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2. RHODIUM

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CONTENTS

INTRODUCTION

This review continues the general form of that published for the 1983 literature [1]. Once again, the chemistry of rhodium and iridium are treated separately this year. The interest in rhodium and iridium complexes as catalysts shows no sign of abating, and numerous new catalytic reactions and modifications to old catalyst systems continue to be reported. This year the chemistry of cluster compounds will not be reported in great detail, except where it is of direct interest to the coordination chemist. The review in this journal covering the 1985

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literature will commence a biennial summary of the application of rhodium and iridium catalysts to organic synthesis.

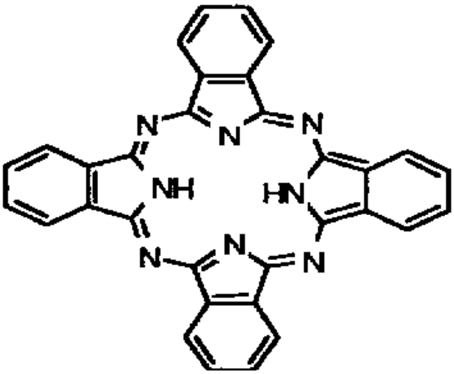
The material included in this review corresponds to the coverage of Volumes 100 and 101 of Chemical Abstracts, although the major journals (*Journal of the American Chemical Society, Inorganic Chemistry, Journal of the Chemical Society, Dalton Transactions and Journal of the Chemical Society, Chemical Communications*) have been covered through December 1984.

As usual, I must thank the staff of the Cambridge Crystallographic Data Centre for their invaluable assistance, and, in particular, Dr John Davies for initiating me into Marks 7, 8 and 9.

Wallbridge and Taylor have produced the Annual Report of the chemistry of the Platinum Group Metals for 1982, which is up to their normal high standard [2]. A volume of Gmelin dealing with rhodium coordination compounds has appeared (Gmelin Handbook of Inorganic Chemistry: Rh - Rhodium Suppl. Vol B2: Coordination Compounds, 8th Ed.) which should be of considerable use [3]. A review of binuclear and polynuclear rhodium complexes incorporating bridging nitrogen donor heterocycles has appeared [4], as has a review dealing with rhodium(III) complexes of H_4edta and related aminopolycarboxylic acids [45].

2.1 RHODIUM(VI), (V) AND (IV)

Interest in these oxidation states is noticeable by its absence. The formally rhodium(V) complex $[(cp^*)RhH_2(SiEt_3)_2]$ is formed by the reaction of Et_3SiH with $[\{(cp^*)RhCl\}]_2$. The complex has been characterised by ^{103}Rh, ^{29}Si, ^{13}C and ^1H n.m.r. spectroscopy, and by X-ray and neutron diffraction structural determinations [95]. Chemical or electrochemical oxidation of [Rh(pc)(MeOH)X] (H_2pc = **1**, X = Cl or Br) leads to the rhodium(IV) complex $[Rh(pc)(MeOH)X]^+$ [5]. No rhodium(IV) compounds were obtained from the attempted oxidation of $K_3[RhCl_6]$ in hydrochloric acid, or $Rh_2O_3.xH_2O$ in sulphuric, perchloric or nitric acids with ozone over a range of temperatures and pH values. However, green $RhO_2.2H_2O$ was obtained from the ozonolysis of $K_2[RhCl_5(H_2O)]$ or $Ba_3[Rh(OH)_6]_2$ in water. The reaction of $RhO_2.2H_2O$ with sulphuric acid in acetone results in the formation of $Rh(OH)_2.(SO_4).2H_2O$. The e.s.r. spectra of the d^5 rhodium(IV) complexes were reported, and that of the blue rhodium(IV) sulphate reinterpreted in terms of two non-equivalent rhodium(IV) sites [6].



(1)

2.2 RHODIUM(III)

2.2.1 Complexes with halides and pseudohalides

The complex $[NH_4]_3[RhCl_6]$ reacts with glycine in the solid state to yield $[RhL_5Cl]Cl_2$ and $[RhL_4Cl_2]Cl$ (L = glycine, $H_2NCH_2CO_2H$) [7]. The attempted oxidation of various chlororhodate(III) complexes is discussed in Section 2.1 [6]. The electronic structures of the ions $[RhCl_6]^{3-}$, $[Rh_2Cl_9]^{3-}$ and $[Rh_2Cl_{10}]^{4-}$ have been investigated by a combination of X-ray spectroscopy using the Rh $L_{\beta 2}$ and Cl K_{β} frequencies and theoretical calculations [8].

The 'reactive' form of rhodium(III) chloride has been investigated in the solid state and solution by a combination of X-ray diffraction and ^{103}Rh, ^{17}O, ^{133}Cs and ^{35}Cl n.m.r. methods. The authors interpret their results in terms of polynuclear species in 'fresh' material, and $[RhCl_5(OH_2)]^{2-}$ in aged samples [9]. Other chloroaqua complexes of rhodium(III) have been investigated by ^{103}Rh and ^{17}O n.m.r. spectroscopy [21,22]. The oxidation of dihydrogen in hydrochloric/perchloric or sulphuric acid media at 95° in the presence of rhodium trichloride has been investigated. A mechanism for the process has been proposed in which $[HRhCl_5]^{3-}$ is a key intermediate [10]. A solid state structural analysis of the related complex $K_3[HRh(CN)_5]$ has been reported; the metal is in a distorted octahedral environment with Rh–C distances in the range 2.000 - 2.005 Å, and an Rh-H distance of 2.082 Å. The ^{13}C n.m.r. spectrum of the complex exhibits two carbon resonances corresponding to the positions *cis* and *trans* to the hydride; each resonance is a doublet of doublets due to coupling to both hydrogen and rhodium ($^1J_{Rh-C}$ 34.5 Hz) [11].

Purple solutions containing the $[Rh(SnCl_3)_5]^{4-}$ ion are obtained from the reaction of $SnCl_2$ with $[Me_4N]_3[RhCl_n(SnCl_3)_{6-n}]$ ($n = 2$, 3 or 4); the kinetics and thermodynamics of these equilibria were investigated [12]. The reaction of rhodium trichloride with K[SCN] gives mixtures of the linkage isomers $[Rh(NCS)_n(SCN)_{6-n}]^{3-}$ ($n = 0$, 1, 2 or 3) rather than the homoleptic species previously reported. Upon heating the $^nBu_4N$ salts of the initially formed mixture of isomers a re-equilibration occurs to favour the *N* bonded isomers. The pure linkage isomers may be separated from the mixtures by ion-exchange chromatography. Extraction of the reaction mixture with a CH_2Cl_2 solution of [ppn]Cl (ppn = $[Ph_3P{=}N{=}PPh_3]^+$) yields the anion $[Rh_2(SCN)_{10}]^{4-}$. It is suggested that this latter anion possesses a structure with two bridging thiocyanates and *only S* bonded terminal thiocyanates [13].

The extraction of rhodium(III) from aqueous acidic chloride rich medium by thiocyanate into a polyurethane/polyether phase is claimed to give excellent separation from iridium; the extracted species is $[Rh(SCN)_6]^{3-}$ (presumably a mixture of the linkage isomers) [14]. Near quantitative extraction of rhodium as $[Rh_2Cl_9]^{2-}$ occurs from low pH aqueous solutions with the extractant N_{1923} [15]. In contrast, the species passing into the organic phase upon treating rhodium trichloride with Aliquat 336 in $ClCH_2CH_2Cl$ is $[R_3NMe][RhCl_4]$ ($R = {}^nC_8H_{17}$); the solution is a very active catalyst for the hydrogenation of olefins, acetylenes and arenes [17]. The extraction of rhodium by phosphoric triamides, $(RNH)_3P{=}O$, has also been reported [16].

The electrochemical reduction (at rotating disc electrodes) of the solution of chloro complexes in the system $RhCl_3/[NH_4]Cl/H_2O/H_3PO_4$ has been investigated [18].

The photoreactivity of the ion $[Rh(NH_3)_5I]^{2+}$ has been investigated in acidic and alkaline aqueous solution. The photolabile species is a ligand field excited state. The hydroxide ion quenches NH_3 and enhances iodide labilisation. These observations are in accord with those previously reported for $[Rh(NH_3)_5X]^{2+}$ (X = Cl or Br) in which results were obtained which suggested that hydroxide reacted with the ligand field state [19]. The photosolvolysis reaction of $[Rh(NH_3)_5Cl]^{2+}$ in dmf or dmso has been investigated and the $\Delta V^{\ddagger}$ values determined from the pressure dependence [20]. A similar study in a wider range of solvents has also been reported [23]. Competing reactions involving displacement of halide and ammonia occur. The process of ammonia loss from $[Rh(NH_3)_5I]^{2+}$ appears to be dissociatively activated, with a $\Delta V^{\ddagger}$ value of +1.4 $cm^3\ mol^{-1}$ [24]. The reaction of $RhCl_3$ with acetamide apparently yields $[Rh(NH_3)_5Cl]Cl_2$ [25]. The base hydrolysis of the complexes $[Rh(RNH_2)_5Cl]^{2+}$ (R = Me, Et or ^nPr) has been investigated; in each case the rate law is of the form

$$\rho = k_{obs}[Rh(RNH_2)_5Cl^{2+}]$$

$$k_{obs} = k_1 + k_2[OH^-]$$

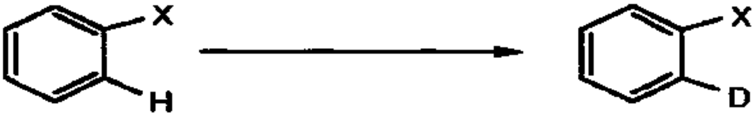
This is interpreted in terms of an S_N1 cb pathway being operative, and the ratio k_1/k_2 was shown to be dependent upon the steric bulk of the amine [26]. A ^1H n.m.r. study of the complexes $[Rh(NH_3)_5X]^{2+}$ (X = Cl or CN) in D_2O and dmso-d_6 has been reported [36].

The photolysis of aqueous solutions of *trans*-$[Rh(NH_3)_4Cl_2]^+$ gives a mixture of *cis* and *trans*-$[Rh(NH_3)_4Cl(H_2O)]^{2+}$. It was shown that the *cis* and *trans* forms of $[Rh(NH_3)_4Cl(H_2O)]^{2+}$ were photochemically interconverted, and the same 17:83 *cis:trans* mixture was obtained from the photolysis of aqueous solutions of *cis*-$[Rh(NH_3)_4Cl_2]^+$, *trans*-$[Rh(NH_3)_4Cl_2]^+$, *cis*-$[Rh(NH_3)_4Cl(H_2O)]^{2+}$, or *trans*-$[Rh(NH_3)_4Cl(H_2O)]^{2+}$. A five coordinate $\{Rh(NH_3)_4Cl\}^*$ intermediate which could interconvert between trigonal bipyramidal and square-based pyramidal geometries was proposed [27]. The photolytic water exchange reaction in *cis* and *trans* $[Rh(NH_3)_4Cl(H_2O)]^{2+}$ has been investigated; the quantum yields are $\Phi = 0.66 \pm 0.02$ (*cis*), $\Phi = 0.39 \pm 0.04$ (*trans*), and both stereoretentive and stereomobile processes were characterised [29]. The base catalysed hydrolysis of *trans*-$[Rh(RNH_2)_4Cl_2]^+$ (R = H, Me, Et or ^nPr) has been studied; in each case, a two term rate law was obeyed which is best interpreted in terms of competing anation and S_N1 cb pathways. A comparison of the behaviour of the rhodium(III) complex with that of chromium(III) and cobalt(III) complexes indicated that the rhodium was less able to participate in π-bonding than the other metals [28].

The preparation of rhodium haloammines is a somewhat serendipitous process, but reliable routes to a number of complexes have been reported. The complex *trans*-$[Rh(NH_3)_4Cl_2]Cl$ is best prepared from $[Rh(NH_3)_5Cl]^{2+}$ by reduction with zinc, followed by a mixture of KCl and HCl and oxidation by acidic hydrogen peroxide. Yields of 70% of the monohydrate were reported. Treatment of *trans*-$[Rh(NH_3)_4Cl_2]Cl$ with NaBr in HBr results in halogen exchange, and the formation of *trans*-$[Rh(NH_3)_4Br_2]Br.H_2O$. The hydrolysis of *trans*-$[Rh(NH_3)_4Cl_2]Cl$ is catalysed by mercury(II) perchlorate, and the complex *trans*-$[Rh(NH_3)_4(H_2O)_2][ClO_4]_3$ may be isolated in good yield. The iodo complex *trans*-$[Rh(NH_3)_4I_2][ClO_4].0.5H_2O$ is best prepared from the reaction of *trans*-$[Rh(NH_3)_4(H_2O)_2][ClO_4]_3$ with NaI [30].

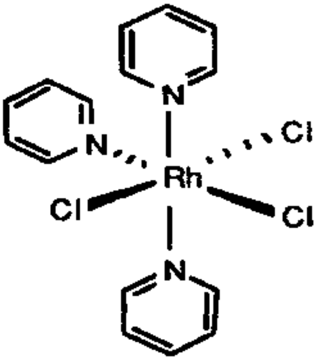
The labelled complex *trans*-$[Rh(NH_3)_4(^{15}NH_3)(CN)]^{2+}$ is prepared by the reaction of $^{15}NH_3$ with *trans*-$[Rh(NH_3)_4Cl(CN)]^+$; photoaquation of the complex occurs almost exclusively by a pathway involving the loss of ammonia from the equatorial plane, rather than from the site *trans* to cyanide [31]. The photoaquation and photophysiscs of the the complexes *cis* and *trans* $[Rh(NH_3)_4XY]^{n+}$ (X = Cl, Br or H_2O; Y = X, H_2O or OH) have been investigated. The photoaquation occurs from a ligand field state, and a dissociative mechanism has been proposed. The effect of the Y substituent on the rate of loss of X was *cis* X > *trans* OH ≈ *trans* X > NH_3 ≈ *cis* OH [32]. The photoaquation of *cis* and *trans* $[RhL_2X_2]^{n+}$ (L = 1,3-pn, $H_2NCH_2CH_2CH_2NH_2$; X = Cl or Br) has also been studied. In this case, halide is the leaving group, and the product is $[RhL_2(H_2O)X]^{2+}$, once again derived from a ligand field state giving rise to a dissociative intermediate [33].

