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2. RUTHENIUM AND OSMIUM

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CONTENTS

INTRODUCTION

The period of this review essentially coincides with the coverage of Vols. 90 and 91 of Chemical Abstracts. Thus, although a majority of the papers covered were published in 1979, many from 1978 are included.

This review concentrates upon the coordination chemistry of ruthenium and osmium. No attempt has been made to cover work of an essentially organometallic nature, although the chemistry of simple carbonyl clusters has been included, to reflect the ever increasing interest in this area. Other areas of special interest this year include valuable work upon the OsO_4 oxidation of organic substrates, the elegant syntheses of ruthenium carboxylate systems, the ever-active $[Ru(bipy)_3]^{2+}$ system, metal—metal bonded and mixed-valence species, and the newer area of electrode modification.

RUTHENIUM

2.1 RUTHENIUM(VIII), (VII), (VI) AND (V)

2.1.1 Fluorides

The fluorination of Ru or RuO_2 yields principally RuF_5, but some RuF_8 was also detected [1]: its IR spectrum was reported. There has only been one previous report [2] of RuF_8, also made by the reaction between Ru metal and fluorine, but no spectroscopic data were given. Reaction of RuF_6 and B_2O_3 gives RuF_5 [3]. Thermochromatographic studies upon a number of ruthenium fluorides have been reported [4].

2.1.2 Oxides

The oxidative cleavage of partially or completely fluorinated alkenes by RuO_4 has been demonstrated [5]

e.g. $(C_8F_{17})CH{=}CH_2 \xrightarrow{RuO_4} C_8F_{17}COOH + CO_2$

$(C_6F_{13})CH{=}CH(C_6F_{13}) \xrightarrow{RuO_4} C_6F_{13}COOH$

$CF_3CF{=}CF_2 \xrightarrow{RuO_4} CF_3COOH + COF_2$

Oxidation of 1,3-disubstituted piperidines with RuO_4 gives the expected 2,6-dione [6]. $K_2[RuO_4]$ has been used catalytically, in the presence of excess $[S_2O_8]^{2-}$, for the oxidation of a large number of organic substrates under mild conditions (e.g. alcohols and aldehydes are oxidised to carboxylic acids and ketones; amines to nitriles or carboxylic acids). The reagent is unreactive towards tertiary alcohols, alkenes and alkynes, making it particularly useful for selective oxidation of unsaturated alcohols and aldehydes [7]. The reduction of RuO_4, $[RuO_4]^-$ and $[RuO_4]^{2-}$ by $[BH_4]^-$ has also been investigated [8].

An anti-resonance Raman effect has been observed for $[RuO_4]^{2-}$: the $\nu_1(a_1)$ stretching vibration shows a de-enhancement of the pre-resonance Raman intensity in the spectral region tentatively assigned to the d ↔ d transitions [9].

2.2 RUTHENIUM(IV)

2.2.1 Halide and oxohalide complexes

The crystal structure of $K_4[Ru_2OCl_{10}]$ has been redetermined, and the accurate parameters are $\bar{r}(RuCl)_{equatorial} = 0.2363$ nm, $\bar{r}(RuCl)_{axial} = 0.2317$ nm, and $\bar{r}(RuO) = 0.1801$ nm [10]. These results differ from the previous determination in that the axial RuCl bond length is significantly shorter than the equatorial bond lengths, a result anticipated by Campbell and Clark in their detailed analysis and reassignment of the resonance Raman spectrum of $K_4[Ru_2OCl_{10}]$ [11]. Also, the crystal structure of $K_2[RuCl_6]$ has been refined anew from the original data, to give $\bar{r}(RuCl) = 0.2318$ nm [10]. Ammonium ion tunnelling has been observed in powdered $[NH_4]_2[RuCl_6]$ [12].

$[Ru_2Cl_6(MeOH)(H_2O)(OH)_2]$ has been suggested as a solution species present in Ru(IV) chloride solutions in aqueous methanol [13].

2.2.2 Oxides and aqueous chemistry

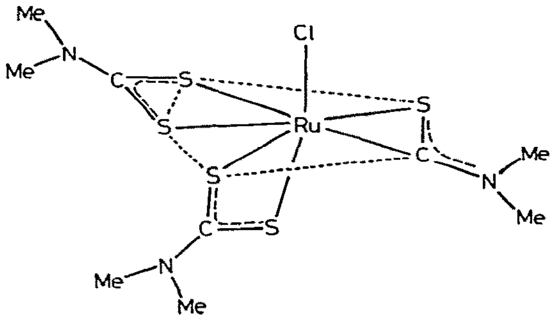
A study of the growth of single-crystals of RuO_2 has been published [14]. The X-ray and UV photoelectron spectra of RuO_2 have been reported [15], and provide verification of the Goodenough model of the band structure [16]. RuO_2 appears to form a well-behaved working electrode in aprotic media (e.g. dmso, MeCN) [17] and has been examined as an electrode material suitable for chemical modification [18]. RuO_2 reacts with HCl at 480--540°C to give $RuCl_3$ [19].

A review of the syntheses and magnetic properties of ternary and quaternary ruthenates(IV) has appeared [20]. The ternary oxides A_2RuO_3 (A = Li or K) have been prepared by the reaction of $A_2[CO_3]$ with RuO_2 and have metallic properties [21]. A particularly important result in the ruthenium--oxygen system is that the pyrochlores $A_2Ru_2O_{7-x}$ (A = Pb, Bi or Tl), particularly $Pb_2Ru_2O_{7-x}$, form efficient *catalytic* oxygen electrodes [22]. An IR study of $B_2Ru_2O_7$ (B = rare earth tripositive ion) has also been reported [23].

The nature of Ru(IV) in nitric acid solution has been reinvestigated: the principal species present is now believed to be $[Ru_4(OH)_{12}]^{4+}$ [24].

2.2.3 *Dithiocarbamates*

Photolysis of $[Ru(S_2CNR_2)_3]$ (R = Me or Et) in $CHCl_3$ in the presence of benzophenone gives $[RuCl(S_2CNR_2)_2(SCNR_2)]$, a mixed dithiocarbamato—thiocarboxamido- complex. The molecular structure of $[RuCl(S_2CNMe_2)_2(SCNMe_2)]$ (1) reveals it to be seven-coordinate [25], and it is fluxional in solution.



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2.2.4 *Mixed valence complexes, Ru(IV/III)*

The aerial oxidation of $[Ru(NH_3)_5(N_2)]^{2+}$ supported on Y-type zeolite produces supported ruthenium red [26].

2.3 RUTHENIUM(III)

2.3.1 *Halides and pseudohalides*

The optical properties of α-$RuCl_3$ have been studied in the IR, visible and UV (240—80 600 cm^{-1}) regions, by reflectance spectroscopy [27].

Ruthenium(III) has been doped into AgX (X = Cl or Br), and its EPR spectra have been interpreted in terms of the $[RuX_6]^{3-}$ moiety [28]. The IR, UV and CD spectra of $[Ru(SCN)_6]^{3-}$ and $[Ru(NH_3)_2(SCN)_4]^-$ confirm that SCN^- bonds via N and S in these complexes [29]. $[Ru(SCN)_6]^{3-}$ has also been studied polarographically [30].

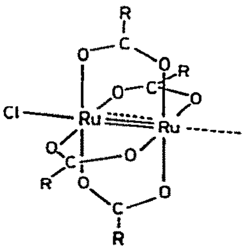
2.3.2 Aqueous chemistry

The rates of reduction of $[Ru(H_2O)_6]^{3+}$ by $[Ru(NH_3)_6]^{2+}$, $[Ru(H_2O)_5Cl]^+$ or $[V(H_2O)_6]^{2+}$ have been studied [31].

2.3.3 Carboxylates and related mixed valence complexes

Under aerobic conditions, $[RuX_2(PPh_3)_3]$ reacts with RCO_2H in benzene to give $[RuX_2(O_2CR)(PPh_3)_2]$ {X = Cl, R = Me, Et, $ClCH_2$, Ph or 4-C_6H_4Y (Y = Cl, Br, OMe, Me or NO_2); X = Br, R = Me, Ph or 4-C_6H_4Y (Y = Br or Me)} [32].

$[Ru_2(O_2CMe)_4(H_2O)_2][BF_4]$ (2) has been prepared by the hydrolysis of $Ru_2(O_2CMe)_4Cl \cdot 2\,H_2O$ (3), and $Cs[Ru_2(O_2CMe)_4Cl_2]$ (4) by the reaction of (3) with CsCl. $K[Ru_2(O_2CH)_4Cl_2]$ (5) was prepared by carboxylate exchange with (3), followed by treatment with KCl. The molecular structures of (2)–(5), along with $Ru_2(O_2CEt)_4Cl$ (6), have been determined, and pertinent data are given in Table 1. (3) and (6) have a polymeric structure (type 7), whereas (2), (4) and (5) form discrete dimers (type 8) [33].



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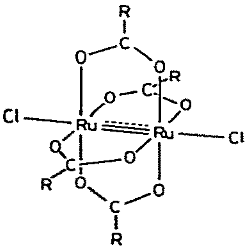

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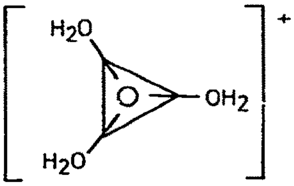
$[Ru_3O(O_2CMe)_6(H_2O)_3][O_2CMe]$ (9) is a good catalyst for the hydrogenation of alkenes. Hydrogenation of (9) in dmf yields $[HRu_3O(O_2CMe)_5(dmf)_3]^+$; this catalyses the isomerisation of alkenes to give $[Ru_3O(O_2CMe)_4(dmf)_n]^+$, which appears to be the active species in alkene hydrogenation. Only one Ru per trimeric unit appears to be involved with coordination to hydrogen and alkenes [34]. Reaction between "monomeric" $[Ru_3O(O_2CMe)_6(py)_2(L-L)]^+$



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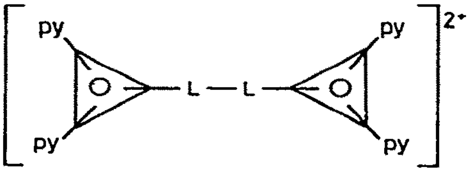

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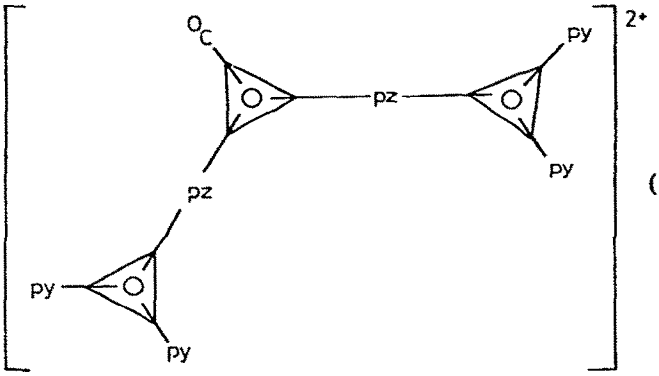
TABLE 1

Structural parameters [33]

Compound	r(RuRu)/nm	r(RuCl)/nm
(2)	0.2248	
(3)	0.2267	0.2566
(4)	0.2286	0.2521
(5)	0.2290	0.2517
(6)	0.2292	0.2566

{L—L = pyrazine, 4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethene or 1,2-bis(4-pyridyl)ethane} and $[Ru_3O(O_2CMe)_6(py)_2(MeOH)]^+$ gives "dimeric" clusters of the type $[\{(py)_2Ru_3O(O_2CMe)_6\}(L{-}L)\{Ru_3O(O_2CMe)_6(py)_2\}]^{2+}$ (**10**) [35], whereas $[Ru_3O(O_2CMe)_6(py)_2(pz)]^+$ reacts with $[Ru_3O(O_2CMe)_6(MeOH)_2(CO)]$ to give a "trimeric" cluster $[\{(py)_2Ru_3O(O_2CMe)_6(pz)\}_2\{Ru_3O(O_2CMe)_6(CO)\}]^{2+}$ (**11**) [36]. These complexes were all isolated as



(**11**)

$[PF_6]^-$ salts. The "dimeric" clusters show an extensive redox chemistry. The oxidised forms behave as electronically discrete, delocalised "monomeric" Ru_3 units, with little coupling across the L—L bridge. As the "dimer" is reduced, coupling between the two "monomeric" Ru_3 units increases [35]. The "trimer" (**11**) shows ten individual redox waves (CV); as with the "dimers", as the cluster is reduced (i.e. as it becomes electron-rich), coupling between the Ru_3 units is enhanced, and the appearance of closely spaced, one-electron waves may indicate the onset of band-like behaviour in this discrete molecular system [36].

Substitution reactions of $[Ru(edta)(H_2O)]^-$ to produce $[Ru(edta)L]^-$ {L = e.g. pz, py, isonic, MeCN or NCS^-} have been studied, and the products studied by electronic spectroscopy and CV [37,38]. In a similar manner, $[Ru(edtaH)(H_2O)]$ reacts with RSH to give $[Ru(edta)(SR)]^{2-}$, whilst thiosulphate gives $[Ru(edta)(S_2O_3)]^{3-}$. Dithiocarbonates, dithiocarbamates and thiourea behave analogously [39]. Complexes of ruthenium(III) with *trans*-

1,2-cyclohexanediaminetetraacetic acid [40] and 3-indoledithiocarboxylic acid [41] have also been reported.

2.3.4 Sulphide complexes

fac-$[RuCl_3\{E(CH_2Ph)_2\}_3]$ (E = S or Se) have been prepared by conventional methods [42].

