Coordination Chemistry Reviews, 57 (1984) 75–154
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2. RHODIUM

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CONTENTS

Introduction

0010-8545/84/$24.00

INTRODUCTION

This review is a continuation of that published previously [1] and corresponds mainly to publications which appeared during late 1980, and 1981. The papers therefore coincide with Chemical Abstracts Volumes 94 and 95.

Although concentrating predominantly upon the coordination chemistry of rhodium, especial emphasis has been placed, as in last years review, upon its catalytic properties and these are the subject of a separate section which cuts across the conventional approach of classifying material according to oxidation state.

An unusually large number of other reviews concerning rhodium were published during 1981 and 1982 and these have to some extent dictated the content of the material described here. For example, this article deliberately excludes asymmetric hydrogenation by chiral rhodium phosphine catalysts since this is adequately covered in reference [2] and further reviewed in [3] and [4].

Some work of an organometallic nature has been included in the review only where, in the author's opinion, it is considered to contain some relevance to co-ordination chemistry. Annual surveys of the organometallic chemistry of rhodium have been published elsewhere {[5] (for the year 1979) and [2] (covering the year of 1980)}.

A review concerning the commercial applications of reactions catalysed by soluble complexes of rhodium has been produced during 1981 [6] and the commercial uses of rhodium salts have been described [7]. The chemistry of recently reported rhodium cluster complexes has been reviewed [8] as has the chemistry of new rhodium carbonyl clusters [9].

An international conference on the chemistry of the platinum group metals (Ru, Os, *Rh*, Ir, Pd and Pt), organised by the Royal Society of Chemistry and the University of Bristol School of Chemistry, was held at Bristol during July, 1981. A brief reveiw concerning the more important developments has been published [10] and a publication containing abstracts of all the papers and posters presented at the meeting is available from the Department of Inorganic Chemistry, The University, Bristol. The second international symposium on the platinum group metals is scheduled for 2-6 July, 1984 at the University of Edinburgh.

2.1 RHODIUM(IV)

Ba[RhO_3] may be prepared by the reaction of BaO and RhO_2 at 1175 °C and 60-65 kbar. The structure consists of a four-layer stacking sequence of close-packed

BaO_3 layers containing tetravalent rhodium in all of the octahedral oxygen interstices [11].

2.2 RHODIUM(III)

2.2.1 Halide complexes

Heating of $[M(NH_3)_4][NH_4][RhCl_6]$ (M = Pd or Pt) results in the formation of *trans*-$[M(NH_3)_2Cl_2]$ and $RhCl_3$. At 800 °C, palladium-rhodium or platinum-rhodium alloys are formed as well as the free metals [12].

The Raman spectrum of $[RhBr_6]^{3-}$ is consistent with an octahedral ground-state structure. Polarisation measurements of the $\nu_1(A_{1g})$ and $\nu_2(E_g)$ vibrational modes are consistent with cubic symmetry and the degree of polarisation of these lines was found to be independant of the laser wavelength - a situation which is not unlike the observations of other d^6 hexahalide systems [13].

2.2.2 Complexes with oxygen donor ligands

2.2.2.1 Oxides and aqueous chemistry

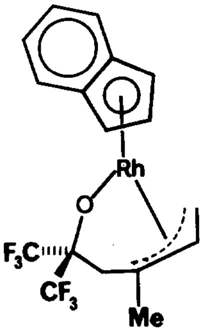
$RhMO_4$ (M = Nb, Ta or Sb) decomposes in the solid phase on heating with the evolution of dioxygen and the formation of rhodium and M_2O_5. Rh_2MO_6 (M = Te or W) melts with decomposition giving MO_3 and Rh_2O_3. $RhVO_4$ melts with decomposition evolving dioxygen and forming rhodium and V_2O_5 [14]. The phase diagram of the niobium(V) oxide-rhodium(III) oxide system has revealed the formation of $RhNbO_4$ and, similarly, $RhTaO_4$ was obtained in the Ta_2O_5-Rh_2O_3 system [15].

$Rh(OH)_3$, obtained from the reaction of aqueous solutions of $RhCl_3$ and NH_3, is reported to be partially dehydrated in the temperature range 135-310 °C. Crystallisation of Rh_2O_3 was reported to occur at 590-640 °C [16]. $[Rh(NH_3)_5(OH)]^{2+}$ reacts rapidly with dissolved SO_2 to form the oxygen-bonded sulphito complex species $[Rh(NH_3)_5(OSO_2)]^+$. The rate constant for SO_2 uptake was found to be 1.8 x 10^8 mol^{-1} s^{-1} at 25 °C [17].

2.2.2.2 Sulphoxide and ketone-related complexes

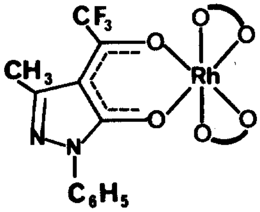
The electronic structures of trans-$[Rh(dmso)_2Cl_4]^-$ and $[Rh(dmso)_3Cl_3]$ have been calculated by a modified version of the SCF-MO-LCAO method in the CNDO approximation. The electronic characteristics of dmso were compared in relation to its type of co-ordination to the metal (sulphur or oxygen bonded) [18].

$(CF_3)_2CO$ reacts with isoprene- or 2,3-dimethylbuta-1,3-diene-(η^5-indenyl) rhodium to give the η^3-allylic complexes $[Rh\{OC(CF_3)_2CH_2C(R')\mathrel{=\!=\!=}C(R^2)\mathrel{=\!=\!=}CH_2\}(\eta^5 - C_9H_7)]$ (1; R' = Me, R^2 = H; R' = H, R^2 = Me) [19].



(1)

A detailed study of the ^{103}Rh NMR spectrum of [Rh(acac)$_3$] has been undertaken [20] and the related complex [RhL$_3$] (2; HL = 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazalone) has been prepared [21].



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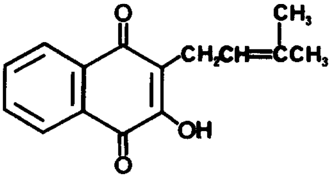
Stability constants and thermodynamic functions of rhodium(III) with 2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthaquinone (3) have been determined; 1:1, 1:2 and 1:3 complexes are formed [22].



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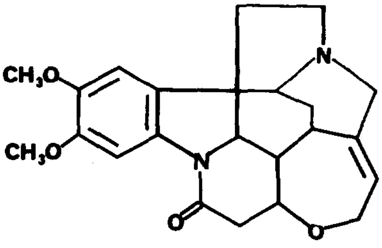
$[Rh_2Cl_6L]$ (L = brucine (4)) has been prepared and found to contain one of the

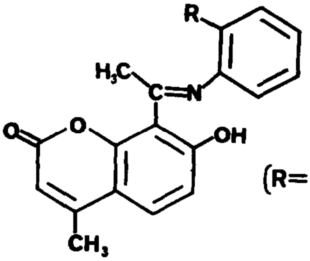


(4)

rhodium atoms co-ordinated *via* the carbonyl oxygen and the other coordinated *via* the ether oxygen atom [23].

2.2.2.3 Complexes with oxygen-nitrogen donor ligands

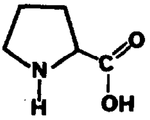
Diamagnetic, octahedral $H[RhL_2]$ {L = (5)} has been prepared and characterised [24]. L-proline {HL = (6)} reacts with $RhCl_3.nH_2O$ in weakly-acidified, boiling,



(R=COOH or OH)

(5)

aqueous solution to give the *mer*- and *fac*- isomers of $[RhL_3]$ [25] and the compound $[Rh(HL')LCl_2]$ {HL' = (7)} has been synthesised [26].



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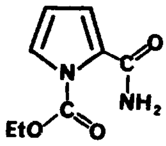

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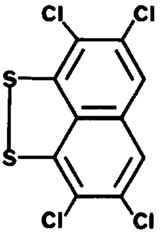
The formation of $[Rh(edta)X(OH)]^{3-}$, $[Rh(edta)X_2]^{3-}$ (X = Br^-, I^-, $[SCN]^-$, $[NO_2]^-$ or $[SO_2]^-$, $[Rh(edta)(S_2O_3)(OH)]^{4-}$ and $[Rh(edta)(S_2O_3)_2]^{5-}$ have been monitored spectrophotometrically. The stability constants are found to depend upon the reducing potential of X (including $[S_2O_3]^{2-}$) and on its oxidative dimerisation capacity [27]. $[NH_4][RhCl_2(edtaH_2)]$ and $Na[RhCl(pdtaH)].3H_2O$ ($pdtaH_4$ = propylene diaminetetraacetic acid) have been prepared from $RhCl_3.3H_2O$ and $Na_2[H_2edta]$ or $Na_2[H_2pdta]$, respectively [28].

2.2.2.4 Nitrito complexes

$RhCl_3$ reacts with molten mixtures of alkali metal nitrites to form $[Rh(NO_2)_6]^{3-}$. At high temperatures nitrogen oxides are evolved from this material and Rh_2O_3 is formed [29].

2.2.3 Complexes with sulphur donor ligands

The reactions of the cyclic disulphides (8–10) with $[RhCl(PPh_3)_3]$ results in the oxidative addition of the S–S bond to rhodium [30].



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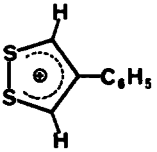

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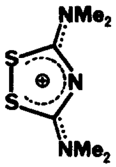

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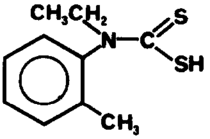
$[Rh(SCN)_2L_2]$ (L = O-methyldimethylglyoximato) contains Rh^{3+} octahedrally co-ordinated, with the SCN groups co-ordinated in trans-positions via the S atoms. The two bidentate rings are contained in the equatorial plane of the complex which crystallises in the monoclinic configuration [31].

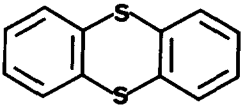
Complexes of the type [RhL(HL)], where HL = methyl β-(2-hydroxy-1-naphthylmethylene)dithiocarbazate or methyl β-[1-(2-hydroxy-5-bromophenyl)-ethylidene]dithiocarbazate, have been prepared and found to possess pseudooctahedral stereochemistry [32]. $[RhL_3]$ {LH = (11)} has been prepared from



(11)

aqueous solution and is a diamagnetic, octahedral species forming a monomeric, non-conducting solution [33].

Thianthrene (12) combines with $RhCl_3.3H_2O$ to give $[RhCl_3(\text{thianthrene})]$, whereas phenoxathiin (13) gives $[RhCl_3(\text{phenoxathiin})_3]$ [34]. Complexation of 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane with $[CpRh(PMe_3)(\eta^2\text{-}C{\equiv}CH)]$ gave (14) [35].



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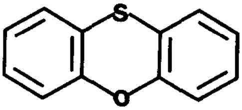

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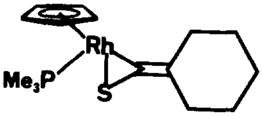

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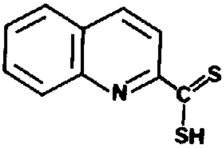
$[Rh(SO_3)_3(NH_3)_3]^{3-}$ is found, from vibrational specta, to contain rhodium-sulphur bonds [36].

Oxidative addition of RCH_2SO_2Cl (R = H, 4-tolyl or $4\text{-}NO_2C_6H_4$) to $[RhCl(PPh_3)_3]$ gives the expected sulphonyl complex $[Rh(PPh_3)_2Cl_2(SO_2CH_2R)]$ [37,38].

Octahedral complexes of formula $[RhL_2Cl_2]Cl$ and $[RhL'Cl_3]$ (L = α-pyridyl-thiosemicarbazide and L' = 1-benzilidine-4-(α-pyridyl)thiosemicarbazone) have been prepared and characterised by IR and UV spectroscopy and by magnetic moment measurements [39]. $RhCl_3$ reacts with 2-quinolinedithiocarboxylate {(15) = HL} to produce RhL_3 [40] and $[Rh(6\text{-methyl-2-thiouracil})_3]$ is proposed to possess the distorted octahedral structure illustrated in (16) [41].



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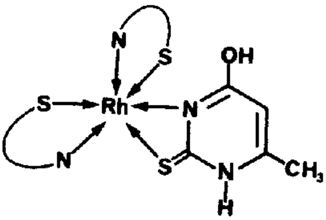

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2.2.4 *Complexes with nitrogen donor ligands*

2.2.4.1 *Ammine and amine complexes*

Thermal decomposition (280-390 °C) of $[Rh(NH_3)_5Cl]Cl_2$ is reported to simultaneously produce both $[Rh(NH_3)_4Cl_2]Cl$ and rhodium metal according to the equations [42]:

$$2\,[Rh(NH_3)_5Cl]Cl_2 \longrightarrow 2Rh + 2NH_3 + 6[NH_4]Cl + N_2$$

$$[Rh(NH_3)_5Cl]Cl_2 \longrightarrow [Rh(NH_3)_4Cl_2]Cl + NH_3$$

The kinetics of H_2O-NH_3 exchange for *trans*-$[Rh(NH_3)_4(OH)_2]^+$ and $[Rh(NH_3)_5(OH)]^{2+}$ has been studied in aqueous ammonia. The observed rate constant, at fixed ammonia concentrations, is proportional to the concentration of ammonium ion.

$$[Rh(NH_3)_4(OH)_2]^+ + [NH_4]^+ \longrightarrow [Rh(NH_3)_5(OH)]^{2+} + H_2O$$

The reaction of $[Rh(NH_3)_5(OH)]^{2+}$ with ammonia results in the formation of an equilibrium mixture of $[Rh(NH_3)_5(OH)]^{2+}$ and $[Rh(NH_3)_6]^{3+}$ [43].

The hydrolysis of $[Rh(NH_3)_5(NO_2)]^{2+}$ at 130-160 °C and of *cis*-$[Rh(NH_3)_4(NO_2)_2]^+$ and *trans*-$[Rh(NH_3)_4(NO_2)_2]^+$ at 140-150 °C and 80-110 °C, respectively, has been studied. Aquation of the *trans*-isomer is accompanied by irreversible loss of nitrite ions but in the other complexes, aquation occurs by loss of ammonia in the rate-determining step of the reaction [44]. The kinetics of ammoniation of $[Rh(NH_3)_5Br][ClO_4]_2$ and $[Rh(NH_3)_5(NO_3)][ClO_4]_2$ have been examined as a function of solution acidity. The base-catalysed reaction of these ammines is reported to follow the conjugate-base mechanism [45].

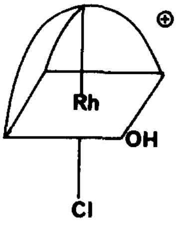
Crystalline powders of $[Rh(NH_3)_6][Rh(CN)_6]$ and $[Rh(ND_3)_6][Rh(CN)_6]$ were examined by emission spectroscopy at low temperatures. Emmission bands associated with the $^3T_{1g} \rightarrow {}^1A_{1g}$ transition of $[Rh(NH_3)_6]^{3+}$ and its deuterated analogue suggest the presence of a Jahn-Teller distortion in the $^3T_{1g}$ excited state [46]. Photochemical, photoluminescence and spectral studies of $[Rh(NH_3)_5(NCR)]^{3+}$ (R = Ph, 2-MePh, $PhCH_2CH_2CH_2$, 3-$HO(C_6H_4)CH_2CH_2$, $PhCH_2$ or 3-$MeO(C_6H_4)CH_2$) have been reported [47]. The electronic absorption spectra shows bands arising from both $\pi \rightarrow \pi^*$ and ligand field transitions, but the luminescence spectra exhibit only ligand field emissions whether or not the π^* or ligand field states are populated initially. Irradiation of either the $\pi \rightarrow \pi^*$ or the ligand field bands in aqueous solution causes photosubstitution of the nitrile ligand:-

$$[Rh(NH_3)_5(NCR)]^{3+} + H_2O \xrightarrow{h\nu} [Rh(NH_3)_5(H_2O)]^{3+} + RCN$$

The standard thermodynamics of formation and stability constants of the complexes $[Rh(en)_3]L^+$ (L = $[SO_3]^{2-}$, $[SeO_3]^{2-}$, $[TeO_3]^{2-}$, $[S_2O_3]^{2-}$, $[CO_3]^{2-}$ or $[SO_4]^{2-}$) have been determined in aqueous solution. The stabilities of the complexes are found to increase in the above order [48]. The stability constants and thermodynamic parameters have also been determined for the formation of the sulphato and selenato outer-sphere complexes of *cis*-$[Rh(en)_2Cl_2]^+$ [49].

Exchange of the anions of $[Rh(en)_3]Cl_3$ by hydroxide ions using a strongly-basic anion-exchange resin gave $[Rh(NHCH_2CH_2NH_2)_3]$ [50]. The preparation of $[Rh(NH_2CH_2CH_2OH)_3]X_3$, $[Rh(NH_2CH_2CH_2OH)_4X_2]X$ and $[Rh(NH_2CH_2CH_2OH)_5X][ClO_4]_2$ (X = Cl or Br) has also been reported [51] and the acid dissociation constants of $[Rh(NH_2CH_2CH_2OH)_4X_2]^+$ are found to be 2.03×10^{-11} and 2.90×10^{-11} for X = Cl and Br, respectively.

cis-$[Rh(en)_2Cl_2][ClO_4]$ combines with liquid ammonia to give *cis*-$[Rh(en)_2(NH_3)_2][ClO_4]_3$; *cis*-$[Rh(en)_2(NH_3)Cl][ClO_4]_2$ is formed as an intermediate. Entropies of activation for the rate-determining step have been determined as 0 and -42 J $mole^{-1}K^{-1}$, respectively. *trans*-$[Rh(en)_2I_2][ClO_4]$ ammoniates to *trans*-$[Rh(en)_2(NH_3)I][ClO_4]_2$ [52]. A kinetic study of the Hg(II)-catalysed aquation of *cis*-$[Rh(en)_2Cl_2]^+$ in methanol and water reveals that the first-order rate constants do not vary over the mercury(I) concentration range of 0.06 - 0.18 mole l^{-1} [53]. Base hydrolysis of $[Rh(tren)Cl_2]^+$ produces β-$[Rh(tren)Cl(OH)]^+$ (17) although earlier work had shown that aquation of $[Rh(tren)Cl_2]^+$ in acidic solution gave the α-isomer (18). Kinetic data have



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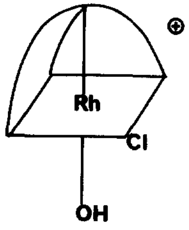


(18)

been collected for the following reactions, the products of which were characterised from both their chemical analyses and electronic spectra [54].

$$\begin{tikzcd}
{[Rh(tren)Cl_2]^+} \arrow[r, "OH^-"] & \beta\text{-}[Rh(tren)Cl(OH)]^- \arrow[d, "OH^-"] \\
\alpha\text{-}[Rh(tren)Cl(OH)]^+ \arrow[r, "OH^-"] & {[Rh(tren)(OH)_2]^+}
\end{tikzcd}$$

$$[Rh(tren)(OH_2)_2]^{3+} \xrightarrow{Cl^-} \beta\text{-}[Rh(tren)Cl(OH_2)]^{2+} \xrightarrow{Cl^-} [Rh(tren)Cl_2]^+$$

trans → *cis* and *cis* → *trans* photoisomerisations are predicted for $[Rh(en)_2(NH_3)(H_2O)]^{3+}$ by the model for five-coordinate excited state rearrangement, and have now been observed experimentally. It is also shown that the photochemistry of a complex may be modified by a change in temperature. The results show that the stereochemical course of a d^6 substitution reaction can be driven and controlled by light, heat or a combination of both light and heat [55].

2.2.4.2 Diimine and porphyrin complexes

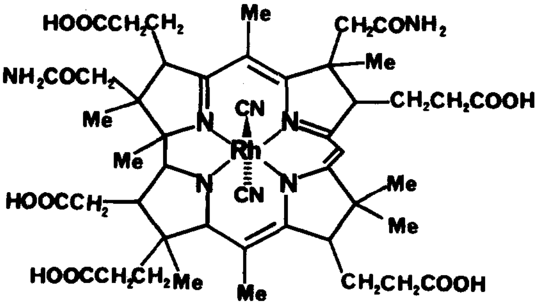
In the intensity luminescence emission of $[Rh(phen)_3]^{3+}$, two different emissions are reported: the first (measured at < 150 K) with a well-structured emission and a maximum centred at 450 nm and the second with a broad emission (330-210 K) and a maximum centred at about 575 nm [56]. $[Rh(phen)_3]^{3+}$ in MeCN exhibits a vibrationless emission band centred around 580 nm originating from the lowest triplet metal-centred excited state. The complex ion is known to emit from a triplet ligand-centred excited state in a rigid matrix at 77 K and this example is believed to be the first observed to exhibit a dual luminescence emission from orbitally different, spatially isolated excited states [57].

