorg. Chem.*, 19 (1980) 3740.

81 A. Yeh and H. Taube, *J. Am. Chem. Soc.*, 102 (1980) 4725.

82 A. Ohyoshi and K. Yoshikuni, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3105.

83 S.E. Diamond, B.S. Tovrog and F. Mares, *J. Am. Chem. Soc.*, 102 (1980) 5908.

84 G.M. Brown, H.J. Krentzien, M. Abe and H. Taube, *Inorg. Chem.*, 18 (1979) 3374.

85 D.M. Stanbury, W.A. Mulac, J.C. Sullivan and H. Taube, *Inorg. Chem.*, 19 (1980) 3735.

86 J. Phillips and A. Haim, *Inorg. Chem.*, 19 (1980) 76.

87 R. Gulka and S.S. Isied, *Inorg. Chem.*, 19 (1980) 2842.

88 M.E. Revek and P.S. Sheridan, *Inorg. Chem.*, 19 (1980) 2646.

89 C-K. Poon and C-M. Che, *J. Chem. Soc., Dalton Trans.*, (1980) 756.

90 C-K. Poon, C-M. Che and Y-P. Kan, *J. Chem. Soc., Dalton Trans.*, (1980) 128.

91 S.S. Isied, *Inorg. Chem.*, 19 (1980) 911.

92 B.T. Khan, M.R. Somayajulu and M.M. Taqui Khan, *Indian J. Chem. Sect. A*, 17 (1979) 359.

93 V. Kumar, M.M. Hao and N. Ahmad, *Indian J. Chem. Sect. A*, 17 (1979) 305.

94 R. Berkoff, K. Krist and H.D. Gafney, *Inorg. Chem.*, 19 (1980) 1.

95 J.S. Littler, G.R. Quick and D. Wozniak, *J. Chem. Soc., Perkin Trans. 2*, (1980) 657.

96 A.J. Audsley, G.R. Quick and J.S. Littler, *J. Chem. Soc., Perkin Trans. 2*, (1980) 557.

97 V.Ya. Shafirovich and V.V. Strelets, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (1980) 7.

98 R.A. Krause, *Inorg. Chim. Acta*, 31 (1978) 241.

99 R.A. Krause, *Inorg. Chim. Acta*, 22 (1977) 209.

100 B. Durham, S.R. Wilson, D.J. Hodgson and T.J. Meyer, *J. Am. Chem. Soc.*, 102 (1980) 600.

101 F.R. Keene, D.J. Salmon, J.L. Walsh, H.D. Abruña and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 1896.

102 B.P. Sullivan, J.M. Calvert and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 1404.

103 J. Chatt and B.L. Shaw, *J. Chem. Soc.(A)*, (1966) 1811.

104 R. Contreras, G.A. Heath, A.J. Lindsay and T.A. Stephenson, *J. Organomet. Chem.*, 179 (1979) C55.

105 P.T. Manoharan, P.K. Mehrotra, M.M. Taqui Kahn and R.K. Andal, *Inorg. Chem.*, 12 (1973) 2753.

106 O.K. Medhi and U. Agarwala, *Inorg. Chem.*, 19 (1980) 1381.
107 G. Mercati and F. Morazzoni, *Gazz. Chim. Ital.*, 109 (1979) 161.
108 D. Gussoni, G. Mercati and F. Morazzoni, *Gazz. Chim. Ital.*, 109 (1979) 545.
109 T. Togano, M. Mukaida and T. Nomura, *Bull. Chem. Soc. Jpn.*, 53 (1980) 2085.
110 D.S. Martin, R.A. Newman and L.M. Vlasnik, *Inorg. Chem.*, 19 (1980) 3404.
111 J.G. Norman, Jr., G.E. Renzoni and D.A. Case, *J. Am. Chem. Soc.*, 101 (1979) 5256.
112 R.I. Crisp and K.R. Seddon, unpublished results.
113 J.L. Walsh, J.A. Baumann and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 2145.
114 N.S. Hush, A. Edgar and J.K. Beattie, *Chem. Phys. Lett.*, 69 (1980) 128.
115 B.C. Bunker, R.S. Drago, D.N. Hendrickson, R.M. Richman and S.L. Kessell, *J. Am. Chem. Soc.*, 100 (1978) 3805.
116 J.W. Lauher, *Inorg. Chim. Acta*, 39 (1980) 119.
117 M.A. Nemzek and R.W. Callahan, *J. Chem. Soc., Chem. Commun.*, (1980) 1231.
118 B.P. Sullivan and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 752.
119 M.J. Powers and T.J. Meyer, *J. Am. Chem. Soc.*, 102 (1980) 1289.
120 L.H. Pignolet and S.H. Wheeler, *Inorg. Chem.*, 19 (1980) 935.
