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COORDINATION CHEMISTRY REVIEWS

3. Rhodium 1993

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CONTENTS

INTRODUCTION

This review details the coordination chemistry of rhodium reported during 1993 and is organized in a similar manner to the corresponding 1992 review [1]. The literature has been searched by using both *Current Contents* and the Cambridge Structural Data Base, and structural

PII S0010-8545 (96) 01270-2

figures have been redrawn using coordinates taken from this data base, implemented through the ETH, Zürich [2]. In most cases, hydrogen atoms have been omitted for clarity.

Most organometallic complexes and rhodium carbonyl clusters have been excluded, although some complexes containing cyclopentadienyl and carbonyl ligands but which are of interest to the coordination chemist are described. The review is not fully comprehensive but does provide an overview of rhodium coordination chemistry for 1993.

A review by Sutton covers the chemistry of diazo compounds, including some of rhodium [3].

3.1 RHODIUM(IV)

The caesium salt $Cs_2[RhCl_6]$ has been studied by X-ray photoelectron spectroscopy; accompanying results focus on rhodium(III) compounds (see below) [4].

3.2 RHODIUM(III)

3.2.1 Complexes with halide ligands

Studies of $Cs_3[RhCl_6]$ by X-ray PES are complemented by an investigation of the barium salt of Claus' blue. The latter was prepared by the reaction of Cl_2 with rhodium(III) chloride in aqueous KOH; this produced a deep purple solution to which $Ba(OH)_2$ was added to precipitate the blue product. Originally proposed to be a rhodium(VI) compound, the present study shows that Claus' blue possesses a rhodium(III) centre and ESR and Raman spectroscopic data confirm the presence of a superoxide group [4]. The crystal structure of $K_3[RhCl_6]$ has been determined [5].

Eight isomers, including three pairs of stereoisomers, of $[Rh(NCS)_n(SCN)_{6-n}]^{3-}$ (n = 0-4) have been prepared and characterized by ^{103}Rh and ^{15}N NMR spectroscopies [6].

3.2.2 Complexes with oxygen donor ligands

The photochemical isomerization of *mer,cis*-[$RhCl_3$(dmso-*S*)$_2$(dmso-*O*)] leads to the formation of *mer,trans*-[$RhCl_3$(dmso-*S*)$_2$(dmso-*O*)], a new linkage isomer of this compound. The latter has been characterized by spectroscopic and X-ray diffraction methods. In aprotic solvents, the *mer-trans*-isomer is thermodynamically unstable with respect to the *mer,cis*-species [7].

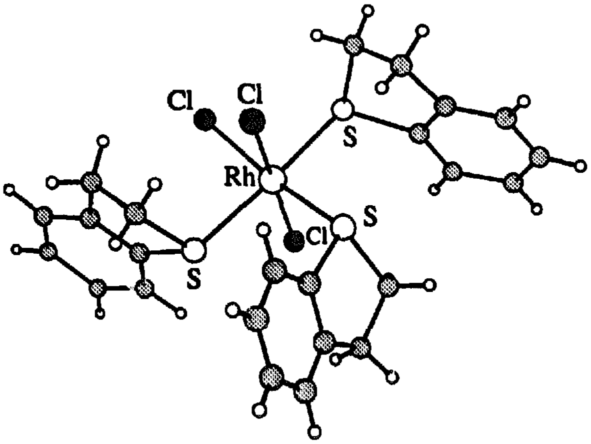
The reaction of dioxygen with $[RhL_2]^+$ where L is ligand (1) leads to the formation of the peroxo complex $[Rh(O_2)L_2]^+$. The cation has been characterized spectroscopically, and the structure has been confirmed by X-ray crystallography [8]. A further peroxo-complex is described in section 3.4.2.

(1)

3.2.3 Complexes with sulfur or selenium donor ligands

The reaction of $[Rh(SPh)(PMe_3)_3]$ (see section 3.4.2) with PhSH results in oxidative addition of the S–H bond and the formation of the rhodium(III) complex *cis,mer*-$[RhH(SPh)_2(PMe_3)_3]$. This isomerizes in hexane to give the *trans,mer*-complex which has been structurally characterized [9]. The reaction of $Pb\{S(C_6F_4)\}_2$ with the dimer $[Cp^*{}_2Rh_2Cl_4]$ yields the ionic compound $[Cp^*{}_2Rh_2\{\mu\text{-}S(C_6F_4)\}_3][Cp^*Rh\{S(C_6F_4)\}_3]$ the structure of which has been confirmed by the results of an X-ray diffraction study. Solution NMR spectroscopic data are consistent with the retention of the ionic structure in methanol, but in less polar solvents an equilibrium exists between the ionic species and $[Cp^*Rh\{S(C_6F_4)\}_2]$. Contrasting behaviour is observed for the iridium analogues (see accompanying review) [10].

The coordination of 2,3-dihydrobenzo[*b*]thiophene, L, to rhodium(III) is observed in the octahedral complex *mer*-$[RhCl_3L_3]$ (**2**), the crystal structure of which has been determined [11].



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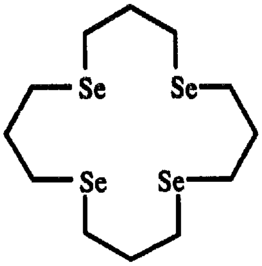


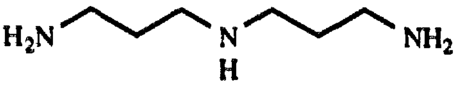
(**3**)

Whilst sulfur macrocyclic chemistry has a rich chemistry, few reports have appeared concerning related selenium-containing ligands. Reid *et al.* point out the advantage of being able to use ^{77}Se NMR spectroscopy to aid the characterization of such ligands and their complexes. The reaction of $RhCl_3.3H_2O$ with ligand (**3**) in aqueous ethanol under reflux gives the cation $[RhCl_2(3)]^+$, isolated as the tetrafluoroborate salt. This has been characterized by FAB mass spectrometry, UV-VIS and NMR spectroscopies, and X-ray diffraction methods. A doublet is observed in the ^{77}Se NMR spectrum — $J(^{103}Rh-^{77}Se) \approx 30$ Hz. Preliminary electrochemical studies (in MeCN, with $[^nBu_4N][BF_4]$ as supporting electrolyte) show that $[RhCl_2(3)]^+$ undergoes an irreversible reduction ($E_{1/2} = -1.16$ V vs. Fc/Fc$^+$) [12].

3.2.4 Complexes with nitrogen donor ligands including cyclometallated 2-phenylpyridine ligands

The preparation (by an improved route), properties and structure of the complex *trans*-$[Rh(CN)_2L_2][ClO_4]$ (L = 1,3-diaminopropane) have been described. In the solid state, the cations occupy special positions at inversion centres and the RhL-chelate rings are in chair-conformations. The perchlorate salt has also been studied by electronic absorption, IR and NMR spectroscopies. Stepwise substitution of the cyano ligands occurs in aqueous solution to yield the *trans*-isomers of $[Rh(CN)ClL_2]^+$, $[RhCl_2L_2]^+$, $[Rh(CN)(SO_3)L_2]$, $[Rh(SO_3)_2L_2]^-$ [13].

The *mer*-, *sym,fac*- and *unsym,fac*-isomers of $[Rh(dien)_2]^{3+}$ have been prepared and separated by using chromatography. Complex characterization by UV-VIS, CD and IR spectroscopies are supported by a structural determinations of *sym,fac*-$[Rh(dien)_2]Br_3$. In the synthesis of $[Rh(4)_2]^{3+}$, only the *mer*-isomer appears to be formed, and this has been confirmed by the single crystal structure determination of *mer*- $[Rh(4)_2]Cl[ClO_4]_2$. Differences between the isomer distributions for cobalt and iridium complexes are discussed; attempts to prepare $[Ir(4)_2]^{3+}$ failed [14].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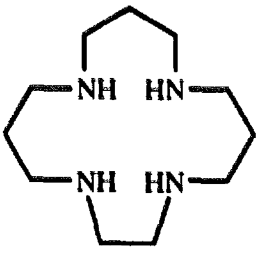
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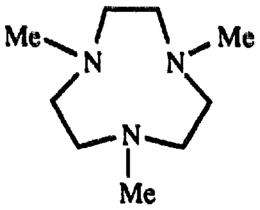
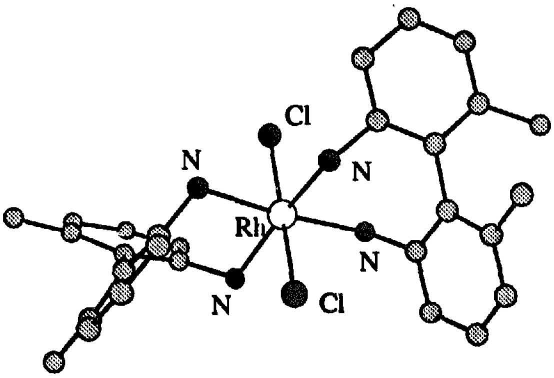

(6)

Macrocycle (5) forms the rhodium(III) complexes *trans*-$[Rh(5)L_2][ClO_4]$ in which HL is succinimide or phthalimide. These products have been studied by conductiometric and IR and UV-VIS spectroscopic methods, and magnetic measurements have been made [15]. Although the compounds $[RhMe_2(6)(OTf)]$ and $[RhMe(6)(OTf)_2]$ have previously been described, new work has investigated their chemistry in aqueous and methanol solutions. The complex $[RhMe(6)(OTf)_2]$ dissolves in water and forms a dihydrate; deprotonation occurs as the pH is altered — pK_a1 = 8.6, pK_a2 = 10.7. Proton NMR spectra have been recorded for these compounds. In D_2O, $[RhMe_2(6)(OTf)]$ eliminates MeD and for this process, a pseudo-first order rate constant of $k = (3.8\pm0.08) \times 10^{-5}\ s^{-1}$ has been determined. The compound [RhMe(6)(OH)(OTf)] has also been isolated. Further transformations in MeOH have been studied and the results discussed [16]. When ligand (6) reacts with $RhCl_3.3H_2O$ in ethanol, the mononuclear complex $[Rh(6)Cl_3]$ is obtained; related experiments lead to the formation of dinuclear species and are described in section 3.5.6 [17].

As part of investigations concerning the asymmetric hydrogen transfer to ketones using rhodium(III) complexes with chiral diaminobiphenyl derivatives as ligands, Lew *et al* have reported the preparation and crystal structure of *trans*-$[RhCl_2L_2]Cl$ in which L is (*S*)-6,6'-dimethyl-2,2'-diaminobiphenyl. The extent of twist around the inter-ring C–C bond in each ligand is evident in (7) which shows the structure of the cation [18].



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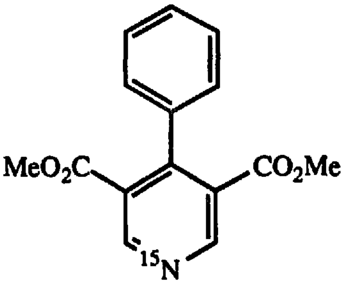
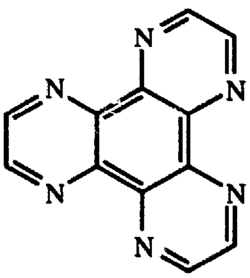


(8)

The ^{15}N-labelled pyridine derivative (8) has been incorporated into the rhodium(III) complexes *cis*-$[Rh(H)_2X(PPh_3)_2(8)]$ (X = Cl, SC_6F_5) and $[Rh(H)(C_2Ph)X(PPh_3)_2(8)]$ (X = Cl, OCN, N_3, C_2Ph) as well as in related rhodium(I) complexes. Multinuclear NMR spectroscopic studies included ^{15}N-observed and a shift range of δ −110.6 to −128.9 (with respect to $MeNO_2$) has been recorded [19].

