9. Rhodium 1992

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of rhodium reported during the year 1992 and is similar in format to the corresponding review dealing with the 1991 literature [1]. The literature has been searched by using both *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Structural figures have been redrawn using coordinates taken from the Cambridge Crystallographic Data Base.

On the whole, organometallic complexes have not been included since reviews of their chemistry are to be found elsewhere. Similarly, rhodium carbonyl and related clusters have been excluded.

As is the current policy in this series of surveys, this review is not fully comprehensive but instead aims to give the reader an overview of the coordination chemistry of rhodium reported in 1992. I apologise to those readers whose work may have been omitted.

Higher (+4 and above) oxidation state chemistry for rhodium reported 1992 appears to be scarce, but the results of Ellison and Gillard are of general interest — they indicate that a large proportion of higher oxidation state species of rhodium which are in aqueous media are actually superoxorhodium(III) species [3].

9.1 RHODIUM(III)

9.1.1 Complexes with halide ligands

During studies of the hydrocarbonylation of MeOAc using a rhodium(III) catalyst, the complex anion *trans*-$[RhI_4(CO)_4]^-$ has been isolated as the 2,6-diphenylpyridinium or isoquinolinium salts. The crystal structure of the 2,6-diphenylpyridinium salt has been determined, and the rhodium(III) centre is in a distorted octahedral environment [4].

Rhodium(III) bromide complexes in aqueous solution have been the subjects of a ^{103}Rh NMR spectroscopic study. Ten complexes of the type $[RhBr_n(H_2O)_{6-n}]^{3-n}$ (n = 0 to 6) and including geometrical isomers for n = 2 to 4 have been investigated. Values of the chemical shift exhibit a nephelauxetic dependence, and δ becomes less positive with increasing n. A correlation has been made between the ligand field parameter ratio $^{\beta}/_{\Delta E}$ and δ (where β = nephelauxetic parameter and ΔE = electronic transition energy). It is also found that δ(*trans* isomer) > δ(*cis* isomer), and δ(*mer* isomer) > δ(*fac* isomer) (where > corresponds to a more downfield resonance) [5].

9.1.2 Complexes with oxygen donor ligands

Spectrophotometric methods have been used to follow the kinetics of the de-aquation of $[Rh(H_2O)_6]^{3+}$ by thiocyanate ion in aqueous solution. The rate is pH dependent (pH range 1–3) and is independent of the concentration of the substituting ligand. A primary H_2O dissociation-controlled process is proposed; activation parameters have been determined [6]. X-ray scattering techniques have been applied to elucidate the hydration structure of rhodium(III) ions in 1M perchlorate solution. The first hydration sphere contains six water molecules with Rh-O distances of 2.03 ± 0.02Å. There is a well-defined second sphere consisting of 13 water molecules (Rh-O = 4.02Å). Hydrogen bonding exists between molecules in the two shells. These results have been compared with those of EXAFS studies of $[Rh(ClO_4)_3].6H_2O$ in both solid and solution states. There appears to be little difference between the structure of the $[Rh(H_2O)_6]^{3+}$ complex ion in the solid, and the metal ion in the first hydration shell in solution [7].

Equilibria between *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ or *cis*-$[Rh(NH_3)_4(H_2O)(OH)]^{2+}$ and dinuclear species such as $[(NH_3)_4Rh(\mu\text{-}OH)_2Rh(NH_3)_4]^{4+}$ have been studied over a range of temperatures from 25 to 100°C in 1M $(Na,H)ClO_4$ with $[H^+]$ lying in the range 1×10^{-7} to 1.0 M [8]. Related hydroxy-bridged species are discussed in section 9.4.

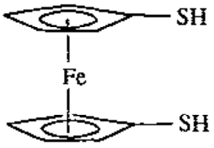
The rhodium(I) complex $[Rh(ONO_2)(PPh_3)_3]$ undergoes oxidative addition with dihydrogen (1 atm., ambient temp.) to give the rhodium(III) compound $[RhH_2(ONO_2)(PPh_3)_3]$. Loss of one PPh_3 ligand leads to the octahedral complex $[RhH_2(ONO_2)(PPh_3)_2]$ in which the nitrate ligand acts in a didentate manner. This has been confirmed crystallographically; the PPh_3 ligands are mutually *trans*, but the hydride ligands have not been located. The results of multinuclear NMR spectroscopic studies have also been reported [9, 10].

The preparation, spectroscopic and electrochemical characterisations of the rhodium(III) complexes $[Rh(cat)\{Ph_2PCH_2)_3CMe\}]X$ (X = BPh_4 or PF_6) where cat^{2-} is one of a range of catecholates have been reported. The complexes exhibit electron transfer processes which involve Rh(III), Rh(II) and Rh(I) states and also show catecholate (cat), semiquinone (SQ) and quinine oxidation levels of the ligands. Dioxygen uptake by the complexes produces adducts, and the crystal structure of an iridium(III) adduct has been determined [11].

9.1.3 Complexes with sulfur, selenium and tellurium donor ligands

The results of the reaction between $[\{Cp^*RhCl_2\}_2]$ and 1,2-dicyanoethene-1,2-dithiolate (L) have been reported. The ligand bonds to the rhodium(III) centre as an *S,S'*-donor and forms the complex $[Cp^*RhL]$ [12]. Related reactions are described in section 9.1.4.

The dilithio derivative of ligand (1), Li_2L, reacts with $[Cp^*Rh(PMe_3)Cl_2]$ to give $[Cp^*Rh(PMe_3)L]$. Analogous selenium and tellurium-containing complexes may also be prepared. The products have been characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopies, and the crystal structure of $[Cp^*Rh(PMe_3)L]$ has been determined. The rhodium(III) centre is 4.304(1)Å distant from the iron atom; the two Rh-S distances are 2.367(1) and 2.360(1)Å [13].



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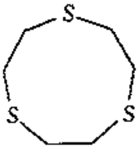


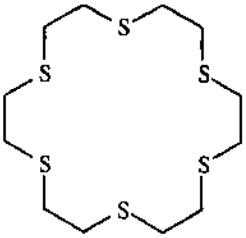
(2)

The reaction of $[Rh_2L_4(\mu\text{-}Cl)_2]$ (L_2 = cod or L = CO) with $Na_2[S_2PPh_2]$ leads to $[Rh(S_2PPh_2)L_2]$. For L = CO, this product reacts with PPh_3 to give $[Rh(S_2PPh_2)(CO)(PPh_3)]$, and the oxidative addition of iodine produces two isomers of the rhodium(III) complex $[RhI_2(S_2PPh_2)(CO)(PPh_3)]$. Related reactions have also been reported, and include the formation of the square pyramidal complex $[RhI(\eta^2\text{-}S_2Ph_2)(COMe)(PPh_3)]$ [14].

A crystal structure determination of the diethyldithiocarbamato complex $[Cp^*Rh(S_2CNEt_2)(dppm)_2]$ has been carried out. Each dppm ligand is monodentate, and the dithiocarbamato is bound in an *S,S'*-mode [15].

Kim *et al.* have determined the structure of the complex $[Cp^*Rh(2)][ClO_4]_2.MeCN$ [16]. The macrocycle (3) and the related open-chain ligands (4) = HL and (5) = HL' have been the subject of study of Schröder and coworkers. Ligand (3) reacts with $[\{RhCl(C_8H_{14})\}_2]$ in

MeOH/H_2O under reflux in the presence of HBF_4 to give [Rh(3)][BF_4]$_3$. This complex exhibits two reversible one-electron redox couples. Similarly, but in the presence of hexafluorophosphate anion, [RhL][PF_6]$_2$ and [RhL'][PF_6]$_2$ have been prepared. The complex cation $[RhL]^{2+}$ shows ill-defined, irreversible reductions, whereas $[RhL']^{2+}$ exhibits reversible reductions which correspond to Rh^{III}/Rh^{II} and Rh^{II}/Rh^{I} couples. The reduction products with the open-chain ligands are less stable than those containing the closed-ring ligand (3) [17].



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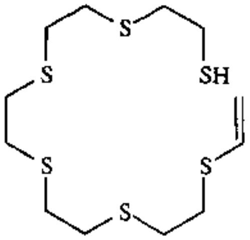

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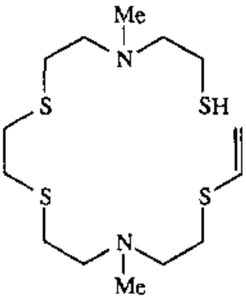

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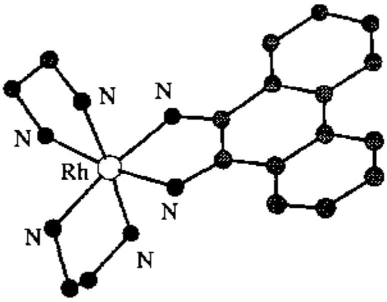
9.1.4 Complexes with nitrogen donor ligands

As part of a wider (see section 9.1.1) spectroscopic study, the ^{103}Rh NMR spectrum of aqueous $[Rh(NH_3)_6]^{3+}$ has been reported. It shows a resonance at δ 4766 (276 K) [5]. Equilibria between cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ or cis-$[Rh(NH_3)_4(H_2O)(OH)]^{2+}$ and dinuclear species which include $[(NH_3)_4Rh(\mu\text{-}OH)_2Rh(NH_3)_4]^{4+}$ were mentioned in section 9.1.2 [8].

From aqueous hydrochloric acid solutions of $ReCl_3$ and $[Rh(en)_3]Cl_3.3H_2O$, it is possible to crystallise the complex $[H_3O][Rh(en)_3][Re_3Cl_{12}]Cl$ which has been structurally characterised. The $[Re_3Cl_{12}]^{3-}$ anions are connected by hydroxonium cations; channels run through the lattice in the [001] direction and within these lie the $[Rh(en)_3]^{3+}$ and chloride ions. The Rh-N distances in the octahedral $[Rh(en)_3]^{3+}$ cation are 2.111(7) and 2.051(7)Å [18]. Rhodium(III) complexes of amino-functionalised silica have been prepared; the anchored complexes are dispersed homogeneously over the surface; characterisation has been by elemental analysis, IR and CP-MAS ^{13}C NMR spectroscopies, XPS, and TEM-energy dispersive X-ray methods [19].



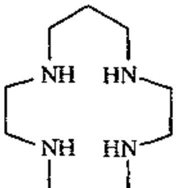
(6)

The single crystal structures of the octahedral rhodium(III) complexes $[Rh\{1,2\text{-}(NH_2)_2C_6H_{10}\}_3][NO_3]_3.3H_2O$ [20], and *rac*-$[Rh(en)_2L]Br_3.3H_2O$ where L = 9,10-phenanthrenequinone diimine and $[Rh(en)_2L]^{3+}$ = (6) [21] have been determined. A crystallographic study of the complex $[Rh(HL)LCl_2]$ (HL = $EtC(NOH)CMe_2NH_2$) has also been carried out. The rhodium(III) centre is octahedrally coordinated with distances of $Rh\text{-}N_{(hydroxyimino)}$ = 2.00 and 1.98Å and $Rh\text{-}N_{(amino)}$ = 2.08 and 2.09Å. The solid state structure exhibits hydrogen bonding between the hydroxyimino groups of the ligands [22].