Solutions of rhodium trichloride in D_2O have been shown to be selective catalysts for exchange of the *ortho* protons in benzoic acid, benzamide and aniline (Scheme 1) [34].



Scheme 1

The crystal and molecular structure of *mer*-[Rh(py)$_3$Cl$_3$] (**2**) has been determined. The average Rh-Cl distance is 2.3345 Å and the average Rh-N distance is 2.057(13) Å [35].



(**2**)

2.2.2 Complexes with Group 16 donor ligands

2.2.2.1 Complexes with water, alcohols and inorganic ligands

An X-ray diffraction study of a solution of rhodium(III) perchlorate in aqueous perchloric acid has been reported. The results suggested that no polynuclear species were present in the experimental solution, and the only solution species was [Rh(H$_2$O)$_6$]$^{3+}$, with an average Rh-O distance of 2.04 Å [37]. Swaddle has reported partial molar volumes for [Rh(H$_2$O)$_6$]$^{3+}$ and [Rh(NH$_3$)$_5$(H$_2$O)]$^{3+}$ [38]. A range of chloroaqua complexes have been studied by ^{17}O and ^{103}Rh n.m.r. spectroscopy [9,21]. The formation of rhodium(IV) compounds from the ozonolysis of Ba$_3$[Rh(OH)]$_2$ or K$_2$[RhCl$_5$(OH$_2$)] has been discussed earlier [6].

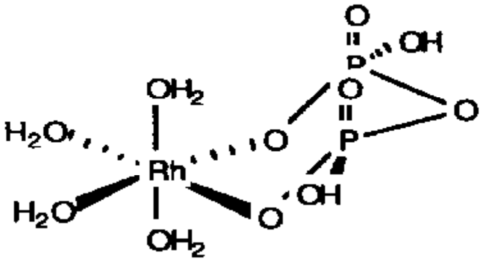
Numerous reports concerning the photoaquation or photosolvation of rhodium(III) ammine and amine complexes have appeared. The bulk of the evidence is in support of a dissociative process in which a short-lived five coordinate intermediate is formed from a ligand field state. The photosolvation of $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br, I, NH_3, py, or SO_4) by H_2C [19,23], $HCONH_2$ [20,23], $HCONMe_2$ [20,23] or Me_2SO [20,23] has been studied. Typical activation volumes $\Delta V^{\ddagger}$ are close to zero (X = NH_3, +3.9; X = I, +1.4; X = SO_4, -3.9), as expected for a dissociatively activated process [24]. Related photosolvation processes have been utilised in the synthesis of $[Rh(NH_3)_4Cl(H_2O)]^{2+}$ [27-29,32]. The photolysis of aqueous solutions of $[Rh(NH_3)_5H]^{2+}$ appears to lead to rhodium(II) complexes rather than photosolvation products. A similar reaction occurs with $[Rh(NH_3)_4(H_2O)H]^{2+}$. The rhodium(II) complexes which are formed are oxygen sensitive, and give rise to rhodium(III) superoxide species [39].

The preparation of $[Rh(NH_3)_4(H_2O)_2][ClO_4]_3$ by the mercury(II) perchlorate catalysed aquation of $[Rh(NH_3)_4Cl_2]Cl$ has been described [30]. The exchange of water in the complexes *cis* and *trans* $[Rh(NH_3)_4(H_2O)_2]^{3+}$ has been investigated. For the *cis* complex, $k_{obs} = 7.5\pm0.3 \times 10^{-6}$ s^{-1}, $\Delta H^{\ddagger} = 108.1\pm1.4$ kJ mol $^{-1}$, whilst for the *trans*, $k_{obs} = 7.2\pm0.5 \times 10^{-9}$ s^{-1}, $\Delta H^{\ddagger} = 145.5\pm1.7$ kJ mol $^{-1}$. These rates may be compared with those for *cis*-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$ ($k_{obs} = 23.8\pm0.3 \times 10^{-6}$ s^{-1}) and *trans*-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$ ($k_{obs} = 32.8\pm0.9 \times 10^{-6}$ s^{-1}). The kinetic *trans* effect for a given fixed set of *cis* ligands is seen to be $H_2O \ll NH_3 < Cl$, and the *trans* effect for rhodium(III) is larger than for chromium(III) [40]. The photoaquation of $[RhL_2X_2]^+$ (L = $H_2NCH_2CH_2CH_2NH_2$, X = Cl or Br) yields $[RhL_2(H_2O)X]^{2+}$ [33].

The photolysis of aqueous solutions of $[Rh(en)_2X(NO_2)]^+$ in the presence of O_2 leads to the superoxo complexes $[Rh(en)_2(OH_2)O_2]^{2+}$ and the peroxy compound $[X(en)_2Rh(\mu-O_2)Rh(en)_2(OH_2)]^{4+}$. The complexes exhibit nitro-nitrito linkage isomerism. The superxoxo complex was characterised as such by e.s.r. spectroscopy, and acts as a one electron oxidising agent [41].

Rhodium(III) dmso complexes in the presence of $^nBuNH_2$ and CCl_4 have been shown to be of use as initiation catalysts for the polymerisation of methyl acrylate and methyl methacrylate [42].

The interaction of $[Rh(H_2O)_6]^{3+}$ with phosphate, polyphosphate and nucleotides has been investigated. The products of these reactions were characterised by n.m.r. and circular dichroism spectroscopy and include $[Rh(H_2O)_4(OPO_3)(OPO_3H)]^{2-}$, $[Rh(H_2O)_4L]$ (HL = $(OH)_2P(=O)OP(=O)(OH)_2$) (**3**), and $[Rh(H_2O)_3L]$ (H_5L = $(HO)_2P(=O)OP(=O)(OH)OP(=O)(OH)_2$) (**4**). Complexes with ATP and ADP were also characterised [43].



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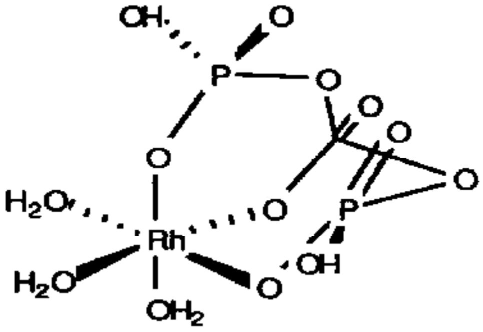


(4)

Trifluoromethanesulphonate is an extremely good leaving group, and a number of synthetic applications of such complexes have been reported this year. Solvation of $[Rh(NH_3)_5(O_3SCF_3)]^{2+}$ by dmf or MeCN proceeds rapidly to yield $[Rh(NH_3)_5L]^{3+}$ (L = dmf or MeCN). The solvento complexes are activated with respect to base hydrolysis, and (unusually) single products are obtained from reaction with hydroxide. No ligand loss occurs by conjugate base mechanisms (to give hydroxo complexes), and the products of these reactions are the acetamido or formato complexes $[Rh(NH_3)_5L]^{2+}$ (L = HNCOMe or O_2CH) from MeCN and dmf respectively [44]. The overall rate enhancement over the hydrolysis of the free ligands is about 10^6 and the rate law is of the form

$$\rho = k_{obs}[Rh(NH_3)_5L]^{3+}$$

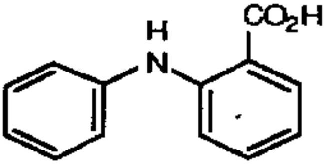
where

$$k_{obs} = k_1[OH^-] + k_2[OH^-]^2$$

2.2.2.2 Complexes with other oxygen donors

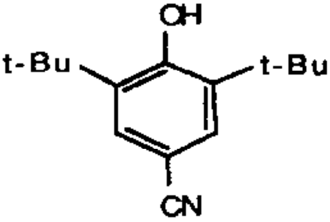
A crystal structural analysis of the complex Λ-$(+)_{546}$-$K_3[Rh(ox)_3].2H_2O$ has been reported. The compound is isomorphous with the corresponding $(-)_{546}$ cobalt(III) complex. The Rh-O distances are 2.019(12) Å, but two of the oxalate ligands are disordered. One potassium counterion is close to a rhodium bonded oxygen atom, giving a short K..O contact of 3.494 Å. These interactions between alkali metal ions and low spin d^6 complexes of cobalt, rhodium and iridium are a feature of such oxalate complexes [46].

Complexes with amino acids and aminopolycarboxylic acids will be dealt with in Section 2.2.3.3. The reaction of rhodium trichloride with *N*-phenylanthranilic acid (**5**) gives three distinct

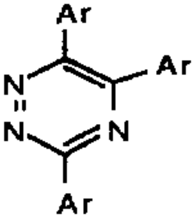


(**5**)

compounds, in each of which the ligand is bonded to the metal only through the carboxylate oxygen atoms. The complexes were not further characterised, but are reported to be extremely active hydrogenation catalysts. The authors issue a *caveat* that the catalytic properties of these complexes (or mixtures?) are not fully reproducible [47].

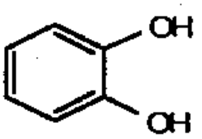


(**6**)



(**7**)

The reaction of 4-cyano-2,6-di-*tert*-butylphenol (**6**) with rhodium trichloride results in the formation of $[RhL_3Cl_3]$ (HL = **6**). Upon oxidation with PbO_2, this complex generates the 4-cyano-2,6-di-*tert*-butylphenoxy radical, which trimerises to the 3,5,6-triaryl-1,2,4-triazine **7** [48]. Catechol (**8**) reacts with rhodium trichloride to yield $[Rh(HL)Cl_3(H_2O)]^-$ and $[Rh(L)Cl_3(H_2O)]^{2-}$ (H_2L = **8**), and the ligand has been suggested as a colorimetric reagent for rhodium [49].



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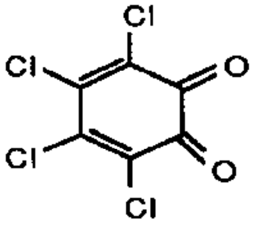

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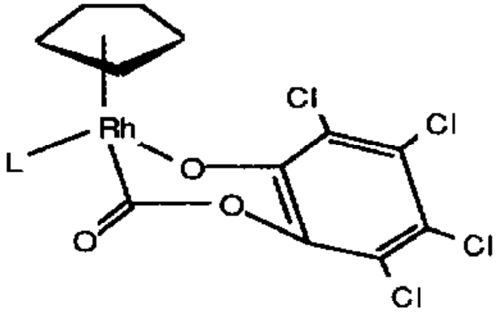
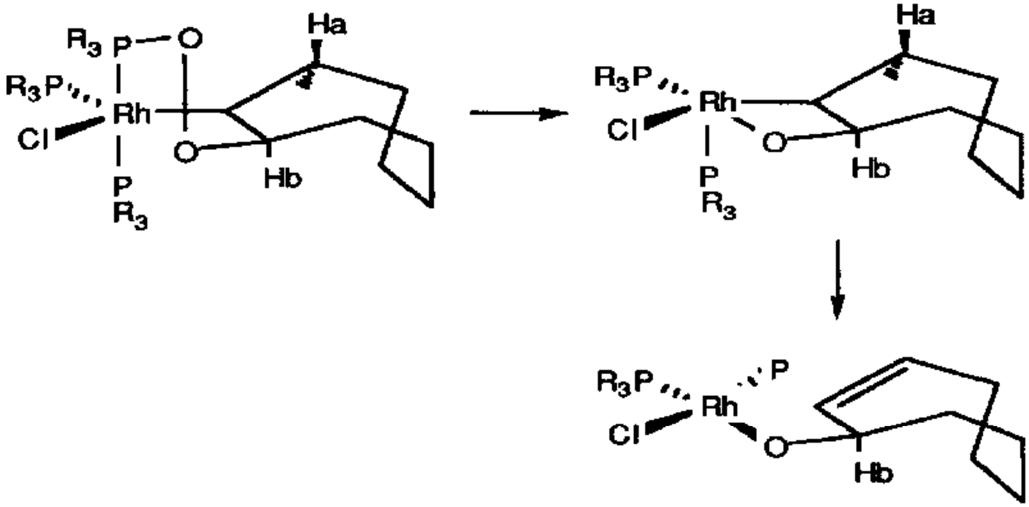


(10)

Tetrachlorobenzo-1,2-quinone (**9**) reacts with [Rh(CO)L(cp)] (L = CO or PPh_3) by attack at the carbonyl ligand to yield [RhL(cp)($C_7Cl_4O_3$)] (**10**). A crystal structural analysis of the complex with L = PPh_3 confirmed the structure; the Rh-C distance to the acyl carbonyl is 1.994(12) Å, longer than in the parent carbonyl complex. The {RhO_2C_3} ring adopts a distorted boat conformation. Treatment of [RhL(cp)($C_7Cl_4O_3$)] with HBF_4 cleaves the C-OAr bond, and leads to [RhL(cp)(OC_6Cl_4OH)(CO)], whilst reaction with CH_2Cl_2 yields [Rh(cp)($C_6Cl_4O_2$)] (containing a chelated catecholato ligand) in the case of L = CO, or [RhL(cp)($C_6Cl_4O_2$)] in the case of L = PPh_3. The ligand exchange reactions (with PPh_3, $AsPh_3$ or $P(OPh)_3$) and electrochemical properties of these rather unusual complexes were investigated [50].