A range of complexes of rhodium(III) involving bpy and related ligands was reported in 1993. A two-phase system consisting of aqueous $NaHCO_3$ and $C_2Cl_3H_3$ with [Cp*Rh(bpy)Cl]Cl and $[Mn^{III}(TPP)]$ functions as a redox-active phase transfer catalyst and epoxidizes alkenes under a pressure of O_2 [20]. The electrochemical properties of the cations $[Cp^*Rh(bpy)Cl]^+$ and $[Cp^*Rh(phen)Cl]^+$ have been investigated — a two-electron reduction occurs at the rhodium centre to give $[Cp^*RhLCl]^-$ (L = bpy or phen) which is in equilibrium with the chloride-free [Cp*RhL]. The position of the equilibrium depends upon whether L is bpy or phen. Further work has been carried out with these complexes immobilized on polypyrrolic films [21]. The results of an optically detected magnetic resonance spectroscopic study of $[Rh(bpy)(ppy)L]^+$ (HL = 2,2'-thienylpyridine) doped into single crystals of $[Rh(bpy)(ppy)_2][PF_6]$ have been described [22]. The complexes $[Rh(ppy)_2L]X$ (L = 1,4,5,8-tetraazaphenanthrene or (9), and X = ClO_4 or PF_6) have been prepared and their electrochemical and absorption and emission spectroscopic characteristics investigated and the results discussed. Two reversible reductions centred on ligand L and an irreversible oxidation are observed [23]. High-resolution laser spectroscopic studies of the complexes $[RhL_2(bpy)]^+$, $[RhL_2(en)]^+$ and $[\{RhL_2\}_2(\mu\text{-}Cl)_2]$ (HL = thienylpyridine) have probed their luminescence and excitation spectra at ≈5 K. Vibrational side bands have been fully resolved [24].

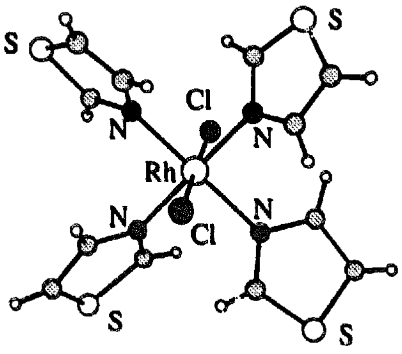


(9)

The 2,2′:6′,2″-terpyridine complex $[Rh(tpy)_2]^{3+}$ has been used as a reduction catalyst for the conversion of NAD^+ to NADH in a photosensitized reaction system containing $[Ru(bpy)_3]^{2+}$ and triethanolamine (as the electron donor). Effective NADH production was observed at pH 7.7 after 90 min irradiation; the yield is pH dependent [25]. In an independent study by Beley *et al.*, a modified electrode which incorporates the $[Rh(tpy)_2]^{3+}$ unit linked by pyrrole groups (electropolymerized onto a reticulated vitreous carbon electrode) has been used in the electrocatalytic reduction of NAD^+. This work has demonstrated the viability of bioreactors with the electrochemical regeneration of the NADH cofactor [26].

Efficient preparations of the complexes $[RhX_4L]^{3+}$ (L = 9,10-phenanthrenequinone diimine; X_4 = $(NH_3)_4$, $(en)_2$, tren, 1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetrathiacyclododecane) have been described. The complexes have been characterized by multinuclear NMR spectroscopy crystallographic studies, and by studies of their photochemical reactivities — the crystal structures are of the compounds $[Rh(NH_3)_4L]Cl_3.3H_2O$, $[RhL'L][SCN]_3.2H_2O$ (L′ = 1,4,7,10-tetraazacyclododecane) and $[RhL'L]Br_3.2H_2O$ (L′ = 1,4,7,10-tetrathiacyclododecane). The detailed results go some way towards an understanding of the contributions of hydrogen-bonding and van der Waals interactions to the sequence-specific recognition of DNA [27].

The chloride salt of *trans*-$[RhCl_2L_4]^+$ (L = pyrazole) has been structurally characterized; each pyrazole ligand is bound through the N(2) atom [28]. A related complex is *trans*-$[RhCl_2L_4]^+$ (**10**) in which L is thiazole; the crystal structure of the perchlorate salt with MeCN solvate has been determined and each thiazole ligand is coordinated through the *N*-donor atom [29].



(10)

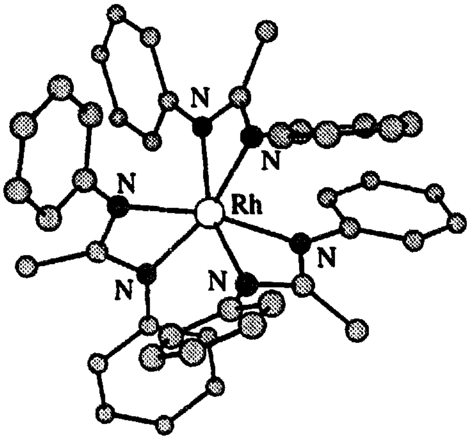
The reaction of $[Cp^*Rh(MeOH)_3][OTf]_2$ with 9-ethylguanine, L, in methanol yields the rhodium(III) complex $[Cp^*RhL(MeOH)_2][OTf]_2$ in which the guanine ligand is coordinated through atom N(7). A related complex containing 9-methylhypoxanthine has also been prepared; the crystal structure of the cation confirms coordination through the N(7)-donor site and also illustrates the presence of significant hydrogen-bonding in the solid state. In solution, there is ^1H NMR spectroscopic evidence for the formation of cyclic trimers — this is pH dependent and the products could not be isolated [30]. In an accompanying paper [31], Smith *et al* show that cyclic timer formation in solutions of $[Cp^*RhL]_3$, in which the ligand is the conjugate base of adenosine 5'-monophosphate (H_2L), is inhibited by the presence of the $P(O)_2{=}O$ group.

Octaethylporpyrinato complexes of rhodium(III) are represented in the 1993 literature by the compounds [Rh(OEP)Cl], $[Rh(OEP)(CO_2Et)]$ and [Rh(OEP)(CHO)] which are formed when the dimer $[Rh_2(OEP)_2]$ reacts with carbon monoxide and ethanol in CH_2Cl_2. Spectroscopic data (^1H and ^{13}C NMR) have been recorded for $[Rh(OEP)(CO_2Et)]$ and [Rh(OEP)(C[illegible])], and $[Rh(OEP)(CO_2Et)]$ has been further characterized by X-ray crystallography. The Rh–C bond is particularly short (1.92Å) and the rhodium atom is drawn slightly out of the plane containing the four nitrogen donor atoms. The solution behaviours of all the complexes, and in addition of [Rh(OEP)H], have been investigated [32]; see also section 3.3. The single crystal structure of the phthalocyaninato complex [RhLMe] (H_2L = octapentylphthalocyanin) has been determined; out-of-plane twisting of just one of the isoindole groups is observed and the cause of the distortion has been attributed to the presence of the pentyl substituents. The rhodium(III) centre is in a square-based pyramidal environment ($Rh{-}C_{Me}$ = 2.031(8)Å, $Rh{-}N_{average}$ = 1.989Å) [33].

The syntheses of mono-, bis- and tris-complexes of rhodium(III) with 2-acetylpyridine hydrazone and 2-benzoylpyridine hydrazone have been reported, in addition to preparations of mono-complexes containing 2-acetylpyridine dimethylhydrazone and 2-benzoylpyridine dimethylhydrazone. The products have been characterized by elemental analysis, conductivity measurements, IR, far-IR, UV-VIS and ^1H NMR spectroscopies. It is proposed that each ligand coordinates through the pyridine *N* and azomethine *N*-donor atoms. Electronic spectroscopic data are consistent with octahedral rhodium(III) centres [34].

The reaction between $RhCl_3.3H_2O$ and PhN=C(Me)NHPh (HL) in boiling ethanol in the presence of Et_3N leads to the formation of the air-stable compound $[RhL_3]$ (**11**), the crystal structure of which has been determined. Under similar conditions, 1,3-diphenyltriazene, HL', reacts with rhodium(III) chloride to yield $[RhL'_3]$, the octahedral nature of which has been crystallographically confirmed; the triazene has a smaller bite-angle than the acetamidinato ligand. Dark red crystals of a second compound were found amongst those grown of $[RhL'_3]$,and these have been shown to be the dimeric compound $[Rh_2L'_4]$. Structural data confirm the presence of four triazene ligands in bridging positions with the Rh–Rh bond distance of 2.377(3)Å and an average Rh–N bond length of 2.050Å [35].

The syntheses and properties of complexes of the type $[Rh(dmgH)_2(4\text{-}R'py)]$ have been described, and for a representative compound with R = R' = ^tBu, the structure of the product (**12**) has been confirmed by X-ray diffraction methods. Photochemical cleavage of the Rh–C bond in these rhodium(III) complexes occurs in the presence of efficient radical traps [36]. With the ultimate aim of labelling monoclonal antibodies with radioisotopes for imaging or therapeutic applications, Efe *et al.* have prepared the complexes [Rh(HL)LCl$_2$] in which HL = (**13**). The products have been characterized by IR and ^{1}H NMR spectroscopies and the crystal structure of [Rh(HL)LCl$_2$] with R = NO$_2$ has been elucidated. The chloro ligands are mutually *trans* and the oxime groups are *cis* to each other. In the IR spectrum, a weak absorption at 1792 cm^{-1} is consistent with the presence of a short O$_{oxime}$–H–O$_{oxime}$ hydrogen bonded interaction [37].



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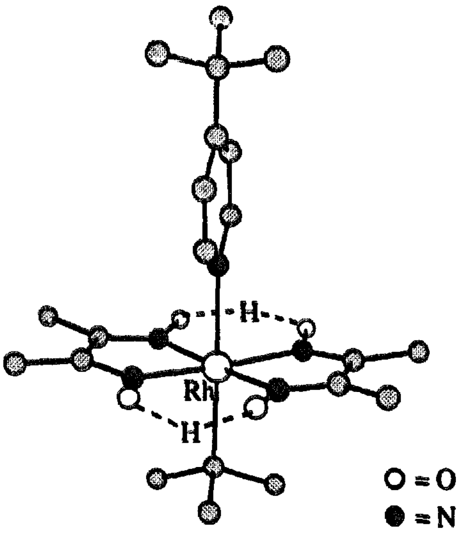

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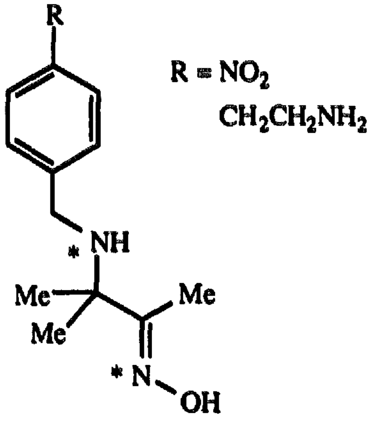


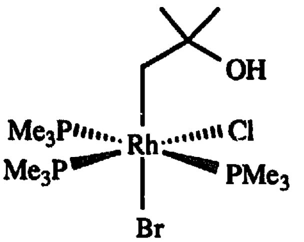
(**13**) * = coordination site

3.2.5 *Complexes with phosphorus donor ligands*

In an investigation of the reactions of tertiary phosphines of phosphino-rhodium complexes with catecholborane (HBcat) Marder and coworkers have included the reactions of the coordinatively saturated complexes [RhH(dppp)$_2$] and [RhH(PMe$_3$)$_4$] with HBcat. The products are [RhH$_2$(dppp)$_2$]$^+$[Bcat]$^-$ and [RhH$_2$(PMe$_3$)$_4$]$^+$[Bcat]$^-$, respectively, both of which are active catalyst precursors for the addition of HBcat to 4-vinylanisole. A crystallographic study of

$[RhH_2(PMe_3)_4][Bcat]$ has established an octahedral environment for the rhodium(III) centre and a *cis*-arrangement of hydride ligands (although these were not directly located) [38].

Although organometallic in nature, the formation and reactivity of $[RhBrCl(PMe_3)_3(CH_2CMe_2OH)]$ is noteworthy because of the end product of the study which features a rhodaoxetane metallacycle. The oxidative addition of the C–Br bond in 2-hydroxy-2-methylpropane to $[Rh(PMe_3)_3Cl]$ gives $[RhBrCl(PMe_3)_3(CH_2CMe_2OH)]$ (**14**) which is deprotonated by $KN(SiMe_3)_2$ to form compound (**15**). Structural data show that the 4-membered metallacycle in (**15**) is planar, and the bonding in this complex has been probed at the extended Hückel level [39].



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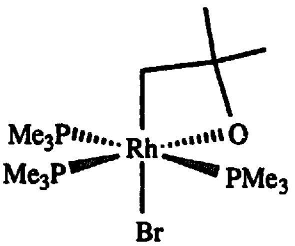
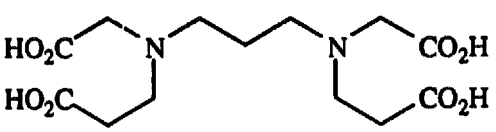


(**15**)

The reaction of $[Cp^*_2Rh_2Cl_4]$ with $Ph_2PCH_2CH_2SiMe_2H$ leads to the formation of the mononuclear complex $[Cp^*RhCl_2(Ph_2PCH_2CH_2SiMe_2H)]$ in which the ligand is coordinated in a monodentate mode through the phosphorus atom; the Si–H bond is sensitive to hydrolysis. Related iridium and ruthenium complexes have also been prepared and IR and ^1H, ^{13}C and ^{31}P NMR spectroscopic data have been reported for the products [40].

