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4. RHODIUM

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CONTENTS

INTRODUCTION

This review continues the general form of that published for the 1982 literature [1]. This year, the chemistry of rhodium and iridium have been treated seperately, and the chemistry of iridium is dealt with in the following chapter. Interest in rhodium coordination chemistry continues at a high level, stimulated to a great degree by the actual and potential catalytic applications of these compounds. Numerous catalytic processes incorporating rhodium complexes of various sophistication have been described, and are treated herein. The search for cluster compounds exhibiting catalytic activity in the polynuclear form continues, and has met with varying degrees of success.

The material included in this review corresponds closely with the coverage in volumes 98 and 99 of Chemical Abstracts, although the major journals (J. Am. Chem. Soc., J. Chem. Soc., Chem. Commun., J. Chem. Soc., Dalton Trans., and Inorg. Chem.) have been covered through December 1983.

As always, I must thank Drs. Olga Kennard and Sharon Bellard for their invaluable assistance in obtaining data from the Cambridge Crystallographic Data Centre.

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4.1 RHODIUM(VI) AND RHODIUM(V)

No reports concerning rhodium(VI) compounds appear to have been made this year. Rhodium(V) complexes have been implicated as intermediates in metallation reactions at rhodium centres [2]. The reaction of the rhodium(III) complex $[Rh(C_5Me_5)Me_2(dmso)]$ with benzene proceeds smoothly to give $[Rh(C_5Me_5)MePh(dmso)]$ [2]. The reaction is much slower than that of the corresponding iridium complex. A rhodium(V) complex, $[Rh(C_5Me_5)Me_2HPh]$ is proposed as an intermediate in the reaction. The slower rate of reaction with the rhodium complex was attributed to the lower stability of a rhodium(V) intermediate as compared to an iridium(V) species. The reaction of rhodium(V) fluoride with lead or strontium fluorides leads to the formation of hexafluororhodate(III) complexes [9].

4.2 RHODIUM(III)

4.2.1 Complexes with halides

A number of workers have concerned themselves with the properties of rhodium(III) halides. Many of these reports are discussed elsewhere in this review, as the prime interest is in the catalytic properties of the compounds. Treatment of rhodium(III) chloride tetrahydrate with aqueous hydroxide results in the formation of the rhodate(III) ion, $[Rh(OH)_6]^{3-}$, which may be isolated in the form of $Sr_3[Rh(OH)_6]_2$ upon the addition of strontium(II) salts [3]. This is the first example of an isolated hexahydroxorhodate(III) salt. Thermogravimetric analysis of the trichloride tetrahydrate has been reported; phases including polynuclear species such as $(H_3O)_3Rh_nCl_{3n+3}.xH_2O$ (n = 4 or 5) were implicated [4]. A similar study of the sodium chloride/ rhodium(III) chloride system confirmed the existence of $Na_3[RhCl_6]$ and $Na[RhCl_4]$ in the solid phase [8].

The hexacyanoferrate(III) oxidation of propan-2-ol or butan-2-ol in alkaline aqueous medium is catalysed by rhodium(III) chloride [5]. It is proposed that the reaction proceeds by the formation of rhodium(III) alkoxide species, which decompose to the ketone and a transient rhodium(III) hydride. It is this latter species which is oxidised by the alkaline hexacyanoferrate.

Aqueous solutions of sodium hexachlororhodate(III) are rapidly aquated to give $[Rh(H_2O)Cl_5]^{2-}$ salts; the hydrolysis occurs even in the presence of excess halide [6]. Changes in the primary and secondary coordination shells were followed by ^{103}Rh NMR studies. The inner sphere chlorine atoms appear to be in a slow exchange regime. Related studies of the aquation of rhodium(III) halide complexes using spectroscopic and potentiometric techniques have also been described [11]. A number of mixed chlorobromo hexahalorhodate(III) complexes have also been investigate by ^{103}Rh NMR techniques. The chemical shift is sensitive to the number and spatial arrangement of halide ligands, and representative values are given below [7].

n	δ
0	7983
1	7848
2 (cis)	7707
2 (trans)	7712
3 (fac)	7556
3 (mer)	7561
4 (cis)	7403
4 (trans)	7409
5	7243
6	7079

^{103}Rh chemical shifts for $[RhCl_{6-n}Br_n]^{3-}$;
all referred to a nominal value of 3.16 MHz for Ξ Rh.

The complexes M_2RhF_7 (M = Sr or Pb) are prepared by the thermal reaction of MF_2 with rhodium(V) fluoride; crystallographic studies have established the formulation $M_2F[RhF_6]$ [9]. The hexafluororhodate(III) ion is found to be a slightly distorted octahedral species.

Tetraalkylammonium salts have been used for the extraction of rhodium from aqueous halide rich medium [10]. Species such as $[R_4N]_3[Rh_2Cl_9]$ and $[R_4N]_3[Rh_3Cl_{12}]$ can also be found in the organic phase. The rhodium may be back extracted into the aqueous phase by mineral acids.

4.2.2 Complexes with Group VI donor atoms

4.2.2.1 Oxygen donor ligands

The preparation of the complex hydroxo anion, $[Rh(OH)_6]^{3-}$ has been discussed above [3]. This promises to be a useful starting material for the preparation of rhodium(III) complexes. The reaction of 'rhodium(III) hydroxide' with perrhenic acid results in the formation of the very hygroscopic compound $Rh(ReO_4)_3$ [12].

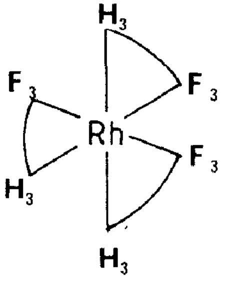
The interaction of nitrite ion with rhodium(III) has been investigated; evidence was presented for the formation of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 complexes in aqueous solution [13].

Several reports have described the formation of polyphosphate complexes of rhodium(III). Polarographic studies of the reduction of $[Rh(HP_2O_7)_3]^{6-}$ and $[Rh(HP_2O_7)_2]^{3-}$ at various acidities have been reported [14,15].

Trifluoromethanesulphonate complexes are being heralded as useful intermediates in synthesis, and the preparation of $[Ir(NH_3)_5(OSO_2CF_3)]^{2+}$ by the reaction of $[Ir(NH_3)_5Cl]Cl_2$ with CF_3SO_3H has been described [16]. The aquation rate has been determined, and a value of $k = 1.8 \times 10^{-2}\ s^{-1}$ reported (c.f. the iridium complex, $k = 1.6 \times 10^{-4}\ s^{-1}$) [16]. The reaction of the trifluoromethanesulphonate complex with urea results in the formation of both O and N-bonded species. The complex catalyses the hydrolysis of urea. Both O and N-bonded ligands are acid labile, and a full kinetic analysis of the behaviour of the complexes has been reported. Treatment of the O bonded complex with hydroxide results in the formation of a deprotonated N bonded species [17].

The photolysis of rhodium(III) oxalate complexes in a variety of matrices at 77 K has been investigated; the predominant process appears to be metal-centred reduction [18].

A detailed study of the gas-phase photochemical behaviour of the cis and trans forms of $[RhL_3]$ (HL = $CF_3COCH_2COCH_3$) (1 and 2) has been reported [19].



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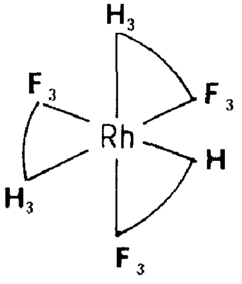

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4.2.2.2 *Sulphur donor ligands*

Sodium hexachlororhodate(III) reacts with ammonium pentasulphide, $[NH_4]_2[S_5]$ to give the purple-red dichroic complex $[NH_4]_3[Rh(S_5)_3]$ [20]. This latter complex reacts with water to yield $[RhS_{10}]^-$ salts, of unknown structure.

SCF X-α calculations have been reported for the complexes $[Rh(X_2)(PH_3)_4]^+$ (X = S or Se); it was concluded that the bond order of the X-X bond was close to one. The bonding between the metal and the disulphur or diseleneium fragment was described in terms of an in-plane π overlap between the metal p_x+d_{xz} hybrid orbitals and the π^* orbitals of the dichalcogenide fragment, and was correlated with the observed optical spectra of these complexes [72].

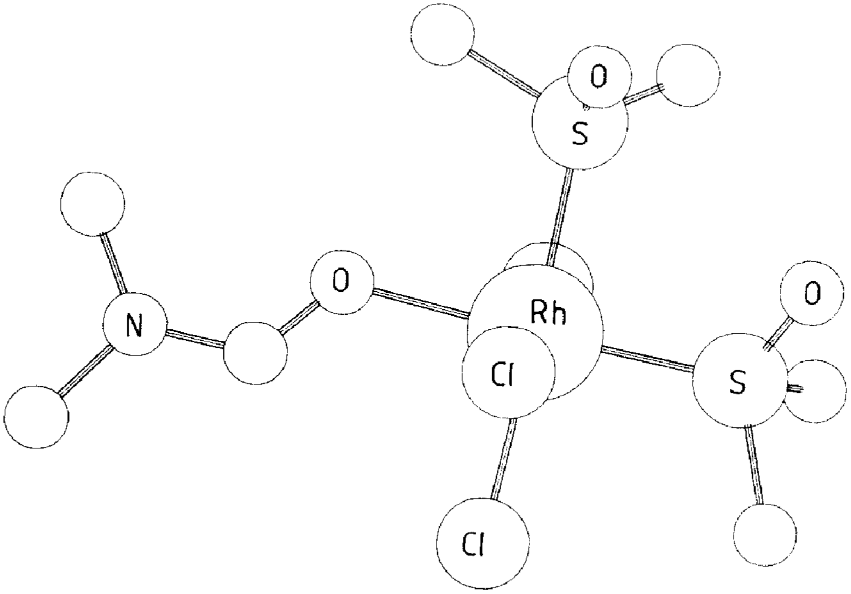
Stability constants have been determined for a range of rhodium(III) thiolate complexes [21]. The thiolate complexes $[Me_4N][MLX_4]$ (L = 2,5-dithiahexane, **3**; X = Cl or Br) have been investigated by ^1H NMR methods, as have the related compounds $[Rh_2L_2Cl_6]$ and $[RhL_2Cl_2]Cl$ [22]. Variable temperature studies were made to investigate the metal ion dependent inversion at sulphur [22].

(3)

A crystal structural analysis of the complex $[Rh(dmso)_2(dmf)Cl_3]$ **(4)** has been reported; the three chlorine atoms lie in the equatorial plane, with one dmso axial and the other equatorial, and the remaining axial site being occupied by the dmf [23]. Both dmso molecules are sulphur bonded to the rhodium (Rh - S, 2.242, 2.290 Å), and the dmf is oxygen bonded to the metal.

Two forms of the L-methionine complex, $[Rh(L)Cl_3(H_2O)]$ (L = **5**) have been described [24]. In one the amino acid is coordinated to the metal through the amino nitrogen atom and the thioether sulphur, whereas in the other the ligand is in the Zwitterionic form with carboxylate oxygen and thioether sulphur bonded to the metal, and a protonated amino group dangling free.

The octahedral complex $[RhLL'(OH)_2H_2O]$ (HL = **6**; L' = piperidine) has been characterised; both of the sulphur atoms of the dithiocarbamate are coordinated to the metal [25]. The reaction of cyclohexanone thiosemicarbazone **(7)** with rhodium(III) halides leads to the formation $[RhL_3]X_3$ (L = **7**; X = Cl, Br or I), in which the ligand is bonded to the metal in a bidentate fashion through sulphur and the hydrazine nitrogen [26]. A similar complex with thiobarbituric acid **(8)**, $[RhL_3]$ (HL = **8**) has been described [27].



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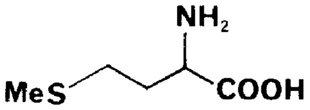

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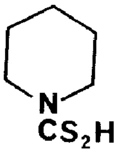

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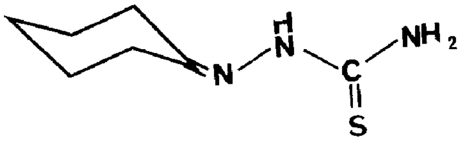

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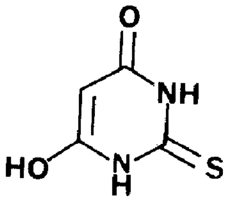

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4.2.3 *Complexes with Group V donor ligands*

4.2.3.1 *Complexes with amines and related ligands*

There have been numerous mechanistic studies concerned with the kinetics and intimate molecular details of the substitution reactions of $[Rh(NH_3)_nX_m]^{p+}$ complexes. The photoreactions of $[Rh(NH_3)_5X]^{n+}$ complexes have also been widely studied. The pressure dependence of the photoaquation of $[Rh(NH_3)_5X]^{2+}$ (X = Cl or Br) has been studied; the activation volume is negative, whereas the activation volume for photolabilisation is positive [28]. It was proposed that the photoaquation reaction is dissociative, and involves a ligand field excited state. These reactions have been reviewed by Ford [29]. In general, the lowest energy electronic absorption bands are spin-allowed singlet-singlet ligand field transitions, with the LMCT and IL bands to higher energy. An efficient internal-conversion/ inter-system-crossing mechanism allows the initially formed singlet state to decay to a lower energy triplet state. The photosubstitution chemistry arises from these lowest energy triplet excited states, which are considerably labilised with respect to the ground state ($\text{rate}_{\text{triplet}} = 10^{14} \times \text{rate}_{\text{ground state}}$). The bulk of the evidence is in accord with a dissociative intimate mechanism. The photoaquation of $[Rh(NH_3)_5I]^{2+}$ immobilised in a Zeolite Y matrix has also been investigated [30].

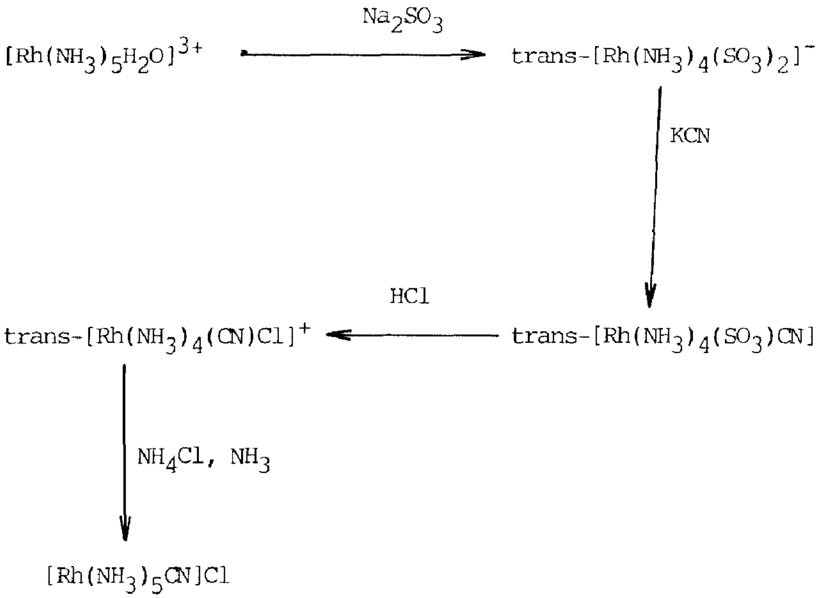
Photosubstitution of aqueous solutions of $[Rh(NH_3)_5CN]^{2+}$ results in the displacement of an ammonia ligand by water, to give cis-$[Rh(NH_3)_4(H_2O)CN]^{2+}$. The same product was obtained from the photolysis of trans-$[Rh(NH_3)_4(H_2O)CN]^{2+}$ [31]. Reliable synthetic routes to these compounds were described [31. The pressure dependence of these photoisomerisation and photolabilisation reactions has also been investigated [32]. In general, the absolute values of the activation volumes for the photoaquation of $[Rh(NH_3)_4XY]^{n+}$ species are small (-8.8 - $+9.3$ cm^3 mol^{-1}). Geometrical changes were frequently associated with photoaquation reactions. Detailed studies of the photochemical behaviour of trans-$[Rh(NH_3)_4Cl_2]^+$ have been reported [11].

Swaddle has determined the partial molar volume of the $[Rh(NH_3)_5H_2O]^{3+}$ cation to be 77.4 pm^3 , virtually identical to that reported for the corresponding iridium compound [33].