The reaction of cyclooctene to 3-hydroxycyclooctene (Scheme 2) by dioxygen and triphenylphosphine is catalysed by [RhCl(PPh_3)O_2]; the reaction is truly catalytic, and no reaction occurs in the absence of the metal complex.

Scheme 2



Scheme 3

A mechanism has now been proposed for the reaction which involves Rh–C bonded peroxy and alkoxy intermediates (Scheme 3). This scheme is supported by deuteration studies [51].

2.2.2.3 Complexes with sulphur donor ligands

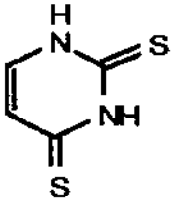
The extraction of rhodium(III) from an aqueous acetate/phosphate medium by unithiol ($HSCH_2CH(SH)CH_2SO_3Na$) has been investigated [52]. Rhodium trichloride reacts with 2-aminoethanethiol to yield $[RhL_3]$ ($HL = HSCH_2CH_2NH_2$), which may be oxidised by hydrogen peroxide to a mixture of complexes $[Rh\{S(=O)CH_2CH_2NH_2\}_n\{S(=O)_2CH_2CH_2NH_2\}_{3-n}]$ [53]. Extraction of aqueous nitric acid solutions containing $[Rh(NO_2)_6]^{3-}$ or $[Rh(H_2O)_6]^{3+}$ by R_2S ($R = PhCH_2$, ^nBu or ^noct) has been studied; the extraction is complicated by nitric acid oxidation of the sulphide to sulphoxide according to

$$R_2S + NO_3^- \longrightarrow R_2SO + NO_2^-$$

Associated with this oxidation is the coordination of the nitrite which is formed to the rhodium - all-in-all, not an overly efficient extractant [54].

The aquation of *trans*-[Rh(Hdmg)$_2$X(tu)] (H_2dmg = MeC(=NOH)C(=NOH)Me, tu = H_2NCSNH_2, X = Br or Cl) has been investigated [55]. A comparison of the thiosemicarbazide complexes [ML_3]Cl_3 (L = $H_2NNHCSNH_2$, M = Rh or Co) has been reported [56]. Dithiouracil (**11**) reacts with rhodium trichloride to yield {RhL_3Cl_3} (L = **11**) [57].

A variable temperature ^{1}H n.m.r. study of $CDCl_3$ solutions of [RhL_3] (HL = MePhNCS$_2$H) over the range -34 to +51° has been reported. The complex is mobile and isomerises by rotation about the C-N bond; the $\Delta G^\ddagger$ value of 61.5±4.2 kJ mol^{-1} is larger than that reported for the corresponding iron(II) and iron(III) complexes, but comparable to those for the cobalt(III) and iron(IV) analogues [58]. Rhodium(III) complexes with PhNHCS$_2$Et have been reported; the ligand is monodentate and bonds to the metal through the thiocarbonyl sulphur atom [59]. The orange, insoluble, and probably polymeric, complex {RhL_2Cl} (HL = **12**) is obtained from the reaction of rhodium trichloride with **12** [60].



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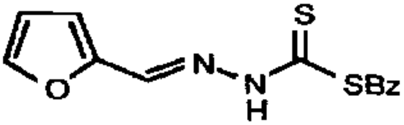

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2.2.3 Complexes with Group 15 donor ligands

2.2.3.1 Complexes with ammines, amines and amides

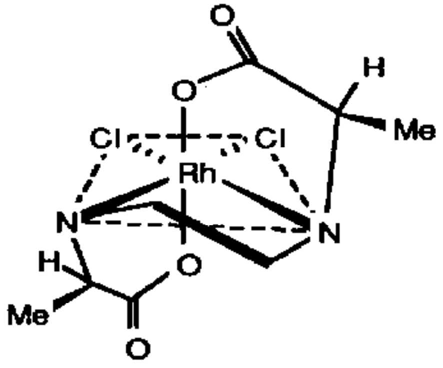
Numerous studies of the aquation of rhodium(III) ammine complexes have been reported, and are discussed in detail in earlier sections. Complexes which have been investigated include $[Rh(NH_3)_6]^{3+}$ [23,24,36], $[Rh(NH_3)_5Cl]^{2+}$ [20,23,25,26,31,36], *trans*-$[Rh(NH_3)_4Cl(CN)]^+$ [31], $[Rh(NH_3)_5(H_2O)]^{3+}$ [38], $[Rh(NH_3)_5I]^{2+}$ [19,23,24], $[Rh(NH_3)_5py]^{3+}$ [23], $[Rh(NH_3)_5(SO_4)]^+$ [23,24], $[Rh(NH_3)_4Cl_2]^+$ [27,30], $[Rh(RNH_2)_4Cl_2]^+$ [28,32], $[Rh(NH_3)_4(H_2O)Cl]^{2+}$ [29,32], $[Rh(NH_3)_4(H_2O)H]^{2+}$ [39], $[Rh(NH_3)_5H]^{2+}$ [39], $[Rh(NH_3)_4(H_2O)_2]^{3+}$ [40], $[Rh(NH_3)_5CN]^{2+}$ [36], $[Rh(NH_3)_5(Him)]^{3+}$ [61] and $[Rh(NH_3)_5(O_3SCF_3)]^{2+}$ [44].

The photolysis of aqueous solutions of $[Rh(en)_2X(NO_2)]^+$ in the presence of O_2 leads to the superoxo complexes $[Rh(en)_2(OH_2)O_2]^{2+}$ and the peroxy compound $[X(en)_2Rh(\mu\text{-}O_2)Rh(en)_2(OH_2)]^{4+}$. The complexes exhibit nitro-nitrito linkage isomerism. The superoxo complex was characterised as such by e.s.r. spectroscopy, and acts as a one electron oxidising agent [41]. In contrast, photoaquation of *cis* or *trans* $[RhL_2X_2]^+$ [L = $H_2NCH_2CH_2CH_2NH_2$, X = Cl or Br) gives the simple substitution compound, $[RhL_2(H_2O)X]^{2+}$ [33]. The outer sphere complexes formed by $[Rh(en)_3]^{3+}$ with a range of carboxylates, RCO_2^-, have been investigated. The stability constants were in the order (R =) CCl_3 > CH > Me > Et [62]. The formation of outer sphere complexes with $[H_2edta]^{2-}$ has also been demonstrated [76]. The solubility product of the complex $[Rh(en)_3][Fe(CN)_6]$ has also been reported [62].

Four diastereomeric *tris* complexes have been isolated from the reaction of rhodium(III) with *racemic* (±)-$H_2NCHMeCHMeNH_2$. A crystal structural analysis of the complex *lel,lel,lel*-$[RhL_3]Br_3$ was also reported. The *ob* conformation is enthalpically disfavoured, but the increase in enthalpy associated with each new *ob* ring is only about 1/3 of that observed for the cobalt(III) complex. The structures of the diastereomers were assigned on the basis of ^{13}C n.m.r. spectroscopic studies [63]. The relative percentages of the various diastereomers for the cobalt(III) and rhodium(III) complexes are given below

	Co	Rh
lel,lel,lel	60	27
lel,lel,ob	28	38
lel,ob,ob	12	29
ob,ob,ob	<1	6

The reaction of rhodium trichloride with the lithium salt of ethylenediamine-*N,N'*-di(*S*)-α-propionic acid results in the formation of only the Δ-*cis*-α **(13)** and Λ-*cis*-β **(14)** isomers of the complex $[RhLCl_2]^-$ (H_2L = (*SS*)-$HO_2CCHMeNHCH_2CH_2NHCHMeCO_2H$). The structures were assigned on the basis of n.m.r., o.r.d. and c.d. spectroscopy [64]. The complex $\{RhCl_3.L.3H_2O\}$ (L = hexamethylenetetramine, **15**) has been reported [65], as has an *S*-bonded complex of the thiocarbamate $PhNHCS_2Et$ [59]. The oxidative addition of H_2S to $[RhCl(PPh_3)_3]$ yields $[Cl(PPh_3)_2HRh(\mu\text{-}SH)_2RhH(PPh_3)_2Cl]$; the non-bonded Rh...Rh and S...S distances are 3.637(1) and 3.083(2) Å respectively [128].



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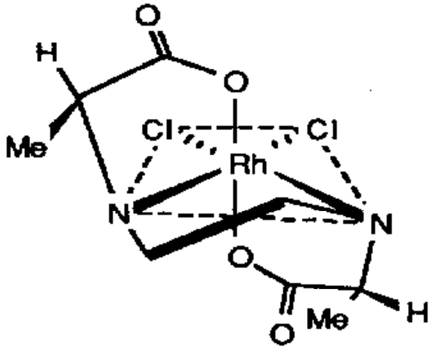

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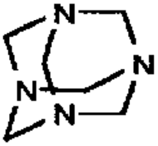
The formation of complexes with $HSCH_2CH_2NH_2$ and their oxidation to mixtures of coordinated sulphoxide and sulphone has been discussed earlier [53]. The complex $[RhLClH_2]$ (L = $Ph_2PCH_2CH_2NHCH_2CH_2PPh_2$) is obtained by hydrogenation of [RhClL], and is an active catalyst for the hydrogenation of cyclohexene [66].



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2.2.3.2 *Complexes with amino acids and aminopolycarboxylic acids*

The reaction of $[NH_4]_3[RhCl_6]$ with glycine in the solid state leads to isomeric complexes of the formulation $\{Rh(HL)_nCl_3\}$ ($HL = H_2NCH_2CO_2H$). These complexes have been shown to contain various ratios of *O* bonded and *N* bonded glycine, $[Rh(H_2\mathit{N}CH_2CO_2H)_3(H_3NCH_2COO)_2Cl]Cl_2$ and $[Rh(H_2\mathit{N}CH_2CO_2H)_2(H_3NCH_2COO)_2Cl_2]Cl$ [7]. The thermal decomposition of the complexes $[RhL_3].H_2O$, $\{Rh(HL)_3Cl_3\}$ (L = glycine, $H_2NCH_2CO_2H$), $[RhL_3].2H_2O$ and $\{Rh(HL)_3Cl_3\}$ (L = β-alanine, $H_2NCHMeCO_2H$) has been studied [67].

A structural analysis of the complex $Na[RhL].3H_2O$ ($H_4L = (HO_2CCH_2)_2NCH_2CH_2CH_2N(CH_2CO_2H)_2$), obtained from the $(-)_{589}$ salt of the acid, has been reported. The metal is in a distorted octahedral environment, with Rh-O distances in the range 2.002(2) to 2.050(2) Å and Rh-N distances of 2.033(3) and 2.031(3) Å [68].

2.2.3.3 *Complexes with imines and related ligands*

The reaction of $[Rh(HL)_2Me(H_2O)]$ (H_2L = HON=CMeCMe=NOH) with a range of nucleophiles to yield $[Rh(HL)_2MeNu]^{n-}$ (Nu = N_3, SCN, I, py or tu) has been studied. The rate law was of the form

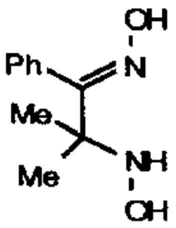
$$\rho = k_{obs}[Rh(HL)_2Me(H_2O)]$$

where

$$k_{obs} = k_1[L] + k_{-1}$$

The overall rates for the methylrhodium(III) complex were about 10^2 times those of the corresponding methylcobalt(III) compounds, and about

10^5 times greater than those in rhodium(III) tetra(sulphonatophenyl)porphyrin complexes. The authors conclude that the methyl group has a strong *trans* labilising effect, and that the reaction is dissociatively activated, although the large negative entropy of activation does not really appear to be in accord with this [69].



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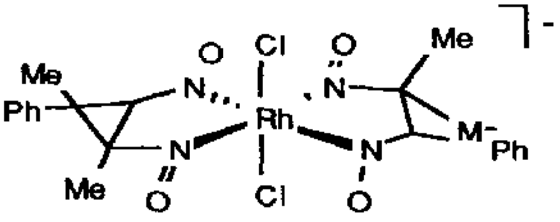

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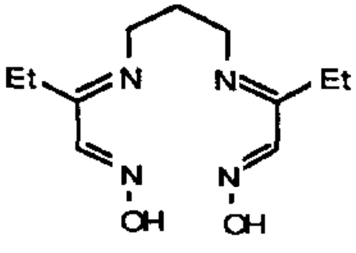
The reaction of rhodium trichloride with HONHCMe$_2$CPh=NOH (**16**) results in an oxidative dehydrogenation of the ligand and the formation of the novel complex H[Rh{N(=O)CMe$_2$CPh=N(O)}$_2$Cl$_2$] (**17**), which was assigned the structure on the basis of vibrational and n.m.r. spectroscopy and conductivity measurements [70]. The ligand HON=CHCEt=NCH$_2$CH$_2$CH$_2$N=CEtCH=NOH (**18**) forms the complex [Rh(HL)Cl$_2$] (H$_2$L = **18**) (**19**) which has been structurally characterised. The



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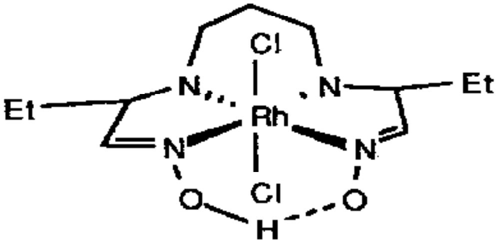

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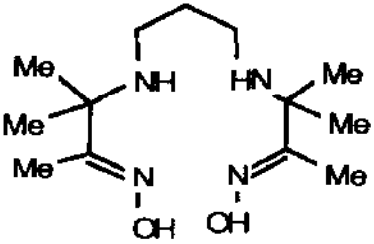
Rh-N_{imine} distances of 2.00(2) Å and Rh-N_{oxime} distances of 1.976(3) Å are slightly longer than those in the isostructural conalt(III) complex (1.917(4) and 1.887(4) Å respectively. The average Rh-Cl distance in the compound is 2.335 Å [71]. The related ligand $HON{=}CMeCMe_2NHCH_2CH_2CH_2NHCMe_2CMe{=}NOH$ (**20**) also forms a *trans*-[Rh(HL)Cl_2] (H_2L = **20**) complex (**21**) which has been structurally characterised [72]. The related bidentate ligand $HON{=}CMeCMe_2NH_2$ (**22**) also forms a structurally characterised complex *trans*-[Rh(HL)Cl_2] (H_2L = **22**) (**23**) [72].