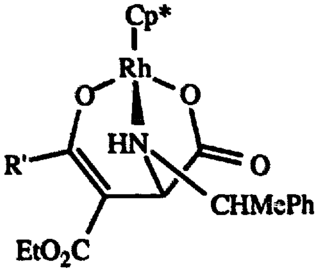
3.2.6 Complexes with mixed donor ligands

The asymmetrical ligand (**16**) coordinates to rhodium(III) in the expected hexadentate *N,N′,O,O′,O″,O‴*-mode and two geometrical isomers have been separated and isolated. Characterization by ^1H and ^{13}C NMR, and UV-VIS spectroscopies show the isomers to have the arrangements *trans*-acetate, *cis*-propanoate and *cis*-acetate, *cis*-propanoate [41].



(**16**)

The complexes $[Cp^*RhCl\{O_2CC(R){=}NCHMePh\}]$ (R = H or Me) have been formed from the respective α-carboxylic acids and optically active 1-phenylethylamine by a template condensation reaction. For R = H, the imino-carbon atom in the rhodium(III) complex is susceptible to nucleophilic attack by $R'C(O)CH_2CO_2Et$ (R′ = Me, Ph) and $H_2NCH(CO_2Et)_2$ to give the products (**17**) and (**18**) respectively. Both compound types have been confirmed by the results of X-ray diffraction studies, and spectroscopic data have been recorded. Borohydride reduction of [Cp*RhCl{$O_2CCH=NCHMePh$}] followed by treatment with HCl yields an *N*-substituted glycine [42].



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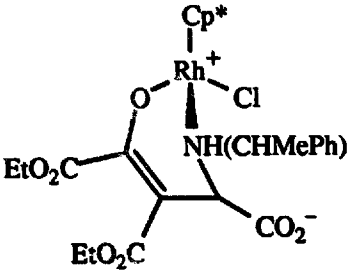
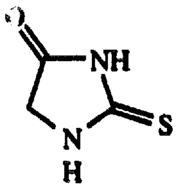


(18)

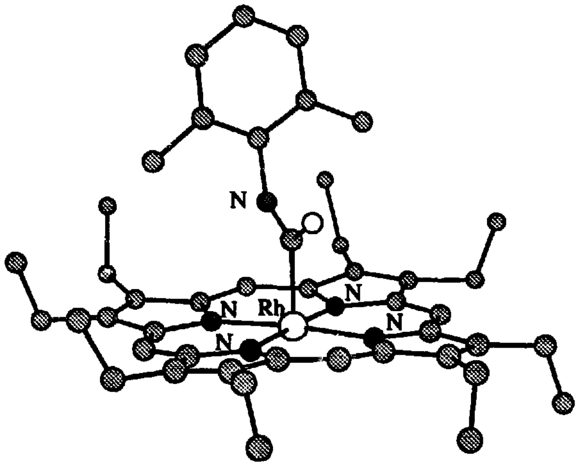
The *O*,*P*-donor ligand (1) complexes with rhodium(I) to yield $[Rh(1)_2]^+$ to which dihydrogen oxidatively adds to give the unstable rhodium(III) dihydride $[RhH_2(1)_2]^+$. The oxidative addition of methyl iodide to $[Rh(1)_2]^+$ has also been investigated, as has the reaction of dioxygen (see section 3.2.2) [8]. A series of complexes of type $[RhL_3]$ in which HL is a derivative of ligand (19) [1-Ph-, 1-naphthyl-, 1-(4-ClC_6H_4) or 1-(2-$MeOC_6H_4$)] has been reported. The compounds have been characterized by elemental analysis, UV-VIS, IR and ^1H NMR spectroscopies, and magnetic susceptibility measurements [43].



(19)

3.3 RHODIUM(II)

Several octaethylporphyrinato complexes of rhodium(III) were described in section 3.2.4, and that work overlaps with further studies that, for convenience, have been detailed under rhodium(II). The reactivity of the $[Rh^{II}(TMP)]^{\bullet}$ radical with carbon monoxide and isocyanides has been compared with those of [Rh(OEP)H] and the dimer $[Rh_2(OEP)_2]$. One product — $[Rh(OEP)C(O)NHC_6H_3Me_2\text{-}2,6]$ (20) — has been crystallographically characterized [44]. The porphyrinato rhodium(II) complexes [Rh(TMP)] and [RhL] (H_2L = tetrakis(2,4,6-triisopropylphenyl)porphyrin) are both low spin d^7 and EPR spectroscopic parameters are consistent with a $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$ ground state. Data on several related 5-coordinate complexes with *N*-, P, or *As*-donor ligands (L) in the apical site again show the presence of a low spin d^7 configuration with the unpaired electron occupying the d_{z^2} metal orbital. The *d* orbital energy separations and ligand spin densities for [Rh(porph)L] are greater than for corresponding cobalt(II) complexes [45].



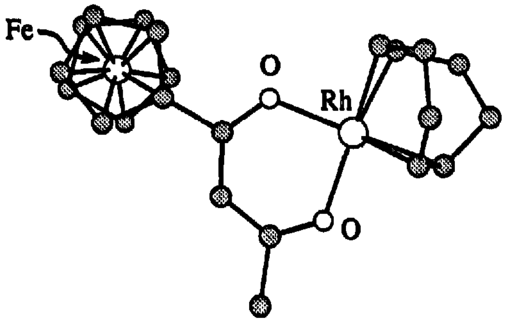
(20)

3.4 RHODIUM(I)

3.4.1 Complexes with oxygen donor ligands

The syntheses, and electrochemical and spectroelectrochemical properties of the oxalate complexes $[Rh(ox)(CO)_2]^-$, $[Rh(ox)(cod)]^-$ and $[Rh_2(ox)(cod)_2]$ have been described. The mononuclear complexes undergo 2-electron oxidations but each is followed by a chemical reaction in which the oxalate ion decomposes to CO_2. The dirhodium complex undergoes an electrochemical oxidation in two 2-electron steps without oxalate decomposition [46].

The crystal structures of several β-diketonate complexes have been determined. In the ferrocenyl-1,3-butanedionato (L^-) complex [Rh(cod)L] (**21**), the β-diketonate is in a chelating mode and the cyclopentadienyl rings are in a conformation that is partway between being staggered and eclipsed [47]. An almost eclipsed conformation is observed in the solid state structure of the (ferrocenylcarbonyl)trifluoroacetonato (L^-) complex $[Rh(CO)(PPh_3)L]$ (**22**) [48]. The $[acac]^-$ ligand in the square-planar complex $[Rh(acac)(\mathbf{23}\text{-}P)_2]$ is also in a chelating mode [49].



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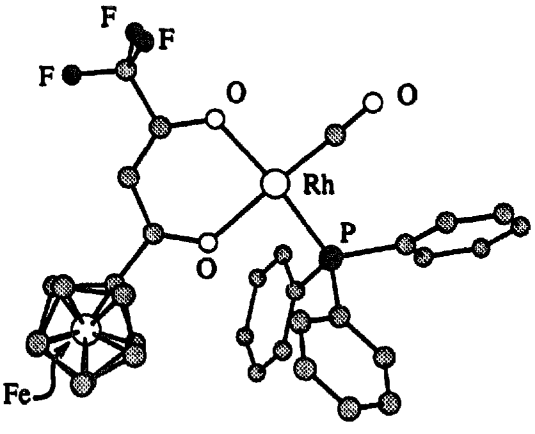

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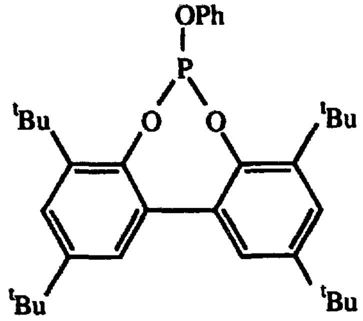
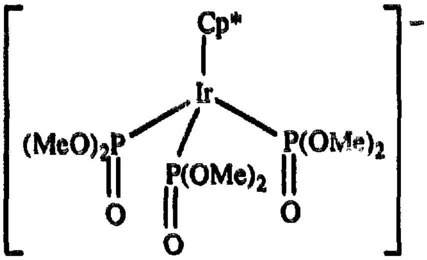


(23)

Infrared and solution ^1H and ^{31}P NMR spectroscopies have been used to elucidate the structure of $[Rh(PPh_3)_3L]$ (HL = anthranilic acid) and that of the dinuclear product formed when $[Rh(PPh_3)_3L]$ reacts with *N*-phenylanthranilic acid, HL'. A square planar geometry incorporating a monodentate carboxylate ligand is proposed for $[Rh(PPh_3)_3L]$. The dirhodium complex is proposed to have the formula $[Rh_2(PPh_3)_2(\mu\text{-}L)(\mu\text{-}L')]$ in which two phosphine ligands are mutually *cis* at each metal centre. Reactions with H_2 give *cis*-dihydrides and variable temperature NMR studies have been used to probe the solution behaviour of these products. Both $[Rh(PPh_3)_3L]$ and $[Rh_2(PPh_3)_2(\mu\text{-}L)(\mu\text{-}L')]$ are catalysts for the hydrogenation of 1-alkenes and cyclohexadiene and for the conversion of pyridine into peperidine [50].

The tripodal *O,O',O''*-ligand (24) reacts with a variety of metal centres including rhodium(I); reaction with $[Rh_2(cod)_2Cl_2]$ leads to the formation of [RhL(cod)], which has been characterized by IR, ^1H and ^{31}P NMR spectroscopies and elemental analysis [51]; the iridium(III) complex (24) is discussed further in the accompanying chapter.



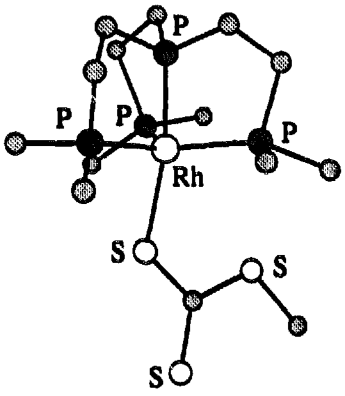
(24)

See section 3.4.3 for mention of the coordination of pyridine *N*-oxide, L, in *cis*-$[Rh(CO)_2(L)X]$ (X = Cl or Br).

3.4.2 Complexes with sulfur or selenium donor ligands

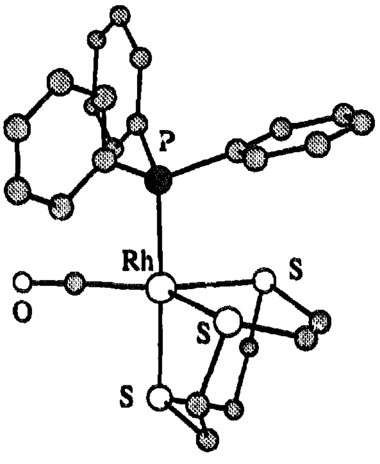
The reaction of NaSPh with $[Rh(PMe_3)_4]Cl$ or $[Rh(PMe_3)_3Cl]$ yields $[Rh(SPh)(PMe_3)_3]$ for which crystallographic data confirm a square-planar geometry. Variable temperature ^1H and ^{31}P NMR spectroscopic results are consistent with intramolecular ligand exchange. The addition of dioxygen to $[Rh(SPh)(PMe_3)_3]$ gives the distorted trigonal bipyramidal rhodium(III) complex

$[Rh(SPh)(O_2)(PMe_3)_3]$ in which the peroxo ligand occupies an equatorial site (O–O = 1.456(6)Å, Rh–O = 2.041(3) and 2.015(4)Å) [9]. The oxidative addition of PhSH to $[Rh(SPh)(PMe_3)_3]$ was described in section 3.2.3. Related to the above preparation of $[Rh(SPh)(PMe_3)_3]$ are the reactions between NaSAr (Ar = 4-MeC_6H_4 or 4-$MeOC_6H_4$) and $[Rh(PMe_3)_4]Cl$ which lead to the rhodium(I) complexes $[Rh(SAr)(PMe_3)_3]$, both of which possess distorted square-planar structures. Further treatment with ArSH results in oxidative addition of the S–H bond and the formation of $[RhH(SAr)_2(PMe_3)_3]$; during the reaction, the conversion of the *cis,mer*- to *trans,mer*-isomer was observed [52]. The trigonal bipyramidal complexes [RhL(EMe)] (L = $N(CH_2CH_2PPh_2)_3$, E = S or Se) have been prepared, and their reactivities with respect to electrophilic attack have been investigated. The sulfur or selenium donor atom in the complex is attacked by Me^+ (from CF_3SO_3Me) or Et^+ (from $[Et_3O][BF_4]$) to yield the cations $[RhL(EMeR)]^+$ (R = Me or Et); treatment with CF_3SO_3H produces the dications $[RhL(H)(EMeR)]^{2+}$ [53]. From the same authors comes a report of the reaction between $[Rh(cod)L]^+$ [L = $P(CH_2CH_2PPh_2)_3$] and NaSMe which leads to the rhodium(I) complex [RhL(SMe)] which has been characterized by ^1H and ^{31}P NMR spectroscopies. Carbon disulfide reacts with [RhL(SMe)] to give the insertion product [RhL{SC(S)SMe}] (25); the structure has been confirmed by the results of an X-ray diffraction study and in solution by ^1H and ^{31}P NMR spectroscopies. Pertinent bond distances in the solid state are Rh–S = 2.409(5)Å, Rh–$P_{trans\text{-}S}$ = 2.206(4)Å, Rh–$P_{cis\text{-}S}$ = 2.339-2.369(5)Å. Methylation of [RhL(SMe)] using CF_3SO_3Me yields $[RhL(SMe_2)][CF_3SO_3]$ [54].