Base hydrolysis of $[Rh(NH_3)_5NCS]^{2+}$ in aqueous ethanol or aqueous acetone leads to the formation of $[Rh(NH_3)_5OH]^{2+}$; the rate law is of a slightly unusual type:

$$[OH]/k_{obs} = [OH]/k + 1/kK$$

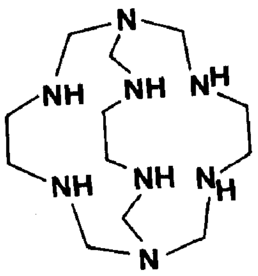
which is interpreted as involving the prior formation of an ion pair between hydroxide and the complex in a rapid pre-equilibrium [34]. This was favoured over alternative explanations involving the more orthodox S_N1_{cb} mechanism, and suggests an associative character to the substitution.



The use of $[Rh(NH_3)_5Cl]^{2+}$ as an agent for quenching the phosphorescence of the ^2E $[Cr(phen)_3]^{2+}$ state has been investigated [35].

It is now clear that the formation of outer sphere complexes is a preliminary stage in substitution reactions. In the case of kinetically inert rhodium(III) and iridium(III) complexes, these outer sphere complexes are sufficiently stable and long-lived that they appear in the rate equations, and provide valuable mechanistic data. A collection of thermodynamic data for such complexes has appeared [36]. The formation of outer-sphere complexes between halide ions (F^-, Cl^- or Br^-) and $[Rh(en)_3]^{3+}$ has been investigated [37]. EPR studies of the octachlorodicuprate(II) salts, $[Rh(en)_3]_2[Cu_2Cl_8]Cl_2.2H_2O$ have also been reported [38].

A template condensation of $[Rh(en)_3]^{3+}$ with formaldehyde and ammonia results in the formation of the rhodium(III) sepulchrate complex $[RhL]^{3+}$ (L = **9**) in 90-100% yield. A similar high yield preparation of the encapsulated complex $[RhL]^{3+}$ (L = **10**) was reported in the reaction of $[Rh(en)_3]^{3+}$ with formaldehyde and nitromethane. Reduction of the nitro derivative $[RhL]^{3+}$ (L = **10**) with zinc in hydrochloric acid resulted in the formation of the amino substituted complex $[RhL]^{3+}$ (L = **11**). Although there were no clear metal centred reductions associated with aqueous solutions of $[RhL]^{3+}$ (L = **9**), acetone solutions exhibited a one-electron reduction to the rhodium(II) derivative; the rhodium(II) complex then undergoes an irreversible two electron reduction to the metal. Perhaps more remarkably, the nitro substituted complexes undergo reversible one electron processes to the rhodium(II) state. These rhodium(II) complexes may also be prepared by pulse radiolysis of aqueous solutions, but are extremely short-lived under these conditions. Spectroscopic properties for the rhodium(III) complexes were reported, and the ligand field bands interpreted in terms of low energy $^1A_{1g}$-$^1T_{1g}$ transitions derived from an octahedral model [39].



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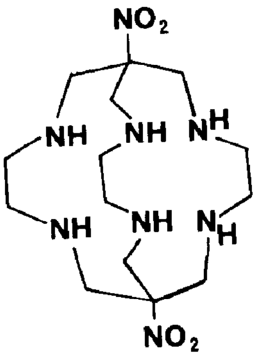

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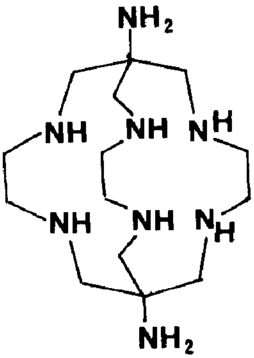
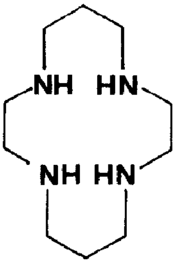


(11)

The photochemical properties of the macrocyclic complex trans-[RhL(CN)$_2$]$^+$ (L = 12) have been investigated, and compared with those of simple monodentate amine complexes [40]. The complex exhibits the strongest d-d phosphorescence ever reported for a rhodium(III) compound. The emisssion lifetime is at least three times greater than that of related ammine complexes. The ligand field spectra and emission spectra were interpreted in terms of D_{4h} symmetry with a lowest lying $^3A_{2g}$ state (derived from the splitting of the $^3T_{1g}$ level in octahedral symmetry). The use of the macrocyclic ligand has prevented photoloabilisation of the ligand, and no substitution photochemistry is observed. The related complex, cis-$[RhL(CN)_2]^+$ (L = **12**) is readily prepared by the reaction of cis-$[RhLCl_2]^+$ with sodium cyanide, although some of the trans isomer is also formed in the reaction [47].



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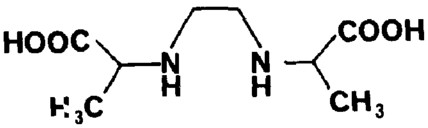
Hydrolysis of the complex cis-α-$[Rh(trien)Cl_2]^+$ results in the formation of $[Rh(trien)(H_2O)Cl]^{2+}$ and $[Rh(trien)(OH)Cl]^+$; this is exhibited in the observed pH dependence of the electrochemistry of these complexes [41]. The reactions are catalysed by rhodium(I) above pH 6 (when rhodium(I) is removed by reaction with water to give a rhodium(III) hydride).

There has been some interest in the coordination chemistry of the chiral ligand S,S-2,7-dimethyl-3,7-diaza-1,8-octanedioic acid (**13**). Reaction with rhodium(III) chloride results in a stereospecific formation of Δ-cis-α- (**14**) and Λ-cis-β-$[RhLCl_2]^-$ (L = 13) (**15**) only. The reactions with amino acids were investigated, and shown to result in inversion [42]. Whereas **14** reacts with R or S alanine, or with glycine to give [RhLL'] with retention of configuration, 15 was shown to give rise to inverted products under some conditions [43]. Even more notable stereospecificity was observed in the reaction of 13 and ethylenediamine with $[Rh(py)_4Cl_2]^+$ to give only Δ-cis-α-$[RhL(en)]^+$, and with Λ-cis-β-$[RhLCl_2]^-$ in the presence of ethylenediamine to give only the Λ-cis-β isomer [44].



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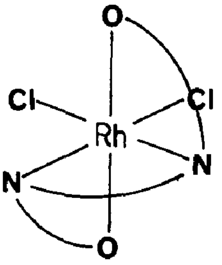

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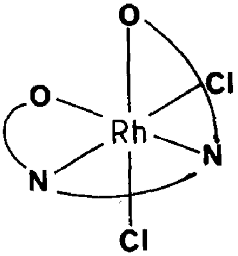

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The preparation of the complex ion $[RhL]^-$ (H_4L = $(HO_2CCH_2)_2NCH_2CH_2CH_2N(CH_2CO_2H)_2$) has been described; CD measurements indicated that the (-)-D enantiomer possesses the Λ absolute configuration [45].

The solid state reaction of glycine with rhodium(III) chloride tetrahydrate has been investigated [46]. The reaction of rhodium(III) chloride with the polydentate ligand $(HO_2CCH_2)_2NCH_2CH_2SCH_2CO_2H$ has been investigated, and the complexes $[Rh(H_2L)Cl_2(H_2O)_2]$ and $[Rh(HL)Cl(H_2O)].H_2O$ (H_3L = $(HO_2CCH_2)_2NCH_2CH_2SCH_2CO_2H$) have been described; the former complex contains a bidentate ligand binding through the nitrogen and one of the edta-like oxygen atoms, whereas the latter incorporates a quadridentate ligand binding through sulphur, nitrogen and two oxygen atoms [57].

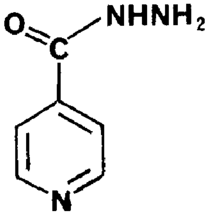
The aquation of the complex cation cis-$[Rh(NO_2)_2L_2]^+$ (L = biguanide, $H_2NC(=NH)NHC(=NH)NH_2$) has been studied [89]. The reaction results in the sequential formation of $[Rh(NO_2)(H_2O)L_2]^{2+}$ and $[Rh(H_2O)(OH)L_2]^{2+}$.

4.2.3.2 Complexes with heterocyclic nitrogen donor ligands

Treatment of trans-$[Rh(py)_4Cl_2]Cl.5H_2O$ with nitric acid results in the formation of trans-$[Rh(py)_4Cl_2][H(ONO_2)_2]$, an example of a compound containing the hydrogen dinitrate anion [48].

The formation of outer sphere complexes is not limited to compounds with aliphatic amines, and the formation of such complexes between $[Rh(phen)_3]^{3+}$ and nitrate, acetate, formate and propionate has been demonstrated [49]. The stability constants for the formation of these complexes are small. Much of the interest in this class of rhodium complexes lies in their potential applications as photocatalysts. A number of new recipes for the bouillabaise technique for the photodecomposition of water have appeared; hydrogen is generated upon photolysis of ternary $[Rh(bipy)_3]^{3+}$/triethanolamine/$K_2[PtCl_4]$ or quaternary $[Rh(bipy)_3]^{3+}$/triethanolamine/$K_2[PtCl_4]$/proflavine systems [50]. A novel system coupling tris(2,2'-bipyridine)rhodium(III) with titanium dioxide has also been described [51]. Laser photolysis of colloidal titanium dioxide leads to conduction band electron transfer to an $[Rh(bipy)_3]^{3+}$ acceptor; the primary product is a rhodium(II) complex, which undergoes subsequent dark reactions.

A number of rhodium(III) complexes with pyridine carboxylic acids have been described [52]. The species reported include $Na[RhL_2]$ and [RhLL'] (H_2L = 2,6-pyridinediacrboxylic acid; HL' = 2-pyridinecarboxylic acid, 3-pyridinecarboxylic acid, glycine or 2-aminophenol); the complexes are probably polymeric. The complex $[RhLCl_2]Cl$ (L = 4-pyridinecarboxylic acid hydrazide, **16**) has been prepared [53]. The reaction of rhodium(III) chloride with 8-hydroxyquinoline results in the formation of $[RhL_3]$ (HL = 8-hydroxyquinoline) in high cis:trans ratio; the two isomers may be separated by chromatography over silica [54]



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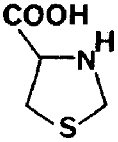

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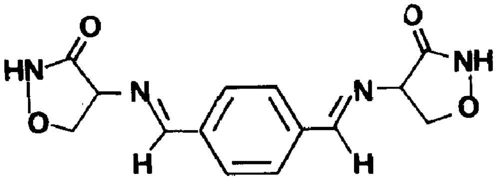
The thiazolidine (thioproline) complexes $[RhL_4X_2]Cl$ (L = thioproline, **17**; X = Cl or Br) incorporate nitrogen bonded ligands, and exhibit no significant antitumour or cytostatic properties [55]. Terzidone (**18**) is a drug implicated in cycloserine release, and has been shown to form a rhodium complex $[RhL_3X_3]$ (L = **18**); the ligand is monodentate, and there is no observed opening of the heterocyclic ligand [56].



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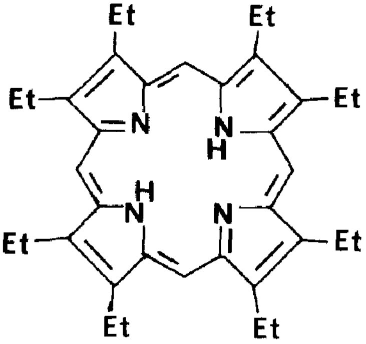
4.2.3.3 *Complexes with macrocyclic nitrogen donor ligands*

A number of complexes of this type have been discussed previously in the context of amino complexes. Photochemical studies of the complexes [RhL(MeOH)X] (L = phthalocyanine, X = Cl, Br or I) have been described [58]. These complexes are also luminescent; upon irradiation at 400 nm, they exhibit an emission centred at 420 nm from a triplet ligand centred $\pi\pi^*$ state [62]. Iterative extended Huckel calculations upon metalloporphyrins have been performed in order to interpret their electronic, vibrational and emission spectra; amongst the species studied were the rhodium(I), rhodium (II) and rhodium(III) complexes [59]. It was suggested that the rhodium(I) complex should exhibit no emission due to d,π^* transitions, nor should the 'true' rhodium(II) species exhibit any emission associated with the low energy π,d state, although it was conceded that this might be the ground state (i.e. Rh(I)(P$^\bullet$) rather than Rh(II)P). The rhodium(III) axially substituted species were predicted to be strongly phosphorescent, but should exhibit no low energy CT or d,d states [59]. The rhodium(III) octaethylporphyrin complex [RhLCl] (L = octaethylporphyrin, **19**) reacts with silver(I) salts in arenes to yield metallated products [RhLAr] (ArH = benzene, anisole, toluene etc.) [60]. It was shown that an unstable intermediate $[\mathrm{RhL}]^+$ species could be isolated from the reaction, and that this reacted with arenes to give the same products. No free radical species were involved in the reaction.

The effect of pressure on the anation reaction of $[\mathrm{RhL(H_2O)_2}]^{3-}$ (H_6L = meso-tetrakis(sulphonatophenyl)porphyrin, **20**) with thiocyanate has been investigated, and an activation volume of 8.8 cm^3 mol^{-1} determined [61]. The macrocyclic ligand is seen to enhance the lability of the axial ligands.

Hydrogen is evolved in the photochemical dehydrogenation of propan-2-ol or cyclohexanol catalysed by [RhL(Cl)] (L = meso-tetraphenylporphyrin) [63]. Rhodium(III) octaethylporphyrin (**19**) complexes are effective catalysts for the anti-Markownikoff oxygenation of olefins by the dioxygen/Na[BH_4]/thf system; cyclohexene is converted quantitatively to cyclohexanol in 130 h at 20° C [64].



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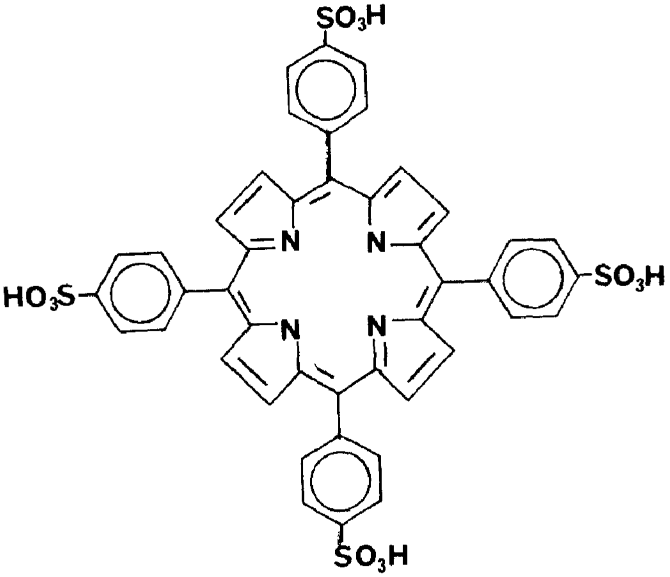

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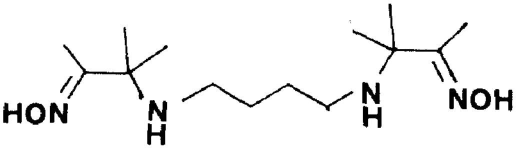
4.2.3.4 Complexes with miscellaneous nitrogen donor ligands

Crystal structural analyses of the binuclear complexes formed with the bis(oxime) ligands 21 and 22 have been reported [65]. The complex $[Rh_2L_2Cl_2]$ (21) exhibits an octahedral geometry about the each rhodium centre, with the four nitrogen atoms in the equatorial plane and the chlorides axial (23). In contrast, a rather different structure is observed in the complex $[Rh_2L(HL)$ [65]



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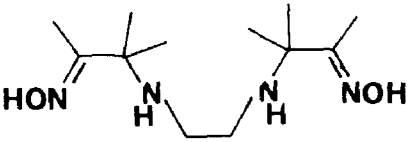