Irradiation of $[Ru(bipy)_3]^{2+}$, $[Rh(bipy)_3]^{3+}$ and triethanolamine mixtures in solution with 450 nm light produces rhodium(I) and dihydrogen. Light absorption by $[Ru(bipy)_3]^{2+}$ produces excited $\{[Ru(bipy)_3]^{2+}\}^*$, which is oxidised by $[Ru(bipy)_3]^{3+}$ to give $[Ru(bipy)_3]^{3+}$ and $[Rh(bipy)_3]^{2+}$, the back-reaction being prevented by the triethanolamine [58]. The reaction of $[Rh(bipy)_3]^{3+}$ with reducing radicals such as e^-_{aq}, $\cdot CO_2^-$ and $Me_2\dot{C}OH$ in aqueous solution also yields $[Rh(bipy)_3]^{2+}$, which slowly loses bipy at room temperature. In alkaline medium $[Rh(bipy)_3]^{2+}$ disproportionates to $[Rh(bipy)_3]^{3+}$ and $[Rh(bipy)_2]^{+}$. $[Rh(bipy)_2]^{+}$ exists in at least four identifiable forms; $[Rh(bipy)_2(OH)_n]^{(1-n)+}$ (red-violet, soluble), $[Rh(bipy)_2X]$ (soluble; X = Cl^- or $[ClO_4]^-$), $[Rh(bipy)_2(OH_2)_n]^{+}$ (transient green - obtained from acidification of $[Rh(bipy)_2(OH)_n]^{(1-n)}$) and a hydride, formulated as $[Rh(bipy)_2]^{2+}$ (colourless, soluble) formed from the protonation of $[Rh(bipy)_2]^{+}$ [59]. The picosecond, time-resolved absorption spectra (following 306 nm sub-picosecond pulse excitation) were obtained for $[RhCl_2(bipy)_2]Cl$ and $[RhBr_2(bipy)_2]Br$. The relaxation processes between excitation and emission involves both changes in multiplicity and in orbital "parentage". The probable energy relaxation path populating the emitting levels of each complex is

$$^1(\pi\pi^*) \rightarrow {}^1(dd) \rightarrow {}^3(dd) \quad [60]$$

The luminescence and polarisation spectra of $[Rh(Hdpa)_2Cl_2]^{+}$ (Hdpa = 2,2-dipyridylamine) have been measured in acid, base and neutral solution. Acidic and neutral solutions show broad, symmetrical and structureless red emissions with microsecond lifetimes assigned as dd* phosphorescence. Basic solutions of the (deprotonated) complex show a blue asymmetrical emission overlapping the red emission band and assigned as a charge-transfer dπ* emission analogous to that obtained for the $[Ru(bipy)_3]^{2+}$ complex [61].

The corrinoid complex (19) is found to have a similar structure to its cobalt analogue [62].



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2.2.4.3 *Complexes with nitrogen-arsenic donor ligands*

In the equilibrium:-

$$trans\text{-}[RhL_2Cl_2] + X^- \rightleftharpoons mer\text{-}[RhL(L')Cl_2X]$$

{X = SCN, SeCN, NO_2 or N_3; L = (2-dimethylaminophenyl)dimethylarsine-*NAs*; L' = (2-dimethylaminophenyl)dimethylarsine - *As*} it is found that the second-order rate constant is hardly affected by the type of entering group. The first-order rate constants of the reverse reaction, however, are greatly affected by the leaving group concerned [63].

2.2.5 *Complexes with phosphorus or arsenic donor ligands*

^{19}F, ^{31}P and ^{103}Rh NMR spectra (single and double resonance) have been recorded for some rhodium(III) trifluorophosphine complexes. Coupling constants, and chemical shifts relative to $CFCl_3$ (for ^{19}F), H_3PO_4 (for ^{31}P) and the arbitrary frequency of 3.16 MHz (for ^{103}Rh), are recorded in Table 1 [64].

Complexes containing a variety of fluorophosphine ligands (L = PF_3, $PF_2(OPh)$, $PF(OPh)_2$ or 2-fluoro-1,3,2-benzodioxaphosphole) have been prepared.

TABLE 1

Chemical Shifts (units of ppm) and Coupling Constants (units of Hz) for some Rhodium(III) Trifluorophosphine Complexes

Complex	$\delta(^{19}F)$	$\delta(^{31}P)$	$\delta(^{103}Rh)$	$^{1}J(RhP)$	$^{2}J(RhF)$	$^{1}J(PF)$	$^{3}J(PF)$	$^{2}J(PP)$	$^{4}J(FF)$
cis-$[NBu_4][RhCl_4(PF_3)_2]$	-34.5	82.6	1934	-211	-12.6	-1375.3	7.9	-1.2	2.7
cis-$[NBu_4][RhBr_4(PF_3)_2]$	-29.5	87.2	1243	-210	-12.8	-1364.1	8.5	8.6	3.2
fac-$[RhCl_3\{PF(OPh)_2\}_3]$	-41.6	83.0	989	-187.1	-12.2	-1274.1	1.8	-20.4	1.6
fac-$[RhBr_3\{PF(OPh)_2\}_3]$	-38.6	81.2	623	-186.8	-12.4	-1260.1	2.1	-15.4	2.0

The compounds, either isolated or detected in solution by NMR spectroscopy include the types $[RhX_2L_2]$, $[RhX_3L]^-$, $[RhX_4L_2]$ and $[RhX_3\{PF(OPh)_2\}_3]$ (X = Cl, Br or I) [65]. The vibrational spectrum of *cis*-$[Bu_4N]$ $[RhX_4(PF_3)_2]$ (X = Cl or Br) has also been assigned [66].

The tridentate ligand, (E)-2-$Ph_2PC_6H_4CH{=}CHCH_2C_6H_4PPh_2$-2, loses a methylene proton upon reaction with $RhCl_3$ to give the chelate η^3-allylic complex, $[RhCl_2(2\text{-}Ph_2PC_6H_4CH{=}CHCHC_6H_4PPh_2\text{-}2)]$ [67].

The complexes $[RhCl_3L_3]$, $[RhCl_3(CO)L_2]$ and $[Rh_2Cl_6L_4]$ $\{L = As(CH_2Ph)_3\}$ have been prepared and characterised by infrared spectroscopy, electrical conductivity and dipole moment measurements [68]. The tribenzylarsine complexes of $[RhCl_3L_3)$ and $[RhCl_3(CO)L_2]$, examined in the range 260–450 cm^{-1}, showed a dependence of the metal-chloride frequency on the nature of the ligand located in the *trans* position relative to the halogen atom [69].

Acyl chlorides, RCOCl (R = Me, Et or $CHMe_2$), oxidatively add to $[RhCl(PMe_2Ph)_3]$ to give six coordinate $[MCl_2(COR)(PMe_2Ph)_3]$ complexes. $[RhCl(COMe)(PMe_2Ph)_3][PF_6]$ is formed upon treatment of $[RhCl_2(COR)(PMe_2Ph)_3]$ with $[NH_4][PF_6]$ and contains an approximate square-pyramidal geometry with an apical ethanoyl group. In solution $[RhCl(COMe)(PMe_2Ph)_3]^+$ is in equilibrium with $[RhCl(Me)(CO)(PMe_2Ph)_3]^+$ [70].

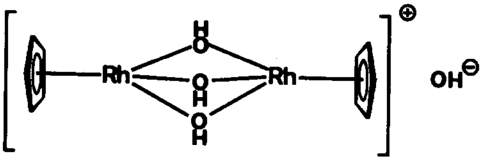
2.2.6 *Complexes with Group IV donor ligands*

2.2.6.1 *Organometallic complexes*

Although the chemistry of organometallic compounds is strictly outside the scope of this review note is made of those papers, in the author's opinion, which have some relevance to coordination chemistry.

The complexes, $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}OH)_3]X$ (X = Cl, $[PF_6]$ or $[BF_4]$), react in $CHMe_2OH$ solution to give $[\{RhH(C_5Me_5)\}_3(\mu_3\text{-}O)]^+$ salts. The structure of the $[PF_6]^-$ salt consists of an equilateral triangle of metal atoms each bonded to a C_5Me_5 and capped on one side by an oxygen and with each pair of rhodium atoms bridged at the other side by hydride. Reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3][PF_6]$ with primary alcohols gives mixtures of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)(\mu\text{-}O_2CR)_2][PF_6]$ and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CR)][PF_6]$. The latter complex contains both rhodium atoms bonded (η^5) to C_5Me_5 and bridged by two hydrides and one ethanoate group [71]. $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3][PF_6]$ reacts with phenol to give $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OPh)_3][PF_6]$, and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]$ X (X = Cl or OH) reacts with phenol to give $[\{Rh(C_5Me_5)\}_2(OPh)_3][(PhO)_5H_4]$ [72]. $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]OH$ reacts with $PhNH_2$ in the presence of $[PF_6]^-$ or $[BF_4]^-$ to produce $[\{Rh(C_5Me_5)\}_2(\mu\text{-}NHPh)(\mu\text{-}OH)_2]^+$. Primary amines react with $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]OH$ to give $[\{Rh(C_5Me_5)(NH_2R)_3]^{2+}$ (R = propyl or benzyl)

[73]. $[\{Rh(C_5H_5)\}_2(\mu\text{-}OH)_3]OH.11H_2O$ contains two metal atoms each η^5-bonded to a C_5H_5 ligand and bridged by three hydroxo ligands (20).

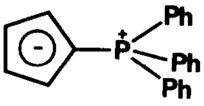


(20)

$[\{Rh(C_5Me_5)\}_2Cl_4]$ reacts with $Ag_2[SO_4]$ to give $Rh(C_5Me_5)(SO_4).2H_2O$. This complex is thought to exist in aqueous solution as $[Rh(C_5Me_5)(H_2O)_3]^{2+}$ and is readily carbonylated at room temperature and atmospheric pressure to $[Rh(C_5Me_5)(CO)_2]$ [74]. $[\{Rh(C_5Me_5)\}_2Cl_4]$ reacts with PMe_3 to give $[Rh(C_5Me_5)Cl_2(PMe_3)]$ which then reacts with silver ethanoate to produce the complex $[Rh(C_5Me_5)(O_2CMe)_2(PMe_3)]$, containing a monodentate ethanoate group [75]. The reaction of $[\{Rh(C_5Me_5)\}_2Cl_4]$ with LiMe gives *cis*-$[\{Rh(C_5Me_5)\}_2(\mu\text{-}CH_2)_2Me_2]$. This material isomerises slowly to the *trans* isomer, pyrolysis of which produces propene, methane and ethene [76].

Studies concerning the Cannizzaro-type disproportionation of ethanal into ethanoic acid and ethanol have continued [77]. The reaction is found to be first-order in aldehyde and half-order in $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$. By using solutions containing $[PF_6]^-$, the μ-hydride complexes, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)_2][PF_6]$ and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H_2)(\mu\text{-}O_2CMe)][PF_6]$ were isolated from reaction of the starting complex with ethanal [66].

$[Rh(C_5Me_5)(O{=}CMe_2)_3][PF_6]_2$ readily reacts with (21) to give the sandwich-type complex $[Rh(C_5Me_5)(Ph_3PC_5H_4)][PF_6]_2$ [78].



(21)

The redox chemistry of the $[Rh_2(1,3\text{-diisocyanopropane})_4]_2{}^{6+}$ ion ($Rh_4{}^{6+}$) has been examined in acidic aqueous media at the rotating glassy carbon electrode. The oxidation was determined to be a two-electron process with the overall stoicheiometry (in the presence of chloride ion) represented by:-

$$Rh_4Cl^{5+} + 3Cl^- \longrightarrow 2Rh_2Cl_2{}^{2+} + 2e^-$$

The reduction process is more complex in the stationary-electrode CV. Reduction peaks, relative to the saturated calomel electrode, are observed at + 160 mV and - 70 mV and, on the reverse scan, a sharp oxidation peak is obtained at + 385 mV with a shoulder at about + 530 mV [79].

2.2.6.2 *Carborane complexes*

Fourier-transform NMR studies on $[RhL_2H(L')]$ $\{L = PPh_3, PEt_3$ or PMe_2Ph; $L' = 1,2\text{-}, 1,7\text{-}$, or $1,12\text{-}C_2B_9H_{10}R$ (R = H, Me, Ph or Bu)$\}$ indicate that the metal vertex undergoes hindered rotation with respect to the five-membered face of the carborane cage [80].

Reaction of an ether solution of Na $[1,3\text{-}C_2B_7H_{12}]$ with $[RhCl(PPh_3)_3]$ or $[\{RhCl(PPh_3)_2\}_2]$ at room temperature gave $[\textit{closo}\text{-}6,6\text{-}(PPh_3)_2\text{-}6\text{-}H\text{-}6,2,3\text{-}RhC_2B_7H_9]$ according to the equation:-

$$Na[C_2B_7H_{12}] + [RhCl(PPh_3)_3] \longrightarrow [RhH(PPh_3)_2(C_2B_7H_9)] + H_2 + PPh_3 + NaCl$$

$[RhCl\{P(4\text{-tolyl})_3\}_2]_2$ reacts in a similar way. The rhodium PPh_3-carbaborane complex acts as a catalyst for the homogeneous hydrogenation of vinyltrimethylsilane under mild conditions [81].

2.2.6.3 *Complexes with tin donor ligands*

Rhodium-tin complexes, generated in aqueous HCl solutions containing $RhCl_3$ and $SnCl_2$, have been examined by ^{119}Sn NMR spectroscopy. The rhodium(III) species, $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1-5) have been assigned [82].

2.2.7 Hydride complexes

A neutron diffraction study of $[HRh\{P(OCHMe_2)_3\}_2]_2$ has confirmed the square-planar coordination around each rhodium atom and has located the hydride ligands at the bridging position [83].

Solvent exchange in $[M(PR_3)_2(solvent)_2H_2]^+$ (R = Ph, solvent = MeCN or Me_2CO; R = cyclohexyl, solvent = MeCN) has been examined. The coordinated solvent molecules are found always to occupy the *trans* position with respect to the hydride ligands [84].

2.2.8 Crystallographic Studies

Those studies dealing only with the crystal structures of rhodium(III) complexes and which are not dealt with earlier in the review are summarised in Table 2.

2.3 RHODIUM(II)

2.3.1 Halide complexes

EPR studies of γ-irradiated $[NH_4]Cl$ single crystals doped with rhodium reveal that Rh(II) (as well as rhodium(O)) is stabilised at interstitial sites in a compressed octahedral (D_{4h}) configuration. The unpaired electron is believed to be contained in the $d_{x^2-y^2}$ orbital and at 77 K super-hyperfine structure is observed as a result of the four equivalent chloride ligands indicating the overlap of the $d_{x^2-y^2}$ orbital with those of the equatorial ligands [92].

2.3.2 Diimine complexes

The chemistry of $[Rh(bipy)_3]^{2+}$ was discussed in Section 2.2.4.2.

2.3.3 Complexes with Group VI donor ligands

2.3.3.1 Carboxylate complexes

The chemistry of rhodium in this relatively uncommon oxidation state remains dominated by the dinuclear carboxylate derivatives. Apart from their unusual structure and oxidation state, these materials are known to have potential as anti-cancer agents and there is continued controversy concerning the electronic

TABLE 2

Crystallographic Studies of some Rhodium(III) Complexes

Complex	Crystal Structure	Space Group	Lattice Parameters	Approximate Metal Geometry	Reference
$[NH_4]_2[RhCl_5(H_2O)]$	Orthorhombic	Pnma	a13.767, b9.787, c7.059Å a13.738, b9.762, c7.042Å	Octahedral	[85] [86]
$[Rh(edtaH_3)Cl_2].2H_2O$	Monoclinic	Bb	a13.591, b14.416, c10.704Å γ101.29°	Square planar	[87]
trans-$[RhCl_2(dmg)(dmgH_2)]^-$	Orthorhombic	Pbca	a28.91, b8.20, c11.70Å	Octahedral	[88]
(-)-$[Rh(en)_3]Br_3.H_2O$	Orthorhombic	Pnma	a10.07, c16.688Å	Octahedral	[89]
$K_2[RhCl_2(dmg)(dmgH)].2H_2O$	Monoclinic	$P2_1/b$	a7.601, b15.123, c15.403Å γ95.04°	Distorted Octahedral (*trans* Cl atoms)	[90]
(±)-$[Rh(en)_3][SCN]_3$	Orthorhombic	-	a14.652, b14.268, c17.48Å	Octahedral	[91]
(+)-$[Rh(en)_3][SCN]_3$	Orthorhombic	-	a14.711, b13.481, c9.166Å	Octahedral	[91]
(+)-$[Rh(en)_3]$(+)$[Cr(en)_3][SCN]_6$	Monoclinic	-	a15.707, b17.739, c9.426Å γ131.04°	Octahedral	[91]

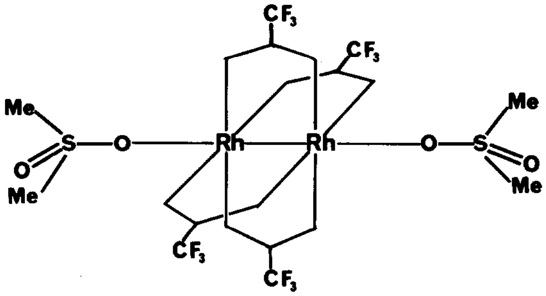
cdta = 1,2-dichlorocyclohexanediaminetetraethanoate properties of the compounds. Recently calculations have demonstrated that π-back-bonding stabilisation is important in the formation of adducts to $[Rh_2(C_3H_7COO)_4]$ [93]. Crystals of $(GuH)_2[Rh_2(CH_3COO)_4Cl_2]$ (Gu = guanine) consist of alternating dinuclear anionic complexes of $[Rh_2(CH_3COO)_4Cl_2]^{2-}$ and GuH cations. The important bond distances are: Rh - Rh; 2.397, Rh_1 - Cl_1; 2.571, Rh_2 - Cl_2; 2.610Å [94]. The rate constants for the forward and reverse reactions:

$$[Rh_2(O_2CMe)_4]^+ + X^- \rightleftharpoons [Rh_2(O_2CMe)_4X] \quad (X = Cl \text{ or } Br)$$

have been measured [95]. Reduction of $[Rh_2(O_2CMe)_4]^+$ by bromide involves the equilibrium:

$$[Rh_2(O_2CMe)_4Br] + Br^- \rightleftharpoons [Rh_2(O_2CMe)_4Br_2]^-$$

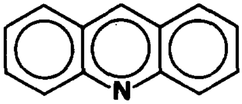
$[Rh_2(O_2CCF_3)_4(Me_2SO_2)_2]$, prepared from $[Rh_2(O_2CCF_3)_4]$ and an excess of dimethyl sulphone, has the molecular structure (22) [96].



(22)

The electronic configurations of the dirhodium tetracarboxylate complexes, $[Rh_2(\mu\text{-}HCO_2)_4]$ and $[Rh_2(\mu\text{-}HCO_2)_4L_2]$ ($L = H_2O$, NH_3 or PH_3) have been calculated by the *ab initio* SCF MO method. The Rh-Rh bond is a weak, single bond and the electronic configuration is $\pi^4\delta^2\pi^{*4}\delta^{*2}\sigma^2$ for $[Rh_2(\mu\text{-}HCO_2)_4]$ and the water and ammonia bonded complexes whilst $[Rh_2(\mu\text{-}HCO_2)_4(PH_3)_2]$ has an electronic configuration of $\delta^2\pi^4\pi^{*4}\delta^{*2}\sigma^2$ [97]. The electronic structure of $[Rh_2(O_2CH)_4(PH_3)_2]$ has also been investigated by Xα - SW MO calculations. The phosphine ligands are strong σ-donors resulting in a HOMO of Rh-Rh σ and Rh-P σ* symmetry. No Rh-P back bonding is evident [98]. The structures of the phosphine and phosphite adducts, $[Rh_2(O_2CMe)_4(PPh_3)_2]$ and $[Rh_2(O_2CMe)_4\{P(OPh)_3\}_2]$ have been determined by single-crystal X-ray diffraction studies. The $\{Rh_2(O_2CMe)_4\}$ nucleus in both complexes is very similar to that found in the bis(aqua) adducts [99]. Electrochemical or radiochemical oxidations of $[Rh_2(O_2CR)_4(PY_3)_2]$ (R = Et, CF_3; PY_3 = PPh_3, $P(OPh)_3$, $P(OCH_2)_3CEt$) gave the respective radical cations which were studied by EPR. The results are consistent with a single metal-metal bond formulation. The odd electron density on the Rh 5s atomic orbital is reported to be less than 15% of that on the rhodium d_σ atomic orbital [100]. $[Rh_2(O_2CCF_3)_4(PPh_3)_2]$ and $[Rh_2(O_2CCF_3)_4\{P(OPh)_3\}_2]$ have been examined by X-ray diffraction. Not surprisingly, the structures are found to be very similar to those of the ethanoate analogues [101].

The anti-tumour complex, $[Rh_2(O_2CMe)_4]$, forms a 1:1 adduct with adenine and adenosine. Binding is considered to be through the nitrogen of the purine rings. The chemical properties of these materials are similar to $[Rh_2(O_2CMe)_4]$/DNA solutions suggesting that similar binding sites are involved [102]. The compounds, $[Rh_2(O_2CC_2H_5)_4(\text{acridine})_2]$, $[Rh_2(O_2CC_2H_5)_4(\text{7-azaindole})_2]$, $[Rh_2(O_2CC_2H_5)_4(\text{phenazine})]$ and $[Rh_2(O_2CC_2H_5)_4(\text{durenediamine})]$ have been prepared each containing the axial nitrogen donor ligands depicted {acridine = (23), 7-azaindole = (24), phenazine = (25), durenediamine = (26)}.



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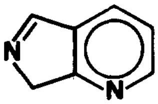

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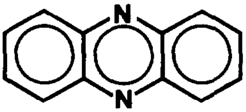

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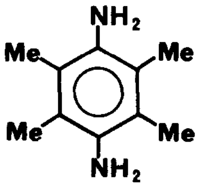


(26)

(25) and (26) link the $Rh_2(O_2CC_2H_5)_4$ units through their bidentate heteroatoms into one-dimensional chains [103].