Ipso-C atoms of Ph rings only are shown

(25)



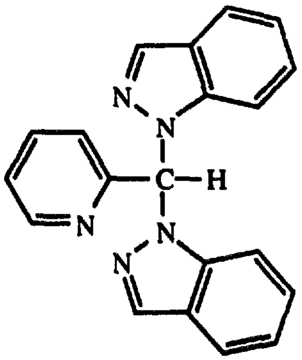
(26)

A further trigonal bipyramidal complex of rhodium(III) is the cation $[Rh(PPh_3)(CO)L]^+$ (L = 1,4,7-triazacyclononane) (26), the crystal structure of which has been reported. The phosphine and one sulfur donor atom occupy the axial sites [55].

3.4.3 Complexes with nitrogen donor ligands

The crystal structure of the square-planar rhodium(I) complex $[Rh(CO)(NCS\text{-}N)(PEt_3)_2]$ has been determined; the phosphine ligands are mutually *trans* [56]. Infrared spectra of the square-planar complexes *cis*-$[Rh(CO)_2(py)X]$ (X = Cl or Br) have been analysed, and incorporated into the study are isotopic labelling experiments and a normal coordinate analysis [57]. The work is extended to cover NMR spectroscopic exchange processes involving the related rhodium(I) complexes *cis*-$[Rh(CO)_2(L)X]$ (L = pyridine *N*-oxide, X = Cl or Br) [58]. The ^{15}N-labelled pyridine derivative (8) has been incorporated into the rhodium(I) complexes *cis*-$[RhX(PPh_3)_2(8)]$ (X = Cl, SC_6F_5) and $[RhCl(PPh_3)L(8)]$ (L = C_2H_4 or CO) as well as in related rhodium(III) species (see section 3.2.4). Multinuclear NMR spectroscopic studies included ^{15}N-observed with a shift range of δ −110.6 to −128.9 (with respect to $MeNO_2$) for the complexes studied [19].

The synthesis and characterization of ligand (27) and its reaction with $[Rh_2(nbd)_2Cl_2]$ in methanol in the presence of KPF_6 have been reported. The complex product is $[Rh(27\text{-}N,N',N'')(nbd)][PF_6]$ — IR, ^1H and ^{13}C NMR spectroscopic are consistent with, and single crystal structural data confirm, a distorted trigonal bipyramidal geometry with the pyridine-*N* atom occupying an axial site with the two pyrrole-*N* atoms equatorially sited. The coordinated ligand is described by the authors as adopting a helical conformation [60].



(27)

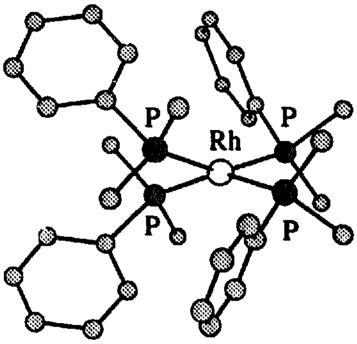
The dimers $[Rh_2(cod)_2Cl_2]$, $[Rh_2(nbd)_2Cl_2]$ and $[Rh_2(CO)_4Cl_2]$ react with α-diimines (L) $RN{=}C(Me)C(Me){=}NR'$ (R = R' = NH_2, NMe_2 or Ph; R = NH_2, R' = OH) or with 2,2'-biquinoline in the presence of tin(II) chloride to yield complexes such as $[Rh(SnCl_3)(cod)L]$ and $[Rh(SnCl_3)(nbd)L]$. Intramolecular rearrangements in solution have been observed using ^1H and ^{119}Sn NMR spectroscopies. In the absence of $SnCl_2$, the reactions proceed to give the fluxional complexes $[RhClL'_2L]$ (L'_2= cod, nbd or $(CO)_2$) or the salts $[RhL'_2L]^+[RhL'_2Cl_2]^-$ [61].

A further rhodium(I) complex containing an *N*-donor atom ligand is [Rh(cod)ClL] where L is 1,5-diazabicyclo[4.3.0]non-5-ene; the compound has been prepared and structurally characterized as part of an investigation of species with *P,N*-donor ligands [77] (see section 3.4.5).

3.4.4 Complexes with phosphorus donor ligands

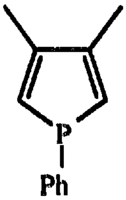
Numerous rhodium(I) complexes which incorporate phosphine ligands [9, 19, 48-50, 52-56] have already been mentioned in earlier parts of section 3.4 and these are not repeated below.

The crystal structure of $[Rh(PMe_2Ph)_4]Cl$ has been determined; the environment about the rhodium(I) centre in the cation **(28)** is in between square-planar and tetrahedral [62]. The results of a detailed vibrational spectroscopic study of $[Rh(PPh_3)_3Cl]$ have been analysed [63]. The conversion of *trans*-$[RhCl(CO)(PPh_3)_2]$ to $[Rh(PPh_3)_3Cl]$ can be accomplished in high yield by using diphenylphosphoryl azide as a CO ligand abstracting agent; the interest in this research is in achieving methods of recycling rhodium [64].



(28)

Complexes of the general formula *trans*-$[RhCl(CO)L_2]$ in which L is PPh_3 or the ligands **(29)** to **(31)** have been prepared and characterized by IR, solution ^1H, ^{13}C and ^{31}P NMR and solid state CP/MAS NMR spectroscopies and conductivity measurements. The data are consistent with the complexes involving ligands **(29)** to **(31)** being square-planar [65].



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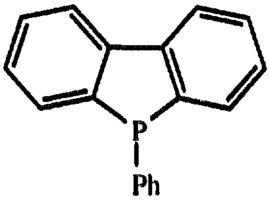

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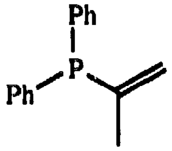

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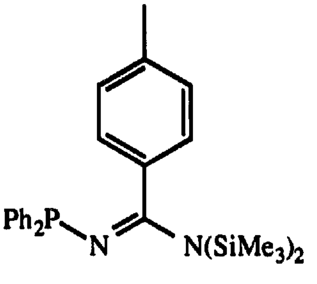

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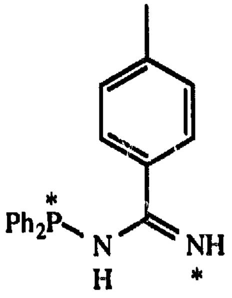


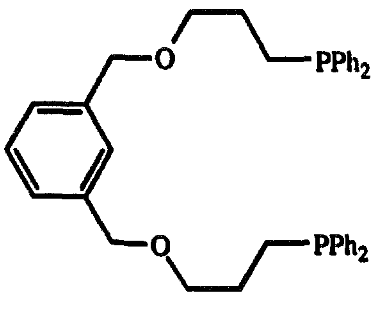
* = coordination site

(33)

Treating the dimer $[Rh_2(cod)_2Cl_2]$ with two equivalents of ligand **(32)** in thf leads to the formation of [Rh(cod)(**32**)Cl] for which ^1H and ^{31}P NMR spectroscopic data are consistent with a *P*-bonded ligand. If the reaction is carried out in acetone in the presence of sodium tetrafluoroborate, the product is [Rh(cod)(33)][BF_4]. This rhodium(I) compound has been fully characterized and an X-ray diffraction study confirms that the ligand is *P*,*N*-bonded, forming a 5-membered chelate ring [66].

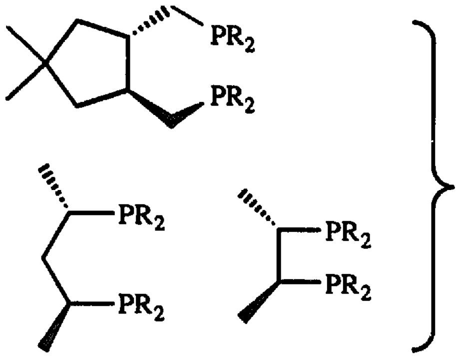
Rhodium(I) complexes containing the ligands $ROP{=}N(C_6H_2\text{-}2,4,6\text{-}^tBu_3)$ (R = Me, 2-MeC_6H_4), L, have been prepared from [$RhCl(PPh_3)_3$] and are of the types [$RhCl(PPh_3)L_2$] for R = Me, or [$RhCl(PPh_3)_2L$] for R = 2-MeC_6H_4. It was noted that when the ligand is XP=NAr where X = Cl, Br or I, reaction with [$RhCl(PPh_3)_3$] leads to oxidative addition of the P–X bond rather than phosphine exchange [67]. Ligands of the form $[R_2PCH_2CR'_2O]^-$ are of interest because they contain both hard and soft donor centres. When [$Rh_2(CO)_4Cl_2$] reacts with $R_2PCH_2C^tBu_2OH$ (where R = Me or Ph), the square-planar complexes *trans*-[$Rh(CO)Cl\{R_2PCH_2C^tBu_2O\}_2$] are formed. For R = Me, crystallographic data illustrate that the ligand is coordinated in a monodentate manner through the phosphorus atom but that there are significant Rh····HO and Cl····HO close contacts in the solid state. The results of solution studies of [$Rh(CO)Cl\{Ph_2PCH_2C^tBu_2O\}_2$] indicate that the Rh····HO interactions are retained, but this is not the case for [$Rh(CO)Cl\{Me_2PCH_2C^tBu_2O\}_2$]; for [$Rh(CO)Cl\{Ph_2PCH_2C^tBu_2O\}_2$], the resonance due to the OH proton in the ^1H NMR spectrum is a doublet with $J(^1H—^{103}Rh)$ 2.7 Hz [68].

Work with didentate bis(phosphine) ligands has included the use of (±)-*trans*-1,2-bis(diphenylphosphine)cyclopentane, L. This ligand reacts with [$Rh_2(OAc)_2(NCMe)_6$][BF_4]$_2$ to give the square-planar mononuclear complex [RhL_2][BF_4] for which a crystal structure determination has been carried out [69]. Ligand (34) has been used to assemble a heterometallic complex in which the bis(oxygen) and bis(phosphine) domains recognize zinc(II) and rhodium(I) centres respectively. The ligand reacts with an excess of $Zn(O_3SCF_3)_2$ to give [$Zn(34)(O_3SCF_3)_2$] in high yield; when treated with [$^nBu_4N$][$RhCl_2(CO)_2$], this complex reacts to produce [Cl(34)Zn(μ-Cl)Rh(CO)] in which the rhodium(I) centre is in a square-planar environment, coordinated by the two PPh_2-groups of (34), the bridging chloride and the CO ligand; the phosphine donors are mutually *trans*. A crystallographic study confirms that the two metal centres are not within bonding distance — the compound is an active hydroformylation catalyst [70].