2.3.5 Ammine, amine and related mixed valence complexes

An excellent account of the chemistry of $[Ru(NH_3)_5L]^{3+}$ complexes has appeared [43].

Reaction of $[Ru(NH_3)_5(OH)]^{2+}$ with ethanoic anhydride yields $[Ru(NH_3)_5(O_2CMe)]^{2+}$ [44]. The rates of electron exchange for the redox couples $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_4(bipy)]^{3+}/[Ru(NH_3)_4(bipy)]^{2+}$ and $[Ru(NH_3)_2(bipy)_2]^{3+}/[Ru(NH_3)_2(bipy)_2]^{2+}$ have been determined [45]. The reduction of $[Ru(NH_3)_5(O_2CMe)]^{2+}$, $[Ru(NH_3)_5(C_2O_4)]^{+}$ or $[Ru(NH_3)_4(C_2O_4)]^{+}$ by Ti(III) occurs by an inner-sphere mechanism [46], whereas that of $[Ru(NH_3)_5X]^{2+}$ (X = Br or I) involves an outer-sphere mechanism [47]. Earlier results upon the thermal decomposition of solid $[Ru(NH_3)_5(H_2O)]X_3$ (X = Cl, Br or I) to give $[Ru(NH_3)_5X]X_2$ and H_2O have been reassessed in terms of the kinetic compensation effect [48], and INDO calculations have been performed upon *cis*-$[RuX_2(NH_3)_4]^{+}$ (X = Cl, Br or I) [49]. The reduction of $[Ru(NH_3)_5L]^{3+}$ (L = py, 4-ethylpyridine or 4-vinylpyridine) by copper(I) has been studied: with 4-vinylpyridine, evidence for ion association {the vinyl group forming a π-complex with the Cu(I)} prior to electron transfer was presented [50].

The molecular structure of a complex of 1-methylcytosine (1-MecytH), $[Ru(NH_3)_5(1\text{-Mecyt})]$ (**12**), shows it to be the first characterised example of a purine or pyrimidine in which coordination occurs through the exocyclic amine nitrogen atom [51]. The structures of the isonicotinamide complexes *cis*-$[Ru(NH_3)_4(isonic)_2][ClO_4]_3 \cdot 2\,H_2O$ (**13**) and *cis*-$[Ru(NH_3)_4(isonic)_2][ClO_4]_2$ (**14**) have also been determined [52]. Comparison of the principal structural parameters (Table 2) for these complexes show the Ru—NH$_3$ bond to be shorter in the Ru(III) complex, but the Ru—isonic bond to be shorter in the Ru(II) complex, clearly illustrating the importance of the d_π—$p_{\pi *}$

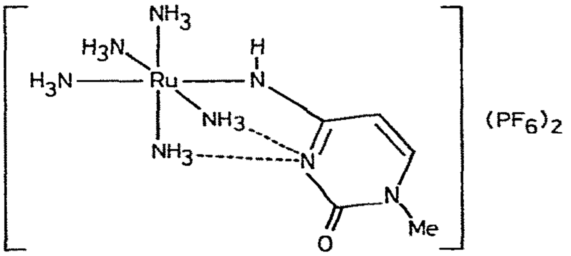


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TABLE 2

Structural parameters [52]

Compound	$\bar{r}$(Ru—NH$_3$)/nm	$\bar{r}$(Ru-isonic)/nm
(13)	0.2125	0.2099
(14)	0.2143	0.2060

backbonding interactions for ruthenium(II) complexes. The kinetics of displacement of H_2O from *trans*-$[Ru(NH_3)_4(isonic)(H_2O)]^{3+}$ by I^- is complicated by the presence of equilibrium amounts of *trans*-$[Ru(NH_3)_4(isonic)(H_2O)]^{2+}$ and $[I_3]^-$ in the solution [53].

The complexes $[Ru(NH_3)_5L]^{3+}$ (L = sulphide ligand) are reported in Section 2.4.4.

A detailed preparation of $[Ru(en)_3]Cl_3$ has been published [54]. Complexes between ruthenium(III) and 6-aminopurine [55], cytosine [55], indazole [56], benzoxazole-2-thione [57], various oximes (e.g. α-furyl monoxime) [58—60] and some thiosemicarbazides and thiosemicarbazones [61,62] have been reported.

$[Ru(NH_3)_5(pzH)]Br_4$ and $[Ru(NH_3)_5(4,4'\text{-bipyH})][ClO_4]_4$ have been prepared by conventional routes. Reaction between $[Ru(NH_3)_5(4,4'\text{-bipy})]^{3+}$ and $[Fe(CN)_5(H_2O)]^{3-}$ gives $[(NH_3)_5Ru(4,4'\text{-bipy})Fe(CN)_5]$, whereas $[Ru(NH_3)_5(pz)]^{2+}$ reacts with $[Fe(CN)_5(NH_3)]^{3-}$ to give $Na[(NH_3)_5Ru(pz)Fe(CN)_5]$, oxidation of which with Ce(IV) or $[S_2O_8]^{2-}$ gives $[(NH_3)_5Ru(pz)Fe(CN)_5]$. Cobalt analogues were also prepared using $[Co(CN)_5(H_2O)]^{3-}$. The complexes $[(NH_3)_5Ru(LL)Fe(CN)_5]$ (LL = pz or 4,4′-bipy) behave as valence-trapped species, containing formally Fe(II) and Ru(III) [63]. The comproportionation constant for $[(NH_3)_5Ru(4,4'\text{-bipy})Ru(NH_3)_5]^{5+}$ (**15**) has been shown to be 24, from analysis of the absorbance of the IT band as a function of the percentage reduction of $[(NH_3)_5Ru(4,4'\text{-bipy})Ru(NH_3)_5]^{6+}$ when it was titrated against Eu^{2+}; the extinction coefficient of the IT band of (**15**) has been recalculated as 880 $l\ mol^{-1}\ cm^{-1}$ [64].

A range of Ru(III) derivatives of imidazole (imH) have been prepared, including monomeric $[Ru(NH_3)_4(SO_4)(im)]$, $[Ru(NH_3)_4(SO_4)(imH)][BF_4]$ and $[Ru(NH_3)_5(imH)][BF_4]_3$, and dimeric $[(SO_4)(NH_3)_4Ru(im)Ru(NH_3)_4(SO_4)][BF_4]$, $[(NH_3)_5Ru(im)Ru(NH_3)_4(SO_4)][BF_4]_3$ and $[(NH_3)_5Co(im)Ru(NH_3)_4(SO_4)][BF_4]_3$. Reduction of the dimers generates mixed-valence species [65].

2.3.6 *Diimine complexes*

A compound originally erroneously reported as $[RuCl_4(bipy)]$ (formed by the prolonged reaction between "$RuCl_3 \cdot x\ H_2O$" and bipy in hydrochloric acid) has been shown to be $RuCl_3(bipy)$ [66]. A review of the electron-transfer reactions of $[Ru(bipy)_3]^{3+}$ has appeared [67], and the effect of micellar sodium dodecyl sulphate solutions upon the rate of electron-transfer between $[Ru(bipy)_3]^{3+}$ and $[Mo(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$ or $[Fe(H_2O)_6]^{2+}$ has been studied [68].

Some rather remarkable chemistry of $[Ru(LL)_3]^{3+}$ (LL = phen or bipy) has been reported, including a purple compound, $[Ru(bipy)_3][ClO_4]_3 \cdot H_2O$ [69].

The perchlorate salts of $[\{(bipy)_2ClRu\}(LL)\{RuCl(bipy)_2\}]^{4+}$ (LL = pz, 4,4′-bipy, 1,2-bis(4-pyridyl)ethane or *trans*-1,2-bis(4-pyridyl)ethene), $[\{(bipy)_2ClRu\}(pz)\{Ru(bipy)_2\}(pz)\{RuCl(bipy)_2\}]^{7+}$ and $[\{(bipy)_2ClRu\}(pz)\{Ru(bipy)_2\}(pz)\{Ru(bipy)_2\}(pz)\{RuCl(bipy)_2\}]^{10+}$ have been prepared by the Ce(IV) oxidation of their Ru(II) analogues. Their electronic and magnetic properties indicate that there is little (if any) interaction between the Ru(III) sites [70].

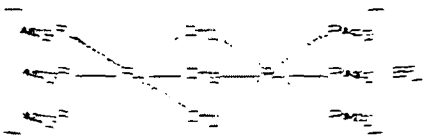
2.8.7 *Phosphine and arsine complexes*

The complexes $[RuCl_3(AsPh_3)_2(py)]$ and $[RuCl_3(PPh_3)_2(py)]$ have been reported: the latter reacts with RNC (R = C_6H_4OMe, CH_2Ph, C_6H_{11}, CMe_3 or CH_2CHCH_2) to give $[RuCl_3(PPh_3)(py)(CNR)]$ [71]. The reaction at room temperature of "$RuCl_3 \cdot x\,H_2O$" with 3-methyl-1-phenylphosphole (mppl) or 3,4-dimethyl-1-phenylphosphole (dmppl) gives $RuCl_3(mppl)$ or $[RuCl_3(dmppl)_3]$, whilst under reflux in ethanol, with mppl, the mixed-valence complex $[Ru_2Cl_5(mppl)_4]$ is formed [72].

2.8.8 *Methylene-bridged dimers*

The reaction between $[Ru_3O(O_2CMe)_6(H_2O)_3][O_2CMe]$ and $MgMe_2$ in the presence of PMe_3 yields $[(Me_3P)_3Ru(\mu\text{-}CH_2)_3Ru(PMe_3)_3]$ (16), which itself reacts with one equivalent of $H[BF_4]$ to give $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3][BF_4]$ (17), and with two equivalents of $H[BF_4]$ to give $[(Me_3P)_3$-

(16)



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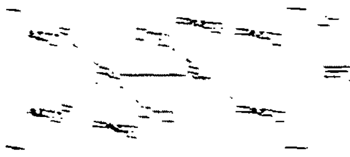

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$Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_3][BF_4]_2$ (18). All three complexes contain single Ru–Ru bonds of length [illegible], [illegible] and [illegible] nm, respectively [73].

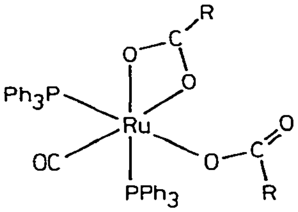
2.4 RUTHENIUM(II)

2.4.1 Aqueous chemistry

The rates of oxidation of $[Ru(H_2O)_6]^{2+}$ by $[Ru(NH_3)_5L]^{3+}$ (L = py or isonic), $[Fe(H_2O)_6]^{3+}$, $[Co(phen)_3]^{3+}$ or $[M(bipy)_3]^{3+}$ (M = Ru or Os) have been investigated [31].

2.4.2 Carboxylates, pentane-2,4-dionates and sulphates

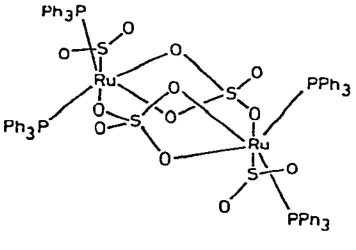
The fluxionality of $[Ru(O_2CR)_2(CO)(PPh_3)_2]$ (R = Me, CF_3, C_2F_5 or C_6F_5) (**19**) has been studied by variable temperature ^1H, ^{19}F and ^{31}P NMR spectroscopy and rapid intramolecular exchange of the monodentate and bidentate carboxylates was observed [74]. The crystal structure of $[Ru(O_2CPh)(CO)Cl(PPh_3)_2]$ shows it to contain bidentate benzoate and *trans*-phosphine groups [75]. The substitution reactions of $[Ru(edta)(H_2O)]^{2-}$ to produce $[Ru(edta)L]^{2-}$ {L = e.g. pz, py, isonic, MeCN or NCS^-} have been reported, and the products studied by electronic spectroscopy and CV [37,38].



(**19**)

The aquation of $[Ru(acac)_3]^-$ {generated by the pulse radiolysis of $[Ru(acac)_3]$} is too slow to be measured by pulse radiolytic techniques: $[Ru(acac)_3H]$ is a strong acid [76].

The complexes $[(Ph_3P)_2(O_2S)Ru(\mu\text{-}SO_4)_2Ru(SO_2)(PPh_3)_2]$ (**20**) and $[Ru(SO_4)(SO_2)(PPh_3)_2(H_2O)]$ have been prepared by passing SO_2 through a solution of $[RuH_2(PPh_3)_4]$. The molecular structure of (**20**) reveals that each sulphate is bidentate with respect to one ruthenium atom, whilst monodentate with respect to the other [77].



(**20**)

2.4.3 *Trithiocarbonate complexes*

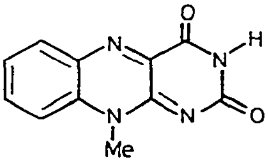
Reaction of $[Ru(CO)_4]^{2-}$ with CS_2, followed by MeI, gives $[Ru(CO)_2(S_2CSMe)_2]$ in very low yield [78].

2.4.4 *Ammine and amine complexes*

An excellent account of the chemistry of $[Ru(NH_3)_5L]^{2+}$ complexes has appeared [43].

The solvent dependence of the electronic spectra of $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$ has been measured and interpreted in terms of charge transfer, complex-to-solvent transitions [79]. The thermolysis of $[Ru(NH_3)_5(N_2)]^{2+}$ supported on Y-type zeolites, and its subsequent reaction with CO, NH_3 or NO, has been reported [26]. Heating solid $[Ru(NH_3)_5(N_2)]X_2$ (X = Cl, Br or I) gives $[Ru(NH_3)_4(N_2)X]X$ [80].