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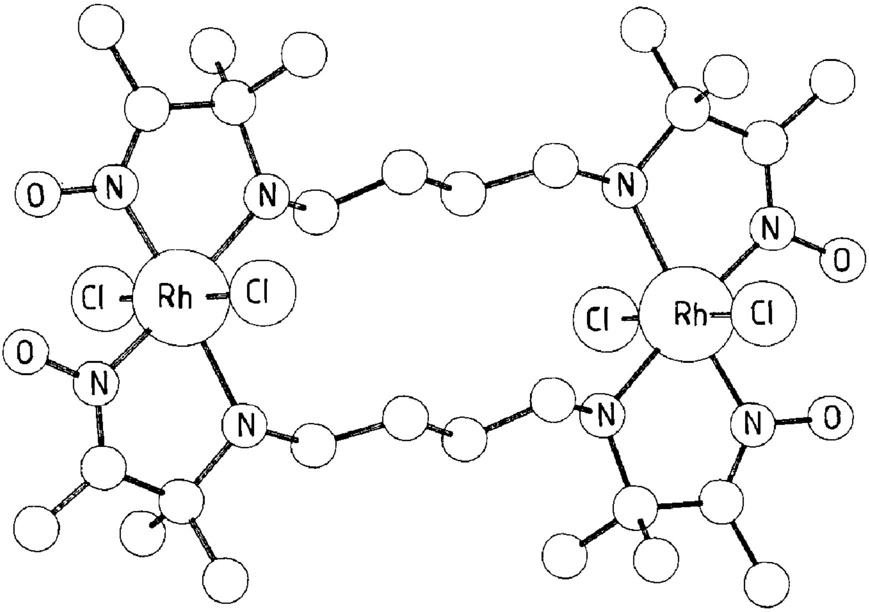

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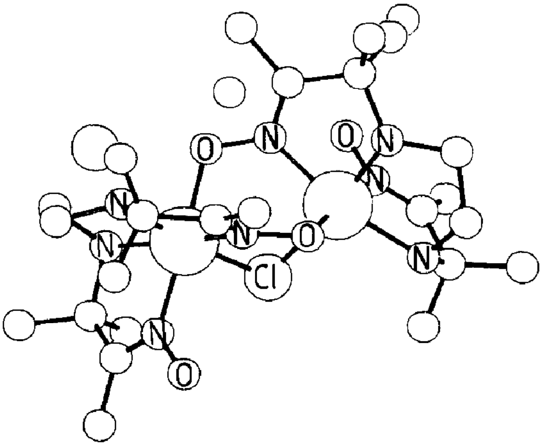

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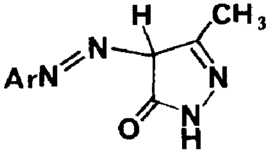
The dioxime complexes $H[RhL_2Cl_2]$ (HL = HON=CRCR=NOH) have been shown to be aquated to give $[RhL_2Cl(H_2O)]$ [66].

Octahedral complexes $[RhL_2Cl_2]Cl$ (L = **25**; Ar = 4-methylphenyl or 2-methoxyphenyl) with the phenylazopyrazolone ligands **25** have been reported [69].

The formamidinato complex $[Rh(Me_5C_5)LCl]]$ (HL = ArN=CHNHAr; Ar = 4-methylphenyl) has been shown to react with carbon monoxide to yield the new carbamoyl complex $[Rh(Me_5C_5)Cl(CONArCH=NAr)]$ (**26**); the reaction was thought to proceed through the insertion of the carbon monoxide into the Rh-N bond, after



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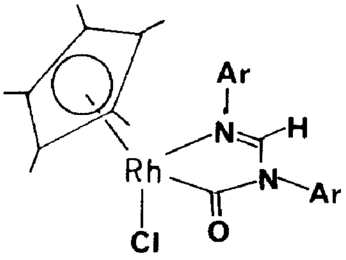
prior coordination to the metal. The same starting complex reacts with phenyl isothiocyanate to give the structurally characterised species $[Rh(Me_5C_5)(PhNC(=S)NArCH=NAr)Cl]$ (27). An exactly analogous reaction occurred with carbon disulphide to give the dithiocarbamato derivative (28) [70]. No pure compound could be isolated from the reaction with carbonyl sulphide, and no reaction could be detected with carbon dioxide.



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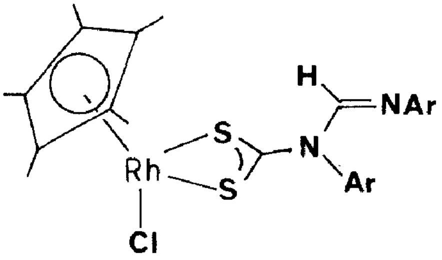

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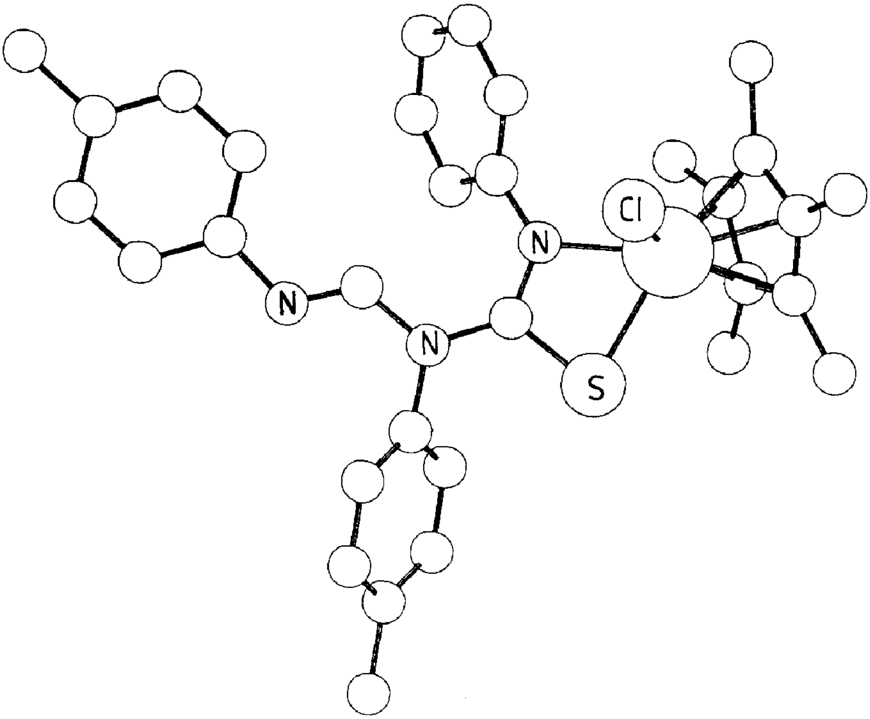
The complex $[RhL_2Cl_3]$ (L = $CO(NH_2)_2$) has been described, and is thought to be a dimeric octahedral species with bridging chloride ligands [71].

4.2.3.5 Complexes with phosphorus donor ligands

The complex $[Rh(O_2COH)H_2(P^iPr_3)_2]$ contains a chelating bicarbonato ligand, and has been shown to react with diphenylacetylene to yield carbon dioxide, trans-stilbene and $[Rh_2(P^iPr_3)_3H_2(PhCCPh)]$ [67]. The latter species has been structurally characterised (29) [67].

In the complex $[RhCl_3L_2]$ (L = $Ph_2PCH_2CO_2Et$) one of the diphenylphosphinoacetate ligands acts as a monodentate phosphorus donor and one as a chelating P,O donor. A dynamic equilibrium exists between the isomer with the monodentate ligand in the equatorial plane and that with it in the axial site. Upon treatment with silver(I) hexafluorophosphate, a chloride ion is removed and the complex cation $[RhL_2Cl_2]^+$ is formed, in which both of the



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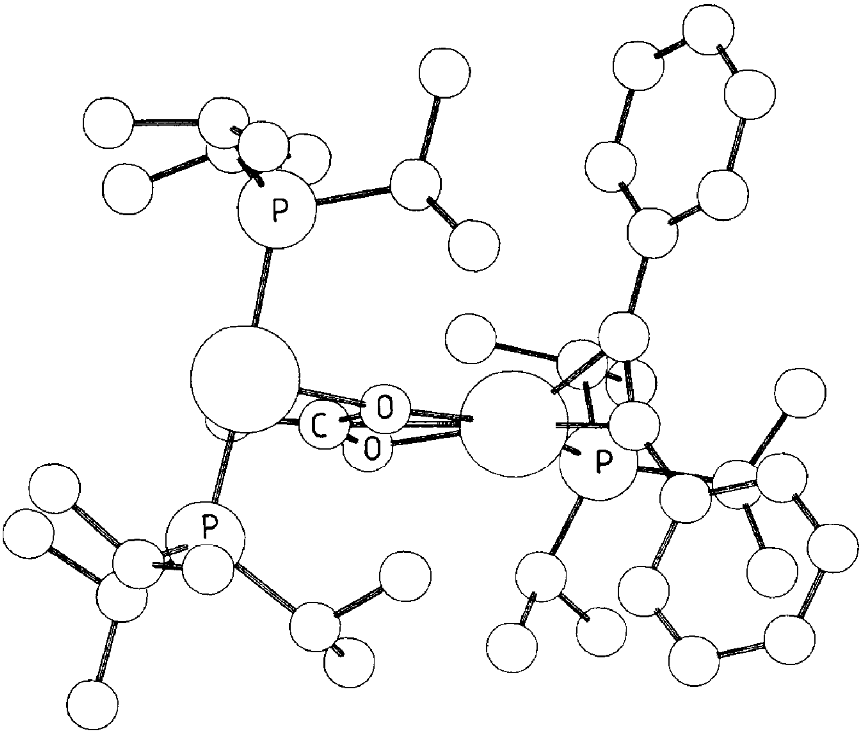

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diphenylphosphinoacetate ligands are bidentate. The axial plane is occupied by the two chloride ions and the two phosphorus atoms [68].

4.2.4 *Complexes with Group IV donor atoms*

The tris(hydroxo)-bridged complex $[(C_5Me_5)Rh(OH)_3Rh(C_5Me_5)]Cl$ has been studied as a catalyst for the chloromercuration of ethene by mercury(II) chloride in alkaline aqueous conditions. The rhodium complex was shown to be an effective catalyst for the decomposition of hydroxyethylmercury chloride to acetate and ethanol. Some dihydrogen was evolved in the reaction, indicating the involvement of water. Two competing processes were detected, one involving the dissociation of acetaldehyde, and the other giving acetate and dihydrogen directly [73].

The reaction of $[Rh(C_3H_5)_3]$ with silica results in the formation of a solid with surface-bound $Rh(C_3H_5)_2$ groups; hydrogen reduction of this material results in the formation of a solid which contains highly dispersed rhodium metal aggregates which are very active catalysts [74].

The reaction of hydrogen fluoride solutions of tin(II) chloride with $H_3[Rh\{Sn(OH)_3\}_5Cl]$ results in the formation of the octahedral complex $K_3[Rh(SnF_3)_6]$ [75].

4.3 RHODIUM(II)

4.3.1 *Mononuclear complexes*

Very few mononuclear complexes of rhodium(II) have been reported. Earlier sections have described the formation of relatively short-lived rhodium(II) derivatives of encapsulating ligands and 2,2'-bipyridine. The majority of rhodium(II) complexes dimerise upon formation, although exceptions include $[Rh(NH_3)_6]^{2+}$, $[Rh(NH_3)_4]^{2+}$ and $[Rh(HL)_2]$ (H_2L = dimethylglyoxime) formed in flash photolysis systems. Pulse radiolysis of $[Rh(bipy)_3]^{3+}$ or $[Rh(bipy)_2(H_2O)_2]^{3+}$ in water results in the formation of rhodium(II) complexes. The complex $[Rh(bipy)_3]^{2+}$ is very labile, and disproportionates to give $[Rh(bipy)_2]^+$ (via $[Rh(bipy)_2]^{2+}$) and $[Rh(bipy)_3]^{3+}$ [76].

4.3.2 *Binuclear complexes*

Ab initio studies of $[Rh_2(O_2CR)_2]$ and $[Rh_2(O_2CR)_2L_2]$ at RHF and UHF levels have been reported [77]. The results were consistent with the description of the Rh-Rh bond as a single σ bond.

The complexes $[Rh_2(O_2CR)_2L_2]$ ($L = H_2O$) are readily oxidised to the monocations $[Rh_2(O_2CR)_2L_2]^+$, and the redox reactions of these species with other inorganic reductants have been studied. From this data, the self-exchange rate for the reaction:

$$Rh_2^+ + Rh_2 \rightleftharpoons Rh_2 + Rh_2^+$$

has been calculated to have a rate constant k_{22} of 1.2 [78]. The electronic spectra of $[Rh_2(O_2CR)_2L_2]$ complexes have been investigated, and a band in the near ultraviolet region assigned to the $\sigma \rightarrow \sigma^*$ transition [79].

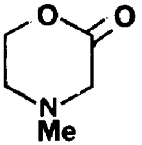
There has been some interest in the transmission of trans influences through metal-metal bonds, and ^{31}P N.M.R. studies of $[LRh_2(OAc)_4L']$ (L' = trimethyl phosphite; L = various) have been reported, in which the chemical shift of the phosphite ligand is used as an indicator for this interaction [80]. There were linear relationships between the chemical shift of the phosphite ligand and the two-bond rhodium-phosphorus coupling, and also with the rhodium-rhodium bond length.

The mixed valence compounds $[Rh_2(O_2CR)_4L_2][ClO_4]$ (L = dmf, R = Me; L = H_2O, R = Et) have been reported [81]. The electronic spectra of the complexes are similar, and electronic configurations were assigned to the compounds. The complexes are paramagnetic, with a temperature independent moment very close to the spin-only value over the temperature range 78 - 296 K.

Optical studies of a derivative with a chiral carboxylate, $[Rh_2(L\text{-}(+)\text{-}PhCHOHCO_2)_4(H_2O)_2]$, have been described [82].

Dirhodium tetraacetate reacts with trifluoroacetamide to give a mixture of all four possible isomers of $[Rh_2(CF_3CONH)_4]$ (**31-35**); the crystal structural analysis of the bis(pyridine) adduct of one of these has been reported (**30**)[83].

A number of catalytic applications of dirhodium(II) complexes have been investigated. Dirhodium tetraacetate catalyses the thermal rearrangement of 2-methylaminoethyl diazoacetate, $N_2CHCO_2CH_2CH_2NHMe$, to give the cyclic compound (35) [84]. The reaction is thought to proceed through the insertion of the carbene into the NH bond.



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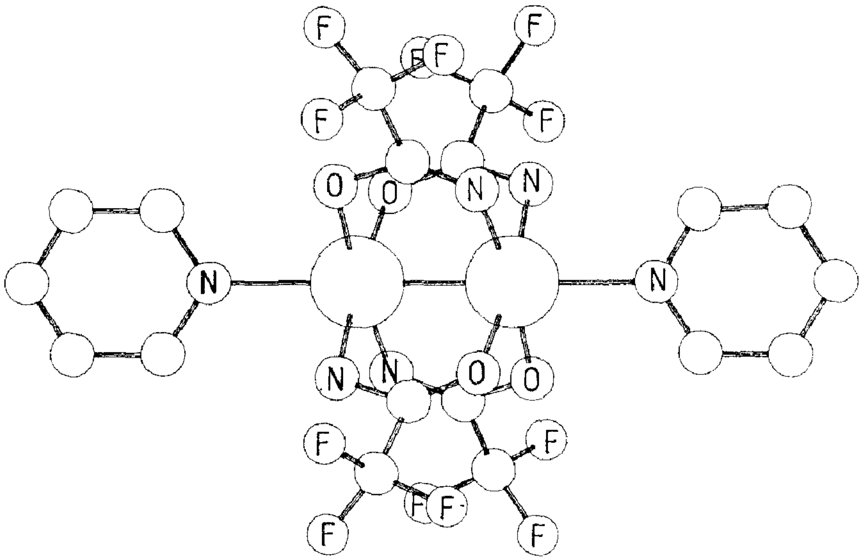

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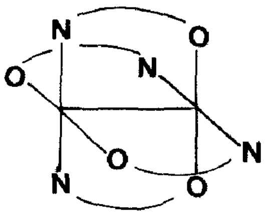

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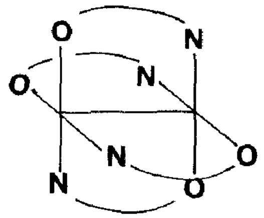

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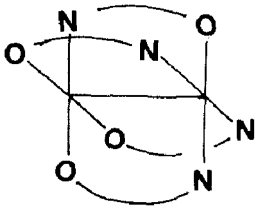

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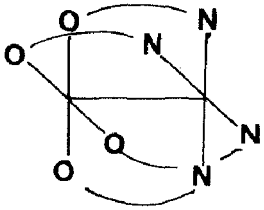

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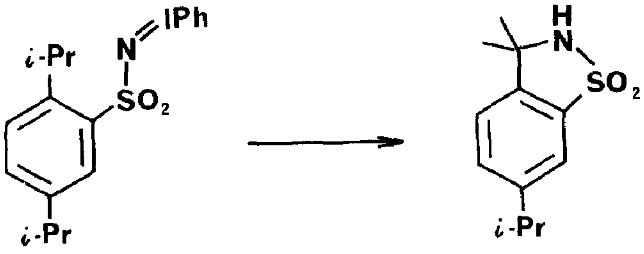
A related reaction is observed in the dirhodium(II) tetracacetate catalysed intramolecular insertion reactions of the nitrene derived from 2-(N-phenyliodo)sulphonimido-1,4-di(isopropyl)benzene (36) [85]. The major product (94%) of the reaction was (37) formed in the intramolecular insertion process.