(34)

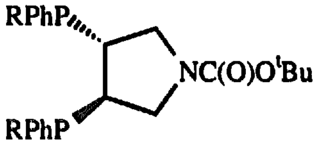
The results of ^1H, ^{13}C, ^{31}P NMR spectroscopic investigations of a series of salts of $[Rh(cod)L]^+$ or $[Rh(nbd)L]^+$, in which L is one of the didentate chiral ligands (35), have been described. The solution data are consistent with each complex possessing C_2 symmetry [71]. The synthesis of a diastereomeric mixture of ligand (36) for R = 2-$MeOC_6H_4$ has been followed by successful chromatographic separation and purification of the diastereomers. The compound $[Rh(cod)_2][BF_4]$ reacts with the bis(phosphine) (36) to yield complexes of the type $[Rh(cod)L]^+$ which are catalysts in enantioselective hydrogenation reactions; further catalytic studies involving rhodium(I) complexes with both the ligands (36) have been described [72, 73]. The synthesis of a tetrasulfonated derivative of BINAP and the complexation of this ligand with rhodium(I) have resulted in the isolation of the compound $[Rh\{(R)\text{-BINAP}(SO_3Na)_4\}(cod)][ClO_4]$. In water, this catalyses asymmetric hydrogenation reactions and the active species is proposed to be $[Rh\{(R)\text{-BINAP}(SO_3Na)_4\}(H_2O)_2]^+$ [74].



R = 4-C_6H_4-X

X = NMe_2, $NMe_3{}^+BF_4{}^-$, $NMe_2H^+BF_4$

(35)

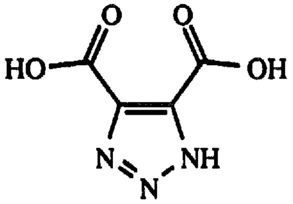


R = Ph, 2-$MeOC_6H_4$

(36)

3.4.5 Complexes with mixed donor ligands

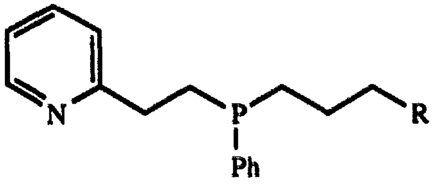
New complexes of rhodium(I) of the form $[(OC)_2Rh(\mu\text{-}L)Rh(CO)_2]^-$ or $[(OC)(PPh_3)Rh(\mu\text{-}L)Rh(PPh_3)(CO)]^-$ where H_3L is (37) have been prepared and characterized. Crystallographic data confirm that in both anions, the rhodium(I) centres are well separated and each is in a square-planar environment; ligand L^{3-} is tetradentate, and behaves as an *N*,*O*-donor to each rhodium atom. Related diiridium complexes are described in the accompanying review article [75].



(37)

Treating the dimer [$Rh_2(cod)_2Cl_2$] with two equivalents of ligand (32) in acetone in the presence of $NaBF_4$ yields the complex [Rh(cod)(33)][BF_4]; compare this to the retention of (32) when the reaction is performed in thf (see section 3.4.4). The compound [Rh(cod)(33)][BF_4] has been fully characterized (multinuclear NMR spectroscopies and crystallographic data) and the ligand is established to be bound as a *P,N*-chelate [66]. The trimethyl substituted compound $Me_3SiN{=}PPh_2CH_2PPh_2$ is a precursor to the new ligands $RN{=}PPh_2CH_2PPh_2$ (R = 4-(CN)C_6F_4, 2,4-$(CN)_2C_6F_3$, 3,4-$(CN)_2C_6F_3$, 5-F-2,4-$(NO_2)_2C_6H_2$, 2,4-$(NO_2)_2C_6H_3$). The reactions of these compounds with [$Rh_2(CO)_4Cl_2$] produces the square-planar chelate complexes [RhCl(CO){$RN{=}PPh_2CH_2PPh_2$}]. The *cis*-arrangement of the chloro and carbonyl ligands has been confirmed in the single crystal structure of [RhCl(CO){(4-(CN)C_6F_4)$N{=}PPh_2CH_2PPh_2$}] [76].

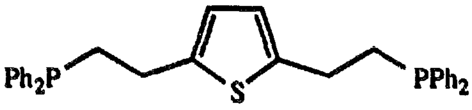
The ligands L (38) react with [$Rh_2(cod)_2Cl_2$] in the presence of $TlPF_6$ at 273 K to yield [Rh(cod)L][PF_6] in which (38) functions as a *P,N*-chelate, leaving the donor atom of the R group uncoordinated. Square-planar geometries are proposed for the complexes. At 298 K, the products polymerized phenylacetylene and polymeric materials have been isolated. In this same work, the synthesis and crystal structure of [Rh(cod)ClL'] where L' is 1,5-diazabicyclo[4.3.0]non-5-ene have also been reported [77].



R = OEt, OPh, NHPh, NHCy

(38)

Ligands capable of acting as *P,S*-donors include (39) which has been prepared from thiophene; potentially this is tridentate but in its reaction with [Rh(cod)(acac)] in the presence of $HClO_4$, (39) forms the complex [Rh(cod)(39)][ClO_4] and in the cation, it bonds through one phosphorus and one sulfur atom. Treatment of [Rh(cod)(39)][ClO_4] with CO produces an equilibrium mixture of [$Rh(CO)_2$(39)][ClO_4] and [Rh(CO)(39)][ClO_4]. The position of the equilibrium depends upon the partial pressure of carbon monoxide and the system represents a change from a 16- to 18-electron complex. In each cation, ligand (39) behaves as a *P,P',S*-donor and the crystal structure of [Rh(CO)(39)][ClO_4] shows that in the complex cation, the CO ligand lies *trans* to the sulfur atom of the thiophene ring. Both species have been investigated in solution by ^{31}P, ^{13} and ^{1}H NMR and IR spectroscopies; a value of $J(^{103}Rh\text{-}^{31}P)$ of 90.3 Hz has been recorded [78].



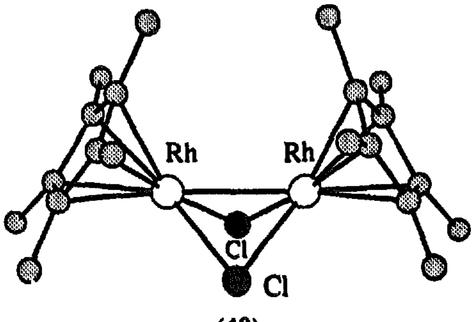
(39)

The reactions of $Ph_2PCH_2P(=Y)R_2$, HL, (E = S, Se; R = Ph, ^tBu) with the dirhodium complex $[Rh_2(cod)_2Cl_2]$ lead to the formation of the cations $[Rh(cod)(HL)]^+$ (isolated as the perchlorate or hexafluorophosphate salts). After deprotonation with NaH, the neutral compounds [Rh(cod)L] are generated. For E = S, an alternative preparative route may be used. The cation $[Rh(cod)(HL)]^+$ with E = S and R = ^tBu, reacts with two equivalents of CO or ^tBuNC, or one equivalent of dppm with displacement of cod. The single crystal structures of $[Rh(cod)(HL)][ClO_4].CH_2Cl_2$ (for E = S and R = Ph or ^tBu) have been determined [78a]. Work from the same group focuses on the preparation and complexation of the anion $[Ph_2PC\{P(S)Ph_2\}_2]^-$; it reacts with $[Rh_2(cod)_2Cl_2]$ to produce $[Rh(cod)\{Ph_2PC\{P(S)Ph_2\}_2\}]$, the solid state structure of which has been determined. This complex reacts with ^tBuNC and I_2 or $PhCH_2Br$; products including $[RhI_2(^tBuNC)_2\{Ph_2PC\{P(S)Ph_2\}_2\}]$ have been isolated and characterized [79]. Related to these results are the independent studies of Contreras *et al.* who have prepared and characterized the compounds $[RhL_2\{H_2C\{P(E)Ph_2\}\}][BF_4]$ (E = S or Se; for example, L_2 = (CO)(PPh_3), $(CO)_2$, cod). Butyl lithium and sodium hydride react deprotonate the coordinated $H_2C\{P(E)Ph_2\}$ ligand giving neutral complexes [80].

3.5 DI- AND POLYNUCLEAR RHODIUM COMPLEXES

3.5.1 Complexes with halide bridges

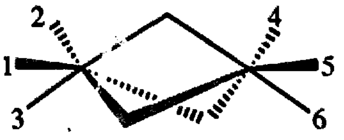
Reduction of $[Cp^*{}_2Rh_2Cl_2(\mu\text{-}Cl)_2]$ by sodium/mercury amalgam gives the deep blue dimer $[Cp^*{}_2Rh_2(\mu\text{-}Cl)_2]$ (40), and the bridging nature of the chloride ligands has been confirmed crystallographically — the Rh–Rh bond distance is 2.617(1)Å in one of two independent molecules. At low temperature, compound (40) reacts with O_2 to produce the unstable adduct $[Cp^*{}_2Rh_2(\mu\text{-}Cl)Cl(\mu,\eta^1{:}\mu^2\text{-}O_2)]$ which is fluxional in solution. The reaction of this compound with PPh_3 yields the mononuclear complex $[Cp^*Rh(O_2)(PPh_3)]$, or with an excess of PMe_3, $[(\eta^4\text{-}C_5Me_4CH_2)Rh(PMe_3)_3]Cl$ is formed; the results of an X-ray diffraction study have confirmed the presence of a fulvene ligand in the latter complex. The reaction of compound (40) with PhNO has also been investigated [81].



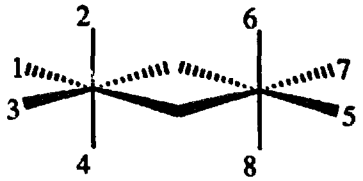
(40)

Cotton *et al.* have reported the preparations and structural characterizations of new chloro and bromo-bridged dirhodium complexes — $[1,5,6\text{-}Rh_2Cl_6(PEt_3)_3]$, $[1,3,6,8\text{-}Rh_2Cl_6(PEt_3)_4]$, $[1,5,6\text{-}Rh_2Cl_6(P^nPr_3)_3]$, $[1,5,6\text{-}Rh_2Br_6(PEt_3)_3]$, $[1,5,6\text{-}Rh_2Br_6(P^nPr_3)_3]$, $[1,5,6\text{-}Rh_2Br_6(P^nBu_3)_3]$

and [1,3,6,8-$Rh_2Br_6(P^nBu_3)_4$] with the numbering schemes in structures (**41**) and (**42**) for 9 or 10 ligands respectively. There is a marked *trans*-effect resulting in significant elongation of the Rh–X_{bridge} bond distances [82]. Further studies have concentrated on the reactions of the anions $[Rh_2X_7(PEt_3)_2]^-$ (X = Cl, Br) (which possess face-sharing bioctahedral structures) with PMe_3, PEt_3 or PMe_2Ph. The addition of one equivalent of phosphine proceeds stereospecifically to generate [1,6,8-$Rh_2X_7(PR_3)_3]^-$. When an equivalent of PEt_3 is added to [1,5-$Rh_2Br_7(PEt_3)_2]^-$, the reaction mixture reaches an equilibrium containing the complexes [1,5-$Rh_2Br_7(PEt_3)_2]^-$, [1,6,8-$Rh_2Br_7(PEt_3)_3]^-$, [1,2,6-$Rh_2Br_6(PEt_3)_3$] and *trans*-$[RhBr_4(PEt_3)_2]^-$. The reactions have been monitored by use of $^{31}P\{^1H\}$ NMR spectroscopy and structural data have been presented for four of the complexes [83].



(**41**)



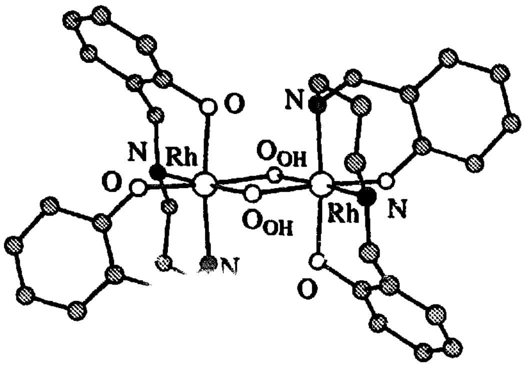
(**42**)

The synthesis of $[Rh_2L_2(\mu\text{-}Cl)_2]$ [L = $(C_5F_5)_2PCH_2CH_2P(C_6F_5)_2$] from $[Rh_2(cod)_2Cl_2]$ has been described. In the product, each rhodium centre is square-planar, coordinated by a chelating bis(phosphine) ligand and two bridging chlorides. The compound $[Rh_2L_2(\mu\text{-}Cl)_2]$ exhibits a high thermal stability, and does not undergo oxidative addition with H_2, O_2 or RX (X = halogen). Related iridium chemistry has also been reported [84, 85].