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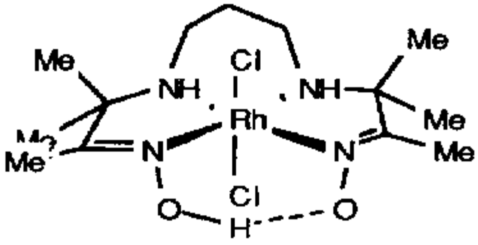

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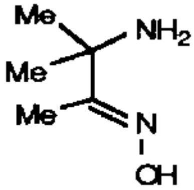

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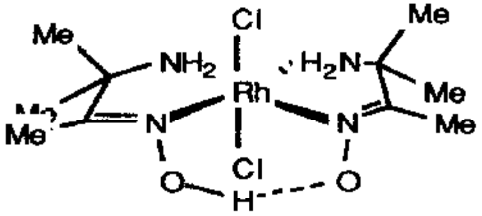


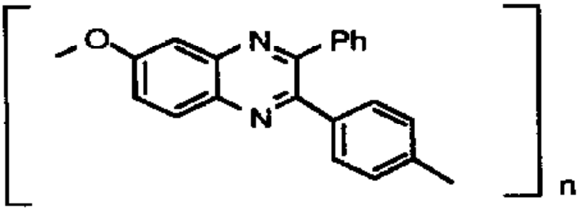
(23)

The formation of complexes with **12** was discussed in an earlier section [60].

2.2.3.4 *Complexes with nitrogen heterocyclic ligands*

The n.m.r. properties of the complex [Rh(NH_3)(Him)$]^{3+}$ and a number of methylated derivatives have been investigated. The pK_a of the coordinated imidazole ligand is 9.97, which is very similar to the value of 10.05 reported for the analogous iridium(III) complex [61]. A number of homoleptic complexes $[RhL_6]^{3+}$ have been reported. The reaction of 1-methylimidazole with $[Rh(H_2O)_6]^{3+}$ leads to $[RhL_6]^{3+}$; other complexes $[RhL_4X_2]X$ (X = halide, L = 1-methylimidazole, 1-vinylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 1-vinyl-2-methylimidazole, 2-*iso*-propylimidazole or 1-*n*-butylimidazole) are made by the reaction of rhodium trihalides with the appropriate ligands [73].

The crystal structure of the complex *mer*-$[Rh(py)_3Cl_3]$ has been reported; the metal is in an octahedral geometry with Rh-Cl_{av} and Rh-N_{av} distances of 2.3345 and 2.057(13) Å [35]. The coordinating quinoxaline-based polymer (**24**) forms a complex with rhodium trichloride which has found application as a catalyst [74]. Oxidative addition of 8-phenylacetylquinoline (**25**) to $[(C_2H_4)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2]$ gives a polymer, which is cleaved upon treatment with pyridine to yield $[RhL(PhCH_2)Cl(py)_2]$ (**26**) (HL = 8-quinolinealdehyde). The latter complex has been structurally



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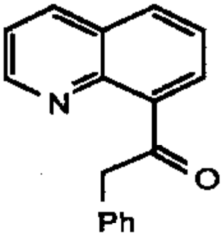

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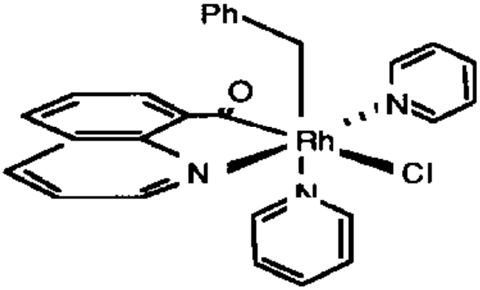


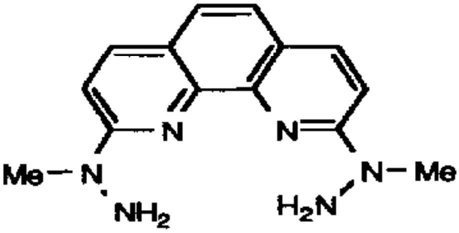
(**26**)

characterised; the metal has inserted into the C–C bond between the benzyl group and the carbonyl group to give an acyl complex [75].

The equilibrium constants for the formation of outer sphere complexes between $[Rh(phen)_3]^{3+}$ and $[H_2edta]^{2-}$ have been determined [76]. Similar outer sphere complexes are formed with chloride, bromide, iodide or perchlorate, with the values of K_{OS} increasing in the order [77]

$$ClO_4 > I > Br > Cl$$

The photophysics of $[Rh(phen)_3]^{3+}$ have been investigated in liquid aqueous phase at room temperature and in water/glycerol glass at 77 K by laser flash photolysis. The excited state is a π–π^* triplet state which is in fast thermal equilibrium with a metal *d–d* triplet. The inter system crossing is very efficient with $\Phi = 1$ [78]. The emission is from ligand centred states only in the case of $[RhL_3]^{3+}$ (L = phen or bipy), but is from both metal and ligand centred states with L = 3,3'-dimethyl-2,2'-bipyridine [81]. The complex $[RhL_2Cl_2]^+$ (L = 3,3'-dimethyl-2,2'-bipyridine) also emits from a ligand centred state [81]. Rhodium(III) complexes of 2,2'-bipyridine have been shown to absorb on platinum/gold binary electrodes [79]. The reaction of rhodium trichloride with 2,9-bis(α-methylhydrazino)-1,10-phenanthroline **(27)** results in the formation of $[RhLCl_2]^+$. This complex has been structurally characterised; the metal is in a distorted octahedral environment with the N_4 donor ligand occupying the equatorial plane, Rh-Cl 2.343(3), 2.312(3) Å, $Rh\text{-}N_{phen}$ 1.928(6), 1.945(7) Å, $Rh\text{-}N_{hyd}$ 2.154(8), 2.150(7) Å [80].



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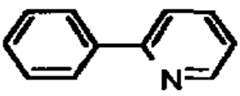
Rhodium trichloride reacts with 2-phenylpyridine (**28**) to yield the cyclometallated (**30**) complex [LRh(μ-Cl)$_2$RhL] (HL = **28**). An exactly analogous complex (**31**) is obtained from the reaction with benzo[h]quinoline (**29**). These rhodium(III) dimers emit light after photoexcitation in glassy solution at 77 K, but do not emit



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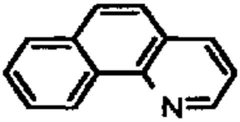

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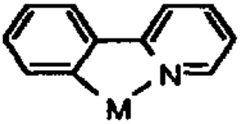

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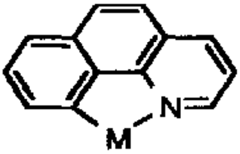
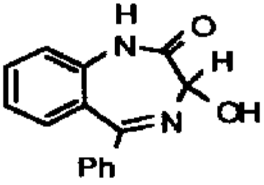


(31)

in liquid CH_2Cl_2 solution at 295 K. The emitting state is thought to be an intraligand π-π^* state in contrast to the MLCT(d-π^*) state seen with the iridium complexes [82].

The formation of a 1:1 complex with dithiouracil has already been mentioned [57]. The complexes {$RhL_3X_3.nH_2O$} and {$RhLI_3$} (L = **32**, X = Cl or Br) have also been described [83].

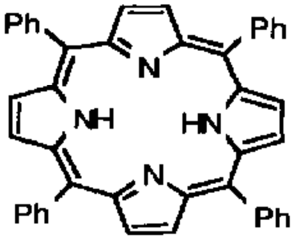


(**32**)

2.2.3.5 *Complexes with nitrogen donor macrocyclic ligands*

There has been considerable interest in the photochemical and photophysical properties of rhodium(III) complexes of phthalocyanine (**1**). The complex [Rh(pc)(MeOH)X] (X = Cl or Br) may be oxidised to [Rh(pc)(MeOH)]$^+$ by either chemical or electrochemical methods [5]. The self exchange reaction between [Rh(pc)(MeOH)X] and its ${}^3\pi-\pi^*$ state has been investigated; the rate constant of 0.22×10^7 dm^3 mol^{-1} s^{-1} is in accord with Marcus-Hush theory [84]. The photoabstraction of hydrogen by [Rh(pc)(MeOH)X] has also been studied. At high photonic flux, biphotonic processes may be detected giving rise to $n-\pi^*$ rather than $\pi-\pi^*$ states [85].

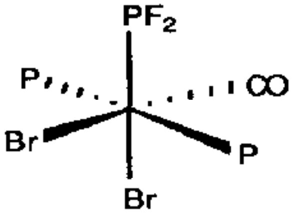
Rhodium(III) complexes of tetraphenylporphyrin (**33**) are of use as catalysts for photodehydrogenation and photohydrogenation reactions. Hydrido intermediates have been detected in the dehydrogenation of *isopropyl* alcohol by [Rh(tpp)Cl]. It is proposed that a radiationless transition from the photoexcited π^* tpp to the σ^* state in a {(tpp)*Rh-H..H-Rh(tpp)} species is responsible for dihydrogen evolution [86,87]. In the case of photodehydrogenation of cyclohexanol by [Rh(tpp)Cl], reduced tpp ligands are found in the products. The system is a reasonably efficient catalyst, with a turnover of 3430 after 530 h [88].



(**33**)

2.2.3.6 Complexes with phosphines and arsines

The reaction of $[Rh(PEt_3)_2(CO)Br]$ with PF_2Br gives the five-coordinate rhodium(I) complex $[Rh(PEt_3)_2(CO)Br(PF_2Br)]$, which is converted thermally to $[Rh(PEt_3)_2(CO)Br_2(PF_2)]$ (**34**). The



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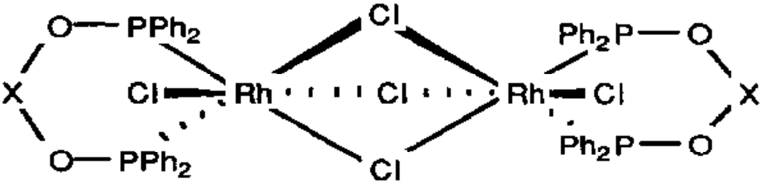
analogous complex [Rh(PEt$_3$)$_2$(CO)I$_2$(PF$_2$)] is obtained from the reaction of PF$_2$I with [Rh(PEt$_3$)$_2$(CO)I]. A similar reaction occurs with PF$_2$Cl and [Rh(PEt$_3$)$_2$(CO)Cl], although it is complicated by halogen exchange reactions, and the products are [Rh(PEt$_3$)$_2$(CO)Cl$_2$(PFCl)] and [Rh(PEt$_3$)$_2$(CO)Cl$_2$(PCl$_2$)]; this latter complex is also obtained from the reaction of PCl$_3$ with [Rh(PEt$_3$)$_2$(CO)Cl] [89].

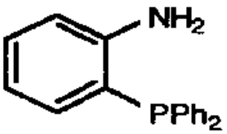
The reaction of PPh$_2$Cl with [(cod)Rh(μ-Cl)$_2$Rh(cod) in aqueous methanol results in hydrolysis of the ligand, and the formation of the complex [{H(OPh$_2$P)$_2$}ClRh(μ-Cl)$_3$RhCl{H(OPh$_2$P)$_2$}] (**35**, X = H). The two rhodium atoms are in octahedral environments,



(35)

with the two octahedra face sharing a *Cl$_3$* face. The hydrogen bonded phosphines form a bidentate chelating ligand. The Rh-Rh non-bonded contact is 3.2662(16) Å. The complex reacts with BF$_3$ to replace the hydrogen bond by a BF$_2$ group (**35**, X = BF$_2$). If a greater amount of methanol is present in the original preparation, a second product, [RhHCl{PPh$_2$(OMe)}$_4$]$^+$ is obtained. The coordinated ligand in [RhHCl{PPh$_2$(OMe)}$_4$]$^+$ is not hydrolysed by water under the reaction conditions for the formation of **35** [90].

Complexes with the *NP*$_2$ donor, $Ph_2PCH_2CH_2NHCH_2CH_2PPh_2$, have already been described [66]. The rhodium(I) complex $[Rh(HL)_2]^+$ (HL = **36**) undergoes an oxidative addition with HCl to yield $[RhH(HL)_2Cl]Cl$, which reacts with O_2 to give $[Rh(HL)LCl_2]$ (**37**), which has been structurally characterised. A mechanism for the formation of this product was proposed, the key intermediate of which is a rhodium(III) hydroperoxide [91]. Complexes with the related arsenic containing ligand **38** have also been studied [92].



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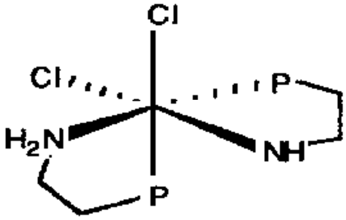

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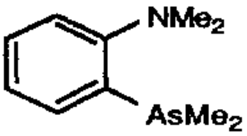


(38)

2.2.4 Complexes with Group 14 donor ligands

A number of examples of compounds incorporating carbon-bonded ligands have been discussed elsewhere in this review [50,51,69,75,82].