$[Rh_2(O_2CMe)_4]$ reacts with CMe_3NC to give the binuclear axial diadduct, $[Rh_2(O_2CMe)_4(CMe_3NC)_2]$, with retention of the metal-metal bond [104].

2.3.3.2 Phosphate complexes

Hydrolysis of $[Rh_2(H_2PO_4)_4(H_2O)_2]$ under inert atmosphere gave $Rh_2(HPO_4)_2(H_2O)_{7.5}$ which on heating gave $[Rh_4(HPO_4)_2(PO_4)_2(H_2O)_{12}]$. The reaction of $[Rh_2(H_2PO_4)_4(H_2O)_2]$ with pyridine in aqueous solution gave $[Rh_2(HPO_4)_2(py)_6].6H_2O$ [105].

2.3.3.3 Complexes with oxygen-nitrogen donor ligands

Seven dinuclear rhodium(II) complexes containing 2-oxopyridine ligands have been characterised. The bridging ligands are either 6-methyl-2-oxopyridine (mhp) or 2-oxo-6-chloropyridine (chp). The complexes are $Rh_2(mhp)_4.H_2O$, $Rh_2(mhp)_4(CH_3CN)$, $Rh_2(mhp)_2(O_2CCH_3)_2(C_3H_4N_2).2CH_2Cl_2$, $Rh_2(mhp)_4(C_3H_4N_2).0.5CH_3CN$, $Rh_2(chp)_4$ and $Rh_2(chp)_4(C_3H_4N_2).3H_2O$. $C_3H_4N_2$ is possibly imidazole, although its chemical origin is not yet known [106].

Monomeric, five-coordinate $[Rh(dmgH)_2PPh_3]$ is generated photochemically from $[Rh(dmgH)_2PPh_3]_2$ or from $[Me_2CHRh(dmgH)_2PPh_3]$ (the latter eliminating propane in the process). Although the rhodium(II) complex is observed only as a transient intermediate its existence has been substantiated by the conversion to the Rh(III) complex, $[RhCl(dmgH)_2PPh_3]$, upon addition of iron(III) chloride, which itself is reduced to iron(II) [107].

2.3.3.4 Complexes with sulphur donor ligands

$[Rh\{S_2C_2(CN)_2\}_2]^{2-}$ is rapidly oxidised by MeI, unlike the corresponding complexes of Co, Ni, Cu and Zn which are methylated by MeI at their sulphur donor atoms [108].

2.3.4 Complexes with Group V donor ligands

2.3.4.1 Complexes with nitrogen donor ligands

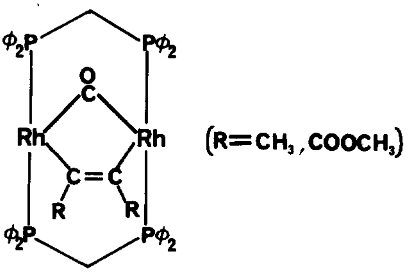
Rhodium(II) octaethylporphyrin $\{Rh(OEP)\}_2$ reacts with $P(OMe)_3$ as follows:

$$\{Rh(OEP)\}_2 + 2P(OMe)_3 \longrightarrow 2Rh(OEP)\{P(O)(OMe)_2\} + 2Me\cdot$$

When the molar ratio of $P(OMe)_3$ to $\{Rh(OEP)\}_2$ is 1:1 or less, $\{Rh(OEP)\}_2$ traps the methyl radical to form Rh(OEP)(Me) [109]. $\{Rh(OEP)\}_2$ also combines with dioxygen to form $Rh(OEP)(O_2)$, which subsequently gives the μ-peroxo species, $\{Rh(OEP)\}(O_2)\{Rh(OEP)\}$ Rh(OEP)(H), Rh(OEP)(Cl) and $\{Rh(OEP)\}(O_2)\{Rh(OEP)\}$ all of which react with NO to produce Rh(OEP)(NO) [110].

2.3.4.2 Complexes with phosphorus donor ligands

The reaction of *trans*-[{RhCl(CO)(dppm)}$_2$] with dimethylacetylenedicarboxylate gives (27). The X-ray structure determination of (27) indicates that it contains



(27)

CO^{2-} (ν(CO) = 1905 cm^{-1}) and the long Rh-Rh separation of 3.354Å suggests that no metal-metal bond is present. Hexafluoro-2-butyne reacts with *trans*-[RhCl(CO)(dppm)]$_2$ to produce a similar compound to the one described [111].

2.4 RHODIUM(I)

2.4.1 Halide complexes

The He-I photoelectron spectra of [Rh$_2$Br$_2$(CO)$_4$] and [Rh$_2$X$_2$(PF$_3$)$_4$] (X = Br, I) have been recorded and the results compared with those obtained for [Rh$_2$Cl$_2$L$_4$] (L = CO, PF$_3$). The He-II photoelectron spectrum of [Rh$_2$Cl$_2$(PF$_3$)$_4$] confirms the previous assignments made from the He-I spectrum above [112].

The interaction of [Rh$_2$Cl$_2$(CO)$_4$] with aluminium oxide has been studied by inelastic electron-tunnelling spectroscopy. The complex adsorbs in a dissociative fashion by interaction with the surface OH groups, resulting in the loss of HCl to form Rh-O bonds [113].

2.4.2 *Complexes with oxygen donor ligands*

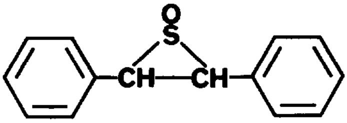
2.4.2.1 *Dioxygen and related complexes*

Decomposition of $[RhCl(PPh_3)_3(O_2)]$, in the absence of air, is said to proceed according to

$$4[RhCl(PPh_3)_3(O_2)] \longrightarrow 4Ph_3PO + [\{RhCl(PPh_3)_2\}_2] + [\{RhCl(PPh_3)_2(O_2)\}_2]$$

The compound $[\{RhCl(PPh_3)_2(O_2)\}_2]$ does not produce a clearly defined ^{31}P NMR spectrum owing to its rapid interconversion into a mixture of isomeric forms [114].

Heating $[RhX(PPh_3)_3]$ with stilbene episulphoxide (28) under reflux in CH_2Cl_2 gives $[Rh(SO)X(PPh_3)]_2$ (X = Cl, Br) [115].



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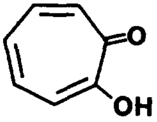
2.4.2.2 *β-diketonate complexes and related species*

$[RhZL_2]$ (Z = 2-benzosemiquinone; L = $P(OPh)_3$ or cod) undergoes oxidative addition with dihydrogen, dioxygen, perbromooxaxanthenequinone or tcne to give the octahedral rhodium(III) complexes with retention of the semiquinolato ligand [116]. The charge distribution in binuclear complexes of rhodium with bis(2-hydroxy)quinones and bis(2-amino)quinones has been established from X-ray photoelectron spectroscopy [117].

$[Rh(CO)_2Cl_2]^-$ reacts with (29) to produce $[Rh(CO)_2(C_7H_5O_2)]$ in which the



(29)

tropolone ligand is found to be bidentate. One of the carbonyl groups in this compound is readily replaced with PPh_3, which has a larger *trans*-influence than the CO group [118].

Ultraviolet irradiation of $[Rh(tfacac)(CO)_2]$ in a methane matrix produces the species $[Rh(tfacac)(CO)]$ $\{\nu(CO) = 2013.7\ cm^{-1}\}$ and $[Rh(\eta^1\text{-}tfacac)(CO)]$ $\{\nu(CO) = 2055.8$ and $1996.7\ cm^{-1}\}$ accompanied by production of carbon monoxide. Irradiation by visible light caused the new bands to decrease and the bands of the original complex to be regenerated [119].

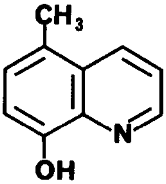
2.4.2.3 *Carboxylate and carbonate complexes*

The carboxylate complexes, *trans*-$[Rh(O_2CR)(CO)(PPh_3)_2]$ (R = C_6F_5; C_6Cl_5; $4\text{-}HC_6F_4$; $3\text{-}HC_6F_4$; $2\text{-}MeOC_6F_4$; $4,5\text{-}H_2C_6F_3$; $3,5\text{-}H_2C_6F_3$ or $2,6\text{-}F_2C_6H_3$), prepared by the action of $[RhH(CO)(PPh_3)_3]$ on the appropriate polyhalobenzoic acid, can be decarboxylated thermally to give the corresponding aryl complexes, $[Rh(R)(CO)(PPh_3)_2]$. The reaction rate increases with increasing fluorosubstitution; derivatives with R = $2\text{-}HC_5F_4$ or $2,6\text{-}F_2C_6H_3$ could not be obtained by this method [120].

The intermediate generated from the interaction of $[HRh(CO)(PPh_3)_3]$ with CO combines with carbon dioxide to form the hydrogen carbonate species *trans*-$[(PPh_3)_2Rh(CO)(OCO_2H)]$, which has a square planar structure; both CO and CO_2 are eliminated from the material upon pyrolysis [121,122]. The reaction of *trans*-$[Rh(OH)(CO)(PPh_3)_2]$ with CO_2 to form $[Rh(OCO_2H)(CO)(PPh_3)_3]$ has been re-examined. In dichloromethane solution, containing a trace of water, the system is found to be first order in complex concentration and the rate is found to be independent of the CO_2 partial pressure [123].

2.4.2.4 *Complexes with oxygen-nitrogen donor ligands*

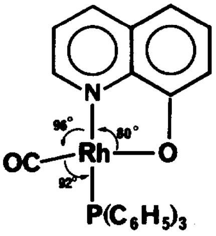
The complexes $[RhL(CO)L^1]$ {HL = 5-methyl-8-hydroxyquinoline (30); L^1 = CO,



(30)

$(4\text{-ClC}_6H_4)_3P$, PPh_3, $(4\text{-MeC}_6H_4)_3P$, $(4\text{-MeOC}_6H_4)_3P$, PEt_3 or PEt_2Ph}, [$RhLL^2$] {L^2 = *cis*-$Ph_2PCH = CHPPh_2$}, and [$RhL(CO)L^3.HgCl_2$] {$L^3 = (4\text{-MeC}_6H_4)_3P$} have been prepared and characterised by infrared and ^{31}P NMR spectroscopy [124].

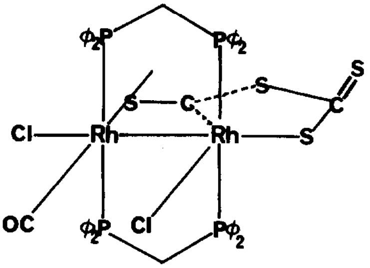
[$Rh(CO)(quin\text{-}8\text{-}0)(PPh_3)$] (31) may be prepared from the action of triphenylphosphine upon [$Rh(quin\text{-}8\text{-}0)(CO)_2$]. The crystal structure of (31) showed that it was the CO group *trans* to the *N*-atom of the quin-8-0 group in [$Rh(quin\text{-}8\text{-}0)(CO)_2$] which was substituted by the PPh_3 ligand, indicating that the *N* atom of the chelate ring has a larger *trans* effect than that of the oxygen atom [125].



(31)

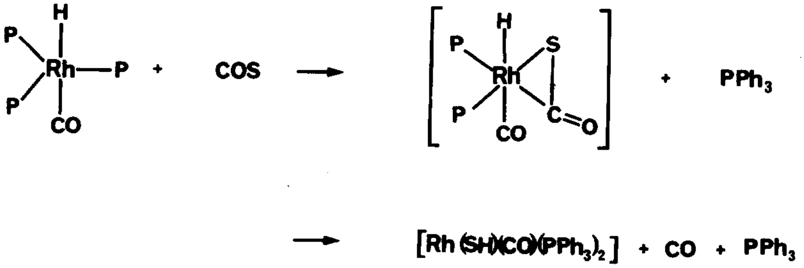
2.4.3 Complexes with sulphur donor ligands

The reaction of *trans*-[$Rh_2Cl_2(CO)_2(dppm)_2$] with CS_2 gives (32). This novel species is also formed in the reaction of [$Rh_2Cl_2(\mu\text{-}CO)(dppm)_2$] with CS_2 [126].

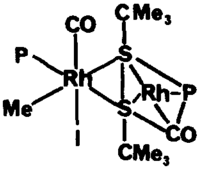


(32)

Although the reaction of $[\{RhCl(PPh_3)_2\}_2]$ with carbonyl sulphide forms $[RhCl(CO)(PPh_3)_2]$, the complex $[RhH(CO)(PPh_3)_3]$ abstracts sulphur from COS to give the rhodium thiol complex, $[Rh(SH)(CO)(PPh_3)_2]$. It is believed that this reaction proceeds by the formation of a COS complex as follows [127]:-



Iodomethane reacts with $[Rh_2(\mu\text{-}SCMe_3)_2(CO)_2(PMe_2Ph)_2]$ to give the oxidative addition product, $[Rh(Me)(I)(CO)(PMe_2Ph)(\mu\text{-}SCMe_3)_2Rh(CO)(PMe_2Ph)]$ (33). This compound rearranges to give the ethanoyl complex (34) [128].



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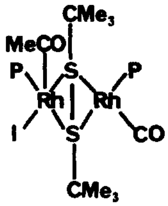
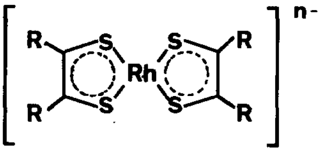


(34)

The reaction of electrochemically-generated $[Rh\{S_2C_2(CN)_2\}_2]^{3-}$ with weak acids gives $[Rh(H)\{S_2C_2(CN)_2\}_2]^{2-}$, containing a rhodium-hydride bond. Oxidation of this compound results in the formation of $[Rh\{S_2C_2(CN)_2\}_2]^{2-}$ [129]. A review on the reactivity patterns of planar bis(dithiolene) complexes (35) has appeared [130]. $[Rh(CO)(PEt_3)\{S_2C_2(CN)_2\}]^-$ reacts readily with $HClO_4$ to form



(35)

$[Rh(H)(CO)(PEt_3)\{S_2C_2(CN)_2\}]$.

$[RhCl(SO_2)(PR_3)_2]$ (R = cyclohexyl) consists of square planar coordination with *trans*-phosphines and a planar SO_2 group (*S*-bonded) [131].

The complex [Rh(eth)(PPh$_3$)Cl]{eth = thio-derivative of (7)} has been prepared [26].

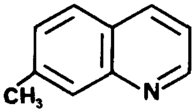
2.4.4 *Complexes with nitrogen donor ligands*

2.4.4.1 *Amine, imine and diimine complexes*

The proton NMR spectrum of $[Rh(CO)_2Cl(L)]$ (L = 2-alkylaniline) showed downfield shifts for the 2-benzylic protons, indicating an above-plane geometry involving an interaction with the metal orbitals [132].

The kinetics of the chelation reaction between $[RhX_2(CO)_2]^-$ (X = Cl, Br) and 2-aminopyridine (L) to give $[RhL_2X]$ has been examined spectrophotometrically. The reaction is first order with respect to the anion and second order with respect to L. Activation energies are 12.5 kJ mole^{-1} (X = Cl) and 23.0 kJ mole^{-1} (X = Br) [133].

$[Rh(CO)_2ClL]$ (L = (36–39)) were prepared from the reaction of $[Rh_2(CO)_4Cl_2]$ with the corresponding ligand. (40 = HL) reacts to give $[Rh(CO)_2L]$ [134].



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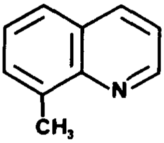

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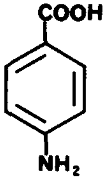

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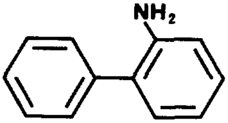

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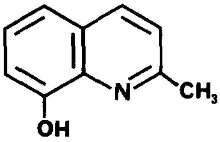
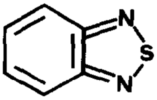


(40)

Compounds of similar formulations with L = $MeNH_2$, $EtNH_2$, Me_2NH, Et_2NH, py, benzothiazole, benzimidazole or 1,2,3-benzotriazole, may be obtained from the reactions of $[Rh(CO)_2ClL']$ with L {L' = (41)}. $[Rh(CO)(PPh_3)ClL]$ is formed by reaction of $[Rh(CO)_2ClL]$ with PPh_3 in benzene solution [135].



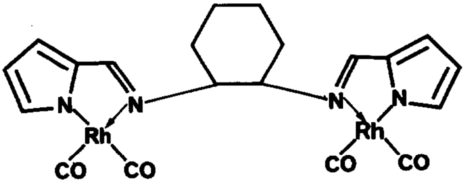
(41)

$[Rh(OClO_3)(CS)\{P(cych)_3\}]$, prepared from $[RhCl(CS)\{P(cych)_3\}]$ and $Ag[ClO_4]$, undergoes exchange reactions with a variety of nitrogen donors to give

$[Rh(CS)\{P(cych)_3\}_2L][ClO_4]$ (L = py, 4-Mepy, bipy, phen and related ligands). $[Rh(CS)(PPh_3)\{P(cych)_3\}L][ClO_4]$ was prepared similarly [136].

Treatment of $[Rh(nbd)_2][ClO_4]$ or $[Rh_2(nbd)_2Cl_2]$ with L (= 2- or 4-benzylpyridine gives $[Rh(nbd)L_2][ClO_4]$ [137].

Complex (42) has been examined by ^{103}Rh NMR spectroscopy. The chemical shift

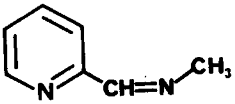


(42)

value of + 46 ppm (vs the 3.16 MHz reference) is one of the highest reported for a Rh(I) complex and is believed to be as a result of nitrogen coordination [138].

The crystal structures of $[Rh_2(\mu\text{-}pzl)_2(CS)_2\{P(OPh)_3\}_2]$ [139] and $[Rh_2(\mu\text{-}L)_2(CS)_2(PPh_3)_2]$ (LH = 3,5-Me_2pzlH) [140] have been determined by X-ray methods. The compounds are isostructural, and consist of dimers containing square-planar coordination, with bridging occurring through the two nitrogen atoms of the pyrazole ligand. The phosphite or phosphine ligands and the CO or CS ligands are in the *trans*- configuration [140]. The complexes $[Rh_2(\mu\text{-}L)_2(CS)_2(PPh_3)_2]$ (LH = various substituted derivatives of pzlH) have also been prepared.

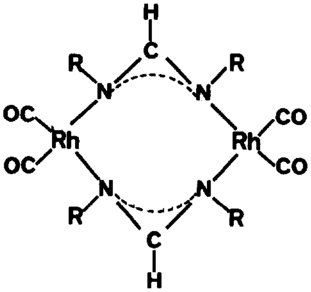
The complexes $[Rh(L\text{-}L)(cod)][PF_6]$ (L-L = pyridinal-methylimine (43),



(43)

pyridinal isopropylimine and pyridinal-α-phenylethylimine) have been studied by polarography and voltammetry in MeCN or CH_2Cl_2, with $[Bu_4N][ClO_4]$ as the supporting electrolyte. The reduction occurs in two reversible one-electron steps, followed by one or two irreversible waves which are complicated by both adsorption phenomena and chemical side-reactions. The oxidation shows only a single one-electron step, associated with catalytic phenomena at the electrode [141].

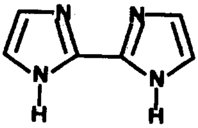
$[Rh_2(CO)_4Cl_2]$ reacts with the formamidine compounds LiN(R)CH:NR {R = Ph or 4-C_6H_4X (X = Me, MeO, Cl or F)} to give (44) [142].



(44)

Five-coordinate complexes of the general formula $[Rh(CO)(L\text{-}L)L'_2]X$ (L-L = substituted phen or biquin; L' = PPh_3, $AsPh_3$ or $SbPh_3$; X = $[ClO_4]$ or $[BF_4]$ were prepared either from the addition of an excess of L-L to $[Rh(CO)_2L_3]X$ or from the addition of a stoicheiometric amount of L' to $[Rh(CO)_2(L\text{-}L)]$ [143].

The salts $[RhL(L'\text{-}L')][ClO_4]$ and $[RhLL''_2][ClO_4]$ (L = cod, nbd or tetrafluorobenzobarrelene; L'-L' = 2,2-biimidazole (45) or 2,2'-bibenziimidazole



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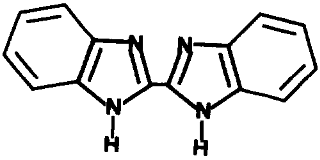


(46)

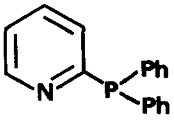
(46); L" = pyrazole or imidazoles) have been described. $[Rh(CO)_2(L'\text{-}L')][ClO_4]$ complexes, prepared by the displacement of the cod from $[Rh(cod)(L'\text{-}L')][ClO_4]$ with CO, react with phosphorus donor ligands (L"') to produce $[Rh(CO)(L''')(L'\text{-}L')][ClO_4]$ [144].

The oxidation of $[Rh(bipy)_2]^+$ was studied by chemiluminescence; the emitting product of this process was found to be *cis*-$[Rh(bipy)_2Br_2]^+$ [145].

