

5. Rhodium

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INTRODUCTION

This chapter surveys the coordination chemistry of rhodium published during 1990. Complexes have been organised according to the oxidation state of the rhodium atom(s) and each section is arranged with respect to the donor atom(s) of the ligand. The final section of this chapter includes selected homo- and heterometallic rhodium clusters. Compounds which are strictly organometallic by nature have not been included in this review. The reader will find several cross references to the previous chapter in which the coordination chemistry of iridium has been described. I express my thanks, as always, to the Cambridge Crystallographic Data Base for allowing access to coordinates for structural figures redrawn for this review. (Hydrogen atoms have been omitted from most figures for clarity).

Of general interest is a review (439 references) by Steel [1] which covers transition metal (including rhodium) complexes incorporating aromatic *N*-heterocycles as bridging ligands; section

headings are azines, azoles, bipyridyldiazines, 2,2'-bipyrimidines, ligands incorporating 2,2'-bipyridine units, tridentate chelates and mixed denticity ligands.

5.1 RHODIUM(VI), RHODIUM(IV)

The synthesis of dark red RhF_6 by the fluorination of RhF_5 carried out at 220°C and under 30 atm pressure has been reported along with the infrared spectral properties of the hexafluoride isolated in nitrogen or argon matrices and the UV-VIS spectrum in a nitrogen matrix. [2]

In the presence of dioxygen or trimethylamine oxide, $\text{RhCl}_3(\text{tht})_3$ reacts with neopentyl-lithium or magnesium bromide to give the diamagnetic rhodium(IV) complex $[(\text{Me}_3\text{CCH}_2)_3\text{Rh}]_2(\mu\text{-O})$. Structural characterisation of this complex confirms a linear Rh-O-Rh arrangement; Rh-O = 1.900 (44) and 1.882 (44) Å. In the infrared spectrum of $[(\text{Me}_3\text{CCH}_2)_3\text{Rh}]_2(\mu\text{-O})$, $\nu_{\text{RhO}} = 802 \text{ cm}^{-1}$. [3]

5.2 RHODIUM(III)

5.2.1 Complexes with nitrogen donor ligands

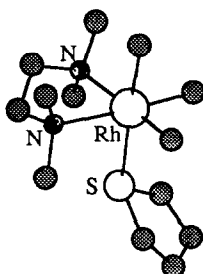
The salt $[\text{Na}][\text{NH}_4]_2[\text{Rh}(\text{NO}_2)_6]$ has been prepared from $[\text{Na}]_3[\text{Rh}(\text{NO}_2)_6]$ and NH_4Cl ; the iridium analogue has also been reported (see Chapter 4). An X-ray structural determination of $[\text{Na}][\text{NH}_4]_2[\text{Rh}(\text{NO}_2)_6]$ illustrates an octahedral anion; Rh-N = 2.11 (8) Å. [4] In related work, the recrystallisation of $[\text{Na}][\text{NH}_4]_2[\text{Rh}(\text{NO}_2)_6]$ from NaNO_2 and NH_4Cl solutions leads to complexes with varying ratios of cations. Structural data are presented. [5] The reaction of $\text{Na}_3[\text{Rh}(\text{NO}_2)_6]$ with phosphoric acid has been investigated by spectrophotometry, TGA and infrared spectroscopy over a range of temperatures. The nature of the phosphate complexes so-formed is dependent upon temperature. Redox properties of the complexes have been reported. [6]

The synthesis of $\text{Rh}(\text{NO})(\text{O}_2\text{CMe})_2(\text{PPh}_3)_2$ has previously been described but it has now been shown that recrystallisation of this complex from dichloromethane yields, instead, $\text{Rh}(\text{NO})\text{Cl}(\text{O}_2\text{CMe})(\text{PPh}_3)_2$; the rhodium atom is trigonal bipyramidal with Rh-N = 1.91 (1) Å, Rh-O_{acetate} = 2.051 (1) Å, Rh-P = 2.368 (4), 2.377 (4) Å, $\angle\text{RhNO} = 130 (2)^\circ$. [7]

The reaction of aqueous rhodium(III) chloride with an excess of ArN_3NNAr ($\text{Ar} = \text{C}_6\text{H}_4\text{-4-X}$, X = H, Me, Cl) and triethylamine in boiling ethanol leads to red-orange tris(triazenido) complexes which have been characterised by elemental analysis, and vibrational and NMR spectroscopy. [8]

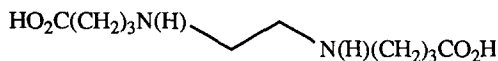
The irradiation (366 nm) of *cis*- and *trans*- $[\text{Rh}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$ leads to loss of chloride ion and, in the case of the *trans*-isomer, ammonia. [9] Some complexes incorporating the tmed ligand have been prepared from $[\text{Li}(\text{tmed})_3][\text{RhMe}_6]$: e.g. *fac*- $\text{RhMe}_3(\text{tht})(\text{tmed})$, (**1**), and *fac*- $\text{RhMe}_3(\text{CO})(\text{tmed})$. Both complexes have been crystallographically characterised. The intra-chelate angle is independent of the ligand L (L = CO or tht), $\angle\text{NRhN} = 81.2 (3)^\circ$; in (**1**), Rh-N =

2.322 (8) and 2.295 (8) Å, Rh-S = 2.460 (4) Å and in *fac*-RhMe₃(CO)(tmed), Rh-N = 2.266 (7) and 2.281 (6) Å. [3]



(1)

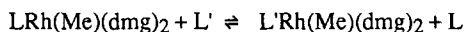
For H₂L = (2), the complexes *s-cis*- and *uns-cis*-[RhLCl₂]⁻ and [RhL(en)]⁺ have been prepared and characterised by infrared, ¹H NMR and electronic absorption spectroscopy. [10]



(2)

Bright yellow crystals of [NH₄][*trans*-Rh(HL)₂I₂], where H₂L = glyoxime, have been the subject of an X-ray diffraction study. The octahedral coordination sphere exhibits, as expected, an equatorial {HL}₂-unit with O---H---O interactions (O---O = 2.713 Å). The *trans*-IRhI units form zig-zag chains running through the *ab*-plane with weak intermolecular I---I interactions (4.010 Å). [11] The kinetics of axial ligand exchange in LRh(Me)(dmg)₂ (summarised in Table 1) have been investigated under pseudo-first order conditions (excess L') at 25°C and in CH₂Cl₂. The data are consistent with a dissociative mechanism. [12]

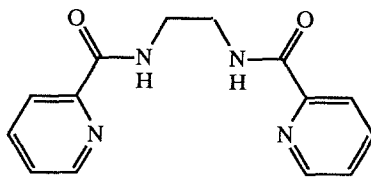
Table 1 Combinations of L and L' in the reaction:



L	tmtu	py	py	N-Meimid	PPh ₃
L'	PPh ₃	PPh ₃	N-Meimid	PPh ₃	N-Meimid

The mixed rhodium(II)/rhodium(III) complex $\text{Rh}_2(\mu\text{-L})_4\text{Cl}$ ($\text{HL} = 2\text{-NHPH-py}$) reacts with NaR or LiR ($\text{HR} = \text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{CPh}$, $\text{HC}\equiv\text{CC}_5\text{H}_{11}$, $\text{HC}\equiv\text{C-C}_4\text{H}_8\text{-C}\equiv\text{CH}$) to yield $\text{Rh}_2(\mu\text{-L})_4\text{R}$. Structural characterisation of this complex for $\text{R} = \text{C}\equiv\text{CH}$ confirms the bridging nature of the four L^- ligands and the presence of one terminal R^- group. The orientations of the bridging ligands are such that each Rh centre exhibits a *cis* array of N_{py} and N_{NPh} donor sets; pertinent distances are $\text{Rh-Rh} = 2.439$ (1) Å, $\text{Rh-N}_{\text{NPh}} = 2.017$ (7), 2.006 (7), 1.999 (7), 2.007 (7) Å, $\text{Rh-N}_{\text{py}} = 2.058$ (7), 2.047 (7), 2.041 (7), 2.053 (7) Å. The results of IR, ESR, NMR, UV-VIS spectroscopic, mass spectrometric and electrochemical studies are also reported. [13]

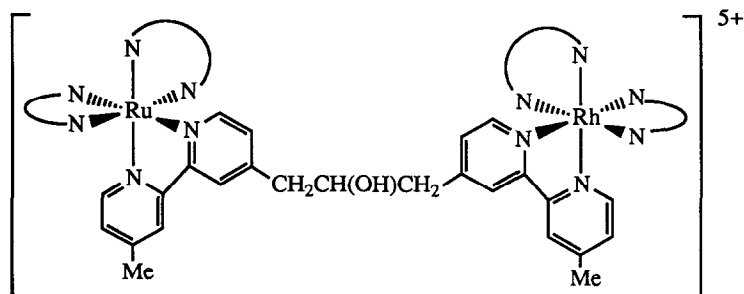
The preparation of ligand H_2L (3) has been reported as well of that of two related ligands $\text{H}_2\text{L}'$ and $\text{H}_2\text{L}''$ (denoted as (13) and (14) respectively in the preceding Chapter). The air stable Rh(III) complexes $[\text{RhLR}]\cdot\text{H}_2\text{O}$ ($\text{R} = \text{Me}$, Et), $\text{Na}[\text{RhL}'\text{Cl}_2]$, $[\text{RhL}'(\text{py})_2][\text{ClO}_4]$, $\text{RhL}'(\text{py})\text{Cl}$, $\text{RhL}'(\text{PPh}_3)\text{Cl}$, $[\text{RhL}'(\text{PPh}_3)_2][\text{ClO}_4]$, $\text{Na}[\text{RhL}'(\text{CN})_2]$, $[\text{RhL}''\text{R}]\cdot\text{H}_2\text{O}$ ($\text{R} = \text{Me}$, Et, $i\text{Pr}$, CHMePh), $\text{Na}[\text{RhL}''\text{Cl}_2]$, $\text{Na}[\text{RhL}''(\text{CN})_2]$, $[\text{RhL}''\text{R}]\cdot\text{H}_2\text{O}$ ($\text{R} = \text{Me}$, Et) have been prepared and characterised by ^1H NMR, IR and electronic absorption spectroscopy. Their electrochemical behaviour is typified by a reversible one electron oxidation. The structure of the complex $[\text{RhL}'(\text{py})_2][\text{ClO}_4]$ has been confirmed by a single crystal X-ray diffraction study; the py ligands occupy axial coordination sites and pertinent distances are $\text{Rh-N}_{\text{py}} = 2.064$ (3), 2.056 (3) Å, $\text{Rh-L}' = 2.094$ (3), 2.091 (3), 1.971 (3), 1.971 (3) Å. [14]



(3)

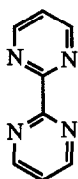
The preparation, spectroscopic and electrochemical properties and molecular structure of $[\text{Rh}(\text{bpy})_2(\text{ppy})][\text{PF}_6]_2$ ($\text{Hppy} = 2\text{-phenylpyridine}$) have been described. The complex cation exhibits a one-electron reduction at -1.59 V and a two-electron feature at -1.83 V (with respect to Fc/Fc^+). Structurally, the cation suffers from a 6-fold disorder; the ppy ligand is a *C,N*-donor and the geometry of the dication is similar to that of $[\text{Rh}(\text{bpy})_3]^{3+}$. [15] The luminescence spectrum of the related monocation $[\text{Rh}(\text{ppy})_2(\text{bpy})]^+$ (in nitrile glass) exhibits lines that are $100\text{-}200\text{ cm}^{-1}$ wide. A comparison of the spectra of $[\text{Rh}(\text{ppy})_2(\text{bpy})]^+$, $[\text{Rh}(\text{ppy})_2(\text{en})]^+$ and $[\text{RhL}_2(\text{bpy})]^+$ ($\text{HL} = \text{thienylpyridine}$) illustrates that L^- rather than the bpy ligand is involved in the lowest energy excited state. [16]

The dimetallic complex (4) has been synthesised and the results of electrochemical studies have been reported. A single reversible wave at 1.27 V (vs. SCE) is assigned to $\text{Ru(II)} \rightarrow \text{Ru(III)}$ oxidation. An irreversible wave at -0.7 V is assigned to the reduction of the rhodium(III) centre. Intramolecular electron transfer in the excited state complex is also discussed. [17]

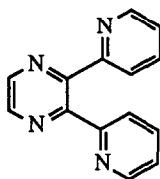


N — N = bpy for Ru(II) and bpy or phen for Rh(III)

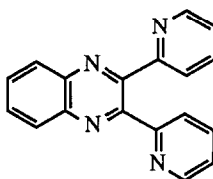
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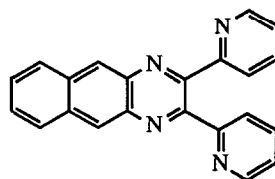
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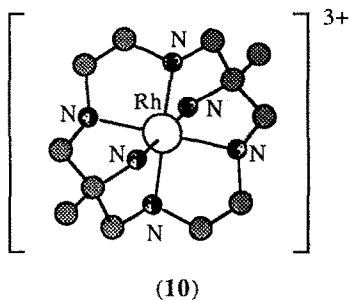
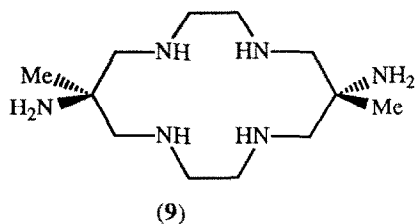
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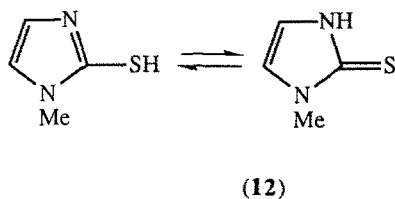
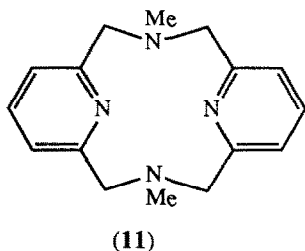
The complexation of ligands L = (5) to (8) to rhodium(III) to give the cations $[\text{RhL}_2\text{Br}_2]^+$ has been reported; related reactions involving iridium(III) are also described (see Chapter 4). The structural characterisation of $[\text{RhL}_2\text{Br}_2]^+$ for L = (7) confirms a *cis* arrangement of the bromide ligands. The conformation of (7) alters upon ligation with rotation about one interannular C-C bond to permit coordination; important distances are Rh-N_{py} = 2.027 (10), 2.031 (10) Å, Rh-N_{pz} = 2.083 (9), 2.071 (9) Å and the trends in these distances are consistent with the weaker σ-donor ability of the pz versus py nitrogen atoms. [18] The rhodium(III) complex cations $[\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}]^{2+}$, $[\text{Rh}(\text{phen})_2(\text{NH}_3)_2\text{Cl}]^{3+}$ and $[\text{Rh}(\text{phen})_2(\text{CN})_2]^+$ have been isolated as their hexafluorophosphate salts. Differences in the photophysical behaviour of the complexes as a function of the monodentate ligands have been assessed. [19]

Elegant work has illustrated enantioselective cleavage by $[\text{Rh}(\text{phen})_2(\text{phi})]^{3+}$ (phi = 9,10-phenanthrenequinone diimine) of DNA, the cleavage occurring at the propeller-twisted sites. The propeller twist at the 5'-pyr-pur-3' site in DNA permits intercalation by Δ - $[\text{Rh}(\text{phen})_2(\text{phi})]^{3+}$ only. Probing the cleavage has been possible after the resolution of $[\text{Rh}(\text{phen})_2(\text{phi})]^{3+}$ into Δ - and Λ -enantiomers. [20] The preparation of $[\text{Rh}(\text{phen})_2(\text{phi})]^{3+}$ from $[\text{Rh}(\text{phen})_2\text{Cl}_2]^+$ has been separately reported along with the molecular structure of $[\text{Rh}(\text{phi})_2(\text{bpy})][\text{BF}_4]$; pertinent distances are Rh-N_{phi} = 2.002 (3), 2.010 (4) Å, Rh-N_{bpy} = 2.071 (4), 2.076 (4), 2.055 (3), 2.054 (3) Å. [21]