The isolation and molecular structure of a stable enantiomeric metalloflavin complex of 10-methylisoalloxazine {10-Meialo, (**21**)}, $[Ru(NH_3)_4(10\text{-Meialo})][PF_6]_2$ (**22**), have been reported, along with details of its electrochemistry [81]. *cis*-$[Ru(NH_3)_4(isonic)_2][ClO_4]_2$ (**14**) has been discussed in Section 2.3.5. Detailed flash photolysis studies of $[Ru(NH_3)_5(L)]^{2+}$ (L = pyridine or substituted pyridine) in aqueous solution have been reported, and some interesting intermediates have been observed [82]. The general rôle of charge-transfer states in these complexes has also been discussed in some detail [83].



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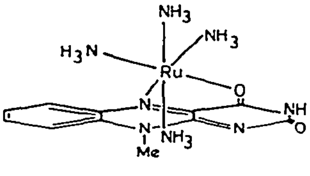
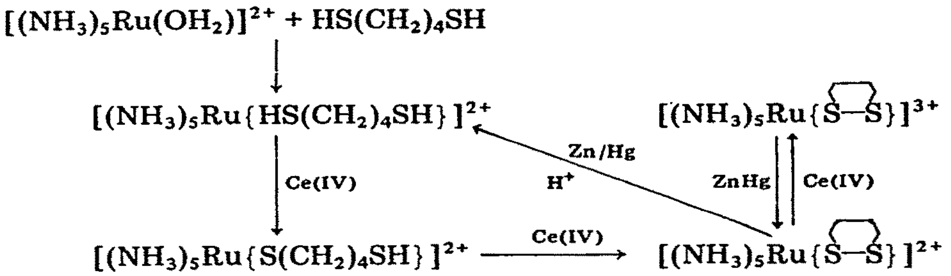


(22)

$[(NH_3)_5Ru(EMe_2)]^{2+}$ (E = S, Se or Te) have been prepared by conventional routes, and isolated as $[PF_6]^-$ salts. The 3+ species have been generated in solution by anodic oxidation, or chemical oxidation by Ce(IV), H_2O_2 or O_2, but have not been isolated as solids. The ruthenium(III) species are less labile towards aquation than the ruthenium(II) species [84]. An exquisite example of synthetic chemistry has been reported by Stein and Taube [85]. The complex $[Ru(NH_3)_5(1,2\text{-dta})][PF_6]_2$ {1,2-dta = 1,2-dithiane (**23**)} has been prepared by the reaction between (**23**) and $[Ru(NH_3)_5\text{-}$

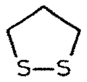
$(H_2O)]^{2+}$. However, it can also be prepared (Scheme I) by the oxidative



Scheme I. Syntheses of dithiane complexes [85].

cyclisation of a 1,4-butanedithiol complex. Similar reactions with 1,3-propanedithiol produce analogous complexes of **(24)**, which cannot be made

(23)

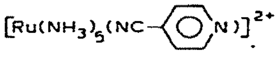


(24)

by direct interaction of **(24)** with $[Ru(NH_3)_5(H_2O)]^{2+}$. $[(NH_3)_5Ru(EPh)]^{2+}$ (E = S or Se) were prepared by reaction of Ph_2E_2 with $[Ru(NH_3)_5(H_2O)]^{2+}$ [85]; these and the corresponding dithiane complexes were characterised by electronic spectroscopy and CV. As expected, evidence for S—S lone pair interactions in the complexes of **(23)** and **(24)** was observed [85].

$[Ru(NH_3)_5(H_2O)]^{2+}$ has been shown to react with a variety of alkenes (e.g. propene) to give $[Ru(NH_3)_5(alkene)]^{2+}$, and $[Ru(NH_3)_4(H_2O)_2]^{2+}$ reacts with dienes to give $[Ru(NH_3)_4(diene)]^{2+}$ [86].

Detailed preparations of $[Ru(en)_3]X_2$ (X = Cl or $\frac{1}{2}[ZnCl_4]$) have been published [54].

The complexes $[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{5+}$ **(25)** and  **(26)** have been prepared by conventional routes. Irradiation of **(25)** produces no significant photoreaction, but irradiation of **(26)** with light of Ru(II)—MLCT energies causes photolability of the Rh—py linkage, to yield  and $[Rh(NH_3)_5(H_2O)]^{3+}$. This nicely demonstrates that intramolecular energy transfer has occurred, light being absorbed at one metal centre, whilst reaction occurs at the other [87].

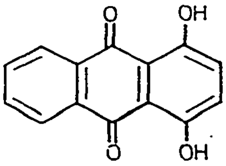
$[Ru(dmso)_4Cl_2]$ reacts with 8-aminoquinoline (amq) to give $[RuCl_2(dmso)_2(amq)]$ [88], and also with 6-aminopurine and cytosine [55].

2.4.5 Diimine complexes

Ruthenium(II) diimine complexes, particularly $[Ru(bipy)_3]^{2+}$ and its derivatives, continue to be at the centre of an active field of chemistry, stimulated by the aim of achieving the photocatalytic decomposition of water with visible light. Their light-induced electron transfer reactions have been reviewed [67,89,90], as have their applications in photogalvanic systems [91]. Methods for the preparation of $[Ru(L—L)_3]^{2+}$ (L—L = bipy, phen, etc.) salts have been reinvestigated and it was concluded that (for high purity samples) the best preparative route was via the reduction of alcoholic "$RuCl_3 \cdot x\,H_2O$" with H_2 in the presence of PtO_2, followed by reaction with excess ligand [66]. *cis*-$[Ru(bipy)_2(dme)][PF_6]_2$ {prepared by the reaction of dme with $[Ru(bipy)_2Cl_2]$ in the presence of $Ag[PF_6]$} has proved a useful precursor to the formation of isocyanide complexes, $[Ru(bipy)_2(CNR)_2]$-$[PF_6]_2$ (R = CH_2Ph, 4-Cl-C_6H_4 or 4-MeO-C_6H_4); it promises to be an important and useful precursor for the reactions with many monodentate and bidentate ligands, both charged and neutral, as dme is an excellent leaving group, but is relatively unreactive [92]. Elegant synthetic work has been described by Valenty et al. for the preparation of the surfactant complexes $[Ru(bipy)_2\{bipy(C_{19}H_{39})_2\}]^{2+}$, $[Ru(bipy)(CN)_2\{bipy(C_{19}H_{39})_2\}]$, and $[Ru\{bipy(COO)_2\}_2\{bipy(C_{19}H_{39})_2\}]^{2-}$. Their monolayer properties, and electronic absorption, luminescence and field-desorption mass spectra were described [93]. The electrochemistry of $[Ru(phen)_3]^{2+}$ has been investigated [94].

O'Donoghue and co-workers have demonstrated conclusively that $[Ru(bipy)_2Cl_2]$ (as prepared by the reaction of "$RuCl_3 \cdot x\,H_2O$" with bipy in dmf at reflux) exists exclusively as the *cis* isomer in dmso solution. Upon heating the non-conducting solution of $[Ru(bipy)_2Cl_2]$ in dmso, solvolysis to yield *cis*-$[Ru(bipy)_2Cl(dmso)]^+$ occurs [95]. A new synthetic route to $[Ru(bipy)_2X_2]$ (X = I, NO_2, N_3 or CN), based upon the photolysis of solutions of $[Ru(bipy)_3]X_2$, has been proposed [96], and *cis*-$[Ru(bipy)_2(NCS)_2]$ and *cis*-$[Ru(py)_4(NCS)_2]$ have also been reported [97]. Oxidation of $[Ru(bipy)_2(py)(H_2O)]^{2+}$ with NO_3^- gives a mixture of $[Ru(bipy)_2(py)(H_2O)]^{3+}$ and $[Ru(bipy)_2(py)(NO)]^{3+}$; in the presence of sulphamate (i.e. an HNO_2 scavanger) only $[Ru(bipy)_2(py)(H_2O)]^{3+}$ is formed [98]. The $[Ru(bipy)_2]^{2+}$ residue has been attached to poly(4-vinylpyridine) and the photochemistry of this polymer-bound complex examined, as was the photochemistry of $[Ru(bipy)_2(py)_2]^{2+}$, $[Ru(bipy)_2(py)Cl]^+$ and $[Ru(bipy)_2(py)(H_2O)]^{2+}$ in methanol. The chemistry of the polymer-bound and the solution species were found to be analogous [99].

The reaction of $[Ru(bipy)_2Cl_2]$ with 1,4-dihydroxyanthraquinone {$dhaqH_2$ (27)} in the presence of LiOMe yields the dimeric species $[(bipy)_2Ru(dhaq)$-$Ru(bipy)_2]^{2+}$, which was isolated as its $[PF_6]^-$ salt, with an intense absorption at 16 720 cm^{-1} ($\epsilon = 25\,600$ l mol^{-1} cm^{-1}) [100]. Reaction between $K_2[RuCl_5(H_2O)]$ and 2,2'-bi-2-thiazoline {bta (28)} in glycerol produces the



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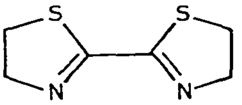
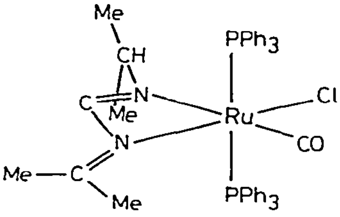


(28)

violet $[Ru(bta)_3]^{2+}$ ion, isolated as its $[PF_6]^-$ and $[ClO_4]^-$ salts. The ligand, although an α,α′-diimine, is non-aromatic. Nevertheless, the complex shows a weak emission at 77 K, assigned to a π^*-d LMCT transition [101]. The complexes $[Ru(bipy)_2(L\!-\!L)][ClO_4]_2$ {L—L = 2-(2-pyridyl)-benzimidazole} and $[Ru(bipy)_2(L\!-\!L')][ClO_4]$ {L—L′H = 2-(2-hydroxyphenyl)-benzimidazole} have been prepared, and characterised by electronic absorption and emission spectroscopy, and CV [102]; these appear to be very interesting complexes, worthy of further attention.

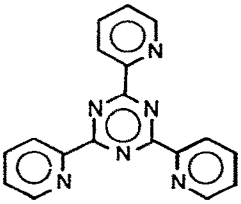
Reaction of $[RuHCl(CO)(PPh_3)_3]$ with the carbodiimide $Me_2CHN{=}C{=}NCHMe_2$ yields $[RuCl(CO)(PPh_3)_2(Me_2C{=}N{-}C{=}NCHMe_2)]$ (**29**) and dihydrogen, a rare example of dehydrogenation of a coordinated alkyl group to give a non-coordinated double bond [103]. In a similar manner, $[RuHCl(PPh_3)_3]$ reacts with the diazadiene $Me_2CH{-}N{=}CHCH{=}N{-}CHMe_2$ (dad) to give *trans*-$[RuHCl(PPh_3)_2(dad)]$; in methanol, this reorganises to give a mixture of $[Ru_2Cl_3(PPh_3)_2(dad)_2]^+$, $[RuH_2(PPh_3)_2(dad)]$ and $[RuH_2(CO)(PPh_3)_3]$. $[Ru_2Cl_3(PPh_3)_2(dad)_2][BPh_4]$ can also be prepared from the reaction between $[RuCl_2(PPh_3)_3]$, dad and $Na[BPh_4]$. $[RuHCl(PPh_3)_2(dad)]$ reacts with water to give $[Ru_2(\mu\text{-}OH)_2(\mu\text{-}Cl)H(PPh_3)_3(dad)]$ [104].



(29)

A new investigation [105] of the reaction between $[Ru(5\text{-}NO_2\text{-}phen)_3]^{2+}$ and Na[OMe] in dmso has concluded that nucleophilic attack occurs at the 6-position of the coordinated ligand, and *not* in the 2 or 9 positions as had been previously suggested. This is an important result, and raises many questions concerning the so-called "pseudo-base" mechanism of Gillard and co-workers [e.g. 106]. Elsewhere, reports of nucleophilic attack on $[Ru(tpt)_2]^{2+}$ {tpt = 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (**30**)} [107,108] and $[Ru(bipym)_3]^{2+}$ {bipym = 2,2′-bipyrimidine (**31**)} [109] by OH^- have appeared.

There have been many photophysical investigations of $[Ru(bipy)_3]^{2+}$ and related species, but perhaps the most interesting is a report of the electronic absorption spectrum of $\{[Ru(bipy)_3]^{2+}\}^*$ [110]. Emission and thermally



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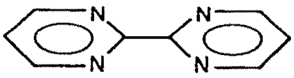
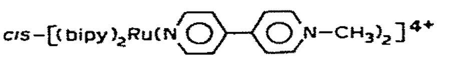


(31)

modulated emission spectra have been reported for $[Ru(bipy)_3]^{2+}$ and $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ [111]. The temperature dependence of the electrochemiluminescence (ECL) of $[Ru(bipy)_3]^{2+}$ in MeCN has been studied, and an ECL generation mechanism discussed, by two different research groups [112,113]. Polarised electronic absorption spectral and CD studies upon $[Ru(bipy)_3]^{2+}$ show that its intense visible absorption is due to two electronic transitions (contrary to much previously published work) [114], and luminescence studies in aqueous solution have also been reported [115].

 has been prepared and has been studied by cyclic voltammetry and electronic absorption and emission spectroscopy; it shows *dual* emission at room temperature in homogeneous solution (at 580 and 680 nm) [116].

The quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by $[Cr(bipy)_3]^{3+}$ has been studied [117], as indeed has the quenching of $\{[Cr(LL)_3]^{3+}\}^*$ by $[Ru(LL)_3]^{n+}$ (LL = bipy, phen or derivatives thereof; n = 2 or 3) [118], and the quenching of $\{[Ru(LL)_3]^{2+}\}^*$ by aqueous Ti(III) [119]. The sensitisation of $[Ru(bipy)_3]^{2+}$ by various aryl ketones has also been investigated [120,121]. The light-induced electron transfer reactions of surfactant derivatives of $[Ru(bipy)_3]^{2+}$ have been discussed [122], and the use of these derivatives (and, of course, $[Ru(bipy)_3]^{2+}$ itself) to induce organic reactions, via oxidative quenching of the excited state of the complex with concomitant formation of free radicals, has been investigated [123]. A linear relationship between the first $t_{2g} \rightarrow \pi^*$ MLCT band and the difference between the first oxidation and first reduction potential of the complexes $[Ru(bipy)_2L_2]^{2+}$ ($L = \frac{1}{2}$ bipy, NH_3, py, $\frac{1}{2}$ en, $\frac{1}{2}$ $acac^-$ or CN^-) has been reported [124]. The effect of poly(vinylsulphate) upon the quenching rate of $\{[Ru(bipy)_3]^{2+}\}^*$ by Cu^{2+} has been investigated [125].

The utilisation of $[Ru(bipy)_3]^{2+}$ derivatives as photocatalysts for the generation of H_2 and/or O_2 from H_2O is discussed in Section 2.9.

In some sense related to diimine chemistry, the reaction between [Ru(oep)(CO)] ($oepH_2$ = octaethylporphyrin) and the alkanethiolate anion, SR^-, has been studied by electronic absorption and ^1H NMR spectroscopy; six-coordinate $[Ru(oep)(CO)(SR)]^-$ is formed [126].

2.4.6 Phosphine, phosphite and arsine complexes

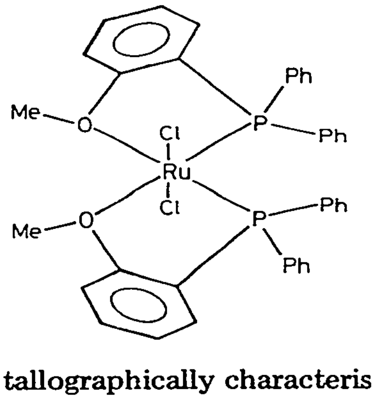
2.4.6.1 Halo, carbonylhalo and thiocarbonylhalo complexes

"$RuCl_3 \cdot x\ H_2O$" reacts with L {L = 1-phenylphosphole or 3,4-dimethyl-1-phenylphosphole} in ethanol at reflux to give $[RuCl_2L_3]$, whereas with 3-methyl-1-phenylphosphole (mppl) in butanol $[RuCl_2(CO)(mppl)_3]$ is formed [72]. $[RuCl_2(PPh_3)_3]$ and $[Ru(CF_3CO_2)_2(CO)(PPh_3)_2]$ are effective catalysts for the hydrogenation of ketones [127]. A number of studies of the catalytic behaviour of $[RuCl_2(PPh_3)_3]$ have appeared [128—131]. The asymmetric hydrogenation of a prochiral ketone with $[Ru_2Cl_4\{(-)\text{-diop}\}_3]$ has been observed [132].

Carbonylation of $[RuCl_2(PR_3)_3]$ $\{R_3 = (4\text{-tolyl})_3$ or $EtPh_2\}$ in dmf gives $[Ru(CO)Cl_2(dmf)(PR_3)_2]$. $[Ru(CO)Cl_2(dmf)\{P(4\text{-tolyl})_3\}_2]$ rearranges in various solvents to give $[Ru_2(CO)_2Cl_4\{P(4\text{-tolyl})_3\}_3]$, and reacts with $[RuCl_2\{P(4\text{-tolyl})_3\}_3]$ to give $[Ru_2(CO)Cl_4\{P(4\text{-tolyl})_3\}_4]$, whereas $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ reacts with $[RuCl_2\{P(4\text{-tolyl})_3\}_3]$ to give $[Ru_2(CO)Cl_4(PPh_3)_2\{P(4\text{-tolyl})_3\}_2]$ [133]. $[RuCl_2\{P(4\text{-tolyl})_3\}_3]$ reacts with CS_2 to give $[Ru_2(CS)Cl_4\{P(4\text{-tolyl})_3\}_4]$ and $[Ru_2(CS)_2Cl_4\{P(4\text{-tolyl})_3\}_4]$, whereas $[RuCl_2(PEtPh_2)_3]$ reacts with CS_2 to give $[RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2]$ and $[Ru_2(CS)_2Cl_4(PEtPh_2)_3]$ [133]. $[Ru_2(CE)Cl_4(PPh_3)_4]$ (E = S or O) reacts with excess L $\{L = PPh_2(OMe)$, $PPh_2(OEt)$ or $PPh(OMe)_2\}$ to give mixtures of $[Ru(CE)Cl_2L_3]$ and $[RuCl_2L_n]$ (n = 3 or 4). $[Ru(CO)Cl_2L_3]$ can also be prepared by reaction of $[RuCl_2L_n]$ with CO, and $[Ru(CS)Cl_2L_3]$ by reaction of $[Ru_2(CS)_2Cl_4(PPh_3)_4]$ with excess L [134]. In alcohols, $[Ru(CE)Cl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) rearranges to give $[Ru(CE)Cl\{PPh_2(OMe)\}_3]^+$ or $[Ru_2(CE)_2Cl_2\{PPh_2(OEt)\}_6]^{2+}$, respectively, whilst $[Ru(CE)Cl_2\{PPh(OMe)_2\}_3]$ does not isomerise [134].

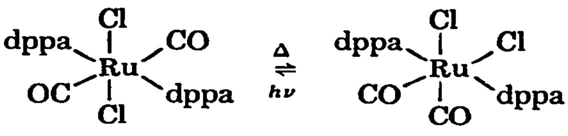
2.4.6.2 Complexes with phosphorus—oxygen and phosphorus—nitrogen donor ligands

Reaction between "$RuCl_3 \cdot x\ H_2O$" and 2-(diphenylphosphino)anisole (dppa) in ethanol yields red *trans*-$[RuCl_2(dppa)_2]$ (**32**), which has been crystallographically characterised [135]. (**32**) undergoes electrochemical or



(32)

chemical (with $NOBF_4$) oxidation to give $[RuCl_2(dppa)_2]^+$, whilst reaction with CO yields $[RuCl_2(dppa)_2(CO)]$ and then $[RuCl_2(dppa)_2(CO)_2]$ (33). Heating (33) produces an isomeric form, (34).



(33) (34)

Me_3CNC reacts with (32) in a similar manner to CO [135]. In a similar reaction to the preparation of (32), *trans*-$[RuCl_2(dppba)_2]$ {dppba = 2-(diphenylphosphino)benzaldehyde} was isolated. This shows no reaction with CO, dppe or py, but upon heating decomposes to give $[Ru(CO)_2Cl_2(PPh_3)_2]$ [136].

$[Ru(dmso)_4Cl_2]$ reacts with 8-(diphenylphosphino)quinoline (dppq) or 8-(diphenylarsino)quinoline (dpaq) to give $[Ru_2Cl_4(dmso)_5]$ or $[RuCl_2(dmso)_2(dpaq)]$, respectively [88].

2.4.6.3 *Mixed phosphine—dithioacid complexes*

Reaction of $[RuCl_2L_4]$ {L = $PPh(OMe)_2$ or $PMePh_2$} and $[RuCl_2(PEtPh_2)_3]$ with $[SS]^-$ {SS = S_2PMe_2, S_2PPh_2, S_2COMe, S_2CNMe_2 or S_2CNEt_2} gives $[Ru(SS)_2L_2]$ under all conditions. In contrast, *cis*-$[RuCl_2(PMe_2Ph)_4]$ and $[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) react with $Na[S_2PR'_2]$ (R′ = Me or Ph) in benzene to give $[RuCl(S_2PR'_2)L_3]$ {which rearranges in alcohol to give $[Ru(S_2PR'_2)L_3]^+$}, whereas treatment with $K[S_2COMe]$ gives $[Ru(S_2COMe)_2L_3]$ {which on heating gives $[Ru(S_2COMe)_2L_2]$}. Reaction of $[RuCl_2(PMe_2Ph)_4]$ with $Na[S_2CNR''_2]$ (R″ = Me or Et) in ethanol gives $[Ru(S_2CNR''_2)(PMe_2Ph)_4]$, but in benzene gives $[Ru(S_2CNR''_2)_2(PMe_2Ph)_3]$ [137].

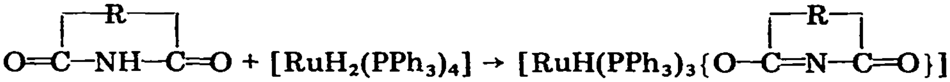
2.4.6.4 *Mixed phosphite—ammine complexes*

$[Ru(NH_3)_5(H_2O)]^{2+}$, $[Ru(NH_3)_5(H_2O)]^{3+}$ or *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)]^{2+}$ reacts with $P(OR)_3$ (R = Me, Me_2CH or Bu) to give $[Ru(NH_3)_4\{P(OR)_3\}_2]^{2+}$; mixed ligand complexes of the type $[Ru(NH_3)_4\{P(OEt)_3\}\{P(OR)_3\}]^{2+}$ have also been prepared. The complexes were isolated as $[CF_3SO_3]^-$ or $[PF_6]^-$ salts [138].

2.4.6.5 *Phosphine hydride complexes*

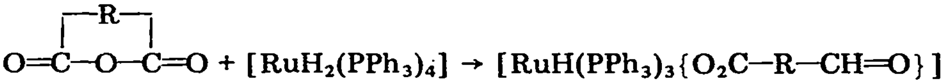
Reaction of alcoholic "$RuCl_3 \cdot xH_2O$" with $P(cych)_3$ gives $[RuHCl(CO)\{P(cych)_3\}_2]$ [139]. Similarly, solutions of "$RuCl_3 \cdot xH_2O$" in 2-methoxyethanol react with L {L = $P(CMe_3)_2Me$ or $P(CMe_3)_2Et$} to give $[RuHCl(CO)L_2]$. These complexes are light- and air-sensitive, and react with CO to give $[RuHCl(CO)_2L_2]$, with MeNC {L = $P(CMe_3)_2Et$} to give $[RuHCl(CO)(CNMe)L_2]$ and with HCl followed by pyridine {L = $P(CMe_3)_2Me$} to give $[RuCl_2(CO)(py)_2L]$ [140]. $[RuH_2(CO)(PPh_3)_3]$ is an effective catalyst for the hydrogenation of ketones [127].

$[RuH_2(PPh_3)_4]$ and $[RuH_4(PPh_3)_3]$ react with RSH (R = Ph or CH_2Ph) or S_2R_2 (R = Me) to give $[RuH(SR)(PPh_3)_3]$, which are thought to be five-coordinate and monomeric [141]. In an interesting series of reactions, RNCO (R = $4\text{-}MeC_6H_4$) reacts with $[RuHX(CO)(PPh_3)_3]$ (X = Cl, Br or H) to give a formamido-complex $[RuX(CO)(PPh_3)_2(RN{\cdots}CH{\cdots}O)]$, with $[RuH_2(CO)(PPh_3)_3]$ under vigorous conditions to give a ureylene complex $[Ru(CO)_2(PPh_3)_2(RN{-}C(O){-}NR)]$, and with $[RuH_2(PPh_3)_4]$ to give a formamidinato-complex $[RuH(CO)(PPh_3)_2(RN{\cdots}CH{\cdots}NR)]$ [142]. Related reactions are observed with cyclic amides (e.g. *d*-camphorimide, phthalimide, succinimide and methyl succinimide) [143] and cyclic anhydrides (e.g. phthalic anhydride and succinic anhydride) [144].



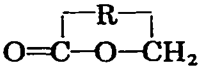
$$O{=}C{-}NH{-}C{=}O + [RuH_2(PPh_3)_4] \rightarrow [RuH(PPh_3)_3\{O{-}C{=}N{-}C{=}O\}]$$

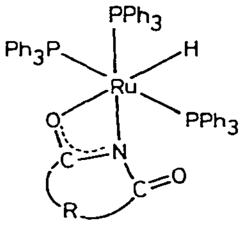
(35)



$$O{=}C{-}O{-}C{=}O + [RuH_2(PPh_3)_4] \rightarrow [RuH(PPh_3)_3\{O_2C{-}R{-}CH{=}O\}]$$

(36)

(36) will react with CO to give  $O{=}C{-}O{-}CH_2$ and CO_2 [144]. Further



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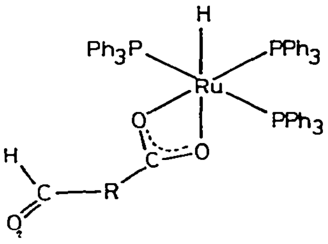


(36)

studies upon the catalytic activity of $[RuH_2(PPh_3)_4]$ have been reported [145].