The syntheses of the dimethylglyoxime complexes $[Rh(py)(dmgH)_2R]$ (R = various alkyl) have been reported, and the three complexes with R = CH_2CF_3, CH_2Cl and ^{n}Pr have been crystallographically characterised. The pyridine and alkyl groups are mutually *trans* in an octahedral coordination sphere. The axial $Rh\text{-}N_{(py)}$ and $Rh\text{-}C_{(R)}$ distances increase with the increasing bulk and σ-donating ability of group R. The kinetics of the substitution reactions given in equation (i) have been studied; k_{obs} is independent of the concentration of the phosphine and a *D* mechanism has been proposed [23].

$$[Rh(py)(dmgH)_2R] + PPh_3 \rightleftharpoons [Rh(PPh_3)(dmgH)_2R] + py \qquad (R = CH_2CF_3 \text{ or } CH_2Cl) \qquad (i)$$

The photophysical properties of the complexes *cis*- and *trans*-$[Rh(7)(CN)_2]^+$ and *trans*-$[Rh(8)(CN)_2]^+$ have been reported. The electronic absorption spectra exhibit broad bands with λ_{max} in the near-UV ($\varepsilon < 300$ dm^3 mol^{-1} cm^{-1}). Details of the emission spectra have been discussed and a Franck-Condon analysis based on a 2-acceptor mode model has been carried out. The results are consistent with average bond displacements in the excited state of approximately 0.14Å for Rh-N and 0.02Å for N-H bonds. In aqueous solution, the *trans*-complexes luminesce strongly. Complexes involving the ligands triazacyclononane and (9) have also been studied [24].



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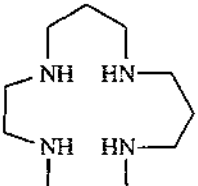

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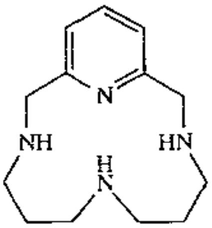
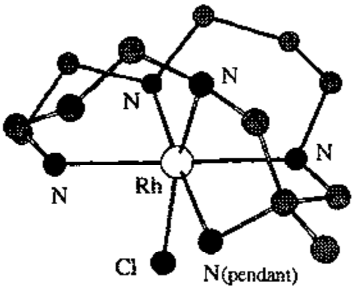


(9)

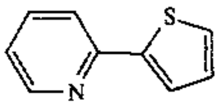
The macrocycle 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine (L) possesses a pendant 'arm'. It reacts with $RhCl_3$ in hot water; after passing the reaction mixture through a cation-exchange column, the product *cis*-$[RhLCl]^{2+}$ (**10**) may be collected and isolated as the perchlorate salt. The results of an X-ray diffraction study of the complex show that the pendant amine (Rh-N = 2.056(6)Å) and the two adjacent secondary amines (av. Rh-N = 2.08Å) are in a *fac*-arrangement. An activation volume for chloride base hydrolysis of +19.5 ± 1.2 cm^3 mol^{-1} is consistent with a conjugate base mechanism [25].



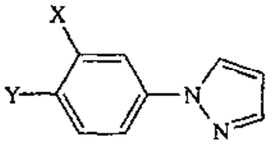
(10)

A range of rhodium(III) complexes involving *N*-donor heterocyclic ligands has been reported. Photosensitisation by biacetyl in aqueous solution is observed for complexes of the type *trans*-$[RhL_4X_2]^+$ (L = heterocyclic amine; X = Cl, Br, I or CN) and *trans*-$[Rh(py)_4Cl(Y)]^+$ (Y = Br or CN). The quantum yields for the direct photo-aquation of halide or cyanide and of amine are approximately the same [26]. Fifteen rhodium(III) and rhodium(I) complexes which feature 2,2'-bpy, 4,4'-bpy and phen ligands have been prepared, and characterised by ^1H, ESR and IR spectroscopies [27]. The luminescence of rhodium(III) complexes with bpy is the basis for a method of determination of rhodium; the relative and absolute detection limits are 0.08 $\mu g\ mL^{-1}$ and 0.008 μg, respectively. The method has a wide dynamic range (0.4 – 20 $\mu g\ mL^{-1}$) and shows good reproducibility [28].

The X-ray crystal structure of $[Rh(bpy)(ppy)_2][PF_6]$ has been elucidated. The two *N*-donors of the 2-phenylpyridine ligands are mutually *trans*. The polarised single crystal absorption spectrum of the $[Rh(bpy)(ppy)_2]^+$ cation, and the excitation and site-selective luminescence spectra of $[Rh(bpy)L_2]^+$ and $[Rh(bpy)(ppy)L]^+$ (HL = 2-thienylpyridine) doped into $[Rh(bpy)(ppy)_2]^+$ have been recorded and discussed. The two lowest energy excitations of $[Rh(bpy)(ppy)_2][PF_6]$ and of $[Rh(bpy)(ppy)_2][BPh_4]$, $[Rh(en)(ppy)_2][PF_6]$ and $[Rh(en)(ppy)_2][BPh_4]$ are observed between 21,400 and 22,200 cm^{-1} and are assigned to electronic transitions involving the 2-phenylpyridine ligand [29]. A report has appeared of the preparation and characterisation of a range of cyclometallated rhodium(III) complexes of the types $[Rh(L\text{-}C,N)_2(L'\text{-}N,N')]^+$ and $[\{Rh(L\text{-}C,N)_2\}_2(\mu\text{-}Cl)_2]$ in which HL is one of ligands Hppy, (**11**) or (**12**), and L' is a diimine ligand (*e.g.* bpy, phen, 2,2'-biquinoline). The configurations of the complexes have been established from ^1H NMR spectroscopic data, and in the case of $[RhL_2bpy]Cl$, [(**13**)]Cl, by X-ray crystallography. In each case, the carbon donor-atoms of the two orthometallated ligands are *cis* to each other. In



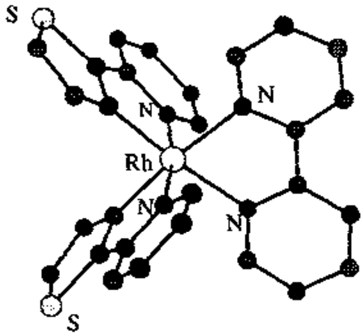
(**11**)



X	Y
H	H
H	NO_2
Cl	H

(**12**)

addition, UV-VIS spectroscopic and electrochemical studies have been carried out [30]. The reaction between [{Cp*RhCl$_2$}$_2$] and 2,2'-diimidazole leads to the formation of [Cp*RhCl(2,2'-diimidazole)] in which the heterocyclic ligand functions as a chelating *N,N'*-donor. Related reactions with iridium(III) and 2,2'-dithiazole have also been investigated and the crystal structure of [Cp*IrCl(2,2'-diimidazole)] has been determined [12].



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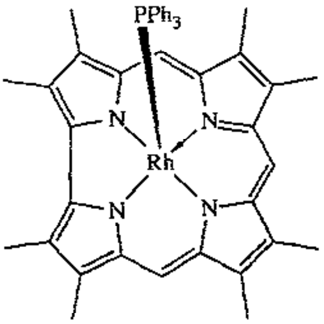


(14)

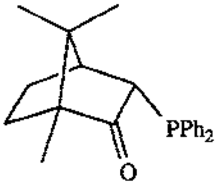
The results of a study of the rhodium porphyrin-catalysed cyclopropanation of alkenes by diazo esters have been described. The complexes involved were [Rh(TTP)I] and [Rh(TTP)Me] where TTPH$_2$ = 5,10,15,20-tetrakis(4-methylphenyl)porphyrin [31]. The electrochemistry of the rhodium(III) corrole complex (**14**) has been studied in thf, dmf, PhCN and CH$_2$Cl$_2$ solutions containing [^{n}Bu$_4$N][ClO$_4$] as supporting electrolyte. Up to three oxidation and two reduction waves are observed depending upon the solvent. The oxidation processes are centred on the corrole π-system, and the reductions are metal-centred [32].

9.1.5 Complexes with phosphorus and antimony donor ligands

Several complexes containing phosphine ligands have already been mentioned; the ones discussed in this section are considered to have a phosphine ligand as the principal ligand of interest.

The crystal structures of the rhodium(III) complexes [Rh(P^{i}Pr$_3$)$_2$H$_2$Cl] and [Rh(P^{i}Pr$_3$)$_2$HCl$_2$] have been elucidated. The former possesses a trigonal bipyramidal array of ligands with *trans*-P^{i}Pr$_3$ groups. In the latter, the *trans*-{Rh(P^{i}Pr$_3$)$_2$Cl$_2$} unit is square planar and the hydride ligand is disordered over two sites related by a centre-of-symmetry [32]. The complexes [Rh(P^{i}Pr$_3$)$_2$H$_2$Cl] and [Rh(P^{i}Pr$_3$)$_2$HCl$_2$] have been reported independently by Rappert *et al.* — [Rh(P^{i}Pr$_3$)$_2$HCl$_2$] has been prepared either from [{RhCl(P^{i}Pr$_3$)$_2$}$_n$] and HCl, or from [RhCl$_2$(P^{i}Pr$_3$)$_n$] and H$_2$, and [Rh(P^{i}Pr$_3$)$_2$HCl$_2$] further reacts with H$_2$ in the presence of Na[N(SiMe$_3$)$_2$] to yield [Rh(P^{i}Pr$_3$)$_2$H$_2$Cl] [32a].

Rhodium(III) chloride reacts with ligand (**15**) in ethanol to give *trans,mer*-[RhCl$_3$L$_2$], and in thf to yield *cis,mer*-[RhCl$_3$L$_2$] (**16**). One ligand is monodentate, coordinating through the phosphorus donor atom, and the other is *P,O*-bonded. In addition to crystallographic data for the *cis,mer*-isomer, both complexes have been characterised by IR, and ^1H and ^{31}P NMR spectroscopic studies [34].



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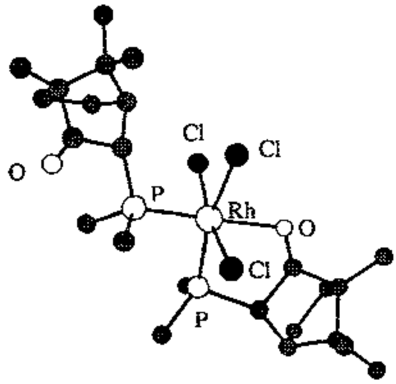


Only the *ipso*-C atoms of phenyl rings are shown.

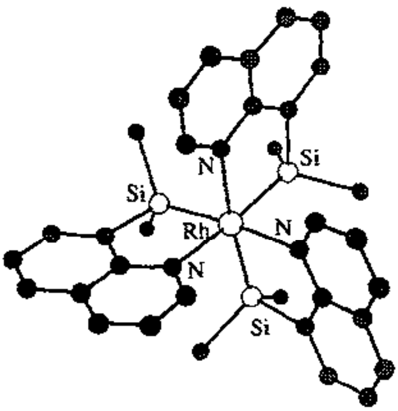
(16)

The reactions of $[\{Rh(CO)_2Cl\}_2]$ with $Me_2PCH_2CH_2SiX_nMe_{3-n}$ (X = F or OMe) yield square planar rhodium(I) complexes of the type $[RhCl(CO)L_2]$ (see section 9.3.5), but when X = Cl and $n = 3$, oxidative addition of a Si-Cl bond occurs to give the octahedral rhodium(III) complex $[RhCl_2(CO)(Me_2PCH_2CH_2SiCl_2)(Me_2PCH_2CH_2SiCl_3)]$ [35].