Ligand L, (9), has the potential to be tetra-, quinque- or sexidentate with respect to rhodium(III) centres. The complex cation $[\text{RhL}]^{3+}$, (10), is one of a series of related species synthesised and characterised. As the perchlorate salt, (10) has been structurally characterised; $\text{Rh-N} = 2.045$ (3), 2.042 (4), 2.055 (3), 2.033 (4), 2.055 (3), 2.058 (4) Å. [22]

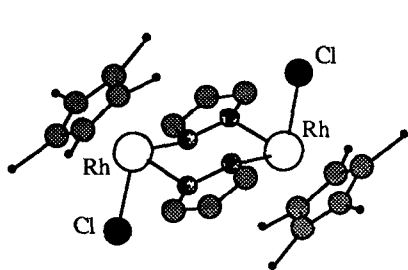
The reaction of the macrocyclic ligand L, (11), with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol (80°C, 2 hr) followed by treatment with NaBF_4 leads to $[\text{RhLCl}_2][\text{BF}_4]$. The 92% yield of this product compares with 96% for the tetraphenylborate and 90% for the hexafluorophosphate salts respectively. Structural analysis of the tetraphenylborate salt has been carried out. The chloride ligands are mutually *cis*, each lying *trans* to a pyridine *N*-donor. Important bond parameters are $\text{Rh-N}_{\text{py}} = 1.958$ (5), 1.960 (5) Å, $\text{Rh-N}_{\text{NMe}} = 2.094$ (5), 2.099 (5) Å, $\text{Rh-Cl} = 2.353$ (2), 2.349 (2), $\angle \text{N}_{\text{py}}\text{RhN}_{\text{py}} = 85.8$ (1)°, $\angle \text{N}_{\text{py}}\text{RhN}_{\text{NMe}} = 82.9$ (1), 83.4 (2), 82.7 (2), 82.5 (2)°. [23]



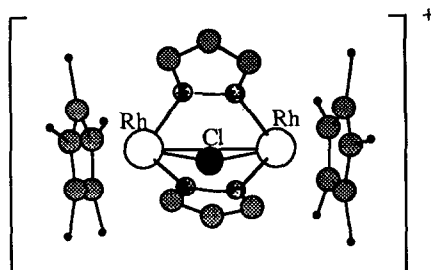
Treating hydrated rhodium(III) chloride with 2-mercapto-1-methylimidazole, L, leads to RhLCl_3 (65% yield). The infrared spectrum of the complex exhibits absorptions at 465, 425 and 190 cm^{-1} ; compared to the spectrum for the free ligand, the loss of an absorption at 2470 cm^{-1} (ν_{SH}) upon coordination implies that it is the thione form of the ligand, (12), that predominates. [24]

The chair conformation adopted by the Rh_2N_4 -core in $[\text{Cp}^*\text{RhCl}(\mu\text{-L})]_2$, (13) (HL = pyrazole), has been confirmed crystallographically. A change to a boat-form occurs upon reaction of the complex with AgBF_4 to give the cation (14). The closure to a "boat" leads to a significant shortening in the $\text{Rh}\cdots\text{Rh}$ distance from 4.059 (2) Å in (13) to 3.588 (2) Å in (14). The reduction of (13) to $[\text{Cp}^*\text{Rh}(\mu\text{-L})]_2$ has also been studied; the Cp analogue of $[\text{Cp}^*\text{Rh}(\mu\text{-L})]_2$ has been synthesised by a parallel route and has been structurally characterised. The Rh_2N_4 -core adopts a

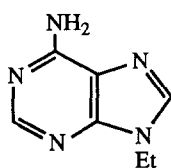
"folded-boat" conformation and a further shortening of the Rh--Rh distance to 2.657 (3) Å is observed. [25] The preparations of the complexes $\text{Cp}^*\text{M}(\mu\text{-L})(\mu\text{-I})_2\text{RhI}(\text{CO}_2\text{R})(\text{CO})$ (HL = pyrazole; M = Rh, R = Me or Et; M = Ir, R = Me) have been reported. An X-ray diffraction study for M = Ir confirms the bridging mode of the pyrazolate ligand. Each of the Rh and Ir atoms is in a distorted octahedral coordination environment; Rh-N = 2.081 (9) Å and Ir-N = 2.095 (8) Å. [26]



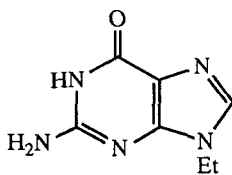
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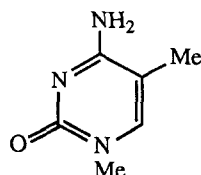
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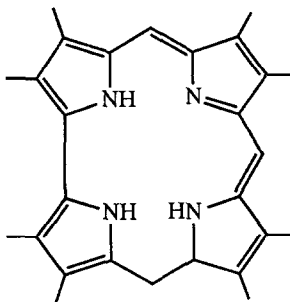
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(16)



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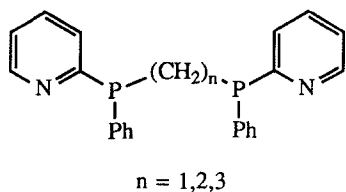
The coordination of nucleobases to rhodium(III) porphyrin complexes RhL or RhLX has been described where H_2L = octaethylporphyrin, TPP, 5,15-*trans*-bis(2-hydroxy-1-naphthyl) octaethylporphyrin and X = Cl, CH_2COMe . The products are 1:1 complexes with tightly bound

axial nucleobases for (15) to (17); however, for 1-methylthymine this is not the case. ^1H NMR and absorption spectroscopic data are presented. [27] In related work, it is reported that RhLCl ($\text{H}_2\text{L} = 5,15\text{-trans-bis}(2\text{-hydroxy-1-naphthyl})\text{octaethylporphyrin}$) forms stable 1:1 adducts with 1- $\text{NH}_2\text{-2-CO}_2\text{Me-C}_6\text{H}_4$ and 1- $\text{NH}_2\text{-4-CO}_2\text{Me-C}_6\text{H}_4$. ^1H NMR spectroscopic data confirm amine to rhodium(III) coordination and also illustrate the formation of a hydrogen bond between the CO_2Me and the hydroxy substituent of the porphyrin ligand. Related complexes are also described and results are assessed in terms of amino acid transport. [28]

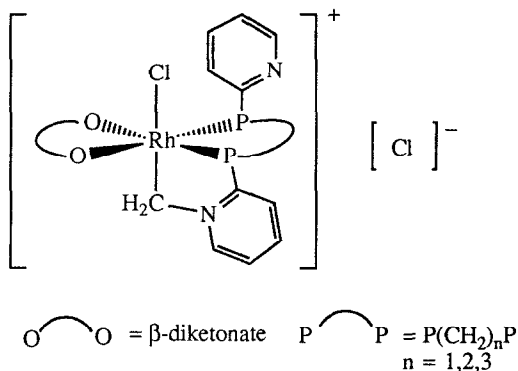
The corrole H_3L , (18), reacts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in benzene under conditions of reflux and in the presence of Ph_3As to give $\text{Rh}(\text{AsPh}_3)\text{L}$ in 75% yield with $\text{Rh}(\text{CO})_2\text{L}$ as a byproduct. The molecular structure of $\text{Rh}(\text{AsPh}_3)\text{L}$ has been determined; the corrole ring is essentially planar and the Rh atom lies 0.26 Å above the plane of the ring, pulled toward the arsenic donor. Pertinent distances in the complex are $\text{Rh-N}_{\text{corrole}} = 1.956$ (10), 1.960 (10), 1.930 (10), 1.932 (11) Å, $\text{Rh-As} = 2.311$ (2) Å. Infrared and electronic spectral data are also presented. [29]

5.2.2 Complexes with phosphorus and arsenic donor ligands

Amongst complexes of rhodium(III) containing simple phosphine ligands is *fac*- $\text{RhMe}_3(\text{PMe}_3)_3$. The latter has been synthesised from PMe_3 and $[\text{Li}(\text{tmed})_3][\text{RhMe}_6]$, an air and thermally stable complex. $\text{RhMe}_3(\text{PMe}_3)_3$ has been structurally characterised and Rh-P distances are 2.321 (5), 2.325 (5) and 2.322 (6) Å. [3] The reaction of the related rhodium(III) complex $\text{RhMe}_3(\text{PMe}_2\text{Ph})_3$ with $\text{HBF}_4\cdot\text{OEt}_2$ leads to the elimination of methane and formation of $\text{RhMe}_2(\text{FBF}_3)(\text{PMe}_2\text{Ph})_3$. The molecular structure of the analogous iridium(III) complex shows a coordinated tetrafluoroborate ion; (see Section 4.2.3 of the previous Chapter). The reactions of ethene and carbon monoxide with $\text{RhMe}_2(\text{FBF}_3)(\text{PMe}_2\text{Ph})_3$ are discussed and compared with those with $\text{IrMe}_2(\text{FBF}_3)(\text{PMe}_2\text{Ph})_3$. [30]



(19)



(20)

The potential for ligand (**19**) to function as a chelating and a bridging ligand leads to an interest in its being used to synthesise heterobimetallic complexes. Initial studies have involved the preparation of mononuclear complexes of the type RhLL' where $\text{L} = (\mathbf{19})$ and $\text{L}' = \beta$ -diketonates (acac or 2,2,6,6-tetramethylheptanedionate). Analogous complexes in which the bis(phosphine) ligand, L , is dpmm, dppe or dppp have also been studied; they undergo oxidative addition with CH_2Cl_2 to give both *cis*- and *trans*- $\text{Rh}(\text{Cl})(\text{CH}_2\text{Cl})\text{LL}'$. However, in the reaction of CH_2Cl_2 with RhLL' where $\text{L} = (\mathbf{19})$, quaternisation occurs and the products are (**20**) and its *cis*-analogue. The latter has been structurally characterised for $\text{O}^-\text{O}^- = 2,2,6,6$ -tetramethylheptanedionate and $n = 2$ in (**19**); $\text{Rh-P}_{\text{trans-Cl}} = 2.206$ (1) Å, $\text{Rh-P}_{\text{cis-Cl}} = 2.261$ (1) Å, $\text{Rh-O} = 2.093$ (3), 2.149 (2) Å, $\angle \text{PRhP} = 83.63$ (4)° and $\angle \text{ORhO} = 87.99$ (9)°. [31] The reaction of $[\text{Cp}^*\text{RhI}_2]_2$ with $\text{P}(\text{OMe})_3$ leads not to simple complex but to $\text{Cp}^*\text{Rh}(\text{I})\{\text{P}(\text{O})(\text{OMe})_2\}\{\text{P}(\text{OMe})_3\}$ which, upon treatment with NaI, gives $\text{Na}[\text{Cp}^*\text{Rh}(\text{I})\{\text{P}(\text{O})(\text{OMe})_2\}_2]$. Replacement of sodium by thallium(I) gives a dimeric complex with a central Tl_2O_4 -core supported by bridging oxygen atoms. Each rhodium(III) centre is tetrahedrally coordinated and $\text{Rh-P} = 2.265$ (2) and 2.262 (2) Å. [32] Other related complexes have also been reported. [33]

The preparation of $[\text{Rh}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_3]_2^{2-}$ and its reactivity with a range of ligands (*N*-, *P*-, and *As*- donors) including PPh_3 or with AgClO_4 in the presence of (for example) $\text{P}(\text{OMe})_3$, PPh_3 and PET_3 have been described. The structure of $\text{Rh}(\text{C}_6\text{F}_5)_3(\text{PET}_3)_2$ (from the previous reaction) confirms a distorted square based pyramidal rhodium(III) atom with the PET_3 ligands occupying mutually *trans*-sites in the basal plane; $\text{Rh-P} = 2.407$ (5) and 2.400 (5) Å. The analogous complex $\text{Rh}(\text{C}_6\text{F}_5)_3(\text{AsPh}_3)_2$ has also been structurally characterised: $\text{Rh-As} = 2.477$ (2) and 2.480 (2) Å. [34]

The diarsine ligand $\text{Me}_2\text{As}(\text{CH}_2)_3\text{AsMe}_2$ (*As-As*) reacts with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ to yield both *trans*- and *cis*- $[\text{RhCl}_2\text{L}_2]^+$. Molecular structures of orange *trans*- $[\text{RhCl}_2\text{L}_2][\text{ClO}_4]$, yellow *cis*- $[\text{RhCl}_2\text{L}_2][\text{PF}_6]$ and yellow *cis*- $[\text{RhCl}_2\text{L}_2][\text{CF}_3\text{SO}_3]$ have been determined. For the *trans*-complex cation, pertinent distances are $\text{Rh-As} = 2.454$ (4), 2.442 (4), 2.442 (4) and 2.447 (4) Å and intra-chelate angles are $\angle \text{AsRhAs} = 89.1$ (1) and 89.9 (1)°. The detailed structure of the *cis*-isomer is anion dependent. For the hexafluorophosphate salt, both chelate rings are in a chair conformation whereas in the triflate salt, one ring exhibits a distorted skew conformation; important distances are given in Table 2. [35]

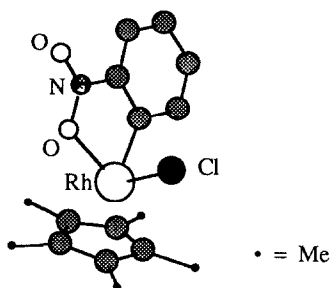
Table 2	Selected bond parameters in <i>cis</i> - $[\text{RhCl}_2\text{L}_2][\text{PF}_6]$ and <i>cis</i> - $[\text{RhCl}_2\text{L}_2][\text{CF}_3\text{SO}_3]$	
	<i>cis</i> - $[\text{RhCl}_2\text{L}_2][\text{PF}_6]$	<i>cis</i> - $[\text{RhCl}_2\text{L}_2][\text{CF}_3\text{SO}_3]$
$\text{Rh-As}_{\text{trans-Cl}}/\text{Å}$	2.385 (3), 2.370 (4)	2.387 (4), 2.367 (5)
$\text{Rh-As}_{\text{cis-Cl}}/\text{Å}$	2.345 (4), 2.484 (6)	2.441 (10), 2.389 (10)
$\angle \text{AsRhAs}_{\text{intra-chelate}}/^\circ$	90.2 (2), 93.9 (1)	92.3 (3), 91.5 (3)

The synthesis of some novel complexes incorporating both the $[P_3]^{3-}$ ligand and 1,1,1-*tris*(diphenylphosphinomethyl)ethane, L, have been reported. Reaction of $LM(P_3)$ ($M = Co, Rh, Ir$) with Ph_3PAuCl , Me_3PAuCl or $ClAu\{Ph_2P(CH_2)_nPPH_2\}AuCl$ ($n = 1,2$) in the presence of $TlPF_6$ gives $[\{LM(P_3)\}_2Au][PF_6]$. All three complexes have been structurally characterised and are isostructural (see structure (24) in Chapter 4). In the rhodium complex, $Rh-P(P_3) = 2.371$ (3)–2.439 (4) Å and $Rh-P(phosphine) = 2.286$ (4)–2.310 (3) Å and the spiro twist at the gold(I) atom is 51.1° . [36]