The addition of MeI to $[Rh(CO)_2I_2]^-$ is promoted by iodide or by 1-methylimidazole, and it is suggested an equilibrium is set up between

$[Rh(CO)_2LI]$, $[Rh(CO)_2LI_2]^-$ and $[Rh(CO)_2I_2]^-$, although other species are also involved [93]. The effect of iodide has been independently confirmed, and it has also been noted that acetate has an effect on the reaction. It is suggested that the MeI can add to either $[Rh(CO)_2I_2]^-$ or $[Rh(CO)_2LI_2]^-$ [94]. These observations are of relevance to the Monsanto acetic acid process.

2.3 RHODIUM(II)

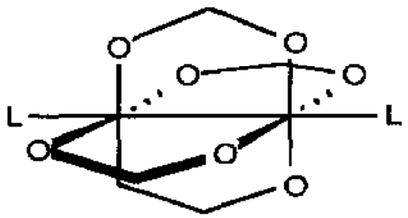
The majority of reports concerning rhodium(II) compounds have dealt with metal-metal bonded dirhodium complexes. The commonest structural feature is a bridging ligand in which the two donor atoms are separated by one non-coordinating atom.

2.3.1 Complexes with bridging **O,O'***-donor ligands*

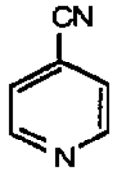
The reaction of $[Rh_2(OAc)_4]$ with sulphuric acid gives the complex $[Rh_2(OAc)_2(HSO_4)_2]$ with two bridging acetate and two bridging bisulphate ligands. Upon treatment of $[Rh_2(OAc)_2(HSO_4)_2]$ with pyridine, two processes occur; the bisulphate ligands are deprotonated to bridging sulphato groups, and pyridine molecules become bound in the terminal sites, to yield $[pyH]_2[Rh_2(OAc)_2(SO_4)_2(py)_2]$. The parent compound $[Rh_2(OAc)_2(SO_4)_2]^{2-}$ has also been described. An analogous reaction occurs when $[Rh_2(HSO_4)_4(H_2O)_2]$ is treated with pyridine to yield $[pyH]_4[Rh_2(SO_4)_4(py)_2]$. Reaction of $[Rh_2(OAc)_2(HSO_4)_2]$ with thiourea gives $\{Rh_2(OAc)_2(HSO_4)_2.H_2O.3tu\}$, although it is not clear whether this possesses metal-bound thiourea ligands, or if it is an inclusion compound. Presumably the complex $\{Rh(HSO_4)_4.H_2O.4.5tu\}$ formed from the reaction of $[Rh_2(HSO_4)_4(H_2O)_2]$ with thiourea in acetone is similar. A slightly different product is obtained when the reaction is performed in water, when $\{Rh_2(SO_4)_2.3H_2O.4tu\}$ is obtained. The hydrogen phosphate analog $\{Rh_2(HPO_4)_2.2H_2O.3.5tu\}$ is obtained from the reaction of $[Rh_2(H_2PO_4)_4(H_2O)_2]$ with thiourea [96].

Single crystal polarised electronic spectra of $[Rh_2(OAc)_4(H_2O)_2]$ and $Li_2[Rh_2(OAc)_4Cl_2].8H_2O$ have been reported. A single crystal structural analysis of $Li_2[Rh_2(OAc)_4Cl_2].8H_2O$ has also been performed.

The Rh-Rh distance in the $[Rh_2(OAc)_4Cl_2]^{2-}$ anion (**39**, L = Cl) is 2.397(1) Å [97]. The axial adduct with 4-cyanopyridine (**39**, L = **40**) has also been structurally characterised, and has an Rh-Rh distance of 2.393(1) Å [98]. The carboxylate ligands in $[Rh_2(OAc)_4]$ undergo a metathesis reaction upon treatment with other carboxylic acids and anhydrides. Thus, the reaction of $[Rh_2(OAc)_4]$ with a mixture of propanoic acid and propanoic anhydride results in the formation of $[Rh_2(O_2CEt)_4]$. This complex has been shown to form adducts with *N*-methylimidazole, pyridine, triphenylphosphine, acetonitrile, tetrahydrothiophen, dmso, pyridine *N*-oxide, methanol and CO. Electrochemical oxidation of $[Rh_2(O_2CPr)_4L_2]$ yields the formally {Rh(II),Rh(III)} complexes $[Rh_2(O_2CPr)_4L_2]^+$, which have been characterised by e.s.r. spectroscopy [99].

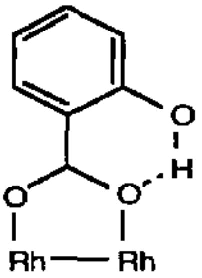


(**39**)



(**40**)

The complex $[Rh_2L_4(EtOH)(H_2O)]$ (HL = salicylic acid, 2-hydroxybenzoic acid) has been structurally characterised. The Rh-Rh distance is within the usual range expected for diaxial adducts of 2.385(2) Å. The phenolic OH group of the salicylate is hydrogen bonded to one of the carboxylato oxygen atoms (**41**) [100].



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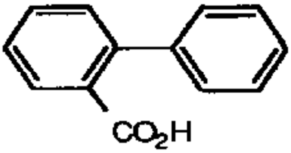
The metathesis of $[Rh_2(OAc)_4]$ with biphenyl-2-carboxylic acid (**42**) yields the expected complex, which was structurally characterised as the *bis*acetonitrile adduct *tris* benzene solvate, $[Rh_2L_4(MeCN)_2].3PhH$ (HL = **42**). The orientation of the *ortho* phenyl substituents are of some interest; two are oriented in the equatorial region, whilst the other two are oriented towards the end of the molecule. The axial acetonitrile ligands (Rh-N, 2.333(3) Å) and carboxylate ligands (Rh-O, 2.026 - 2.051 Å) are otherwise normal. The Rh-Rh distance is 2.396(1) Å. An analogous metathesis occurs with adamantane-1-carboxylic acid (**43**) to yield



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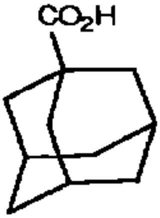
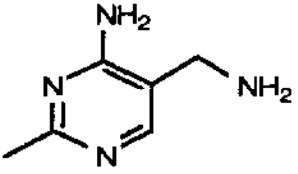


(43)

$[Rh_2L_4(MeOH)_2].5MeOH$ (HL = **43**). This complex exhibits a very short Rh-Rh distance of 2.371(2) Å, with otherwise normal interactions with the axial methanol (Rh-O, 2.296 Å) and carboxylates (Rh-O, 2.008 - 2.066 Å). Attempted metathesis of $[Rh_2(OAc)_4]$ with Ph_3CCO_2H results in only partial replacement of acetate, and the formation of $[Rh_2(OAc)_2(O_2CCPh_3)_2(MeCN)_2].PhMe$. The acetato and triphenylacetato ligands are mutually *cis*. The two axial acetonitrile ligands are no longer equivalent, and Rh-N distances of 2.21(1) and 2.17(1) Å are observed. The Rh-Rh distance is 2.388(2) Å [101]. The direct reaction of rhodium trichloride with $Na(O_2CCH{=}CHPh)$ gives the green rhodium(II) cinnamato complex $[Rh_2(O_2CCH{=}CHPh)_4]$ which forms diaxial adducts with pyridine, imidazole and *N,N*-dimethylacetamide [102].

The interaction of rhodium(II) complexes with thiamine has been modelled in the reaction of $[Rh_2(OAc)_4]$ with 4-amino-5-aminomethyl-2-methylpyrimidine (**44**). The product of the reaction is a polymer of the form shown in **45**. This has been structurally characterised; two separate Rh-Rh distances of 2.405(1) and 2.404(1) Å have been observed [103]



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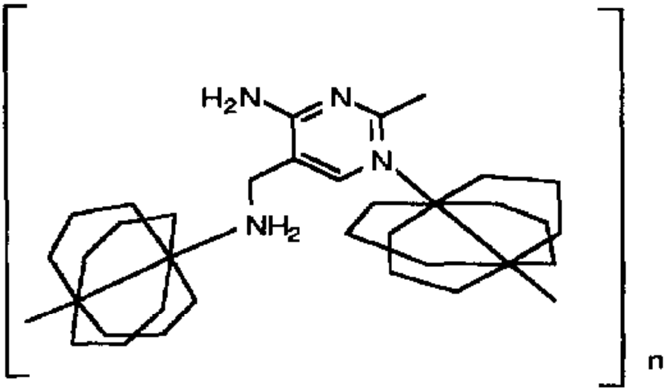

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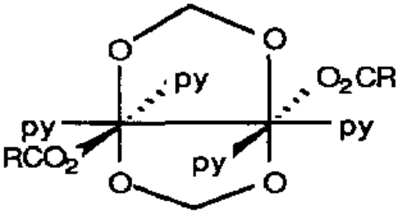
The electrooxidation of a range of $[Rh_2(O_2CR)_4L_2]$ complexes (R = Me, *t*-Bu, *n*-Pr, Ph, $MeOCH_2$ or $ClCH_2$; L = 3,5-Cl_2py, 3-CNpy, 3-Brpy, 3-Acpy, py, 4-Mepy or 3,4-Me_2py) to the radical cations has been studied. The observed potentials were related to the strength of the Rh-Rh bonds in the parent compounds [104].

Compound	Rh-Rh Å	Reference
$[Rh_2(OAc)_4Cl_2]^{2-}$	2.397	[97]
$[Rh_2(OAc)_4(4\text{-}CNpy)_2]$	2.393	[98]
$[Rh_2(sal)_4(EtOH)(H_2O)]$	2.385	[100]
$[Rh_2(bpa)_4(MeCN)_2]$	2.396	[101]
$[Rh_2(adam)_4(MeOH)_2]$	2.371	[101]
$[Rh_2(OAc)_2(O_2CCPh_3)_2(MeCN)_2]$	2.388	[101]
$[\{Rh_2(OAc_4)(\mathbf{44})\}_n]$	2.405,2.404	[103]
$[Rh_2(OAc)_2(Ph_2PC_6H_4)_2(OAc)_2]$	2.508	[106]
$[Rh_2(O_2CCF_3)_4(\mathbf{49})_2]$	2.417	[110]
$[Rh_2(O_2CC_3F_7)_4(\mathbf{49})_2]$	2.424	[110]
$[Rh_2(PhCONH)_4(py)_2]$	2.437	[115]
$[Rh_2(PhCONH)_4(SbPh_3)_2]$	2.463	[115]
$[\{Rh_2(MepyO)_4\}]$	2.369	[118]
$[\{Rh2(MepyO)_3(OTs)\}_2]$	2.377, 2.376	[118]
$[Rh_2(FpyO)_4(dmso)]$	2.410	[119]
$[Rh_2(OAc)_3(\mathbf{56})]^+$	2.405	[122]
$[Rh_2(\mathbf{58})_3Cl_2]^{2+}$	2.5668	[123]

Rhodium-rhodium bond lengths in structurally characterised rhodium(II) dimers

A number of axial adducts of $[Rh_2(O_2CCF_3)_4]$ have been described. and the expected $[Rh_2(O_2CCF_3)_4L_2]$ complexes obtained. However, a number of other types of reaction have also been detected. Decomposition occurred upon treating $[Rh_2(O_2CCF_3)_4]$ with N-methylimidazole in piperidine, and monomers appear to be formed upon reaction with triphenylphosphine. Treatment with pyridine gives the complex $[Rh_2(O_2CCF_3)_4(py)_4]$ **(46)**, in which two of the trifluoroacetato groups are bidentate and two are monodentate. The reaction with *tert*-butylisocyanide proceeds in a similar manner, but a mixture of isomers of $[Rh_2(O_2CCF_3)_4(t\text{-}BuNC)_4]$ is obtained. Upon reaction with PMe_2Ph, the complex $[Rh_2(O_2CCF_3)_4(PMe_2Ph)_2]$ **(47)** is obtained; once again, this complex possesses two bidentate and two monodentate trifluoroacetate ligands [105].

Treatment of $[Rh_2(OAc)_4(MeOH)_2]$ with triphenylphosphine might be expected to lead to a simple displacement of the axial ligands by triphenylphosphine. However, the product is the compound $[Rh_2(OAc)_4L_2]$ **(48)** (HL = Ph_3P). This has been structurally characterised, and shown to contain two *cis*-bidentate acetate groups, two axial monodentate acetates and two head-to-tail *cis* cyclometallated triphenylphosphines. The Rh-Rh distance is rather longer than in the parent acetate and is found to be 2.508(1) Å [106].



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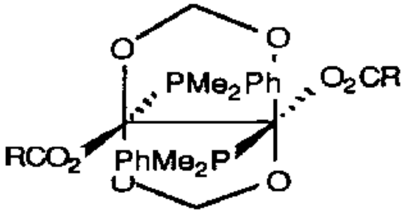

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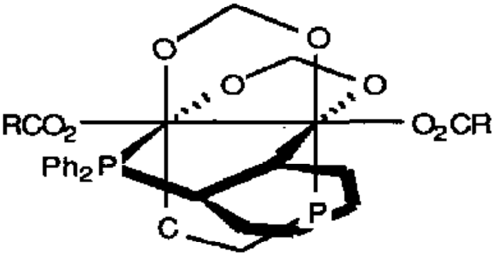

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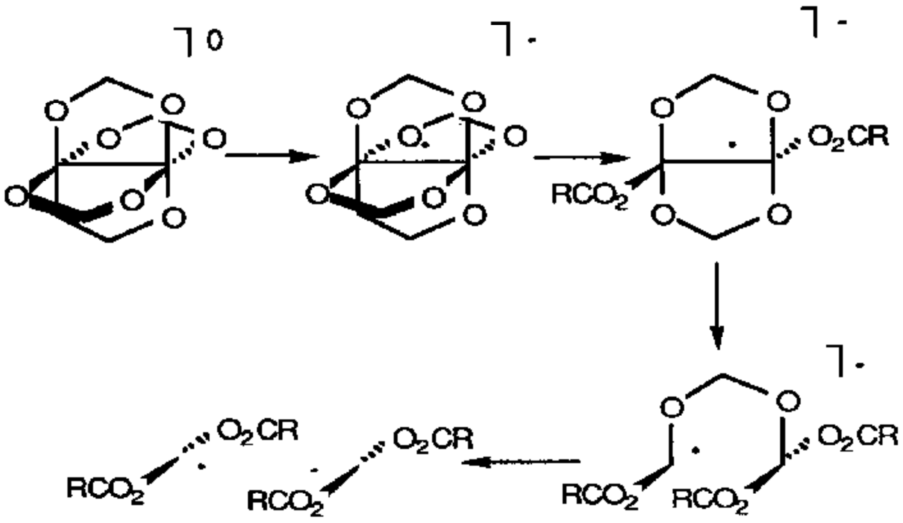
Irradiation of $[Rh_2(O_2CR)_4]$ (R = Me or CF_3) with ^{60}Co γ radiation results in electron capture and the formation of transient $[Rh_2(O_2CR)_4]^-$ species. These were shown by e.s.r. spectroscopy to have the electron localised in d_{z^2} orbitals. The decomposition pathway involves cleavage of the Rh-Rh bond, and was thought to proceed as shown in Scheme 4.