The syntheses of *mer*-$[RhCl_3(SbPh_3)_3]$ and *trans*-$[RhCl_2(Ph)(SbPh_3)_2]$ from $RhCl_3$ and $SbPh_3$ have been reported. The complex *mer*-$[RhCl_3(SbPh_3)_3]$ may also be obtained in high yield by treating rhodium(III) chloride with $SbPh_3$ in the presence of excess chloride ion in ethanol under reflux. Pyridine reacts with *mer*-$[RhCl_3(SbPh_3)_3]$ in MeOH under reflux to give *trans*-$[RhCl_2(py)_4]^+$ [36].

9.1.6 Complexes with mixed donor atom ligands

The preparation and characterisation of the complex *fac*-$[RhL_3]$ (**17**), in which HL = (8-quinolyl)dimethylsilane, have been described. The complex is stable to air and moisture and does not decompose when heated to 150°C. ^1H and ^{29}Si NMR spectroscopic properties are reported ($J_{Rh\text{-}Si} = 41.7$ Hz), and the crystal structure of (**17**) has been determined. Each ligand functions as an *N,Si*-donor [37]. The rhodium(I) complex $[RhL(CO)\{P(C_6H_4R)_3\}]$ (HL is the substituted quinoline (**18**); R = 4-OMe, 4-Me, 4-F, 4-Cl or 3-Me) undergoes oxidative addition when it reacts with MeI or I_2. The effects of the steric and electronic properties of the phosphine ligands of the reactions have been investigated. The products have been characterised by IR, and ^1H and ^{31}P NMR spectroscopies and results indicate that only one isomer of the rhodium(III) complex is formed in each case. The crystal structure of $[Rh(I)(Me)L(CO)\{P(C_6H_4Me\text{-}4)_3\}].0.5Et_2O$ has been determined. The metal centre is octahedrally coordinated as shown in structure (**19**) with ligand L^- functioning as an *N,O*-donor. The iodide and methyl groups lie *cis* to each other [38].



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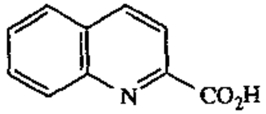

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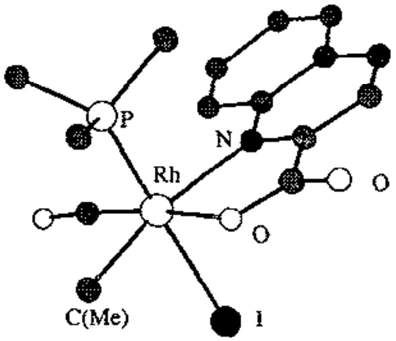
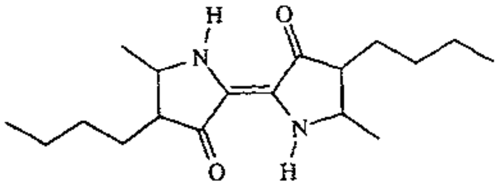


Only *ipso*-C atoms of the *o*-tolyl groups are shown.

(19)

Treatment of the dimer $[\{Cp^*RhCl_2\}_2]$ with the pyrrole derivative (**20**) leads to the formation of $[\{Cp^*RhCl\}_2(\mu\text{-}L)]$ in which each rhodium centre is coordinated by one *N,O*-donor set of the di-deprotonated ligand. The complex has been characterised by IR and UV-VIS spectroscopies. A significant bathochromic shift of absorption in the visible region is observed in going from free (**20**) to the complex [39].



(20)

A series of rhodium(III) complexes has been made incorporating ligands such as 3-(*N*-phenylamino)-3-methyl-2-butanone oxime (HL) and 3-(*N*-2-phenylethylamino)-3-methyl-2-butanone oxime (HL'). The products have been spectroscopically and, for four complexes including $[Rh(HL)LCl_2]$ and $[Rh(HL')L'Cl_2]$, crystallographically characterised. In each, the rhodium(III) centre is octahedral with *trans*-chloride ligands; both ligands are *N,N'*-bonded [40].

The preparation and crystal structure of *fac*-$[RhL_3]$ (HL = *N,N*-diethyl-*N'*-benzoylthiourea) have been reported. Pertinent distances around the octahedral rhodium(III) centre are Rh-S = 2.284(3)Å and Rh-O = 2.033(5)Å [41]. In the products of the reactions of rhodium(III) chloride with *S*-methyl-L-cysteine (HL) there is evidence for competition for different coordination modes and this is dependent upon the reaction conditions and whether or not the ligand is deprotonated. Mononuclear complexes that have been isolated and characterised are $[Rh(HL\text{-}S,N)(L\text{-}S,O)Cl_2].2H_2O$, $[Rh(HL\text{-}S)(L\text{-}S,N)Cl_3].2H_2O$ and $[Rh(HL\text{-}S)_3Cl_3]$. In addition, the tetranuclear compound $[Rh_4(L\text{-}S,O)_2(L\text{-}S,N,O)_4Cl_6]$ has been reported [42].

9.2 RHODIUM(II)

An article that reviews the chemistry of d^7 metal ion complexes including those of rhodium(II) has appeared (242 references); syntheses, structural data, and magnetic, IR and UV-VIS spectroscopic, and X-ray PES properties are discussed [43].

The preparation [32a] and crystal structure [32, 32a] of *trans*-$[RhCl_2(P^iPr_3)_2]$ have been reported. The structure confirms a square planar geometry; the Rh-P distance is 2.373(1)Å.

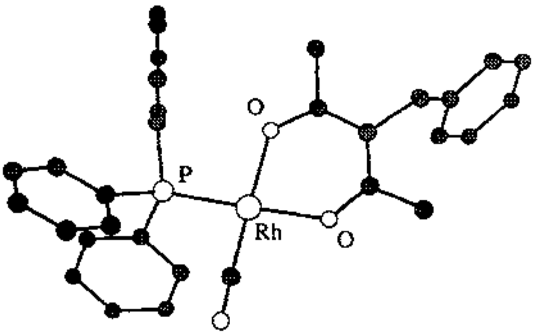
The preparations of the nitrosubstituted derivatives of the ligand 3-(1-imidazoyl)propanoic acid (HL) have been described. Rhodium(II) complexes of HL are amongst a series of compounds synthesised and characterised. Rhodium(II) acetate reacts with HL, and the isolated products are the purple complexes $[Rh(HL)(OAc)_2]$.solv (solv = H_2O or EtOH). Spectroscopic data are consistent with the ligands being coordinated to the rhodium(II) centre through the imidazole *N*-donor atom. Related copper(II), cobalt(II) and platinum(II) complexes have also been prepared and characterised, and the radiosensitiser activities have been assessed [33].

9.3 RHODIUM(I)

9.3.1 Complexes with oxygen donor ligands

The products of the reaction of rhodium(III) nitrate dihydrate with excess PPh_3 in methanol/ethanol are dependent upon the conditions. At room temperature, $[Rh(ONO_2)(PPh_3)_3]$ is obtained, but at reflux temperature (> 48 hr), the product is *trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$. Both complexes have been studied by X-ray diffraction methods, and in each, the nitrate ligand is monodentate [9, 10].

The single crystal structure of the square planar complex $[Rh(CO)L(PPh_3)]$ (**21**), where HL = 3-benzylacetylacetone, has been determined [44]. Basson *et al.* have elucidated the solid state structure of the rhodium(I) complex $[Rh(CO)LL']$ (**22**) in which HL = *N*-hydroxy-*N*-nitrosoaniline and L' = 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. The ligand L^- coordinates in an *O,O'*-mode [45].



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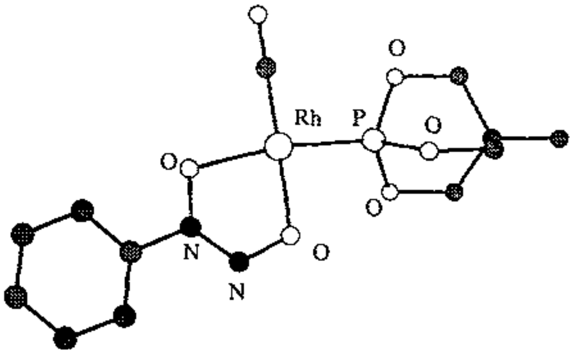
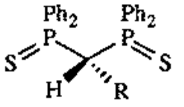


(22)

It has previously been reported that crystals of $[Rh(CO)_2L]$ (L^- = 3,6-di^{t}butyl-1,2-semiquinone) bend reversibly when they are exposed to light in the near-infrared. The solid state structure of this complex has now been determined and illustrates that the molecules are stacked in columns with a non-linear oligomeric Rh_x-backbone. The magnetic properties of $[Rh(CO)_2L]$ show a temperature dependence with both ferro- and anti-ferromagnetic interactions (5-330 K). Coupling between the semiquinone ligands is propagated through rhodium-rhodium interactions within the aforementioned stacks. The near-IR spectrum of the complex, and the origins of the photomechanical properties of the crystals have been discussed [46].

9.3.2 *Complexes with sulfur donor ligands*

The reactions of $[\{Rh(cod)Cl_2\}_2]$ with ligands **(23)** yield the complexes $[Rh(cod)\{$**(23)**-$S,S'\}]^+$. Facile loss of H^+ from the ligand occurs and the neutral complex, for R = H, has been structurally characterised [47].



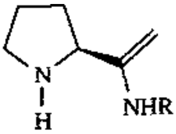
R = H or Me

(23)

9.3.3 Complexes with nitrogen donor ligands

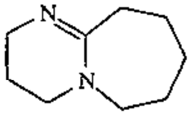
The reactions of [Rh(CO)(PPh$_3$)$_2$(OSO$_2$CF$_3$)] with 1,4-dicyanobenzene and 1,4-dicyano-2-butene (L) lead to the complexes [(CO)(Ph$_3$P)$_2$Rh(μ-L)Rh(CO)(PPh$_3$)$_2$](OSO$_2$CF$_3$)$_2$ which have been characterised by ^{1}H and ^{31}P NMR and IR spectroscopies [48].

Optically active complexes of the type [RhCl(cod)L], [RhCl(CO)$_2$L] and [RhCl(PPh$_3$)$_2$L] in which L = **(24)** (an *N,N'*-donor) have been synthesised and characterised by IR and ^{1}H NMR spectroscopies. Cationic species may be derived by displacing the chloride ligand in these complexes by non-coordinating anions such as hexafluorophosphate. The results of catalytic studies involving the new rhodium(I) complexes have been reported; they are selective catalysts for the hydrogenation of prochiral alkenes [49].