121 A. Bino and F.A. Cotton, *J. Am. Chem. Soc.*, 102 (1980) 608.
122 R.I. Crisp and K.R. Seddon, *Inorg. Chim. Acta*, 44 (1980) L133.
123 S.P. Gabuda, E.P. Zeer and A.G. Lundin, *Yader. Magnit. Rezonans v Kristallakh, Krasnoyarsk*, (1978) 58 [*Chem. Abstr.*, 91 (1979) 201731].
124 K.W. Hicks and G.A. Chappelle, *Inorg. Chem.*, 19 (1980) 1623.
125 S. Bagger, *Acta Chem. Scand. Ser. A*, 34 (1980) 63.
126 M.C. Mehra and J.C. Landry, *Talanta*, 27 (1980) 445.
127 F. Abraham, G. Nowogrocki, S. Sueur and C. Brémard, *Acta Crystallogr. Sect. B*, 36 (1980) 799.
128 J.R. Barnes and R.J. Goodfellow, *J. Chem. Res.(S)*, (1979) 350, *J. Chem. Res.(M)*, (1979) 4301.
129 N. Farrel and N.G. de Oliveira, *Inorg. Chim. Acta*, 44 (1980) L255.
130 C. Preti, G. Tosi and P. Zannini, *J. Inorg. Nucl. Chem.*, 41 (1979) 485.
131 S.K. Sahni, P.C. Jain and V.B. Rana, *Indian J. Chem. Sect. A*, 18 (1979) 161.
132 A. Deak and J.L. Templeton, *Inorg. Chem.*, 19 (1980) 1075.
133 J.N. Murrell, A. Al-Derzi, G.J. Leigh and M.F. Guest, *J. Chem. Soc., Dalton Trans.*, (1980) 1425.
134 P.C. Ford, *Rev. Chem. Intermediates*, 2 (1979) 267.
135 E. Tfouni and P.C. Ford, *Inorg. Chem.*, 19 (1980) 72.
136 D.A. Johnson and V.C. Dew, *Inorg. Chem.*, 11 (1979) 3273.
137 M.J. Clarke, M.G. Dowling, A.R. Garafalo and T.F. Brennan, *J. Biol. Chem.*, 255 (1980) 3472.
138 H. Lehmann, K.J. Schenk, G. Chapuis and A. Ludi, *J. Am. Chem. Soc.*, 101 (1979) 6197.
139 V.B. Shur, I.A. Tikhonova, G.G. Aleksandrov, Yu.T. Struchkov, M.E. Vol'pin, E. Schmitz and K. Jähnisch, *Inorg. Chim. Acta*, 44 (1980) L275.
140 R.A. Scott and H.B. Gray, *J. Am. Chem. Soc.*, 102 (1980) 3219.
141 C.S. Glennon, T.D. Hand and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1980) 19.
142 D.M. Stanbury, O. Haas and H. Taube, *Inorg. Chem.*, 19 (1980) 518.
143 F.J. Kristine, C.R. Johnson, S. O'Donnell and R.E. Shepherd, *Inorg. Chem.*, 19 (1980) 2280.
144 B.S. Tovrog, S.E. Diamond and F. Mares, *J. Am. Chem. Soc.*, 101 (1979) 5067.
145 C-K. Poon and C-M. Che, *J. Chem. Soc., Chem. Commun.*, (1979) 861.
146 A.R. Middleton, J.R. Thornback and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1980) 174.
147 J.L. Templeton, *J. Am. Chem. Soc.*, 101 (1979) 4906.
148 D.P. Rillema, D.S. Jones and H.A. Levy, *J. Chem. Soc., Chem. Commun.*, (1979) 849.
149 R.H. Fabian, D.M. Klassen and R.W. Sonntag, *Inorg. Chem.*, 19 (1980) 1977.
150 P. Belser and A. von Zelewsky, *Helv. Chim. Acta*, 63 (1980) 1675.
151 M.A. Weiner and A. Basu, *Inorg. Chem.*, 19 (1980) 2797.
152 M. Hunziker and A. Ludi, *J. Am. Chem. Soc.*, 99 (1977) 7370.
153 R.J. Crutchley and A.B.P. Lever, *J. Am. Chem. Soc.*, 102 (1980) 7128.

154 B. Durham, J.L. Walsh, C.L. Carter and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 860.

155 B.P. Sullivan, D.J. Salmon, T.J. Meyer and J. Peedin, *Inorg. Chem.*, 18 (1979) 3369.

156 E.C. Johnson, B.P. Sullivan, D.J. Salmon, S.A. Adeyemi and T.J. Meyer, *Inorg. Chem.*, 17 (1978) 2211.

157 J.L. Walsh, R.M. Bullock and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 865.

158 J.M. Clear, J.M. Kelly, C.M. O'Connell, J.G. Vos, C.J. Cardin, S.R. Costa and A.J. Edwards, *J. Chem. Soc., Chem. Commun.*, (1980) 750.