2.4.7 Aryl, naphthyl and cycloruthenated complexes

Reaction of $MgPh_2$ with $[Ru_2(O_2CMe)_4Cl]$ in the presence of Me_3P gives the species $[RuPh_2(PMe_3)_4]$. With $Mg(2\text{-}CH_3OC_6H_4)_2$, the metallocycle $[Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4]$ is formed and its structure has been confirmed crystallographically [146].

cis-[HRu(dmpe)$_2$(np)] reacts with aromatic hydrocarbons, RH (RH = anthracene, C_6H_5CN or C_6D_6) to give a mixture of *cis*- and *trans*-[HRu(dmpe)$_2$(R)] and npH. The anthracyl anion bonds via the 2-position, whereas C_6H_4CN is attached via the 2, 3 or 4 positions, yielding an isomeric mixture of products [147]. Similarly, *cis*-[HRu(dmpe)$_2$(np)] reacts with HCN to give *cis*- and *trans*-[$HRu(CN)(dmpe)_2$], with MeCN to give *cis*-[$HRu(dmpe)_2(CH_2CN)$] and with Me_2CO to give *cis*- and *trans*-[$HRu(dmpe)_2\{CH_2C(O)CH_3\}$] [148].

The yellow solution formed from $RuCl_3 \cdot x\,H_2O$ and CO in 2-methoxyethanol reacts with HC—N (HC—N = 1-phenylpyrazole, 2-phenylpyridine or benzo[*h*]quinoline) to give the chloro-bridged dimers [$\{RuCl(C—N)(CO)_2\}_2$]. These species react with Tl[acac] or 4-Me-py to give [$Ru(acac)(C—N)(CO)_2$] or [$RuCl(C—N)(CO)_2(4\text{-Me-py})$] [149].

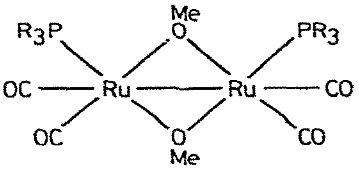
2.4.8 Tin halide complexes

$RuCl_3$ reacts with SnF_2 in aqueous HF, followed by treatment with AF (A = Na, K or NH_4), to yield $A_4[Ru(SnF_3)_6]$. This reacts with HCl or HBr to give, in the presence of $[Me_4N]^+$, $[Me_4N]_4[Ru(SnF_3)_5X]$ (X = Cl or Br) [150].

$[RuCl(SnCl_3)_5]^{4-}$ has been spectroscopically characterised [151], and will react with L (L = thiourea or its substituted derivatives) to give $[Me_4N]_2[Ru(SnCl_3)_4L_2]$, $[Me_4N][Ru(SnCl_3)_3L_3]$, $[Ru(SnCl_3)_2L_4]$ and $[RuL_6][SnCl_3]_2$ [152].

2.5 RUTHENIUM(I)

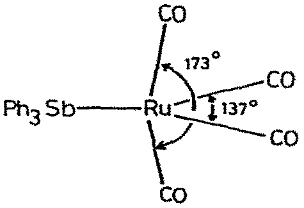
Prolonged reaction of [$Ru_3(CO)_{12}$] with $P(CMe_3)_3$ in methanol, or heating [$Ru(CO)_3\{P(CMe_3)_3\}_2$] under reflux in methanol, yields a metal—metal bonded dimer, (37) [153].



(37)

2.6 RUTHENIUM(0)

[$Ru_3(CO)_{12}$] reacts with $P(CMe_3)_3$, in butanol to give [$Ru(CO)_4\{P(CMe_3)_3\}$] and in methanol to give [$Ru(CO)_3\{P(CMe_3)_3\}_2$] [154]. Photolysis of a hexane solution of [$Ru_3(CO)_{12}$] in the presence of $SbPh_3$ gives [$Ru(CO)_4(SbPh_3)$] (38), which has a molecular structure with a geometry between trigonal



(38)

bipyramidal and square pyramidal, more resembling the former [155]. Reaction of alcoholic solutions of "$RuCl_3 \cdot x\,H_2O$" with $P(cych)_3$ yields $[Ru(CO)_3\{P(cych)_3\}_2]$ [139].

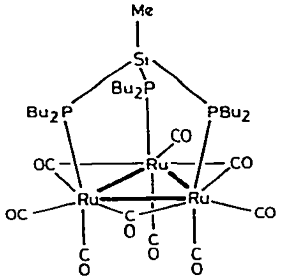
2.7 RUTHENIUM CARBONYL CLUSTERS

The UV photoelectron spectra (He-I and He-II) of $[Ru_3(CO)_{12}]$ have been reported [156] and are discussed in Section 2.18. The low frequency Raman spectra of $[Ru_xOs_{3-x}(CO)_{12}]$ ($x = 0, 1, 2$ or 3) have been measured ($x = 3$, $\nu(Ru_3) = 187$ cm^{-1}; $x = 0$, $\nu(Os_3) = 160$ cm^{-1}) [157].

The preparation of $[Et_4N][HRu_3(CO)_{11}]$ from the reaction of $[H_4Ru_4(CO)_{12}]$ with alcoholic KOH has been described [158]. $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ are effective homogeneous catalysts for the water gas shift reaction ($H_2O + CO \rightleftharpoons H_2 + CO_2$) [158,159]. Stepwise deprotonation of $[H_4Ru_4(CO)_{12}]$ with KH in thf has been observed and the salts $A[H_3Ru_4(CO)_{12}]$ and $A_2[H_2Ru_4(CO)_{12}]$ $\{A = (Ph_3P)_2N\}$ isolated. $[HRu_4(CO)_{12}]^{3-}$ is unstable, decomposing to form $[H_2Ru_4(CO)_{12}]^{2-}$ and $[Ru_4(CO)_{12}]^{4-}$ [160]. Solid state NMR (multiple pulse) studies upon $[H_4Ru_4(CO)_{12}]$ provide evidence for anisotropic proton motion at room temperature [161].

The diazene complexes $[Ru_3(CO)_9(L\text{—}L)]$ {where L—L = 2,3-diazanorbornene or 4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline} have been prepared by reaction of $[Ru_3(CO)_{12}]$ with the free ligand; fluxional behaviour was examined by ^{13}C NMR spectroscopy [162].

The molecular structure of $[H_4Ru_4(CO)_{10}(PPh_3)_2]$ holds no surprises [163]. The photocatalytic activity of $[Ru_3(CO)_9(PPh_3)_3]$ and $[Ru(CO)_4(PPh_3)]$, with respect to the isomerisation of pent-1-ene, have been compared [164,165] and the effect of solvent upon the same process (when using $[H_4Ru_4(CO)_{11}L]$ or $[H_4Ru_4(CO)_{10}L_2]$ $\{L = P(OEt)_3, P(OPh)_3$ or $PPh_3\}$) has been described [166]. The reactions of $[Ru_3(CO)_9L_3]$ $\{L = PBu_3$ or $P(OPh)_3\}$ with excess L have been studied in decalin. Reaction proceeds via thermal fragmentation to give mononuclear products, the rate determining step being the initial loss of CO from the cluster [167]. $MeSi(PBu_2)_3$ reacts with $[Ru_3(CO)_{12}]$ to give $[Ru_3(CO)_9\{MeSi(PBu_2)_3\}]$ (**39**), which contains three bridging carbonyls [168].



(**39**)

$[Ru_3(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$ react with Me_3CNC to give $[Ru_3(CO)_{12-n}$-

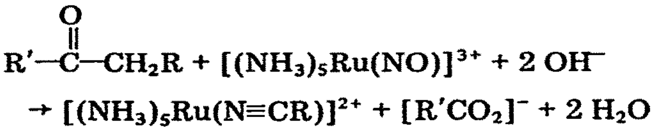
$(CNCMe_3)_n]$ (n = 1, 2, or 3) and $[H_4Ru_4(CO)_{12-n}(CNCMe_3)_n]$ (n = 1, 2 or 4), respectively [169]. The molecular structure of $[Ru_3(CO)_{11}(CNCMe_3)]$ shows the isocyanide ligand to be axial, whilst variable temperature ^{13}C NMR spectra reveal the molecule to be fluxional in solution [169]. It reacts with H_2 to give principally $[HRu_3(CO)_9(HC{=}NCMe_3)]$, along with small amounts of $[H_4Ru_4(CO)_{12-n}(CNCMe_3)_n]$ (n = 0, 1 or 2) and $[HRu_3(CO)_8(CNCMe_3)(HC{=}NCMe_3)]$ [170].

The reaction of $[Ru_3(CO)_{12}]$ with $MeSC{\equiv}CSMe$ gives $[Ru_3(CO)_9(MeSC{\equiv}CSMe)]$, along with $[Ru(CO)_3\{\overline{C(SMe){=}C(SMe){-}C(SMe){=}C(SMe){-}C{=}O}\}]$ and $[Ru_2(CO)_6(Me_2S_2C_2)_2]$ [171].

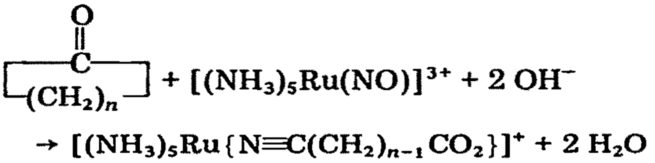
2.8 RUTHENIUM NITROSYLS

The ^{14}N NMR spectra of $[Ru(NH_3)_5(NO)]^{3+}$ and $[RuCl_5(NO)]^{2-}$ have been reported [172]. Kinetic studies of the ligand substitution reactions of $[Ru(NO)Cl_3L_2]$ (L = $AsPh_3$ or $SbPh_3$) indicate that the reactions proceed via a dissociative mechanism involving formation of $[Ru(NO)Cl_3L]$ [173].

Facile oxidative cleavage of ketones by $[Ru(NH_3)_5(NO)]^{3+}$ in basic solution has been reported [174].



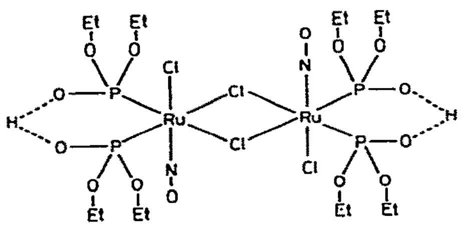
$$R'{-}\overset{O}{\overset{\|}{C}}{-}CH_2R + [(NH_3)_5Ru(NO)]^{3+} + 2\,OH^- \rightarrow [(NH_3)_5Ru(N{\equiv}CR)]^{2+} + [R'CO_2]^- + 2\,H_2O$$



$$\overset{O}{\overset{\|}{C}}(CH_2)_n + [(NH_3)_5Ru(NO)]^{3+} + 2\,OH^- \rightarrow [(NH_3)_5Ru\{N{\equiv}C(CH_2)_{n-1}CO_2\}]^+ + 2\,H_2O$$

The reaction of "$RuCl_3 \cdot x\,H_2O$" with *N*-methyl-*N*-nitroso-4-toluenesulphonamide in the presence of $[P(OR)_3]$ (R = Et or Ph) gives the dimeric complex $[H\{(RO)_2PO\}_2Cl(NO)Ru(\mu\text{-}Cl)_2Ru(NO)Cl\{(RO)_2PO\}_2H]$; the molecular structure of the $P(OEt)_3$ complex (40) has been determined [175].

$[Ru(LL')_2(NO)X]$ {LL' = 2,4,6-trioxo-5-oximinopyrimidine or 1,3-dimethyl-2,4,6-trioxo-5-oximinopyrimidine (41); X = Cl, Br, OH or NO_2}



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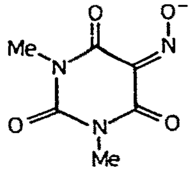


(41)

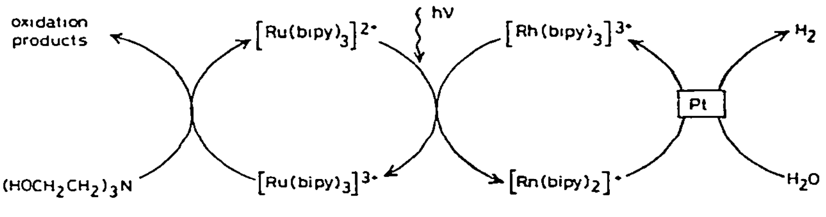
reacts with β-diketonates. Nitrosation of the diketonate occurs, resulting in the formation of coordinated oximes [176]. The glycinato-complex $K[Ru(NH_2CH_2COO)(OH)_3(NO)]$ has also been reported [177].

2.9 PHOTOCATALYTIC DECOMPOSITION OF WATER

Perhaps the most exciting area of current ruthenium chemistry is that of the use of ruthenium(II) complexes (e.g. $[Ru(bipy)_3]^{2+}$) as catalysts for the photodecomposition of water, to give dihydrogen and dioxygen. There have been a number of major developments in this area during the period covered by this review, principally due to the efforts of Lehn and Sauvage in France, Grätzel in Switzerland, Memming in Germany, and Goodenough in England.

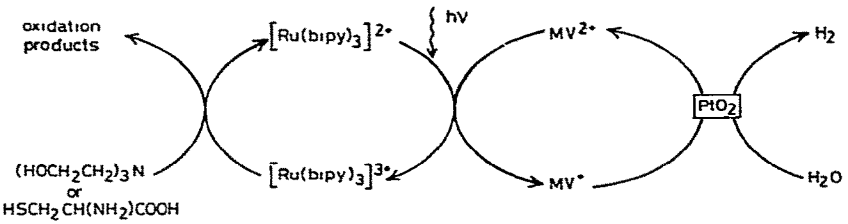
The first approach to the problem of the photodecomposition of water may be thought of as the "bouillabaisse" technique, in which light is shone upon a chemical soup (comprising a homogeneous or colloidal mixture of an inorganic chromophore, an inorganic or organic redox reagent, a reducing agent, an oxidising agent, and one or more catalysts), causing the evolution of dihydrogen and/or dioxygen. In an idealised system, both the reducing agent and the oxidising agent should be water.