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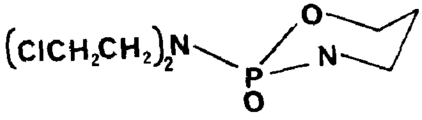

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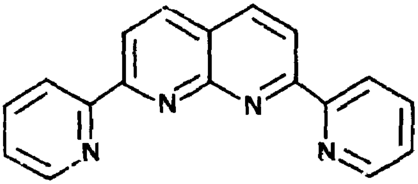

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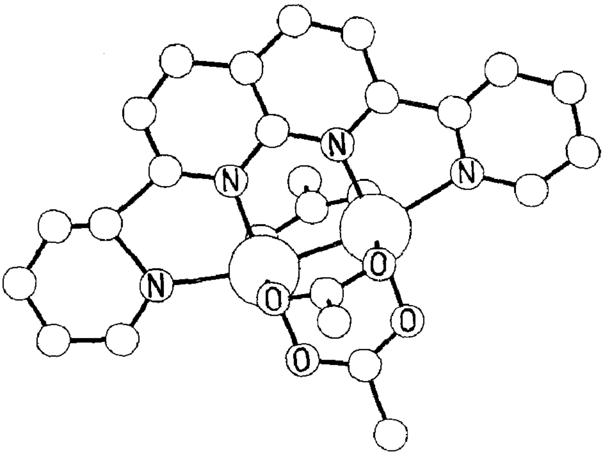
The adducts $[Rh_2(OAc)_4L_2]$ (L = **38**) are readily prepared by the reaction of dirhodium(II) tetraacetate with L [86]. The unusual tetradentate ligand, 2,7-(2-pyridyl)-1,8-naphyridine (**39**), reacts with $[Rh_2(OAc)_4]$ to yield salts of the cation $[Rh_2(OAc)_3L]^+$ (L = **39**); a crystal structural analysis of the latter complex has been reported (**40**), and the terminal pyridyl groups shown to occupy the terminal axial sites [87].



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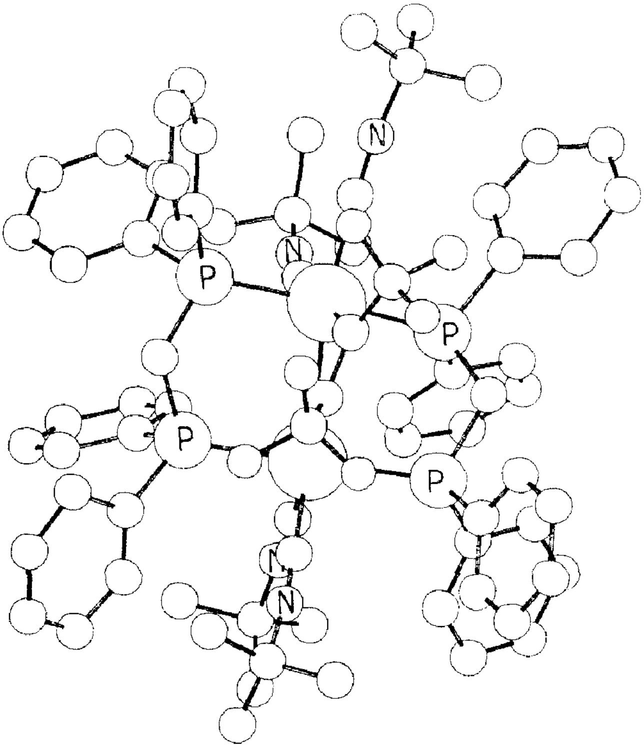
A crystal structural analysis of the complex $[Rh_2(^tBuNC)_4(F_3CC{=}CCF_3)(dppm)_2][PF_6)_2$ **(41)**, resulting from the reaction of $[Rh_2(^tBuNC)_4(dppm)_2][PF_6]_2$ with hexafluorobut-2-yne, has been reported [88].



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4.4 RHODIUM(I)

To a certain extent, the assignment of compounds to particular classes in this section is arbitrary. Many of the complexes are multi-functional and could appear under several headings. The selection has been made on this author's consideration of the most important feature in the structure. It is also true that the assignment of some reports to the rhodium(III) or rhodium(I) sections is slightly arbitrary, either on tha basis of oxidation state ambiguity, or because the key feature is oxidative addition to a rhodium(I) centre.

4.4.1 Complexes with halides

As discussed above, numerous examples of compounds involving rhodium(I) halo complexes will be found elsewhere in this review. In particular, $[Rh_2(Cl_2(CO)_4]$ is one of the most widely used starting materials in rhodium(I) chemistry; reactions involving this complex as a reagent will be discussed in the section appropriate to the other ligands introduced.

$[Rh_2Cl_2(CO)_4]$ is an effective catalyst precursor for the rhodium(I)/copper(II) co-catalysed aerial oxidation of olefins to ketones, in a variant on the Wacker process. A model system has been investigated in an attempt to characterise the active catalyst [90]. The rhodium dimer reacts with dioxygen in acidic ethanol to yield acetaldehyde and a rhodium(III) ethanol complex:

$$[Rh_2Cl_2(CO)_4] + 4HCl + 2O_2 + 4EtOH \rightarrow 2[RhCl_3(H_2O)_2EtOH] + 2MeCHO + 4CO$$

The reaction has been shown to proceed by a number of discreet steps. The first is the aerial oxidation of ethanol to produce aldehyde and peroxide

$$CH_3CH_2OH + O_2 \rightarrow CH_3CHO + H_2O_2$$

which reacts with the rhodium(I) dimer in the presence of acid to give a mononuclear rhodium(I) hydroperoxide complex

$$2H_2O_2 + [Rh_2Cl_2(CO)_4] + 2HCl \rightarrow 2[Rh(CO)Cl_2(O_2H)]^{2-} + 4H^+ + 2CO$$

This latter complex may deprotonate to a peroxide complex

$$[Rh(CO)Cl_2(O_2H)]^{2-} \rightarrow [Rh(CO)Cl_2(O_2)]^{3-} + H^+$$

which is oxidised to the rhodium(III) product

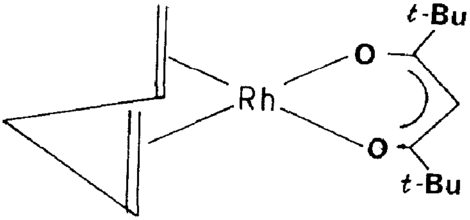
$$[Rh(CO)Cl_2(O_2)]^{3-} + 4H^+ + Cl^- + EtOH \rightarrow [RhCl_3(H_2O)_2EtOH] + CO$$

4.4.2 Complexes with Group VI donor ligands

A number of rhodium(I) diketonate complexes have been shown to be of utility as catalysts for the hydroformylation of 1-hexene [91]. In particular, the complex [Rh(acac)L] (L = $P(OPh)_3$) has been demonstrated to be an effective catalyst; under hydroformylation conditions the reaction mixture contains a wide range of complexes, including $[Rh(acac)(CO)_nL_{2-n}]$ (n = 0,1 or 2),

$[Rh(acac)L_{3-n}(CO)_n]$ (n = 0 or 1), trans-$[Rh(acac)L_{4-n}(CO)_n]$ (n = 1 or 2), trans-$[Rh(acac)L_2H_2]$, trans-$[Rh(acac)L_2H(CO)]$ and trans-$[Rh(acac)L_2(CO)(hexyl)]$. The complex $[Rh(acac)(CO)(PPh_3)]$ has been shown to act as a catalyst for the hydroformylation of propene [97]. High pressure infra-red studies indicated that the active catalyst was $[RhH(CO)_2(PPh_3)_2]$.

A novel carbon-carbon bond formation reaction occurs when the complex $[RhL(C_2H_4)(F_3CCCCF_3)]$ (HL = $^tBuC(=O)CH_2C(=)^tBu$) is heated [92]. The product of the reaction is the complex $[LRh(H_2C{=}CHCH_2C(CF_3){=}CH(CF_3))]$ (**42**).



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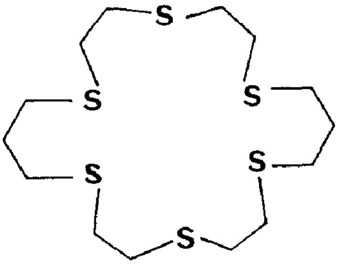
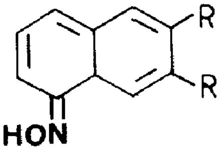
The preparation and spectroscopic properties of the complex $[RhL(CO)_2]$ (HL = 8-hydroxyquinoline) have been investigated; the ^{13}CO enriched complex was prepared, and a ^2J coupling between the two ^{13}C atoms of 9.15 Hz demonstrated [93]. The mixed donor complexes $[RhL_2]^+$ (L = $Ph_2PCH_2CH_2SR$) catalyse the aerial oxidation of terminal alkenes or secondary alcohols to ketones and of primary alcohols to acetals [94]. The key step in the reactions appears to be the formation of a dioxygen complex $[RhL_2(O_2)]^+$.

$[Rh_2Cl_2(cod)_2]$ reacts with the hexathia crown ether 1,4,7,11,14,17-[20]ane-S_6 (**43**) in the presence of silver(I) to give the binuclear complex $[Rh_2L(cod)_2][PF_6]_2$ (L = **43**) (**44**) [95]. Each rhodium atom is coordinated to three sulphur atoms of the macrocycle. The ligand adopts a tridentate bridging mode in an 'inside-out' conformation reminiscent of that adopted by the free ligand [18]ane-S_6.



(**43**)



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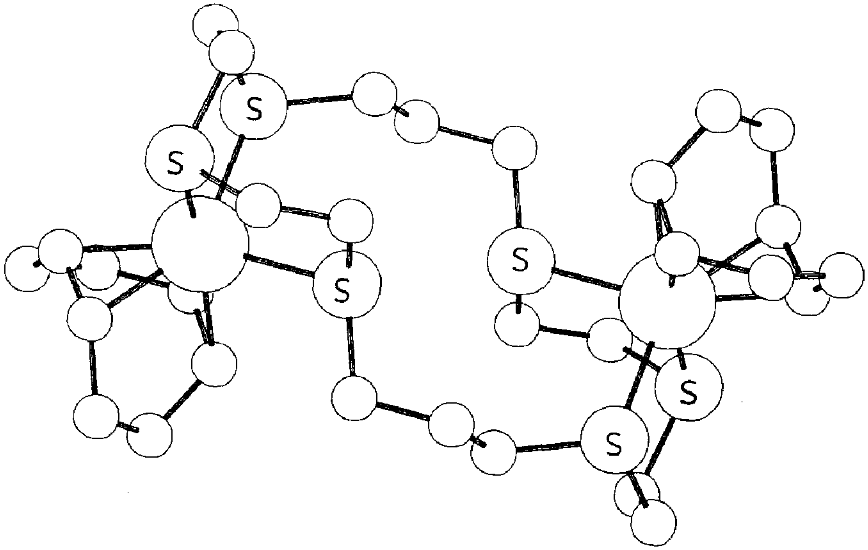

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The dicyanodithiolene complexes $[RhL_2l']^-$ (L = CO or $P(OPh)_3$; H_2L' = HSC(CN)=C(CN)SH) have been shown to possess interesting photochemical and photophysical properties [96].

4.4.3 Complexes with group V donor ligands

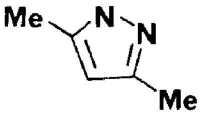
4.4.3.1 Complexes with nitrogen donor ligands

An investigation of a series of complexes $[RhL(CO)_2Cl]$ (L = **45**; R = various) have been investigated by ^1H NMR methods [98]. The binding of $[(Ph_3P)_2(CO)Rh]^+$ fragments to inosine, guanosine, 6-mercaptoguanosine and 8-mercaptoguanosine has been investigated. The relevance of these studies to the carcinostatic properties of planar transition metal complexes is apparent. It was found that the binding sites varied from ligand to ligand; with 6-mercaptoguanosine the only binding site was at the sulphur, whereas in 8-mercaptoguanosine binding to a deprotonated N(7) was also implicated, whilst inosine and guanosine bound the metal at O(6) [99]. Related studies indicated that the rhodium fragment exhibited stronger binding to cytidine than other nucleotides [100].

The complex $[Rh(CO)_2(NH_3)_2]Cl$ reacts with acetyl chloride at room temperature to yield a chloro-bridged dimer, whereas upon heating, acetylation of the coordinated ammonia occurs to give $[Rh_2(CO)_2Cl_5L_2]Cl$ (L = $MeCONH_2$)

[101]. Similar reactions are observed with other alkylamine complexes. Thermolysis of the related complexes $[Rh(CO)_2(NH_3)_2]Cl$ and $[Rh(CO)_2LCl]$ (L = $MeNH_2$, benzothiazole, benzimidazole or benzotriazole) in air leads to the evolution of carbon dioxide [102].

The hindered ligand 3,5-dimethylpyrazole (**46**) behaves as a neutral, non-bridging two-electron donor, and a number of rhodium(I) complexes have been characterised [103]. A crystal structural analysis of the complex [(cod)RhClL] (L = **46**) has been reported (**47**); the heterocyclic ligand is perpendicular to the square-plane of donor atoms about the rhodium, and there is no significant rhodium-rhodium interaction (Rh...Rh, 4.487 Å).



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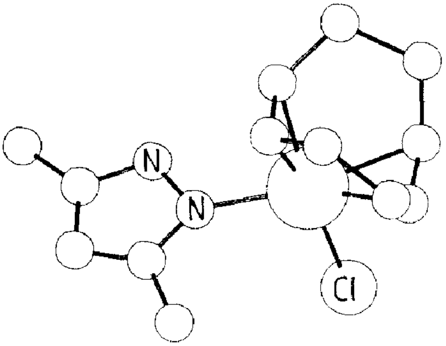
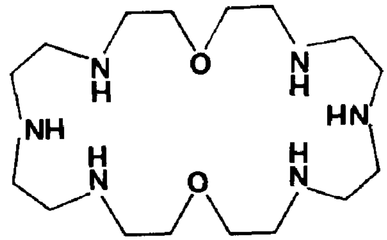


(47)

This is in contrast to the structure of the complex with pyrazole itself in which there is a short rhodium-rhodium distance of 3.452 Å [103]. These complexes may be converted to pyrazolate bridged species.

The 24-membered macrocyclic ligand (**49**) reacts with $[Rh_2Cl_2(CO)_4]$ to give the binuclear complex $[Rh_2(CO)_3L]Cl_2$ (L = **49**) [104]. The compound has been structurally characterised (**50**); each rhodium is coordinated to three nitrogen atoms of the macrocycle, and the two rhodium centres are brdged by the three carbonyl groups. The rhodium-rhodium distance is 2.58 Å.