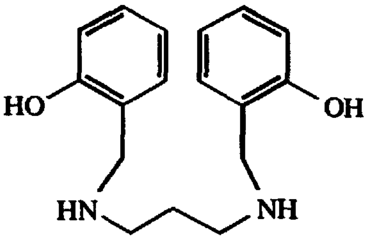
3.5.2 Complexes with hydroxy and dioxygen bridges

The crystal structure of the hydroxy-bridged complex $[Rh_2L_2(\mu\text{-}OH)_2]$ (**43**) in which H_2L = (**44**) has been determined; each rhodium centre is octahedrally sited [86]. The reaction of $[\{Cp^*Rh(H_2O)(OTf)_2\}_n]$ with the nucleobase 1-methylcytosine (L) is solvent dependent. In acetone, the product is mononuclear but on recrystallization from water at pH 5.1, the isolated product has been shown to be *trans*-$[Cp^*_2Rh_2(\eta^1\text{-}N(3)\text{-}L)_2(\mu\text{-}OH)_2](OTf)_2$. Both products have been characterized by ^1H NMR spectroscopy, mass spectrometry and X-ray crystallography. In the solid state, extensive hydrogen bonding between the bridging OH and exocyclic amine groups is present in the structure of *trans*-$[Cp^*_2Rh_2(\eta^1\text{-}N(3)\text{-}L)_2(\mu\text{-}OH)_2](OTf)_2$ [87].

Substitution reactions involving the complex cation $[Rh_2(O_2)(OH)_2(H_2O)_n]^{3+}$ have been carried out at room temperature using chloride and bromide ion. Products have been characterized by ESR, Raman and UV-VIS spectroscopies [88]. The results of ESR spectroscopic studies on the complex *trans*-$[Cl(py)_4Rh(\mu\text{-}O_2)Rh(py)_4Cl]^{3+}$ both as a pure salt and when magnetically diluted in diamagnetic *trans*-$[Rh(py)_4Cl_2]Cl.5H_2O$ have confirmed that a superoxide bridge is present [89].

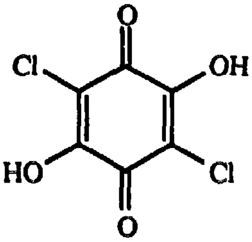


(43)



(44)

Chloranilic acid (45) and 2,5-dihydroxy-1,4-benzoquinone (H_2L) react with [$Rh_2(\mu$-$OMe)_2L'_2$] (*e.g.* L' = cod, nbd) to give the complexes [$Rh_2L'_2(\mu$-L)] and for the chloranilate complex, crystallographic data confirm that the ligand is planar in the quinone-form; structure (46) shows the structure of [$Rh_2(cod)_2(\mu$-L)] for H_2L = (45). The reaction between [Rh(cod)(acac)] and (45) yields the tetranuclear compound [$Rh_4(cod)_4(\mu$-L$)_2$] — here, each chloranilate dianion is non-planar and interacts with three metal centres. The results of electrochemical investigations complement the structural data [90].



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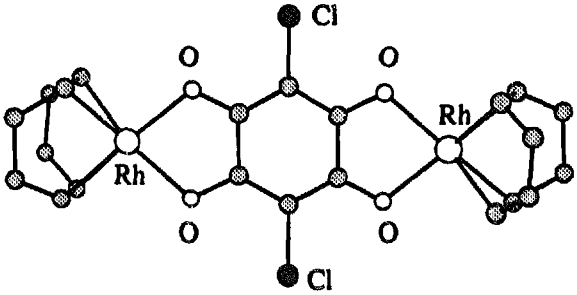
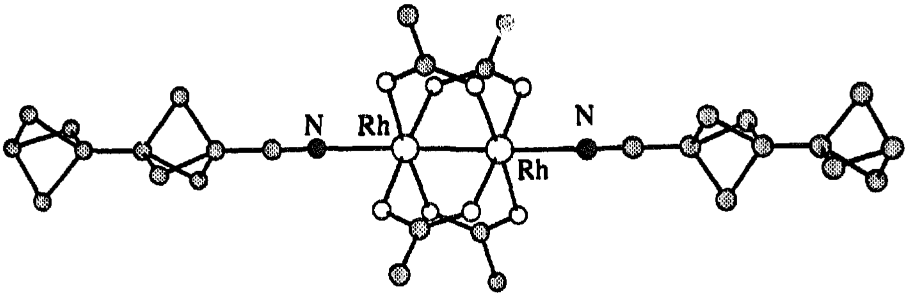


(46)

3.5.3 Complexes with carboxylate bridges

Several crystallographic studies have dealt with derivatives of [$Rh_2(\mu$-$OAc)_4$] with axial ligands and these include [$Rh_2(\mu$-$OAc)_4L_2$] in which L is [2]staffane-3-carbonitrile-*N*, complex (47) [91], L is 2-(pyrrol-1-yl)pyrazine [92], and L is MeOH [93].

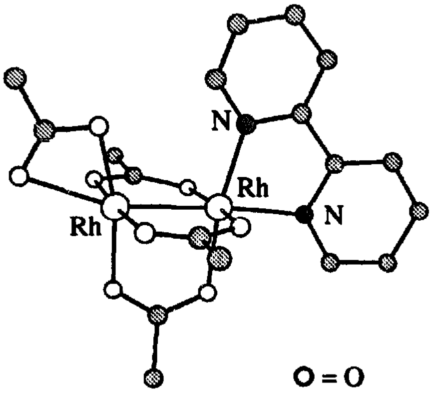


(47)

After recrystallization from tcne/benzene, the product of the reaction of $[Rh_2(\mu\text{-}O_2CCF_3)_4]$ with tcne in CH_2Cl_2 has been isolated as the novel compound $[\{Rh_2(\mu\text{-}O_2CCF_3)_4\}_2.tcne].2C_6H_6$ in which the four *N*-donor atoms of the tcne ligand coordinate in axial sites of the dirhodium units. The overall effect is that the ligand adopts a μ_4,η^4-mode and the solid state lattice of the complex consists of a beautiful infinite sheet structure. The Rh-N bond distances lie in the range 2.16 to 2.19(1)Å [94]. Two related papers report syntheses and spectroscopic studies of the complexes $[Rh_2(\mu\text{-}O_2CR)_4L_2]$ (R = Me, Et, Pr, CF_3, PhCH=CH, and $PhCH_2CH_2$; L = sulfadiazine); ligand L coordinates through the pyrimidine-*N* atom except when R = CF_3 when it bonds through the aniline-*N* atom [95, 96]. Treatment of $[Rh_2(\mu\text{-}O_2CCF_3)_4]$ with PPh_3 leads to $[Rh_2(\mu\text{-}O_2CCF_3)_4(PPh_3)_2]$ which, at room temperature and in solution, undergoes slow orthometallation of two phenyl groups to yield $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}C_6H_4PPh_2\}_2]$. Phosphorus-31 NMR spectroscopic data have been recorded. (Further complexes of this type are described in section 3.5.8). In the same paper, Lahuerta *et al.* have reported the reaction of $[Rh_2(\mu\text{-}O_2CCF_3)_4]$ with an excess of pyridine. The heterocycle coordinates in both axial sites as well as in two equatorial sites, the latter being at the expense of two bridging carboxylate ligands which become monodentate [97]. Further work from this group has focused on the syntheses and characterization of the dimers $[Rh_2(\mu\text{-}O_2CCR_3)_2(CO)_2(PCy_3)_2]$ and $[Rh_2(\mu\text{-}O_2CCR_3)_2(CO)_3(PCy_3)]$ (R = H, F); the compounds have been prepared by the displacement of rhodium-bound cod by CO and then phosphine. The additions of the alkyne $MeO_2CC{\equiv}CCO_2Me$ across the metal-metal bond in these complexes have also been studied, as has the reaction of $[Rh_2(\mu\text{-}OAc)_2(CO)_2(PCy_3)_2]$ with pyrazole (HL) to give $[Rh_2(\mu\text{-}OAc)(\mu\text{-}L)(CO)_2(PCy_3)_2]$. Interestingly, an attempt to perform the analogous reaction between pyrazole and $[Rh_2(\mu\text{-}O_2CCF_3)_2(CO)_2(PCy_3)_2]$ was unsuccessful [98].

2,2'-Bipyridine reacts with $[Rh_2(\mu\text{-}OAc)_4(MeOH)_2]$ in acetone with the formation of $[Rh_2(\mu\text{-}OAc)_3(OAc)(bpy)]$ (**48**) in high yield. The solid state structure of this dinuclear complex has been confirmed by a crystallographic study, and the Rh–Rh bond distance is 2.475(2)Å. With MeOH, ligand displacement in complex (**48**) results in the formation of $[Rh_2(\mu\text{-}OAc)_3(MeOH)(bpy)][OAc].2MeOH$ which has been characterized by ^1H NMR spectroscopy and conductance measurements. Treatment of $[Rh_2(\mu\text{-}OCCF_3)_4(Me_2CO)_2]$ with 2,2'-bipyridine and recrystallization of the product from thf/water yields crystals of the compound $[Rh_2(OCCF_3)_4(bpy)(thf)(H_2O)].thf$. A single crystal X-ray diffraction study shows that two carboxylate ligands bridge the dimetal unit whilst two are monodentate, both associated with the same rhodium centre. In another reaction in this work, bpy and $[Rh_2(OAc)_2(MeCN)_6]^{2+}$ combine to give $[Rh_2(\mu\text{-}OAc)_2(bpy)(MeCN)_4]^{2+}$ (**49**) isolated as the tetrafluoroborate salt [99].

The dimer $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ reacts with adenosine, but not with guanosine, cytidine or uridine, and solution NMR spectroscopic investigations have been carried out to attempt to understand this specificity. The experimental work has been complemented by theoretical studies aimed to probe the role of π-bonding [100]. With adenine and N^6,N^6-dimethyladenine, $[Rh_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}L)_2(H_2O)_2]$ (L^- = *N,N'*-di-4-tolylformamidinate) reacts to give adducts in which the adenine ligands are bound to the rhodium centres through the N(3) atoms. When sites N(3) and N(9) are blocked, and the ligand is adenosine (HL'), the complex that forms incorporates the adenosine ligand in a didentate mode, coordinated through the N(1) and deprotonated amino-N atoms. The reactions of $[Rh_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}L)_2(H_2O)_2]$ (L^- = *N,N'*-di-4-tolylformamidinate) with cytosine, 1-methylcytosine and cytidine result in one-electron oxidations and the formation of paramagnetic compounds [101].



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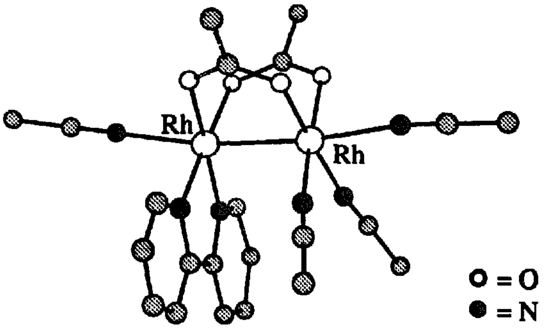
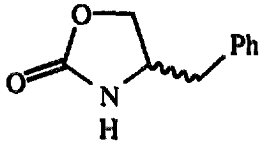


(49)

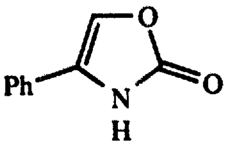
Chiral heterocyclic ligands which include (50) react with $[Rh_2(\mu\text{-}OAc)_4]$ by displacement of all four carboxylate ligands. The new complexes have been characterized in solution by ^1H NMR spectroscopies and by representative solid state structure determinations. The interest in the structural data arises from efforts to understand the relative effectiveness of such complexes as catalysts for the enantiocontrol of metal-carbene transformations; the results of catalytic studies have also been reported [102].



(*R*)- or (*S*)-(50)

3.5.4 Complexes with bridging ligands containing N,O-donors

The formation of the dimer $[Rh_2L_4]^+$ in which HL is 2-hydroxy-6-methylpyridine has been described. The analogous neutral complex was previously known and it undergoes an electrochemical one-electron reversible oxidation ($E_{1/2}$ +0.48 V vs. Fc/Fc^+) — chemical oxidation to the radical cation can be achieved by using tris(4-bromophenyl)aminium hexachloroantimonate. The results of a crystallographic study of $[Rh_2L_4][SbCl_6].2CH_2ClCH_2Cl$ reveal that the *N*-donor atoms are mutually *trans*, and there is a *cis*-arrangement of *N*- and *O*-donor atoms; the Rh–Rh bond distance is 2.3591(7)Å. Further data on the cation include EPR spectra and an analysis of the electronic structure [103]. The conjugate base L^- of the ligand (4*S*)-(51) has been incorporated into the dirhodium complex $[Rh_2(\mu\text{-}L)_4]$. Solution ^1H and ^{13}C NMR spectra are consistent with a *cis*-arrangement of *N*-donor atoms at each metal centre and this has been confirmed in the solid state by crystallographic data for the adduct $[Rh_2L_4(MeCN)_2].2MeCN$. The complex has been used in studies of enantioselective carbene transformations [104].