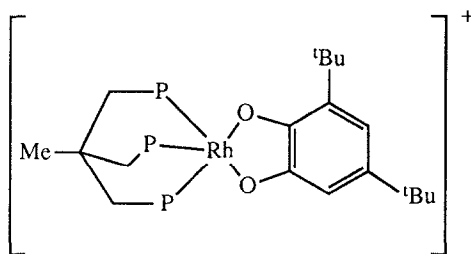
5.2.3 Complexes with oxygen donor ligands

The atomic radial distribution method has proved successful in the determination of the structures of two rhodium(III) sulphates formed upon treatment of $Rh_2O_3 \cdot xH_2O$ with sulphuric acid at $280^\circ C$. The sulphates are formulated as $Rh_3O(HSO_4)_5(SO_4)$ and $[Rh_3O(SO_4)_9]^{11-}$ (isolated as the hydrated potassium salt). In both, Rh_3 -triangular arrays are capped by μ_3 -O atoms and edge bridged by sulphate ions; the $Rh \cdots Rh$ separations are 3.28 Å and 3.36 Å in $Rh_3O(HSO_4)_5(SO_4)$ and $K_{11}[Rh_3O(SO_4)_9]$ respectively. [37]

The reaction of $[Cp^*RhCl_2]_2$ with $Hg(C_6H_4NO_2-2)_2$ or $Hg(C_6H_4NO_2-2)Cl$ in the presence of excess Me_4NCl leads to complex (21). The molecular structure of (21) has been determined and is described as possessing a pseudo-octahedral $Rh(III)$ centre. Selected bond parameters are $Rh-O = 2.142$ (3) Å, $\angle C_{Ph}RhO = 77.6$ (1)° and $\angle ORhCl = 86.2$ (1)°. The reactivity of the complex with PPh_3 , *py* and *bpy* in the presence of $AgClO_4$ has been investigated. [38]



(21)



(22)

The rhodium(III) complex $(Me_3P)_3Rh(Br)[CH_2CMe_2(OH)]$ is obtained upon treatment of $Rh(PMe_3)_3Cl$ with $Me_2C(OH)CH_2Br$. An X-ray structure for the complex confirms a *mer*-arrangement of phosphine ligands and shows that the terminal organic fragment is involved in an intramolecular hydrogen-bond with the coordinated chloride ion. Reaction of $(Me_3P)_3Rh(Br)-$

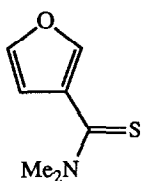
{CH₂CMe₂(OH)} with [(Me₃Si)₂N]K results in loss of Cl⁻ and ring closure to give a metallaioxetane complex which has also been structurally characterised (Rh-O = 2.099 (8) Å). [39]

The coordinatively unsaturated complex cation (22) has been isolated as both the hexafluorophosphate and tetraphenylborate salts. The electrochemical behaviour of complex (22) has been studied; it undergoes electron transfer reactions resulting in both changes in oxidation state of the rhodium atom and oxidation levels of the quinoid ligand. Cation (22) reacts with dioxygen to give an η¹-O₂ coordinated ligand; oxygen transfer reactions are discussed. [40]

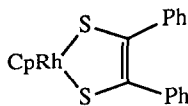
Work relating to the complexes Rh(NO)(O₂CMe)₂(PPh₃)₂ and Rh(NO)Cl(O₂CMe)(PPh₃)₂ is described in Section 5.2.1. [7] Complexes of rhodium(III) containing both β-diketonate and phosphine ligands have been discussed in Section 5.2.2. [31]

5.2.4 Complexes with sulphur donor ligands

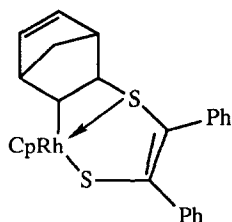
The reaction of HL, (23), with RhCl₃(P^{*n*Bu₃)₂ leads (55% yield) to the cyclometallated product LRhCl₂(PBu₃)₂. An analogous bromo-derivative may be produced in 72% yield. ³¹P and ¹³C NMR and infrared spectroscopic data are presented giving evidence for *S*-coordination (and thus an octahedral Rh(III) centre) and *cis*-halides. Related Pd(II), Pt(II) and Ru(II) complexes are also reported. [41]}



(23)



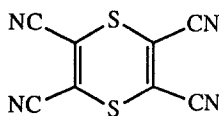
(24)



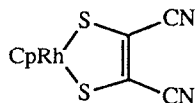
(25)

The reaction of RhCl₃(tht)₃ with MeLi in tmed and diethyl ether leads to [Li(tmed)₃][RhMe₆] which may then be used to prepare the tetrahydrothiophene derivative *fac*-RhMe₃(tht)(tmed), (1); see Section 5.2.1. [3] It has been shown that insertion of quadricyclane into the Rh-S bond of (24) occurs when the two compounds react together under reflux. The product of the reaction is complex (25); it is photoreactive and on irradiation it regenerates (24) with elimination of norbornadiene. However, norbornadiene itself does not react with (24). ¹H NMR and UV-VIS spectroscopic data are presented. [42] Cleavage of the heterocycle (26) occurs upon reaction with CpRh(cod) to give (27); the product has been characterised by elemental analysis, mass spectrometric and NMR and IR spectroscopic data. Related cobalt chemistry is also reported. [43]

The cubane-like compound $[\text{Cp}^*\text{RhW}(\text{O})(\mu\text{-S}_2)(\mu\text{-S})_2]_2$, has been reported along with its iridium analogue. Full structural details for the latter were given in Section 4.2.4, see structure (29) in Chapter 4. [44]



(26)



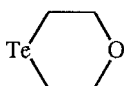
(27)

5.2.5 Complexes with tellurium donor ligands

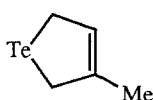
The tellurium containing heterocycles (28) to (34) react with hydrated rhodium(III) chloride to yield orange, red or brown complexes of formula L_3RhCl_3 . Complex characterisation is by elemental analysis, conductivity measurements and IR and UV-VIS spectroscopy and it is proposed that each product has a *mer*-configuration and that the heterocycles function as Te-donors. The complex $[\text{RhL}(\text{PPh}_3)\text{Cl}]_2$ ($\text{L} = 29$) is also reported. [45] In related work by the same authors, ligands (29) and (32) are included in a study of the thermal stability of L_3RhCl_3 , and of $\text{Rh}(\text{cod})\text{LCl}$ for $\text{L} = (28)$ and (29) and of $\text{RhCl}_3(\text{CO})\text{L}_2$ for $\text{L} = (28)$. It is observed that loss of two tellurium-donor ligands occurs for L_3RhCl_3 and $\text{RhCl}_3(\text{CO})\text{L}_2$ while for $\text{Rh}(\text{cod})\text{LCl}$, loss of L results in the formation of the dimeric $[\text{Rh}(\text{cod})\text{Cl}]_2$. [46]



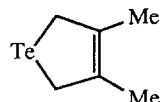
(28)



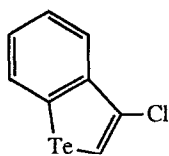
(29)



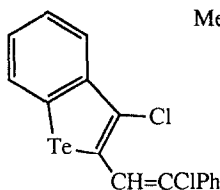
(30)



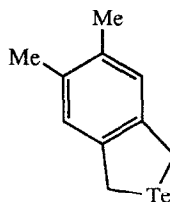
(31)



(32)



(33)



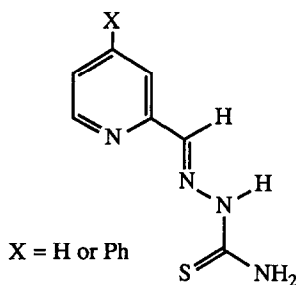
(34)

5.2.6 Complexes with mixed donor sets

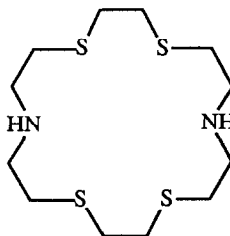
This section deals with Rh(III) complexes containing ligands with *N,O*-, *O,P*-, *O,S*- and *N,S*-donor sets. In $[(\text{Rh}(\eta^2\text{-C}_6\text{H}_4\text{-2-PPh}_2)\{\eta^2\text{-P(2-Cl-C}_6\text{H}_4)\text{Ph}_2\}_2(\mu\text{-salen})][\text{SbF}_6]_2$, the salen ligand is bidentate with respect to each rhodium(III) atom and bridges between the two metal atoms. Important structural data are Rh-P = 2.231 (3), 2.298 (3) Å, Rh-Cl = 2.527 (3) Å, Rh-O = 2.075 (11) Å and Rh-N = 2.111 (10) Å. [47] A series of optically active complexes containing octahedrally coordinated rhodium(III) or iridium(III) atoms with α -amino acidato ligands (HL = L-proline and L-analine) have been reported; see Section 4.2.6 in Chapter 4 for structural details of $\text{Cp}^*\text{IrCl(L-Pro)}$. [48] Related to this work is a report of the reactions of $\text{Cp}^*\text{ClM}(\mu\text{-Cl})_2\text{MClCp}^*$ (M = Rh or Ir) with various α -amino acidato ligands; see details in the previous Chapter. The structure of $\text{Cp}^*\text{ClRh(L-azetidine-2-carboxylate)}$ is reported. [49]

The oxidative addition of diphenylphosphinoacetic acid to rhodium(I) gives rise, first to $\text{RhCl(H)}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{-O,P}\}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{H-P}\}_2$ and then to *fac*- $\text{Rh}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{-O,P}\}_3$. Structural determinations for the two complexes have been carried out. The hydride ligand in $\text{RhCl(H)}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{-O,P}\}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{H-P}\}_2$ has not been located but a vacancy in the otherwise octahedral coordination sphere implies that it lies *trans* to the chloride ligand; Rh-P_{terminal} = 2.244 (7), 2.396 (7) Å, Rh-P_{P,O} = 2.359 (7) Å, Rh-O_{P,O} = 2.13 (2) Å, Rh-Cl = 2.488 (7) Å. In *fac*- $\text{Rh}\{\text{Ph}_2\text{PCH}_2\text{CO}_2\text{-O,P}\}_3$ pertinent distances are Rh-P = 2.294 (3), 2.296 (3), 2.293 (3) Å and Rh-O = 2.100 (6), 2.074 (6), 2.076 (6) Å. [50]

Both *O,S*- and *N,S*-coordination is observed in the products resulting from the reaction of H_3RhCl_6 with cysteine (H_2L): $\text{Rh}_4(\text{HL-O,S})_2(\text{HL-N})_4(\text{L-O,S})_4\text{Cl}_2\cdot\text{H}_2\text{O}$, $\text{Rh}(\text{HL-O,S})(\text{HL-N,S})\text{Cl}(\text{H}_2\text{O})\cdot\text{H}_2\text{O}$, $[\text{Rh}(\text{HL-O,S})(\text{HL-N,S})\text{Cl}]_2\cdot n\text{H}_2\text{O}$ ($n = 2,3,4$) and $[\text{Rh}(\text{HL-N,S})\text{Cl}_2(\text{H}_2\text{O})]_2\cdot\text{H}_2\text{O}$. Complexes have been characterised by XPS, IR spectroscopy and TGA. In those complexes in which the cysteinato ligand coordinates via an *N,S*-donor set, a betain form is present. [51] The crystal structure of $\text{Rh}(\text{MeC(S)CHC(O)CF}_3)_3$ has been described. A *fac*-configuration is confirmed: Rh-S = 2.256 (2), 2.254 (2), 2.259 (2) Å, Rh-O = 2.091 (4), 2.073 (5), 2.081 (4) Å, $\angle\text{SRhO}_{\text{intra-chelate}} = 94.95$ (14), 96.17 (14), 96.40 (14)°. [52]



(35)



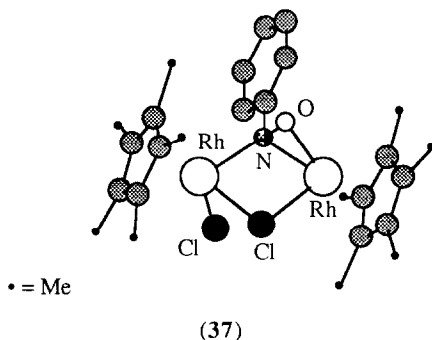
(36)

The ligands (**35**) are *N,N,S*-donors in the *bis*(chelate) complexes $\text{Rh}_2\text{LCl}(\text{H}_2\text{O})_2$ and $[\text{RhL}_2][\text{ClO}_4]$. The complexes have been characterised by elemental analysis, IR and electronic spectroscopy. In the electronic spectra, the bands are intense thereby implying that the *N,N,S*-donor atoms are in a *mer*-configuration. The biological activity of both the ligands (**35**) and their rhodium(III) complexes have been assessed by observing their *in vitro* antibacterial activities towards *E. coli*. [53] The reaction of aqueous Rh(III) ions with the macrocyclic ligand H_2L , (**36**), under reflux in aqueous methanol for 12 hr leads to $[\text{RhL}]^{3+}$ isolated as the hexafluorophosphate salt. Single crystal X-ray diffraction data have been presented; the ligand encapsulates the rhodium(III) atom with the *N*-donors mutually *trans* as would be expected. Bond distances in the coordination sphere are Rh-S = 2.3289 (14), 2.3416 (14), 2.3353 (14), 2.3349 (14) Å, Rh-N = 2.083 (4), 2.101 (5) Å. [54]

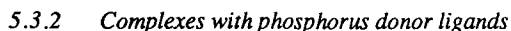
5.3 RHODIUM(II)

5.3.1 Complexes with nitrogen donor ligands

The rhodium(II) dimer $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})]_2$ has been synthesised from $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$ by reduction with Na/Hg. After the addition of hexane, the rhodium(II) complex is isolated as blue-black crystals in 65-75% yield. A single crystal X-ray diffraction study reveals the presence of 2 independent molecules in the unit cell: for molecule *A*, Rh-Rh = 2.617 (1) Å and for molecule *B*, Rh-Rh = 2.628 (1) Å. The highly reactive Rh-Rh bond leads to some interesting chemistry. For example, with PhNO complex (**37**) is formed. The structure of (**37**) is disordered with 2 molecular orientations being observed. For the major orientation, Rh-N_{bridged} by O = 2.016 (4) Å, Rh-N_{unbridged} = 2.083 (6) Å, Rh-O_{NO} = 2.020 (5) Å, $\angle\text{RhNO} = 69.4 (3)^\circ$, $\angle\text{RhON} = 69.1 (3)^\circ$. A related complex is obtained when $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})]_2$ reacts with dioxygen. [55]



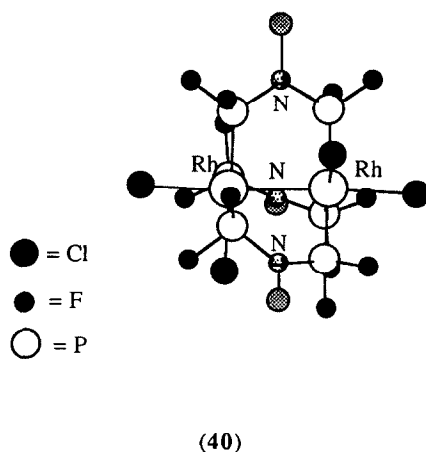
The reaction of the mixed rhodium(II)/rhodium(III) complex $\text{Rh}_2(\mu\text{-L})_4\text{Cl}$ (HL = 2-NHPh-py) with various acetylides to yield $\text{Rh}_2(\mu\text{-L})_4\text{R}$ was described in Section 5.2.1. [13] The