2.4.4.2 Complexes with nitrogen-phosphorus donor ligands

Reaction of $[Rh_2(CO)_4Cl_2]$ with $(MeO)_2PNEtP(OMe)_2$ gives $[\{Rh(CO)[(MeO)_2PNEtP(OMe)_2]Cl\}_2]$, which has an asymmetrical structure with one of the carbonyl groups occupying a terminal position and the other a bridging position. Both chlorine atoms are found to be in terminal positions [146].

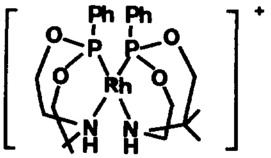
Addition of Ph_2Ppy (47) to $[Rh(CO)_2(\mu\text{-}Cl)]_2$ gives $[Rh(Ph_2Ppy)_2(CO)Cl]$ which



(47)

reacts further with $[Rh(CO)_2(\mu\text{-}Cl)]_2$ to give $[Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2]$. Treatment then with SO_2 produces $[Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2]$ - a reaction which can be reversed by adding CO. $[Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2]$ and its SO_2 analogue are both "A"-frame complexes [147].

$[RhL_2][ClO_4]$ and $[RhL_2]Cl$ ($[RhL_2]^+$ = (48)), *cis*-$[RhL'(CO)Cl]$ and *cis*-$[RhL(CO)Cl]$ (49) (L = $PhP\overline{OCH_2CH_2N(H)CH_2CH_2O}$, L' = $PhP\overline{OCH_2CMe_2N(H)CH_2CH_2O}$) have been found from single-crystal X-ray diffraction studies to have the structures shown [147].



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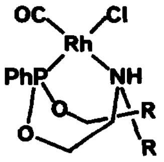
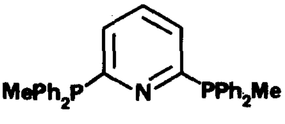


(49)

The reactions of $[RhCl(pnp)]$ (pnp = (50)), {prepared from the reaction of $[RhCl(cyclooctene)_2]$ with pnp} with small neutral molecules (L = PPh_3, CO, CO_2, O_2, SO_2, or Cl_2) gave the complexes $[RhCl(pnp)L]$. The dioxygen compound $[RhCl(O_2)(pnp)]$ reacts at room temperature with sulphur trioxide to give the



(50)

sulphato species [$RhCl(SO_4)(pnp)$]. Reaction of [$RhCl(O_2)(pnp)$] with CO at about 60 °C is more complicated, but the predominant reaction may be represented by:

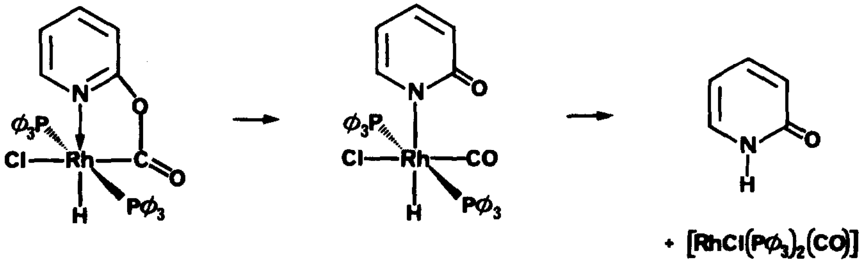
$$[RhCl(O_2)(pnp)] + 2CO \longrightarrow [RhCl(CO)(Opnp)] + CO_2$$

Reaction of [$RhCl(O_2)(pnp)$] with diiodine, however, yields free dioxygen [148]:

$$[RhCl(O_2)(pnp)] + I_2 \longrightarrow [RhClI_2(pnp)] + O_2$$

2.4.4.3 Complexes with nitrogen-carbon donor ligands

[$RhCl(PPh_3)_3$] reacts cleanly with the methanoate C-H bonds of 2-pyridylmethanoate and of 8-quinolinylmethanoate to give (51) and (52), respectively. C-H bond cleavage is shown to be the rate-determining step in the



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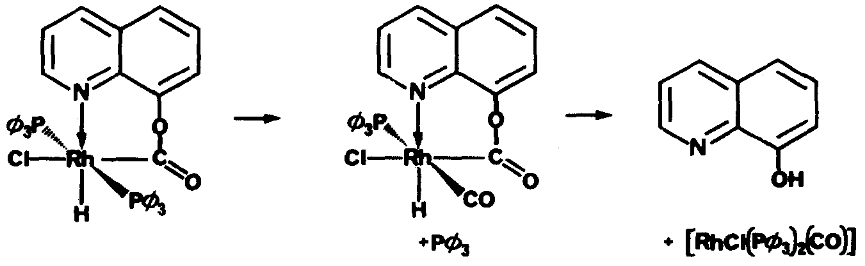


(52)

reaction by the observation of substantial deuterium isotope effects. The reaction is considered to proceed *via* an initial interaction of the antibonding C-H orbital with the highest-occupied molecular orbital on the metal. This interaction is consistent with a triangular C-H——M transition state [149].

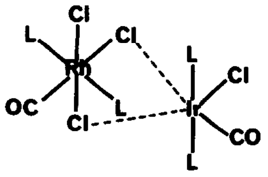
2.4.5 *Complexes with phosphorus donor ligands*

2.4.5.1 *Phosphine, phosphite and related complexes*

Contradictory to earlier reports, the stoicheiometric decarbonylation of benzoyl chloride by [$RhCl(PPh_3)_3$] at low temperature does not take place (although the high-temperature catalysed reaction does produce chlorobenzene). The product of the reaction is [$RhCl_2(PPh_3)_2(Ph)$], which is also derived from the thermal decomposition of [$RhCl_2(CO)(PPh_3)_2(Ph)$] without accompanied formation of chlorobenzene. In a similar fashion, [$RhCl(PPh_3)_3$] reacts with 4-methylbenzoyl chloride to give [$RhCl_2(PPh_3)_2(C_6H_4$-4-Me)] with elimination of CO; 4-chlorotoluene is not formed upon thermal decomposition of the complex [150]. Similarly, α,β-unsaturated acid chlorides, RCH = CHCOCl (R = H, Ph, Me, n-C_4H_9), are not decarbonylated to the respective chloroalkenes by using a stoicheiometric amount of [$RhCl(PPh_3)_3$] [151]. The reactions proceed as follows:-

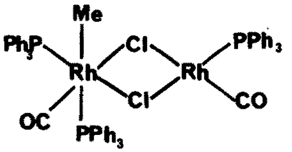
$$\mathrm{RCH = CHCOCl + [RhCl(PPh_3)_3] \longrightarrow [RCH = CH\overset{+}{P}Ph_3]Cl^- + [RhCl(CO)(PPh_3)_2]}$$

[$RhCl_3(CO)L_2$] and [$IrCl(CO)L_2$] (L = $PMePh_2$ or PEtPh) react together to give what is presumed to be a double chloro-bridged intermediate (53). Oxidative addition-reductive elimination then occurs to give [$IrCl_3(CO)L_2$] and the rhodium(I) species, [$RhCl(CO)L_2$]. *trans*-[$RhCl(CO)(PMe_2Ph)_2$] reacts similarly with [$RhCl_3(CO)(PEt_2Ph)_2$] to give [$RhCl_3(CO)(PMe_2Ph)_2$] and *trans*-[$RhCl(CO)(PEt_2Ph)_2$]



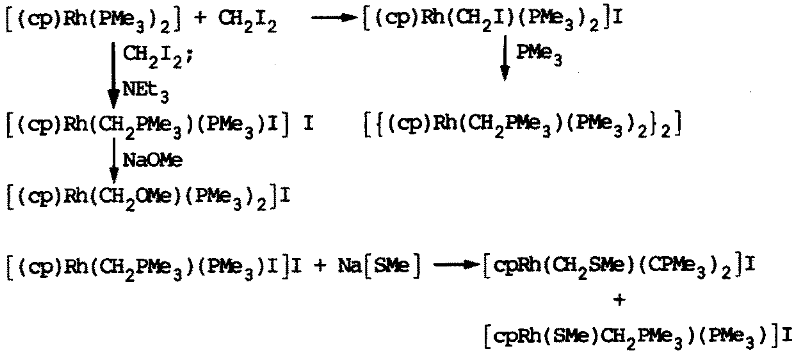
(53)

[152]. Treatment of $[(Ph_3P)_2RhCl_2\{C(O)Me\}]$ (from $[(PPh_3)_3RhCl]$ and MeCOCl) with carbon dioxide at room temperature in dichloromethane gave (54). Using benzene as solvent, $(Ph_3P)_3Rh(CO)_2MeCl$ was formed which reacts with CO to give $[(Ph_3P)_2Rh(CO)Cl]$ [153].



(54)

$[Rh(PMe_3)_4]Cl$ or $[RhCl(PMe_3)_3]$ interact with sodium amalgam in thf to give $[Hg_6Rh_4(PMe_3)_{12}]$. This cluster contains an $\{Hg_6\}$ octahedron with four tetrahedrally-related faces capped by $\{Rh(PMe_3)_3\}$ groups. Na/Hg reduction of $[RhH_2(PMe_3)_4]Cl$ yields $[RhH(PMe_3)_4]$, and $[RhCl(CO)(PMe_3)_2]$ gives $[\{RhH(CO)(PMe_3)_3\}_2]$. Syntheses of $[RhMe(PMe_3)_3]$, $[Rh(C_6H_4Me\text{-}3)(PMe_3)_3]$, $[RhCl(PMe_2Ph)(PMe_3)_2]$, $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)_2]$, $[Rh(O_2)(PMe_3)_4]PF_6$ and *trans*-$[RhCl(PPh_3)(PMe_3)_2]$ have also been reported [154]. Some interesting reactions of rhodium-phosphine complexes with CH_2I_2 have also been observed and these are summarised in Scheme I [155].



$$\begin{tikzcd}
{[(cp)Rh(PMe_3)_2] + CH_2I_2} \arrow[r] \arrow[d, "CH_2I_2;\ NEt_3"] & {[(cp)Rh(CH_2I)(PMe_3)_2]I} \arrow[d, "PMe_3"] \\
{[(cp)Rh(CH_2PMe_3)(PMe_3)I]\ I} \arrow[d, "NaOMe"] & {[\{(cp)Rh(CH_2PMe_3)(PMe_3)_2\}_2]} \\
{[(cp)Rh(CH_2OMe)(PMe_3)_2]I} &
\end{tikzcd}$$

$$[(cp)Rh(CH_2PMe_3)(PMe_3)I]I + Na[SMe] \longrightarrow [cpRh(CH_2SMe)(CPMe_3)_2]I + [cpRh(SMe)CH_2PMe_3)(PMe_3)]I$$

Scheme I: Some reactions of rhodium phosphine complexes with CH_2I_2, and the chemistry of the products

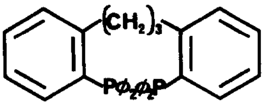
Both $[Rh_2Cl_2(PMe_3)_4]$ and $[Rh(PMe_3)_4]Cl$ react with lithium indenyl to produce $[(C_9H_7)Rh(PMe_3)_2]$. This material combines with $[NH_4][PF_6]$, CH_3I or CH_3COCl to form the cationic species $[C_9H_7RhR(PMe_3)_2]^+$ (R = H, CH_3 or CH_3CO), and the compound $[(C_9H_7)RhR(PMe_3)_2][PF_6]$ reacts with 1,5-C_8H_{12}, CO or PMe_3 to give $[Rh(PMe_3)_2(C_8H_{12})][PF_6]$, $[Rh(PMe_3)_2(CO)_3][PF_6]$ or $[Rh(PMe_3)_4][PF_6]$, respectively. An equilibrium mixture containing $[Rh(PMe_3)_2(C_2H_4)_3]^+$ is produced from the reaction of $[(C_9H_7)RhH(PMe_3)_2][PF_6]$ with ethene [156].

The $^{31}P\{^1H\}$ dynamic NMR spectra of *trans*-$[RhX(CO)L_2]$ (L = $(CMe_3)_2PMe$, $(CMe_3)_2PCl$ or $(CMe_3)_2PPh$; X = Cl, Br or I) have been recorded. The spectra shows the existence of different conformers and the differences in the free energies of rotation between the rotamers have been evaluated [157].

In the oxidative addition of MeI to $[RhCl(CO)(PR_3)_2]$ to give $[RhClI(CH_3)(CO)(PR_3)_2]$ the rate of reaction is found to be in the sequence $P(C_8H_{17})_3 \geqslant P(C_4H_9)_3 > P(C_{18}H_{37})_3$. When PR_3 is a triarylphosphine, two products are formed - *trans*-$[RhClI(CH_3)(CO)(PAr_3)_2]$ and a rhodium(III) acyl complex. The oxidative addition product was found not to be an intermediate in the formation of the acyl complex. Trialkylphosphines were found to be more effective than triarylphosphines at promoting the oxidative addition to rhodium(I); alkyl chains of length greater than C_4 are said to be marginally less effective than butyl [158]. 2- or 4-$C_6H_4(C{\equiv}CH)_2$ add oxidatively to *trans*-$[RhCl(CO)L_2]$ {L = PPh_3 or $P(C_6H_4F)_3$}. In the presence of diethylamine, HCl is lost from these complexes to yield $[Rh(CO)(C{\equiv}CR)L_2]$ {R = 2- or 4-$C_6H_4(C{\equiv}CH)$} [159].

Treatment of $[Rh(CO)_3\{P(4\text{-}RC_6H_4)_3\}_2][ClO_4]$ (R = Cl, F, Me or MeO) with MeCN followed by L (L = py, 2-MeOpy, bipy or phen) gives $[Rh(CO)L\{P(4\text{-}RC_6H_4)_3\}_2]$ $[ClO_4]$ [160].

Heating of $[Rh_2(cod)_2Cl_2]$ and (55) under reflux in toluene gave (56), in which the alkane moiety is dehydrogenated and the alkene is bound to the rhodium atom [161].



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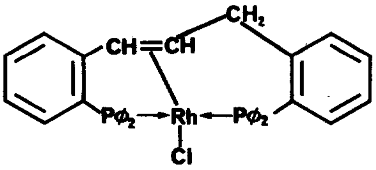
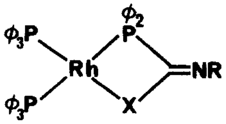
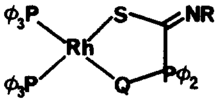


(56)

The complexes (57) and (58) have been prepared and are found to combine with CO to displace one PPh_3 group at the position which is *trans* to that chelate donor atom with the lowest *trans* influence [162].



(X=S,O,NR)

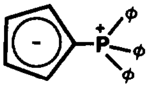


(Q=S,O)

(57)

(58)

Species (59) reacts with $[Rh_2(CO)_4Cl_2]_4$, $[Rh_2(1,5\text{-}C_8H_{12})_2Cl_2]_4$ or



(59)

$[Rh_2(C_7H_8)_2Cl_2]$ in the presence of $Ag[PF_6]$ to produce $[Rh(Ph_3PC_5H_4)(CO)_2][PF_6]$, $[Rh(Ph_3PC_5H_4)(1,5\text{-}C_8H_{12})][PF_6]$ and $[Rh(Ph_3PC_5H_4)(C_7H_8)][PF_6]$, respectively. Addition of PPh_3 to $[Rh(Ph_3PC_5H_4)(CO)_2][PF_6]$ gave $[Rh(Ph_3PC_5H_4)(CO)(PPh_3)][PF_6]$ and addition of $Ph_2PCH_2PPh_2$ gave $[(Ph_3PC_5H_4)(CO)Rh(\mu\text{-}Ph_2PCH_2PPh_2)Rh(CO)(Ph_3PC_5H_4)][PF_6]_2$ [163].

The NMR parameters of some fluorophosphine rhodium(I) complexes have been recorded, Table 3, [164] and the infrared and Raman spectra of *cis*-$[Bu_4N][RhX_2(PF_3)_2]$ and $[Rh_2X_2(PF_3)_4]$ (X = Cl, Br) have been reported and assigned [165].

$[Rh_2(CO)_4Cl_2]$ reacts with trialkyl phosphites (L) to form $[RhCl(CO)L_2]$ and $[Rh_2Cl_2L_4]$ depending upon the Rh:L ratio. L is hydrolysed to $P(OR)_2OH$ which also reacts with $[Rh_2(CO)_4Cl_2]$ to give $[RhCl(CO)\{P(OR)_2O\}_2]$ [166]. $[Rh(C_6H_5Me)\{P(OPh)_3\}_2][ClO_4]$ was prepared by treating $[RhCl\{P(OPh)_3\}_2]_2$ with $Ag[ClO_4]$. The rhodium atom is found from the crystal structure determination to be π-bonded to the arene ring which exists in a boat-like conformation. Treatment of $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ with CO gives $[Rh(CO)_3\{P(OPh_3)_2\}]ClO_4$ [167].

TABLE 3

NMR Parameters[a] of Some Fluorophosphine Complexes

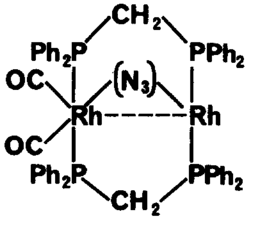
Complex	$\delta(^{19}F)$	$\delta(^{31}P)$	$\delta(^{103}Rh)$	$^{1}J(RhP)$[b]	$^{2}J(RhF)$[b]	$^{1}J(PF)$[b]	$^{3}J(PF)$[b]	$^{2}J(PP)$[b]	$^{4}J(FF)$[b]
$[\{RhCl(PF_3)_2\}_2]$	−16.9	110.8	−353	−344	−31.6	−1328.7	+19.1	−65.2	+4.4
$[\{RhBr(PF_3)_2\}_2]$	−15.8	112.8	−493	−343	−31.4	−1332.6	+21.1	−41.7	+4.7
cis-$[NBu^n{}_4][RhCl_2(PF_3)_2]$	−20.6	110.4	−382	−333	−31.6	−1312.7	+15.7	−43.3	+4.4
cis-$[NBu^n{}_4][RhBr_2(PF_3)_2]$	−19.9	112.6	−491	−334	−31.7	−1319.9	+18.1	−22.6	+4.8

a Chemical shifts in ppm. ^{19}F relative to $CFCl_3$, ^{31}P relative to H_3PO_4 and ^{103}Rh relative to 3.16 MHz

b Units of Hz

2.4.5.2 Diphosphine complexes

The following "A-frame" complexes have been prepared; $[Rh_2(\mu\text{-}X)(\mu\text{-}CO)(CO_2)(\mu\text{-}dppm)_2]Y$ (X = Br or I; Y = Br, I, $[RhBr_2(CO)_2]$ or $[BPh_4]$, $[Rh_2(CN)_2(CO)_n(\mu\text{-}dppm)_2]$ (n = 3 or 4), $[Rh_2(NCS)_2(CO)_4(\mu\text{-}dppm)_2]$, $[Rh_2(NCO)_2(CO)_2(\mu\text{-}dppm)_2]$ and $[Rh_2Cl(N_3)(CO)_2(\mu\text{-}dppm)_2]$. The unusual azide complex is proposed to have the structure illustrated by (60) [168].

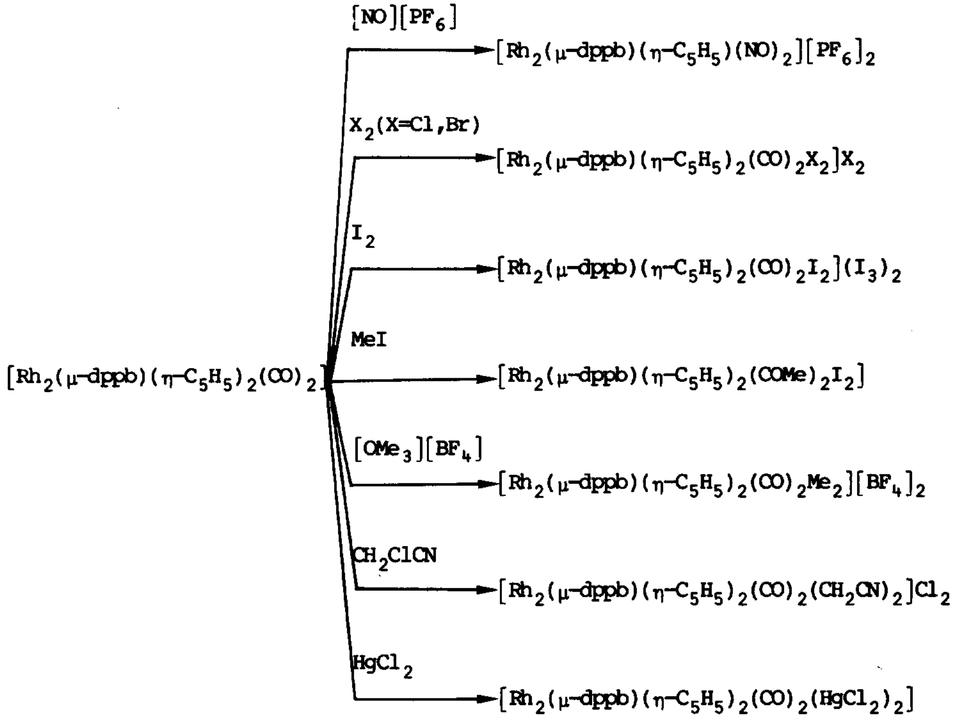


(60)

$[Rh_2Cl_2(\mu\text{-}CF_3C_2CF_3)(\mu\text{-}dppm)_2]$ contains two rhodium atoms bridged by two transoid dppm ligands. The alkyne bridges the two rhodium atoms, and is bound as a *cis*-dimetalated alkene. Reaction of the complex with carbon monoxide gives $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)(\mu\text{-}dppm)_2]$, which contains a bridging carbonyl, an alkyne molecule bound in a similar way to the parent complex and no metal-metal bond [169]. Addition of dppm to $[Rh(Ph_3PC_5H_4)(CO)_2][PF_6]$ gave $[(Ph_3PC_5H_4)(CO)Rh(\mu\text{-}Ph_2PCH_2PPh_2)Rh(CO)Ph_3PC_5H_4][PF_6]_2$ [169].