159 D.J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, (1980) 1213.

160 R.O. Gould, T.A. Stephenson and M.A. Thomson, *J. Chem. Soc., Dalton Trans.*, (1980) 804.

161 R. Salcedo and H. Torrens, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 247.

162 R.A. Krause and K. Krause, *Inorg. Chem.*, 19 (1980) 2600.

163 B. Chaudret and R. Poilblanc, *J. Chem. Soc., Dalton Trans.*, (1980) 539.

164 R.D. Gillard, K.W. Johns and P.A. Williams, *J. Chem. Soc., Chem. Commun.*, (1979) 357.

165 R.D. Gillard, C.T. Hughes, W.S. Walters and P.A. Williams, *J. Chem. Soc., Dalton Trans.*, (1979) 1769.

166 J.A. Arce Sagüés, R.D. Gillard and P.A. Williams, *Inorg. Chim. Acta*, 44 (1980) L253.

167 H.D. Abruña, A.Y. Teng, G.J. Samuels and T.J. Meyer, *J. Am. Chem. Soc.*, 101 (1979) 6745.

168 C.M. Elliott, *J. Chem. Soc., Chem. Commun.*, (1980) 261.

169 D.J. Salmon, PhD thesis, University of North Carolina at Chapel Hill, 1976.

170 T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, 110 (1980) 329.

171 M. Venturi, S. Emmi, P.G. Fuochi and Q.G. Mulazzani, *J. Phys. Chem.*, 84 (1980) 2160.

172 T. Matsumura-Inoue, I. Ikemoto and Y. Umezawa, *J. Electroanal. Chem. Interfacial Electrochem.*, 102 (1979) 131.

173 A.B. Bocarsly, D.C. Bookbinder, R.M. Dominey, N.S. Lewis and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 3683.

174 L.F. Schneemeyer and M.S. Wrighton, *J. Am. Chem. Soc.*, 101 (1979) 6496.

175 T. Boschi, G. Bontempelli and G-A. Mazzocchin, *Inorg. Chim. Acta*, 37 (1979) 155.

176 G. Domazetis, B. Tarpey, D. Dolphin and B.R. James, *J. Chem. Soc., Chem. Commun.*, (1980) 939.

177 J.W. Faller, C.C. Chen and C.J. Malerich, *J. Inorg. Biochem.*, 11 (1979) 151.

178 T.S. Srivastava, *Indian J. Chem. Sect. A*, 18 (1979) 284.

179 D.R. Paulson, A.W. Addison, D. Dolphin and B.R. James, *J. Biol. Chem.*, 254 (1979) 7002.

180 T.S. Srivastava, *Biochim. Biophys. Acta*, 491 (1977) 599.

181 D. Dolphin, B.R. James, A.J. Murray and J.R. Thornback, *Canad. J. Chem.*, 58 (1980) 1125.

182 S. Omiya, M. Tsutsui, E.F. Meyer, Jr., I. Bernal and D.L. Cullen, *Inorg. Chem.*, 19 (1980) 134.

183 L.J. Boucher and P. Rivera, *Inorg. Chem.*, 19 (1980) 1816.

184 M. Atkinson and K.R. Seddon, unpublished results; M. Atkinson, Part II thesis, Oxford, 1981.

185 C.K. Choy, J.R. Mooney and M.E. Kenney, *J. Magn. Reson.*, 35 (1979) 1.

186 H. Schmidbaur and G. Blaschke, *Z. Naturforsch. Teil B*, 35 (1980) 584.

187 M.M. Taqui Khan, R. Mohiuddin and M. Ahmed, *J. Coord. Chem.*, 10 (1980) 1.

188 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Chem. Commun.*, (1979) 489.

189 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 511.

190 T. Arthur, R. Contreras, G.A. Heath, G. Hefter, A.J. Lindsay, D.J.A. Riach and T.A. Stephenson, *J. Organomet. Chem.*, 179 (1979) C49.