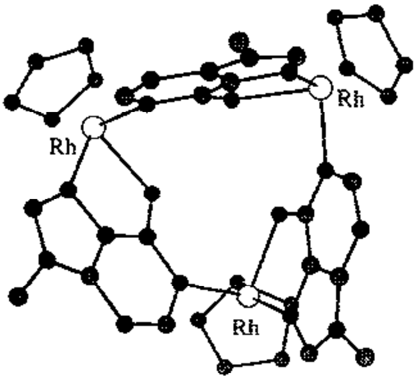
R = ^{t}Bu or (CH$_2$)$_3$Si(OEt)$_3$

(24)



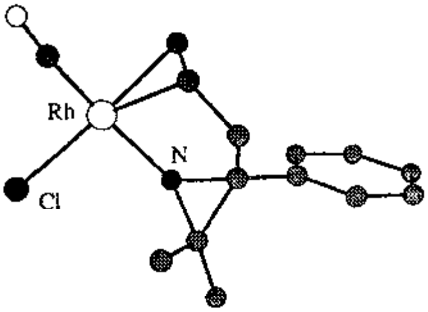
(25)

Rhodium(I) complexes involving *N*-donor heterocyclic ligands include the following. The complexes [Rh(cod)(DBU-*N*)], DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, **(25)**, and [Rh(cod)(L-*N*)], L = 1,5-diazabicyclo[4.3.0]non-5-ene, have been the subjects of X-ray diffraction studies. In both, the heterocyclic ligands function as monodenate *N*-donors [50]. In acetonitrile, the rhodium(I) complexes [Rh(CO)Cl(ER$_3$)$_2$] react with AgX (E = P, R = Ph, X = BF$_4$; E = P, R = *c*-C$_6$H$_{11}$, X = CF$_3$SO$_3$; E = As, R = Ph, X = BF$_4$) to give *trans*-[Rh(CO)(MeCN)(ER$_3$)$_2$]X. The two tetrafluoroborate salts react with 8-methylquinoline (HL) at room temperature to yield *trans*-[Rh(CO)(HL)(EPh$_3$)$_2$][BF$_4$] (E = P or As). For E = P, the product has been confirmed crystallographically. The plane of the 8-methylquinoline ligand lies perpendicular to the square coordination-plane of the rhodium(I) centre. The methyl group is involved in a weak agostic interaction; the Rh-H distance of the Rh-H-C$_{\text{methyl}}$ grouping is 2.21Å [51]. 9-Methyladenine (L) reacts with the water soluble complex [{Cp*Rh(H$_2$O)$_2$(CF$_3$SO$_3$)$_2$}$_n$] (the preparation and characterisation of which are reported) to yield [{Cp*RhL}$_3$][CF$_3$SO$_3$]$_3$. This crystallises as a hydrate, and its structure has been determined. The cation, **(26)**, is a cyclic trimer in the solid state; the 9-methyladenine ligand coordinates to each rhodium(I) centre as an *N,N'*-donor, and one nitrogen atom binds to a second metal atom. Spectroscopic data suggest that the product of the reaction of [{Cp*Rh(H$_2$O)$_2$(CF$_3$SO$_3$)$_2$}$_n$] with adenosine is also a cyclic trimer, whereas a monomer is formed when guanosine is the ligand. The coordination differences between these ligands are discussed [52].



(26)

Although organometallic in nature, complex (27) is included in this article because of its novelty. 2,2-Dimethyl-3-phenyl-3-allylaziridine (L) reacts with [{Rh(ethene)$_2$Cl}$_2$] to give [RhL(ethene)Cl]; treatment with CO then leads to (27). The CO ligand can be displaced by PPh$_3$. The crystal structure of (27) reveals that the organic ligand is coordinated through the heterocyclic *N*-donor atom and the unsaturated unit — a 4-electron donor overall, giving a 16-electron rhodium(I) centre. This appears to be the first example of a didentate aziridine [53].



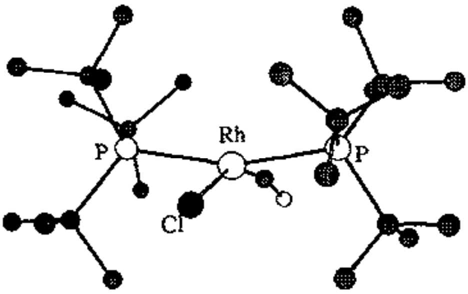
(27)

9.3.4 Complexes with phosphorus donor ligands

Phosphine ligands are involved in a number of the rhodium(I) complexes already described in section 9.3 [9, 10, 44, 48, 49, 51, 53]. The following complexes are considered to contain phosphines as the principal ligand(s) of interest.

The results of studies which look at the diastereoselective hydrogenation of folic acid using optically active rhodium(I) diphosphane complexes have been reported [54].

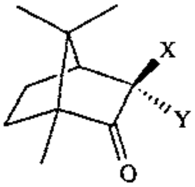
Wilkinson's catalyst is, of course, a well known compound. The preparation and characterisation of a solvated, orthorhombic form of the complex — $[RhCl(CO)(PPh_3)_2].2CH_2Cl_2$ — have now been described. Comparisons are made with earlier work, and Dunbar *et al.* show that the previously reported orthorhombic "$[RhCl_2(PPh_3)_2]$" and $[RhCl(CO)(PPh_3)_2]$ are one and the same compound [55]. Harlow *et al.* have described a simple rhodium(I) complex that is not square planar as might have been expected. Prepared from $[\{Rh(CO)_2Cl_2\}_2]$ and P^tBu_3, $[Rh(CO)Cl(P^tBu_3)_2]$ (**28**) has been the subject of an X-ray diffraction study. In the distorted tetrahedral coordination sphere, the angles P-Rh-P and C_{CO}-Rh-Cl are 162.3 and 148.7° respectively in one of two crystallographically independent forms [56].



(**28**)

The rhodium(I) complexes *trans*-$[Rh(CO)X(PEt_3)_2]$ (X = Cl, Br, I or NCS) react with PH_3 at 183 K in dichloromethane to give the five-coordinate cations $[Rh(CO)(PH_3)_2(PEt_3)_2]^+$. Further reaction with carbon monoxide (213 K) leads to the formation of $[Rh(CO)_2(PH_3)(PEt_3)_2]^+$. Related reactions are also reported, along with detailed ^{13}C, ^{31}P and ^1H NMR spectroscopic data [57].

Related to the work involving ligand (**15**) [34] (section 9.1.4) is that of Perera *et al.* The series of ligands (**29**) has been prepared. For X = H, and Y = PPh_2, the reaction of the ligand with $[\{Rh(CO)_2Cl\}_2]$ to give *trans*-$[RhCl(CO)(\mathbf{29})_2]$ has been investigated. The product has been characterised by ^1H, ^{31}P and ^{13}C NMR spectroscopies. An alternative route to the complex is the reaction between $RhCl_3.3H_2O$, CO, and the corresponding enolate of the ligand [58].



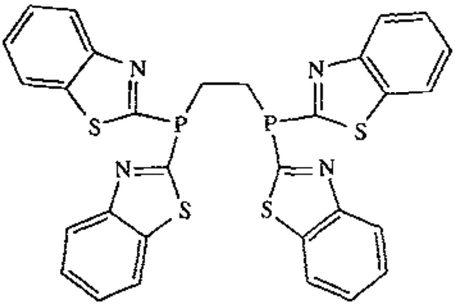
X	Y
PPh_2	H
H	PPh_2
H	$P(O)Ph_2$
H	$P(S)Ph_2$

(**29**)

Rhodium(III) chloride reacts with an excess of 1,3,5-triaza-7-phosphaadamantane (L) in ethanol to yield $[RhClL_3]$. This is an active catalyst for alkene hydrogenation whilst being effectively inactive for the hydrogenation of aldehyde functionalities. With HCl, $[RhClL_3]$ reacts to give $[RhClL_2].2HCl$ for which an X-ray diffraction study has been carried out. A square planar coordination sphere around the rhodium(I) centre has been confirmed; each 1,3,5-triaza-7-phosphaadamantane ligand is protonated and is bonded through one phosphorus atom. One chloride ion is hydrogen-bonded between the two protonation sites [59].

Unsaturated, fourteen-electron metal fragments such as those of the general form $\{Rh(PR_3)_2X\}$ (*e.g.* X = halide) are important, reactive intermediates in a range of catalytic processes. Molecular orbital calculations have been carried out at the extended Hückel level on the model complexes $[RhCl(L\text{-}P,P')]$ and $[RhCl(L'\text{-}P,P')]$, where $L = H_2PCH_2PH_2$ and $L' = {}^{t}Bu_2PCH_2P{}^{t}Bu_2$. Details of the electronic structures of these species are presented. In addition, the crystal structure of $[RhCl(L'\text{-}P,P')(PMe_3)]$ has been determined. As expected, it has a square planar geometry; pertinent distances are $Rh\text{-}P_{L'} = 2.225(1)$ and 2.289(1)Å, and $Rh\text{-}P_{PMe_3} = 2.297(1)$Å. Within the chelate ring, the angle P-Rh-P is 75.47(4)° [60].

Reactions of $[RhCl(PPh_3)_3]$ with two potentially mixed-donor atom ligands have been investigated (see also section 9.3.5). In one reaction, the ligand (**30**) is found to coordinate only through the two phosphorus atoms; the product is $[RhCl(PPh_3)\{(\mathbf{30})\text{-}P,P'\}]$. This complex undergoes oxidation and disproportionation in $CHCl_3$ to yield $[\{RhCl\}_2\{\mu\text{-}(\mathbf{30})\}_2][RhCl_4(\mathbf{30})]_2$, and the identity of the product has been confirmed crystallographically. The rhodium(III) anion contains an octahedral metal centre and ligand (**30**) is coordinated in a *P,P'*-mode. In the dinuclear species, each ligand functions as a *P,P'*-chelate to one of the two metal centres, whilst also acting as a bridging ligand by using two of the four *P,N*-donor sets [61]. The versatility of ligand (**31**) (the synthesis of which is reported) has also been demonstrated. The products of the reaction between $[\{Rh(cod)Cl\}_2]$ and (**31**) are dependent upon the ratio of the reagents. When the ligand is present in a 2-fold excess, the rhodium(I) complex $[Rh(cod)Cl(\mathbf{31})]$ is formed. Here, the ligand coordinates only through the phosphine group. In solution, ^{1}H and ^{13}C NMR spectroscopic data provide evidence for fluxionality. When the ratio of $[\{Rh(cod)Cl\}_2] : (\mathbf{31})$ is 1 : 1, a dinuclear compound is produced — $[\{Rh(cod)Cl\}_2\{\mu\text{-}(\mathbf{31})\}]$ — in which the ligand functions as an *N*-donor to one metal centre and a *P*-donor to the other. There is evidence that an equilibrium can be established in solution between the mononuclear and dinuclear complexes, with loss of one equivalent of the ligand (**31**) accompanying the transition from monomer to dimer. A further dinuclear species $[\{Rh(CO)Cl\{\mu\text{-}(\mathbf{31})\}\}_2]$ has also been prepared and characterised by X-ray diffraction methods; the two bridging ligands are in a 'head-to-tail' arrangement [62]. A not unrelated ligand is the substituted pyridine (**32**). It reacts with $[\{Rh(cod)Cl\}_2]$ to give a square planar complex $[Rh(cod)Cl(\mathbf{32})]$ in which the heterocyclic ligand is *P*-bonded. The cod ligand may be displaced by carbon monoxide and the rhodium(I) complex $[Rh(CO)_2Cl(\mathbf{32})]$ has been characterised by IR and NMR spectroscopies. Further reaction of $[Rh(CO)_2Cl(\mathbf{32})]$ with ligand (**32**) leads to the formation of *trans*-$[Rh(CO)Cl(\mathbf{32})_2]$, again with *P*-coordinated ligands. This new complex forms a trinuclear species when treated with $[Cu(NCMe)_4]^+$; structural data reveal that the copper(I) centre is in a linear environment, and interacts with the pyridine-*N* donors which remain uncoordinated in the precursor *trans*-$[Rh(CO)Cl(\mathbf{32})_2]$. Further reactions in this series are also discussed [63].