$[Rh(C_2H_4)_2Cl_2]$ reacts with dppe to give $[Rh(C_2H_4)(dppe)Cl]$ which eliminates C_2H_4 to give solvated $[RhCl(dppe)]$, which is subsequently converted to a dimer. Exposure of $[RhCl(dppe)]$ to CO_2 gives $[Rh(CO_2)(dppe)Cl]$, which decomposes to $[Rh_2(dppe)_2Cl_2]$. Reaction of $[Rh(dppe)Cl]$ with $Na[BPh_4]$ gives $[Rh(dppe)(BPh_4)]$ in which one of the phenyl rings is coordinated to the metal. This species also coordinates CO_2 at room temperature, under pressure, and is converted into $[Rh(dppe)Ph]$ when heated at 70°C under a CO_2 atmosphere, subsequently inserting CO_2 to give $[Rh(dppe)(O_2CPh)]$ [170].

Low-temperature ^{31}P NMR spectroscopy reveals that $[Rh(dppp)_2][BF_4]$ has a trigonal bipyramidal geometry with an equatorial solvent (propanone) molecule. For $[Rh(dppb)_2][BF_4]$, the solution geometry is more complex. Single-crystal X-ray studies, performed on $[Rh(dppb)_2][BF_4].C_4H_{10}O$ reveal that the cation has a distorted tetrahedral arrangement, whereas $[Rh(cod)(dppb)]^+$, in the $[BF_4]^-$ salt, is found to have an approximately square-planar geometry [171]. The dimer, $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2]$, is obtained by heating $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ under reflux with dppb in benzene. Smaller chelating phosphines such as dppe and dppp do not behave in a similar way [172]. The transformations illustrated in Scheme II have also been observed:

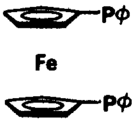


Scheme II: Some reactions of rhodium-dppb complexes

Dichloromethane solutions of $[Rh(dppb)_2]X$ (X = $[BF_4]$ or $[PF_6]$) react with CO to yield the dinuclear complex $[Rh_2(dppb)_3(CO)_4]^{2+}$. This species, isolated as the $[PF_6]$ salt, consists of two trigonal bipyramidal $\{RhP_3(CO)_2\}$ groups bridged by a dppb ligand through axial coordination sites. The CO groups are *cis*, and occupy equatorial sites. The chelating dppb ligands span the equatorial and axial sites [173].

The X-ray structural characterisation of $[RhH(diop)_2]$ reveals that the metal is coordinated to two chelating diop ligands, each with *S*, *S* chirality, and a hydride in a distorted trigonal bipyramid [174].

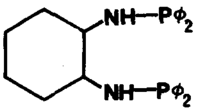
Complexes of the type $[HRh(CO)(P\text{-}P)(PR_3)]$, $[HRh(CO)(P\text{-}P)_{1\cdot5}]_2$ and $[HRh(CO)(\eta^2\text{-}P\text{-}P)(\eta^1\text{-}P\text{-}P)]$ {R = PPh_3 or $PEtPh_2$, P-P = various diphosphines {e.g. (61)} have been examined by $^{31}P\{^1H\}$ NMR spectroscopy. The complexes are found to have approximately trigonal-bipyramidal geometry [175].



(61)

The effect of temperature (2–100 K) on the emission spectra and lifetimes of [RhL$_2$][ClO$_4$] (L = *cis*-1,2-bis(diphenylphosphino)ethylene) is interpreted with a two-level, spin-orbit split emitting manifold with $\Delta\varepsilon$ = 38 cm^{-1}, τ(lower) = 5920 μs and τ(higher) = 20.3 μs [176].

[Rh(cod)(L-L)][ClO$_4$].CH$_2$Cl$_2$ {L-L = (62)} has a triclinic crystal structure,



(62)

space group $P\bar{1}$, with a distorted square planar geometry around the metal [177].

2.4.6 *Complexes with arsenic donor ligands*

The complexes, [RhX(CO)L$_2$] (X = Cl, Br or I), [RhH(CO)L$_3$] and [RhClL$_3$] {L = (PhCH$_2$)$_3$As} have been prepared and characterised from infrared spectroscopy, electrical conductivity and dipole moment measurements [178].

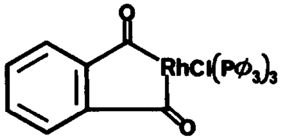
The "A-frame" complexes; [Rh$_2$(μ-X)(μ-CO)(CO)$_2$(dpam)$_2$]Y (X = Br or I; Y = Br, I, [RhBr$_2$(CO)$_2$] or [BPh$_4$]), [Rh$_2$(CN)$_2$(CO)$_4$(dpam)$_2$], [Rh$_2$(NCS)$_2$(CO)$_4$(dpam)$_2$] and (Rh$_2$(NCO)$_2$(CO$_2$)(dpam)$_2$] have been prepared [179]. [Rh$_2$Cl$_2$(CO)$_2$(dpam)$_2$].CH$_2$Cl$_2$ consists of two square-planar rhodium atoms bridged by two diarsine ligands. The rhodium atoms each possess *trans*- chloro and carbonyl ligands and the Rh-Rh separation is found to be about 5% shorter than that in the unsolvated species [180].

2.4.7 Complexes with carbon donor ligands

2.4.7.1 Organometallic complexes

Reaction between sodium or lithium nitrocyclopentadienide and $[Rh(CO)_2Cl]_2$ gives $[\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2]$. This is the first example of an η^5-nitrocyclopentadienyl transition metal compound to be synthesised directly from the nitrocyclopentadienide anion [181]. $[Rh(acac)(CH_2 = CHSiR_3)_2]$ and $[Rh(acac)\{CH_2 = CH)_2SiR_2\}]$ (R = Me, EtO or Ph) were prepared by ligand exchange of $[Rh(acac)(CH_2 = CH_2)_2]$ with the vinyl silanes [182]. A propanone solution of $[Rh_2(tfb)_2Cl_2]$ (tfb = tetrafluorobenzobicyclo[2,2,2]octatriene) reacts with $Ag[ClO_4]$ to form $[Rh(tfb)_2][ClO_4]$. This material combines with various nitrogen or phosphorus donor ligands to give $[Rh(tfb)L_2][ClO_4]$ (L = MeCN, PhCN, py, $PhNH_2$, 2-Mepy, 2-Etpy or 2,4-Me_2py) or $[Rh(tfb)(L\text{-}L)][ClO_4]$ (L-L = phen, bipy, amq, tmen, 2,2'-diquinoline or dppe) [183]. The organosodium compounds $[C_5H_4C(O)R]Na$ (R = H, Me or MeO) are found to be useful intermediates in the preparation of $[(\eta^5\text{-}C_5H_4CHO)Rh(CO)_2]$, which may be readily converted into the corresponding acrylate and vinyl derivatives [184]. $[Rh(nbd)\{P(4\text{-}RC_6H_4)_3\}_2]X$ (X = $[ClO_4]$ or $[BPh_4]$; R = Cl, F, Me or MeO) were prepared by reaction of $[Rh_2Cl_2(nbd)_2]$ with $P(4\text{-}RC_6H_4)_3$, followed by NaX. Treatment of these complexes with dihydrogen gave $[RhH_2\{P(4\text{-}RC_6H_4)_3\}_2]X$ or $[Rh\{P(4\text{-}RC_6H_4)_3\}_2PhBPh_3]$; the latter complex contains $[BPh_4]$ coordinated to rhodium *via* an arene. $[Rh(CO)_3\{P(4\text{-}RC_6H_4)_3\}_2][ClO_4]$ was isolated by carbonylation [185].

Complex (63) was prepared by treatment of (64) with $[RhCl(PPh_3)_3]$ [186].



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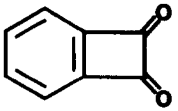


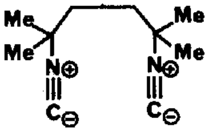
(64)

Carbon suboxide, C_3O_2, reacts with $[RhCl(PPh_3)_3]$ in benzene to produce *trans*-$[RhCl(CO)(PPh_3)_2]$ and polymeric C_2O. In toluene solution, C_3O_2 reacts with $[Rh_2Cl_2(cyclooctene)_4]$ to give $[\{RhCl(cyclooctene)(CO)(C_2O)\}_n]$. This species combines with pyridine to form $[\{RhCl(cyclooctene)(CO)(C_2O)(py)\}_2]$ [187].

2.4.7.2 Isonitrile complexes

The low-temperature, single-crystal polarised absorption spectrum of $[Rh_2(1,3\text{-diisocyanopropane})_4][BPh_4]_2$ has been obtained in the lowest triplet ← singlet transition. Analysis of the band shape of the absorption shows that the excited state is greatly distorted from the ground state along the Rh-Rh coordinate [188]. The ground ($^1A_{1g}$) and excited ($Eu(^3A_{2u})$) states of $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$ have been examined by time-resolved Raman spectroscopy. The results reveal that the Rh-Rh bond order is much higher in the excited state than in the ground state and the Rh-Rh bond energy has been estimated to be 176 kJ mol^{-1} from analysis of the vibronic structure [189].

$[Rh_4(1,3\text{-diisocyanopropane})_8]^{6+}$ forms 1:1 and 1:2 complexes with $[Rh_2L_4]^{2+}$ {L = (65)} in aqueous, non-complexing, acid solutions at room temperature. The formation constants of the oligomers were determined [190]. The oxidation state of rhodium in this material is formally 1.5.



(65)

The reaction of $[Rh(cod)Cl]_2$ with *meso*-1,3-diisocyanocyclohexane (L) gave $[Rh_2L_4][BPh_4]_2$ in the presence of $[BPh_4]^-$ ions [191]. The complexes $[Rh_2L_4]^{2+}$ (L = *meso*-1,3-diisocyanocyclohexane or *meso*-2,4-diisocyanopentane) were prepared and characterised from their electronic spectra. Thermal and photochemical reaction with HCl produces dihydrogen and the dimers $[\{Rh_2L_4Cl\}_2]^{4+}$ which react further with HCl to give $[Rh_2L_4Cl_2]^{2+}$ [192].

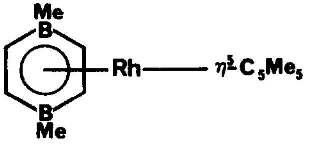
The radical anion salts, $[Rh(RNC)_4]^+ [TCNQ]^{\overline{\cdot}}$ (R = Me_3C, cyclohexyl, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $2,6\text{-}Me_2C_6H_3$ or $2,4,6\text{-}Me_3C_6H_2$); $[Rh(RNC)_4]^+ [TCNQ]^{\overline{\cdot}}.TCNQ$ (R = cyclohexyl, Ph, $4\text{-}MeC_6H_4$, $2,6\text{-}Me_2C_6H_3$ and $2,4,6\text{-}Me_3C_6H_2$) and $[Rh(4\text{-}MeC_6H_4NC)_4]^+ [TCNQ]^{\overline{\cdot}}[TCNQ]_2$ have also been prepared [193].

$[Rh_2L_4][PF_6]_2$ (L = 1,8-diisocyanomenthane) is triclinic, space group $P\bar{1}$, with lattice parameters: a = 13.688, b = 13.9445Å; α = 95.79, β = 104.54 and γ = 62.15°. The metal geometry is approximately square planar [194].

2.4.7.3 Carborane complexes

^1H and ^{31}P NMR spectra have been recorded for $[3,3\text{-}(PPh_3)_2\text{-}3,4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10}]$. The free energy of activation for hindered metal-cage rotation is found to be 41.0 kJ mole^{-1} [195]. The metallacarbaborane, *closo*-$[1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}RhC_2B_{10}H_{12}]$ has been synthesised from the reaction of $[RhCl(PPh_3)_3]$ with $[Me_4N][C_2B_{10}H_{13}]$ and its molecular structure has been determined by X-ray diffraction [196].

Complexation of (66) with $[C_5Me_5)RhC_2]_2$ gave (67) containing a bridging diborabenzene ligand [197].



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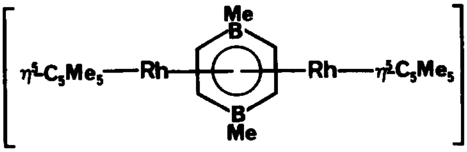


(67)

2.4.8 Complexes with mercury donor ligands

$[Rh_2Cl_2L_2]$ (L = cod or nbd) reacts with $[Hg(RN_3R')_2]$ (R = Me, Et or 4-tolyl; R' = 4-tolyl) to give the triazenido complex, $[L(RN_3R')_2RhHgCl]_2$ containing a Rh-Hg bond. This compound was also prepared by reaction of $[LRhCl(HgCl_2)]_2$ with $[Ag(RN_3R')_n]$. Intramolecular exchange is reported to occur between the two triazenide groups. The structure is believed to be similar to the analogous iridium complex for which a crystal structure determination has been carried out [198].

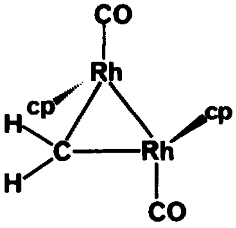
2.5 RHODIUM(O)

The EPR spectrum of γ-irradiated, rhodium-doped, $[NH_4]Cl$ single crystals is consistent with the stabilisation of Rh(O) {and of Rh(II)} at interstitial sites in a compressed octahedral (D_{4h}) symmetry. The g-values are consistent with the unpaired electron being in a pure $d_{3z^2-r^2}$ orbital [199].

2.6 BIMETALLIC COMPLEXES

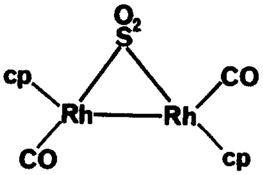
2.6.1 Homometallic complexes

$[\mu\text{-}CH_2)\{(\eta^5\text{-}cp)Rh(CO)\}_2]$ (68) has been examined by neutron diffraction at low temperature. The H-C-H angle of the bridging methylene group is very close to the tetrahedral angle [200].



(68)

$[(\mu\text{-CO})\{(cp)Rh(CO)\}_2]$ reacts with SO_2 in ethoxyethane at room temperature to give (69) through quantitative substitution of CO with SO_2 [201]. Addition of diphenylcarbene to the Rh = Rh bond of (70) gives (71). CO elimination and addition of the CH_2 moiety gives (72) [202].



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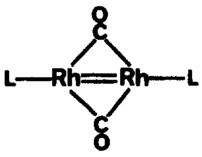

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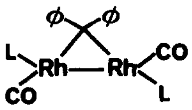

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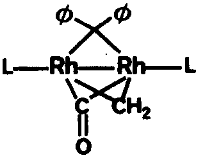
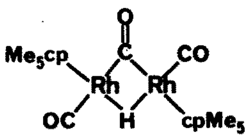


(72)

Reaction of $[(\eta^5\text{-}C_5Me_5)Rh(CO)_2]$ with $H[BF_4]$ produced a high yield of the metal-metal bonded species (73), which gave (74) upon reaction with NaOMe. CO was eliminated from (74) to give (75) [203]. The binuclear species (76) reacts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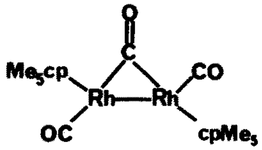
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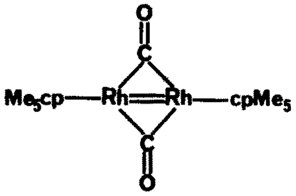
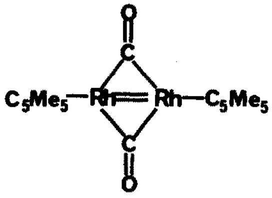

(75)

with $RR'CN_2$ (R = H, R' = H, Me or CO_2Et; R = R' = CO_2Me or Ph) to give (77), which rearranges to (78). On heating (78) gives (79) [204,205].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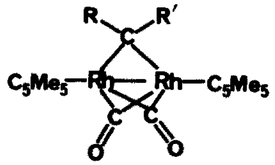
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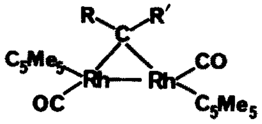
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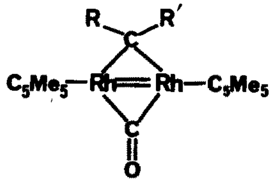
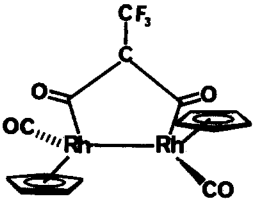

(79)

$[(cp)_2Rh_2(CO)_3(CF_3C_2CF_3)]$ (80) is formed from the reaction of $[Rh_2(CO)_4Cl_2]$ with $CF_3C \equiv CCF_3$ after treatment with (cp)Tl. (80) is believed to be in equilibrium with the isomer (81), which increases in concentration as the temperature is lowered. Decarbonylation of (80) is achieved at 25°C upon treatment with Me_3NO producing *cis*- and *trans*-$[Rh(cp)_2(CO)_2(CF_3C_2CF_3)]$ and $[Rh_2(cp)_2(\mu\text{-}CO)(CF_3C_2CF_3)]$ [206].



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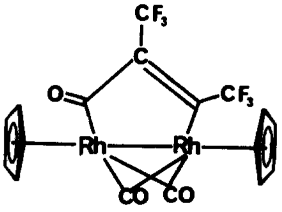


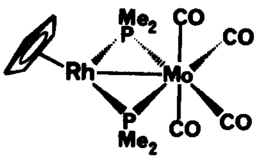
(81)

The electron-deficient alkynes $RO_2CC_2CO_2R$ (R = H or Me) cyclotrimerise on heating in the presence of $[\{Rh(CO)_2(PPh_3)_2\}_2]$. Thus, $MeO_2CC_2CO_2Me$ gives $[Rh_2(CO)_2(PPh_3)_4(MeO_2CC_2CO_2Me)]$ and $[Rh(CO)_2\{\overline{C_4(CO_2Me)_4Rh}(CO)_2(PPh_3)\}]$ [207].

CO combines with $[(\mu\text{-}H)_2Rh_2\{P(OCHMe_2)_3\}_4]$ to produce $[(\mu\text{-}H)_2Rh_2(\mu\text{-}CO)\{P(OCHMe_2)_3\}_4]$ which transforms slowly in solution to $[Rh_2(\mu\text{-}CO)_2\{P(OCHMe_2)_3\}_4]$. This material reacts reversibly with carbon monoxide to give $[Rh_2(\mu\text{-}CO)_2(CO)_2\{P(OCHMe_2)_3\}_4]$ [208].

2.6.2 Heterometallic complexes

The phosphido-bridged, binuclear species $[(C_5Me_5)\overline{Rh(\mu\text{-}PMe_2)Mo}(CO)_4]$ has a crystallographically determined Rh-Mo bond. The structure is shown schematically in (82). NMR studies have demonstrated that the complex is fluxional with a facile axial-equatorial interchange [209]. The "triple-decker" sandwich complexes $[CoRh(P_3)(triphos)_2][BF_4]_2.0.75CH_2Cl_2$, $[CoRh(P_3)(triphos)_2][BPh_4]_2.2(CH_3)_2CO$, $[NiRh(P_3)(triphos)_2][BF_4]_2$,



(82)

$[NiRh(P_3)(triphos)_2][BF_4]_2.C_4H_8O$ and $[NiRh(P_3)(triphos)_2][BPh_4]_2.CH_2Cl_2$ (analogous to $[Rh_2(P_3)(triphos)_2][BPh_4].(CH_3)_2CO$) have been prepared and characterised $\{(P_3)$ is the η^3-bonded *cyclo* triphosphorus unit and triphos is 1,1,1-tris(diphenylphosphinomethyl)ethane$\}$ [210].

Heating of $[(Cp)(CO)Co(\mu\text{-}CH_2)Co(CO)(cp)]$ with $[Rh(cp)(CO)_2]$ gave a mixture of the known species, $[cp(CO)Rh(\mu\text{-}CH_2)Rh(CO)cp]$ and the novel heterobinuclear species, $[cp(CO)Co(\mu\text{-}CH_2)Rh(CO)cp]$ [211].

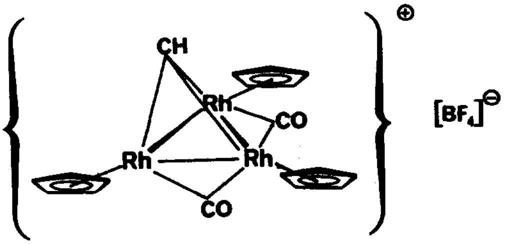
$[IrH_5(PEt_3)_2]$ reacts with $[(PEt_3)_2Rh(\mu_2\text{-}Cl)_2(PEt_3)_2]$ or $[(dppe)Rh(\mu_2\text{-}Cl)_2(dppe)]$ to give, respectively, the hydrido-bridged binuclear complexes $[(PEt_3)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PEt_3)_2]$ or $[(dppe)Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(dppe)]$ [212].