The oxidation of the rhodium(I) complex $[\text{Rh}\{\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2\}(\text{CO})]_2$ generates the corresponding dication. Analogous complex cations with py or $\text{P}(\text{OMe})_3$ replacing CO have also been reported and for $[\text{Rh}\{\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{PPh}_2\}(\text{py})]_2^{2+}$ a full structural determination has been carried out. The Rh_2 -framework is supported by two bridging $\eta^5\text{-C}_5\text{H}_4\text{PPh}_2$ ligands, each functioning as a ferrocenyl ligand to one rhodium atom and as a *P*-donor to the second. Each rhodium atom carries a terminal py ligand. The observed Rh-Rh separation of 2.7796 (9) Å is short, particularly when compared to that in the Rh(I) starting material, viz 4.3029 (6) Å. The observations underline the flexibility of the phosphinoferrocenyl ligand. [58]

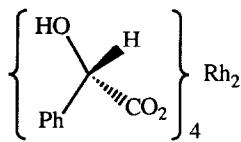
A novel group of complexes involving the *bis*(difluorophosphino)methylamino ligand has been synthesised and structurally and electronically characterised. The reaction of $[\text{RhCl}(\text{PF}_3)_2]$ and

with $\text{MeN}(\text{PF}_2)_2$ leads to the Rh(0) species $\text{Rh}_2[\text{MeN}(\text{PF}_2)_2]_3(\text{PF}_3)_2$ under reducing conditions. Under oxidising (Cl_2) conditions, the Rh(II) complex $\text{Rh}_2[\text{MeN}(\text{PF}_2)_2]_3\text{Cl}_4$, (**40**), is formed. The molecular structure of (**40**) has been determined; three bridging $\text{MeN}(\text{PF}_2)_2$ ligands are observed ($\text{Rh-P} = 2.277$ (2), 2.226 (2), 2.184 (2) Å and $\text{Rh-Rh} = 2.707$ (1) Å) and there are two terminal chloride ligands per rhodium atom. If the synthesis described above is carried out under stringent (non-reducing or non-oxidising) conditions a mixed Rh(0)-Rh(II) complex is obtained in which $\text{Rh-Rh} = 2.785$ (1) Å. The two coordination environments are octahedral Rh(II) and trigonal bipyramidal Rh(0). [59]

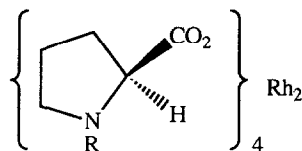


5.3.3 Complexes with oxygen donor ligands

Homochiral rhodium(II) carboxylates, (**41**) and (**42**), have been shown to catalyse carbon-carbon bond forming reactions of α -diazoketones. This is the first time that such rhodium(II) complexes have been utilised thus. [60]



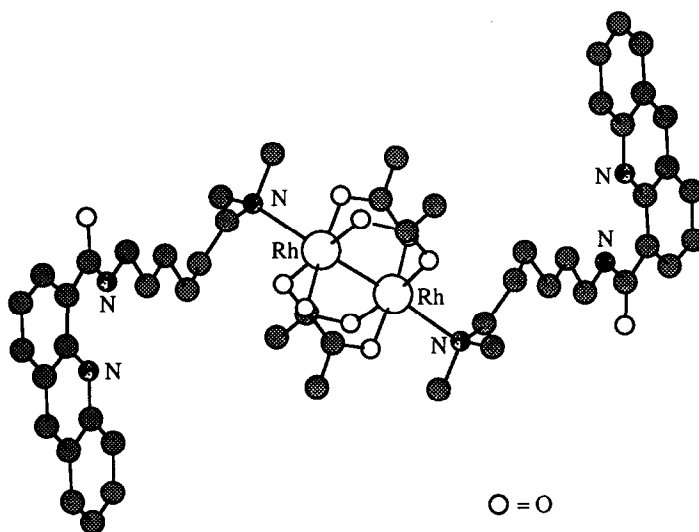
(41)



R = benzenesulphonyl
or 1-naphthalenesulphonyl

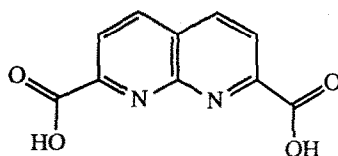
(42)

A report has appeared of the convenient use of the Raman spectroscopy as a method of investigating solid-liquid crystal phase transitions in dirhodium(II) alkanoates. Complexes of the type $\text{Rh}_2(\mu\text{-O}_2\text{CR})_4$ are mesogens. The ν_{RhRh} band maximum and halfwidth vary as a function of temperature and exhibit inflection points which correspond to mesophase transitions. [61] The resonance Raman spectra of the one electron oxidised products of $\text{Rh}_2(\mu\text{-L})_4\text{L}'_2$ ($\text{HL} = \text{MeCO}_2\text{H}$, $\text{CD}_3\text{CO}_2\text{H}$, MeCONH_2 , CF_3CONH_2 ; $\text{L}' = \text{PPh}_3$, AsPh_3 , SbPh_3) have been presented. The band assigned to the $\nu_{\text{Rh-Rh}}$ mode occurs between 264 and 302 cm^{-1} and the $\nu_{\text{Rh-L}}$ band appears in the range 258 to 366 cm^{-1} . The observed shifts in bands upon oxidation are discussed. [62] An interest in potential multifunctional anti-cancer complexes has prompted an investigation of the species $\text{Rh}_2(\mu\text{-O}_2\text{CR})_4\text{L}_2$ ($\text{R} = \text{Me}$, Et , MeOCH_2 ; $\text{L} = N\text{-}[2\text{-(dimethylamino)alkyl}]$ acridine-4-carbox-amide in which the alkyl group is ethyl, butyl or hexyl). For the hexyl derivative, a structural characterisation of $\text{Rh}_2(\mu\text{-O}_2\text{CMe})_4\text{L}_2$, (43), reveals that the acridine units stack through the crystal. [63]

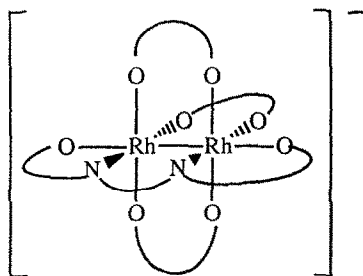


(43)

The ligand H_2L , (44), has been prepared and its reaction with $\text{Rh}_2(\text{O}_2\text{CMe})_4$ leads to the complex anion $[\text{Rh}_2(\text{O}_2\text{CMe})_3\text{L}]^-$ the structure of which is represented schematically by (45). The anion has been characterised by ^1H NMR, UV-VIS spectroscopy and electrochemically. In the UV-VIS spectrum exhibits MLCT absorption bands. [64]



(44)



(45)

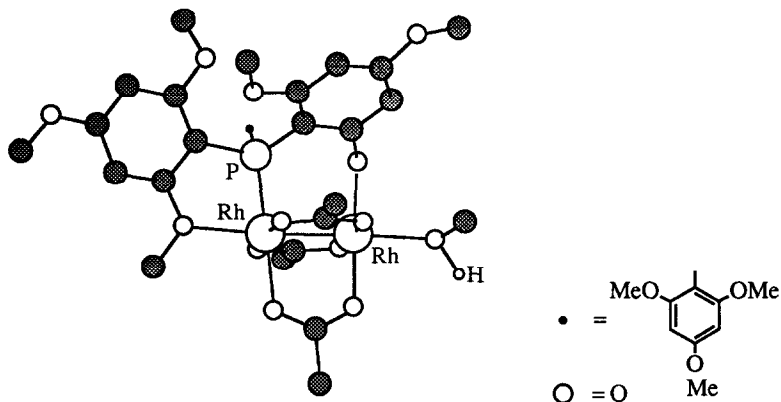
5.3.4 Complexes with sulphur donor ligands

The reaction of $\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$ with $\text{Na}(\text{S}_2\text{CNR}_2)$ ($\text{R} = \text{Me}, \text{Et}$) in benzene under reflux for 4 hr is reported to lead to the square planar rhodium(II) complexes $\text{Rh}(\text{S}_2\text{CNMe}_2)_2$ (orange, 83% yield) and $\text{Rh}(\text{S}_2\text{CNEt}_2)_2$ (yellow-orange, 74% yield). When the same reagents are combined in benzene at room temperature and stirred for 6 hr, square pyramidal $\text{Rh}(\text{S}_2\text{CNR}_2)_2(\text{PPh}_3)$ ($\text{R} = \text{Me}, \text{Et}$) is formed. An axial site for the phosphine ligand is proposed. Infrared, electronic, ^1H NMR and ESR spectroscopic data are reported for the complexes. Magnetic moments have been measured: $\mu_{\text{eff}} = 2.10, 2.02, 2.08$ and 2.12 B.M. for $\text{Rh}(\text{S}_2\text{CNMe}_2)_2(\text{PPh}_3)$, $\text{Rh}(\text{S}_2\text{CNEt}_2)_2(\text{PPh}_3)$, $\text{Rh}(\text{S}_2\text{CNMe}_2)_2$ and $\text{Rh}(\text{S}_2\text{CNEt}_2)_2$ respectively. [65]

5.3.5 Complexes with mixed donor sets

The reaction of $\text{Rh}_2(\mu\text{-O}_2\text{CMe})_4(\text{MeOH})_2$ with *tris*(2,4,6-trimethoxyphenyl)phosphine, L, yields complex (46) in which oxidative addition of one O-C_{Me} bond of L has occurred to give an *O,P*-bridging ligand. The mode of coordination has been confirmed crystallographically; selected distances are $\text{Rh-Rh} = 2.4228$ (3) Å, $\text{Rh-O}_{\text{metallated}} = 2.048$ (2) Å. Restricted by the metallocyclic unit, the phosphorus atom exhibits significant angular distortion. Electronic and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data for (46) are reported in addition electrochemical results. [66]

Dependent upon the molar ratio of reagents, reaction of $\text{PhCH}_2\text{SCH}_2\text{PPh}_2$, L, with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ generates either the Vaska-type rhodium(I) complex *trans*- $\text{RhCl}(\text{CO})(\text{L-P})$ or the ionic species $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-L})][\text{RhCl}_2(\text{CO})_2]$. The tetraphenylborate salt of $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-L})]^+$ is produced by treating $[\text{RhCl}_2(\text{CO})_2]^-$ with an equivalent of L in the presence of $\text{Na}[\text{BPh}_4]$. In the presence of HCl, $\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-L})_2$ is formed. The latter has been structurally characterised and exhibits two *cis*-bridging ligands; $\text{Rh-Rh} = 2.733$ (3) Å, $\text{Rh-S} = 2.390$ (3) Å, $\text{Rh-P} = 2.291$ (1) Å. [67]



(46)

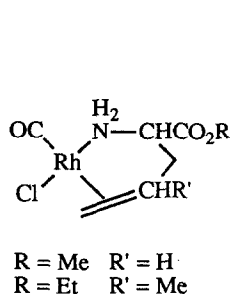
5.4 RHODIUM(I)

5.4.1 Complexes with nitrogen donor ligands

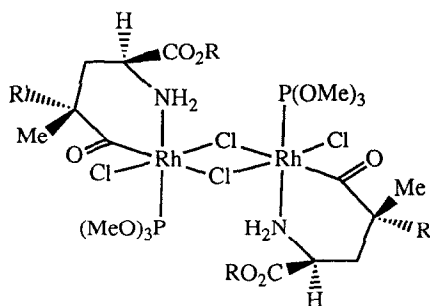
The kinetics of the displacement of the ClO_4 group in $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)$ by RCN (see Table 3 for R) have been investigated; a mechanism for the reaction has been proposed. The reaction is first order with respect to each of the rhodium(I) substrate and the incoming nitrile; kinetic data are summarised in Table 3. [68]

Table 3 Kinetic data for the reaction of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)$ with RCN (k = overall rate constant at 10°C)			
R	$k / \text{M}^{-1}\text{s}^{-1}$	$\Delta H^\ddagger / \text{kcal mol}^{-1}$	$\Delta S^\ddagger / \text{cal deg}^{-1}\text{mol}^{-1}$
Me	395 ± 32	11 ± 1.4	-8.7 ± 1.4
$\text{CH}_2=\text{CHCH}_2$	564 ± 51	11 ± 0.9	-8.4 ± 0.4
$\text{CH}_2=\text{CH}$	4900 ± 420	4.4 ± 0.3	-26 ± 1.0
$\text{CH}_2=\text{CMe}$	5370 ± 620	4.6 ± 0.2	-25 ± 0.8
$\text{MeCH}=\text{CH}$	10010 ± 1010	2.4 ± 0.2	-32 ± 0.8

The rhodium(I) dimer $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ or the rhodium(III) complex $[\text{Cp}^*\text{RhCl}_2]_2$ reacts with C-allylglycine esters to give 4-coordinate rhodium(I) or rhodium(III) complexes with chelating organic ligands. The structure of the tetrafluoroborate salt of $[\text{Cp}^*\text{IrCl}(\eta^2, \sigma\text{-CH}_2=\text{CHCH}_2\text{CH}(\text{CO}_2\text{Me})\text{NH}_2\text{-N})]^+$ was described in Section 4.4.1 of the preceding Chapter. Addition of HCl and $\text{P}(\text{OMe})_3$ to (47) occurs regiospecifically and stereoselectively to give a dimeric species (48), the structure of which has been confirmed crystallographically for $\text{R} = \text{Et}$ and $\text{R}' = \text{Me}$; $\text{Rh-Cl}_{\text{terminal}} = 2.330$ (3) Å, $\text{Rh-Cl}_{\mu} = 2.363$ (2) Å, $\text{Rh-N} = 2.133$ (7) Å, $\text{Rh-P} = 2.233$ (3) Å. [69]



(47)

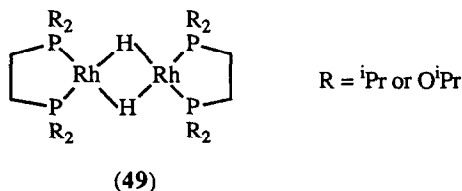


(48)

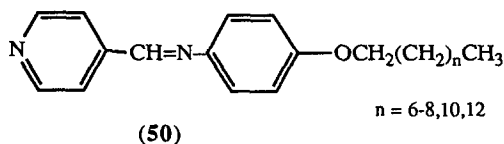
Members of a series of complexes incorporating bridging imido or amido groups in A-frame dirhodium complexes have been prepared and characterised. $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-L})_2$ ($\text{L} = \text{dppm}$ or dmpm) reacts with LiNHR ($\text{R} = \text{Me}$, Ph , 4-MeO- C_6H_4 , 4-Me- C_6H_4 , 2-Me- C_6H_4 , 2,6-Me $_2$ - C_6H_3 , 4-F- C_6H_4 , 4-Br- C_6H_4 , 4-NO $_2$ - C_6H_4) to yield $\text{Rh}_2(\mu\text{-NR})(\text{CO})_2\text{L}_2$, its tautomer $\text{Rh}_2(\mu\text{-NHR})(\text{CO})_2\text{L}(\text{L-H})$ or an equilibrium mixture of the two depending upon the electronic properties of R . The hydrolysis of these species leads to the corresponding oxo-bridged complexes. The structures of $\text{Rh}_2(\mu\text{-N}(4\text{-NO}_2\text{-C}_6\text{H}_4))(\text{CO})_2(\mu\text{-dppm})_2$, $\text{Rh}_2(\mu\text{-NHMe})(\text{CO})_2(\mu\text{-dppm})\{\mu\text{-}(\text{dppm-H})\}$ and $\text{Rh}_2(\mu\text{-O})(\text{CO})_2(\mu\text{-dppm})_2$ have been determined crystallographically; each rhodium atom in each complex carries one terminal carbonyl ligand and the two ligands per complex are mutually *cis*. In going from $\text{Rh}_2(\mu\text{-N}(4\text{-NO}_2\text{-C}_6\text{H}_4))(\text{CO})_2(\mu\text{-dppm})_2$ to $\text{Rh}_2(\mu\text{-NHMe})(\text{CO})_2(\mu\text{-dppm})\{\mu\text{-}(\text{dppm-H})\}$, the Rh-N distance lengthens from 2.042 (2) Å to 2.098 (5) Å. [70] Results from the same authors describe the addition of CH_2Cl_2 or MeI to the phenyl substituent of the bridging *N*-donor ligand in the tautomers $\text{Rh}_2\{\mu\text{-N}(4\text{-Me-C}_6\text{H}_4)\}(\text{CO})_2(\mu\text{-dppm})_2$ and $\text{Rh}_2\{\mu\text{-NH}(4\text{-Me-C}_6\text{H}_4)\}(\text{CO})_2(\mu\text{-dppm})\{\mu\text{-}(\text{dppm-H})\}$. For example, in CH_2Cl_2 , $[\text{Rh}_2\{\mu\text{-N}=(4\text{-Me-4-CH}_2\text{Cl-C}_6\text{H}_4)\}(\text{CO})_2(\mu\text{-dppm})_2][\text{Cl}]$ forms slowly. This ionic complex has been characterised both by NMR spectroscopy and by single crystal X-ray diffraction. Selected bond parameters are $\text{Rh-N} = 2.05$ (1), 2.04 (1) Å, $\text{N-C}_{\text{ipso}} = 1.29$ (2) Å and $\angle \text{RhNRh} = 97.3$ (4)°. [71]