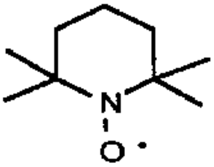


Scheme 4

The reaction of $[Rh_2(O_2CR)_4]$ (R = H or Me) with acetamide at room temperature results in the formation of the axial adducts $[Rh_2(O_2CR)_4(MeCONH_2)_2]$ [25].

The first example of olefins binding to rhodium(II) dimers has been reported in the formation of 1:1 adducts from the reaction of $[Rh_2(O_2CCF_3)_4]$ with 2,5-dimethylhexa-2,4-diene. The stability of the olefin adducts vary considerably from styrene (K_{eq} = 6.1) to 2-methoxypropene (K_{eq} = 578) [108]. The dications $[Rh_2(O_2CPr)_2]^{2+}$ are formed in the reaction of $[Rh_2(O_2CPr)_4]$ with CF_3SO_3H or HBF_4 [109].

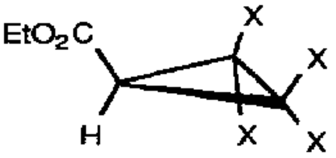
Complexes with nitroxyl ligands in the axial sites have been prepared by the reaction of $[Rh_2(O_2CR)_4]$ (R = CF_3, n-C_3F_7 or C_6F_5) with 2,2,6,6-tetramethylpiperidineoxyl (**49**). Structural analyses of the compounds $[Rh_2(O_2CR)_4L_2]$ (R = CF_3 or n-C_3F_7; L = **49**) have



(49)

been reported; the Rh-Rh distances are relatively long, Rh-Rh, 2.417(0) (CF_3), 2.424(1) (n-C_3F_7). This is in accord with the magnetic properties of the complexes which have been shown to exhibit large anti-ferromagnetic exchange interactions. This is interpreted in terms of superexchange through the metal-metal bond, as the radical centres are 6.8 Å apart [110].

The pivalate complex $[Rh_2(O_2CR)_4]$ (R = *t*-Bu) is prepared by the reaction of pivalic acid and sodium pivalate with rhodium trichloride in ethanol, and acts as a catalyst for the *cyclo*addition of *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, 1,1-dichloroethene or vinyl bromide to ethyl diazoacetate (N_2=$CHCO_2Et$). The products of the reactions are cyclopropanecarboxylic acids (**50**) [111]. Dirhodium(II) tetracetate in fluorobenzene solution has been shown to be an effective catalyst for the novel cyclisation reaction shown in Scheme 5 [112]. A similar catalytic reaction of $[Rh_2(OAc)_4]$ is shown in Scheme 6 [113].



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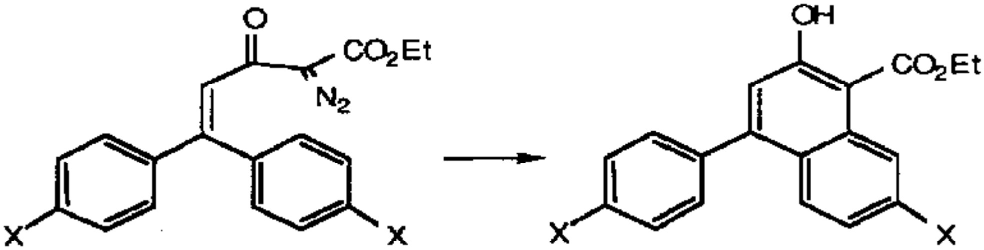


Scheme 5

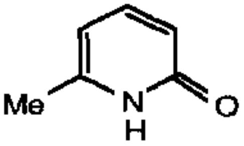
Scheme 6

2.3.2 Complexes with amides

Attempts to prepare rhodium(II) complexes with bridging amides by the reaction of rhodium trichloride with acetamide led only to the formation of $[Rh(NH_3)_5Cl]Cl_2$. Similarly, the reaction of $[Rh_2(O_2CR)_4]$ (R = H or Me) with acetamide at room temperature led to the diaxially substituted species $[Rh_2(O_2CR)_4(MeCONH_2)]$. However, on warming $[Rh_2(O_2CR)_4]$ or $[Rh_2(O_3C)_2]$ with acetamide, the complex $\{Rh_2L_4(HL)_4.4H_2O\}$ (HL = $MeCONH_2$) is obtained. Thermolysis of this leads to $[Rh_2L_4]$, whilst treatment with water yields $[Rh_2L_4].4H_2O$. These complexes are diamagnetic, metal-metal bonded rhodium(II) species analogous to the tetracarboxylates. Reaction with a range of ligands allows the preparation of the axially substituted derivatives $[Rh_2L_4(L')_2]$ (L' = NH_3, py or $PhNH_2$) [25]. A detailed study has shown that the reaction of $[Rh_2(OAc)_4]$ with molten acetamide leads to mixtures of the complexes $[Rh_2(OAc)_3L]$, $[Rh_2(OAc)_2L_2]$, $[Rh_2(OAc)L_3]$ and $[Rh_2L_4]$. The electrochemical properties of these complexes have been investigated. Each compound exhibits a one-electron oxidation, and the potential decreases steadily from $[Rh_2(OAc)_4]$ (1.17 V *vs.* SCE) to $[Rh_2L_4]$ (0.15 V *vs.* SCE). The complexes $[Rh_2(OAc)L_3]$ and $[Rh_2L_4]$ also exhibit second oxidation processes at 1.65 V and 1.41 V respectively [114].

The reaction of $[Rh_2(OAc)_4]$ with benzamide leads to the complex $[Rh_2L_4(HL)_2]$ (HL = $PhCONH_2$), which is exactly analogous to the corresponding acetamide compound. The axial benzamide ligands may be replaced by a range of other species, and the complexes $[Rh_2L_4(L')_2]$ (L' = py, PPh_3 or $SbPh_3$) have been prepared. Crystal structural analyses of the complexes $[Rh_2L_4(py)_2]$ and $[Rh_2L_4(SbPh_3)_2]$ have been reported; the Rh-Rh distances are 2.437(1) and 2.463(1) Å respectively [115]. The electrochemical properties of the complex $[Rh_2(MeCONHPh)_4]$ have also been investigated [117].

The reaction of $[\{Rh_2L_4\}_2]$ (HL = 6-methylpyridone, **51**) with 4-methylbenzenesulphonic acid (TsOH) has been investigated. The structurally characterised product is $[\{Rh_2L_3(OTs)\}_2]$, which possesses a framework similar to that on the parent $[\{Rh_2L_4\}_2]$ compound. The central feature is a *$\{Rh_2O_2\}$* ring. The complex exhibits two differing Rh-Rh distances of 2.377(3) and 2.376(3) Å [118]. A ^{103}Rh n.m.r. spectroscopic investigation of the the 6-methylpyridone complexes has been reported. The ^{103}Rh chemical shift of $[Rh_2L_4]$ is δ 5745, and of $[\{Rh_2L_4\}_2]$ δ 7644 and 4322 (relative to Ξ Rh = 3.16 MHz). A direct $^1J_{Rh-Rh}$ coupling of 35 Hz was observed [120]. In contrast to the behaviour of 6-methylpyridone, 6-fluoropyridone (**52**) gives a discrete complex



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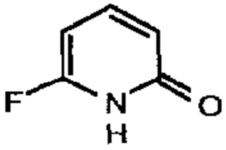

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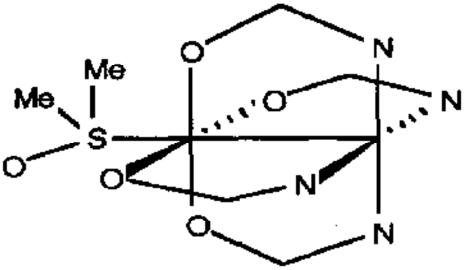
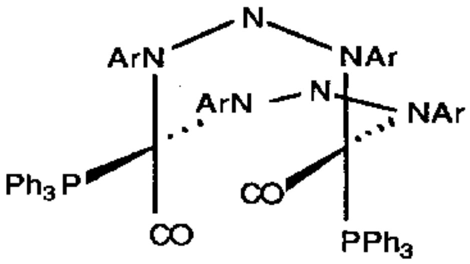


(53)

$[Rh_2L_4(dmso)]$ (**53**), the crystal structure of which reveals an Rh-Rh distance of 2.410(1) Å. The 6-fluoropyridinate ligands are all arranged with the oxygen donor atoms to the same end of the dimer, and it is clear that this arrangement results in considerable steric hindrance at the other end, since a single axial dmso molecule is observed at the oxygen donor end [119].

2.3.3 *Complexes with nitrogen donor ligands*

The electrochemical properties of a range of triazenato complexes $[Rh_2(CO)_2(PR_3)_2(\mu\text{-}ArNNNAr)_2]$ have been investigated. These rhodium(I) complexes undergo reversible one-electron oxidations. The crystal structure of the neutral rhodium(I) complex $[Rh_2(CO)_2(PR_3)_2(\mu\text{-}TolNNNTol)_2]$ (**54**) has been reported. There is no direct Rh-Rh interaction, and the Rh...Rh contact is 2.960(4) Å. Upon oxidation, the mixed oxidation state complex ({Rh(II),Rh(I)}) $[Rh_2(CO)_2(PR_3)_2(\mu\text{-}TolNNNTol)_2]^+$ (**55**) is produced. This has also been structurally characterised, and has a Rh-Rh distance of 2.698 Å [121].



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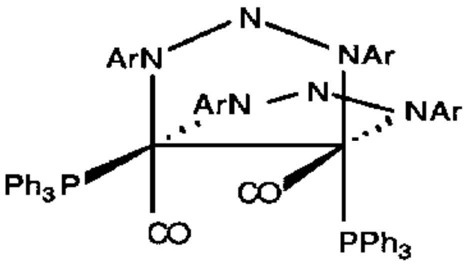

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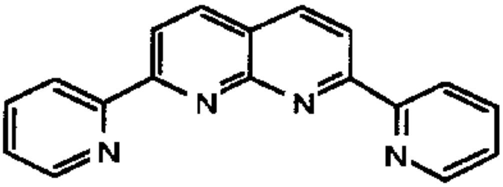
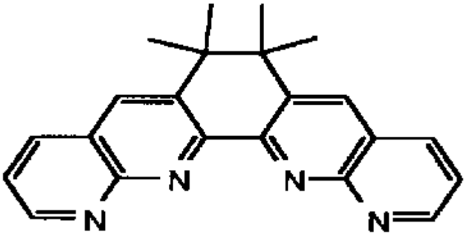
The potentially tetradentate ligand 2,7-*bis*(2-pyridyl)-1,8-naphthyridine (**56**) possesses the 1,3-arrangement of donors required to bridge a Rh-Rh bond, and reaction of $[Rh_2(OAc)_4]$ with **56** yields $[Rh_2(OAc)_3L]^+$ (L = **56**). This complex has been structurally characterised, and the pyridyl groups shown to be weakly



(56)

coordinated to the axial sites. The Rh-Rh distance is 2.405(2) Å, and the Rh-Rh-N_{py} angle is 166.9°. Related complexes $[Rh_2(OAc)_3L]^+$ (L = **57** or **58**), $[Rh_2(OAc)_2L_2]^{2+}$ (L = **58**) and $[Rh_2L_4]^{4+}$ (L = 1,8-naphthyridine, **59**) have also been described [122]. A structural analysis of the complex $[Rh_2L_3Cl_2]^{2+}$ (**60**) (L = **58**),



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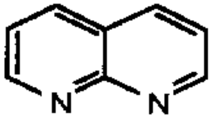

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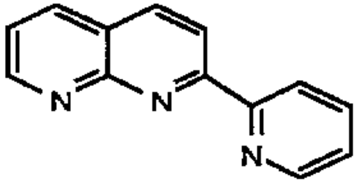

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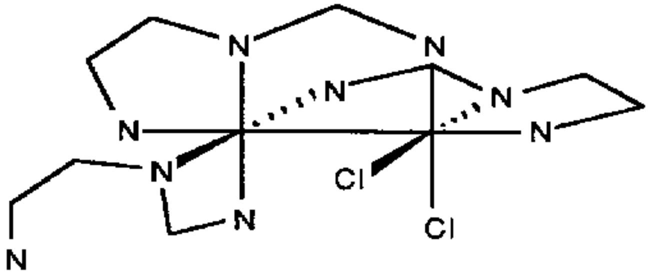


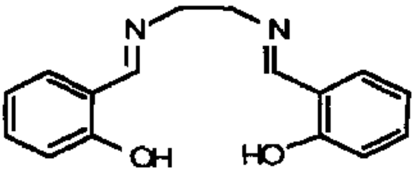
(60)

obtained from the reaction of $[Rh_2(OAc)_4]$ with **58** has also been described. In this case, two the pyridyl ligands are coordinated to the axial sites, and one is 'dangling'. The Rh-Rh distance is 2.5668(7) Å [123].