2,2'-Biimidazole (**51**) is a versatile ligand which may exhibit a range of bonding modes. Treatment of [Rh(acac)L] (L = cod or nbd) with 2,2'-biimidazole results in the formation of [Rh(HL')L] (H_2L' = 51), in which the 2,2'-biimidazolate anion acts as a bidentate chelating ligand. Reaction of this complex with trialkylphosphinegold(I) chlorides in the presence of silver(I) gives $[LRh(HL')AuPR_3]$, in which the gold is bonded to the free imine type nitrogen of the 2,2'-biimidazolate ligand. In contrast, the reaction of the gold 2,2'-biimidazolate complexes $[L'(AuPR_3)_2]$ with $[Rh(cod)X_2]^+$ results in the ternuclear complex $[(cod)RhL'(AuPR_3)_2]^+$, the triphenylphosphine analogue of which has been structurally characterised (52) [105]. The rhodium is squareplanar, and coordinated to a bidentate chelating 2,2'-biimidazolate dianion. A



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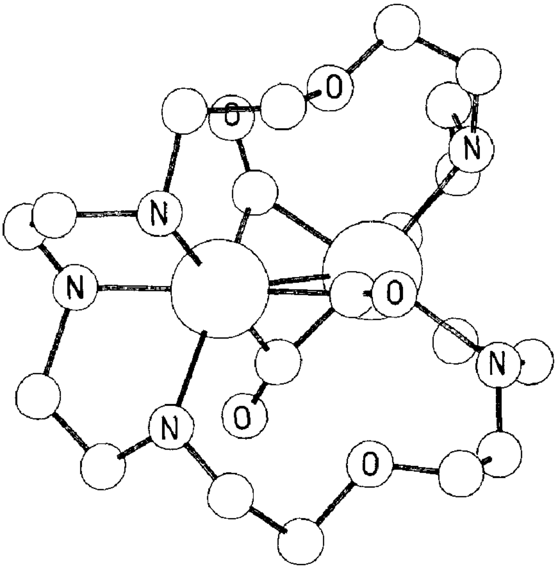

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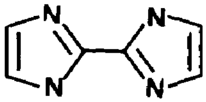

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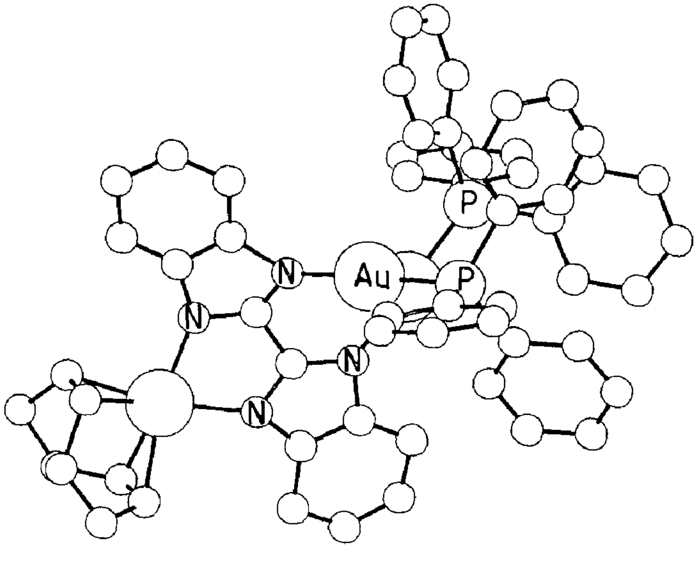
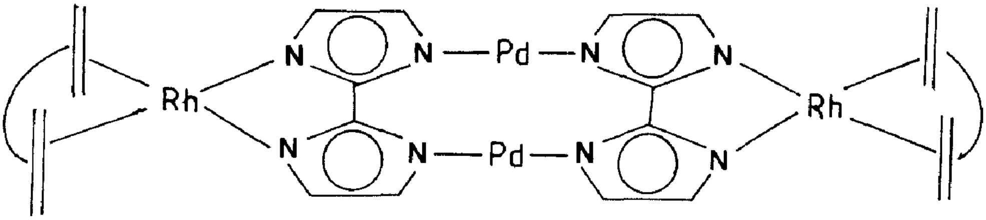


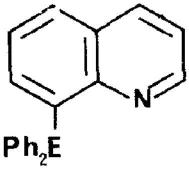
(52)

related complex in which two (cod)RhL' units are linked by two allylpalladium(II) units , (53), is formed in the reaction of [Pd(C_3H_5)(acac)] with [Rh(HL')(cod)] [106].



(53)

A number of rhodium(I) complexes with arsenic and other mixed donor atom ligands have been reported [107]. The complexes [Rh(CO)ClL] (L = 8-diphenylarsinoquinoline, **54**, 8-diphenylphosphinoquinoline or 8-aminoquinoline) are prepared by the reaction of [$Rh_2Cl_2(CO)_4$] with the ligand.

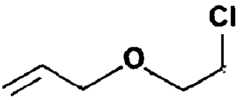


(54) E = As
(55) E = P

Enantioselective hydrogen transfer from propan-2-ol to ketones is catalysed by the complex [$LRhCl_2RhL$] (L = 1,5-hexadiene) in the presence of the chiral ligand (-)-2-pyridinalphenylethylimine [142]

4.4.3.2 Complexes with phosphorus donor ligands

Numerous applications of tris(phosphine)rhodium(I) chloride complexes in catalytic systems have been reported. Allyl chloroacetate (**56**) is converted to the 2-methylene-4-pentene derivative (**57**) upon treatment with [$Rh(PPh_3)_3Cl$] in thf [109]. Other allylic alcohol derivatives underwent analogous coupling reactions. It was shown that free allenes are not involved in the reactions, and it was suggested that the catalytic cycle involved oxidative addition to give an allylrhodium chloroacetate, which undergoes reductive elimination to a



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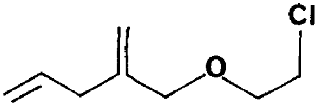
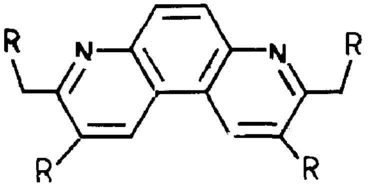


(57)

rhodium(I) allene complex. The same rhodium complex has been shown to be an effective catalyst for the enantioselective hydrogenation of PhCH=C(NHAc)CO_2H to (-)-PhCH_2CH(NHAc)CO_2H in cholesteryl tridecanoate liquid crystal medium [110,111]. Up to 16% optical yield of the (-) enantiomer was obtained.

An interesting synthetic application is seen in the preparation of 4,7-phenanthrolines (**58**) from 1,4-dinitrobenzene or 4-nitroaniline and aldehydes, or 1,7-phenanthrolines (**59**) from 1,3-dinitrobenzene or 3-nitroaniline with aldehydes [112]. The reaction is co-catalysed by palladium(II) chloride and [Rh(PPh_3)$_3$Cl], although other rhodium compounds may be used less effectively.



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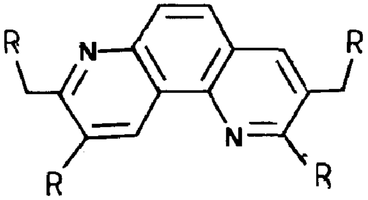
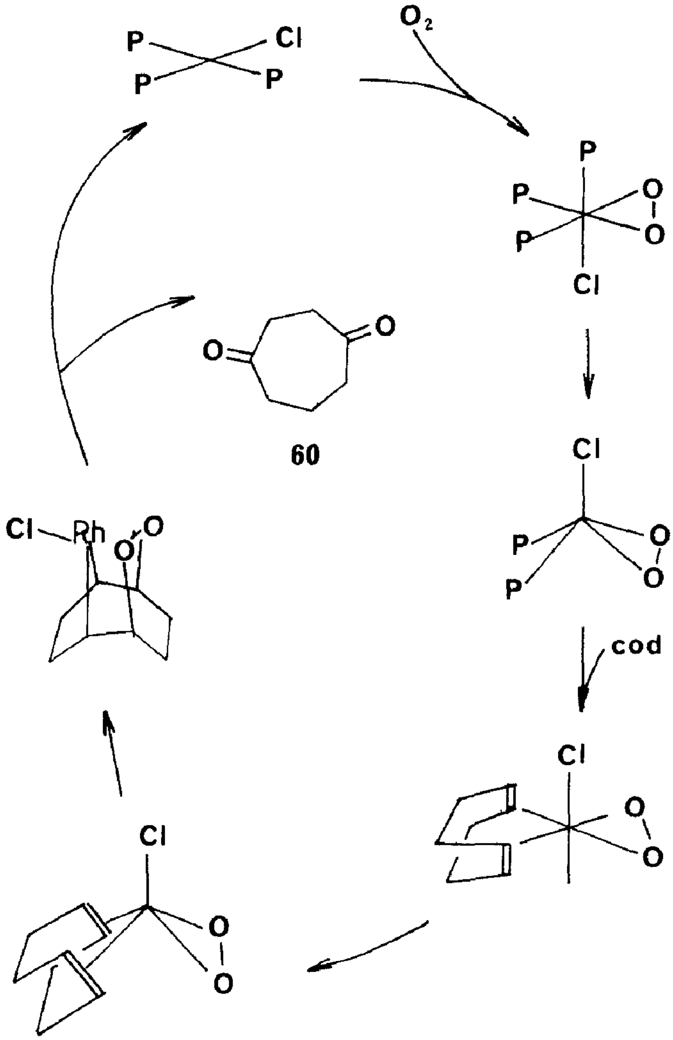


(59)

The oxygenation of 1,5-cyclooctadiene by molecular dioxygen in the presence of [Rh(PPh_3)$_3$Cl] and triphenylphosphine has been reported [119]. The product is cycloctane-1,4-dione (**60**), which is formed in good yield. The initial step appears to be the formation of a dioxygen complex [Rh(PPh_3)$_3$Cl(O_2)], which undergoes phosphine loss, followed by coordination of the diene to yield [RhPPh_3(cod)(O_2)Cl]. This was then thought to undergo an electrocyclic process, to give a metal coordinated dione precursor complex.

Water soluble derivatives of the catalyst have been developed, and are being evaluated. The sulphonated complex [Rh(NaL)$_3$Cl] (HL = 3-diphenylphosphinobenzene sulphonic acid) has been used as a catalyst for the Leuckert-type reduction of olefins or aldehydes by formic acid and sodium



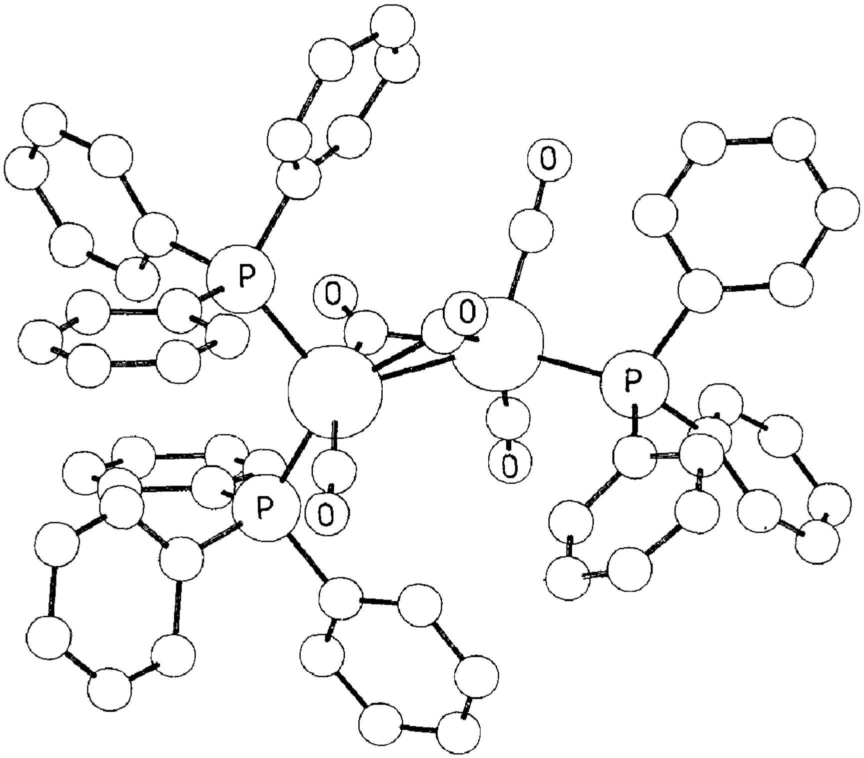
formate in aqueous conditions [113]. This same catalyst is effective in the emulsion polymerisation of chloroprene in the presence of a thiol regulator [114]. In the presence of the regulator, soluble trans-1,4-polychloroprene (MW 150,000 - 250,000) was obtained in 90-96% yield, whereas in its absence insoluble polymers resulted.

The addition of hydrogen to [Rh(PAr$_3$)$_2$ClL] (Ar = 4-methylphenyl; L = PAr$_3$, pyridine or tetrahydrothiophene) has been investigated [115]. The two hydrogen atoms in the octahedral [Rh(PAr$_3$)$_2$ClLH$_2$] product are cis to each other, whilst the two phosphines are trans to each other. Analysis of thermodynamic data led to calculated rhodium-hydrogen bond enthalpies of about 60 kcal mol^{-1} [115].

The reduction of vinylketones by alcohols has been shown to proceed in the presence of the transfer hydrogenation catalyst [$HRh(PPh_3)_4$] [116]. The insertion of olefins into Rh-H bonds has been studied [117]. Treatment of [$HRh(N_2)(P^iPr_3)_2$] with ethylene results in the formation of [$HRh(C_2H_4)(P^iPr_3)_2$]; a rapid cis-trans isomerisation was thought to proceed by an intramolecular olefin insertion/de-insertion pathway. This same catalyst has been shown to be effective in regiospecific hydrogen transfer reactions [138].

An analysis of the available structural data for [$Rh(PR_3)_3L$] complexes has been made, and the conformational changes correlated with molecular motion and the implications for catalytic activity considered [118].

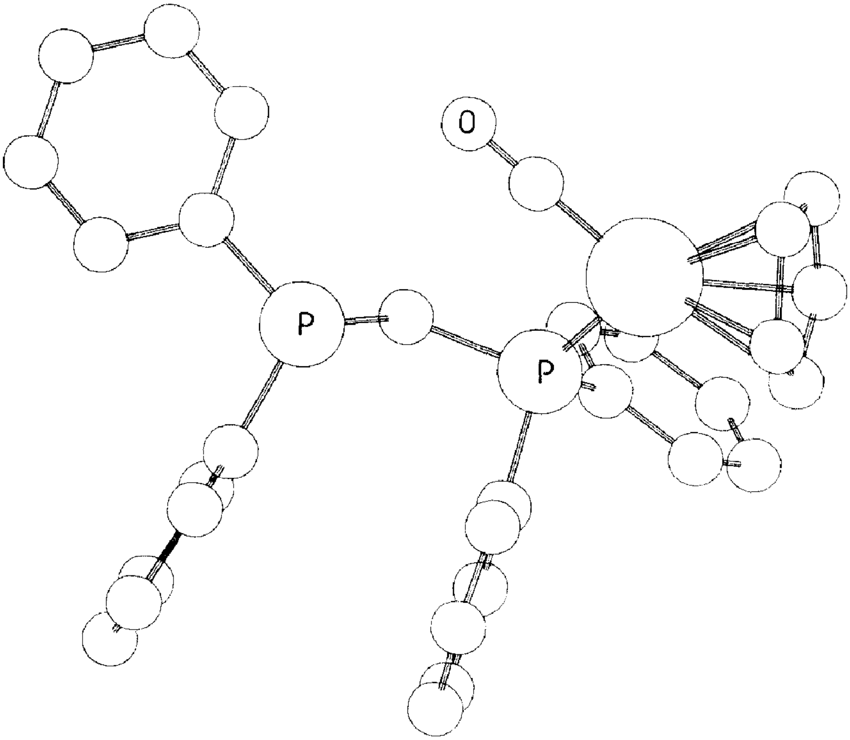
A dimeric complex of the form [$(CO)(PR_3)_2Rh(CO)_2Rh(PR_3)_2(CO)$] was thought to be involved in the rhodium catalysed hydroformylation of olefins. A complex of this type has been prepared by the reduction of [$RhCl(CO)(PPh_3)_2$] in thf by sodium amalgam under an atmosphere of carbon monoxide. Upon releasing the gas pressure the desired complex was obtained as a yellow solid. The complex was characterised crystallographically, and shown to be the tris(phosphine) derivative, [$(CO)(PPh_3)_2Rh(CO)_2Rh(CO)_2PPh_3$] (**61**), with a metal-metal distance of 2.769 Å [120].