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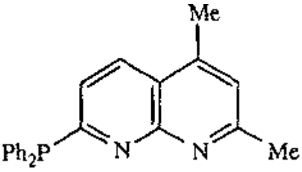

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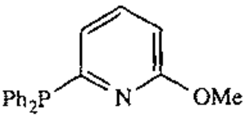
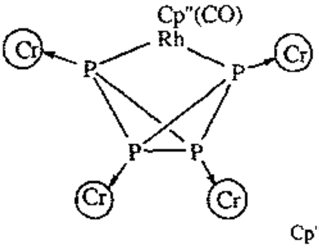
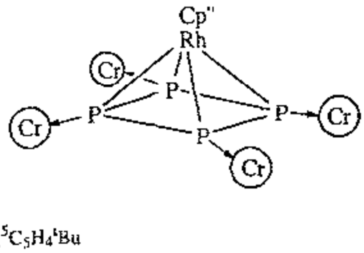


(32)

The coordination of members of a series of 'donor-acceptor' ligands, L, of the type $Me_2PCH_2CH_2SiX_nMe_{3-n}$ (X = F, Cl, OMe; n = 0-3 — not all combinations) with rhodium(I) have been studied. Mononuclear complexes of the formula $[RhCl(CO)L_2]$ have been prepared, and spectroscopically (IR, and ^1H, ^{31}P and, where appropriate, ^{19}F NMR) characterised. The crystal structures of $[RhCl(CO)(Me_2PCH_2CH_2SiF_3)_2]$ and $[RhCl(CO)(Me_2PCH_2CH_2Si(OMe)_3)_2]$ have been determined. In each, a square planar geometry and a *trans*-configuration are observed, with each $Me_2PCH_2CH_2SiX_3$ ligand functioning as a *P*-donor, leaving the silane moiety pendant [35].

The last piece of work to be discussed in this section involves what are best described as derivatives of *p*-block clusters. Elemental phosphorus reacts with the rhodium(I) complex $[Cp''Rh(CO)_2]$ ($Cp'' = \eta^5\text{-}C_5H_4{}^tBu$) in the presence of a five-fold excess of $[Cr(CO)_5(thf)]$ to yield **(33)**, but if a larger excess of $[Cr(CO)_5(thf)]$ is used, **(34)** results. The IR and NMR spectroscopic properties of these new products have been described, as have their single crystal structures. In **(33)**, the Cp''Rh(CO)-fragment bridges between the wingtips of a P_4-butterfly. The wingtip-wingtip P·····P separation is 2.815(4)Å. In compound **(34)**, the P_4-unit is planar with Rh-P distances of 1.88Å [64].





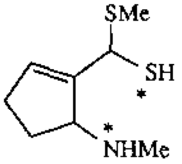
$Cp'' = \eta^5C_5H_4{}^tBu$

Ⓒr = $Cr(CO)_5$

(33) (34)

9.3.5 Complexes with mixed donor atom ligands

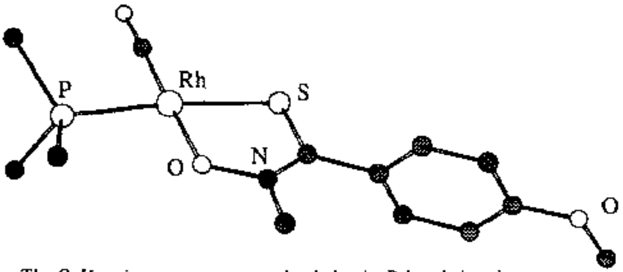
The preparation and structural characterisation of the square planar rhodium(I) complex [Rh(CO)L(PPh$_3$)] in which HL = (**35**) have been reported. The conjugate base of (**35**) functions as an *N,S*-donor, and the nitrogen-donor atom lies *trans* to the phosphine ligand. The kinetics of the oxidative addition of methyl iodide to [Rh(CO)L(PPh$_3$)] have been studied [65].



* = site of coordination in deprotonated ligand

(**35**)

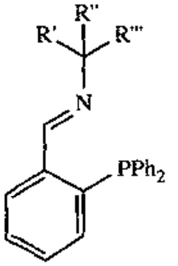
The conjugate base of 4-MeOC$_6$H$_4$C(S)N(Me)OH (HL) coordinates to a rhodium(I) centre in the square planar complex [Rh(CO)L({P(*c*-C$_6$H$_{11}$)$_3$})] (**36**) as an *O,S*-donor. The crystal structure of the compound (**36**).C$_6$H$_6$ has been determined [66].



The C_6H_{11} rings are represented only by the P-bonded carbon atoms.

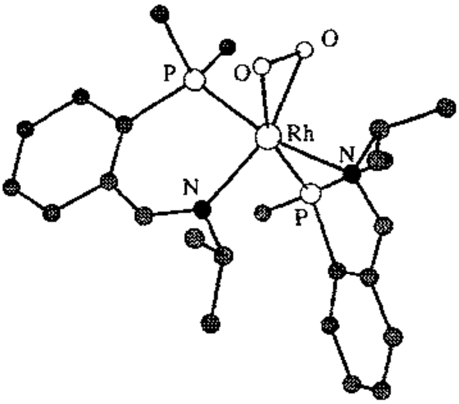
(**36**)

Some ligands with phosphorus and nitrogen donor atoms were mentioned in the previous section; in mononuclear complexes involving these ligands, each was *P*-bonded, but use was made of the *N,P*-donor set to generate di- or trinuclear species. Amongst mononuclear complexes featuring chelates with an *N,P*-donor set is a series incorporating ligands in the family (**37**). Rhodium(I) complexes with these ligands have been synthesised and characterised spectroscopically. The reactivity patterns of these species are interesting — depending upon the steric hindrance exhibited by each ligand of type (**37**), the complexes (in solutions of organic solvents) may reversibly bond dioxygen at room temperature. The oxygenation–deoxygenation cycles have been monitored by using ^{31}P NMR spectroscopy and may be repeated several times. reactions with carbon monoxide have also been investigated. The structure of one dioxygen complex, [Rh(**37**)$_2$(O$_2$)][BF$_4$] (for R' = H, R'' = R''' = Me) has been elucidated. The rhodium(I) centre in the cationic complex (**38**) is in a distorted trigonal bipyramidal environment, if the description places the O_2 molecule in one site. The Rh-$O_{dioxygen}$ distances are equal (1.436(9)Å) [67].



R' = R'' = H, R''' = Me, Et
R' = H, R'' = R''' = Me
R' = R'' = R''' = Me

(37)

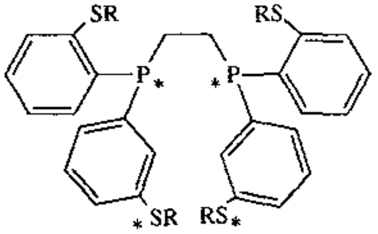


Only the *ipso*-C atoms are shown for the Ph rings.

(38)

Another *N,P*-donor to be studied is the ligand $^iPr_2PCH_2CH_2NMe_2$. In this same work, the coordination to rhodium(I) centres of the related *O,P*-donor $^iPr_2PCH_2CH_2OMe$ has also been investigated. The complex cation $[Rh(^iPr_2PCH_2CH_2OMe)_2]^+$ reacts with carbon monoxide to give the complex $[Rh(CO)(^iPr_2PCH_2CH_2OMe)_2]^+$ in which one of the two $^iPr_2PCH_2CH_2OMe$ ligands is chelating and the other is monodentate. With H_2, $[Rh(^iPr_2PCH_2CH_2OMe)_2]^+$ reacts to give a relatively unstable product of formula $[RhH_2(^iPr_2PCH_2CH_2OMe)_2]^+$. Other related reactions have also been described [68].

The reactions of $[RhCl(PPh_3)_3$ with ligands (**39**) lead to the rhodium(I) compounds [Rh(**39**)]Cl, in which the ligand functions as an *P,P',S,S'*-donor generating a square planar complex cation in each case. Studies with a related and, again potentially mixed-donor, ligand have given a mononuclear product in which the ligand is *P,P'*-bonded (see section 9.3.4) [61].



R = Me, ^iPr

* = site of coordination

(39)

9.4 DINUCLEAR RHODIUM COMPLEXES

Several dinuclear complexes containing rhodium have been described in previous sections.

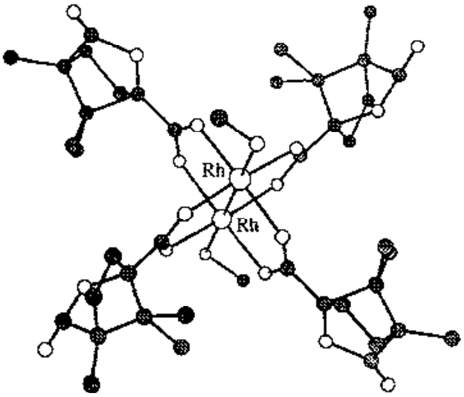
9.4.1 Hydroxy- and superoxo-bridged complexes

Metastable hydrolysis products of rhodium(III) have been separated chromatographically and their ^{1}H, ^{103}Rh and ^{17}O NMR spectroscopic properties recorded. A dimer and trimer have been characterised as solution species. The dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ is centrosymmetric, whilst the NMR spectroscopic data for the trimer are consistent with a linear structure (see section 9.5) [69]. When chromium(III) ions are added to alkaline solutions of rhodium(III), heteronuclear species are formed which may be separated by using an ion-exchange column. The mesitylsulfate salt of the dinuclear species $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ has been isolated as a hydrate, and structurally characterised. The cation possesses a centre-of-symmetry and it proved impossible to distinguish the two metal centres. The metal----metal separation is 3.031(2)Å [70].

Reactions of $[Rh(py)_3Cl]$, water and dioxygen are reported to give blue superoxo-bridged dirhodium(III) complexes. These have been characterised by ESR and UV-VIS spectroscopies, and their reactions have been investigated [71].

9.4.2 Carboxylate-bridged complexes

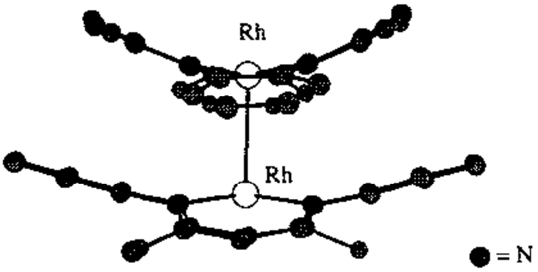
The role of carboxylate bridged rhodium dimers of the type $[Rh_2(OAc)_4]$ as enantioselective catalysts has been the subject of a 'highlight' article [72]. The electronic, IR, Raman and resonance Raman spectroscopic properties of the complexes $[Rh_2(OSCMe)_4L_2]$ (L = PPh_3, $AsPh_3$, $SbPh_3$ and MeCOSH) have been studied and the results discussed. The electronic and resonance Raman spectroscopic results are consistent with X-ray diffraction data in showing that the Rh-Rh distances in the tetrakis(thiocarboxylate) complexes are significantly longer than those in the corresponding tetrakis(carboxylate) compounds. In the visible (blue) region of the absorption spectrum of each thiocarboxylate complex, a strong band has been assigned to the $\sigma(Rh_2)\rightarrow\sigma^*(Rh_2)$ transition; the absorption exhibits a bathochromic shift [73].



(40)

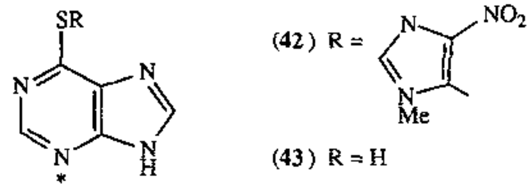
The reaction of $[Rh_2(O_2C^tBu)_4]$ with 1,4-benzoquinone (L) leads to the formation of $[Rh_2(O_2C^tBu)_4.L]_n$. This complex possesses a chain-structure in which the $\{Rh_2(O_2C^tBu)_4\}$-units are connected by difunctional 1,4-benzoquinone ligands. The latter coordinate through one oxygen atom, and through one C-C π-bond [74]. For RCO_2H = camphanic acid, the structure of $[Rh_2(O_2CR)_4(MeOH)_2]$ **(40)** has been determined. The structure is as expected with four bridging carboxylate ligands and two axially-bound methanol molecules [75].