Treatment of the dirhodium(I) hydride (49) with a variety of aldimines or with ketimine or isoquinoline gives products with bridging amido groups. For example, when the reacting aldimine

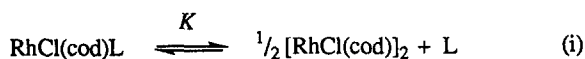
is PhCH=NPh , the product contains a $\mu\text{-NPh(CH}_2\text{Ph)}$ group. Synthetic work is complimented by NMR spectroscopic data for the products and kinetic data for their formation. [72]

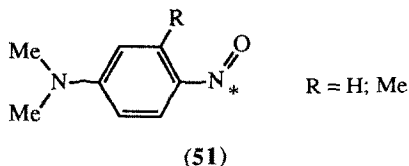


Twenty-seven new rhodium(I) complexes containing *N*-iminophosphorane ligands have been prepared by the reaction of $[\text{RhL}_2\text{Cl}]_2$ ($\text{L}_2 = \text{cod}$ or $\text{L} = \text{CO}$) with $\text{R}_3\text{P=NR}'$ (various substituents). In solution and for $\text{L}_2 = \text{cod}$, a given product lies in equilibrium with its respective precursors; values of K depend upon R and R' . The structure of $\text{Rh}(\text{cod})\text{Cl}\{\text{Et}_3\text{P=N(C}_6\text{H}_4\text{-4-Me)}\}$ has been determined and pertinent bond parameters are $\text{Rh-N} = 2.142(3) \text{ \AA}$, $\text{N-P} = 1.608(3) \text{ \AA}$, $\angle \text{RhNP} = 121.0^\circ$. [73]

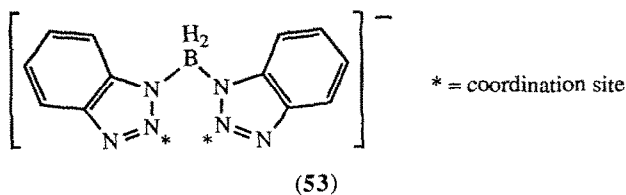
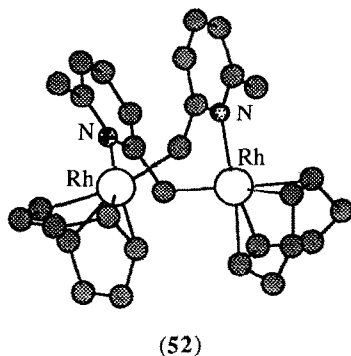


The complexes $\text{RhCl}(\text{cod})\text{L}$ in which $\text{L} = (50)$ have been synthesised and characterised by infrared and ^1H and ^{31}P NMR spectroscopy. Treatment of $\text{RhCl}(\text{cod})\text{L}$ with carbon monoxide results in exchange of the cod ligand for two CO ligands. The $\text{RhCl}(\text{CO})_2\text{L}$ complexes exhibit mesogenic properties and these experimental results illustrate the formation of liquid crystalline materials which are produced by the coordination of a ligand which itself is non-mesogenic. [74] $\text{RhCl}(\text{cod})\text{L}$ for $\text{L} = 1\text{-NMe}_2\text{-3-R-4-NO-C}_6\text{H}_3$ ($R = \text{H or Me}$) has been reported. ^1H and ^{13}C NMR spectroscopic data are presented to compliment a structural study of the complex, (51), for $R = \text{Me}$; selected structural data are $\text{Rh-N} = 2.050(4) \text{ \AA}$, $\angle \text{RhNC}_{\text{ipso}} = 124.5(3)^\circ$, $\angle \text{RhNO} = 117.1(2)^\circ$. The NMR spectroscopic data have been used to determine dissociation constants K for the reaction in equation (i); for $R = \text{Me}$, $K_{259\text{ K}} = (3.03 \pm 0.15) \times 10^{-3} \text{ mol}^{-1/2} \text{ kg}^{-1/2}$ while for $R = \text{H}$, the high stability of the complex precludes the determination of K by an NMR spectroscopic method. [75]





Substituted pyridines, 2-, 3- or 4-R-py, HL, in which R is carboxaldehyde react with the rhodium(III) complex $\text{Cp}^*\text{RhMe}_2(\text{Me}_2\text{SO})$ to give $\text{Cp}^*\text{Rh}(\text{Me})(\text{CO})(\text{HL})$. Further reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ leads to a mixed Rh(I)/Rh(III) complex. In this, the pyridine molecule bridges between the two rhodium centres being C-bonded to rhodium(III) and N-bonded to rhodium(I). A structural study of $\text{Cp}^*\text{Rh}(\text{Me})(\text{CO})(\text{L})\text{Rh}(\text{CO})_2\text{Cl}$ (HL = 3-R-py); Rh-N = 2.110 (4) and 2.104 (15) Å for two inequivalent molecules in the unit cell and Rh----Rh = 5.89 Å. [76] $[\text{Rh}(\text{cod})\text{Cl}]_2$ reacts with LiL (LiL = 2-Me-6- CH_2Li -py) and generates complex (52) in which the dirhodium(I) framework is supported by two bridging ligands, each C,N-bonded. (An analogous iridium complex has also been described; see the previous Chapter). Complex (52) has been structurally characterised and selected distances are Rh-N = 2.118 (2) Å and Rh---Rh = 3.6806 (3) Å. [77]



The reaction of the iridium(I) complex $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with KL where $\text{L}^- = (53)$ was described in Section 4.4.1 of the previous Chapter; the analogous rhodium(I) complex has also been synthesised along with *trans*-(Ph_3P) $_2\text{RhL}(\text{CS})$. [78]

The heterometallic complexes $(\text{Ph}_3\text{P})_2(\text{CO})(\text{H})\text{M}(\mu\text{-L})_2\text{M}'(\text{dialkene})$ ($\text{M} = \text{Ru}$ or Os ; $\text{M}' = \text{Rh}$ or Ir ; $\text{H}_2\text{L} = 2,2'$ -bi-imidazole or 2,2'-bibenzimidazole; dialken = cod or tetrafluorbenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene) have been synthesised by the reaction of $\text{M}(\text{H})(\text{CO})(\text{HL})(\text{PPh}_3)_2$ with $[\text{M}'(\text{dialkene})(\mu\text{-OMe})]_2$. For $\text{H}_2\text{L} = 2,2'$ -bi-imidazole, the complex $(\text{Ph}_3\text{P})_2(\text{CO})(\text{H})\text{Ru}(\mu\text{-L})_2\text{M}'(\text{cod})$ has been structurally characterised. The rhodium(I) atom is in a square planar coordination environment; the two bi-imidazolate rings are mutually twisted by 2.6° . Important distances are $\text{Rh-N} = 2.127$ (5) and 2.134 (5) Å, $\text{Ru-N}_{\text{trans-H}} = 2.283$ (5) Å, $\text{Ru-N}_{\text{trans-CO}} = 2.180$ (5) Å, $\text{Rh}\cdots\text{Ru} = 5.579$ (2) Å. [79]

5.4.2 Complexes with phosphorus donor ligands

The *bis*(triphenylphosphine) rhodium(I) complex *trans*- $\text{Rh}(\text{CO})(\text{I})(\text{PPh}_3)_2$ has been the subject of a single crystal structure determination. For the square planar rhodium atom, $\text{Rh-P} = 2.336$ (2) and 2.316 (2) Å and $\text{Rh-I} = 2.683$ (1) Å. [80]

The oxidative addition of MeI to $\text{Rh}(\text{Sacac})(\text{CO})(\text{PX}_3)$ has been investigated for $\text{X} = \text{Ph}$, 4- $\text{Cl-C}_6\text{H}_4$, 4- $\text{MeO-C}_6\text{H}_4$ or *c*- C_6H_{11} . The reactions follow second order kinetics and it is proposed that the path goes via a rhodium(III) alkyl derivative before forming the final acyl complex. The reaction rate is influenced by the solvent and by the steric and electronic properties of the phosphine or phosphite ligand. For PPh_3 , values of k_{obs} as a function of solvent are collected in Table 4. [81] The flash photolysis of $\text{RhCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{PPh}_3$, $\text{P}\{4\text{-Me-C}_6\text{H}_4\}_3$ or PMe_3) is reported to lead to a tricoordinate complex RhClL_2 . The reactivity of this intermediate has been investigated. [82]

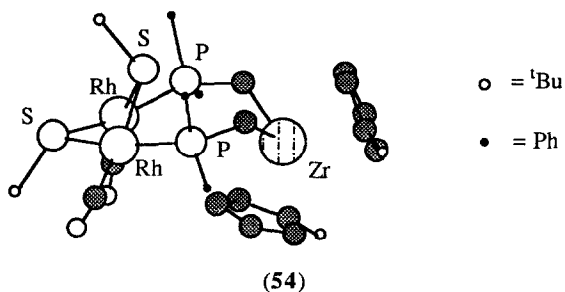
Table 4 k_{obs} for the reaction of MeI with $\text{Rh}(\text{Sacac})(\text{CO})(\text{PPh}_3)$ as a function of solvent

Solvent	$k_{\text{obs}} \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
toluene	2.17 (4)
ethylacetate	5.47 (5)
chlorobenzene	8.36 (6)
acetone	30.1
1,2-dichloroethane	56.0 (7)
acetonitrile	82.7 (7)

The preparation and characterisation of $\text{RhX}(\text{P}^i\text{Pr}_3)_2(\text{CNR})$ ($\text{X} = \text{Cl}$ or I ; $\text{R} = \text{Me}_3\text{CCH}_2$ or 2,6- $\text{Me}_2\text{-C}_6\text{H}_4$) and *cis*- $\text{Rh}(\text{Cl}(\text{iPr}_2\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)(\text{CNCH}_2\text{CMe}_3))$ have been reported. Catalytic studies of the isocyanide insertion into aromatic C-H bonds have also been described; it has been

noted that the rate for the chloro complex is greater than that for the iodo complex and the presence of the chelating *bis*(phosphine) inhibits the reaction. [83] The results of a $^{31}\text{P}\{^1\text{H}\}$ DNMR spectroscopic study of *trans*-($^t\text{Bu}_2\text{PhP}$) $_2\text{M}(\text{CO})\text{Cl}$ ($\text{M} = \text{Ir}$ or Rh) has been reported. The spectra show decoalescence of each complex into four diastereomers; details were summarised in Section 4.4.2 of the previous Chapter. [84] The complex $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{NCMe})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ has been crystallographically studied; $\text{Rh-P} = 2.340$ (1), 2.336 (1) Å and $\text{Rh-N} = 2.048$ (3) Å. [85] The reaction of $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})][\text{HC}(\text{SO}_2\text{CF}_3)_2]$ with $[\text{XM}_{12}\text{O}_{40}]^{n-}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{X} = \text{Si}, \text{P}$) in an acetonitrile-ethanol solution generates *trans*- $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{MeCN})]_n[\text{XM}_{12}\text{O}_{40}]$ which, upon heating, loses acetonitrile. The oxometallate complexes have been characterised by IR, NMR and X-ray absorption spectroscopy; the cations $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{MeCN})]^+$ or $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})]^+$ respectively are stabilised within the metallate lattice. The activity of the complexes as catalysts for alkene isomerisation and hydroformylation reactions has also been investigated. [85]

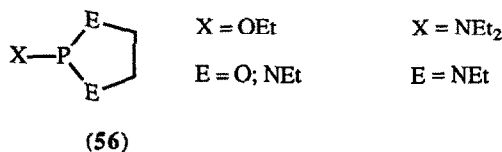
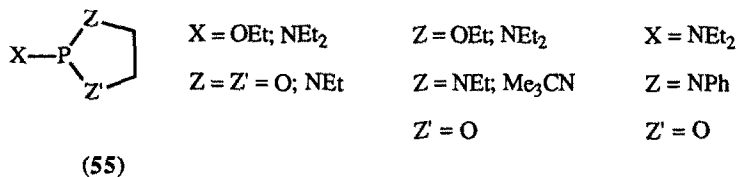
An interesting dirhodium(I) complex in which the Rh_2 -unit is bridged by a zirconium containing ligand has been described. The complex $\{\mu\text{-Cp}''_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\}\text{Rh}_2(\text{CO})_2\{\mu\text{-S}^t\text{Bu}\}_2$, (**54**), has been prepared by the reaction of $\text{Cp}''_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2$ with $\text{Rh}_2(\text{CO})_4\{\mu\text{-S}^t\text{Bu}\}_2$ ($\text{Cp}'' = \eta^5\text{-}^t\text{BuC}_5\text{H}_4$). A related complex cation $[\text{Cp}''_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2\text{Rh}(\text{cod})]^+$ has also been synthesised. The molecular structure of (**54**) confirms the expected square planar nature of each rhodium(I) atom; the zirconium atom resides in a pseudo-tetrahedral coordination sphere. Pertinent bond parameters are $\text{Rh-P} = 2.277$ (1), 2.275 (1) Å, $\text{Rh-S} = 2.356$ (1), 2.394 (1), 2.408 (1), 2.365 (1) Å, $\angle \text{RhSRh} = 80.28$ (3), 78.68 (3)°. Complex (**54**) has been assessed for its catalytic activity in the hydroformylation of hex-1-ene; a high selectivity of conversion has been achieved. [86]



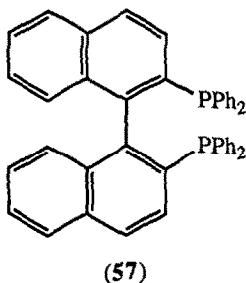
Rhodium(I) complexes of type $\text{Rh}(\text{acac})(\text{CO})\text{L}$ where $\text{L} = (\text{55})$, (**56**), $\text{P}(\text{NEt}_2)_3$ or $\text{P}(\text{NEt}_2)(\text{OEt})_2$ have been prepared and characterised by ^{31}P NMR spectroscopy; the chemical shift of the ^{31}P NMR spectroscopic resonance is a function of the electronegativity of the *P*-substituent. A single crystal X-ray analysis of one complex $\text{Rh}(\text{acac})(\text{CO})\text{L}$ for $\text{L} = (\text{55})$ and $\text{X} = \text{NEt}_2$, $\text{Z} = \text{NEt}$, $\text{Z}' = \text{O}$ has been carried out. [87]