(61)

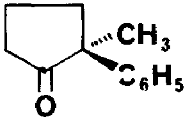
The reaction of $[Rh(dppe)(MeOH)_2]^+$ with $[IrH_5(P^iPr_3)_2]$ in methanol results in the formation of the binuclear hydride bridged complex $[(dppe)RhH_2IrH_2(P^iPr_3)_2]$, which has been structurally characterised [121].

Surface modified silica gels have been prepared in which 1-phenoxy-1,2-bis(diphhenylphosphino)ethyl ligands have been randomly attached over the surface. reaction with [Rh(nbd)(acac)] results in the formation of a rhodium(I) modified surface, which has been investigated as a potential immobilised catalyst [122]. Numerous model compounds are also described in this study. An unusual example of a monodentate dppm ligand has recently been reported [123]. The reaction of $[Rhcp(CO)_2]$ with dppe or dppp results in the formation of the expected chelated complexes [Rhcp(dppe)] or [Rhcp(dppp)]. In the case of dppb, the chelate ring would be too large, and a bridging mode is adopted in the complex [cp(CO)Rh(dppb)Rh(CO)cp]. The reaction with dppm is exceptional, and results in the formation of [Rhcp(CO)(dppm)] **(63)**, which has been shown to possess a monodentate dppm ligand in the solid state [123]. The reactions with acids to give hydrido species were also reprorted.



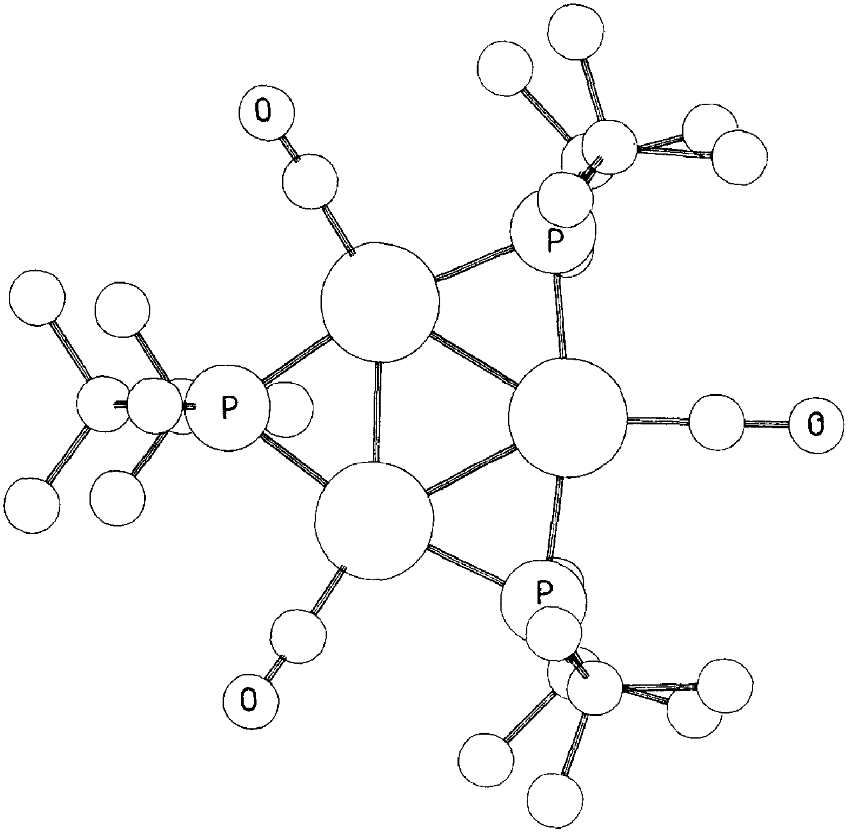
(63)

The chiral complex $[RhL_2]Cl$ (L = 2S,3S-bis(diphenylphosphino)butane. $Ph_2PCHMeCHMePPh_2$) has been shown to be an effective catalyst for the asymmetric cyclisation of pent-4-enals to cyclopentanones. Thus, a 52% enantiomeric excess of the (-)-S enantiomer of 2-methyl-2-phenylcyclopentanone **(64)** is obtained in the catalysed cyclisation of $MePh(CHO)CCH_2CH=CH_2$ [124].



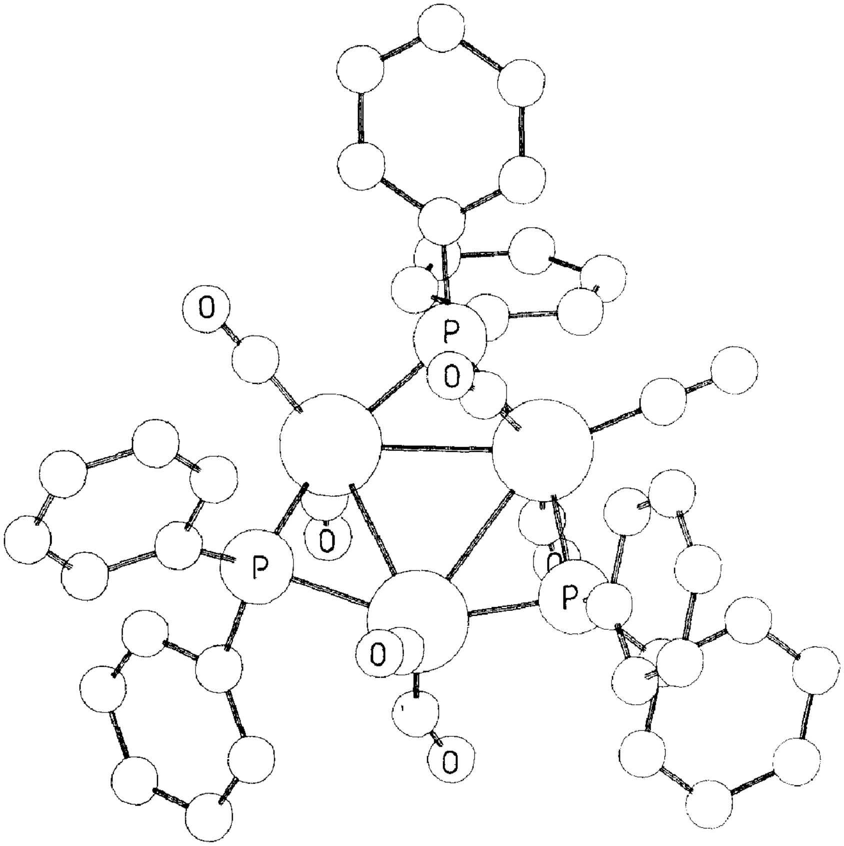
(64)

There has been some recent interest in the formation and properties of phosphido derivatives of transition metals, and a number of such rhodium complexes have been described. The reaction of $[Rh_2(CO)_4Cl_2]$ with $^tBu_2PLi$ results in the formation of the triangulo cluster, $[Rh_3(CO)_3(^tBu_2P)_3]$ **(65)**, in which each rhodium atom bears a terminal carbonyl ligand, and each rhodium-rhodium edge is bridged by a phosphido ligand [125].



(65)

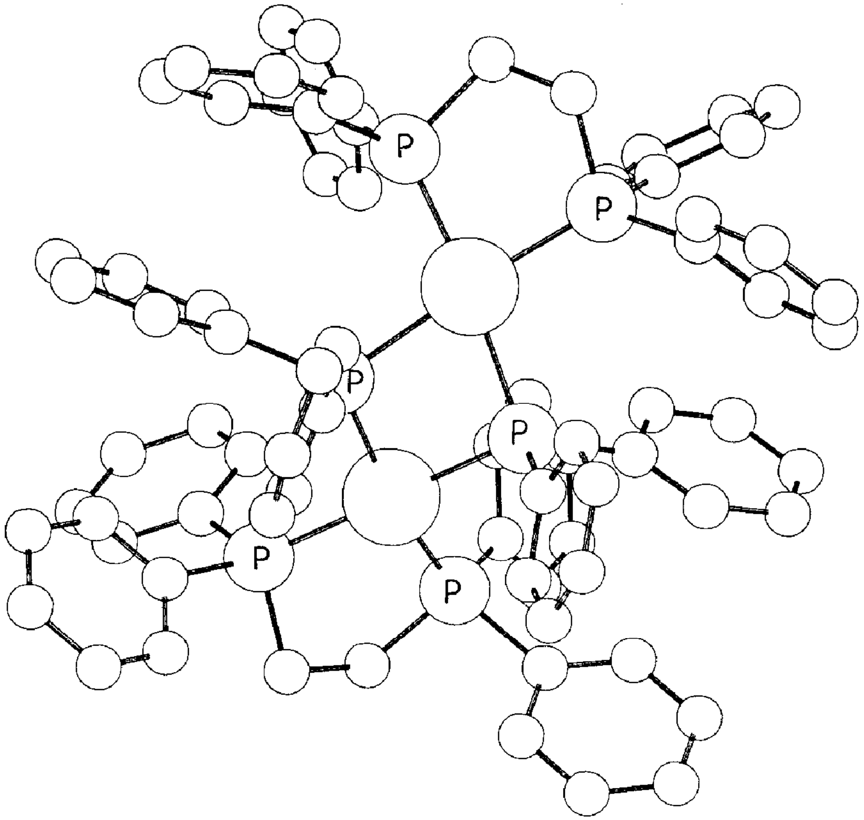
In contrast, the reaction of Ph_2PLi with $[Rh_2(cod)_2Cl_2]$ results in the formation of a phosphido-bridged dimer $[(cod)Rh(PPh_2)_2Rh(cod)]$ [126]. The diene ligands are relatively labile in this complex, and substitution products in which they have been replaced by dppm, dppe, dppp, cis-$Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2AsPh_2$, PPh_3, PEt_3 or PPh_2Me have been described. The reaction of $[Rh_3(PPh_2)_3(CO)_5]$ with carbon monoxide results in the formation of $[Rh_3(PPh_2)_3(CO)_7]$ **(66)**, which has been shown to possess the structure shown [127].



(66)

The crystal structure of $[(dppe)Rh(PPh_2)_2Rh(dppe)]$ **(67)** has also been reported [128].

The triphosphine ligand $Ph_2PCH_2PPhCH_2PPh_2$ reacts with $[Rh_2Cl_2(CO)_4]$ to give the trinuclear complex $[Rh_3(triphos)_2(CO)_3Cl_2][Cl]$ **(68)** [129]. Each rhodium atom bears a terminal carbonyl ligand, and the two terminal rhodiums also bear a chloride ligand, one of which is bridging to the central metal.



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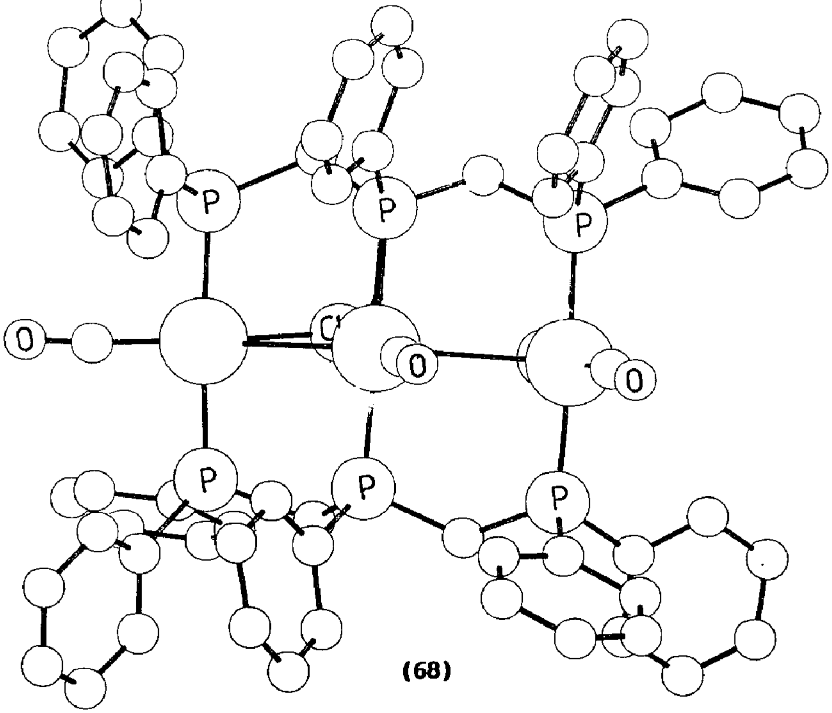
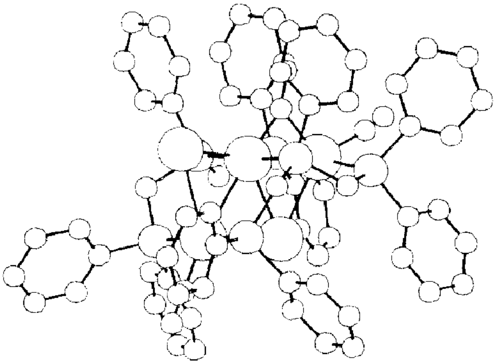


(68)

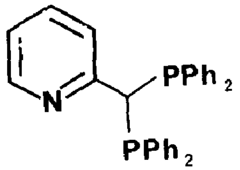
Upon reaction with sodium iodide, metathesis reactions occur, and the bonded chloride ligands are replaced by iodide [130]. An X-ray structural analysis of the product cation $[Rh_3(triphos)_2I_2(CO)_3]^+$ (**69**) reveals that the reaction is not quite as simple as might be expected; a framework rearrangement has occurred, and the complex now contains a rhodium-rhodium bond (2.865 Å), and a more distant non-bonded interaction (3.149 Å). The metal-metal bond is bridged by a carbonyl and iodide ligand.



(69)

Complexes with mixed nitrogen/phosphorus donor ligands have come in vogue over the last few years, and a number of interesting examples of rhodium complexes with these species have been reported. The PNP ligand, 2-bis(diphenylphosphino)methylpyridine (**70**) forms the complex $[RhL(nbd)][BF_4]$, which has been shown by ^{31}P NMR spectroscopy and by a crystallographic determination to possess a bidentate ligand, in which one of the diphenylphosphino groups is non-coordinated (**71**) [131]. Treatment of the complex with carbon monoxide results in dimerisation to give $[Rh_2L_2(CO)_2]$ (**72**). The displacement of the diene by the monodentate carbon monoxide leaves a vacant site, and the free phosphorus atoms coordinate to the metal. The metal-metal distance is 3.054 Å, on the basis of an unpublished crystallographic determination. The reaction of this latter complex with sulphide, results in the introduction of a sulphido bridge between the two rhodium atoms, and the displacement of the pyridine nitrogen atoms (**73**).

The related PNP ligand, 2,6-bis(diphenylphosphino)pyridine (**74**) reacts with $[Rh_2(CO)_4Cl_2]$ to give the green tetranuclear complex $[Rh_4L_2Cl_4(CO)_3]$ (**75**) [133]. A crystallographic determination of the complex has revealed it to possess the 'phase-shifted' structure indicated. The two central rhodium atoms are directly bonded to each other, with a carbonyl bridge. The two terminal



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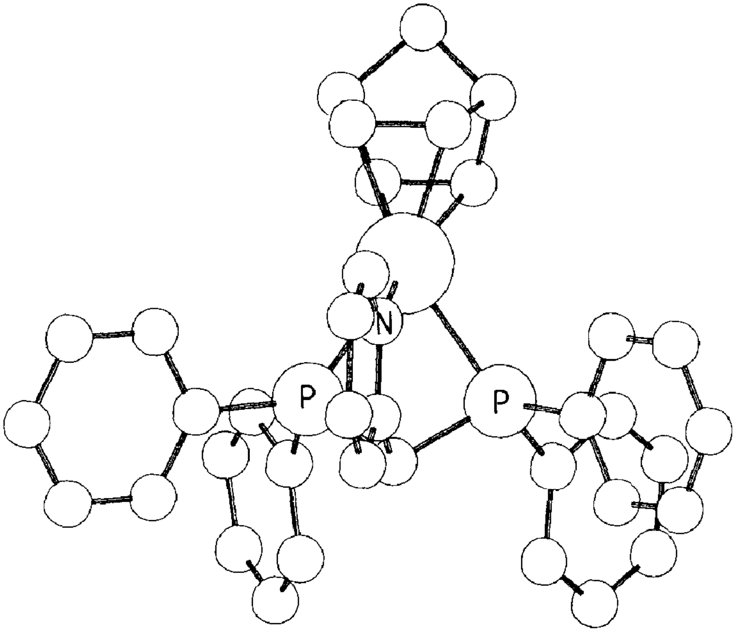

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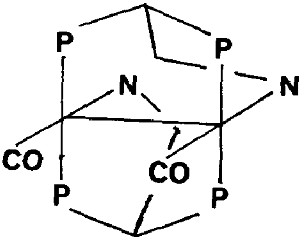

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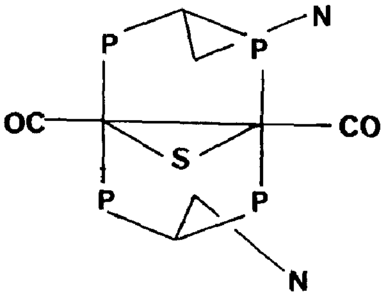
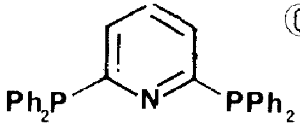


(73)

metal atoms each bear a terminal carbonyl and chloride ligand, and also a bridging chloride to the central Rh_2 unit. Reaction of the complex with excess carbon monoxide in methanol yields a binuclear complex $[Rh_2L_2(CO)_2(MeOH)Cl]^+$ **(76)**, which has also been structurally characterised [132]. Each rhodium atom is four coordinate, and coordinated to the phosphorus of the ligand. The reactions of the complex with other small molecules, notably sulphur dioxide, was also investigated.