191 J. Blum, I. Pri-Bar and O. Buchman, "Catalysis in Chemistry and Biochemistry

Theory and Experiment" (ed. B. Pullman), (1979) 265.
192 V.Z. Sharf, B.M. Savchenko, V.N. Krutii and L.Kh. Freidlin, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (1980) 456.
193 W. Strohmeier, M. Michel and L. Weigelt, *Z. Naturforsch. Teil B*, 35 (1980) 648.
194 R.A. Sanchez-Delgado and O.L. De Ochoa, *J. Mol. Catal.*, 6 (1979) 303.
195 E.J. Kuhlmann and J.J. Alexander, *J. Organomet. Chem.*, 174 (1979) 81.
196 K. Ohkubo, I. Terada and K. Yoshinaga, *Inorg. Nucl. Chem. Lett.*, 15 (1979) 421.
197 H. Singer, E. Hademer, U. Oehmichen and P. Dixneuf, *J. Organomet. Chem.*, 178 (1979) C13.
198 Z. Toth, F. Joo and M. Beck, *Magy. Kem. Foly.*, 85 (1979) 571.
199 Z. Toth, F. Joo and M. Beck, *Magy. Kem. Foly.*, 86 (1980) 20.
200 Z. Toth, F. Joo and M. Beck, *Magy. Kem. Foly.*, 86 (1980) 173.
201 E. Roland and H. Vahrenkamp, *Chem. Ber.*, 113 (1980) 1799.
202 T.V. Ashworth, M.J. Nolte and E. Singleton, *S. Afr. J. Chem.*, 31 (1978) 155.
203 T.V. Ashworth, M.J. Nolte and E. Singleton, *S. Afr. J. Chem.*, 31 (1978) 149.
204 A. Dobson, D.S. Moore and S.D. Robinson, *J. Organomet. Chem.*, 177 (1979) C8.
205 B. Cetinkaya, M.F. Lappert and S. Torroni, *J. Chem. Soc., Chem. Commun.*, (1979) 843.
206 K. Kurtev, D. Ribola, R.A. Jones, D.J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1980) 55.
207 K.G. Srinivasamurthy, N.M.N. Gowda and G.K.N. Reddy, *Indian J. Chem. Sect. A*, 18 (1979) 322.
208 T. Tsuihiji, T. Akiyama and A. Sugimori, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3451.
209 S.M. Boniface and G.R. Clark, *J. Organomet. Chem.*, 184 (1980) 125.
210 P. Pertici, G. Vitulli, W. Porzio and M. Zocchi, *Inorg. Chim. Acta*, 37 (1979) L521.
211 R.O. Rosete, D.J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1979) 1618.
212 A. Sahajpal and S.D. Robinson, *Inorg. Chem.*, 18 (1979) 3572.
213 R.G. Ball, B.R. James, J. Trotter, D.K.W. Wang and K.R. Dixon, *J. Chem. Soc., Chem. Commun.*, (1979) 460.
214 B.R. James and D.K.W. Wang, *Can. Symp. Catal.*, (1979) 29.
215 B.R. James and D.K.W. Wang, *Can. J. Chem.*, 58 (1980) 245.
216 R.A. Jones, G. Wilkinson, I.J. Colquohoun, W. McFarlane, A.M.R. Galas and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1980) 2480.
217 J.M. Towarnicky and E.P. Schram, *Inorg. Chim. Acta*, 41 (1980) 55.
218 L. Vaska and E.M. Sloane, *J. Am. Chem. Soc.*, 82 (1960) 1263.
219 K. Hiraki, Y. Sasada and T. Kitamura, *Chem. Lett.*, (1980) 449.
220 T. Ito and A. Yamamoto, *Ventron Alembic*, 16 (1979) 2.
221 J.K. Stille and Y. Becker, *J. Org. Chem.*, 45 (1980) 2139.
222 R.A. Grey, G.P. Pez, A. Wallo and J. Corsi, *J. Chem. Soc., Chem. Commun.*, (1980) 783.
223 R.A. Grey, G.P. Pez and A. Wallo, *J. Am. Chem. Soc.*, 102 (1980) 5948.
224 D.J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1979) 1283.
225 E.O. Sherman, Jr. and P.R. Schreiner, *J. Chem. Soc., Chem. Commun.*, (1976) 3.
226 E.O. Sherman, Jr. and M. Olson, *J. Organomet. Chem.*, 172 (1979) C13.
227 P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc., Dalton Trans.*, (1980) 1961.
228 L. Bednarik and E.W. Neuse, *J. Org. Chem.*, 45 (1980) 2032.
229 M.A. Bennett, T-N. Huang and T.W. Turney, *J. Chem. Soc., Chem. Commun.*, (1979) 312.
230 J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1980) 144.
231 H. Wagner, A. Jungbauer, G. Thiele and H. Behrens, *Z. Naturforsch. Teil B*, 34 (1979) 1487.
232 C.F.J. Barnard, J.A. Daniels and R.J. Mawby, *J. Chem. Soc., Dalton Trans.*, (1979) 1331.