Reactions of the functionalised phosphine ligands $(\text{Me}_2\text{CH})_2\text{PCH}_2\text{CH}_2\text{R}$ ($\text{R} = \text{NMe}_2$ or OMe) with $[\text{RhCl}(\text{C}_6\text{H}_{14})]_2$ leads to the square planar complexes $\text{RhCl}\{(\text{Me}_2\text{CH})_2\text{PCH}_2\text{CH}_2\text{R}\}_2$ in which one phosphine ligand is in a chelating mode and one is monodentate. The reactions of

$\text{RhCl}\{(\text{Me}_2\text{CH})_2\text{PCH}_2\text{CH}_2\text{R}\}_2$ with carbon monoxide, ethene and alkynes have been described. [88] The dinuclear complex $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ reacts either with two equivalents of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$, L, in dmf or ethanol to give $\text{Rh}(\text{CO})\text{ClL}_2$ and $[\text{Rh}(\text{CO})\text{ClL}_2]_n$ or with one equivalent of L to yield $[\text{Rh}(\text{CO})_2\text{L}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$. In $\text{Rh}(\text{CO})\text{ClL}_2$ and $[\text{Rh}(\text{CO})_2\text{L}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$, the ligand is *P*-bonded whereas in $[\text{Rh}(\text{CO})\text{ClL}_2]_n$, both *N*- and *P*-coordination are observed. [89]

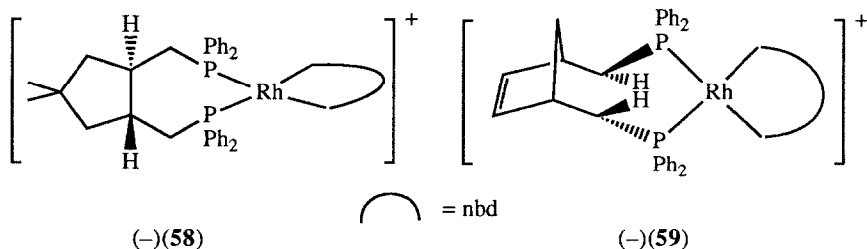


The dppe containing complex $[\text{Rh}(\text{dppe})_2][\text{BF}_4]$ catalyses the oxygenation of alkenes and alkanes using oxidants such as perchlorate ion. [90] The phosphine substituted ferrocene ligand dppf chelates to rhodium to give the red complex $[\text{Rh}(\text{dppf})_2][\text{BF}_4]$; the preparation, structure and solution properties of the analogous iridium complex were described in Chapter 4. Under conditions of reflux in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ solution, the red complex transforms to a yellow species. The red and yellow complexes are proposed to be dimorphic forms of the same compound. [91]



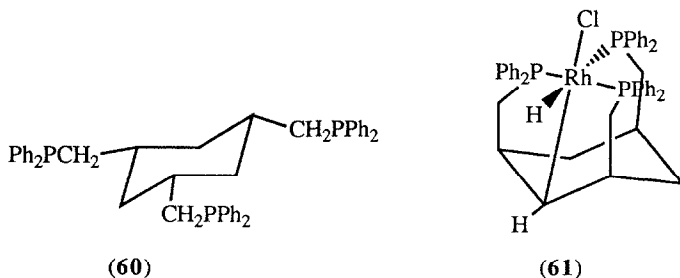
Rhodium(I) complexes incorporating the chiral ligand (57) have been shown to catalyse the isomerisation of diethylgeranylamine or diethylnerylamine with high enantioselectivity. A mechanism for the process has been proposed. [92] For the enantioselective hydrogenation of cinnamic acid derivatives (low pH in aqueous HBF_4), an active catalyst is $[(\text{MeCHP}(\text{HMe}_2\text{N}-4-\text{C}_6\text{H}_4)_2\text{CH}_2\text{CHP}(\text{C}_6\text{H}_4-4-\text{NMe}_2\text{H})_2\text{Me})\text{Rh}(\text{nbd})]^{5+}$ (nbd = norbornadiene). Quaternisation of the

Me₂N-substituents by protonation allows the design of a recyclable catalyst; a mechanism for the catalytic cycle has been proposed. [93] The rhodium(I) complexes (–)(**58**), (–)(**59**) and (+)(**59**) have been prepared and the impregnation of barium sulphate, cellulose, silica gel, aluminium oxide, silver nitride and charcoal supports with these complexes produces catalysts which are active for the hydrogenation of (*Z*)- α -*N*-acetamidocinnamic acid in aqueous sodium hydroxide. The activity decreases after repeated use of the catalysts. [94]



The cationic complex $\text{Rh}(\text{R,R-L})(\text{MeOH})_2]^+$ ($\text{L} = \text{Ph}(\text{C}_6\text{H}_4-2\text{-OMe})\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4-2\text{-OMe})\text{Ph}$) is an asymmetric hydrogenation catalyst for enamides. It reacts with methyl(*Z*)- β -propyl- α -acetamidoacrylate, L' , to give $[\text{RhLL}']^+$ for which the binding constant has been determined ($1.4 \times 10^4 \text{ M}^{-1}$ at 25°C). The tetrafluoroborate salt of the adduct has been structurally characterised and pertinent bond parameters are $\text{Rh-P} = 2.272$ (6), 2.239 (6) Å, $\text{Rh-O}_\text{L}' = 2.108$ (13) Å, $\angle\text{PRhP} = 83.1$ (2)°. [95]

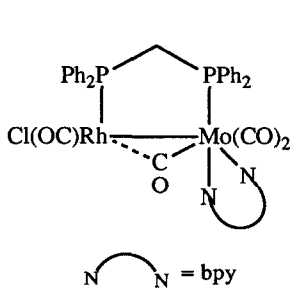
The reaction of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with ligand (**60**) leads to complex (**61**) via C-H activation of the cyclohexyl ring. Complex (**61**) reacts with CO with loss of the Rh-C_{ring} bond. The complexes have been characterised by NMR and IR spectroscopy. [96]



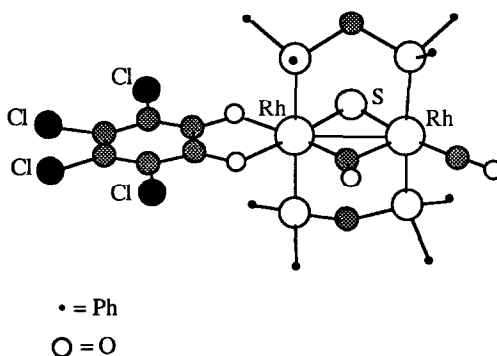
The ligand $(\text{Me}_2\text{OPO})_2\text{H}$ incorporates an acidic hydrogen atom bound between two oxygen atoms. It can thus function as a bidentate *P*-donor. This is confirmed after determination of the structure of $\{(\text{Me}_2\text{OPO})_2\text{H}\}_2\text{RhPPh}_2\text{Me}$; the complex has a square pyramidal array of donor atoms with the PPh_2Me ligand in the axial site with the phenyl rings in non-equivalent positions. The

conformations of the two chelating ligands are not equivalent and this is explained in terms of the steric requirements of the unique phosphine ligand. [97]

The A-frame complexes $\text{Rh}_2(\mu\text{-NR})(\text{CO})_2\text{L}_2$ ($\text{L} = \text{dppm}$ or dmpm ; $\text{R} = \text{Me}$, Ph , $4\text{-MeO-C}_6\text{H}_4$, $4\text{-Me-C}_6\text{H}_4$, $2\text{-Me-C}_6\text{H}_4$, $2,6\text{-Me}_2\text{-C}_6\text{H}_3$, $4\text{-F-C}_6\text{H}_4$, $4\text{-Br-C}_6\text{H}_4$, $4\text{-NO}_2\text{-C}_6\text{H}_4$) and its tautomer $\text{Rh}_2(\mu\text{-NHR})(\text{CO})_2\text{L}(\text{L-H})$ were described in Section 5.4.1. [70] The related species $\text{Rh}_2\{\mu\text{-N}(4\text{-Me-C}_6\text{H}_4)\}(\text{CO})_2(\mu\text{-dppm})_2$ and $\text{Rh}_2\{\mu\text{-NH}(4\text{-Me-C}_6\text{H}_4)\}(\text{CO})_2(\mu\text{-dppm})\{\mu\text{-(dppm-H)}\}$ were also discussed. [71] The reaction of $\text{Mo}(\text{CO})_3(\text{N,N'-bpy})(\text{dppm-P})$ with $[\text{RhCl}(\text{nbd})]_2$ has been investigated. A blue-violet complex results for which, based on IR and ^{31}P NMR spectroscopic data, structure (62) is proposed. [98] The A-frame complex $\text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2(\mu\text{-S})$ reacts with $1,2\text{-(O)}_2\text{-C}_6\text{Cl}_4$ to give complex (63) which has been structurally characterised. The Rh-Rh distances in (63) is 2.966 \AA compared with 3.154 \AA in the starting complex. [99] In related work, the complexes $\text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2(\mu\text{-X})$ in which $\text{X} = \text{S}$, SO or SO_2 have been prepared by insertion of X into $\text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2$. The products have been characterised by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and for $\text{X} = \text{SO}$, $2\text{D-}(^{31}\text{P}, ^{31}\text{P})$ COSY results have been reported. [100] The reaction of RSiH_3 with $\text{Rh}_2(\text{CO})_2(\mu\text{-H})_2(\mu\text{-L})_2$ ($\text{L} = \text{dppm}$ or $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$; $\text{R} = \text{}^n\text{C}_6\text{H}_{13}$, Et , Ph) gives the complexes $\text{Rh}_2(\mu\text{-SiHR})_2(\text{CO})_2(\mu\text{-L})_2$ which have been characterised by ^1H and ^{31}P NMR and IR spectroscopy. The molecular structures of $\text{Rh}_2(\mu\text{-SiHPh})_2(\text{CO})_2(\mu\text{-dppm})_2$ and $\text{Rh}_2(\mu\text{-SiHEt})_2(\text{CO})_2(\mu\text{-dppm})_2$ have been presented and for the ethyl derivative relevant distances and angles are Rh-Rh = $2.814 (1) \text{ \AA}$, Rh-Si = $2.354 (2)$, $2.342 (2) \text{ \AA}$, Rh-P = $2.363 (2)$, $2.367 (2) \text{ \AA}$, $\angle\text{RhSiRh } 73.62 (6)^\circ$. [101]



(62)



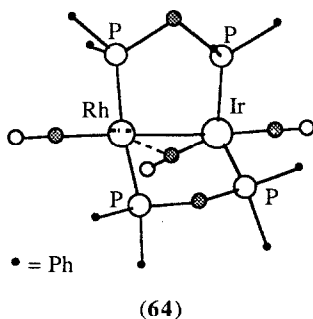
(63)

The dication $[\text{Rh}_2\text{L}_2(\mu\text{-dppm})_2]^{2+}$ ($\text{L} = 2,5\text{-diisocyano-2,5-dimethylhexane}$) has been synthesised and its optical spectral properties reported. An intense absorption at 595 nm has been assigned to the $^1\text{A}_{1g}[(d\sigma^*)^2] \rightarrow ^1\text{B}_{1u}[(d\sigma^*)^1(p\sigma)^1]$ transition; fluorescence (677 nm) emanates from the $^1\text{B}_{1u}$ excited state. Mechanisms of the photoreactions are discussed. [102]

The reaction of $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ with $(\text{PhO})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OPh})_2$ generates a trinuclear complex $\text{Rh}_3(\mu\text{-Cl})_3(\text{CO})_4\{\mu\text{-(PhO)}_2\text{PCH}_2\text{CH}_2\text{P}(\text{OPh})_2\}$ for which the results of a single crystal

X-ray diffraction study have been reported. The Rh_3 -framework is triangular with three bridging chlorine atoms supporting the unit; Rh-Rh distances lie in the range 3.2023 (3) - 3.4627 (4) Å, the differences being due to the fact that one edge is also bridged by the *bis*(phosphine) ligand. The structure is compared with that of $\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2$ in which one dppm ligand is replaced by a $\text{Rh}(\text{CO})_2\text{Cl}_2$ -unit. [103]

A series of dimetallic RhM -complexes has been described in which, in a formal sense, a $\text{M} \rightarrow \text{Rh}$ dative bond may be drawn. For example, in $\text{Rh}(\text{CO})(\mu\text{-dppm})_2\text{Re}(\text{CO})_3$, oxidation states of Rh(I) and Re(-I) are assigned. This complex reacts with H_2S , HSEt or HSPh to give $\text{Rh}(\text{CO})(\mu\text{-dppm})_2(\mu\text{-S})\text{Re}(\text{CO})_3$, $\text{Rh}(\text{CO})(\mu\text{-dppm})_2(\mu\text{-H})(\mu\text{-SEt})\text{Re}(\text{CO})_3$ or $\text{Rh}(\text{CO})(\mu\text{-dppm})_2(\mu\text{-H})(\mu\text{-SPh})\text{Re}(\text{CO})_3$ respectively. Spectroscopic data for the complexes have been reported along with the molecular structure of $\text{Rh}(\text{CO})(\mu\text{-dppm})_2(\mu\text{-H})(\mu\text{-SEt})\text{Re}(\text{CO})_3$; pertinent distances are $\text{Rh} \cdots \text{Re} = 2.9697$ (8) Å, $\text{Rh-S} = 2.521$ (3) Å, $\text{Re-S} = 2.505$ (3) Å, $\text{Rh-P} = 2.287$ (3), 2.299 (3) Å, $\text{Rh-H} = 1.4$ (1) Å and $\text{Re-H} = 2.1$ (1) Å. [104] Related to this work is a study of $\text{RhIrCl}_2(\text{CO})_2(\mu\text{-dppm})_2$ in which an $\text{Ir}(-\text{I}) \rightarrow \text{Rh}(\text{I})$ bond is assigned. Reduction with NaBH_4 yields $\text{RhIrH}(\mu\text{-H})(\text{CO})_2(\mu\text{-dppm})_2$ while reaction with carbon monoxide gives $\text{RhIr}(\text{CO})_3(\mu\text{-dppm})_2$, (64); the two new products may be interconverted by treatment with CO or H_2 respectively. The stepwise diprotonation of $\text{RhIr}(\text{CO})_3(\mu\text{-dppm})_2$ has been described. The molecular structure of (64) illustrates a distorted A-frame type complex with the desire for the rhodium(I) and iridium(-I) atoms to adopt square planar and tetrahedral geometries respectively causing the observed structural perturbation; $\text{Rh-P} = 2.312$ (2), 2.295 (2) Å, $\text{Ir-P} = 2.309$ (2), 2.321 (2) Å, $\text{Ir-Rh} = 2.7722$ (7) Å. [105] A general method of preparing A-frame $\text{M}(-\text{I}) \rightarrow \text{Rh}(\text{I})$ containing complexes from $\text{Rh}_2\text{Cl}_2(\mu\text{-dppm})_2$ has been established. The systems characterised, two structurally, are $\text{RhCo}(\text{CO})_3(\mu\text{-dppm})_2$, $\text{RhMn}(\text{CO})_4(\mu\text{-dppm})_2$, (the Rh-Mn distance has been determined to be 2.8428 (8) Å), $\text{RhRe}(\text{CO})_4(\mu\text{-dppm})_2$, ($\text{Rh-Re} = 2.7919$ (6) Å), $\text{Rh}(\text{CpFe})(\mu\text{-CO})(\mu\text{-dppm})_2$, $\text{RhFe}(\mu\text{-H})(\text{CO})_3(\mu\text{-dppm})_2$, $\text{RhRu}(\mu\text{-H})(\text{CO})_3(\mu\text{-dppm})_2$, $\text{RhOs}(\mu\text{-H})(\text{CO})_3(\mu\text{-dppm})_2$, $\text{RhCr}(\mu\text{-H})(\text{CO})_4(\mu\text{-dppm})_2$, $\text{RhW}(\mu\text{-H})(\text{CO})_4(\mu\text{-dppm})_2$ and $\text{Rh}(\text{CpMo})(\text{CO})(\mu\text{-CO})(\mu\text{-dppm})_2$. [106]