When 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecine (H_2L) reacts with $[Rh_2(OAc)_4]$, the dirhodium complex $[Rh_2L_2]$ **(41)** is formed. Crystal structural data reveal the presence of an unsupported Rh-Rh bond (2.619(1)Å) and a staggered arrangement of the two macrocyclic ligands. In the presence of diphenylacetylene, the reaction between H_2L and $[Rh_2(OAc)_4]$ proceeds to give a tetrarhodium product which is described in section 9.5 [76].



(41)

The heterocyclic ligand **(42)** is a derivative of the anticancer agent **(43)**; ligand **(42)** reacts with $[Rh_2(OAc)_4(H_2O)_2]$ to yield $[Rh_2(OAc)_4(\mathbf{42})_2]$. The ^1H NMR, UV-VIS and IR spectroscopic and electrochemical properties of this complex have been studied. It crystallises with dimethylacetamide solvate, and the structure has been determined. Each heterocyclic ligand is *N*-bonded in an axial site. Hydrogen-bonding plays an important role in stabilising the solid state structure [77].



* = site of coordination to rhodium

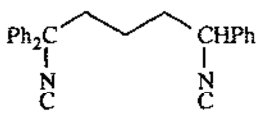
The reaction of $[Rh_2(OAc)_4(MeOH)_2]$ with PPh_3 has been followed by using spectroscopic methods and as a function of the reaction conditions. Intermediates have been observed and one, $[Rh_2(OAc)_3\{C_6H_4PPh_2\}(AcOH)_2]$, has been isolated and structurally characterised. Metallation of one phenyl ring occurs, allowing the $[C_6H_4PPh_2]^-$ ligand to function as a *C,P*-donor and capable of bridging between the two rhodium centres. $[Rh_2(OAc)_3\{C_6H_4PPh_2\}(AcOH)_2]$ readily reacts further with PPh_3 to generate the doubly metallated product $[Rh_2(OAc)_2\{C_6H_4PPh_2\}_3(AcOH)_2]$ in which the two *C,P*-bridging ligands are in a 'head-to-tail' arrangement. This has been crystallographically confirmed. On the other hand, under thermal conditions, a 'head-to-head' product is observed [78]. Stepwise exchange occurs between $[CD_3CO_2]^-$ and the acetate and acetic acid ligands in $[Rh_2(OAc)_3\{C_6H_4PPh_2\}(AcOH)_2]$, and the kinetics of this process have been investigated. The first step is the fast exchange of the acetate ligand which is *trans* to the metallated ligand, and also fast exchange of the axially-bound acetic acid molecules. The remaining two acetate bridges are exchanged in a slow step [79]. Lahuerta *et al.* have also synthesised the related complexes $[Rh_2(OAc)_3\{(4\text{-}XC_6H_3)P(C_6H_4\text{-}4\text{-}X)_2\}(AcOH)_2]$ where X = Cl or Me. These species under ligand exchange and metallation when they are treated with $P(C_6H_4\text{-}4\text{-}Y)_3$ where Y = H, Cl or Me. When the reagents combine in a 1 : 1 ratio, the doubly metallated products exhibit a 'head-to-tail' arrangement of metallated ligands for X = Y. In contrast, when the ratio of $P(C_6H_4\text{-}4\text{-}Y)_3$: dirhodium complex is 3 : 1, a mixture of 'head-to-tail' and 'head-to-head' products is obtained for X = Y = Cl, but only a 'head-to-head' product if observed for X = Y = Me; both 'head-to-tail' and 'head-to-head' products are formed if X ≠ Y [80]. The crystal structure of $[Rh_2(OAc)_3\{C_6H_4P(Ph)(C_6H_4\text{-}2\text{-}Cl)\}(AcOH)_2]$ has been determined; the Rh-Rh distance is 2.401(1)Å. Ligand exchange reactions have been investigated, as well as thermal transformations [81]. Orthometallation has also been observed in the case of a bridging dppe ligand in a dirhodium complex [82].

9.4.3 Complexes with dppm and related ligands as bridging units

When *trans*-$[RhCl(CO)(Me_2PCH_2PMe_2)_2]$ reacts with aqueous sodium hydroxide and carbon monoxide, the product is $[Rh_2(CO)_3(\mu\text{-}Me_2PCH_2PMe_2)_2]$. Under an atmosphere pressure of carbon monoxide, this complex is in equilibrium with $[Rh_2(CO)_2(\mu\text{-}CO)_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$. $[Rh_2(CO)_3(\mu\text{-}Me_2PCH_2PMe_2)_2]$ reacts with tetrafluoroboric acid to give $[Rh_2(CO)_3(\mu\text{-}H)(\mu\text{-}Me_2PCH_2PMe_2)_2][BF_4]$. Other related chemistry has also been described [83].

In solution, the dirhodium complexes $[Rh_2(CO)_2(\mu\text{-}dppm)_2(\mu\text{-}NR)]$ (R = Me, Ph, 4-MeC_6H_4, 4-FC_6H_4 and 4-BrC_6H_4) are in equilibrium with their respective tautomers in which one dppm ligand is deprotonated and the imido bridge is protonated. Carbon monoxide inserts into the Rh-N bond, and the nature of one product which forms in the presence of excess CO — $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2\{\mu\text{-}\eta^1{:}\eta^1\text{-}C(O)NMeC(O)\}]$ — has been confirmed by crystallographic studies [84].

Ligands which are similar to (**31**) and (**39**), but having only one methylene group between the two phosphorus atoms, react with $[\{RhCl(CO)_2\}_2]$ to yield the 'A-frame' type complexes $[ClRh(\mu\text{-}CO)(\mu\text{-}L)_2Rh(CO)]Cl$ and *cis*-$[\{RhCl(CO)\}_2(\mu\text{-}L')_2]$ where L is related to (**30**), and L' is related to (**39**) (R = Me). Structural data for *cis*-$[Rh_2Cl_2(CO)_2(\mu\text{-}L')_2]$ reveal that each rhodium centre is in a square planar environment [85]. In the presence of ammonium hexafluorophosphate, $[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$ reacts with ligand (**44**) to give 'head-to-head' *RR*- and *SS*-isomers the dirhodium complex $[Rh_2(\mu\text{-}dppm)_2\{\mu\text{-}(\mathbf{44})\}_2]^{2+}$. Characterisation of this cationic complex has been by IR, UV-VIS and ^{31}P NMR spectroscopies, electrochemical and X-ray diffraction methods [86]. The single crystal structure of $[Rh_2(CN^tBu)_2(\mu\text{-}dppm)_2(\mu\text{-}3,5\text{-}pz)]$ (**45**) ($[3,5\text{-}pz]^-$ = 3,5-dimethylpyrazolato) has been elucidated [87].



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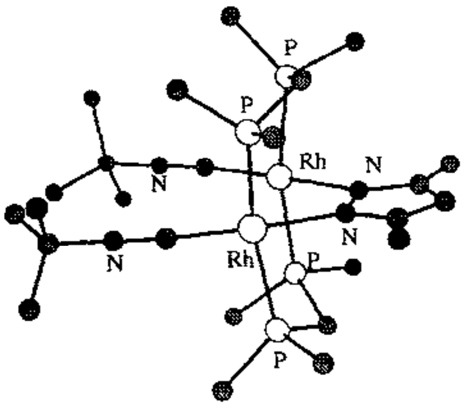


Only the *ipso*-C atoms are shown for the Ph substituents.

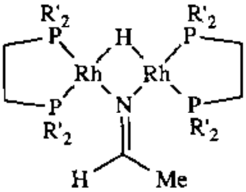
(45)

Heterometallic complexes with dppm bridges include $[(MeCN)Pt(\mu\text{-dppm})_2Rh(NCMe)_3]^{3+}$ [88], $[(OC)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ and $[(OC)(\eta^2\text{-phen})M(\mu\text{-CO})_2(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ (M = Mo or W) [89]. The platinum-rhodium complex is isolated as the hexafluorophosphate salt when $[Rh(NCMe)_4]^+$ is treated with $[Pt(dppm)_2]Cl_2$ in a methanol solution containing $[NH_4][PF_6]$. The structure of $[(MeCN)Pt(\mu\text{-dppm})_2Rh(NCMe)_3]^{3+}$ has been crystallographically confirmed; the platinum and rhodium centres are in square planar and octahedral environments if a metal-metal bond is included in the description. The Pt-Rh distance is 2.708(2)Å. Related chemistry has also been described, and attention is paid to the variation in the coordination geometries within a family of platinum-rhodium species [88]. When $[Rh(S_2CNEt_2)(CO)_2]$ reacts with $[Mo(CO)_4(\eta^2\text{-dppm})]$ or with $[M(CO)_3(\eta^2\text{-phen})(\mu^1\text{-dppm})]$ (M = Mo, W), the dimetallic complexes $[(OC)_4Mo(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ and $[(OC)(\eta^2\text{-phen})M(\mu\text{-CO})_2(\mu\text{-dppm})Rh(S_2CNEt_2)(CO)]$ (M = Mo or W), respectively, are formed. These have been characterised by IR, ^1H and (in part) ^{31}P NMR spectroscopic methods. The presence of dative bonds ($Rh \rightarrow M$) is proposed [89].

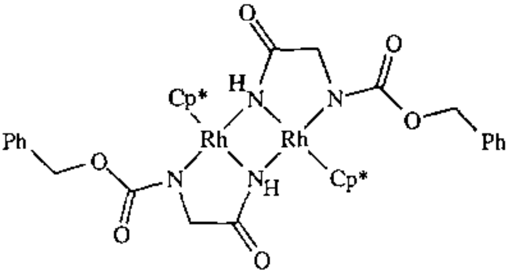
Orthometallation has been observed in the case of a bridging dppe ligand in a dirhodium complex [82]. Dirhodium complexes containing dppp ligands have also been studied. The hydrogenation of $[Rh_2(CO)_2(dppp)_2(\mu\text{-CO})_2]$ in the presence of dppp leads to catalytically important species. Two such products are the dinulear complex $[Rh_2H_2(CO)_2(dppp)_2(\mu\text{-dppp})_2]$ and the mononuclear $[RhH(CO)(dppp)_2]$. In the latter, one bis(phosphine) ligand is monodentate and one is didentate. Mechanistic aspects of this work have been addressed [90].

9.4.4 Complexes with N-donor ligands involved in bridging units

A study of the reactions of nitriles RCN (R = Me, Ph or 2-MeC_6H_4) with the hydrido dimers $[Rh_2(R'_2PCH_2CH_2PR'_2)_2(\mu\text{-}H)_2]$ (R' = ^iPr or O^iPr) has shown that the products include those of the type (**46**). For R' = ^iPr, the structure of compound (**46**) has been crystallographically confirmed. The Rh-N bond lengths are 2.030(3) and 2.044(3)Å [91].