Lehn and co-workers [178] have now reported, at length, details of their pioneering work [179] upon the photoevolution of dihydrogen, in which the chromophore is $[Ru(bipy)_3]^{2+}$, the redox reagent is $[Rh(bipy)_3]^{3+}$, the reducing agent is triethanolamine $\{(HOCH_2CH_2)_3N\}$, the oxidising agent is water, and the catalyst is colloidal platinum. The process is represented in Scheme II,



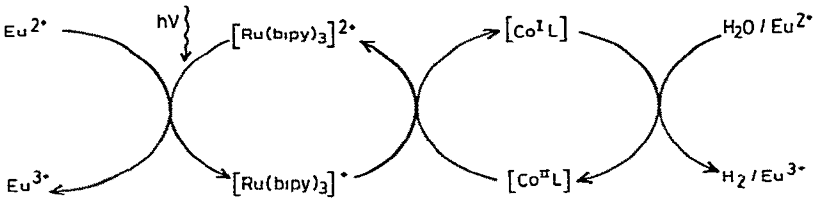
SCHEME II

but is not truly catalytic, as ethanolamine is irreversibly consumed during the cycle. This system has also latterly been investigated by Sutin and co-workers [180], who confirm the experimental observations reported above, but differ in their interpretation as to the rôle of the rhodium complex. A related system is that of Grätzel and co-workers [181], in which $[Rh(bipy)_3]^{3+}$ is replaced by the *N*,*N*′-dimethyl-4,4′-bipyridinium (MV^{2+}) cation, the catalyst is Adams catalyst (PtO_2), and the reducing agent may be triethanolamine or cysteine $\{HS \cdot CH_2 \cdot CH(NH_2) \cdot COOH\}$, as represented in Scheme III. The photoreduction of MV^{2+} by a surfactant derivative of $[Ru(bipy)_3]^{2+}$ in micellar solution has also been studied [182]. The rôle of the colloidal catalyst (using $edtaH_4$ as reducing agent) has been investigated [183,184], as has the use of triethylamine as combined reducing agent/redox agent in aqueous ethanenitrile [122,185]. The $edtaH_4/[Ru(bipy)_3]^{2+}/MV^{2+}/Pt$ (or Au)



SCHEME III

system has been independently investigated [186], and the triethanolamine/ $[Ru(bipy)_3]^{2+}/MV^{2+}$ system has also been shown to be active for dihydrogen production if the Pt catalyst is replaced by a hydrogenase from *Desulphovibrio vulgaris* [187]. A related system, this time involving reduction of $\{[Ru(bipy)_3]^{2+}\}^*$ (rather than its oxidation) is illustrated in Scheme IV,



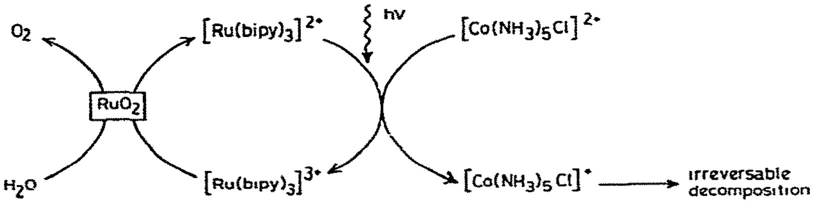
SCHEME IV

where $Co^{II}L$ is a cobalt(II) macrocycle of $(Me_6[14]dieneN_4)^+$. The Eu^{2+} can be replaced by ascorbic acid, being irreversibly oxidised during the reactions to dehydroascorbic acid [188]. None of the above systems are truly catalytic, as they all involve irreversible oxidation of an organic (or inorganic) reducing agent, which fuels the production of H_2 from water.

RuO_2 has been shown to be an active catalyst for the generation of dioxygen from water in the reaction [184,189]

$$4\,Ce^{4+} + 2\,H_2O \xrightarrow{RuO_2} 4\,Ce^{3+} + 4\,H^+ + O_2$$

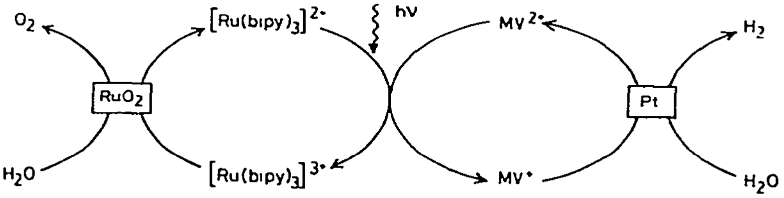
It also catalyses the thermal oxidation of water by $[Ru(bipy)_3]^{3+}$, and has been used in a broth for the photogeneration of dioxygen (Scheme V) [190].



SCHEME V

As with the photogeneration of dihydrogen, these processes for the generation of dioxygen are not truly catalytic, since the oxidising agent is consumed.

The "potage de l'année" is the recipe of Kalyanasundaram and Grätzel [191], and the overall reaction is illustrated in Scheme VI. This is the only scheme, to date, which effects the simultaneous evolution of H_2 and O_2 using visible light, and is truly catalytic, in that only H_2O is consumed.



SCHEME VI

The second approach to the problem of achieving the catalytic photodecomposition of water is to employ a photoelectrochemical technique, in which the production of H_2 and O_2 occurs separately at electrode surfaces, rather than simultaneously in homogeneous solution. Thus, Meyer and coworkers [192] have shown that illumination of a solution of $[Ru(bipy)_3]^{2+}$, MV^{2+} and triethanolamine, in an anodic compartment of an electrochemical cell, results in the production of H_2 at the cathode, and appreciable photocurrents. However, as with most of the homogeneous systems, here the photoreduction of the water is being fuelled by triethanolamine, which is consumed during the operation of the cell.

The photosensitisations of SnO_2 [193] and TiO_2 [194] by $[Ru(bipy)_3]^{2+}$ have been reinvestigated and both systems reveal the presence of previously unreported cathodic photocurrents. These results argue against the feasibility of dye sensitisation from homogeneous solutions as a viable photoelectrochemical process. However, two groups working independently have demonstrated that when derivatives of $[Ru(bipy)_3]^{2+}$ are attached in a monolayer upon an electrode surface, either by deposition of surfactant derivatives (by a Langmuir—Blodgett technique) upon SnO_2 [195] or bonded by the chemical modification of TiO_2 [196], direct catalytic photoelectrochemical oxidation of water is observed at the semiconductor—electrolyte interface. In both cases, irradiation of the system with visible light results in electron-transfer from the Ru(II) species to the electrode. The resultant Ru(III) species then chemically oxidises the water to regenerate the photoactive Ru(II) complex.

2.10 ELECTRODE MODIFICATION

The new field of electrode modification has been the subject of an excellent review [197], and a relatively large number of papers this year have been concerned with attaching ruthenium complexes to electrode surfaces, especially semiconducting and graphitic electrodes.

Well-defined ruthenium/2,2'-bipyridine complexes have been attached to silanised platinum oxide electrodes, and these electrodes are reasonably stable towards cycling between the ruthenium(II) and ruthenium(III) oxidation states. The complexes on the surface have only slightly altered electrochemical properties but quenched photochemical behaviour was observed. The surfaces were characterised by CV and XPES [198]. Similarly, $[Ru(bipy)_2(bipy\text{-}(COO)_2)]$ was attached to the surfaces of SnO_2 and TiO_2 electrodes, and these latter modified electrodes were shown to catalyse the photoelectrochemical decomposition of water [196]. SnO_2 electrodes have also been modified by direct exposure to solutions of commercial $RuCl_3 \cdot x\,H_2O$ (i.e. solutions in which there are a number of ill-defined components); the surfaces were characterised by CV and XPES but the identity of the surface-attached complexes was not established [199]. Modification of the photoelectrochemical properties of *n*-GaAs [200,201] by exposure to the same indeterminate mixture has also been observed.

Pyrolytic graphite electrodes have been coated with poly(4-vinylpyridine) or polyacrylonitrile and then used to anchor $[Ru^{II}(edta)]$ and $[Ru^{II}(NH_3)_5]$ fragments to the electrode surfaces, which were characterised by CV [202, 203]. $[Ru^{II}(edta)]$ has also been attached to graphite via 4-(aminomethyl)-pyridine [204,205], and $[Ru^{II}(bipy)_2Cl]$ via vinylpyridine [206,207]. $[Ru(bipy)_2(LL)Ru(bipy)_2][PF_6]_2$ (LL = 1,5-dihydroxyanthroquinone) has been dip-coated onto a glassy carbon electrode and the electrochemical characterisation indicated that a stable multi-layer film had been formed [208].

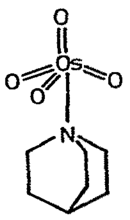
OSMIUM

2.11 OSMIUM(VIII)

The force constants of OsO_3F_2 have been calculated [209].

The absorption spectrum of OsO_4 has been studied using a high-pressure tunable CW—CO_2 laser [210] and multiple IR absorptions have been observed [211]. The γ-radiolysis of alkaline OsO_4 solution has also been investigated [212].

The molecular structures of $[OsO_4(quinuclidine)]$ (42) and $[(OsO_4)_2$-



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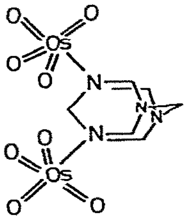


(43)

(hmta)] (**43**) (hmta = hexamethylenetetraamine) have been determined [213]. (**42**) has $\bar{r}$(Os=O) = 0.1706 nm {cf. 0.1712 nm in OsO_4} and r(OsN) = 0.237 nm; this Os—N bond is very long and it is somewhat surprising that the complex does not dissociate in solution. The Os—N bond in (**43**) is even longer (0.242 nm) [213]. Complexes between OsO_4 and various thiosemicarbazides and thiosemicarbazones have been reported [61].

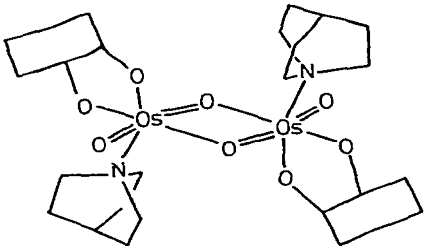
2.12 OSMIUM(VI)

2.12.1 Oxofluorides and oxides

The reaction between OsF_6 and B_2O_3 yields $OsOF_4$ [3]. A_3OsO_6 (A = Ca or Sr) was prepared, by heating AO with OsO_2 at high pressure and at 1000—1200° C, and characterised crystallographically and magnetically [214]. Cd_3OsO_6 has a perovskite structure [215]. The structure of $La_3Os_2O_{10}$ reveals isolated (Os_2O_{10}) clusters {r(OsOs) = 0.2462 nm}, which are formally mixed-valence dimers [216].

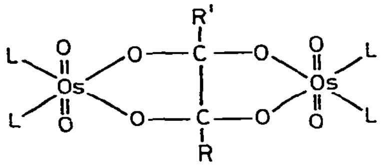
2.12.2 Complexes

Good progress is being made in understanding the oxidations performed by OsO_4. [OsO_4(quinuclidine)] (**42**) reacts with cyclohexene to give a dimeric solid [$(C_6H_{10}O_2)(C_7H_{13}N)OsO(\mu\text{-}O)_2OsO(O_2C_6H_{10})(C_7H_{13}N)$] (**44**),

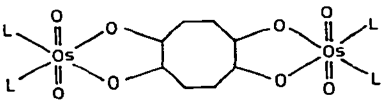


(**44**)

which has been characterised crystallographically. The complex dissociates in solution to give a five-coordinate monomer [217]. In the presence of L (L = pyridine or isoquinoline), OsO_4 will oxidise RC≡CR′ (R, R′ = H, H; Ph, Ph; Ph, H or Me, Ph) to give osmium(VI) esters of type (**45**). Hydrolysis of these

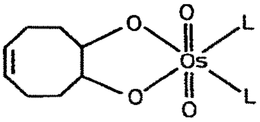


(**45**)



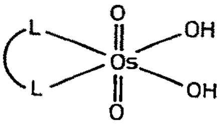
(**46**)

esters yields benzil (R, R′ = Ph, Ph), benzoic acid (R, R′ = Ph, H) or 1-phenylpropane-1,2-dione (R, R′ = Me, Ph) [218]. Catalytic amounts of OsO_4 in the presence of $KClO_4$ can be used to catalytically oxidise these alkynes. Similar results were obtained for the oxidation of dienes. Thus, cycloocta-1,5-diene gives (46) when OsO_4 is in excess. When the diene is in excess, (47) is formed



(47)

[218]. OsO_4 also reacts with phenols containing *ortho* hydroxy groups, $R(OH)_2$ (e.g. catechol and its derivatives), to give $[Os(O_2R)_3]$ and polymeric $\{OsO(O_2R)_2\}_n$. The reaction of *cis*-$[OsO_4(OH)_2]^{2-}$ or *trans*-$[OsO_2(OH)_4]^{2-}$ with $R(OH)_2$ gives *trans*-$[OsO_2(O_2R)_2]^{2-}$, whilst the reaction between OsO_4



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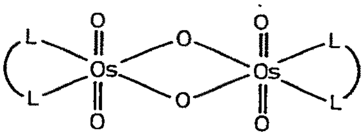


(49)

and $R(OH)_2$ in the presence of L (L = pyridine or substituted pyridines) gives *trans*-$[OsO_2(O_2R)L_2]$ [219].

The complexes $[OsO_2(OH)_2(L{-}L)]$ (L—L = phen or tmen) have been isolated from the reactions between OsO_4 and L—L in both monomeric (48) and dimeric (49) forms. The monomer ⇌ dimer interconversion is pH dependent, and has been followed by NMR spectroscopy [220].

The complexes $[LH][OsNX_4(H_2O)]$, $[OsNX_3L]$ (L = bipy or phen; X = Cl or Br) and $[OsNBr_3(py)(H_2O)]$ have been reported [221].