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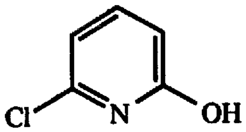
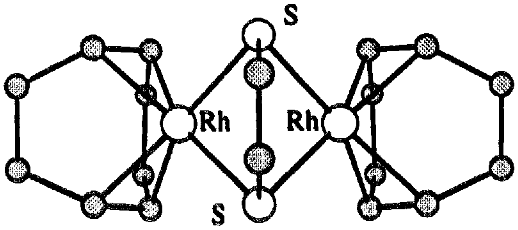


(52)

The reaction between the substituted pyridine (52), HL, and the dimer [$Rh_2(\mu$-$OAc)_2(NCMe)_6][BF_4]_2$ leads to the formation of [$Rh_2(\mu$-OAc)(μ-L)$_2$(NCMe)$_3$], characterized by UV-VIS spectroscopy and an X-ray diffraction study — one axial site is occupied by an acetonitrile ligand [69].

3.5.5 Complexes with sulfur-containing bridging ligands

The single crystal structures of the thiolate bridged complexes [$Rh_2(CO)_4(\mu$-$SR)_2$] (R = Et or Ph) have been determined [105]. The dithiols $HS(CH_2)_nSH$ (n = 2-4) react with [$Rh_2(cod)_2(\mu$-$OMe)_2$] to yield the dirhodium compounds [{$Rh_2(cod)_2(\mu$-$S(CH_2)_nS)$}$_x$] (x = 1 or 2). Confirmation of the bridged structure comes from crystallographic studies of [$Rh_2(cod)_2(\mu$-$S(CH_2)_2S)$] (53) and [$Rh_2(cod)_2(\mu$-$S(CH_2)_3S)$]. Despite the structures indicating a formal Rh–Rh zero bond order, the results of molecular orbital calculations suggest a degree of direct metal-metal bonding character [106].



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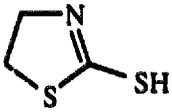
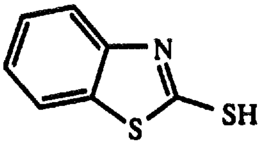


(54)



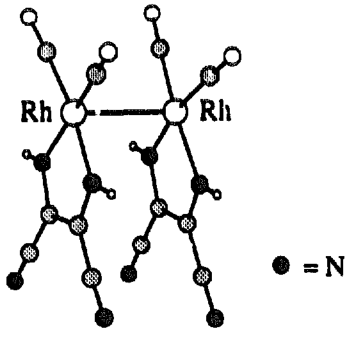
(55)

The thiazole derivatives L⁻, where HL is (54), bridge the dirhodium framework in the compounds [$Rh_2(CO)_2(\mu$-$L)_2(\mu$-dppm)] and [$Rh_2(CO)_2(\mu$-$L)_2(\mu$-dppe)], and addition of dppm to [$Rh_2(CO)_2(\mu$-$L)_2(\mu$-dppm)] leads to a change in the bonding mode of one L⁻ ligand. The solution properties of these and related iridium complexes have been detailed. Diiodine adds to the dimetal unit and the crystal structure of [[$Rh_2I_2(CO)_2(\mu$-$L)_2(\mu$-dppe)] confirms an *N*,*S*-bridging mode for the heterocycles with a head-to-tail arrangement of ligands [107]. In independent work, complex formation involving the conjugate base of the related ligand (55), HL, has included the preparation and characterization of [$Rh_2(\mu$-$L)_2(CO)_3(PPh_3)$] — the phosphine ligand lies *trans* to the sulfur-donor atom. In solution, $[Rh_2(\mu\text{-}L)_2(CO)_3(PPh_3)]$ is in dynamic equilibrium with $[Rh_2(\mu\text{-}L)_2(CO)_4]$ and $[Rh_2(\mu\text{-}L)_2(CO)_2(PPh_3)_2]$. Treatment of $[Rh_2(\mu\text{-}L)_2(CO)_2(PPh_3)_2]$ with triphenylphosphine leads to cleavage of the dirhodium framework and the formation of $[RhL(CO)(PPh_3)_2]$ in high yield [108].

3.5.6 *Complexes with nitrogen-containing ligands*

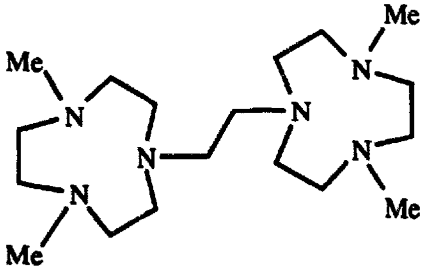
A number of dirhodium complexes involving nitrogen-donor ligands which are *not* in bridging modes were reported in 1993. In work that aims to show the potential of combining polyoxoanions and dinuclear complexes with possible implications for a new area of solid state chemistry, Dunbar *et al.* have prepared and characterized a number of novel systems including $[Rh_2(NCMe)_{10}][Mo_6O_{19}]_2$, $[Rh_2(NCMe)_{10}][Mo_8O_{26}]$ and $[Rh_2(NCMe)_{10}][W_6O_{19}]_2$. The synthetic strategy is to combine, for example, $[Rh_2(NCMe)_{10}][BF_4]_2$ and $[^nBu_4N]_2[Mo_6O_{19}]$. The compounds have been characterized from infrared and electronic spectroscopic data and elemental analyses, as well as a single crystal structure determination of $[Rh_2(NCMe)_{10}][Mo_6O_{19}]_2$. The solid state lattice consists of discrete cations and anions, and the ligands in $[Rh_2(NCMe)_{10}]^{2+}$ adopt a staggered conformation; the Rh–Rh bond distance is 2.616(3)Å [109].

The reaction of Z-$(NC)(H_2N)C{=}C(NH_2)(CN)$, H_2L, with $[Rh_2Cl_2(CO)_4]$ followed by oxidation in air, leads to the formation of the dirhodium complex $[Rh_2(CO)_4L_2]$ (**56**). The ligand coordinates through the deprotonated amino-*N* atoms and adopts a chelating mode. In the solid state, molecules stack to give one-dimensional columns running parallel to the *a*-axis; the rhodium atoms form the core of each column. For the two crystallographically independent molecules, intramolecular Rh–Rh distances are 2.822 and 2.843Å, and the intermolecular Rh----Rh separations are 4.081 and 4.109Å [110].

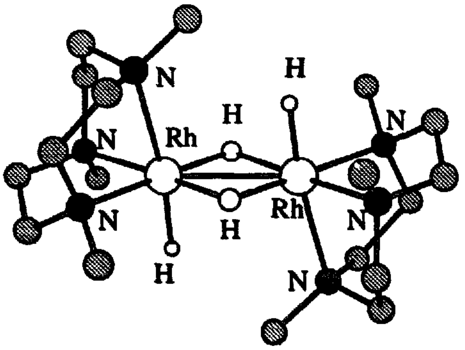


(56)

Whereas the reaction between ligand (**6**) and $RhCl_3.3H_2O$ in ethanol gives the mononuclear complex $[Rh(\mathbf{6})Cl_3]$, that between (**57**) and $RhCl_3.3H_2O$ leads to the dirhodium complex $[Rh_2(\mathbf{57})Cl_6]$. When aqueous suspensions of $[Rh(\mathbf{6})Cl_3]$ or $[Rh_2(\mathbf{57})Cl_6]$ are treated with sodium borohydride followed by KPF_6, the hydride complexes *anti*-$[Rh_2(\mathbf{6})_2(H)_2(\mu\text{-}H)_2][PF_6]_2$ and *syn*-$[Rh_2(\mathbf{57})_2(H)_2(\mu\text{-}H)_2][PF_6]_2$ are formed respectively. The structure of the former has been determined both by X-ray and neutron diffraction methods and the modes of hydride attachment in the cation (**58**) have been confirmed; the $\{HRh(\mu\text{-}H)_2RhH\}^{2+}$ core is planar. In solution, *anti*-$[Rh_2(\mathbf{6})_2(H)_2(\mu\text{-}H)_2]^{2+}$ shows fluxional behaviour on the NMR spectroscopic timescale but $[Rh_2(\mathbf{57})_2(H)_2(\mu\text{-}H)_2]^{2+}$ is static [17].



(**57**)



H atoms omitted except for hydrides

(**58**)

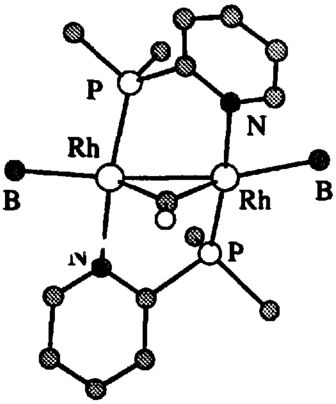
Laser flash photolysis of $[RhX(dmgH)_2(PPh_3)]$ (X = Cl, Br) with $[\{CpW(CO)_3\}_2]$ is reported to lead to the formation the dirhodium complex $[Rh_2(dmgH)_4(PPh_3)_2]$. The reaction proceeds through the radical $[Rh(dmgH)_2(PPh_3)]^{\bullet}$ followed by dimerization ($k = 2.1 \times 10^8$ dm^3 mol^{-1} s^{-1}) and the dimer has been observed by UV-VIS spectroscopy (λ_{max} =452 nm, $\varepsilon_{max} = 5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) [111].

A bridging nitrosyl ligand is present in the compound $[Rh_2(\mu\text{-}NO)(\mu\text{-}H)(P^iPr_3)_4]$ which has been prepared from $RhCl_3.3H_2O$, P^iPr_3, $NaO^iPr/^iPrOH$ and *N*-methyl-*N*-nitroso-4-tosylamide. The new compound has been characterized both in solution (where the fluxional properties have been studied) and in the solid state; the Rh_2NO-unit is planar [112].

3.5.7 Complexes with bridging dppm and related ligands

Detailed NMR spectroscopic data have been recorded for a family of complexes of general formula $[Rh_2X_2(\mu\text{-}Y)(\mu\text{-}dppm)_2]^{n+}$ (n = 0, Y = CO, X = Cl, Br, I; n = 0, Y =SO_2, X = Cl; n = 0, Y = S, X = CO; n = 1, Y = Cl, X = CO) and for $[Rh_2(CO)_2(\mu\text{-}Y)(\mu\text{-}CO)(\mu\text{-}dppm)_2]^+$ (Y = H, Cl). The work includes other related A-frame type complexes [113]. The dirhodium compound $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ reacts with $LiAlH_4$ in thf to yield $[Rh_2(AlH_4)_2(\mu\text{-}CO)(dppm)_2]$ but this product was obtained only *in situ*. With $NaBH_4$ in toluene and methanol, $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ reacts to produce $[Rh_2(BH_4)_2(\mu\text{-}CO)(dppm)_2]$, whereas in thf and methanol, the reaction proceeds to give $[Rh_2(\mu\text{-}H)_2H_2(CO)(dppm)_2]$. This undergoes reversible loss of H_2. The new compounds have been characterized by ^1H, ^{13}C and ^{31}P NMR and IR spectroscopies, and the crystal structure of the related species $[Rh_2(\mu\text{-}CO)(BH_4)_2(\mu\text{-}2\text{-}Ph_2Ppy)_2]$ (**59**) (the preparation of which is also reported) has been determined. Only the boron atoms of the borohydride ligands were crystallographically located and the ^1H NMR spectrum of the compound did not provide unambiguous data with regards to the hydrogen atom locations — at room temperature, one signal at δ –0.09 was observed which, on cooling to 198 K, gave rise to three broad signals at δ –3.25,

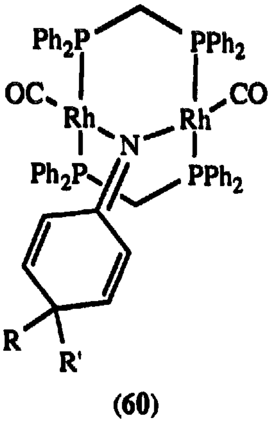
−3.77 and +0.05. Infrared spectroscopic data do however suggest that each borohydride ligand coordinates in an η^2-mode [114].



For Ph rings, only the ipso-C atoms are shown.