233 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem.*, 182 (1979) C46.
234 S.G. Davies and F. Scott, *J. Organomet. Chem.*, 188 (1978) C41.
235 P.M. Treichel and D.A. Komar, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 205.
236 R.K. Pomeroy, *J. Organomet. Chem.*, 177 (1979) C27.
237 R.K. Pomeroy and K.S. Wijesekera, *Inorg. Chem.*, 19 (1980) 3729.
238 R.K. Pomeroy and K.S. Wijesekera, *Can. J. Chem.*, 58 (1980) 206.
239 I. Fernandez, R. Greatrex and N.N. Greenwood, *J. Chem. Soc., Dalton Trans.*, (1980) 918.
240 D.F. Gill, B.E. Mann and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1973) 311.
241 H. Schumann and J. Opitz, *J. Organomet. Chem.*, 186 (1980) 91.
242 H. Schumann, J. Opitz and J. Pickardt, *Chem. Ber.*, 113 (1980) 1385.
243 H. Schumann and J. Opitz, *Chem. Ber.*, 113 (1980) 989.
244 H. Schumann and J. Opitz, *Z. Naturforsch. Teil B*, 35 (1980) 38.
245 H.B. Abrahamson, M.C. Palazzotto, C.L. Reichel and M.S. Wrighton, *J. Am. Chem. Soc.*, 101 (1979) 4123.
246 P. McArdle and A.R. Manning, *J. Chem. Soc.(A)*, (1970) 2128.
247 J.A.S. Howell and A.J. Rowan, *J. Chem. Soc., Chem. Commun.*, (1979) 482.
248 R. Huq, A.J. Poë and S. Chawla, *Inorg. Chim. Acta*, 38 (1980) 121.
249 M.S. Wrighton, J.L. Graff, C.L. Reichel and R.D. Sanner, Report 1979, AD-A067603 [*Chem. Abstr.*, 91 (1979) 199513].
250 D.C. Moody and R.R. Ryan, *J. Chem. Soc., Chem. Commun.*, (1980) 1230.
251 R.K. Pomeroy and R.F. Alex, *J. Chem. Soc., Chem. Commun.*, (1980) 1114.
252 R. Holderegger and L.M. Venanzi, *Helv. Chim. Acta*, 62 (1979) 2154.
253 J-M. Bassett, D.E. Berry, G.K. Barker, M. Green, J.A.K. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1979) 1003.
254 K.D. Schramm and J.A. Ibers, *Inorg. Chem.*, 19 (1980) 2441.
255 L.H. Staal, L.H. Polm, G. van Koten and K. Vrieze, *Inorg. Chim. Acta*, 37 (1979) L485.
256 L.H. Staal, L.H. Polm, R.W. Balk, G. van Koten, K. Vrieze and A.M.F. Brouwers, *Inorg. Chem.*, 19 (1980) 3343.
257 J.M. Maher and N.J. Cooper, *J. Am. Chem. Soc.*, 102 (1980) 7604.
258 H. Nyman and S. Andersson, *Acta Crystallogr. Sect. A*, 35 (1979) 934.
259 K. Hiebl, P. Rogl, E. Uhl and M.J. Sienko, *Inorg. Chem.*, 19 (1980) 3316.
260 B.F.G. Johnson (ed.), "Transition Metal Clusters", Wiley-Interscience, Chichester, 1980.
261 P.R. Raithby, in [260], p. 5.
262 K. Wade, in [260], p. 193.
263 C.D. Garner, in [260], p. 225.
264 J.A. Connor, in [260], p. 345.
265 A.J. Deeming, in [260], p. 391.
266 B.F.G. Johnson and R.E. Benfield, in [260], p. 471.
267 R. Whyman, in [260], p. 545.
268 R.G. Woolley, in [260], p. 607.
269 R.E. Benfield and B.F.G. Johnson, *J. Chem. Soc., Dalton Trans.*, (1980) 1743.
270 R.E. Benfield and B.F.G. Johnson, *J. Chem. Soc., Dalton Trans.*, (1978) 1554; B.F.G. Johnson, *J. Chem. Soc., Chem. Commun.*, (1975) 211
271 P.B. Hitchcock, R. Mason and M. Textor, *J. Chem. Soc., Chem. Commun.*, (1976) 1047.
272 A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1980) 2509.
273 M.Z. Iqbal, *Arabian J. Sci. Eng.*, 5 (1980) 119.
274 R.L. Kump and L.J. Todd, *J. Chem. Soc., Chem. Commun.*, (1980) 292.
275 W.C. Trogler and J. Berkowitz, Report 1979, CONF-790658-7 [*Chem. Abstr.*, 92 (1980) 101993].
276 D. Ajò, G. Granozzi, E. Tondello and I. Fragalà, *Inorg. Chim. Acta*, 37 (1979) 191.
277 W.M. Bowser and W.H. Weinberg, *J. Am. Chem. Soc.*, 102 (1980) 4720.
278 G.A. Battiston, G. Bor, U.K. Dietler, S.F.A. Kettle, R. Rossetti, G. Sbrignadello and P.L. Stanghellini, *Inorg. Chem.*, 19 (1980) 1961.