Another polyfunctional ligand, 2,5-bis(diphenylphosphino)furan (77), has been shown to react with $[Rh(nbd)_2][BF_4]$ to yield $[(nbd)RhL_2Rh(nbd)][BF_4]$ **(78)**, in which the ligand acts as a bridging bidentate P_2 donor [134]. The complex has been structurally characterised, and shown to react with dihydrogen to give



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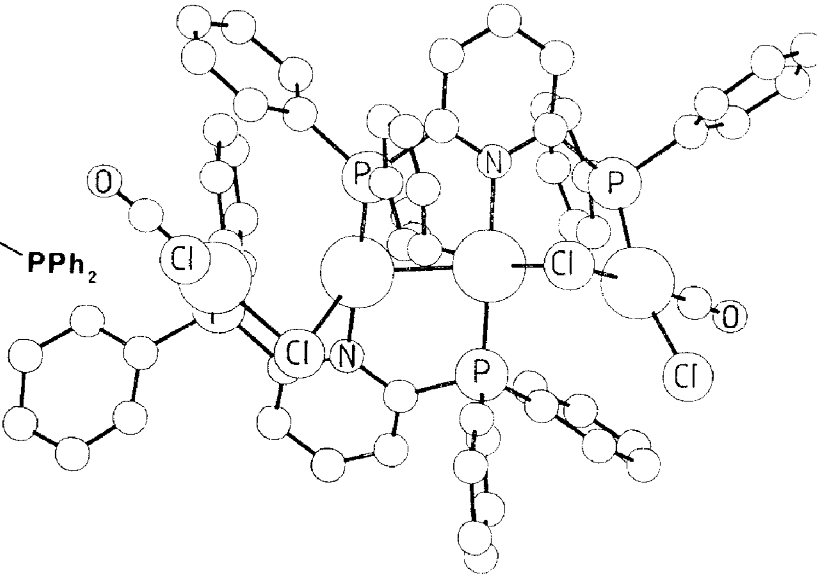

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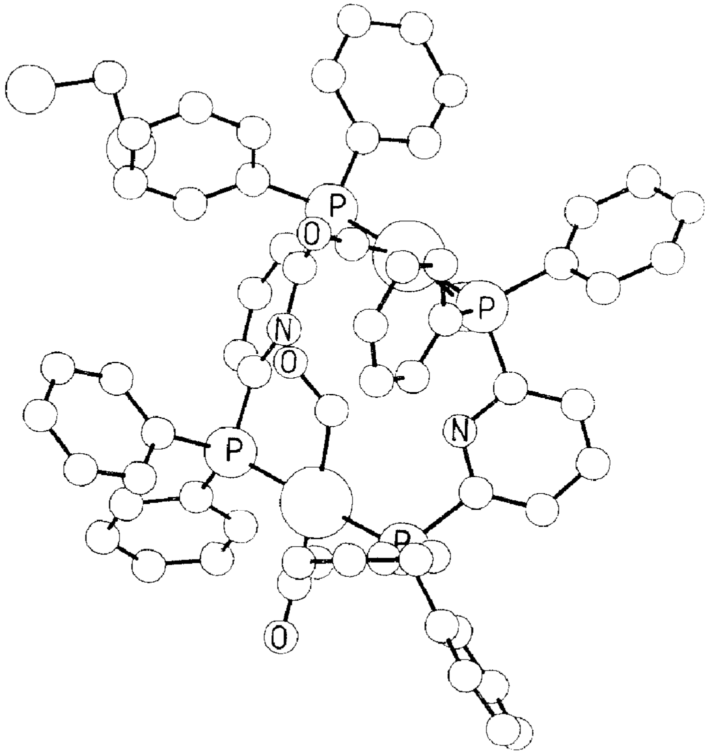
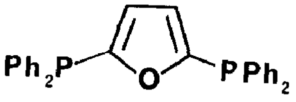


(76)

a tetrahydride, $[Rh_2L_2H_4(MeOH)_4]^{2+}$ (79). The reaction of the ligand with $[Rh_2(CO)_4Cl_2]$ also gives a dimeric product, $[(CO)ClRhL_2Rh(CO)Cl]$ [134].



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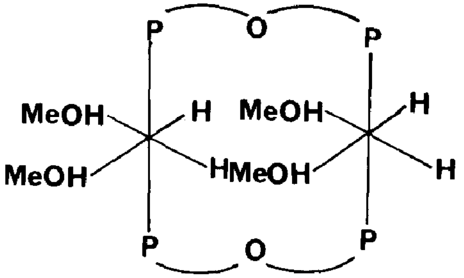

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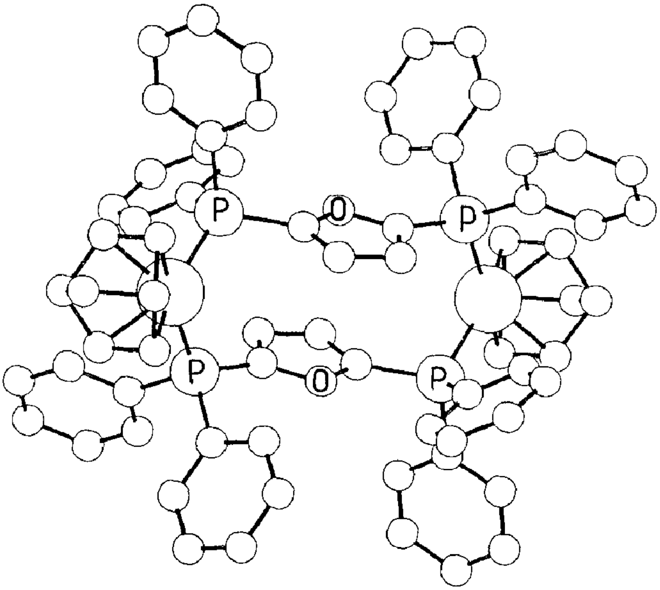
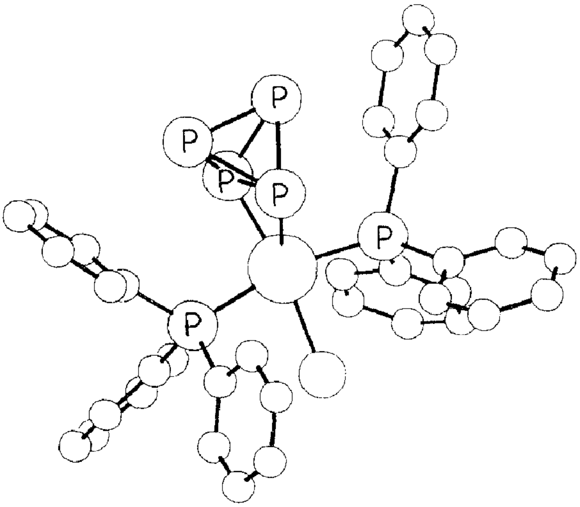


(78)

The unusual complex $[Rh(P_4)(PPh_3)_2Cl]$ (80) has been structurally characterised [135]. A tetrahedral P_4 unit is bonded to the metal in a bidentate fashion, by two adjacent phosphorus atoms. The P-P vector of the two metal bound phosphorus atoms is perpendicular to the square-plane of ligands about the metal. This is the first example of the bidentate bonding mode for a P_4 tetrahedron. Extended Huckel calculations were reported for the complex.



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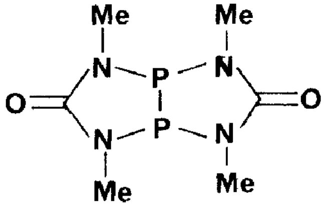


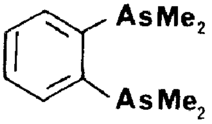
(81)

The unusual heterocycle **(81)** reacts with $[Rh_2Cl_2(CO)_4]$ to give $[Rh_2L_2(CO)_2Cl_2]$ [136]. There is no cleavage of the P-P bond in the heterocycle, which acts as a bridging bidentate P_2 ligand. The dimeric complex contains a six-membered P_4Rh_2 ring.

The complexes $[RhL(P_3E_3)]$ ($L = MeC(CH_2PPh_2)_3$; E = S or Se) **(82)** have been prepared, and the sulphur compound structurally characterised. The rhodium is bonded to the three phosphorus atoms of the triphosphine, and two phosphorus atoms of the heterocycle. The remaining coordination site is occupied by the terminal sulphur atom of the ligand [137].

4.4.3.3 Complexes with arsenic donor ligands

The reaction of 1,2-bis(dimethylarsino)benzene **(83)** with $[Rh_2Cl_2(C_2H_4)_4]$ results in the formation of $[RhL_2]Cl_2$ (L = **83**) [108]. This complex reacts with carbon dioxide to give an octahedral species $[RhL_2(CO_2)Cl]$ **(84)** which has been structurally characterised. The carbon dioxide is bonded to the metal through the carbon, and the Rh-C distance of 2.05 Å is typical of rhodium-acyl complexes [108].



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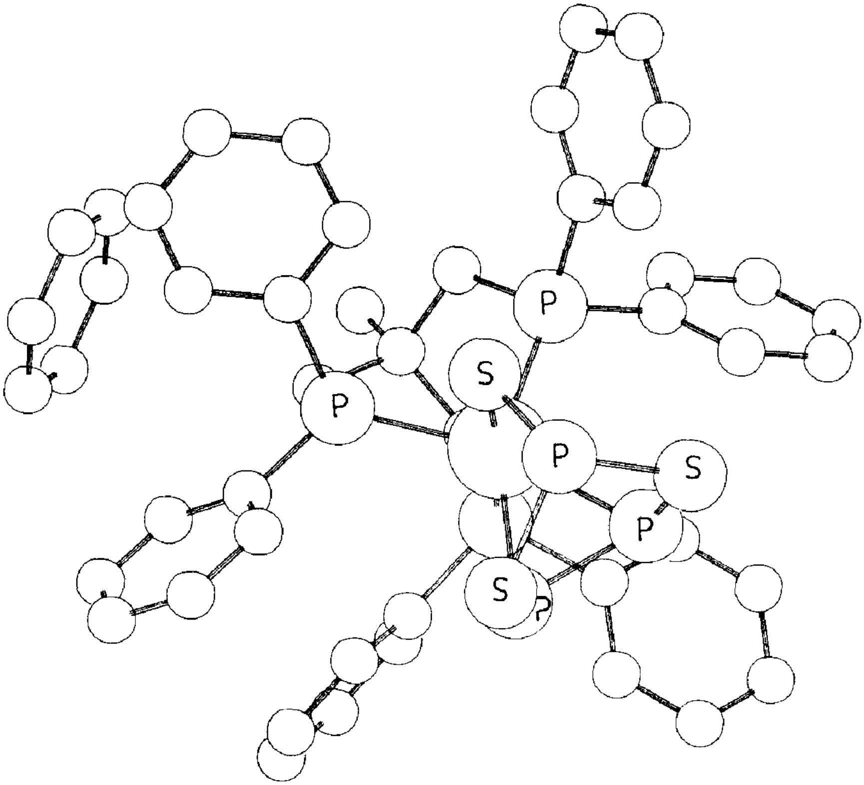

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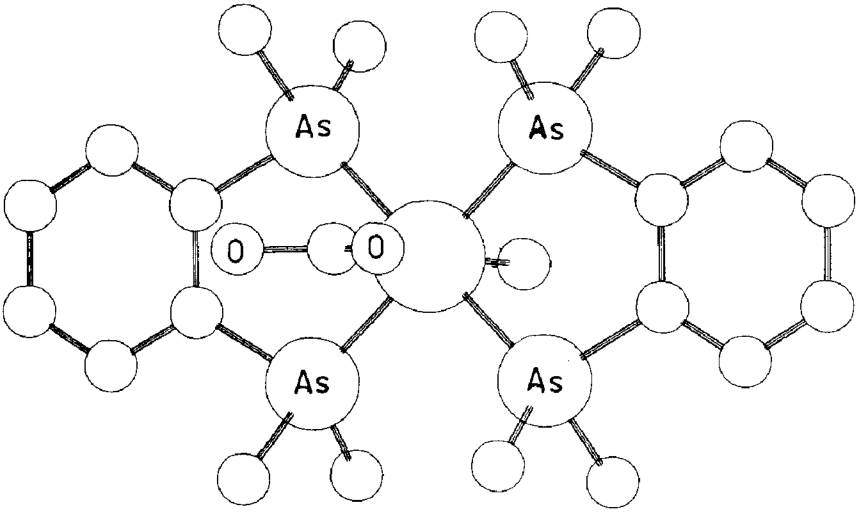

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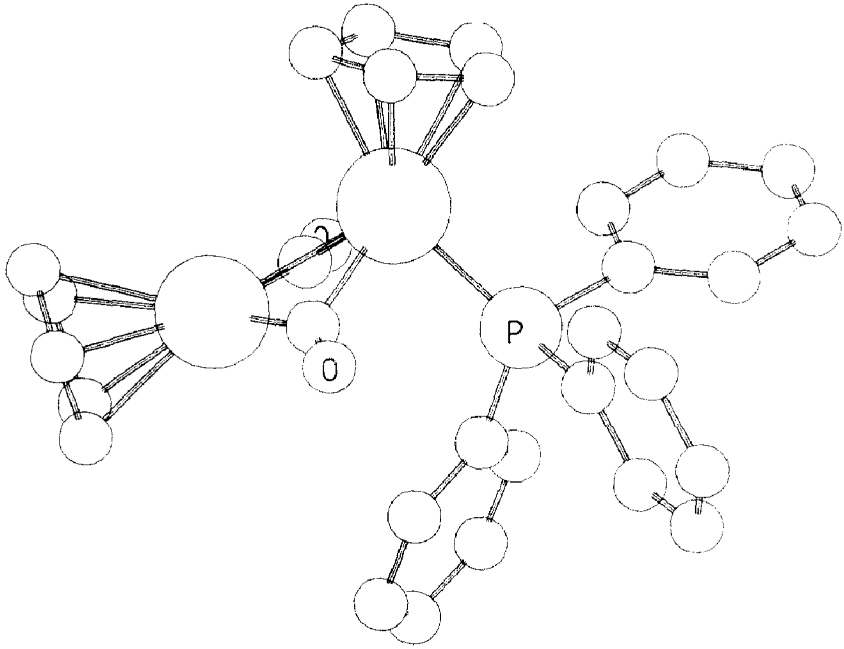
4.4.4 Complexes with carbon, silicon and tin donor ligands

4.4.4.1 Complexes with dienes and cyclopentadienyl ligands

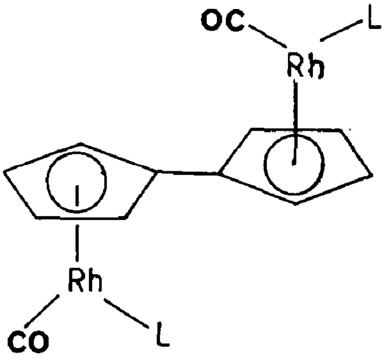
The carbonyl bridged complex [cp(CO)Rh(CO)Rh(CO)cp] reacts with triphenylphosphine to yield [cpRh$(CO)_2$Rh(PPh_3)cp] **(85)**, which has been shown crystallographically to possess a bis(carbonyl) bridged structure [139].