2.3.4 Complexes with other ligands

The rhodium tetraphenylporphyrin complexes [{(CO)$_2$Rh}$_2$tpp] (H_2L = **33**) are photoactive, and photolysis generates the rhodium(II) complex [Rh(tpp)], which has been characterised by its optical and e.s.r. spectra. The paramagnetic mononuclear species dimerises to diamagnetic [Rh$_2$(tpp)$_2$] [124,125].

The reaction of [(CO)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] with H$_2$salen (**61**) in the presence of triethylamine or bicarbonate gives [{(CO)$_2$Rh}$_2$(salen)], which may be converted to [Rh$_2$(salen)$_2$]. The reactions of the related ligands **62** and **63** have also been investigated. Both of the new ligands give [Rh_2L_2] (H_2L = **62** or **63**) complexes. Whereas the complex with H$_2$salen is partially dissociated at room temperature (μ_{eff} 0.90 B.M., g_1 2.418, g_2 2.33, g_3 1.99), the complexes with **62** and **63** are diamagnetic. The new complexes react with dioxygen to give paramagnetic (μ_{eff} 1.80 B.M.) adducts. Solutions of [Rh_2L_2(py)$_2$] in pyridine are e.s.r. silent, but on treatment with O_2 they develop an e.s.r. signal consistent with the formation of a rhodium(III)



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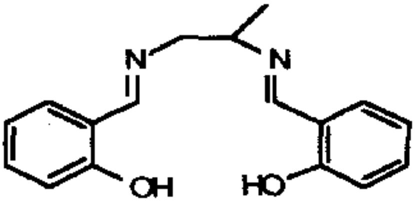

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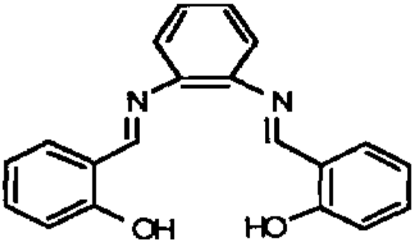


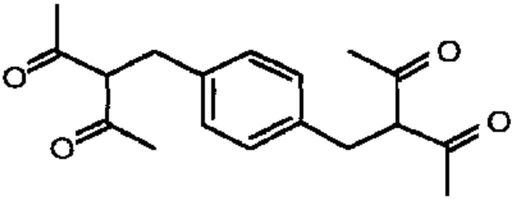
(63)

superoxo complex. The authors are emphatic that the rhodium(II) complexes do *not* arise by O_2 oxidation during the preparation, and cite the evolution of dihydrogen as evidence for this [126].

2.4 RHODIUM(I)

2.4.1 Complexes with Group 16 donor ligands

The complex [(cod)RhLRh(cod)] ($H_2L' =$ **64**) has been prepared by the reaction of [(cod)Rh(μ-Cl)$_2$Rh(cod)] with H_2L. Treatment of [(cod)RhLRh(cod)] with PPh_3 or Co gives the complexes [(CO)$_2$RhLRh(CO)$_2$] and [(PPh$_3$)$_2$RhLRh(PPh$_3$)$_2$] respectively. These complexes have been assessed as hydrogenation catalysts [127].



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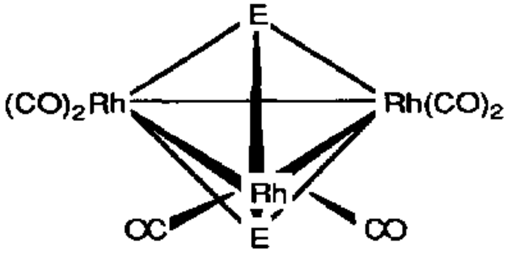
The cluster anion $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ **(65)** has been prepared by the reaction of $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ with KSCN or K_2S_n ($n = 1 - 8$), by the reaction of $[Rh_6(CO)_{15}]^{2-}$ with elemental sulphur, or from $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ with S^{2-}. The selenium analog may be prepared in a similar manner; crystal structural analyses of both $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ and $[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$ have been reported [129]. The zirconium(IV) complex $[Zr(cp)_2(CH_2PPh_2)_2]$ can act as a bidentate P_2 donor, and reaction with $[(CO)_2Rh(\mu\text{-}S^tBu)_2Rh(CO)_2]$



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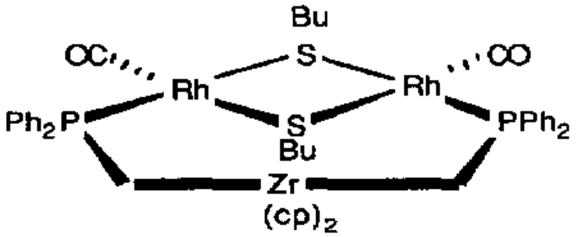
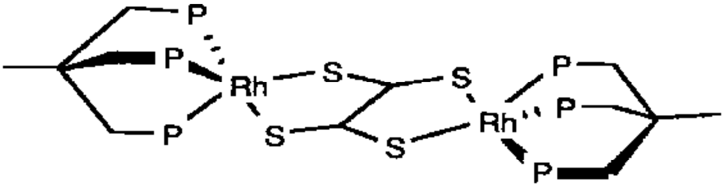


(66)

gives $[(CO)_2Rh(\mu\text{-}S^tBu)_2(\mu\text{-}\{Zr(cp)_2(CH_2PPh_2)_2\}Rh(CO)_2]$ **(66)**. The complex is a very active hydroformylation catalyst for hex-1-ene, comparable in activity to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2\{P(OMe)_3\}_2]$ and superior to $[RhH(CO)(PPh_3)_2]$. The catalyst exhibits a short induction period, and only produces aldehydes. The corresponding complex with dppb, $[(CO)_2Rh(\mu\text{-}S^tBu)_2(\mu\text{-}dppb)Rh(CO)_2]$ was also prepared; this was also catalytically active, but had a considerably longer induction period [130].

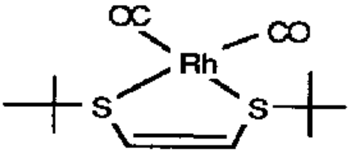
The complex $[LRh(\mu\text{-}S_4C_2)RhL]^{2+}$ (L = triphos, $MeC(CH_2PPh_2)_2$) results from the reaction of $[(C_2H_4)_2Rh(\mu\text{-}Cl)_2Rh(C_2H_4)_2]$ **(67)** with carbon disulphide in the presence of triphos. A crystal structural analysis of the complex has been reported, and analysis of the bond lengths suggest that the compound is best formulated as a rhodium(III) complex with a bridging $(S_2C{=}CS_2)^{4-}$ ligand [131].

There has been some interest in thioethers as auxiliary ligands in rhodium(I) hydrogenation catalysts. The complexes $[Rh(CO)_2L]^+$ (L = $MeSCH_2CH_2CH_2SMe$ or $^tBuSCH_2CH_2S^tBu$) are prepared by



(67)

the reaction of the ligands with $[Rh(CO)_2(Me_2CO)_x]^+$. However, a crystal structural analysis of the reaction product with $^tBuSCH_2CH_2S^tBu$ revealed that the ligand had been dehydrogenated to yield $[Rh(CO)_2(^tBuSCH{=}CHS^tBu)]$ (**68**). The complexes $[Rh(cod)L_2]^+$



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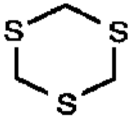
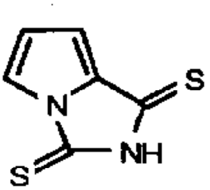


(69)

(L_2 = $MeSCH_2CH_2CH_2SMe$ or L = tetrahydrothiophen, Me_2S or Et_2S) react with CO to yield oils [132]. Trithiahexane (**69**) reacts with $[Rh_4(CO)_{12}]$ to yield $[Rh_4(CO)_9L]$ (L = **69**). A structural analysis of the product reveals the rhodium cluster has opened up to a butterfly structure, in which the ligand face caps one of the wings, and the wing-tips are linked by a bridging carbonyl. This structure is in equilibrium with a face-capped tetrahedral isomer in the solid state [133].



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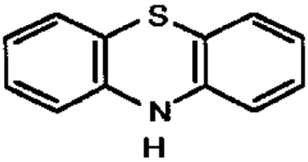

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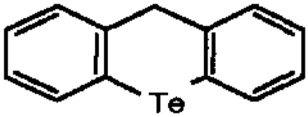

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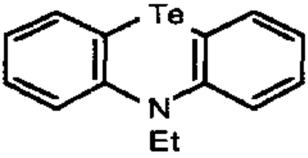


(73)

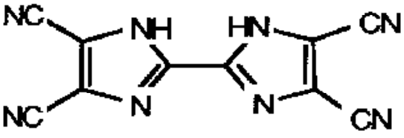
Complexes with the ligand $PhNHCS_2Et$ have been reported [59]. The cyclic compound **70** is reported to behave as a monodentate *S* donor in the complex $[Rh(CO)Cl(PPh_3)_2L]$ [134].

Phenothiazine (**71**) reacts with $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ to yield $[RhL_2(CO)Cl]$ and $[RhL(CO)_2Cl]$ (L = **71**). The related complexes $[RhL_2(CO)Cl]$ (L = **72** or **73**) are obtained from the reaction of the tellurium ligands **72** or **73** with $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$. The complexes are oxidised by iodine to $[RhL_2(CO)ClI_2]$. The ternary complexes [RhL(L')(CO)] (L = **72** or **73**, L' = 8-hydroxyquinoline) are obtained from the reaction of **72** or **73** with [RhL'(cyclooctene)(CO)] [135].

2.4.2 Complexes with Group 15 donor ligands

2.4.2.1 Complexes with nitrogen donor ligands

The interaction of $[Rh(CO)(PPh_3)_2]^+$ with the base pairs 6-mercaptoguanosine-cytidine and 8-mercaptoguanosine-cytidine has been investigated by ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy [136]. Tetracyano-2,2'-biimidazole (H_2L, **74**) is a versatile binucleating ligand, and reacts with [Rh(cod)(acac)] to yield $[(cod)(MeCN)Rh(\mu\text{-}L)Rh(cod)]$ and $[(cod)Rh(\mu\text{-}L)Rh(cod)]$; in the

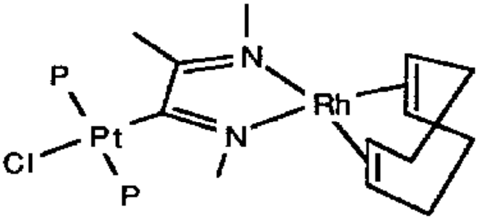


(74)

former complex the ligand acts as a bridging terdentate, and in the latter as a bridging tetradentate. The reaction of the complex [(cod)Rh(μ-L)Rh(cod)] with CO yields [$Rh_4(CO)_4(PPh_3)_4L_2$] [137].

The unusual *pseudo*halide complex *trans*-[$Rh(CO)_2(PPh_3)_2(NSO)$] is formed (together with Ph_3PO) from the reaction of $CsNSO_2$ with [$Rh(CO)H(PPh_3)_3$]; the complex has been structurally characterised and contains an *N* donor NSO ligand [138].

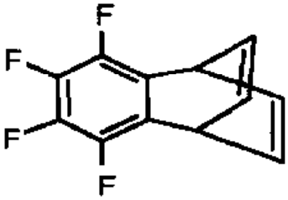
The complex *trans*-[$PtCl(PPh_3)_2L$] (HL = ArN=CMeCH=NTol, Ar = 4-methoxyphenyl, Tol = 4-methylphenyl) reacts with the dimer [(cod)Rh(μ-Cl)$_2$Rh(cod)] to yield the salt [$PtCl(PPh_3)_2$(μ-L)Rh(cod)] [$RhCl_2(CO)_2$] (**75**). The crystal structure of the complex reveals the diazabutadiene to act as a monodentate *C* donor to platinum and a bidentate N_2 donor to rhodium. The rhodium square-plane is



(75)

inclined at 81° to the platinum square-plane in the solid state. Solution n.m.r. studies indicate considerable cation-anion association, and partial breaking of the Rh-N bonds [139]. Complexes with RN=CR'CR'=NR (R = cych, Ph, 4-hydroxyphenyl, 4-methylphenyl or 4-methoxyphenyl, R' = H or Me) have also been studied; in general they resemble those discussed above

[142].



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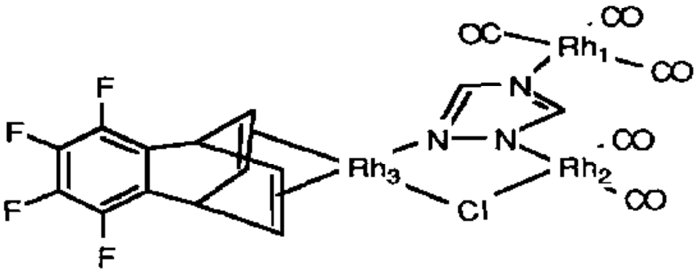


(77)

The reaction of [Rh(acac)(tfb)] (tfb = **76**) with 1,2,4-triazole (HL) and $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ yields $[Rh_3(\mu_3\text{-}L)(\mu_2\text{-}Cl)Cl(tfb)(CO)_4]$ (**77**), the structure of which has been confirmed by a crystal structure. In the solid state there is a stacking interaction between Rh(2) and Rh(2') (Rh(2)...Rh(2'), 3.425(4) Å, Rh(2)...Rh(3), 3.817(3) Å) [140].

An analysis of the ^1H n.m.r. spectrum of the acrylonitrile ligand in $[Rh(CH_2{=}CHCN)(CO)(PPh_3)_2]^+$ suggests that it is bonded to the metal through nitrogen [141].