2.13 OSMIUM(V)

A detailed preparation of OsF_5 has been published [222].

The pyrochlores $A_2Os_2O_7$ (A = Ca, Cd or Pb) have been prepared, by reaction between OsO_2 and AO, and structurally and magnetically characterised [214]. Thermal decomposition of $Ca_2Os_2O_7$ above 855°C gives rise to a defect pyrochlore, $Ca_2Os_2O_{7-x}$ [223]. The strontium system has also been studied [224,225].

2.14 OSMIUM(IV)

2.14.1 Halides

$[(C_{12}H_{25})_3NH]F$ has been used as a phase transfer reagent with $[OsX_6]^{2-}$ (X = Cl, Br or I) to form mixed halide complexes of the type $[OsF_nX_{6-n}]^{2-}$ (n = 1, 2, 3 or 4) under mild conditions [226].

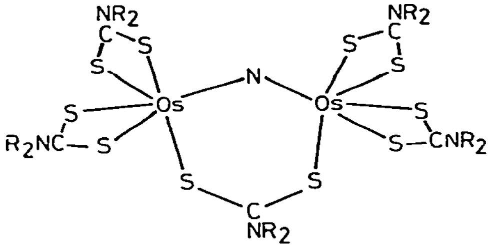
2.14.2 Oxides

The ternary oxides $AOsO_3$ (A = Ca, Sr or Ba) have been prepared by reaction of OsO_2 with AO at high temperatures and pressures, and characterised structurally and magnetically [214]. The thermal decomposition of $SrOsO_3$ has been studied [224,225], and the novel oxides A_2OsO_3 (A = Li or Na) have been prepared [21].

2.14.3 Complexes

Reaction of $K_2[OsX_6]$ (X = Cl, Br or I) with aqueous pentane-2,4-dione gives a mixture of *cis*- and *trans*-$[OsX_2(acac)_2]$. The complexes were separated by chromatography and spectroscopically characterised [227].

$[Os(S_2CNEt_2)_3]$ (prepared by reaction of $[NH_4]_2[OsCl_6]$ with $Na[S_2CNEt_2]$) reacts with HCl, I_2 or BF_3(aerobic) to give $[ClOs(S_2CNEt_2)_3]$, $[IOs(S_2CNEt_2)_3]$ or $[Os(S_2CNEt_2)_3][BF_4]$, respectively. The latter reacts with L (L = MeCN or PPh_3) or X^- (X = Cl or I) to give seven-coordinate $[Os(S_2CNEt_2)_3(L)][BF_4]$ or $[XOs(S_2CNEt_2)_3]$, respectively, all of which are fluxional in solution [228]. Prolonged reaction between $[NH_4]_2[OsCl_6]$ and $Na[S_2CNMe_2]$ gives $[Os_2(S_2CNMe_2)_5]Cl$; the reaction between $K_2[OsNCl_5]$ and $[Os(S_2CNR_2)_3]$ (R = Me or Et), in the presence of excess $[S_2CNR_2]^-$, gives $[Os_2N(S_2CNR_2)_5]$ (50) [228]. All these dithiocarbamato-complexes were characterised spectroscopically and electrochemically.



(50)

Reaction of the metalloporphyrin complex $[Os(oep)(N_2)(thf)]$ with CBr_4 gives the osmium(IV) complex $[Os(oep)Br_2]$ [229].

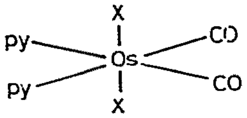
2.15 OSMIUM(III)

Under aerobic conditions, $[OsBr_2(PPh_3)_3]$ reacts with RCO_2H (R = Ph, 4-Br-C_6H_4 or 4-Me-C_6H_4) in benzene to give $[OsBr_2(O_2CR)(PPh_3)_2]$ [32], and $OsX_3 \cdot x\,H_2O$ (X = Cl, Br or I) reacts with benzoxazole-2-thione (bot) to give $MX_3(bot)_3$ [57]. Reaction of $[OsX_4(L)(CO)]^-$ (L = H_2O, MeOH or Me_2CO; X = Cl, Br or I) with one equivalent of diars gives $[OsX_4(diars)(CO)]^-$, which contains unidentate diars [230]. The kinetics of reduction of $[Os(L—L)_3]^{3+}$ (L—L = bipy, 4,4′-Me_2-bipy or 5-Cl-phen) by aqueous Ti(III) has been investigated [119]. A series of complexes $[Os(NH_3)_5(L)]X_3$ (L = isonic, py, pz or pyridazine; X = Cl, Br or PF_6) has been prepared, by the oxidation of $[Os(NH_3)_5(N_2)]Cl_2$ in triethylphosphate, in the presence of L. These were studied by electronic spectroscopy and cyclic voltammetry; the analogous Os(II) complexes were unstable in acid solution [231]. An overview of the chemistry of $[Os(NH_3)_5L]^{3+}$ species has appeared [43].

2.16 OSMIUM(II)

2.16.1 Carbonyl complexes

Reaction of *cis*-$[OsX_4(CO)_2]^{2-}$ (X = Cl, Br or I) with pyridine gives, stereospecifically, $[OsX_2(py)_2(CO)_2]$ (51). These complexes undergo step-wise halogen exchange with Y_2 (Y = Br or Cl), with retention of stereochemistry, according to [232]



(51)

$$[OsX_2(py)_2(CO)_2] \xrightarrow{Y_2} [OsXY(py)_2(CO)_2] \xrightarrow{Y_2} [OsY_2(py)_2(CO)_2]$$

(X = Br or I)

The fluxionality of $[Os(O_2CR)_2(CO)(PPh_3)_2]$ (R = Me or CF_3) {cf. (19)} has been studied by variable temperature NMR spectroscopy; rapid intramolecular interconversion of the monodentate and bidentate carboxylate ligands occurs [74].

2.16.2 Ammine complexes

An excellent description of the chemistry of $[Os(NH_3)_5L]^{2+}$ complexes has appeared [43]. Oxidation of $[Os(NH_3)_5(CO)]^{2+}$, in acidic solution, by Ce(IV) or $[S_2O_8]^{2-}$ gives $[\{(CO)(NH_3)_4Os\}(\mu\text{-}N_2)\{Os(NH_3)_4(CO)\}]^{4+}$; the same species can be generated by anodic oxidation [233]. Reaction of $[Os(NH_3)_5(H_2O)]^{3+}$ with $[S_2O_5]^{2-}/SO_2$ in hydrochloric acid yields $[Os(NH_3)_5(SO_2)]Cl_2$ [231].

2.16.3 Diimine complexes

In comparison with ruthenium, the attention being attracted by osmium(II) diimine species is meagre and almost exclusively centres upon photochemistry. The emission spectra, relative quantum yields and luminescence lifetimes of $[Os(bipy)_3]^{2+}$ and $[Os(phen)_3]^{2+}$ have been measured (77—300 K) [234]. Polarised electronic absorption spectra and the CD of $[Os(bipy)_3]^{2+}$ have also been measured and interpreted [114]. The quenching of

{$[Cr(bipy)_3]^{3+}$}* by $[Os(bipy)_3]^{2+}$ has also been investigated [118] and the photochemistry of $[Os(LL)_3]^{2+}$ has been reviewed [89].

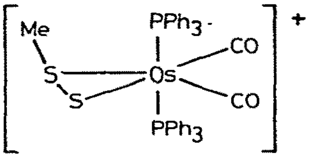
The redox behaviour of $[Os(bipy)_2Cl_2]$ in dmf has been studied by CV, polarography and controlled potential coulometry [235].

2.16.4 Porphyrin complexes

Reduction of $[OsO_2(oep)]$ in thf with hydrazine gives $[Os(oep)(N_2)(thf)]$ which reacts with CS_2/py to give $[Os(oep)(CS)(py)]$ [229].

2.16.5 Phosphine complexes

RNCO (R = 4-Me-C_6H_4) reacts with $[OsHX(CO)(PPh_3)_3]$ (X = Br or H) to give a formamido-complex $[OsX(CO)(PPh_3)_2(RN{\cdots}CH{\cdots}O)]$, with $[OsH_2(CO)(PPh_3)_3]$ under vigorous conditions to give a ureylene complex $[Os(CO)_2(PPh_3)_2(RN{-}C(O){-}NR)]$, and with $[OsH_4(PPh_3)_3]$ to give a formamidinato-complex $[OsH(CO)(PPh_3)_2(RN{\cdots}CH{\cdots}NR)]$ [142]. Methylation of $[Os(S_2)(CO)_2(PPh_3)_2]$ with methyltrifluoromethylsulphonate gives $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]^+$ (**52**), the perchlorate salt of which has been characterised by

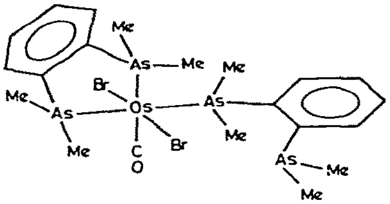


(**52**)

X-ray crystallography [236].

2.16.6 Arsine complexes

The reaction of $[OsX_4(L)(CO)]^-$ (L = H_2O, MeOH or Me_2CO; X = Br or I) with two equivalents of diars gives $[OsX_2(CO)(diars)_2]$. Crystallographic studies upon the bromide (**53**) reveal that the complex contains both mono-



(**53**)

dentate and bidentate diars [230]. Heating $[OsX_2(CO)(diars)_2]$ (or reaction between $[OsX_4(L)(CO)]^-$ and diars in alcohol at reflux) gives *cis*-$[OsX(CO)(diars)_2]^+$, which isomerises to the *trans* form on further heating [230].

2.16.7 Naphthyl, alkyl and hydride complexes

cis-[$HOs(dmpe)_2(np)$] reacts with HCN to give a mixture of *cis*- and *trans*-[$HOs(CN)(dmpe)_2$] [148]. The chemistry of osmium(II) hydrides and alkyls has been well reviewed, particularly with respect to elimination reactions [237,238].

2.16.8 Tin halide complexes

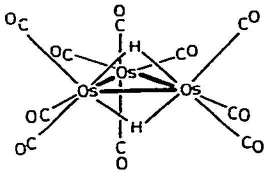
$H_2[OsCl_6]$ reacts with SnF_2 in aqueous HF, followed by treatment with AF (A = Na, K or NH_4), to yield $A_4[Os(SnF_3)_6]$; this reacts with HX (X = Cl or Br) to give, in the presence of $[Me_4N]^+$, $[Me_4N]_4[Os(SnF_3)_5X]$ [150]. The reaction of $[Os(SnCl_3)_5Cl]^{4-}$ with thiourea (tu) gives $[Me_4N]_2[Os(tu)_2(SnCl_3)_4]$, $[Me_4N][Os(tu)_3(SnCl_3)_3]$, $[Os(tu)_4(SnCl_3)_2]$ or $[Os(tu)_6][SnCl_3]_2$, dependent upon the amount of ligand added [239]. A salt of $[Os(SnCl_3)_5Cl]^{4-}$ has been crystallographically characterised [151].

2.17 OSMIUM(0)

The reaction between "$[Os(CO)_2(PPh_3)_2]$" and formaldehyde yields the very interesting complex $[Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)]$, whose structure reveals that the $H_2C{=}O$ is side-bonded to the osmium with a very long (0.159 nm) $H_2C{-}O$ bond length [240]; this is, perhaps, better considered as an osmium(II) complex.

2.18 OSMIUM CARBONYL CLUSTERS

The UV photoelectron spectra (He-I and He-II) of $[Os_3(CO)_{12}]$ and $[Os_6(CO)_{18}]$ have been reported, and interpreted in terms of an extended Hückel calculation. The first observed ionisation energies are ca. 3 eV higher than the work function of the metal, and change by only 0.3 eV upon doubling the size of the metal cluster (i.e. $Os_3 \rightarrow Os_6$). These results suggest that metal carbonyl cluster compounds have electronic properties which differ significantly from those of metal surfaces (in either their pure or chemisorbed states) and thus question the popular belief that clusters of this type are reliable models for heterogeneous catalytic reactions at metal



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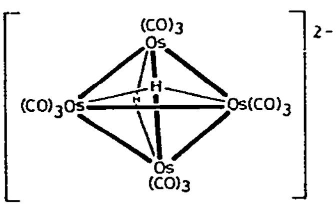
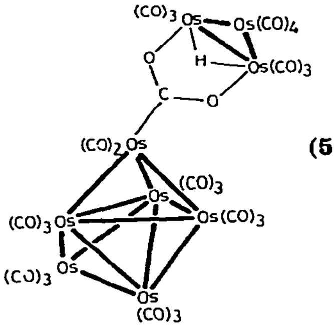


(55)

surfaces [156]. Low frequency Raman studies upon $[Os_3(CO)_{12}]$ have also been reported [157].

The structure of $[(\mu\text{-}H)_2Os_3(CO)_{10}]$ (54) has been solved independently by neutron diffraction [241] and a combined X-ray/neutron diffraction study [242], the hydrogen atoms being directly located. The solid state NMR spectra of $[H_2Os_3(CO)_{10}]$ and $[H_4Os_4(CO)_{12}]$ have been reported [161] and $[H_2Os_3(CO)_{10}]$ has been shown to be a good catalyst for the isomerisation of pent-1-ene [243].