(**46**)

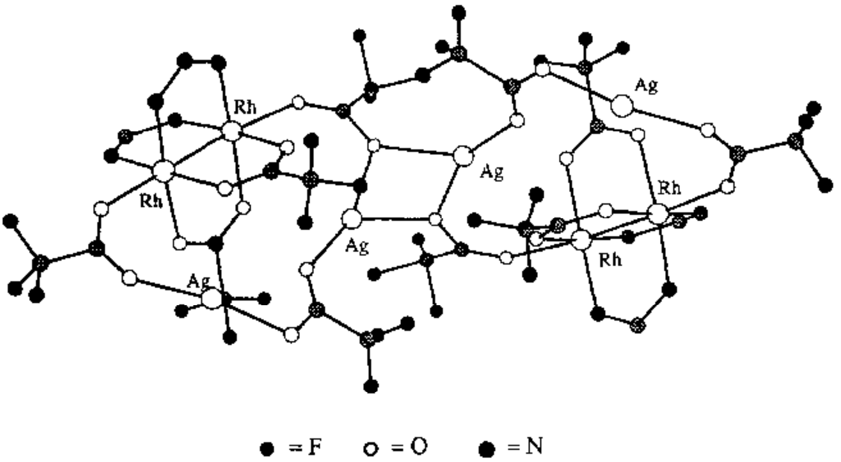


(**47**)

As part of a study of the coordination to rhodium of biologically important ligands, the results of the reaction between $[\{Cp^*RhCl_2\}]_2$ and *N*-carbobenzoxy-glycine amide in the presence of sodium methoxide have been reported. The dinuclear complex (**47**) is formed and has been isolated and structurally characterised [92].

The chemistry of some dirhodium complexes involving triazenide ligands have been reported by Connelly *et al.* [93, 94]. Treating $[Rh_2I(CO)(bpy)(\mu\text{-}RNNNR)_2]^{2+}$ (R = 4-MeC_6H_4) with silver hexafluorophosphate and dppm leads to iodide abstraction and the addition of the dppm ligand. The product is $[Rh_2(\mu\text{-}CO)(bpy)(dppm)(\mu\text{-}RNNNR)_2]^{2+}$ and the results of an X-ray diffraction study show that each of the bpy and dppm ligands is associated with a particular metal centre and is chelating; the electronic structure of the complex has been investigated by using extended Hückel MO calculations. The complex cation is described as possessing an 'open-book' structure, and the bridging carbonyl ligand appears to have the character of a ketonic CO^{2-} unit. Solution data evidence the existence of an isomer equilibrium. Electrochemical results are also discussed. In the presence of a catalytic amount of $[^nBu_4N][BH_4]$, one triazenide ligand in the dication $[Rh_2(\mu\text{-}CO)(bpy)(dppm)(\mu\text{-}N,^1N^3\text{-}RNNNR)_2]^{2+}$ undergoes a rearrangement and adopts an unprecedented $\mu\text{-}N^{1,3},N^{1,3}$-mode. The new structure has been confirmed crystallographically. Electrochemical studies have been carried out and the results discussed.

The bridged complex $[Rh_2L_4]$ which contains the *N,N'*-di-4-methylphenyl-formamidinate ligand (L^-) is chemically oxidised by silver nitrate or silver trifluoroacetate, giving $[Rh_2L_4][NO_3]$ and $[Rh_2L_4(H_2O)][O_2CCF_3]$ respectively. Infrared and EPR spectroscopic data for the two complexes have been recorded; in the latter spectrum, an interaction is observed between the unpaired electron and the two equivalent rhodium centres. An X-ray diffraction study of $[Rh_2L_4(H_2O)][O_2CCF_3]$ has been carried out. In the cation, the single water molecule is axially bound to the$\{Rh_2L_4\}$-core. The Rh-Rh and Rh-O_{water} distances are 2.452(2) and 2.165(2)Å respectively. Comparison of the structural parameters with those of the neutral precursor indicate that oxidation causes a degree of lengthening of the Rh-Rh bond; this is in contrast to the shortening that is predicted on the basis of MO calculations [95]. In a later paper which continues work with the *N,N'*-di-4-methylphenyl-formamidinate ligand, Bruno *et al.* report the formation of the paramagnetic 'dimer-of-dimers' $[\{Rh_2L_2(O_2CCF_3)_3(AgO_2CCF_3)_2\}_2]$ **(48)**, which formally contains two $\{Rh_2\}^{5+}$ cores. In the EPR spectrum, coupling is observed between each unpaired electron and two of the ^{103}Rh centres. The solid state structure of **(48)** illustrates that the $\{Rh_2L_2(O_2CCF_3)_3\}$-radicals are linked through the axial positions by silver trifluoroacetate molecules. Two other related species containing $\{Rh_2\}^{5+}$-cores have also been reported — $[Rh_2L_2(O_2CCF_3)_2(H_2O)_2][ClO_4]$ and $[Rh_2L_2(O_2CCF_3)\}[NO_3]_2$ [96]. The *N,N'*-diphenylphenylbenzamidinate ligand, $[L']^-$, has been incorporated into the complexes $[Rh_2L'_4]$ and $[Rh_2L'_4(CO)]$. The absorption spectroscopic and redox properties of $[Rh_2L'_4]$ are reported. The results of structural studies show that the Rh-Rh distance lengthens from 2.389(1)Å to 2.435(1)Å upon coordination in of the CO molecule in an axial site. Comparisons have been made between these dirhodium systems and similar dicobalt ones [97].

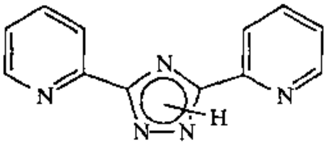


p-tolyl substituents omitted for clarity.

(48)

Pyrazolate ($[pz]^-$) bridges feature in several dirhodium complexes, and one example has already been mentioned — $[Rh_2(CN^tBu)_2(\mu\text{-dppm})_2(\mu\text{-}3,5\text{-pz})]$ (45) [87]. The two complexes $[Rh_2(cod)_2(\mu\text{-pz})(\mu\text{-SPh})]$ and $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-pz})(\mu\text{-SPh})]$ have been synthesised and their reactivity patterns investigated [98]. Sodium and thallium salts of $[Cp^*Rh\{PO(OMe)_2\}_2(pz)]^-$ have been prepared. These anions are ideal units from which to access heterometallic or asymmetrical homometallic complexes containing rhodium. Reactions of the anion $[Cp^*Rh\{PO(OMe)_2\}_2(pz)]^-$ with $[\{Cp^*RhCl_2\}_2]$, $[\{Cp^*IrCl_2\}_2]$ and $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ have been studied. The crystal structure of $[Cp^*Rh\{\mu\text{-}PO(OMe)_2\}_2(\mu\text{-pz})Ru(\eta^6\text{-}C_6H_6)][ClO_4]$ has been elucidated; there is no direct metal-metal bonding interaction [99].

Two triazole-bridged homo- and heterometallic complexes containing rhodium have been described — these are the cationic species $[(bpy)_2Ru(\mu\text{-}L)Rh(ppy)_2]^{2+}$ and $[(ppy)_2Rh(\mu\text{-}L)Rh(ppy)_2]^{+}$ where HL = (49). The formal oxidation state of the rhodium centres in each complex is +3. Electrochemical studies of these and analogous iridium-containing complexes show that the heterometallic species exhibit an oxidation step centred on ruthenium, and a reduction step centred on the bpy ligand. The reduction of the dirhodium (and also the diiridium) complex is triazole-centred. Bands in the absorption spectra of $[(bpy)_2Ru(\mu\text{-}L)Rh(ppy)_2]^{2+}$ can be assigned to the transitions Ru→bpy and Rh→$[ppy]^{-}$. Energy transfer processes in this cation are discussed [100].



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9.4.5 Complexes with porphyrin ligands

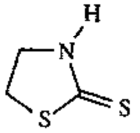
A series of articles has described dirhodium porphyrin complexes. The reactions between a series of (tetraarylporphyrinato)rhodium(II) complexes and CO give results that illustrate the role of ligand steric effects in promoting or inhibiting carbonyl coupling and the associated formation of dirhodium complexes of the type [(porph)RhC(O)C(O)Rh(porph)]. For example, a combination of CO and the radical $[Rh(TMP)]^{\bullet}$ gives an equilibrium mixture of the diamagnetic compound [(TMP)RhC(O)C(O)Rh(TMP)] and (a smaller proportion of) the paramagnetic [Rh(TMP)(CO)] ($S = {}^{1}/_{2}$). On the other hand, reacting CO with $[Rh(TTiPP)]^{\bullet}$ ($TTiPPH_2$ = 5,10,15,20-tetrakis(2,4,6-tri-*iso*-propylphenyl)porphyrin) leads only to the formation of the monomer [Rh(TTiPP)(CO)]. The EPR spectra of the monomeric compounds are consistent with the presence of non-linear Rh-C-O units. Further studies reveal that [Rh(TMP)(CO)] behaves similarly to an acyl radical [101]. Further work by the same authors shows that the reaction of $[Rh(TTEPP)]^{\bullet}$ ($TTEPPH_2$ = 5,10,15,20-tetrakis(1,3,5-triethylphenyl)porphyrin) with ethene (≈ 0.25 atm) in benzene gives rise to the dirhodium complex $[(TTEPP)Rh(CH_2)_4Rh(TTEPP)]$ which has been characterised by ^{1}H and ^{13}C NMR spectroscopies. A similar pattern of reactivity is exhibited by $[Rh(TTiPP)]^{\bullet}$. Low temperature EPR spectroscopic studies of this system illustrate the formation of a 1 : 1 ethene π-complex [102].

The dimer $[Rh_2(OEP)_2]$ undergoes addition reactions with acrylates with reduction of the alkene group. The products are $[(OEP)Rh(CH_2CH(CO_2X)Rh(OEP)]$ where X = H, Me or Et. Stereoisomers, which arise because of hindered rotation about the $CH—CO_2X$ bond, have been observed. The effects of changing the porphyrin ligands to TMP^{2-} are discussed [103].

9.4.6 Complexes with sulfur-containing ligands

Thiolate bridges in dirhodium complexes are seen in $[Rh_2(cod)_2(\mu\text{-}pz)(\mu\text{-}SPh)]$ and $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}pz)(\mu\text{-}SPh)]$ which have been synthesised; their reactivity has been investigated [98]. Bridge-cleavage may be effected in $[Rh_2(PPh_3)_4(\mu\text{-}SC_6F_5)_2]$ by reaction with phosphines, phosphites, or nitrogen-containing species such as pyridines and quinolines. These transformations have been used as a means of preparing a range of mononuclear pentafluorophenylthiolate complexes of rhodium [104].

Dirhodium complexes with mixed donor-atom ligands involving sulfur have been reported. The first work comes from Ciriano *et al.* and incorporates the ligand benzothiazole-2-thiol (HL). The complex $[Rh_2(\mu\text{-}L)_2(CO)_2(PPh_3)_2]$ reacts with $[MCl_2(cod)]$ (M = Pd or Pt) to yield the diamagnetic heterometallic compound $[(Ph_3P)M(\mu\text{-}L)_2Rh(CO)Cl]$. These products have been characterised by IR, ^1H and ^{31}P NMR spectroscopies, and for M = Pt, by X-ray diffraction methods. Each ligand L^- acts as an *N,S*-donor, binding to the rhodium centre through the nitrogen atom of the heterocyclic ring, and to the group 10 metal centre through the sulfur atom. The two bridging ligands lie *trans* to one another across the metal-metal bond [106]. The coordination of some related *N,S*-donor bridging ligands has been explored by Gopinathan *et al.* Ligands HL = **(50)** to **(52)** react with $[Rh_2(OAc)_4]$ and ligands, L', such as pyridine and triphenylphosphine to yield the complexes $[Rh_2(\mu\text{-}L)_2(OAc)_2].2L'$. If an excess of the ligands HL is present, compounds of the form $[Rh_2(\mu\text{-}L)_4].L'$ are obtained. The IR, UV-VIS and ^1H NMR spectroscopic properties of the new products have been reported, and the crystal structure of $[Rh_2\{\mu\text{-}(\mathbf{51})\}_4].PPh_3$ (R = Me) has been elucidated [106].