Extremely good catalysts for the reduction of nitrobenzene to aniline by CO/H_2 mixtures are obtained from $[Rh_6(CO)_{16}]$ and 1,10-phenanthroline or 3,4,5,6,7,8-hexamethyl-1,10-phenanthroline; the active catalysts are mononuclear complexes [143].

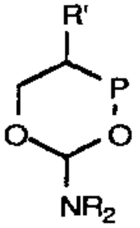
2.4.2.2 Complexes with phosphorus donors ligands

A detailed analysis of the ^{31}P n.m.r. spectra of the series of complexes $[Rh(CO)Cl(PR_3)_2]$ (R = H, Me, Et, ^{n}Bu or Ph) has been reported [144]. The reaction of $[Rh\{P(OPh)_3\}_2(acac)]$ with deuterium has been investigated. Specific deuteration occurred at the *ortho* positions of the phenyl groups of the coordinated phosphite and at the central carbon of the acac ligands [145]. The site exchange processes in $[Rh_4(\mu\text{-}CO)_2(CO)_4(\mu\text{-}PPh_2)_4]$ have been investigated by $\{^1H\}^{31}P\text{-}^{31}P$ correlation and *J* resolved COSY experiments [146]. *DANTE* experiments on $[RhCl(PPh_3)_3]$ hydrogenation systems have provided evidence for a *cis*

$Rh(PPh_3)_2$ intermediate at a key step [155].

The reactions of $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$ with phosphides have been investigated. The complex $[(cod)Rh(\mu\text{-}PMePh)_2Rh(cod)]$ is obtained from the reaction of $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$ with LiPMePh; replacement of the cod ligands by PEt_3 is facile, to yield $[(PEt_3)_2Rh(\mu\text{-}PMePh)_2Rh(PEt_3)_2]$. The diphenylphosphido complexes $[(cod)Rh(\mu\text{-}Cl)(\mu\text{-}PPh_2)Rh(cod)]$ and $[(cod)Rh(\mu\text{-}Cl)(\mu\text{-}PPhMe)Rh(cod)]$ have also been prepared [147].

A series of novel phosphorus ligands **78** (R = Ph, Et, Me, Cl or morpholino; R' = H or Me) have been shown to give complexes [Rh(CO)L(acac)] upon reaction with $[Rh(CO)_2(acac)]$ [148]. A range of complexes with $Ph_2PCH_2CO_2H$ have been described. The ligand acts as a *P* donor in the complexes [Rh(CO)X(HL)] (X = Cl, Br or I; HL = $Ph_2CH_2CO_2H$), which are prepared from HL and $[(cod)Rh(\mu\text{-}Cl)_2Rh(cod)]$. A number of different isomers of [Rh(CO)L(HL)] (**79**) have been isolated from the reaction of $[Rh(CO)_2(acac)]$ with HL; a structural analysis has revealed the presence of monodentate *P* donor HL ligands, and bidentate chelating *PO* donor L^- in [Rh(CO)L(HL)]. The α, β and γ forms differ in the lattice hydrogen bonding [149]. The complex [LRhH] (L = $N(CH_2CH_2PPh_2)_3$) reacts with CO_2 to yield $[RhL(CO)]^+$ [150].



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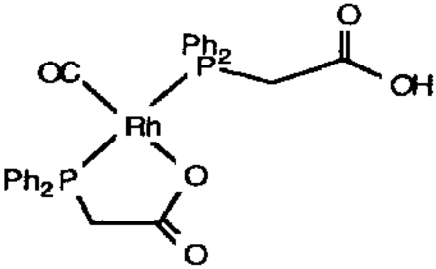

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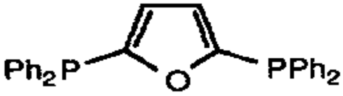
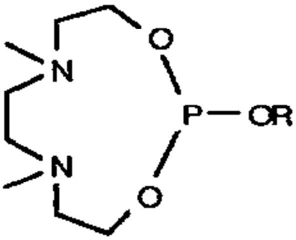
The bidentate phosphine **80** forms the complex $[(nbd)Rh(\mu\text{-}L)_2Rh(nbd)]$, which has been investigated as a hydrogenation catalyst [151]. The macrocyclic ligand **81** has been



(80)

shown to form the complexes [RhCl(L')L] (L = **81**, L' = CO or C_2H_4). A structural analysis of the five-coordinate complex [RhCl(CO)L] **(82)** reveals one of the Rh–N bonds to be considerably longer than the other (2.570(5) *vs* 2.330(5) Å). The complex is a good, mild hydroformylation catalyst, and its activity is thought to be



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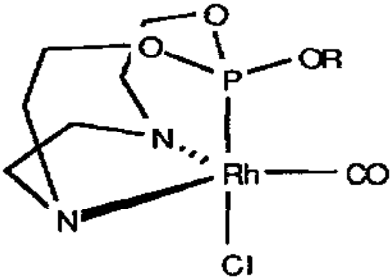
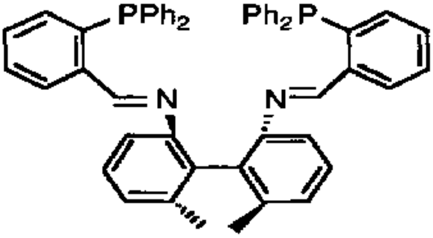


(82)

related to this weakening of the Rh–N bonding in the fifth site [152]. The complex $[RhL]^+$ (L = **83**) has been prepared in racemic and enantiomeric forms. A crystal structural analysis has revealed the ligand to act as an N_2P_2 donor to the metal. The complex is not significantly active as a hydrogenation or hydroformylation catalyst, and is unreactive to H_2 and only reacts slowly and incompletely with CO [153].

Each of the diastereomeric pair of ligands **84** and **85** react with $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ to give a diastereomeric complex. The ligands act as *NP* donors. The complexes are active hydrogenation



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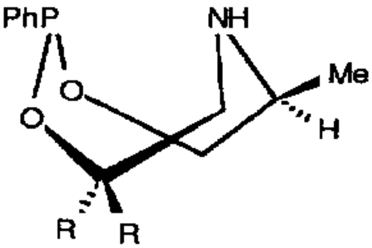
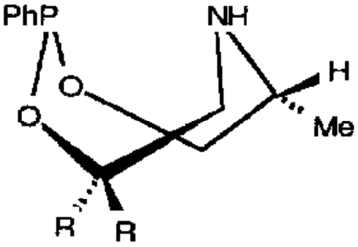
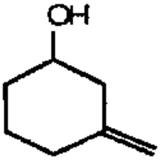



(84) (85)

catalysts, but only low enantiomeric excesses are obtained with prochiral substrates [154].

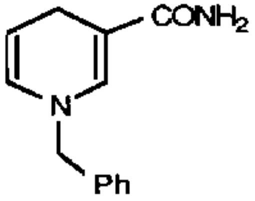
Numerous studies of phosphine containing rhodium catalytic systems have been reported. The detailed study of the reduction of prochiral alkylamines by chiral $[Rh(diphos)_2]^+$ complexes has been reported [156]. The hydrogenation of 3-methylcyclohex-2-enol, 4-methylcyclohex-3-enol or 4-hydroxymethyl-1-methylcyclohex-1-ene in the presence of a $[Rh(dppb)_2]^+$ catalyst has also been studied. Yields of 95% 3-methylcyclohexanol are reported [157]. The related complexes $[Rh(dppb)(nbd)]^+$ and $[Rh(PPh_3)_2(nbd)]^+$ are also active catalysts, and yields of 98% *trans*-3-methylcyclohexanol are reported from **86** [158].



(86)

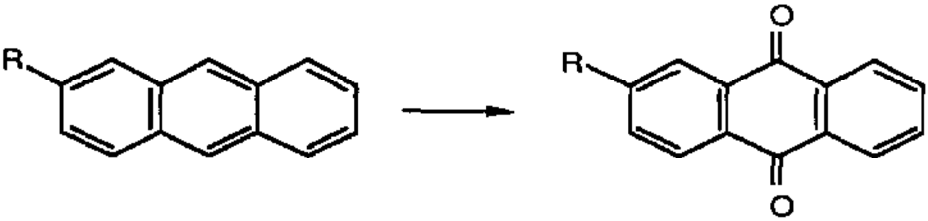
Rhodium complexes may also act as hydrogen transfer catalysts from other reducing agents, and extremely high yields of arenes are obtained from aryl iodides by reduction with the NADH model, *N*-benzyl-1,4-dihydropyridine-3-carboxamide **(87)**, in the presence of [Rh(PPh$_3$)$_3$Cl] [160].

The use of rhodium complexes as oxidation catalysts is increasing, and a mechanistic study of the oxidation of cyclooctene



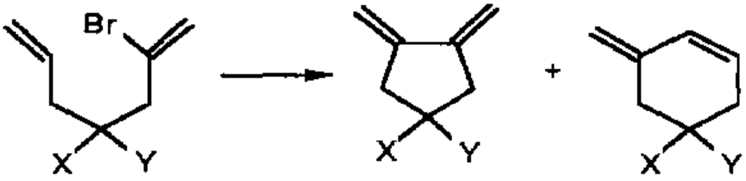
(87)

by dioxygen and triphenylphosphine in the presence of [RhCl(PPh$_3$)O$_2$] has been reported [51]. High yields (>95%) of cyclohexenyl hydroperoxide are obtained from cyclohexene and cumyl hydroperoxide in the presence of [Rh(PPh$_3$)$_3$Cl], [Rh(PPh$_3$)$_2$(CO)Cl] or [(C$_2$H$_4$)$_2$Rh(μ-Cl)$_2$Rh(C$_2$H$_4$)$_2$] [161]. The oxidation of anthracenes to anthraquinones (Scheme 7) by *tert*-butyl hydroperoxide is catalysed by [Rh(PPh$_3$)$_3$Cl] [162,163].



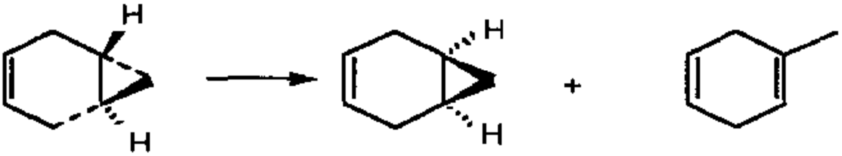
Scheme 7

The electroreduction of CO$_2$ to cyanoacetate in acetonitrile is catalysed by [Rh(dppe)$_2$]$^+$ [164].



Scheme 8

The preparation of 1,4-dihydroxybenzene from acetylene and carbon monoxide is catalysed by [Rh(PAr$_3$)$_2$(CO)Cl] (Ar = Ph, 4-Mephenyl or 4-MeOphenyl) [165]. The novel cyclisation of vinyl halides (Scheme 8) has been shown to be catalysed by [Rh(PPh$_3$)$_3$Cl] [166].



Scheme 9

Investigations of the methyl iodide oxidative addition step in the Monsanto acetic acid process have been discussed elsewhere [93,94].

A novel *cis-trans* isomerisation of cyclopropanes (Scheme 9) has been shown to be catalysed by [(CO)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] or [(cod)Rh(μ-Cl)$_2$Rh(cod)] [167].

2.4.2.3 Homonuclear dimers

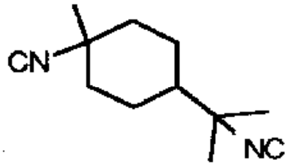
Numerous examples of dimeric complexes with bridging diphosphine ligands are known, those in which heterometals are present are not covered in this review. The reaction of [(CO)ClRh(μ-dppm)$_2$Rh(CO)Cl] with NaBH$_4$ yields the hydrido bridged dimer [(CO)Rh(μ-dppm)$_2$(μ-H)$_2$Rh(CO)]. The reaction is reversed by HCl. Loss of hydrogen from [(CO)Rh(μ-dppm)$_2$(μ-H)$_2$Rh(CO)] to yield the metal-metal bonded complex [(CO)Rh(μ-dppm)$_2$Rh(CO)] is facile. The reaction of [(CO)Rh(μ-dppm)$_2$(μ-H)$_2$Rh(CO)] with MeI yields methane and [(CO)Rh(μ-dppm)$_2$(μ-H)(μ-I)Rh(CO)] [168]. Lengthening of the Rh-Rh bond to

2.7464(7) Å occurs upon the addition of HA to [ClRh(μ-dppm)$_2$(μ-CO)RhCl] to yield [ClRh(μ-dppm)$_2$(μ-H)(μ-CO)RhClA] (A = BF_4, Cl or TsO) [169]. The complex [$RhL_2(CO)_2$] (H_2L = 1,2-dihydroxy-3,4,5,6-tetrachlorobenzene) reacts with dppm to yield the metal-metal bonded species [(CO)Rh(μ-dppm)$_2$Rh(CO)L]; the Rh-Rh distance is short (2.637(1) Å, but there is an ambiguity over the oxidation states resulting from the various bonding modes open to the non-innocent ligand L [170].

The reaction of dppm with [(cp)(CO)Rh(μ-CO)Rh(CO)(cp)] yields [(cp)Rh(μ-dppm)(μ-CO)Rh(cp)]; the Rh-Rh distance is 2.683(1) Å. The complex reacts with SO_2, $SnCl_2$ or Br_2 to give [(cp)Rh(μ-dppm)(μ-SO_2)Rh(cp)], [(cp)Rh(μ-dppm)(μ-$SnCl_2$)Rh(cp)], [(cp)Br_2Rh(μ-dppm)Rh(cp)Br(CO)]$^+$ or [(cp)Br_2Rh(μ-dppm)RhBr_2(cp)] respectively [171].

2.4.3 Complexes with Group 14 donor ligands

The complex $[Rh_2L_2]^{2+}$ (L = $Me_2C(NC)CH_2CH_2C(NC)Me_2$) may be converted to $[Rh_2L_2]^+$ by pulse radiolysis [172]. The related complex $[Rh_2L_2]^{2+}$ (L = **88**) has also been investigated [159].



(88)

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