Reduction of $[Os_3(CO)_{12}]$ by $Na[BH_4]$ gives $[HOs_3(CO)_{11}]^-$, $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ (55). The latter was isolated as a $[(PPh_3)_2N]^+$ salt, and studied crystallographically; the hydrides were not located [244]. $[HOs_3(CO)_{11}]^-$ has also been generated by treatment of $[Os_3(CO)_{12}]$ with methanolic KOH, and it is fluxional in solution. It reacts with $[Os_6(CO)_{18}]$ to give $[\{HOs_3(CO)_{10}\}(\mu\text{-}CO_2)\{Os_6(CO)_{17}\}]^-$ (56), which has been structurally characterised as a $[(PPh_3)_2N]^+$ salt [245]. In a similar manner, $[HOs_3(CO)_{11}]^-$ reacts with $[Os_5(CO)_{16}]$, $[Os_7(CO)_{21}]$ or $[Ru_6C(CO)_{17}]$ to give $[\{HOs_3(CO)_{10}\}(\mu\text{-}CO_2)\{Os_5(CO)_{15}\}]^-$, $[\{HOs_3(CO)_{10}\}(\mu\text{-}CO_2)\{Os_7(CO)_{20}\}]^-$ or $[\{HOs_3(CO)_{10}\}(\mu\text{-}CO_2)\{Ru_6C(CO)_{16}\}]^-$, respectively [246]. $[Os_5(CO)_{16}]$ reacts with OH^- to produce $[Os_5(CO)_{15}]^{2-}$; $[Os_6(CO)_{18}]$, $[Os_7(CO)_{21}]$ or $[Os_8(CO)_{23}]$ also react with OH^-, but with cluster fragmentation, to give $[Os_5(CO)_{15}]^{2-}$, $[Os_6(CO)_{18}]^{2-}$ or $[Os_7(CO)_{20}]^{2-}$, respectively [247]. The kinetics of reduction of $[Os_6(CO)_{18}]$ to $[Os_6(CO)_{18}]^{2-}$ by I^- have been investigated [248].



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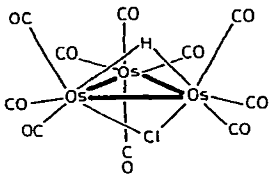
The structures of $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}Cl)]$ (57) [249] and $[(\mu\text{-}H)_2Os_3(CO)_9\text{-}$



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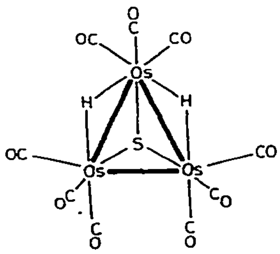

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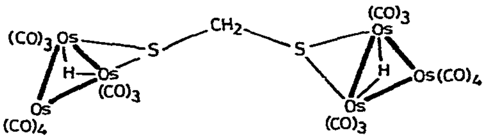
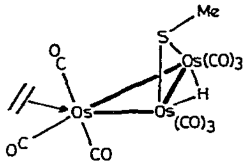


(59)

(μ_3-S)] (58) [250] have been determined, but only in the latter case were the hydrido-ligands directly located. $[H_2Os_3(CO)_{10}]$ reacts with CS_2 to give $[\{HOs_3(CO)_{10}\}(\mu\text{-}SCH_2S)\{HOs_3(CO)_{10}\}]$ (59), which has been crystallographically characterised [251]. The following reaction scheme illustrates the synthetic versatility of the $(SR)^-$ ligand [252]:

$$\begin{tikzcd}
{[}Os_3(CO)_9(H_2S){]} \arrow[r, "KOH", "MeOH"'] & {[}HOs_3(CO)_9(S){]}^- \arrow[r, "R_3O^+", "R = \text{Me or Et}"'] & {[}HOs_3(CO)_9(SR){]} \arrow[d, "L", "(L = CO,\ PPh_3,\ \text{MeCN or } C_2H_4)"'] \\
 & & {[}HOs_3(CO)_9(SR)(L){]}
\end{tikzcd}$$

Of especial interest is the complex $[HOs_3(CO)_9(SR)(L)]$ ($L = C_2H_4$) (60),



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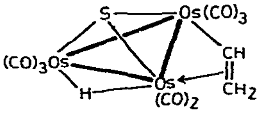
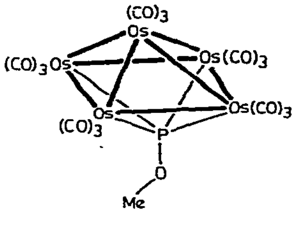


(61)

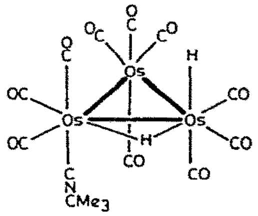
which is the first crystallographically characterised example of ethene bound to a single metal atom in a cluster [252]. (60), upon heating, reverts to $[HOs_3(CO)_9(SR)]$, but in the presence of excess ethene at 125°C it rearranges to give a vinyl derivative (61) [252]. The structure of $[H_2Os_3(CO)_9(PPh_3)]$ reveals the expected structure, analogous to (54), the PPh_3 replacing a CO from an $Os(CO)_3$ group adjacent to the $(\mu\text{-}H)_2$ bridge [253]. Pyrolysis of $[Os_3(CO)_{11}\{P(OMe)_3\}]$ gives $[Os_5(CO)_{15}\{POMe\}]$ (62), which has been



(62)

crystallographically characterised [254,255].

Reaction of $[H_2Os_3(CO)_{10}]$ with CNR (R = Ph, Me or CMe_3) gives $[H(\mu\text{-}H)Os_3(CO)_{10}(CNR)]$ (63). Thermolysis of (63) in pentane, octane or Bu_2O gives initially $[(\mu\text{-}H)_2Os_3(CO)_9(CNR)]$ (R = Ph, Me or CMe_3) (64) and then $[(\mu\text{-H})Os_3(CO)_{10}\{\mu_2\text{-HC=NR}\}]$ (R = Ph or Me); further heating produces $[(\mu\text{-H})Os_3(CO)_9\{\mu_3\text{-HC=NR}\}]$ (R = Ph or Me). $[(\mu\text{-H})Os_3(CO)_9\{\mu_3\text{-HC=NPh}\}]$ **(65)** reacts with $P(OMe)_3$ to give $[(\mu\text{-H})Os_3(CO)_9\{P(OMe)_3\}(\mu_2\text{-HC=NPh})]$ **(66)**. Thermolysis of **(63)** in thf produces $[(\mu\text{-H})Os_3(CO)_{10}\{\mu_2\text{-C=N(H)R}\}]$ **(67)** [256]. The molecular structures of **(63**; R = CMe_3**)** [257], **(64**; R = CMe_3**)** [257], **(65)** [256], **(66)** [256] and **(67**; R = CMe_3**)**



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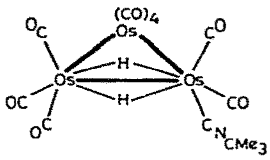

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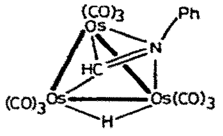

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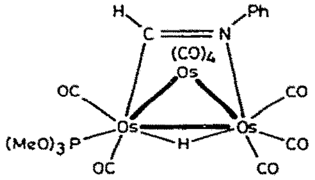

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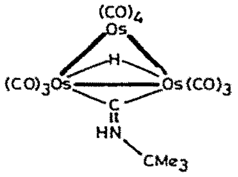
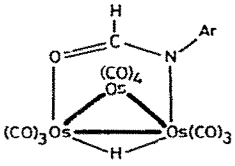


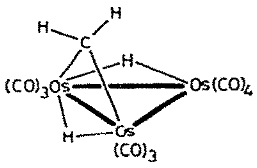
(67)

[258] have been determined. In a similar manner, $[H_2Os_3(CO)_{10}]$ reacts with ArNCO (Ar = Ph or 4-Me-C_6H_4) and PhNCS to give $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-ArNC(O)H}\}]$ **(68)** and $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-PhNC(S)H}\}]$. The structure of **(68**; Ar = 4-Me-C_6H_4**)** has been determined [259] and is clearly related to that of **(66)**.



(68)

$[(\mu\text{-H})_2Os_3(CO)_{10}]$ reacts with CH_2N_2 to give $[(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)]$ **(69)** and a neutron diffraction study of the latter directly located the four hydrogen atoms [260]. A combined X-ray/neutron diffraction study also led



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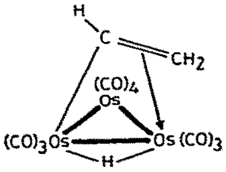
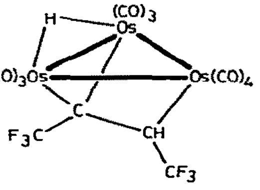


(70)

to the direct location of the hydrogen atoms in $[(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}C_2H_3)]$ **(70)**. Reaction of $[(\mu\text{-H})_2Os_3(CO)_{10}]$ with $CF_3C{\equiv}CCF_3$ gives $[(\mu\text{-H})Os_3(CO)_{10}(CF_3CCHCF_3)]$ **(71)**; the hydrogens of the latter were not directly located in this structure [261]. $[Os_3(CO)_{10}(NCMe)_2]$ reacts with Et_3N to give an equimolar mixture of $[H_2Os_3(CO)_{10}]$ and the iminium species, $[(\mu\text{-H})Os_3(CO)_{10}(CHCHNEt_2)]$ **(72)** [262,263].



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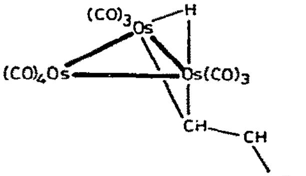
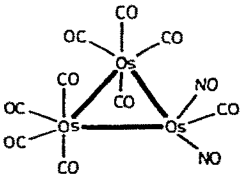


(72)

Reaction of $[Os_3(CO)_{12}]$ with NO in octane at 126°C gives $[Os_3(CO)_9(NO)_2]$ **(73)**, which is fluxional in solution; it reacts with L ($L = NH_3$, $NEtH_2$ or CO) to give the unstable adducts $[Os_3(CO)_9(NO)_2(L)]$, and with L′ ($L' = P(OMe)_3$ or PPh_3) or py to give the stable complexes $[Os_3(CO)_8(NO)_2(L')]$ **(74)** or $[Os_3(CO)_9(\mu_2\text{-}NO)_2(py)]$ **(75)**, respectively. **(74)** reacts with CO to



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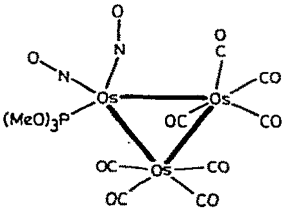

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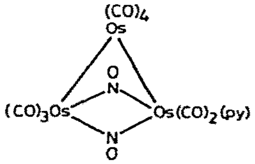
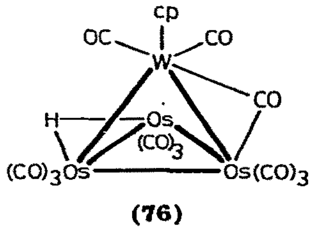


(75)

give $[Os_3(CO)_9(\mu_2\text{-}NO)_2(L')]$ [264]. (**74**; $L' = P(OMe)_3$) was characterised crystallographically [264].

A mixed-metal cluster, $[(\mu\text{-H})Os_3W(CO)_{12}(cp)]$ **(76)** has been prepared by



(76)

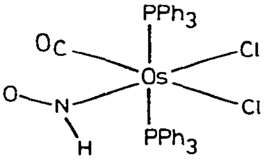
the reaction between $[Os_3(CO)_{10}(NCMe)_2]$ and $[HW(CO)_3(cp)]$, and characterised crystallographically [265]. $[(\mu\text{-H})_3Os_3W(CO)_{11}(cp)]$ has been similarly characterised [266].

An excellent example of synthetic chemistry has resulted in various osmium clusters $\{[Os_3(CO)_{11}\{PPh_2(CH_2CH_2R)\}]$, $[H_2Os_3(CO)_{10}\{PPh_2(CH_2CH_2R)\}]$ and $[HOs_3(CO)_9(CCR)]$ (where R = silica gel)$\}$ being successfully anchored to silica gel, and characterised by IR spectroscopy [267].

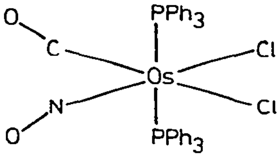
Although osmium shows a wide-ranging cluster chemistry with alkenes, alkynes, etc., these are outside the scope of this review.

2.19 OSMIUM NITROSYLS AND THIONITROSYLS

The ^{14}N NMR spectra of $[Os(NH_3)_5(NO)]^{3+}$ and $[OsCl_5(NO)]^{2-}$ have been reported [172]. $[OsCl(CO)(NO)(PPh_3)_2]$ reacts with HCl to give $[OsCl_2(CO)(HNO)(PPh_3)_2]$ (77); the reaction involves electrophilic attack upon the NO to give a coordinated nitrosyl hydride, which is coplanar with the $Os(CO)Cl_2$ moiety [268]. (77) has been studied by ^{1}H and ^{31}P NMR spectroscopy, and has been prepared with a ^{15}NO label. $[OsCl(CO)(NO)(PPh_3)_2]$ reacts with the non-coordinating acid, HBF_4, to give (amongst other products) $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$ (78) {n.b. the NO and CO were crystallographically disordered} [268].



(77)



(78)

$[OsX_3NL_2]$ (L = $AsPh_3$, PMe_2Ph or $\frac{1}{2}$ bipy; X = Cl or Br) reacts with S_2Cl_2 to give the green thionitrosyl complexes, $[OsClX_2(NS)L_2]$. Treatment of $[NBu_4][OsNCl_4]$ with S_2Cl_2, followed by pyridine, gives $[OsCl_3(NS)(py)_2]$. The phosphines in $[OsCl_3(NS)(PMe_2Ph)_2]$ are mutually *trans* [269].

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