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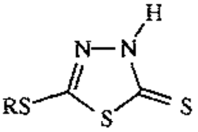
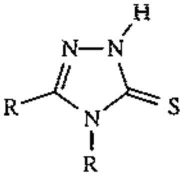


R = Me, Et, Pr

(51)



R = Me, Ph, CH_2CH_2Ph

(52)

9.4.7 *Complexes with chloro-bridges*

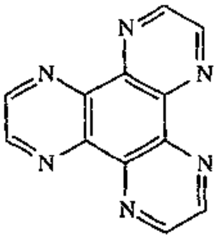
One particular complex should be mentioned here. This is the dirhodium compound $[Rh_2Cl_6(SeCl_2)_4]$, the solid state structure of which has been determined by single crystal X-ray diffraction methods. Two bridging chloro-ligands support the dimetal framework, and each rhodium centre is in a distorted octahedral environment. The $SeCl_2$-groups are terminally bonded [107].

9.5 *POLYNUCLEAR RHODIUM COMPLEXES*

Metastable hydrolysis products of rhodium(III) have been separated and spectroscopically characterised. A dimer (see section 9.4) and a trimer have been observed as solution species. The NMR spectroscopic data for the trimer are consistent with a linear structure with octahedral rhodium centres — $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_2(\mu\text{-}OH)_2Rh(H_2O)_4]^{5+}$. Two resonances are observed in the ^{103}Rh spectrum; the signals at δ 9967.1 and 10,004.3 are assigned to the terminal and central rhodium sites respectively, and the ^{103}Rh-^{103}Rh spin-spin coupling is 1.5 Hz [69].

Didier *et al.* have illustrated that fast atom bombardment mass spectrometry can be a useful means of characterising polymetallic complexes, for example, when NMR spectral data are difficult to analyse. Complexes used in this study include those of ligand **(53)** with rhodium(III), as well as mixed rhodium-ruthenium complexes [108].

Rhodium(III) complexes involving some biologically important ligands have been investigated. As part of this study [92], the reaction of [Cp*RhClL] where HL = **(54)** with silver tetrafluoroborate has been investigated. A trirhodium complex is formed; the ligand L^- is *O*-bonded to one rhodium centre, and *O,N*-coordinated to the next. The trimerisation process, which gives a cyclic array, occurs with "chiral self-recognition" [92].



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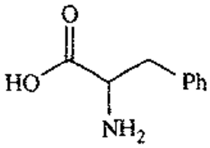
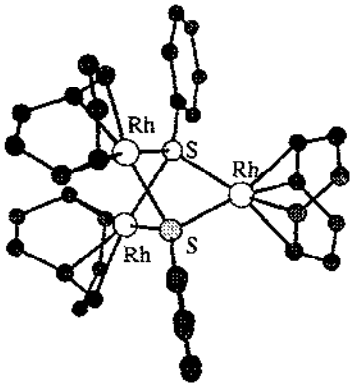


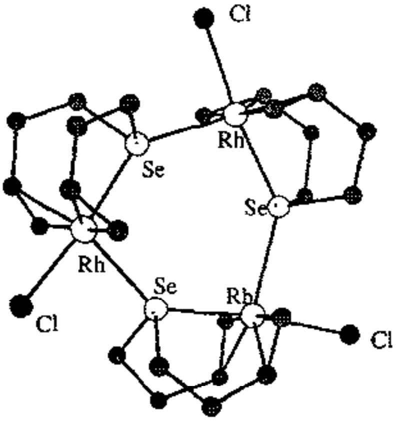
(54)

Thiolate bridges feature in a series of trinuclear homo- and heterometallic involving rhodium and iridium atoms; the complex cations that have been synthesised are of the general type $[Rh_{3-x}Ir_x(\mu_3\text{-SPh})(diene)_3]^+$ ($3 \leq x \leq 0$). The new products have been characterised by ^1H NMR spectroscopy, and the crystal structure of $[Rh_3(\mu_3\text{-SPh})(cod)_3][ClO_4]$ has been determined. In the cation **(55)**, each rhodium centre is square planar. The Rh····Rh distances of 2.9797(8) to 3.4937(8)Å are considered to be indicate that there are no metal-metal bonding interactions. Related dinuclear species have also been prepared and characterised [109]. The reactions of $[\{RhCl(C_2H_4)_2\}_2]$ with $S(CH_2CH_2CH{=}CH_2)_2$ or its selenium analogue lead to the trinuclear complexes $[\{RhCl(E(CH_2CH_2CH{=}CH_2)_2)\}_3]$ (E = S or Se). Crystallographic data for the selenium-containing complex **(56)** show that the complex contains a cyclic core in which each rhodium centre is coordinated by an *Se*-donor atom and two alkene functionalities as well as a chloride ligand. The cyclic structure is supported by the selenium donors which bridge between adjacent metal centres. The environment of each rhodium centre is a distorted trigonal bipyramid. Studies which use one- and two-dimensional NMR spectroscopic techniques confirm that the trimeric structure is retained in solution [110].

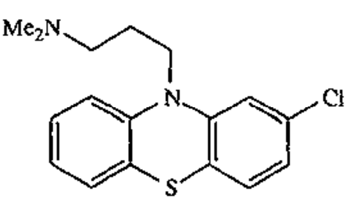
Rhodium complexes of chlorpromazine **(57)**, promethazine **(58)** with R = Me, or ethopropazine **(58)** with R = Et are among a series of species that have been prepared and which incorporate phenothiazine ligands. The products, which include $[Rh_3L_2(H_2O)_2Cl_8][Rh(H_2O)_2Cl_4]$ (L = **(58)** with R = Et) and $[Rh_3L_2(H_2O)_2Cl_8]Cl$ (L = **(57)** or **(58)**, R = Me), have been characterised by elemental analysis, molar conductivities and spectroscopic data [111].



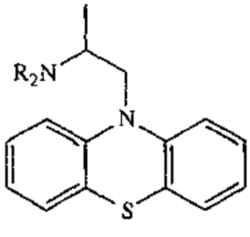
(55)



(56)



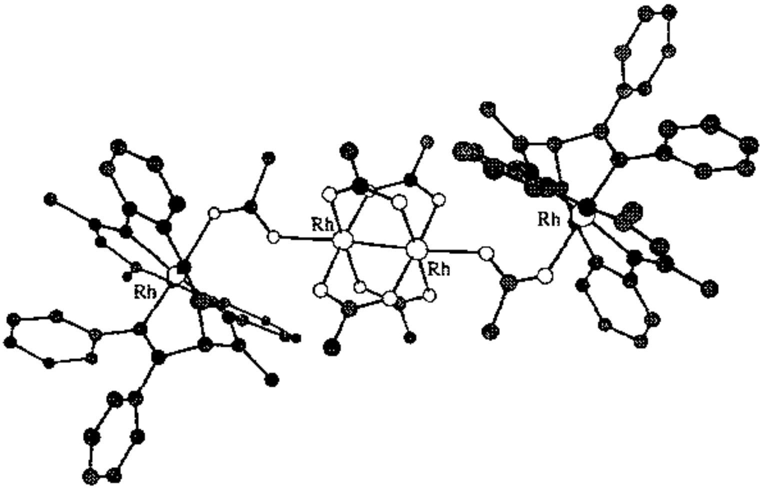
(57)



R = Me, Et

(58)

In the presence of diphenylacetylene, the dimer [$Rh_2(OAc)_4$] reacts with 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine (H_2L) to yield the complex [{$Rh_2(OAc)_4(OAc)$}{RhL(PhC≡CPh)}$_2$] (**59**); (see also section 9.4.2). Crystallographic characterisation of compound (**59**) reveals the presence of a central $Rh_2(OAc)_4$ unit with one additional acetate group coordinated in a monodentate fashion to each axial site. Each axial acetate ligand bridges to a RhL(PhC≡CPh) unit. Each acetylene molecule has inserted between the ligand L^{2-} and the rhodium centre to which the macrocycle is bonded [76].



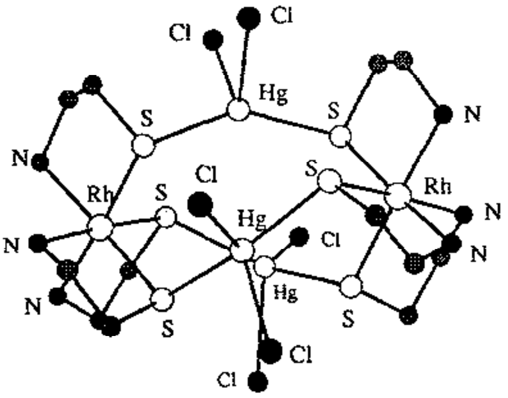
(59) ● = N ○ = O

The formation and structure of a trinuclear complex cation containing a Rh_2Cu core and supported by the *O,P*-donor ligand (**32**) were described in section 9.3.5 [63].

The reaction of lithium hexamethyldisilazane with [Cp*Ir(PMe$_3$)SHCl] leads, after heating at 150°C, to the cubane complex [$Cp^*_4Ir_4S_4$]. Related systems which include the heterometallic complex [$Cp^*_4Ir_2Rh_2S_4$] have also been prepared. [$Cp^*_4Ir_2Rh_2S_4$] has been characterised by ^1H and ^{13}C NMR spectroscopies and by X-ray crystallographic methods. The structure possesses a disordered Ir_2Rh_2-core [112].

A new group of *S*-bridged pentanuclear complexes which possess triple helical chirality has been reported. Members of this class of compound are formed in the reactions of *fac*(*S*)-[RhL_3] (HL = $HN_2CH_2CH_2SH$) with mercury(II) chloride or mercury(II) nitrate. Each product contains two Δ- or two Λ-*fac(S)*-RhL_3 units linked by three mercury atoms. The crystal structure of [{RhL_3}$_2${$HgCl_2$}$_3$] (**60**) has been determined. Each rhodium centre is octahedrally sited and each mercury(II) centre is in a distorted tetrahedral environment. The crystal data support the selective formation of a racemic complex possessing either a ΔΔ– or ΛΛ–configuration for the two *fac*(*S*)-RhL_3 sub-units. Poor solubility has meant that the complex could not be optically resolved [113]. In further studies, Konno *et al* have shown that the reaction of *fac*(*S*)-[RhL_3] (HL = $HN_2CH_2CH_2SH$) with hydrated copper(II) nitrate leads to a complex hexacation with a Cu_4Rh_4-core supported by thiolato ligands and a coordinated disulfide unit. Analogous iridium species have also been synthesised [114].

The preparation and structural characterisation of the complex dication [$(Cp^*Rh^{III})_8(Mo^{V}{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$ have been reported. The synthesis involves the reaction of $MoO_3.2H_2O$ and [$(Cp^*Rh)_2(OH)_3$]Cl at 190°C. Crystallographic data show that the central unit of the structure consists of twelve molybdenum atoms in a truncated tetrahedral array; the Cp*Rh units each cap one face of this core [115].



(60)

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