279 G.A. Battiston, G. Sbrignadello and G. Bor, *Inorg. Chem.*, 19 (1980) 1973.
280 A. Bradshaw, *J. Chem. Soc., Chem. Commun.*, (1980) 365.
281 A.A. Barkatin, A.K. Baev, I.L. Gaidym and S.A.R. Knox, *Khim. Khim. Tekhnol. (Minsk)*, 14 (1979) 14 [*Chem. Abstr.*, 91 (1979) 221698].
282 A.K. Baev, *Zh. Fiz. Khim.*, 54 (1980) 1.
283 G. Cetini, O. Gambino, E. Sappa and M. Valle, *Atti Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat.*, 101 (1967) 855; A.J. Poë and M.V. Twigg, *J. Organomet. Chem.*, 50 (1973) C39.
284 P. Banditelli, A. Cuccuru and F. Sodi, *Thermochim. Acta*, 16 (1976) 89.
285 P.A. Dawson, B.M. Peake, B.H. Robinson and J. Simpson, *Inorg. Chem.*, 19 (1980) 465.
286 R.M. Laine, *Ann. N.Y. Acad. Sci.*, 333 (1980) 124.
287 R.M. Laine, *J. Org. Chem.*, 45 (1980) 3370.
288 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Süss, *J. Chem. Soc., Dalton Trans.*, (1979) 1356.
289 R.L. Pruett, R.C. Schoening, J.L. Vidal and R.A. Fiato, *J. Organomet. Chem.*, 182 (1979) C57.
290 J.B. Keister, *J. Organomet. Chem.*, 190 (1980) C36.
291 G. Süss-Fink, *J. Organomet. Chem.*, 193 (1980) C20.
292 B.F.G. Johnson, J. Lewis, A.G. Orpen, P.R. Raithby and G. Süss, *J. Organomet. Chem.*, 173 (1979) 187.
293 J.B. Keister, *J. Chem. Soc., Chem. Commun.*, (1979) 214.
294 J.B. Keister and T.L. Horling, *Inorg. Chem.*, 19 (1980) 2304.
295 B.F.G. Johnson, P.R. Raithby and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, (1980) 99.
296 E.J. Forbes, N. Goodhand, D.L. Jones and T.A. Hamor, *J. Organomet. Chem.*, 182 (1979) 143.
297 B.F.G. Johnson, J. Lewis, P.G. Lodge, P.R. Raithby, K. Henrick and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, (1979) 719.
298 E. Sappa, O. Gambino and G. Cetini, *J. Organomet. Chem.*, 39 (1972) 169.
299 B.F.G. Johnson, R.L. Kelly, J. Lewis and J.R. Thornback, *J. Organomet. Chem.*, 190 (1980) C91.
300 R. Szostak, C.E. Strouse and H.D. Kaesz, *J. Organomet. Chem.*, 191 (1980) 243.
301 E.W. Abel and G.W. Farrow, *J. Inorg. Nucl. Chem.*, 42 (1980) 541.
302 N. Cook, L.E. Smart, P. Woodward and J.D. Cotton, *J. Chem. Soc., Dalton Trans.*, (1979) 1032.
303 C.C. Nagel and S.G. Shore, *J. Chem. Soc., Chem. Commun.*, (1980) 530.
304 H.W. Walker, C.T. Kresge, P.C. Ford and R.G. Pearson, *J. Am. Chem. Soc.*, 101 (1979) 7428.
305 G.R. Steinmetz, A.D. Harley and G.L. Geoffroy, *Inorg. Chem.*, 19 (1980) 2985.
306 M.R. Churchill, R.A. Lashewycz, J.R. Shapley and S.I. Richter, *Inorg. Chem.*, 19 (1980) 1277.
307 J.L. Graff and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 2123.
308 P.M. Lausarot, G.A. Vaglio and M. Valle, *Gazz. Chim. Ital.*, 109 (1979) 127.
309 P.M. Lausarot, G.A. Vaglio and M. Valle, *Inorg. Chim. Acta*, 36 (1979) 213.
310 M. Bianchi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani and C. Botteghi, *J. Organomet. Chem.*, 188 (1980) 109.
311 P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, *J. Chem. Soc., Chem. Commun.*, (1979) 735.
312 C.R. Eady, P.F. Jackson, B.F.G. Johnson, J. Lewis, M.C. Malatesta, M. McPartlin and W.J.H. Nelson, *J. Chem. Soc., Dalton Trans.*, (1980) 383.
313 P.F. Jackson, B.F.G. Johnson, J. Lewis, P.R. Raithby, M. McPartlin, W.J.H. Nelson, K.D. Rouse, J. Allibon and S.A. Mason, *J. Chem. Soc., Chem. Commun.*, (1980) 295.
314 C.R. Eady, B.F.G. Johnson, J. Lewis, M.C. Malatesta, P. Mackin and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, (1976) 945.
315 P. Chini, G. Longoni, S. Martinengo and A. Ceriotti, *Adv. Chem. Ser.*, 167 (1978) 1.
316 I.A. Oxton, S.F.A. Kettle, P.F. Jackson, B.F.G. Johnson and J. Lewis,

J. Chem. Soc., Chem. Commun., (1979) 687.

317 J.S. Bradley, G.B. Ansell and E.W. Hill, *J. Organomet. Chem.*, 184 (1980) C33.

318 G.B. Ansell and J.S. Bradley, *Acta Crystallogr. Sect. B*, 36 (1980) 726.

319 B.F.G. Johnson, J. Lewis, S.W. Sankey, K.W. Wong, M. McPartlin and W.J.H. Nelson, *J. Organomet. Chem.*, 191 (1980) C3.

320a W.L. Gladfelter and G.L. Geoffroy, *Inorg. Chem.*, 19 (1980) 2579.

320b J.R. Fox, W.L. Gladfelter and G.L. Geoffroy, *Inorg. Chem.*, 19 (1980) 2574.

321 W.L. Gladfelter, G.L. Geoffroy and J.C. Calabrese, *Inorg. Chem.*, 19 (1980) 2569.

322 P.C. Steinhardt, W.L. Gladfelter, A.D. Harley, J.R. Fox and G.L. Geoffroy, *Inorg. Chem.*, 19 (1980) 332.

323 R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio and M. Tiripicchio Camellini *J. Am. Chem. Soc.*, 102 (1980) 3626.

324 N.M. Sinitsyn and A.A. Svetlov, *Koord. Khim.*, 6 (1980) 281.

325 A.B. Nikol'skii, A.M. Popov and N.B. Batalova, *Koord. Khim.*, 5 (1979) 1851.

326 S. Sugimoto, *Radioisotopes*, 28 (1979) 425.

327 E. Akatsu, C. Yonezawa and K. Motojima, *Ann. Nucl. Energy*, 6 (1979) 399.

328 S. Bhaduri, B.F.G. Johnson, A. Khair, I. Ghatak and D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1980) 1572.