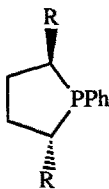


The reaction of hydrated rhodium(III) chloride with cobalt(II) chloride and dppm under a flow of carbon monoxide followed by treatment with NaBH_4 leads to $\text{Rh}(\text{CO})(\mu\text{-CO})(\mu\text{-$

$\text{dppm})_2\text{Co}(\text{CO})$ which is isostructural with its dirhodium analogue. The reactivity of the mixed metal complex with CHCl_3 , HgCl_2 , I_2 , S_8 , Ph_2PH and H^+ has been investigated. [107]

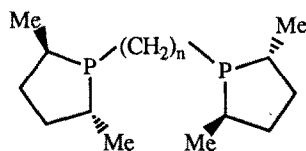
The structural characterisation of $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{RhCl}(\text{C}_2\text{H}_4)$ has been carried out. The alkene ligand occupied two sites of the octahedral coordination sphere; $\text{Rh}-\text{P} = 2.222$ (7), 2.352 (6), 2.371 (6) Å. Related complexes have been synthesised and a detailed investigation of alkene hydrogenation and hydroformylation reactions discussed. [108] The reaction of the rhodium(III) complex $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{RhMe}_3$ with carbon monoxide leads to $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\text{CO})\text{Me}$ and the concomitant formation of Me_2CO . Further treatment with CO results in methyl migration and the formation of $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}\{\text{C}(\text{O})\text{Me}\}(\text{CO})$. The *tris*(phosphine) ligand is restricted to a *mer*-configuration and this has been confirmed crystallographically for $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\text{CO})\text{Me}$. The carbonyl ligand lies in the equatorial plane of the trigonal bipyramidal array of donor atoms; $\text{Rh}=\text{P} = 2.3683$ (12), 2.3446 (14), 2.3135 (14) Å, $\angle\text{P}_{\text{equat}}\text{RhP}_{\text{equat}} = 90.80$ (5)°, $\angle\text{P}_{\text{axial}}\text{RhP}_{\text{equat}} = 87.14$ (5)°, $\angle\text{P}_{\text{equat}}\text{RhP}_{\text{equat}} = 89.28$ (5)°. [109] For the ligand $\text{L} = \text{N}\{\text{CH}_2\text{CH}_2\text{PPh}_2\}_3$, reactions of the complex cations $[\text{LRh}=\text{C}=\text{CRR}']^+$ ($\text{R} = \text{Ph}$, CO_2Et ; $\text{R}' = \text{H}$, Me) with a variety of nucleophiles and hydride donors have been described. Redox chemistry has also been studied. [110,111] The same authors have reported the reactions of $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\text{H})_3$ with alkenes and also the molecular structure of $\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Rh}(\text{H})(\eta^2\text{-L})$ where $\text{L} = \text{dimethyl fumarate}$. [112,113]

The complexation of a series of related ligands containing both *P*- and *N*-donors with $\text{Rh}(\text{I})$ has been investigated. $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ reacts with $\text{Ph}_2\text{PCH}_2\text{NPh}_2$ or $\text{Ph}_2\text{NCH}_2\text{P}(\text{Ph})\text{CH}_2\text{NPh}_2$, L , to give *trans*- $\text{RhL}_2(\text{CO})\text{Cl}$ the structures of which have been determined. Both ligands are *P*-bonded; for $\text{L} = \text{Ph}_2\text{PCH}_2\text{NPh}_2$, $\text{Rh}-\text{P} = 2.331$ (1), 2.325 (2) Å and for $\text{L} = \text{Ph}_2\text{NCH}_2\text{P}(\text{Ph})\text{CH}_2\text{NPh}_2$, $\text{Rh}-\text{P} = 2.299$ (2) and 2.307 (2) Å. The ligands $\text{Ph}_2\text{PCH}_2\text{N}(\text{Ph})\text{CH}_2\text{PPh}_2$ and $\{\text{Ph}_2\text{PCH}_2\}_2\text{NCH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{PPh}_2\}_2$ have also been prepared and studied. [114] Another *P,N*-ligand is $\text{MeN}(\text{PF}_2)_2$ and the reaction of this with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ leads to the dark red-orange trinuclear complex $\text{Rh}_3(\mu\text{-Cl})_3\{\mu\text{-(F}_2\text{P)}_2\text{NMe}\}_3$ in which each $\text{Rh}-\text{Rh}$ edge of the triangular frame is bridged by both chloride and $\text{MeN}(\text{PF}_2)_2$ ligands, the latter as a *P,P'*-donor. Structural characterisation of $\text{Rh}_3(\mu\text{-Cl})_3\{\mu\text{-(F}_2\text{P)}_2\text{NMe}\}_3$ shows that the chloride ligands all lie on one side of the Ru_3 -unit and similarly for the phosphorus ligands; $\text{Rh}\cdots\text{Rh} = 3.1180$ (4), 3.0956 (4), 3.0755 (4) Å and $\text{Rh}-\text{P}$ lie in the range 2.128 to 2.136 (1) Å. [115]



$\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}$

(65)



$n = 2 \text{ or } 3$

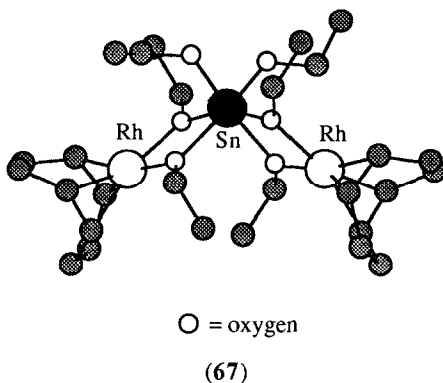
(66)

The chiral phosphine ligands *R,R*-(**65**) and *R,R*-(**66**) have been prepared and used in the syntheses of cations $[\text{Rh}(\text{cod})\text{L}]^+$ where the ligands are represented by L. For L = *R,R*-(**66**) and $n = 2$, the crystal structure of the rhodium(I) complex has been reported; Rh-P = 2.258 (2), 2.276 (2) Å. It has been shown that the new complexes are efficient precursors for the enantioselective hydrogenation of unsaturated reagents such as methyl acetamidocinnamate or dimethylitaconate. [116] The complexation of related ligands *bis*(dioxaphospholane) ligands has also been reported. [117]

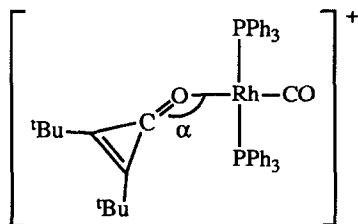
5.4.3 Complexes with oxygen donor ligands

The reaction of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with $\text{LiO}-\text{C}_6\text{H}_3-2,6-\text{Ph}_2$ leads to $\text{Rh}_2(\text{CO})_4(\mu-\text{O}-\text{C}_6\text{H}_3-2,6-\text{Ph}_2)_2$. Structural characterisation of the complex confirms square planar rhodium(I) centres; Rh-O = 2.083 (3), 2.101 (3), 2.063 (3), 2.067 (4) Å. Related iridium species were discussed in Section 4.4.3 of the previous Chapter. [118]

An interesting complex (**67**) results after the treatment of $\text{Rh}_2(\text{cod})_2\text{Cl}_2$ with $\text{Ti}_2\text{Sn}(\text{OEt})_6$. ^1H and ^{13}C NMR spectroscopic data illustrate that (**67**) is fluxional on the NMR timescale even at 193 K. However, replacement of the cod ligands by CO generates an analogous complex in which the fluxional process may be frozen out at -80°C . Complex (**67**) has been crystallographically characterised and pertinent bond parameters are Rh-O = 2.059 (4), 2.082 (4), 2.063 (5), 2.065 (4) Å, $\angle\text{ORhO} = 74.4 (1)^\circ$, $74.6 (2)^\circ$. [119]



The phenoxy derivative *trans*-Rh(OPh)(CO)(PPh₃)₂ has been prepared and structurally characterised. As expected, the rhodium(I) environment is square planar; Rh-O = 2.044 (2) Å and $\angle\text{RhOCPh} = 125.52 (19)^\circ$. The reactivity of MeI and $\text{Ph}_2\text{CHC}(\text{O})\text{Cl}$ towards *trans*-Rh(OPh)(CO)(PPh₃)₂ has been discussed. [120] The coordination of cyclopropenones to rhodium(I) has been the subject of study. Complex decarbonylation leads to 1-rhodacyclopentene-2,5-diones as well as cationic σ -oxygen complexes. The structure of (**68**) has been determined; Rh-O = 2.086 (7), $\text{C}_{\text{ring}}-\text{O} = 1.24 (1)$ Å, $\angle\alpha = 128.3 (8)^\circ$. [121]



(68)

The salicylaldehyde derivative $\text{Rh}(\text{O}-\text{C}_6\text{H}_4-\text{CHO})(\text{CO})(\text{PPh}_3)_2$ has been studied along with related iridium complexes described in the previous Chapter (Section 4.4.3). [122] An investigation of the kinetics of the oxidative addition of $\text{Hg}(\text{CN})_2$ to $\text{RhL}(\text{P}(\text{OPh})_3)_2$ in acetone solution where HL = benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, trifluorobenzoylacetone or hexafluoroacetylacetone. The results are consistent with the rate equation given in equ. (ii). The proposed mechanism for the reaction involves an octahedral intermediate with an $\text{Rh}(\text{I})\{\text{NC}-\text{HgCN}\}$ interaction. [123]

$$-\frac{d[\text{Rh}(\beta\text{-ketonate})\{\text{P}(\text{OPh})_3\}_2]}{dt} = k[\text{Rh}(\beta\text{-ketonate})\{\text{P}(\text{OPh})_3\}_2][\text{Hg}(\text{CN})_2] \quad (\text{ii})$$

The trigonal bipyramidal rhodium(I) complex *trans*- $\text{Rh}(\text{CO})(\text{PPh}_3)_2\{\text{ON}=\text{N}(\text{O})\text{Ph-}O,O'\}$ has been crystallographically characterised. Relevant bond parameters are $\text{Rh}-\text{O} = 2.147$ (8), 2.339 (9) Å, $\text{N}-\text{N} = 1.30$ (1) Å, $\angle\text{ONO} = 124$ (1)°, 114 (1)° and $\angle\text{ORhO} = 69.6$ (3)°. [124] The oxo-complexes $[\text{Cp}_2\text{M}=\text{O}-\text{M}'(\text{PPh}_3)_2(\text{CO})]^+$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Rh}, \text{Ir}$) have been prepared from a combination of $\text{Cp}_2\text{M}=\text{O}$ and $[\text{M}'(\text{CO})(\text{PPh}_3)_2(\text{NCMe})]^+$. ^1H NMR spectroscopic studies of the complexes in CD_3CN solution show that they undergo rapid chemical transformation with the solvent and with excess $\text{Cp}_2\text{M}=\text{O}$. The cation $[\text{Cp}_2\text{Mo}-\text{O}-\text{Rh}(\text{PPh}_3)_2(\text{CO})]^+$ has been structurally characterised; $\text{Rh}-\text{O} = 2.034$ (6) Å, $\text{Mo}-\text{O} = 1.78$ (6) Å, $\angle\text{MoORh} = 167.1$ (4)°. [125]

5.4.4 Complexes with sulphur or selenium donor ligands

The reaction of $[\text{Rh}(\text{cod})_2][\text{BF}_4]$ with $\text{Cp}_2\text{Ti}(\text{SMe})_2$ in the presence of $\text{P}(c\text{-hexyl})_3$ yields $\text{Rh}_2(\text{cod})_2(\mu\text{-SMe})_2$. ^{31}P NMR spectroscopic data suggest that the initial part of the reaction involves the coordination of the phosphine ligand which is then displaced by the thiolate ligand. $\text{Rh}_2(\text{cod})_2(\mu\text{-SMe})_2$ has been structurally characterised; $\text{Rh}-\text{S} = 2.338$ (2), 2.353 (2), 2.340 (2), 2.363 (2) Å, $\text{Rh}-\text{Rh} = 2.948$ (1) Å. [126] Related complexes are $\text{Rh}_2(\text{CO})_4(\mu\text{-L})_2$ in which $\text{HL} = \text{HSC}_6\text{F}_5$, $\text{HS-4-C}_6\text{F}_4\text{H}$ or $\text{HS-4-C}_6\text{H}_4\text{F}$. Their preparation and the structural characterisation of $\text{Rh}_2(\text{CO})_4(\mu\text{-S-4-C}_6\text{H}_4\text{F})_2$ have been reported. The two thiolate bridges lie *cis*-to one another and the two aryl substituents face down towards to carbonyl ligands; for two independent molecules, important bond parameters are $\text{Rh}-\text{S} = 2.353$ (4), 2.367 (5), 2.364 (5), 2.360 (4) Å and 2.350 (4),

2.377 (4), 2.363 (4), 2.350 (4) Å, Rh-Rh = 3.076 (2) Å and 3.070 (2) Å. The role of derivative complexes as catalyst precursors is assessed. [127]

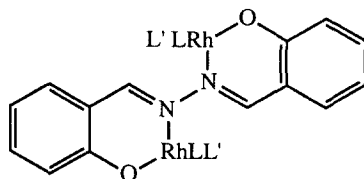
The oxidation of $\text{Me}_2\text{NCS}_2\text{RhL}_2$ is reported to give the octahedral complexes $\text{Me}_2\text{NCS}_2\text{RhL}_2(\eta^2\text{-O}_2)$ with $\text{L}_2 = \text{cis}\text{-}\{\text{PPh}_3\}_2$ or dppe. In the presence of CO, oxidation yields $\text{Me}_2\text{NCS}_2\text{RhL}_2(\text{O}_3\text{CO})$. However, for $\text{L} = \text{PPh}_3$, oxidation followed by treatment with CO leads to the formation of *trans*- $\text{Me}_2\text{NCS}_2\text{RhL}_2(\text{O}_2\text{CO})$ which isomerises in the presence of PPh_3 at 70°C in a sealed tube to the *cis*-isomer. The molecular structure of *trans*- $\text{Me}_2\text{NCS}_2\text{RhL}_2(\text{O}_2\text{CO})$ has been determined; Rh-S = 2.347 (3), 2.346 (3) Å, Rh-O = 2.083 (8), 2.071 (8) Å, Rh-P = 2.356 (3), 2.398 (3) Å. [128] The synthesis and crystallographic characterisation of $(\text{cod})\text{Rh}(\mu\text{-SPPH}_2)_2\text{Pt-S}_2\text{CNEt}_2$ has been reported. The $\text{RhS}_2\text{P}_2\text{Pt}$ -unit adopts a "boat"-conformation; Rh-S = 2.370 (4) and 2.328 (4) Å. The iridium analogue was described in Section 4.4.4 of the previous Chapter. [129]

The reactivity of some singly and doubly selenium bridged complexes has been investigated. $\text{Cp}^*\text{Rh}_2(\text{CO})_2(\mu\text{-Se})$ reacts with SO_3 to give the unusual complex $\text{Cp}^*\text{Rh}_2(\text{CO})_2(\mu\text{-SeSO}_3)$, the molecular structure of which has been determined. Important distances are Rh-Rh = 2.769 (2) Å, Rh-Se = 2.417 (2), 2.440 (3) Å, Se-S = 2.301 (6) Å. The analogous complexes $\text{Cp}^*\text{Rh}_2(\text{CO})_2(\mu\text{-S})$ and $\text{Cp}^*\text{Rh}_2(\text{CO})_2(\mu\text{-Se})$ disproportionate in solution, one product being the cluster species $\text{Cp}^*\text{Rh}_3(\mu_3\text{-CO})(\mu_3\text{-X})$ ($\text{X} = \text{S}$ or Se). Upon warming, $\text{Cp}^*\text{Rh}_2(\text{CO})_2(\mu\text{-Se})$ dimerises with loss of CO to yield $\text{Cp}^*\text{Rh}_4(\mu_3\text{-Se})_4$. [130]

5.4.5 Complexes with mixed donor sets

The donor sets to be discussed in this Section arise from *N,O*-, *N,P*-, *P,O*-, *N,S*- and *P,As*-ligands.