(59)

The reaction of hydrogen sulfide with $[Rh_2(CO)_3(\mu\text{-dppm})_2]$ results in the loss of CO and H_2 and the formation of $[Rh_2(CO)_2(\mu\text{-S})(dppm)_2]$; the reaction is quantitative. An analogous reaction with H_2Se gave an unidentified product, although a hydridic species was obtained when a diiridium precursor was used. With the heterometallic complex, $[IrRh(CO)_3(\mu\text{-dppm})_2]$, H_2S and H_2Se react to yield the complexes $[IrRh(H)(CO)_2(\mu\text{-EH})(dppm)_2]$ (E = S or Se), and their formation is followed either by rearrangement or loss of dihydrogen. A series of related reactions has also been reported and the rhodium-containing products have been characterized by IR and NMR spectroscopies [115]. The sulfur-bridged compound $[Rh_2(CO)_2(\mu\text{-S})(dppm)_2]$ also features in a separate work in which it has been shown that the catalytic dehydrogenation of cyclooctane can be brought about by the irradiation (λ_{max} = 475 nm) of $[Rh_2(CO)_2(\mu\text{-S})(dppm)_2]$ in the presence of the cycloalkane; the initial turnover frequency was 32.8 hr^{-1} [116].



(60)

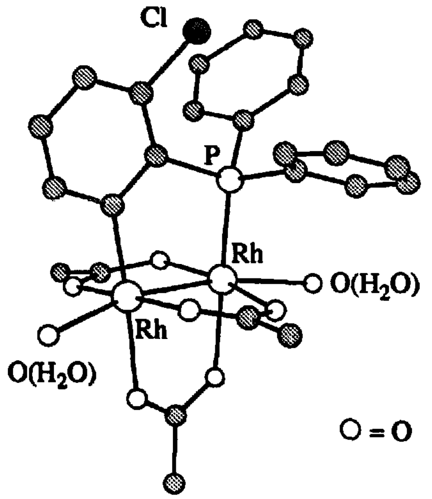
The reactions between carbon-based electrophiles and a tautomeric mixture of the arylimido and arylamido complexes $[Rh_2\{\mu\text{-N}(4\text{-}RC_6H_4)\}(CO)_2(\mu\text{-dppm})_2]$ and $[Rh_2\{\mu\text{-NH}(4\text{-}RC_6H_4)\}(CO)_2(\mu\text{-dppm})(\mu\text{-L})]$ (HL = dppm; R = various) yield addition products of the type shown in structure (**60**)— the group R' originates from the electrophile. In addition to ^1H and ^{31}P and IR spectroscopic characterization, the nature of the products has been illustrated by a representative crystal structure determination [117].

3.5.8 *Complexes with cyclometallated bridging ligands*

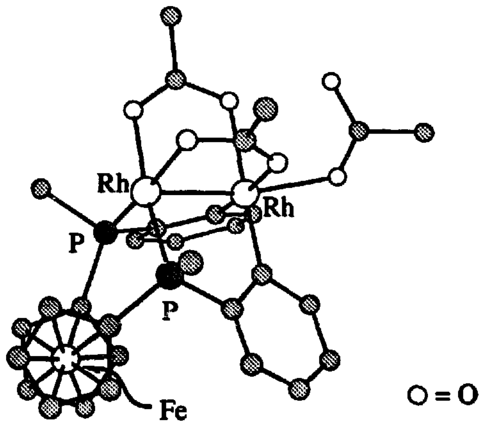
We have already mentioned the slow orthometallation of two phenyl groups which occurs in solutions of $[Rh_2(\mu\text{-}O_2CCF_3)_4(PPh_3)_2]$ to give $[Rh_2(\mu\text{-}O_2CCF_3)_2\{\mu\text{-}C_6H_4PPh_2\}_2]$ [97], and this section surveys similar compounds with dirhodium cores.

When trifluoroacetic acid is added to $[Rh_2(\mu\text{-}OAc)_3\{\mu\text{-}(C_6H_4)PPh_2\}(HOAc)_2]$, a substitution reaction occurs and the axial sites are occupied by two CF_3CO_2H molecules. The monodentate coordination mode of each axial ligand has been confirmed by a single crystal X-ray diffraction study (Rh-Rh = 2.438(1)Å). The reaction has been monitored by ^1H NMR spectroscopy and this includes the use of a ^2H labelled precursor, with the deutero-label present the phosphine ligand; D/H exchange at the *ortho*-positions of the Ph rings has been observed and this has been interpreted as showing that the reaction pathway involves reversible Rh–C bond cleavage followed by orthometallation [118]. The reaction between $PPh_2(2\text{-}ClC_6H_4)$ and $[Rh_2(\mu\text{-}OAc)_4(MeOH)_2]$ in hot aqueous acetic acid leads to the formation of the two dirhodium complexes $[Rh_2(\mu\text{-}OAc)_3\{(C_6H_4)P(2\text{-}ClC_6H_4)Ph\}(HOAc)_2]$ and $[Rh_2(\mu\text{-}OAc)_3\{(2\text{-}ClC_6H_3)PPh_2\}(H_2O)_2]$ (**61**), depending upon the site of orthometallation. Both compounds have been characterized by X-ray diffraction methods — in the former, acetic acid ligands occupy the axial sites but in complex (**61**), water ligands are present, but these can be replaced by acetic acid [119]. The way in which $[Rh_2(\mu\text{-}OAc)_3\{(C_6H_4)P(2\text{-}ClC_6H_4)Ph\}(HOAc)_2]$ reacts with trifluoroacetic acid has been studied. The product is $[Rh_2(\mu\text{-}O_2CCF_3)_3(\eta^1\text{-}O_2CCF_3)\{\eta^2\text{-}P(2\text{-}ClC_6H_4)Ph_2\}(H_2O)]$ and crystallographic data confirm the change in mode of attachment of the phosphine ligand. However, in $CHCl_3$ solution, the new compound undergoes reversible metallation [120]. The synthesis and crystal structure of the cyclometallated complex $[Rh_2(\mu\text{-}OAc)_3\{(C_6H_4)P(2\text{-}BrC_6H_4)Ph\}(HOAc)_2]$ have also been described. The kinetics of the stepwise exchange of $[AcO]^-$ ligands for $[CD_3CO_2]^-$ have been examined by use of ^1H NMR spectroscopy and a pathway for the process has been proposed [121].

The reactions of $[Rh_2(\mu\text{-}OAc)_4(MeOH)_2]$ with dppf or $(\eta^5\text{-}Cp)Fe(\eta^5\text{-}C_6H_4PPh_2)$, L, have been shown to give $[\{Rh_2(\mu\text{-}OAc)_4(MeOH)\}_2(dppf)]$ or $[Rh_2(\mu\text{-}OAc)_4L]$ respectively. On heating, $[Rh_2(\mu\text{-}OAc)_4L]$ undergoes orthometallation to generate $[Rh_2(\mu\text{-}OAc)_3\{(C_6H_4)PPh(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}Cp)\}(HOAc)_2]$. Further treatment with ligand L leads to an adduct, which, after heating gives $[Rh_2(\mu\text{-}OAc)_2\{(C_6H_4)PPh(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}Cp)\}_2(HOAc)]$, present as a mixture of two conformational isomers. The dirhodium compound $[\{Rh_2(\mu\text{-}OAc)_4(MeOH)\}_2(dppf)]$ also undergoes orthometallation when heated, and the product is $[Rh_2((\mu\text{-}OAc)_2\{\{(C_6H_4)PhP(\eta^5\text{-}C_5H_4)\}_2Fe\}(HOAc)]$ (**61**); crystallographic data reveal that the two cyclopentadienyl rings of the ferrocenyl unit are mutually staggered and the *P*-donor atoms are *cis*-to one another [122]. Although not dinuclear, the complexes $[RhCl(\eta^2\text{-}C_6H_4PPh_2)\{\eta^1\text{-}PPh_2(2\text{-}ClC_6H_4)\}L]^+$ (L = bpy or phen) are mentioned here because of their relationship to the orthometallated species above [123].



(61)



For two phenyl substituents, only the ipso-C shown.

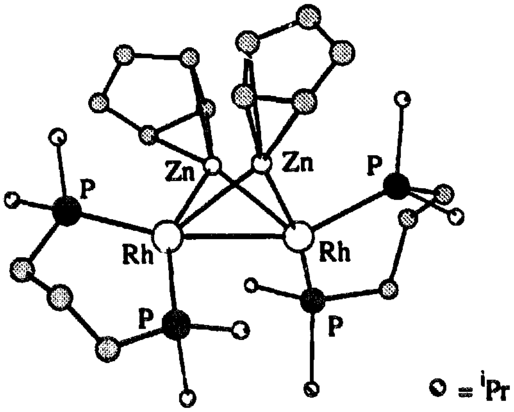
(62)

3.5.9 Heterometallic complexes

Several heterometallic species have already been described and in this final section we extend the discussion. Separate dirhodium and polyoxoanion domains are present in the complexes $[Rh_2(NCMe)_{10}][Mo_6O_{19}]_2$, $[Rh_2(NCMe)_{10}][Mo_8O_{26}]$ and $[Rh_2(NCMe)_{10}][W_6O_{19}]_2$ [109], but an example of direct combination of rhodium and polyoxoanion has been reported in the reaction of $[Cp^*{}_2Rh_2Cl_4]$ with $[Bu_4N]_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}].3MeOH$. After recrystallization from CH_2Cl_2, the isolated product is $[(Cp^*Rh)_2(\mu\text{-}Cl)Mo_5O_{13}(OMe)_4(NO)]$. The corresponding bromide complex has also been formed in addition to related chloride-free compounds. A single crystal X-ray diffraction study of the bromide compound shows that each rhodium centre is coordinated by two terminal oxo groups of the polyoxoanion and the bromo-ligand bridges the two rhodium atoms. The crystal structure of the halide-free compound $[\{Cp^*(H_2O)Rh\}Mo_5O_{13}(OMe)_4(NO)].2H_2O$ reveals that the rhodium centre is again associated with two terminal oxo groups of the polyoxoanionic fragment [124].

The preparations and characterizations of the cation $[LHRh(\mu\text{-}H)_2Cu(\mu\text{-}H)_2RhHL]^+$ and its silver(I) analogue $[L = MeC(CH_2PPh_2)_3]$ have been described; IR and ^1H and ^{31}P NMR spectroscopic data have been reported. A crystal structure determination for salts of the two complexes confirm the presence of near linear Rh–M–Rh (M = Cu, Ag) arrays [125]. The reactions of $[Rh_2(CO)_4Cl_2]$ with *trans*-$[Mn(CN)(CO)(dppm)_2]$ or *cis*- and *trans*-$[Mn(CN)(CO)_2(PR_3)(dppe)]$ (R = OEt or OPh) lead to the formation of the heterometallic species *trans*-$[(dppm)_2(OC)Mn(\mu\text{-}CN)Rh(CO)_2Cl]$, or *cis*- and *trans*-$[(OC)_2(dppe)(R_3P)Mn(\mu\text{-}CN)Rh(CO)_2Cl]$ respectively. The electrochemical properties of the complexes have been investigated and each undergoes an oxidative process centred on manganese, and the chemical oxidation of *trans*-[$(dppm)_2(OC)Mn(\mu\text{-}CN)Rh(CO)_2Cl$] results in the formation of an isolable cation. A comparison of structural parameters for these neutral and cationic complexes indicate that the oxidation is accompanied by significant geometrical changes *only* around the manganese centre. The reaction of *cis*-[$(OC)_2(dppe)(R_3P)Mn(\mu\text{-}CN)Rh(CO)_2Cl$] with $TlPF_6$ produces a heterometallic complex with a Mn_2Rh-core, the electrochemical behaviour and solid state structure of which have been investigated [126].

The zinc(II) alkyls $Zn(CH_2Ph)_2$, $ZnCp_2$ and $Zn(C_3H_5)_2$ react with [$LRh(\mu\text{-}H)_2RhL$] (L = $^iPr_2PCH_2CH_2P^iPr_2$ or $^iPr_2PCH_2CH_2CH_2P^iPr_2$) to yield heterometallic compounds of general formula [$\{LRh\}_2(\mu\text{-}H)_2(\mu\text{-}ZnR)_2$]. In solution, ^1H and ^{31}P NMR spectroscopies have been used to probe fluxional behaviour, and the solid state structure of [$\{(^iPr_2PCH_2CH_2CH_2P^iPr_2)Rh\}_2(\mu\text{-}H)_2(\mu\text{-}ZnCp)_2$] (63) illustrates that the four metal atoms define a butterfly framework with the zinc atoms in wingtip sites. The Rh_2-core is retained, but the Zn–Zn separation is >2.8 Å; the Cp ligands adopt η^3-bonding modes. The results of related reactions have also been reported [127].



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