329 G. Innorta and G. Piazza, *J. Electroanal. Chem. Interfacial Electrochem.*, 106 (1980) 137.

330 R. Holderegger, L.M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, *Helv. Chim. Acta*, 62 (1979) 2159.

331 R.P. Cheney, S.D. Pell and M.Z. Hoffman, *J. Inorg. Nucl. Chem.*, 41 (1979) 489.

332 T.G. Southern, P.H. Dixneuf, J-Y. Le Marouille and D. Grandjean, *Inorg Chem.*, 18 (1979) 2987.

333 J.V. Dubrawski and R.D. Feltham, *Inorg. Chem.*, 19 (1980) 355.

334 T. Ishiyama and T. Matsumura, *Annu. Rep. Radiat. Cent. Osaka Prefect.*, 19 (1978) 1.

335 N.K. Roy and C.R. Saha, *J. Inorg. Nucl. Chem.*, 42 (1980) 37.

336 K.K. Pandey and U.C. Agarwala, *Z. Anorg. Allg. Chem.*, 461 (1980) 231.

337 G.A. Crosby, Report 1979, AD-A080219 [*Chem. Abstr.*, 93 (1980) 160401].

338 General Electric Co., Report 1979, COO-4395-1 [*Chem. Abstr.*, 93 (1980) 160495].

339 E.B. Sveshnikova and S.P. Naumov, *Opt. Spektrosk.*, 47 (1979) 502.

340 K. Nakamaru, K. Nishio and H. Nobe, *Sci. Rep. Hirosaki Univ.*, 26 (1979) 57.

341 O. Johansen, C. Kowala, A.W.-H. Mau and W.H.F. Sasse, *Aust. J. Chem.*, 32 (1979) 1453.

342 G.L. Gaines, Jr., *Inorg. Chem.*, 19 (1980) 1710.

343 F. Bolletta, A. Juris, M. Maestri and D. Sandrini, *Inorg. Chim. Acta*, 44 (1980) L175.

344 K.W. Hipps and G.A. Crosby, *J. Am. Chem. Soc.*, 97 (1975) 7042.

345 F. Felix, J. Ferguson, H.U. Güdel and A. Ludi, *J. Am. Chem. Soc.*, 102 (1980) 4096.

346 S. Decurtins, F. Felix, J. Ferguson, H.U. Güdel and A. Ludi, *J. Am. Chem. Soc.*, 102 (1980) 4102.

347 K.R. Seddon and E.A. Seddon, "The Chemistry of Ruthenium", Chapter 15, Elsevier, manuscript approaching completion (at last!).

348 P. Belser, C. Daul and A. von Zelewsky, manuscript in press; C. Daul, private communication.

349 C.A. Daul and J. Weber, *Chem. Phys. Lett.*, 77 (1981) 593.

350 M. Král, *Theor. Chim. Acta*, 55 (1980) 333.

351 K.W. Hipps, *Inorg. Chem.*, 19 (1980) 1390.

352 R.F. Dallinger and W.H. Woodruff, *J. Am. Chem. Soc.*, 101 (1979) 4391.

353 M.K. De Armond, C.M. Carlin and W.L. Huang, *Inorg. Chem.*, 19 (1980) 62.

354 G.A. Crosby and W.H. Elfring, Jr., *J. Phys. Chem.*, 80 (1976) 2206.

355 J.E. Baggott, M.J. Pilling, S. Anderson and K.R. Seddon, submitted for publication.

356 J. Ferguson, A.W.-H. Mau and W.H.F. Sasse, *Chem. Phys. Lett.*, 68 (1979) 21.

357 S. Anderson, K.R. Seddon, R.D. Wright and A.T. Cocks, *Chem. Phys. Lett.*, 71 (1980) 220.

358 B.P. Sullivan, H. Abruña, H.O. Finklea, D.J. Salmon, J.K. Nagle, T.J. Meyer and H. Sprintschnik, *Chem. Phys. Lett.*, 58 (1978) 389.

359 S.H. Peterson and J.N. Demas, *J. Am. Chem. Soc.*, 101 (1979) 6571.

360 K. Kawasumi, T. Kimura, Y. Kaizu and H. Kobayashi, *Kokagaku Toronkai Koen Yoshishu*, (1979) 68 [*Chem. Abstr.*, 92 (1980) 171784].

361 R.E. Sassoon and J. Rabani, *J. Phys. Chem.*, 84 (1980) 1321.

362 C.R. Bock, J.A. Connor, A.R. Gutierrez, T.J. Meyer, D.G. Whitten, B.P. Sullivan and J.K. Nagle, *Chem. Phys. Lett.*, 61 (1979) 522.

363 M. Brezeanu, L. Patron and M. Andruh, *Rev. Chim. (Bucharest)*, 30 (1979) 745.

364 O. Johansen, C. Kowala, A.W.-H. Mau and W.H.F. Sasse, *Aust. J. Chem.*, 32 (1979) 2395.

365 J.H. Baxendale and M.A.J. Rodgers, *Chem. Phys. Lett.*, 72 (1980) 424.

366 Y. Tsutsui, K. Takuma, T. Nishijima and T. Matsuo, *Chem. Lett.*, (1979) 617.

367 T. Nagamura, K. Takuma, Y. Tsutsui and T. Matsuo, *Chem. Lett.*, (1980) 503.

368 G.L. Gaines, Jr., *J. Phys. Chem.*, 83 (1979) 3088.

369 C.R. Bock, J.A. Connor, A.R. Gutierrez, T.J. Meyer, D.G. Whitten, B.P. Sullivan and J.K. Nagle, *J. Am. Chem. Soc.*, 101 (1979) 4815.