2.7 RHODIUM CARBONYL CLUSTERS

2.7.1 Trimeric clusters

Treatment of $[Rh_2(CO)_4Cl_2]$ with PPh_2H in benzene in the presence of a base gives $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, which consists of an edge-bridged triangular cluster [213]. By employing a $[Rh_2(CO)_4Cl_2]$:PPh_2H molar ratio of 1:2, the 56-electron trinuclear cluster, $[Rh_3(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)_2(\mu\text{-}CO)(CO)_3]$, was isolated in which each Rh-Rh edge is bridged by a PPh_2 group. Two of the rhodium-rhodium bonds are further bridged by chlorine and the third is bridged by a carbonyl group [214].

Reaction of $[(cp)_2Rh_2(CO)_2(\mu\text{-}CH_2)]$ with $H[BF_4]$ gives the protonated derivative, $[(cp)_2Rh_2(CO)_2(\mu\text{-}CH_2)(\mu\text{-}H)]$, which can be readily de-protonated with bases such as methoxide, or thf. On warming, the methylidyne-rhodium cluster (83) is formed along with the elimination of dihydrogen and methane [215].

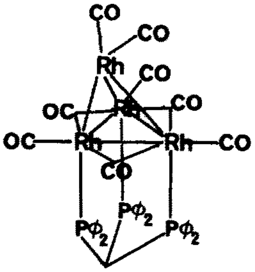


(83)

Reaction of the indene species, $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$, with buta-1,3-diene, *trans*-penta-1,3-diene, isoprene, *trans*, *trans*-hexa-2,4-diene, cyclopentadiene or cyclohexa-1,3-diene gives the stable complexes $[Rh_2(\mu\text{-}CO)(\mu\text{-}1,3\text{-}diene)(\eta^5\text{-}C_9H_7)_2]$. The X-ray crystal structure of the cyclohexa-1,3-diene complex indicates that the diene is more weakly held than in the corresponding mononuclear systems [216]. Reaction of the trimeric complex with allene in toluene affords $[Rh_2(\mu\text{-}CO)_2(C_3H_4)(\eta^5\text{-}C_9H_7)_2]$ which reacts further with $H[BF_4]\text{-}Et_2O$ to give $[Rh_2(CO)_2(CH_3C{=}CH_2)(\eta^5\text{-}C_9H_7)_2][BF_4]$ [217].

2.7.2 *Tetrameric clusters*

Methane formation from the stoicheiometric reaction of molecular hydrogen with $[Rh_4(CO)_{12}]$, supported on γ-alumina, has been studied using temperature-programmed decomposition. The temperature at which methane is first observed is 150 °C [218]. Fragmentation of $[Rh_4(CO)_{12}]$ occurs under 1241-1379 bar of CO at 5-12 °C in dodecane solutions to give $[Rh_2(CO)_8]$. The introduction of small amounts of dihydrogen causes spectral changes in the high-pressure infrared spectrum and Fourier subtraction of the $[Rh_4(CO)_{12}]$ and $[Rh_2(CO)_8]$ bands reveals a series of bands consistent with the species $[HRh(CO)_4]$ [219]. Other carbonyl clusters under high pressures of CO and H_2 have been observed to fragment to $[Rh(CO)_4]^-$, $[HRh(CO)_4]$ and $[Rh_2(CO)_8]$ [220]. The far-infrared and Raman spectrum of $[Rh_4(CO)_{12}]$ in the solid state and in dichloromethane has been examined. The IR band at 198 cm^{-1} has been assigned to the a_1-type $\delta(M\text{-}M\text{-}CO)$ vibration of the bridging carbonyl ligands and this has been confirmed by analysis of the ^{13}CO-enriched spectra. The IR band at 176 cm^{-1} is assigned to t_2, $\nu(M\text{-}M)$. Raman bands of $[Rh_4(CO)_{12}]$ solution are found at 125 (e, $\nu(M\text{-}M)$), 170 (t_2, $\nu(M\text{-}M)$) and 219 cm^{-1} (a_1, $\nu(M\text{-}M)$) [221]. The "tripod" ligand, $HC(PPh_2)_3$, was reacted with $[Rh_4(CO)_{12}]$ to give (84). $[Co_2Rh_2(CO)_{12}]$ behaves in a similar way to $[Rh_4(CO)_{12}]$ [222].



(84)

Although ^{31}P NMR studies on $[Rh_4(CO)_{12-x}\{P(OPh)_3\}_x]$ (x = 1, 2 or 3) show that each compound consists of one isomer in solution, the analogous PPh_3 derivatives exist as different isomers. On mixing $[Rh_4(CO)_{12-x}L_x]$ with $[Rh_4(CO)_{12-y}L_y]$ ($L = P(OPh)_3$; x = 0, 1 or 2, y = x + 2; x = 0, y = x + 4) a distribution of the phosphite ligands takes place to produce $[Rh_4(CO)_{12-x}L_z]$ (z = 1/2(x + y)). It is also found that interchange of carbonyl groups occurs on mixing $[Rh_4(^{12}CO)_{12}]$ with $[Rh_4(^{13}CO)_{12}]$ [223]. The "butterfly" cluster $[Rh_4(\mu\text{-}CO)_4(\mu\text{-}SO_2)_3\{P(OPh)_3\}_4]$ has been prepared from the passage of SO_2 through a benzene solution of $[Rh_4(CO)_8\{P(OPh)_3\}_4]$ at room temperature. The SO_2 ligand is bonded to two metal atoms through the sulphur atom and a third metal atom is bonded through one of the oxygen atoms [224].

2.7.3 Hexameric clusters

The thermal properties of $[Rh_6(CO)_{16}]$ have been studied by thermogravimetry and IR spectroscopy. The temperature of the transition of the cluster to metallic rhodium is increased by a matrix effect of the KBr support [225]. Methane is formed above 140 °C by the stoicheiometric reaction of dihydrogen with $[Rh_6(CO)_{16}]$ supported upon $\gamma\text{-}Al_2O_3$ [218] and XPES indicates that the cluster remains intact when impregnated onto alumina. When completely decarbonylated by exposure to air, regeneration is achieved by treatment with moist CO [226].

The precursor clusters, $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$, when impregnated onto silica containing TiO_2 or ZrO_2 were shown by IR and XPES to form hydrido carbonyl clusters such as $[Rh_6(CO)_{15}H]^-$ owing to the reaction with surface OH from the acid sites of the titanium or zirconium oxides. These oxides are also believed to prevent the aggregation of rhodium on the silica support and to enhance CO dissociation [227]. The anions, $[Rh_6(CO)_{15}X]^-$ (X = COEt, CO_2Me) are found to contain octahedral rhodium clusters and the stereochemistry of the carbonyls is found to be similar to that of $[Rh_6(CO)_{16}]$ with one terminal CO group replaced by X [228].

$[Rh_6(CO)_{14}(C_3H_5)]^-$ is obtained by reaction of allyl chloride ($CH_2 = CHCH_2Cl$) with $[Rh_6(CO)_{15}]^{2-}$ and contains an octahedral rhodium cluster with a mean rhodium-rhodium bond length of 275.3 pm. The structure of the complex is similar to that of $[Rh_6(CO)_{16}]$ except that two of the terminal CO groups of one of the metal atoms are replaced by a π-bonded allyl group [229].

$[Rh_6C(CO)_{13}]^{2-}$, prepared from CO evolution of $K_2[Rh_6C(CO)_{15}].6CH_3O(CH_2)_4OCH_3$, has been characterised in its tetraphenylphosphonium salt. It contains a distorted octahedron of rhodium atoms with a central carbon atom. Six of the CO ligands are edge-bridging, spanning consecutive edges of the three octahedron equators and seven of the CO ligands are terminal [230].

$[Rh_6(\mu_3\text{-}CO)_4(CO)_8\{P(OPh)_3\}_4]$ is found to contain a slightly-distorted octahedral cluster of rhodium atoms. The ligand geometry is derived from that of the parent $[Rh_6(CO)_{16}]$ species with four of the terminal CO groups substituted by $P(OPh)_3$ ligands [231].

2.7.4 High nuclearity clusters

Decomposition of $[Rh_6(CO)_{14}(SCN)_2]^{2-}$ in thf gives the anion $[Rh_{10}S(CO)_{10}(\mu\text{-}CO)_{12}]^{2-}$. The structure of the anion in the $[(Ph_3P)_2N]_2[Rh_{10}S(CO)_{22}]$ salt consists of a bicapped square-antiprismatic metal atom cluster containing an interstitial sulphur atom at the cluster centre [232]. $[Rh_{10}P(CO)_{22}]^{3-}$, as the $[C_6H_5CH_2N(Et)_3]$ salt, has been characterised by X-ray methods and found to have a similar structure [233], as has the analogous anion of $[Rh_{10}As(CO)_{22}]$ in its benzyl triethylammonium salt.

The arsenic species is found to be stable under a high pressure (537 bar) of CO/H_2 up to 150 °C, but at ~ 1000 bar, total pressure, the material decomposes into $[Rh(CO)_4]^-$ and $[Rh_9As(CO)_{21}]^{2-}$ [234].

^{13}C NMR spectroscopy has revealed that $[Rh_{12}(CO)_{30}]^{2-}$ is converted under high CO/H_2 pressure, into $[Rh_5(CO)_{15}]^-$. On the NMR time scale at low temperature, the exchange of carbonyls is found not to be fast [235]. The structure of the anion in $[Ph_3PNPPh_3]_2[Rh_{12}C_2(CO)_{24}]$ consists of a closed $\{Rh_{12}\}$ polyhedron containing two prismatic cavities in which the carbide atoms are located. The CO groups are bonded by eight edge bridges and sixteen terminal links [236].

The anion in $[NMe_4]_4[Rh_{13}H(CO)_{24}].3C_5H_9NO$ has an idealised C_s symmetry and contains a centred twinned-cuboctahedron of metal atoms similar to the $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ series [237].

A new and convenient high-yield synthesis of $[Rh_{14}(CO)_{25}]^{4-}$ from commercially-available rhodium carbonyl complexes has been reported; its previously reported structure has been verified [238].

Heating of a mixture of $[Rh_4(CO)_{12}]$ and NaOH under reflux in 2-propanol produces $[Rh_{17}(\mu_3\text{-}CO)_3(\mu\text{-}CO)_{15}(CO)_{12}]^{3-}$ which contains a tetracapped twinned-cuboctahedral cluster of C_s symmetry [239].

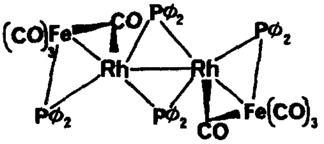
The high-nuclearity cluster, $[Cs_9(18\text{-crown-}6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$ has been isolated and all of the non-hydrogen atoms located in its structure [240].

2.7.5 *Mixed-metal clusters*

$Ag[PF_6]$ and $[Rh(CO)(PPh_3)(cp)]$ combine to form $[Ag\{Rh(CO)(PPh_3)(cp)\}_2][PF_6]$ which contains Ag–Rh bonds. The crystal structure of the material reveals the presence of discrete $[Ag\{Rh(CO)(PPh_3)(cp)\}_2]^+$ ions [241].

Irradiation of $[Mn_2(CO)_{10}]$ in the presence of $[Rh_2(L\text{-}L)_4][PF_6]$ (L-L = 2,5-dimethyl-2,5-diisocyanohexane) produces the mixed-metal, linear, tetranuclear cluster, $[Rh_2(L\text{-}L)_4Mn_2(CO)_{10}][PF_6]_2.2(CH_3)_2CO$, comprising $[(CO)_5MnRh_2(L\text{-}L)_4Mn(CO)_5]^{2+}$ cations having approximate D_{2d} symmetry and two propanone molecules of crystallisation. The geometry about each metal is approximately octahedral [242].

Treatment of $[Rh_2(\eta\text{-}C_3H_5)_4Cl_2]$ with an excess of $[Fe(CO)_4(PPh_2H)]$ in benzene at room temperature and in the presence of CO results in the formation of $[Rh_2Fe_2(PPh_2)_4(CO)_8]$ (85) [243]. $[Rh_3Fe(\mu\text{-}PPh_2)_3(\mu\text{-}CO)_2(CO)_6]$ has been prepared by treatment of $[Rh_2(CO)_4Cl_2]$ with $[Fe(CO)_4(PPh_2H)]$ in the presence of base.



(85)

Reaction of this mixed metal cluster with CO gives $[Rh_2(CO)_6(PPh_2)_2]$, which subsequently eliminates CO to form $[Rh_4(CO)_6(PPh_2)_4]$ [244].

The triosmium cluster, $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ reacts with $[Rh(acac)(C_2H_4)_2]$ to form $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$. The acac ligand in this cluster is chelated to the rhodium atom at one end but one of its oxygen atoms also bridges to an osmium atom. The ligand thus functions as a five-electron donor so that the cluster is a 60-electron system. Reaction of PPh_3 with the $\{Os_3Rh\}$ cluster produces the unstable species $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}(PPh_3)]$ [245].

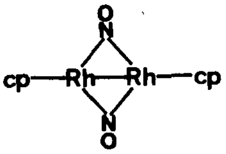
The mixed metal clusters, $[PtRh_4(CO)_{14}]^{2-}$ and $[PtRh_4(CO)_{12}]^{2-}$ have been prepared and characterised by X-ray crystallography. The equilibrium:

$$[PtRh_4(CO)_{12}]^{2-} \xrightleftharpoons[-\,CO]{+\,CO} [PtRh_4(CO)_{14}]^{2-}$$

takes place at room temperature and atmospheric pressure. During this conversion, the trigonal bipyramidal clusters undergo structural rearrangements - the movement of the platinum atom from the apical position to one in the equatorial plane being of particular note [246]. Reaction of $[Pt(C_2H_4)_3]$ with $[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ in toluene at 0 °C produces $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ containing Pt at the centre of a pseudotetrahedral geometry. $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$ is formed by addition of $H[BF_4]$ to, for example, $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ which has a structure similar to that of its precursor. It is speculated that the hydrido ligand must bridge a Pt-Rh bond [247].

2.8 RHODIUM-NITROSYLS AND THIONITROSYLS

NOX (X = Cl or Br) adds to $[RhCl(PPh_3)_3]$ to give $[Rh(NO)X_2(PPh_3)_2]$.solvate and $[Rh(NO)X_3(PPh_3)_2]$ [248]. $[NO][PF_6]$ reacts with $[Rh(CO)_2(\eta\text{-}C_5R_5)]$ (R = H or Me) to give $[Rh(CO)(NO)(\eta\text{-}C_5R_5)]^+$ which decarbonylates to $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5R_5)_2]^+$. Further reaction of the latter compound with NO^+ produces $[\{Rh(\mu\text{-}NO)(\eta\text{-}C_5R_5)\}_2]^{2+}$ [249]. The compounds, $[(cp)_2Rh_2(NO)_2]$ (86) and $[(cp)_3Rh_3(NO)_3]$ (87) have been synthesised by the addition of nitric oxide to thf solutions of $[Rh_2(CO)_4Cl_2]$ under an inert atmosphere. Pyrolysis of $[(cp)_2Rh_2(NO)_2]$ dissolved in xylenes under dinitrogen gave a clean conversion to $[(cp)_3Rh_3(NO)_2]$. $[(cp)_2Rh_2(NO)(NO_2)]$ (88) is formed from the passage of NO through a dichloromethane solution of $[cpRh(CO)_2]$, following the ingress of a small volume of air [250].



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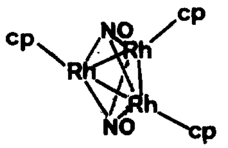

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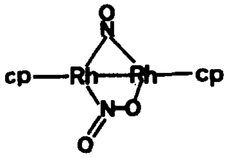
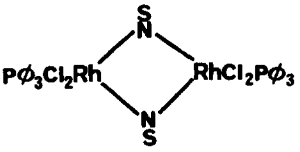


(88)

Reactions of the nitrosyl halides (X = Cl or Br) with the thionitrosyl complexes, $[Rh(CO)(NS)Cl_2L_2]$ and $[Rh(CO)(NS)(PPh_3)_2]$, produces $[Rh(CO)(NO)ClXL_2]$ (L = PPh_3 or $AsPh_3$) [251].

$(NSCl)_3$ reacts with various Rh(I) carbonyl complexes to give $[\{Rh(CO)(NS)Cl_2L\}_2]$ (L = PPh_3 or $AsPh_3$). Reaction of this compound with an excess of PPh_3 or $AsPh_3$ gave $[Rh(CO)(NS)Cl_2L_2]$ and $[Rh(CO)(NS)(PPh_3)_2]$.

Reactions of the nitrosyl halides with these carbonyl thionitrosyl complexes gave [Rh(CO)(NO)ClXL$_2$] (X = Cl or Br; L = PPh$_3$ or AsPh$_3$) [251]. Reaction of (NSCl)$_3$ in thf with [Rh(NO)(PPh$_3$)$_3$] gives (89) [252].



(89)

The complexes [Rh(NS)ClXL$_2$] (X = Cl, L = PPh$_3$ or AsPh$_3$; X = Br, L = PPh$_3$) and [Rh(CO)(NS)Cl$_2$L$_2$] (L = PPh$_3$ or AsPh$_3$) have been derived from (NSCl)$_3$ [253]. [Rh(NO)X$_2$(PPh$_3$)$_2$] (X = Cl or Br) reacts with (NSCl)$_3$ in thf to give the bridging thionitrosyl complex [Rh(NS)X$_2$(PPh$_3$)]$_2$ which, with excess of PPh$_3$ or AsPh$_3$, gives [Rh(NS)X$_2$(PPh$_3$)L] (L = PPh$_3$ or AsPh$_3$) containing a terminal thionitrosyl group [254]. Similarly, reaction of (NSCl)$_3$ with [Rh(NO)Cl$_2$(AsPh$_3$)$_2$] gives [Rh(NS)Cl$_2$(AsPh$_3$)]$_2$ which combines with PPh$_3$ to produce [Rh(NS)Cl$_2$(PPh$_3$)$_2$]. Addition of either PPh$_3$ or AsPh$_3$ (L) to [Rh(NS)Cl$_2$(AsPh$_3$)]$_2$ gives [Rh(NS)Cl$_2$(AsPh$_3$)L] [255].

2.9 RHODIUM CATALYSTS

A number of review articles appeared in 1981 concerning catalysis by rhodium complexes. In particular the chemical and catalytic reactions of Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$], have been reviewed in an article which includes details of the preparation and physical properties of the compound, as well as its stoicheiometric and catalytic reactions. The discussion of the catalytic reactions of [RhCl(PPh$_3$)$_3$] includes its rôle in hydrogenation, dehydrogenation and hydrogen transfer, hydroformylation and carbonylation, hydrosilylation, oxidation, isomerisation, and oligomerisation [256].

A report on the heterolytic activation of dihydrogen by transition metal complexes has appeared in which the catalytic reactions of rhodium(I) and rhodium(III) are discussed [257], and a review of the theoretical chemistry of the homogeneous, [RhCl(PPh$_3$)$_3$]-catalysed hydrogenation of alkenes has been published [258]. Hydrogenations catalysed by rhodium complexes have also been discussed within Volume 4 of the Advances Series; "Aspects of Homogeneous Catalysis" [259] and a review of rhodium-catalysed, asymmetric hydrogenations has appeared in which the experimental data on chiral phosphines used as ligands are highlighted [260]. The mechanistic pathways in the catalysis of alkene hydrocarboxylation by rhodium has been reviewed [261] and the commercial applications of reactions catalysed by rhodium have been described by Parshall [262]. Reviews concerning hydroformylation and carbonylation by rhodium catalysts are described in the relevant sections.

2.9.1 Hydrogenation

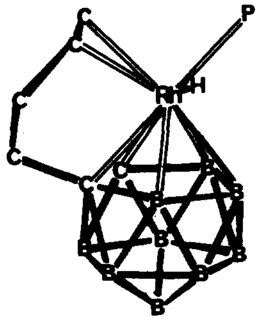
2.9.1.1 Reactions of carbon-to-carbon multiple bonds

$[RhCl(PPh_3)_3]$, anchored onto a linear polystyrene, has been examined as a catalyst for alkene hydrogenation. The results of this work indicate that the mechanism is similar to that found under homogeneous conditions [263]. Catalytic deuterogenation using $[RhCl(PPh_3)_3]$ in benzene, under an atmosphere of dideuterium, occurs in the preparation of palmitic acid-d_2 and stearic acid-d_6 from the corresponding 9,10-unsaturated methyl esters [264].

In conjunction with $AlEt_3$, $[RhCl_2(PR_3)_2]$ is found to be an active hydrogenation catalyst. When R is tolyl, the complex can reduce both alkenes or internal alkynes, but when R is cyclohexyl, the complex is then inactive for the reduction of internal alkynes [265].

The selective oxidation of the hydrido- and carboxylato- triphenylphosphine rhodium(I) complexes $[RhH(PPh_3)_4]$, $[RhH(PPh_3)_3]$, $[RhH(CO)(PPh_3)_3]$ or $[Rh(OCOCHMe_2)(PPh_3)_3]$ in the solid state, using dioxygen, produces the paramagnetic species $\{Rh^{II}(O_2)\}^-$, detected by EPR, indicating the presence of coordinatively-unsaturated metal centres. The catalytic hydrogenation activity of these complexes is affected by the presence of metal centres with a vacant site [266].