The preparation of the complexes (69) has been reported and the products have been characterised by ^1H and ^{31}P NMR and IR spectroscopy. [131] An *N,O*-donor set is also observed upon complexation of the ligands L^{2-} to rhodium(I) where $\text{H}_2\text{L} = 2,5\text{-pyrazinedicarboxylic}$ or $2,3\text{-pyrazinedicarboxylic}$ acid. The complexes which have been characterised are $\text{Rh}_2\text{L}(\text{cod})_2$, $\text{Rh}_2\text{L}(\text{CO})_2(\text{PPh}_3)_2$ and $\text{Rh}_2\text{L}(\text{CO})_2\{\text{P}(\text{OR})_3\}_2$ ($\text{R} = \text{Me}, \text{Ph}$) along with some iridium(I) analogues. In each case, the ligand bridges between the two rhodium(I) centres being *N,O*-bonded to each metal. [132]

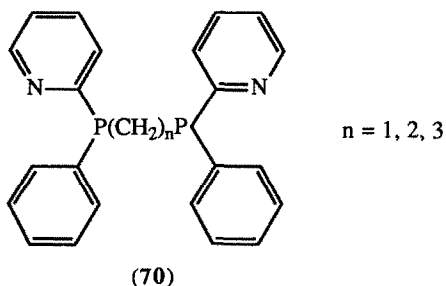


(69)

$\text{L} = \text{P}(\text{OR})_3$

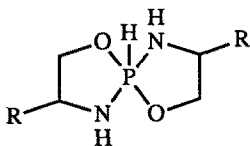
$\text{L}' = \text{P}(\text{OR})_3$ or CO

$\text{R} = \text{Me}, \text{Ph}, \text{Pr}$

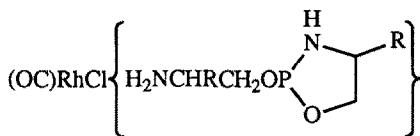


The reaction of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ with two equivalents of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (L) in dmf or EtOH leads to $[\text{Rh}(\text{CO})\text{ClL}_2]_n$ in which the ligand binds through both phosphorus and nitrogen atoms. Related complexes were described in Section 5.4.2. [89] Complexes of the type LRhCl have been prepared from $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and L for L = *bis*{3-(diphenylphosphino)propyl}amine or *bis*{4-(diphenylphosphinobutyl)benzyl}amine). The ligands are coordinated to the square planar rhodium(I) via a P_2N -donor set. The catalytic activity of the complexes with respect to hydrogenation reactions has been addressed. [133] Ligands of type (70) have been designed so as to exhibit a *cis*- P_2N_2 -donor set. The ligands have been produced as equimolar mixtures of the *meso*- and *rac*-forms. The complexation of (70) to rhodium(I) has been studied and the molecular structures of (*rac*- $L_{n=1}$) $\text{Rh}_2(\text{CO})_2\text{Cl}_2$ and the rhodium(II) complex cation [*meso*- $L_{n=3}$] Rh_2Cl_2] $^{2+}$ have been determined. In the former complex, the ligand bridges between the two Rh atoms being an NP_2 -donor to each metal; the Rh---Rh separation is 3.093 (1) Å, Rh-P = 2.212 (2), 2.219 (2) Å and Rh-N = 2.134 (5), 2.148 (5) Å. In the latter, the complex is supported by a Rh-Rh bond (2.650 (1) Å) and the dirhodium unit is bridged by two ligands, each coordinated via a P,P -donor set to one rhodium atom and an N,N -donor set to the other metal atom; Rh-P = 2.244 (3), 2.261 (2) Å and Rh-N = 2.193 (6), 2.185 (7) Å. [134]

A single crystal X-ray diffraction study of $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{MeO}_2\text{CCCCO}_2\text{Me})(\text{Ph}_2\text{PC}_5\text{H}_4\text{N})_2$ and of the related iridium complex cation [$\text{Ir}_2(\text{CO})_2(\text{C}_6\text{H}_5)(\text{CN}^t\text{Bu})(\mu\text{-MeO}_2\text{CCCCO}_2\text{Me})(\mu\text{-dppm})_2$] $^+$ (see Section 4.4.2 of the previous chapter) has been presented. In the dirhodium complex, the Rh-Rh distance is 2.6528 (5) Å and the Rh_2 -unit is bridged by two 2-(PPh_2)-py ligands; Rh-N = 2.171 (7), 2.148 (8) Å and Rh-P = 2.259 (4), 2.244 (4) Å. [135]

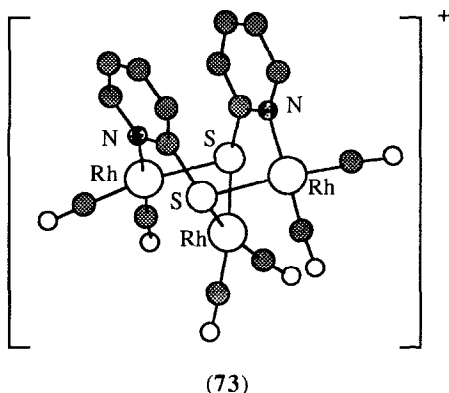


$R = \text{H or Et}$



The hydrospiroposphoranes (71) react with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ to give complexes (72) which have been characterised by infrared and ^{31}P and ^{15}N NMR spectroscopy. [136] The ligand

$\text{Pr}_2\text{P}(\text{CH}_2)_2\text{OMe}$ (L) binds to rhodium(I) in $[\text{Rh}(\text{cod})\text{L}_2]^+$ in an $\eta^1\text{-P}$ -mode. Displacement of the cod ligand by carbon monoxide gives a complex which readily eliminates CO to give $[\text{Rh}(\text{CO})(\eta^1\text{-P-L})(\eta^2\text{-P,O-L})]^+$. The oxidative addition of MeI to $[\text{Rh}(\text{CO})(\eta^1\text{-P-L})(\eta^2\text{-P,O-L})]^+$ and the kinetics of this reaction have been investigated. The ability of L to rearrange from an $\eta^1\text{-P}$ - to $\eta^2\text{-P,O}$ -mode promotes acyl formation after the initial addition of the methyl iodide. [137] In related work, the reaction of $\text{Rh}_2(\text{CO})_4\text{I}_2$ with $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{P}(\text{Ph})(\text{CH}_2)_2\text{OMe}$, L, gives *trans*- $\text{L}_2\text{Rh}(\text{CO})\text{I}$ in which L functions as a monodentate *P*-donor. The oxidative addition of MeI occurs and, as in the previous case, closure of L to an $\eta^2\text{-P,O}$ -mode promotes acyl formation. [138]



Treatment of *cis*- $[\text{RhL}'_2(\text{Me}_2\text{CO})_x]^+$ with $[\text{Rh}(\mu\text{-L})\text{L}'_2]_2$ (HL = 2-HS-py or benzothiazole-2-thiol; $\text{L}'_2 = (\text{CO})_2$, $(\text{CO})(\text{PPh}_3)$, cod, norborna-2,5-diene or tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfbb)) has been shown to give the trirhodium complexes $[\text{Rh}_3(\mu\text{-L})_2(\text{L}'_2)_3]^+$. In particular, the method gives a controlled route to a single isomer of $[\text{Rh}_3(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2(\text{CO})_2(\text{PPh}_3)_2\text{L}'_2]^+$. All the complexes have been characterised by ^1H and ^{31}P NMR and UV-VIS spectroscopy. The structures of $[\text{Rh}_3(\mu\text{-2-S-py})_2(\text{CO})_6]^+$, (73), and $[\text{Rh}_3(\mu\text{-2-S-py})_2(\text{CO})_2(\text{tfbb})(\text{PPh}_3)_2]^+$ have been determined. In (73), pertinent distances for the two independent molecules are Rh-S = 2.407 (6), 2.366 (5), 2.388 (6) Å and 2.401 (5), 2.365 (5), 2.378 (5) Å, Rh-N = 2.106 (13), 2.085 (14) Å and 2.080 (14), 2.088 (13) Å, Rh----Rh = 2.891 (15), 2.907 (4) Å and 2.927 (5), 2.920 (4) Å. [139]

The complex dication $[\text{Rh}(\text{CO})\text{Cl}\{\text{Au}_2(\text{Ph}_2\text{PCH}_2\text{As}(\text{Ph})\text{CH}_2\text{PPh}_2)\}_2]^{2+}$ has been prepared from $\text{ClAu}(\text{Ph}_2\text{PCH}_2\text{As}(\text{Ph})\text{CH}_2\text{PPh}_2)\text{AuCl}$ and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$. A structural determination of the complex confirms that the rhodium atom is centred within an $\text{Au}_2\text{P}_4\text{As}_2$ -macrocycle but bonded to two Au and two As atoms with axial chloride and carbonyl ligands; for two independent molecules distances are Rh-Au = 3.028 (2), 3.006 (2) Å and 3.034 (2), 3.074 (2) Å and Rh-As = 2.406 (5), 2.418 (5) Å and 2.418 (5), 2.414 (5) Å. [140]

5.5 CLUSTERS CONTAINING RHODIUM

5.5.1 Homometallic clusters

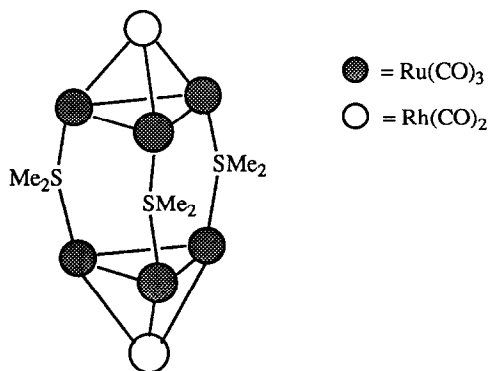
The cluster anions $[\text{Rh}_5(\text{CO})_{14}\text{X}]^{n-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ and $n = 2$; $\text{X} = \text{PPh}_3$, $n = 1$) have been synthesised from $\text{Rh}_4(\text{CO})_{12}$ and X^- or PPh_3 . The molecular structures of $[\text{PPN}][\text{Rh}_5(\text{CO})_8(\mu\text{-CO})_6(\text{PPh}_3)]$ and $[\text{PPN}]_2[\text{Rh}_5(\text{CO})_8(\mu\text{-CO})_6(\text{SCN})]$ have been determined; each anion has a trigonal bipyramidal core, elongated as expected for a cluster with 76 valence electrons. The PPh_3 or SCN^- ligands are terminally bonded and attached to the apical rhodium atoms; $\text{Rh-P} = 2.382(3) \text{ \AA}$ in $[\text{Rh}_5(\text{CO})_8(\mu\text{-CO})_6(\text{PPh}_3)]^-$ and $\text{Rh-S} = 2.582(5) \text{ \AA}$, $\angle \text{RhSC} = 105.5(8)^\circ$ in $[\text{Rh}_5(\text{CO})_8(\mu\text{-CO})_6(\text{SCN})]^{2-}$. The clusters are stable under an atmosphere of CO but decompose under nitrogen. [141]

Variable temperature solid state ^{13}C NMR (magic angle spinning) spectral data have been gathered for $\text{Rh}_4(\text{CO})_{12}$ and $[\text{Me}_3\text{BzN}]_2[\text{Rh}_6(\text{CO})_{15}\text{C}]$. In both cases the results are consistent with the solid state static structures determined by single crystal X-ray diffraction. The ^{13}C NMR spectrum of $\text{Rh}_4(\text{CO})_{12}$ exhibits eight resonances in the carbonyl region although some signals are overlapping. The spectrum for $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ shows five signals, one assigned to terminal carbonyl ligands and four assigned to bridging CO ligands. [142]

The results of a study of the acidity of the interstitial H atoms in Rh_{13} -clusters have been presented. For $[\text{H}_3\text{Rh}_{13}(\text{CO})_{24}]^{2-}$ in MeCN solution, the pK_a corresponding to the removal the first proton is 11.0, and for the second is 16.5. However, the deprotonation step $[\text{H}_3\text{Rh}_{13}(\text{CO})_{24}]^{2-}$ to $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ using aniline as the base has an activation barrier of 21.3 kcal mol^{-1} and deprotonation is therefore slow despite the low pK_a values. [143]

5.5.2 Heterometallic clusters

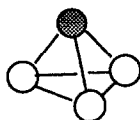
Two tetrahedra linked via Me_2S -bridges are present in $\{\text{HRuRh}_3(\text{CO})_9\}_2(\mu\text{-SMe}_2)_3$, (74).



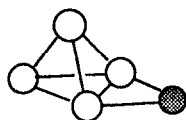
(74)

The preparation and structural determination of compound (74) have been reported. The dimethylsulphido unit is a four electron donor and provides a flexible bridging unit; $\angle \text{RhSRh} = 125.1$ (1) Å. The two Rh_3 -triangles are eclipsed in (74). [144]

It has been shown that ketylenidene clusters are useful precursors to heterometallic systems. For example, the reaction of $[\text{Ru}_3(\text{CO})_9\text{CCO}]^{2-}$ with $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in thf gives the carbido cluster $[\text{Rh}_3\text{Ru}_3(\text{CO})_{15}]^-$. The observation of ^{103}Rh - ^{13}C spin coupling ($J = 23$ Hz) lends supporting evidence for the presence of the three rhodium atoms. [145] Treatment of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{CpRh}(\text{CO})_2$ in toluene at 90°C yields a mixture of $\text{CpRhOs}_2(\text{CO})_9$, $\text{H}_2\text{CpRhOs}_3(\text{CO})_{10}$ and $\text{H}_2\text{CpRhOs}_4(\text{CO})_{13}$. The molecular structures of $\text{H}_2\text{CpRhOs}_3(\text{CO})_{10}$ and $\text{H}_2\text{CpRhOs}_4(\text{CO})_{13}$ have been determined. The metal core (75) of $\text{H}_2\text{CpRhOs}_3(\text{CO})_{10}$ is a tetrahedron as expected for a cluster with 60 valence electrons; the core (76) of $\text{H}_2\text{CpRhOs}_4(\text{CO})_{13}$ is an edge bridged tetrahedron consistent with its 74 valence electrons. Under hydrogen, the same preparative route (again in toluene) leads to $\text{H}_3(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RhOs}_3(\text{CO})_9$ as the major product. The interconversion of some of the new rhodium containing clusters is discussed. [146]



(75)



(76)

A method of metal exchange, rhodium for iron, has been used to synthesise the alkyne containing cluster $\text{H}(\text{CpMo})\text{RuRh}(\text{CO})_8\text{C}_2\text{Me}_2$. Other heterometallic cluster species also reported include $\text{Rh}_2\text{Co}_2(\text{CO})_{10}\text{C}_2\text{MeR}$ ($\text{R} = \text{Me}, \text{Ph}$). [147] The preparation, spectroscopic and structural characterisation of the paramagnetic clusters $(\text{Cp}^*\text{M})(\text{CpCo})_2(\text{CO})_2$ and $(\text{Cp}^*\text{M})_2(\text{CpCo})(\text{CO})_2$ for $\text{M} = \text{Rh}$ or Ir have been reported. Each cluster is a 46 electron species. A detailed examination of the structures provides an insight into the cluster bonding. It appears realistic to describe the molecules in terms of a dinuclear species interacting with a single metal centre. The paramagnetically shifted ^1H NMR spectra of the clusters are discussed. [148]

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