370 P.J. De Laive, T.K. Foreman, C. Giannotti and D.G. Whitten, *J. Am. Chem. Soc.*, 102 (1980) 5627.

371 C. Creutz, M. Chou, T.L. Netzel, M. Okumura and N. Sutin, *J. Am. Chem. Soc.*, 102 (1980) 1309.

372 B.A. De Graff and J.N. Demas, *J. Am. Chem. Soc.*, 102 (1980) 6169.

373 M.I.C. Ferreira and A. Harriman, *J. Chem. Soc., Faraday Trans. 2*, 75 (1979) 874.

374 Y. Ohsawa, T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, 106 (1980) 327.

375 K. Chandrasekaran and P. Natarajan, *Inorg. Chem.*, 19 (1980) 1714.

376 Y. Kurimura and R. Cnimura, *Inorg. Chem.*, 19 (1980) 3516.

377 A. Deronzier and T.J. Meyer, *Inorg. Chem.*, 19 (1980) 2912.

378 B.A. De Graff, J.N. Demas and D.G. Taylor, *Sol. Energy: Chem. Convers. Storage (Symp.), 1978*, (1979) 189 [*Chem. Abstr.*, 92 (1980) 224149].

379 G.B. Porter and R.H. Sparks, *J. Chem. Soc., Chem. Commun.*, (1979) 1094.

380 G.B. Porter and R.H. Sparks, *J. Photochem.*, 13 (1980) 123.

381 W.M. Wallace and P.E. Hoggard, *Inorg. Chem.*, 19 (1980) 2141.

382 A.I. Krasna, *Photochem. Photobiol.*, 31 (1980) 75.

383 I. Okura and N. Kim-Thuan, *J. Chem. Soc., Chem. Commun.*, (1980) 84.

384 P-A. Brugger and M. Grätzel, *J. Am. Chem. Soc.*, 102 (1980) 2461.

385 R.H. Schmell and D.G. Whitten, *J. Am. Chem. Soc.*, 102 (1980) 1938.

386 N. Getoff, S. Solar and M. Gohn, *Naturwissenschaften.*, 67 (1980) 7.

387 E. Amouyal, P. Keller and A. Moradpour, *J. Chem. Soc., Chem. Commun.*, (1980) 1019.

388a V.Ya. Shafirovich and A.E. Shilov, *Kinet. Katal.*, 20 (1979) 1156.

388b V.Ya. Shafirovich, N.K. Khannanov and V.V. Strelets, *Dokl. Akad. Nauk S.S.S.R.*, 250 (1980) 1197.

389 J.M. Lehn, J.P. Sauvage and R. Ziessel, *Nouv. J. Chim.*, 4 (1980) 355.

390 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, (1980) 694.

391 T. Kawai and T. Sakata, *Nature*, 282 (1979) 283.

392 M.Z. Hoffman and N.N. Lichtin, *Sol. Energy: Chem. Convers. Storage (Symp.), 1978*, (1979) 153 [*Chem. Abstr.*, 92 (1980) 166440].

393 C. Daul, O. Haas and A. von Zelewsky, *J. Electroanal. Chem. Interfacial Electrochem.*, 107 (1980) 49.

394 C. Daul, O. Haas, A. Lottaz, A. von Zelewsky and H-R. Zumbrunnen, *J. Electroanal. Chem. Interfacial Electrochem.*, 112 (1980) 51.

395 W.J. Albery, W.R. Bowen, F.S. Fisher and A.D. Turner, *J. Electroanal. Chem. Interfacial Electrochem.*, 107 (1980) 11.

396 W.J. Albery, A.W. Foulds, K.J. Hall, A.R. Hillman, R.G. Egdell and A.F. Orchard, *Nature*, 282 (1979) 793.

397 W.J. Albery, A.W. Foulds, K.J. Hall and A.R. Hillman, *J. Electrochem. Soc.*, 127 (1980) 654.

398 D.P. Rillema, W.J. Dressick and T.J. Meyer, *J. Chem. Soc., Chem. Commun.*, (1980) 247.

399 A. Mackor and J. Schoonman, *Rec. Trav. Chim. Pays-Bas*, 99 (1980) 71.

400 R.W. Murray, *Acc. Chem. Res.*, 13 (1980) 135.

401 P.K. Ghosh and T.G. Spiro, *J. Am. Chem. Soc.*, 102 (1980) 5543.

402 H.D. Abruña, J.L. Walsh, T.J. Meyer and R.W. Murray, *J. Am. Chem. Soc.*, 102 (1980) 3272.

403 D.C. Bookbinder and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 5123.

404 A.B. Bocarsly, E.G. Walton and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 3390.

405 N. Oyama and F.C. Anson, *J. Electrochem. Soc.*, 127 (1980) 640.

406 N.S. Scott, N. Oyama and F.C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, 110 (1980) 303.

407 N. Oyama and F.C. Anson, *Anal. Chem.*, 52 (1980) 1192.

408 N. Oyama and F.C. Anson, *J. Electrochem. Soc.*, 127 (1980) 247.

409 I. Rubinstein and A.J. Bard, *J. Am. Chem. Soc.*, 102 (1980) 6641.

410 C.U. Pittman, Jr. and G. Wilemon, *Ann. N.Y. Acad. Sci.*, 333 (1980) 67.

411 G. Innorta, A. Modelli, F. Scagnolari and A. Foffani, *J. Organomet. Chem.*, 186 (1980) 271.

412 M. Kaneko, S. Nemoto, A. Yamada and Y. Kurimura, *Inorg. Chim. Acta*, 44 (1980) L289.

413 M. Kaneko, J. Motoyoshi and A. Yamada, *Nature*, 285 (1980) 468.