(85)

Electrochemical or chemical oxidation of [Rhcp(PPh_3)CO] gives rise to a metal-metal bonded fulvalene complex **(86)**. This undergoes a two electron reduction, which involves cleavage of the metal-metal bond to form the fulvalene complex **(87)**. Attempted oxidation of [Rhcp(CO)PPh_3] by silver(I) hexafluorophosphate lead to the formation of the metal-metal bonded species [cp(PPh_3)CORhAgRhcp(CO)PPh_3]. The Rh-Ag-Rh bond angle is 171°, and the Rh-Ag bond lengths of 2.651 and 2.636 Å are indicative of single bond order [140].

The complex [RhL$(CO)_2$] (HL = indene, **89**) has been shown to undergo a remarkably rapid substitution reaction upon treatment with triphenylphosphine to give [RhL(CO)PPh_3] [141]. It was proposed that an associative mechanism is operative, in which the electron count at the rhodium is maintained by an η^5-η^3 change at the indenyl group. The substitution of the indenyl complex proceeded 10^8 times faster than that of the cyclopentadienyl compound.



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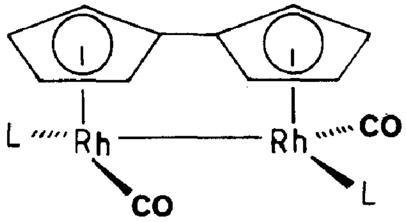

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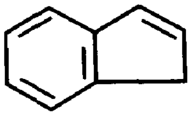


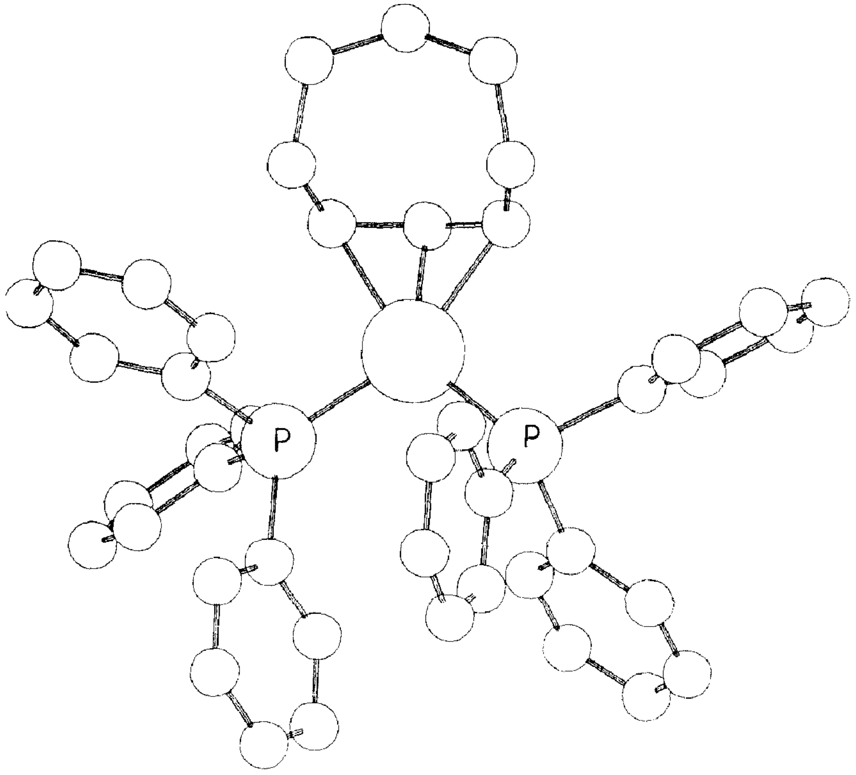
(89)

Under metal vapour synthesis conditions, rhodium reacts with 1,3-cyclooctadiene to give a product, which yields a rhodium(I) complex upon the addition of triphenylphosphine [143]. The complex $[RhL(PPh_3)_2]$ (HL = 1,3-cyclooctadiene) **(90)** has been structurally characterised, and shown to contain an η^3 bonded cyclooctadienyl ligand.

4.4.4.2 Complexes with σ-bonded carbon ligands

Rhodium isocyanide complexes have been of some application as components of systems for the generation of dihydrogen, and electrochemical studies of the complexes $[(RNC)_2Rh(dppm)_2Rh(CNR)_2]^{2+}$ (R = Bu, ^{i}Pr, ^{sec}Bu or ^{tert}Bu) have been reported [144]. A crystal structural analysis of the complex $[(MeO)_3PRh(dppm)_2L(CO)Rh(OAc)]$ (H_2L = $MeO_2CCH{=}CHCO_2Me$) derived from dimethyl acetylenedicarboxylate has been reported [145]. The two dppm ligands, the carbonyl and the alkene fragment are all bridging the two rhodium centres.

The complex $[L_2RhH_2RhL_2]$ (L = $P(^iOPr)_3$) is a catalyst precursor for the hydrogenation of alkynes to trans-alkenes [146]. The alkyne and dihydrogen compete for reaction with the rhodium complex. Amongst the early products of the reaction are $[H_4Rh_2L_4]$ and $L_2Rh(RC{=}CR)H_2RhL_2]$. The addition of alkyne to the former tetrahydride results in the formation of η^2 vinyl complexes, and



(90)

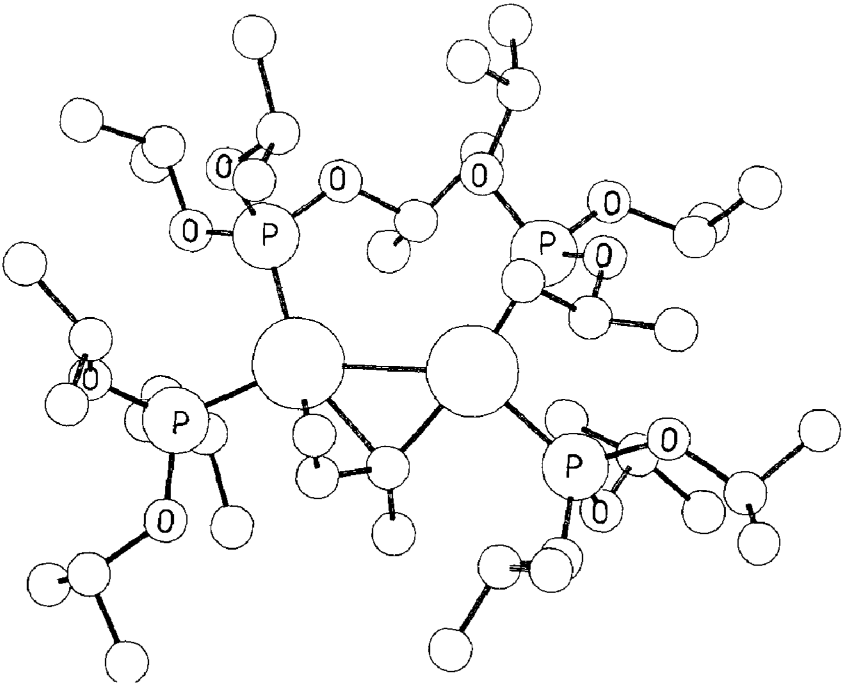
crystal structural analyses have been reported for the products of the reaction with 1,2-bis(4-methylphenyl)ethyne and 2-butyne **(91)** [146]. The addition of further alkyne to the vinyl complex results in carbon-carbon bond formation, and the complex so formed has also been structurally characterised **(92)**.

4.4.4.3 Complexes with tin donor ligands

The dimerisation of ethylene to mixtures of but-2-enes has been shown to be catalysed by the complex $[Rh_2Cl_2(SnCl_3)_4]^{4-}$, which more active and stable than rhodium(III) chloride [147]. The major products were a mixture of cis and trans but-2-ene (97%), although some but-1-ene (3%) was also formed.

4.5 HETEROMETALLIC COMPOUNDS, CLUSTERS AND RHODABORANES

The reaction of $[LRhCl_2RhL]$ (L = $Ar_2PCH_2CH_2PAr_2$; Ar = 4-methylphenyl) with $Li[(\eta^5\text{-}C_5H_4PAr_2)Mo(CO)_3]$ gave the Rh-Mo bonded species (**93**) [148]. The



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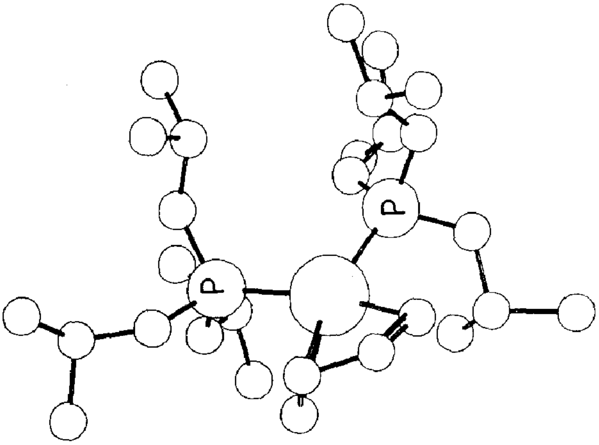
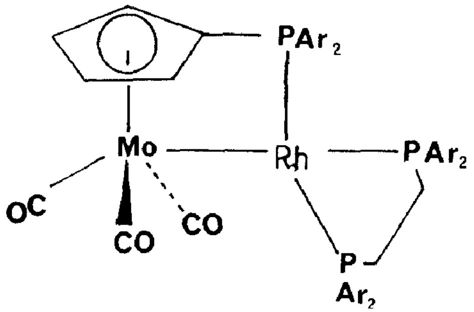


(92)

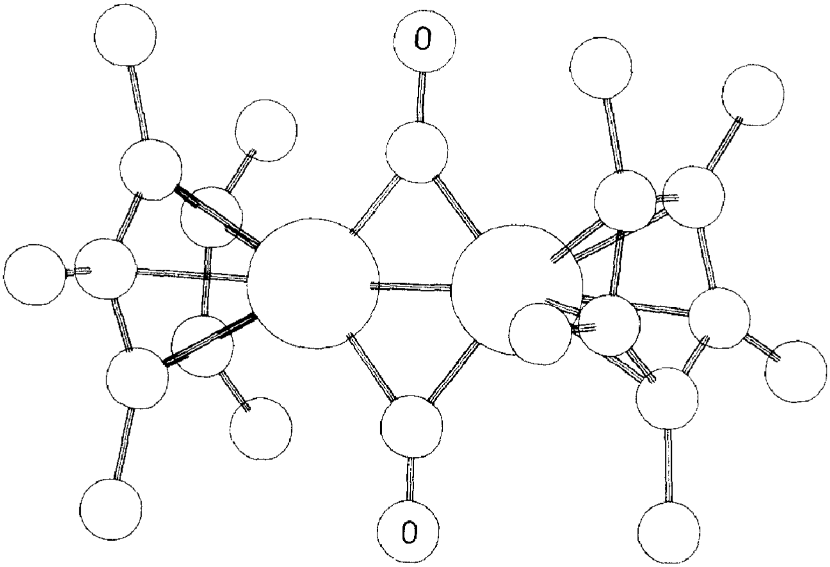
structure was asigned on the basis of the spectroscopic properties of the complex. Reaction with carbon monoxide resulted in the displacement of the diphosphine, and the introduction of two carbonyl ligands [148].

The complex $[Fe_2Rh_2(PPh_2)_4(CO)_8]$ has been structurally characterised, and is the product of the reaction of $[Rh_2(C_3H_5)_2Cl_2]$ with $[Fe(CO)_4(PPh_2H)]$ [149].



(93)

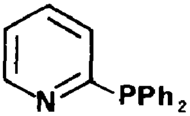
A facile reaction occurs when $[LRh(CO)_2RhL]$ ($HL = C_5HMe_5$) is treated with $[Co(C_2H_4)_2L]$; the product of the reaction is $[LRh(CO)_2CoL]$ **(94)**, which has been structurally characterised [150]. There is a formal double bond between the rhodium and the cobalt (Rh-Co, 2.404 Å). Numerous reactions of this compound with other metallic fragments, to give tetrahedro clusters were described.



(94)

Related complexes, [cp(CO)Co(CH_2)Rh(CO)cp] and [cp(CO)Rh(CH_2)Rh(CO)cp], are prepared in a facile exchange reaction of [cpRh$(CO)_2$] with [cp(CO)Co(CH_2)Co(CO)cp] [151]. The various isomers of these complexes were detected, and the mechanism of interconversion of cis-trans was discussed. Mechanisms involving breaking of the metal-metal bond, or the methylene bridge were considered, together with one involving the formation of carbonyl bridges.

2-(Diphenylphosphino)pyridine (95) is a useful NP donor, and the complex [Cl_2(CO)RhL_2PdCl] is formed from the reaction of [$Rh_2(CO)_4Cl_2$] with [PdL_2Cl_2] or of [RhL_2(CO)Cl] with [Pd(cod)Cl_2] [152]. An X-ray analysis of the product has revealed it to possess a head to tail arrangement of the bridging PN ligands. Related isonitrile complexes have been reported, and the precise nature of the ligands used appears to dictate whether head-to-head or head-to-tail arrangements of the bridges are obtained. Thus, the reaction of [Rh$(MeNC)_2L_2]^+$ with [Pd(cod)Cl_2] results in the formation of head-to-tail [Cl$(MeNC)_2L_2$PdCl$]^+$, whereas the reaction with [Pd$(PHCN)_2Cl_2$] gives head-to-head (P at rhodium) [Cl$(MeNC)_2$RhL_2PdCl$]^+$.



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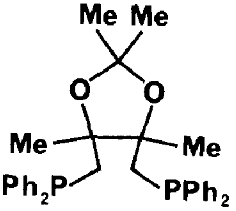

(96)

The hexanuclear cluster, [$Rh_6(CO)_{16}$] has been shown to co-catalyse the oxidation of carbon monoxide and triphenylphosphine [153]. Detailed mechanistic studies have shown that cluster breakdown is an early stage of the reaction, and that intermediate stages in the reaction involve the species [$Rh_2(CO)_2(PPh_3)_4(PhH)_2$], [$Rh_2(CO)_6(PPh_3)_2$] and [$Rh_4(CO)_{10}PPh_3$]. The same cluster also catalyses the reduction of nitrobenzene by carbon monoxide/water mixtures in the presence of 3,4,7,8-tetramethyl-1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline [154]. Very good yields and enantiomeric excesses have been observed in the asymmetric hydrogenation of amino acid precursors by the complex [$Rh_6(CO)_{10}L_3$] (L = (-)-DIOP, 95) [156].

The tetranuclear clusters, [$Rh_4(CO)_{12-x}L_x$] (L = $P(OPh)_3$; x = 1 - 4) have been investigated by ^{103}Rh NMR. The location of the phosphite ligands on the tetrahedron were assigned [155].

Pyrolysis of $Na[Rh_5Pt(CO)_5]$ in methanol in the presence of $NaHCO_3$ gives a mixture of products, from which the complexes $K_3[Pt_2Rh_{11}(CO)_{24}]$ and $Cs_4[PtRh_{12}(CO)_{24}]$ were isolated. Both of these compounds were structurally characterised. The compounds are ESR silent, and exhibit no hydrido signals in their ^{1}H NMR spectra [157].

The reaction of $[cpRh(CO)_2]$ with $[H_2Os_3(CO)_{10}]$ in the presence of hydrogen in aromatic solvents gives $[H_3(ArH)RhOs_3(CO)_9]$ and $[H_2(cp)RhOs_3(CO)_{10}]$ [158]. Replacement of the cyclopentadienyl ligand by pentamethylcyclopentadienyl introduced sufficient steric hindrance that the aromatic solvent was not coordinated to the metal; instead, $[H_4(C_5Me_5)RhOs_3(CO)_9]$ was obtained [158].

The triangulo cluster $[Rh_3(PPh_2)_3Cl_2(CO)_4]$ is obtained from the reaction of $[Rh_2(CO)_4Cl_2]$ with two equivalents of Ph_2PH [159].

A number of rhodaboranes and rhodacarboranes have been reported this year [160-165].

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