[*Closo*-1,3-μ-2,3-μ-$\{1,2\text{-}\mu\text{-}(\eta^2\text{-}3,4\text{-}CH_2CH_2C(Me)\text{=}CHCH_2CH_2CH_2)\}$-3-H-3-$PPh_3$-3,1,2-$RhC_2B_9H_9$] has been prepared from $[RhCl(PPh_3)_3]$ and Cs[7,8-bis(butenyl)-7,8-$C_2B_9H_{10}$]. This compound is found to catalyse the hydrogenation of terminal alkenes (such as 3,3-dimethylbut-1-ene) but is found not to be active towards alkynes [267]. When [*closo*-1,3-$\{\mu\text{-}(\eta^2\text{-}3\text{-}CH_2\text{=}CHCH_2CH_2)\}$-3-H-3-$PPh_3$-3,1,2-$RhC_2B_9H_{10}$] (90) was exposed to conditions employed for the hydrogenation of alkenes or alkynes, the alkenyl ligand was hydrogenated to a non-coordinating butyl group thus leaving an open coordination site on the metal and which greatly enhanced the rate of hydrogenation of added alkene [268].



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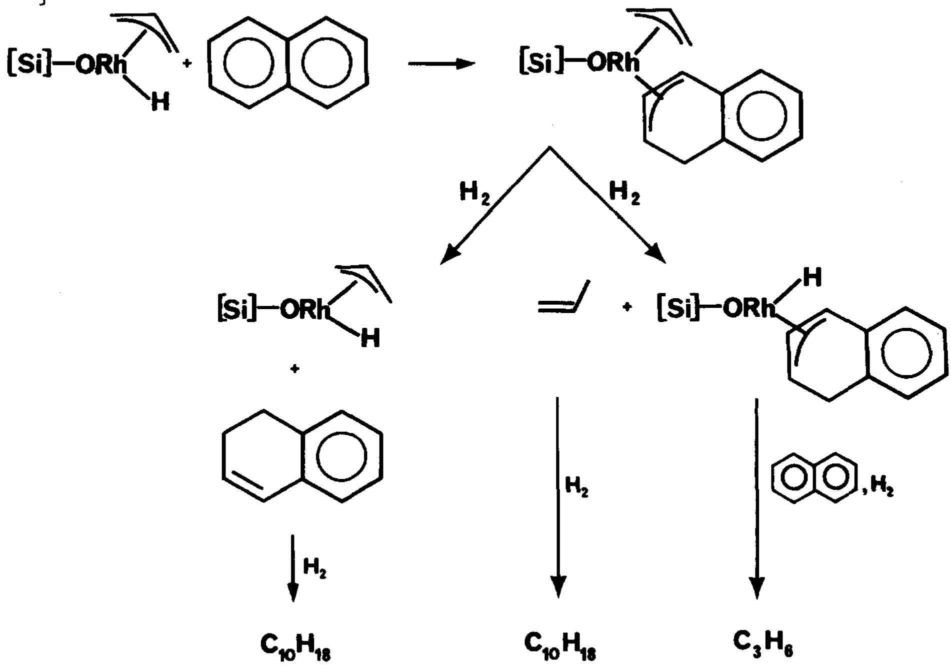
The silica-bound hydride complex, [Si]-ORh(allyl)H, catalyses the hydrogenation of benzene under mild conditions. Naphthalene hydrogenation to decalin also occurs when catalysed by this complex but the activity slowly decreases from the initial rate until a new constant rate is achieved, over which time propane is evolved. The reactions involved are outlined in Scheme III [269].

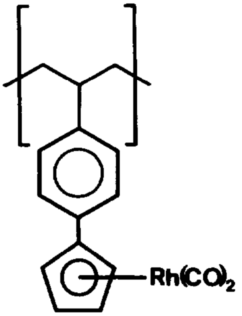


Scheme III: Reactions involved in the [Si]-ORh(allyl)H-catalysed hydrogenation of naphthalene [269]

Various other silica-supported rhodium hydride complexes {e.g. [Si]-ORhH$_2$, [Si]-ORh(allyl)H(PMe$_3$)$_2$ and [Si]-ORhH$_2$(PMe$_3$)$_3$} have been prepared and examined for activity as alkene hydrogenation catalysts. It is confirmed that the Rh-H species are the active sites for hydrogenation because the metal-hydride IR band disappears on exposure of the supported allyl hydride complex to 1-butene, but reappears (with equal intensity) when subsequently exposed to dihydrogen. No activity is obtained with [Si]ORhH$_2$(PMe$_3$)$_3$ owing to the lack of an available coordination site for the incoming alkene. The order of decreasing hydrogenation activity of the catalysts towards various alkenes is as written above, but with [Si]-ORh(allyl)H at the head of the series [270].

LCAO-MO-SCF calculations have been carried out for the reaction [H$_2$RhCl(PH$_3$)$_2$(C$_2$H$_4$)] → [HRhCl(PH$_3$)$_2$(C$_2$H$_5$)]. In the early stages of the process (up to the transition state), the reaction may best be described as an ethene insertion into the Rh-H bond. This insertion is calculated to be exothermic (70 kJ mol^{-1}) with a small energy barrier (75 kJ mol^{-1}) [271]. Catalysts prepared *in situ* from μ,μ'-dichlorobis{di(alkene)rhodium(I)} and phosphines of the type RPPh$_2$ {R = (CH$_2$)$_n$Si(OEt)$_3$; n = 1-6, R = CH$_2$SiMe$_{3-m}$(OEt)$_m$; m = 1-3} have been studied, along with their heterogeneous analogues anchored to silica, in the hydrogenation of alkenes. Rates were found to be first order in alkene concentration and deactivation of the catalysts is believed to occur as a result of dimerisation of the active species [272]. Rhodium anchored to the non-cross-linked polymers [4-Ph$_2$PC$_6$H$_4$CHCH$_2$]$_n$, [4-cych$_2$PC$_6$H$_4$CHCH$_2$]$_n$ or [4-Ph$_2$PC$_6$H$_4$CHMeN:C]$_n$ by addition of either [{RhCl(C$_2$H$_4$)$_2$}$_2$] or [{RhCl(cod)}$_2$], acts catalytically in the hydrogenation of cyclohexane and of cod. The polymer-anchored species have a higher activity and are more stable than their corresponding monomers (the rhodium complexes of PPh$_3$ and of P(cych)$_2$ph) owing to the reduced tendency to dimerise [271]. A solution prepared from the interaction of [{RhCl(cyclooctene)$_2$}$_2$] and poly[(R)-glutamic acid] in CH$_3$CONMe$_2$ showed a high catalytic activity for the hydrogenation of 1-hexene, methyl acrylate and dimethyl maleate [274]. Complexes prepared *in situ* from [{RhCl(cyclooctene)$_2$}$_2$] and PPh$_2$R (R = Me or Me$_3$Si(CH$_2$)$_n$; n = 1-4) have been examined for their activity as 1-heptene hydrogenation catalysts. The SiMe$_3$ group is considered to increase the catalytic activity by increasing the electron density on the metal [275]. The cationic complexes, [Rh(nbd)L$_2$][ClO$_4$] and [Rh(nbd)L(PR$_3$)][ClO$_4$] (L = Mepy, Me$_2$py, *etc*; PR$_3$ = triarylphosphine or a tritolylphosphine) have been prepared and examined for their catalytic activity. Although the catalysts are selective in alkene hydrogenation they have a tendency to decompose under reaction conditions [276]. The complexes [Rh(tfb)L$_2$][ClO$_4$] (Section 2.4.5), containing tertiary phosphine ligands {L = PPh$_2$Et, P(4-MeOC$_6$H$_4$)$_3$, P(4-MeC$_6$H$_4$)$_3$, P(4-FC$_6$H$_4$)$_3$, P(4-ClC$_6$H$_4$)$_3$ or P(3-MeC$_6$H$_4$)$_3$}, show high selectivities in the hydrogenation of 1-hexyne and of various dialkenes to monoalkenes [183].

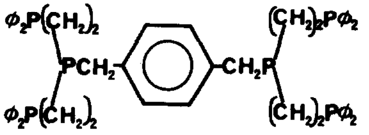
$[Rh_6(CO)_{10}L_6]$ $\{L_6 = (PPh_3)_6, (P(OMe)_3)_6, (-)\text{-}(diop)_3\}$ are good catalysts or catalyst precursors for cyclohexene hydrogenation. IR spectroscopy reveals that the major part of the cluster remains intact during the reaction. For $[Rh_6(CO)_{10}(PPh_3)_6]$, the reaction is first order with respect to dihydrogen pressure, cyclohexene concentration and catalyst concentration [277]. The hydrogenation of *trans*-1,3-pentadiene (1 bar H_2 and 60–80 °C) has been examined using $[Rh_2Cl_2(CO)_4]$ both in toluene solution and anchored to a γ-Al_2O_3 support. Both the homogeneous and heterogeneous systems display good specificity toward the terminal C = C bond. Partial substitution of the CO ligands by PPh_3 leads to a reduction in activity (but not selectivity) in the homogeneous reaction but the activity of the heterogeneous reaction can increase or decrease depending upon whether the introduction of the phosphine preceeds or follows the anchoring of the complex onto the alumina [278]. $[Rh_2Cl_2(CO)_4\{PhS(CH_2)_nSPh\}]$ (n = 1-6) is catalytically active in the hydrogenation of alkenes but has a short life-time owing to its decomposition under the hydrogenation conditions. Similar complexes of PhSMe, Ph_2S, $PhS(O)CH_2S(O)Ph$ and $Ph_2P(CH_2)_mSPh$ (m = 1-3) are reported [279]. The polymer-bound complex (91) is effective in catalytic hydrogenations,



(91)

particularly for aromatic systems containing electron-donating substituents such as CH_3O- and CH_3- [280]. $[Rh_2(CO)_4Cl_2]$, when anchored to γ-Al_2O_3, has been found to be more active towards the hydrogenation of 1- and 2-pentyne than when the reaction is carried out in toluene solution, although the activity of $[Rh_4(CO)_{12}]$ is not appreciably altered upon going from the homogeneous to the heterogeneous system [281].

$[RhCl_3(py)_3]$-Na$[BH_4]$ was found not to be selective in the hydrogenation of PhC≡CPh to *cis*-stilbene owing to over-hydrogenation [282]. The mixed complexes, $[(PEt_3)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PEt_3)_2]$ and $[(dppe)Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(dppe)]$ are claimed to show catalytic activity in alkene hydrogenation [193]. $[Rh_2Cl_2(tddx)]$ {tddx = (92)} and $[Rh_2Cl_2(tdadx)]$ {tdadx = (93)} activate molecular hydrogen by



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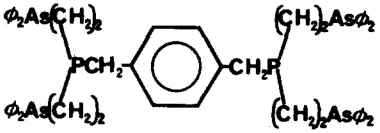


(93)

forming a tetrahydrido species of the type $[Rh_2Cl_2H_4L]$ (L = tddx or tdadx). Transfer of hydrogen is then said to occur to alkenes, such as cyclohexene and 1-heptene, to form the saturated product. The reaction is first order in catalyst concentration and a fractional order with respect to the alkene [283].

$RhCl_3.4H_2O$, $[edtaH_2]Na_2$ and EtOH were combined to give Na[Rh(edtaH)Cl]. In the presence of $Na[BH_4]$, Na[Rh(edtaH)Cl] catalyses the reduction of unsaturated compounds, for example, allyl alcohol, $CH_2 = CHCH_2OH$, is hydrogenated to PrOH [284]. The thiolato-bridged dimers of general formula $[\{Rh(\mu\text{-}SR)[P(OR')_3]_2\}_2]$ (R = R' = Me_3C, Ph or Et; R = Me_3C, R' = $PhCH_2$) are active catalysts for 1-hexene or cyclohexene hydrogenation at low temperature and pressure [285].

2.9.1.2 Reactions of CO, CO_2 and oxygen- or nitrogen- containing organic compounds

$[Rh_6(CO)_{16}]/ThO_2$ catalysts show varying activities and selectivities in the hydrogenation of carbon monoxide to alcohols, depending upon the additive used (*e.g.* CeO_2, CaO or Na_2O). When the undoped catalyst is employed at 250 °C, methanol, ethanol and iso- and normal propanol are formed in the concentrations 0.21, 0.35 and 0.005%, respectively. Hydrogenation under similar conditions, using CeO_2-doped catalysts, gave 0.46% MeOH, 0.49% EtOH and 0.047% Me_2CHOH/PrOH [286]. Impregnation of Rh_4-R_{13} carbonyl clusters onto silica containing TiO_2 or ZrO_2 has lead to the production of highly-dispersed rhodium catalysts which showed a high activity for ethanol production from synthesis gas at atmospheric pressure [227].

$[Rh_6(CO)_{16}]$ acts catalytically in the homogeneous reduction of benzaldehyde:

$$PhCHO + CO + H_2O \longrightarrow PhCH_2OH + CO_2$$

For CO partial pressures below 28 bar the order of reaction in CO is about one; at higher pressures a shift to zero-order dependence is obtained. The reaction is zero order for water and PhCHO, although the aldehyde is involved in the rate-determining step for substituted benzaldehydes. The mechanism of the reaction is said to involve hydride transfer from the catalyst [287]. Ketones (for example, cyclohexanone) may be reduced by hydrogen transfer from isopropanol in the presence of $[Rh(cod)L_2]^+$ catalysts (L = monodentate or bidentate phosphine ligand). The complexes containing the chelating ligands are reported to exhibit highest activity [288].

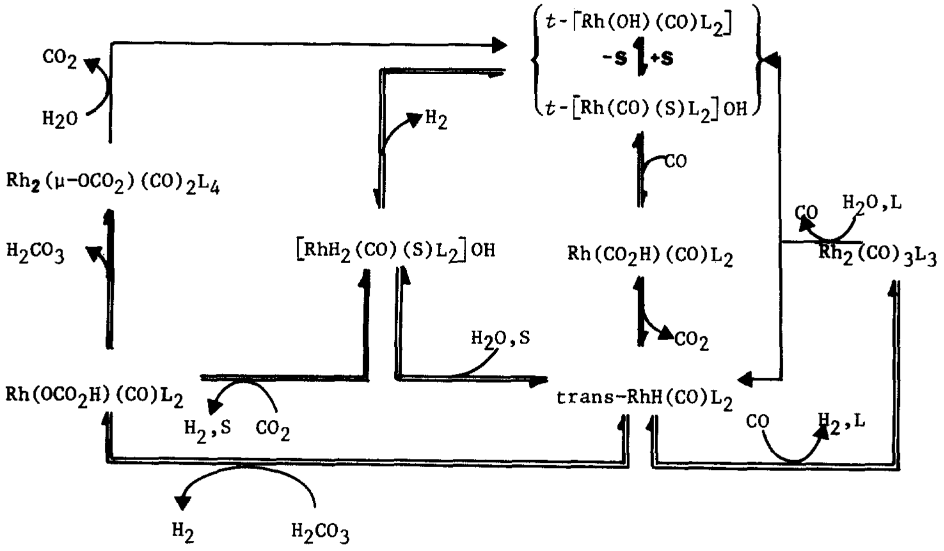
Cationic rhodium complexes derived from the precursors $[Rh(nbd)(PR_3)_n][ClO_4]$ (n = 2 or 3; R = Et, Me or Ph) serve as efficient catalysts for the hydrogenation of styrene oxide to the alcohol, $PhCH_2CH_2OH$. $[Rh(nbd)(dppe)][ClO_4]$ was found to be a poor hydrogenation catalyst in this system and generated a large proportion of $PhCH_2CHO$ and oligomers [289].

$[Rh_4(CO)_{12}]$ and $[\{Rh(CO)_2Cl\}_2]$ catalyse the reduction of CO_2 to CO in the presence of $AlBr_3$ and dihydrogen. Traces of C_1–C_5 alkanes are formed along with CO; no carbonyl compounds are generated [290]. In the water gas-shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

when catalysed by $[RhH(PR_3)_3]$, turnover rates for CO at 100 °C in pyridine are found to be between 15 and 33 mol CO (mol catalyst)$^{-1}$h^{-1}. The rate-determining step is nucleophilic attack of OH^- on CO. *Trans*-$[Rh(CO)(py)(PR_3)_2]^+$ was isolated from the reaction mixture [291]. The reaction is also catalysed by $[Rh(cod)L_2]^+$ (L = nitrogen or phosphorus donor ligands) [292]. The thermodynamics of the water gas-shift reaction are more favoured at low temperature and the rhodium(I) hydrido species; $[RhHL_3]$ $\{L = PEt_3$ or $P(Me_2CH)_3\}$, $[Rh_2H_2(\mu\text{-}N_2)\{P(cych)_3\}_4]$, trans-$[RhH(N_2)\{PPh(CMe_3)_2\}_2]$ and $[RhH\{P(CMe_3)_3\}_2]$ behave as catalysts for the reaction under mild conditions. The catalytic cycle, represented by $[RhH\{P(Me_2CH)_3\}_3]$ is illustrated in Scheme IV [293]. It is assumed that this compound is readily transformed into *trans*-$[Rh(OH)(CO)L_2]$ $\{L = P(Me_2CH)_3\}$ which starts the cycle.

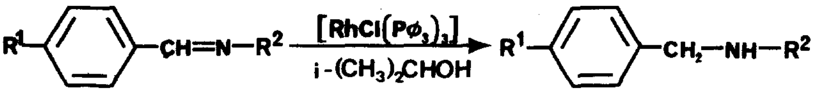
By using 1,2-diaminoethane with $[\{Rh(CO)_2Cl\}_2]$, $[Rh_4(CO)_{12}]$ or $[Rh_{12}(CO)_{30}]^{2-}$, catalytic activities for the shift reaction were found to be comparable to those found for $[Rh_6(CO)_{16}]$-en [294].



$(L = p\{(CH_3)_2CH\})$

Scheme IV: Mechanistic cycle for the $[RhH\{P(Me_2CH)_3\}_3]$-catalysed water gas-shift reaction [293]

Various aldimines (94) may be reduced to secondary amines (95) by hydrogen



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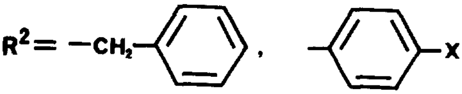
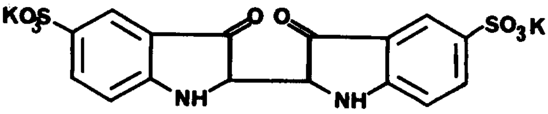


transfer from propan-2-ol in the presence of $[RhCl(PPh_3)_3]$ and sodium carbonate. Catalysts based upon ruthenium, iridium or osmium were found to be inactive but replacement of PPh_3 by $P(4\text{-fluorophenyl})_3$ gave a slightly faster reaction. $[RhH(PPh_3)_3]$ is more active than $[RhCl(PPh_3)_3]$ and is believed to be produced *in situ* during the reaction [295].

The 2:1 complex formed between $RhCl_3$ and K indigosulphonate (96) catalyses



(96)

the hydrogenation of $PhNO_2$ to $PhNH_2$. The reaction is reported to follow pseudo-first order kinetics and the mechanism is said to involve the formation of $[PhNO_2]^+$ followed by PhNO [296].

2.9.2 *Dehydrogenation*

$[RhCl(PPh_3)_3]$ catalyses the dehydrogenation of propan-2-ol when irradiated by UV radiation at room temperature [297]. Under conditions appropriate to alkene hydrogenation the primary alcohols used as solvents were converted into the corresponding aldehydes owing to hydrogen transfer. The *in situ* catalysts derived from $[\{Rh(diene)Cl\}_2]$ and phosphines cause the aldehydes to decarbonylate and the catalyst is partially converted into complexes of the type $[Rh(CO)(PR_3)_2Cl]$ and is thereby deactivated [298]. The dehydrogenation of secondary alcohols {*e.g.* PhCH(Me)OH} to the corresponding carbonyl compounds is achieved by the phase-transfer catalysed reaction using $[\{Rh(CO)_2Cl\}_2]$ and benzene, aqueous NaOH and $[PhCH_2NEt_3]Cl$. *O*-metallated complexes are believed to be the intermediates in these reactions [299]. Photogeneration of dihydrogen occurs in the UV photochemical reaction of water with a triethanolamine $-RhCl_3\text{-bipy-}K_2[PtCl_6]$ system [300].

2.9.3 *Hydroformylation*

A review of the hydroformylation of alkenes and alkadienes using rhodium catalysts has been produced highlighting the recent advances and developments in hydroformylation [301].

In the hydroformylation of ethene (and propene) using $[RhH(CO)(PPh_3)_3]$, there is said to be no observable difference in catalytic activity or activation energy between a non-supported solid catalyst and a supported liquid-phase catalyst. It follows that only the rhodium complex at the gas-PPh_3 phase boundary is involved in the reaction [302]. $[RhCl(CO)(PPh_3)_2]$ catalyses the hydroformylation of ethene in toluene. At 80-130 °C and 5 MPa the reaction was found to be first order in ethene with an activation energy of 33 $kJ\ mol^{-1}$ [303].

The hydroformylation of propene in the presence of $[RhH(CO)(PPh_3)_3]$ and PPh_3 (toluene solutions) shows a zero order dependence in the partial pressures of both CO and H_2. The n-butanal:isobutanal ratio derived depends only upon the relative quantities of CO and triphenylphosphine [304]. The catalyst, $[RhH(CO)(PPh_3)_3]$, is reported to undergo decomposition during the reaction into $\{Rh(CO)_2(PPh_2)\}_n$ [305]. When supported on alumina or silica, $[RhH(CO)(PPh_3)_3]$ also catalyses the hydroformylation of propene: a strong affinity is said to exist between the metal complex and the support [306]. With an excess of PPh_3, also supported on silica, it is found that the catalytic activity may be modified if additional solvents are present. At high loadings of PPh_3 the overall reaction rate is increased and the regioselectivity for PrCHO production is decreased. At low PPh_3 loadings both rate and regioselectivity are increased for small additions of other solvents. The results are consistent with an increasing tendency for PPh_3 to become highly mobile at sufficiently high loadings. The choice of support appears not to influence the catalytic behaviour [307]. When dissolved into one of the various molten tertiary phosphines and capillary-condensed into the pores of Kieselguhr, $[RhH(CO)(PPh_3)_3]$ catalyses the hydroformylation of propene at 90-200 °C and 1.6 MPa total pressure. The normal/iso- butanal selectivity varies considerably with the nature of the tertiary phosphine [308]. $[RhH(CO)(PPh_3)]$ has been anchored to the surface of porous polystyrene-divinylbenzene and the hydroformylation of propene tested at 90 °C and atmospheric pressure. It is found that the method of coupling of the rhodium complex to the catalyst support strongly influences the activity and selectivity of the catalyst [309]. Catalysts prepared *via* chloromethylation rather than chlorophosphonation are found to have a higher selectivity to n-butanal and the selectivity can be increased further by the addition of a small amount of PPh_3 to the anchored catalyst [310].

The hydroformylation of 5,5,5-d_3-1- and of 5,5,5-d_3-2- pentene was carried out in the presence of $[Rh_4(CO)_{12}]$ as catalyst precursor under low or high pressure of CO. Intramolecular H shift decreases with increasing p(CO) and intermolecular H exchange (including exchange between substrate and gaseous hydrogen) at both low and high partial pressures of carbon monoxide [311].

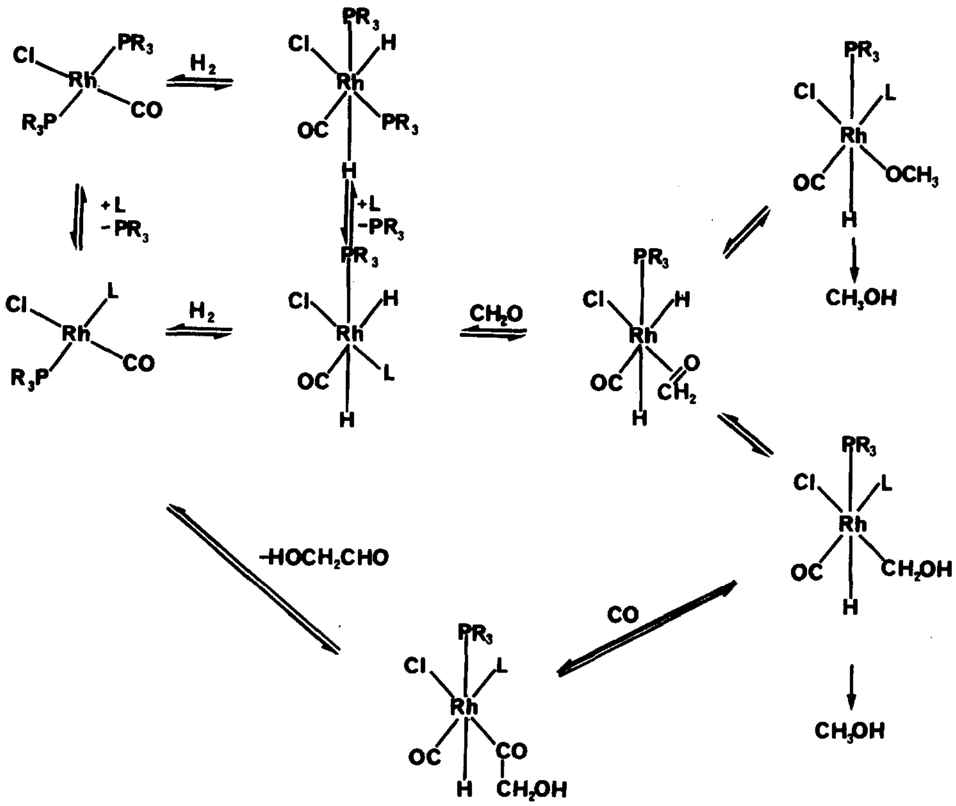
The catalytic hydroformylation of 1-hexene has been studied using $[RhH(CO)(PPh_3)_3]$ in the absence of solvent. The selectivity of the process (the ratio of normal- to iso- butanal) was found to increase with increase in the concentration of PPh_3 to the CO/H_2 feed. The selectivity was also found to be independent of the catalyst concentration and to increase with reduction in total pressure [312]. When catalysed by *trans*-$[RhCl(CO)L_2]$ {L = PPh_3, $(4\text{-}EtC_6H_4)_3P$, $(4\text{-}BuC_6H_4)_3P$ or $(4\text{-}C_5H_{11}C_6H_4)_3P$}, the linear:branched aldehyde ratio is enhanced by the presence of 4-alkyl groups in the phosphine ligand. The optimum catalyst, in terms of a compromise between rate and isomer ratio, is found to be *trans*-$[RhCl(CO)(4\text{-}BuC_6H_4)_3P$ [313]. When dissolved in molten PPh_3, $[RhH(CO)(PPh_3)_3]$ produces a similar high linear:branched ratio of aldehydes as found in the bulk hydroformylation of 1-hexene. When the temperature and pressure are reduced an increase in the linear:branched ratio is obtained along with a decrease in the isomerisation of the starting material to its 2-isomer [314]. The selectivity of catalysts of the type, $[RhCl(CO)(PPh_2NRR')]$ towards 1-hexene hydroformylation, depends upon the electron distribution between nitrogen, phosphorus, phenyl and carbon monoxide. An increase in π-acceptor ability of the amino-phosphine ligand is obtained when R and R' are aryl owing to the delocalisation of the nitrogen lone pair. This leads to a higher selectivity [315]. The polymer-bound material represented by (91) is effective in the hydroformylation of 1-hexene in benzene at 90 bar and 110 °C ($CO:H_2$ = 1:1). Complete conversion to heptanal and 2-methylhexanal is achieved in less than an hour (linear:branched = 2:3) [280]. This reaction has also been examined using $[RhCl(CO)(PPh_3)_2]$ supported on silica or alumina. On silica, reaction with CO is reported to produce a square-planar dicarbonyl species and at high CO pressures a dimeric species is formed. On alumina, both the square-planar and penta-coordinated dicarbonyls are formed. The observed activity and selectivity during hydroformylation is said to correlate with the nature of the rhodium species on both of the supports [316].

Rhodium catalysts formed *in situ* from Rh_2O_3 and an excess of tertiary phosphines are found to be active for the hydroformylation of conjugated dienes to dialdehydes. Secondary phosphines are also found to be active in the hydroformylation of 1,3-butadiene to the 1,4-dialdehyde [317].

$[RhH(CO)(PPh_3)_3]$, dissolved in molten PPh_3 or $P(4\text{-}MeC_6H_4)_3$ and capillary-condensed in the pores of a support material, catalyses the gas-phase hydroformylation of allyl alcohol, $CH_2 = CHCH_2OH$, giving high selectivities to 4-hydroxybutanal [318].

The compounds $[Rh(CO)Cl(PR_3)_2]$ (R = Ph, 3- and 4- tolyl or $4\text{-}FC_6H_4$) are efficient catalysts for the hydroformylation of methanal to $HOCH_2CHO$ in *N,N*-dialkylamide solvents. Methanol formation (from the hydrogenation of CH_2O)

predominates in other solvents. The reaction mechanisms proposed are outlined in Scheme V [319].



Scheme V: Proposed mechanisms for the rhodium-catalysed hydroformylation of methanal [319]

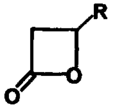
2.9.4 *Carbonylation*

The chemistry and applications of rhodium-catalysed carbonylations have been reviewed by Forster [320].

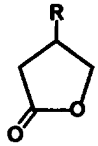
[$\{Rh(CO)_2Cl\}_2$] catalyses the carbonylation of cyclopropane under CO pressure to give cyclobutanone, Pr_2CO, $PrCOCHMe_2$ and a methylcyclohexanone [321].

A catalyst active for the carbonylation of MeOH to ethanoic acid has been prepared from Linde 13X zeolite by exchange with $[Rh(NH_3)_5Cl]Cl_2$ [322]. Ionically-supported $[Rh(CO)_2I_2]^-$ is found to be equal in catalytic activity to the homogeneous complex in methanol carbonylation to ethanoic acid [323].

The carbonylation of the lactones (97) and (98) is catalysed by $RhCl_3$ and MeI in $MeCOOH-H_2O$ under CO at 180 °C to give the dicarboxylic acids $HO_2C(CH_2)_nCHRCO_2H$ quantitatively [324].

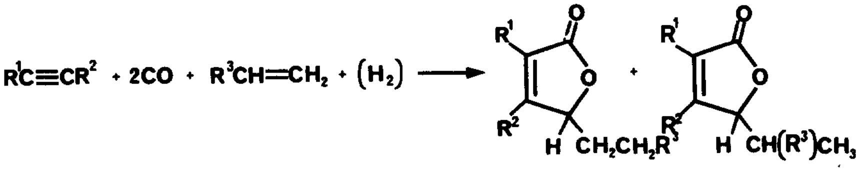


(97)



(98)

Several rhodium carbonyl complexes (e.g., $[Rh_6(CO)_{16}]$, $[RhCl(CO)(PPh_3)_2]$, $[RhCl(PPh_3)_3]$ and $RhCl_3.3H_2O$) are found to be effective for the catalysed carbonylation of alkynes in the presence of alkenes and proton donors (H) (e.g. alcohol or water) to produce 5-alkyl-2(5H)-furanones, (99) and (100) [325]. Thus:



(99) (100)

In the presence of py, the $RhCl_3$- catalysed reduction and carbonylation of $PhNO_2$ to PhNCO is accelerated by a factor of between 9 and 13. Under the experimental conditions (205 °C and 50 bar) $RhCl_3$-py is said to be converted to a $[\{Rh(CO)_2Cl\}_2]/py_2COCl_2/py$ catalytic system [326]. Indeed, $[\{Rh(CO)_2Cl\}_2]$, activated by pyridine or pyridinium chloride, catalyses the carbonylation of $RC_6H_4NO_2$ (R = H, 3-Me, 4-Cl or 4-MeO) to the isocyanate, RC_6H_4NCO at 205 °C, 50 bar CO pressure and 40 min reaction time [327]. The homogeneous carbonylation of nitrobenzene in MeOH using either $[RhCl(CO)(PPh_3)_2]$ or $[RhH(CO)(PPh_3)_3]$ gives methyl-*N*-phenylcarbamate, $PhNHCO_2Me$, with a yield of almost 30% [328].

The reaction of $[Rh_6(CO)_{16}]$ with a phosphinated silica surface at room temperature is reported to form metal particles bonded to the support in the Rh_6-cluster configuration. Carbonylation is thought to produce a thermally stable $[Rh_6(CO)_{13}]$. The interaction of $[Rh_6(CO)_{16}]$ with the support at 80 °C forms a mixture of Rh(O) and Rh(I) species which are said to be inconvertible by mild oxidation or reduction, respectively [329]. At room temperature, the $\{Rh_6\}$ cluster is said to remain intact during the oxidative decarbonylation and subsequent carbonylation of $[Rh_6(CO)_{16}]$ supported on alumina. At temperatures in excess of 250 °C however, the catalyst is reported to lose its ability to undergo the reversible carbonylation/decarbonylation cycle and the resulting material is representative of a highly-dispersed conventional rhodium catalyst [330].

2.9.5 Oxidation and oxygenation

$[Rh_6(CO)_{16}]$, deposited from solution onto alumina or silica supports, is decarbonylated from the surface by exposure to air. Gas adsorption and IR measurements on the Al_2O_3-supported material indicate that CO and O_2 react with a surface component to produce CO_2 and that the surface rhodium material is reversibly converted from the fully carbonylated $[Rh_6(CO)_{16}]$ form to the fully-decarbonylated form which may retain the $\{Rh_6\}$ cluster intact [331].

The reaction:

$$2NO + CO \longrightarrow N_2O + CO_2$$

is catalysed by $[Rh(NO)_2(PPh_3)_2][PF_6]$ in dmf [332]. On the basis of infrared data, the species $[Rh(CO)_2(NO)]^+$ is proposed as an intermediate in the catalysed reduction of NO by CO to form N_2O using rhodium ions in zeolite Y. The species $\{Rh(CO)_2\}^+$ and $\{Rh(NO)_2\}^+$ are also detected on the zeolite surface [333].

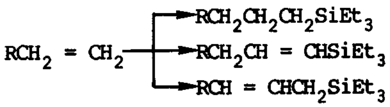
The silica-supported species, $[Si]$-$SRh(CO)_2(solvent)_n$ (solvent = thf or EtOH), co-impregnated with copper(II) ions, is an active catalyst for the oxidation of 1-hexene into 2-hexanone [334]. $[RhX(PPh_3)_3]$ (X = CN, OCN or SCN) are catalysts for the co-oxygenation of 1-octene and PPh_3. The catalytic oxygenation is less efficient with styrene [335]:

$$RCH = CH_2 + PPh_3 + O_2 \longrightarrow R(CO)CH_3 + Ph_3PO$$

$[Rh_2(C_5Me_5)_2(\mu\text{-}OH)_3]Cl.4H_2O$ catalyses the oxygenation of thf to γ-butyrolactone in the presence of small quantities of water. The same complex also catalyses the conversion of Ph_3P to Ph_3PO, although $(EtO)_3P$ is not oxidised but rather substitutes into the rhodium compound to give $[Rh(C_5Me_5)\{(EtO)_3P\}_3]^{2+}$ [336].

2.9.6 Hydrosilylation

$[RhCl(PPh_3)_3]$, applied as a catalyst precursor to the surface of an aminated silica support, has been examined in the hydrosilylation of the 1-alkenes; hexene, heptene and octene [337]. $[(RhC_5Me_5)_2Cl_4]$ (and $[RhCl(PPh_3)_3]$) catalyses the reactions of 1-alkenes with Et_3SiH at < 40 °C as follows [338].



$$RCH_2 = CH_2 \longrightarrow \begin{cases} RCH_2CH_2CH_2SiEt_3 \\ RCH_2CH = CHSiEt_3 \\ RCH = CHCH_2SiEt_3 \end{cases}$$

The complexes $[RhCl(PPh_3)_3]$, and those formed between $RhCl_3.3H_2O$ and PBu_3, $P(OEt)_3$ or $P(OBu)_3$, are found to be active photocatalyst precursors in hydrosilylation. The substrates examined were *sym*-tetramethyldisiloxane, 1,3-divinyltetramethyldisiloxane and simple terminal alkenes. The reaction rates were considerably increased when the photolysis was conducted in the presence of dioxygen or soluble oxidising agents [339]. A series of heterogenised catalysts was prepared by reaction of $[\{RhCl(C_2H_4)_2\}_2]$ and phosphinated silica. The activity of the catalysts towards the hydrosilylation of 1-hexene was found to depend upon the length of the phosphine-alkyl chain, $-(CH_2)_nPPh_2$, used to couple the rhodium centre to the silica surface. Those containing one methylene group were some ten times more active than those containing between two and six methylene groups [340]. $[RhCl(PPh_3)_3]$ has been studied in the catalytic hydrosilylation of styrene by MeR_2SiH (R = Et, CMe_2H or Me_2CHCH_2). Steric factors are responsible for the change in the distribution of reaction products, $PhCH(SiR_2Me)CH_3$, $PCH_2CH_2SiR_2Me$, and *trans*-$PhCH = CHSiR_2Me$, with change in R [341].

$[RhCl(PPh_3)_3]$ or $[RhH(PPh_3)_4]$ catalyse the hydrosilylation of ethyne: $HSiCl_3$, $HSi(OEt)_3$, $HSiMeCl_2$, $HSi(OEt)_2Me$ and $HSi(n\text{-}hexyl)Cl_2$ are converted into the corresponding vinyl silanes in yields of between 40 and 80% [342]. Rhodium catalysts, formed by the displacement of cyclooctene from $[Rh_2Cl_2(cyclooctene)_4]$ by phosphines were studied for the hydrosilylation of 1-pentyne by triethylsilane. The results were interpreted in terms of the isomerisation of an intermediate vinyl rhodium complex [343].

The hydrosilylation of $C_6H_5COCMe_3$ by diphenylsilane to give $C_6H_5CH(OSiHPh_2)CMe_3$ is catalysed by $[Rh(cod)\{(-)\text{-diop}\}][ClO_4]$. A kinetic and spectroscopic study of the system reveals that cod is displaced from the catalyst by Ph_2SiH_2 to give $[Rh(Ph)\{(-)\text{-diop}\}]^+$ which oxidatively adds Ph_2SiH_2 to form $[(Ph_2SiH)RhH\{(-)\text{-diop}\}]^+$. The attack of this species upon $PhCOCMe_3$ is the rate-determining step of the reaction [344]. The initial rates of the enantioselective hydrosilylation of $CMe_3COC_6H_5$ by diphenylsilane to give (R)(+)-$Me_3CCH(OH)C_6H_5$, catalysed by $[Rh\pm\{(-)\text{-diop}\pm\}_2][ClO_4]$, were determined in toluene at 50 °C. $[(Ph_2SiH)RhH\{(-)\text{-diop}\}]$ is considered to be an intermediate in the reaction and its reaction with $Me_3CCH_2C_6H_5$ is believed to constitute the rate-determining step [345].

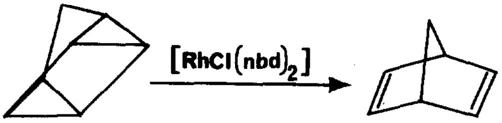
2.9.7 Isomerisation and oligomerisation

[*Closo*-1,3-μ-2,3-μ-{1,2-μ-(η^2-3,4-CH_2CH_2CMe) = $CHCH_2CH_2CH_2$)}-3-H-3PPh_3-3,1,2-$RhC_2B_9H_9$] catalyses the isomerisation of alkenes [265] and [*closo*-1,3-{μ-(η^2-3-CH_2 = $CHCH_2CH_2$)}-3-H-3-PPh_3-3,1,2-$RhC_2B_9H_{10}$] was found to catalyse the isomerisation of 1-hexene [268].

The NMR spectral assignments have been established for $[RhCl(nbd)_2]$ and new equilibrium constants have been determined for the reaction:

$$[\{RhCl(nbd)\}_2] + 2nbd \rightleftharpoons 2[RhCl(nbd)_2]$$

At 40 °C, the equilibrium is sufficiently displaced to the left hand side of the equation that the concentration of monomer is insignificant with respect to its ability to catalyse the reaction (101) to (102). At 1 °C, in the presence of nbd, the equilibrium concentration of the monomer is sufficient to observe the isomerisation. It is therefore demonstrated that the monomer is a more efficient isomerisation catalyst than the dimer [346].



(101) (102)

$Na[Rh(edtaH)Cl]$ catalyses the hydrogenation and isomerisation of $CH_2 = CHCH_2OH$ to PrOH and EtCHO, respectively [284].

$[RhCl(PPh_3)_3]$-$SnCl_2$ was found to be an especially efficient catalyst for the isomerisation of $MeO_2CCH_2C(=CH_2)CO_2Me$ to (E)- and (Z)-$MeO_2CCMe = CHCO_2Me$ at 100 °C [347].

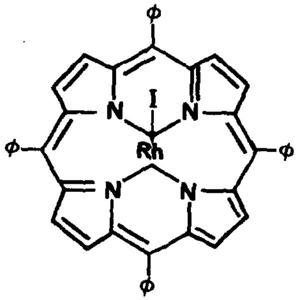
The reaction of $[RhCl(CO)(PPh_3)_2]$ with Et_2AlCN gives $RhCl(CO)(PPh_3).NCAlEt_2$, $(Ph_3P)(Et_2Al)Rh(CO)(CH)Cl.NCAlEt_2$ or $(Ph_3P)(Et_2Al)Rh(CO)(CN)_2$, depending upon the conditions. Reactions of $(Ph_3P)(Et_2Al)Rh(CO)(CN)_2$ with dmf gave $(Ph_3P)RhH(Me_2NCHO)(CN)_2$. The combination of $[RhCl(CO)(PPh_3)_2]$ and Et_2AlCN in dmf and py catalyses the conversion of 1,3-butadiene into 4-vinylcyclohexene and 1,5-cyclooctadiene. In EtOH, polybutadiene was formed [348].

2.9.8 Miscellaneous catalytic reactions

Rhodium(I) complexes, typically $[\{RhCl(PPh_3)_2\}_2]$, catalyse the reaction of anthroquinone with alkylamines to give 1-(alkylamino)anthroquinones. This amination occurs through the α-position of the anthroquinone, giving a high product selectivity. The formation of a monomeric, coordinatively-unsaturated rhodium(I) complex is believed to be the important active species for the catalysed amination [349].

Alkenyl-, alkynyl- and arylmercurials undergo catalytic methylation with MeI in the presence of $MeRh(PPh_3)_2I_2$. For example, PhCH = CHHgCl gave a yield of 77% PhCH = CHMe [350].

The complex porphyrin (103) behaves as a sterically-hindered alkene cyclopropanation catalyst and shows a remarkable selectivity towards formation of the *cis*-isomers of the product esters. Ethyldiazoacetate was used as the cyclopropanation reagent [351].

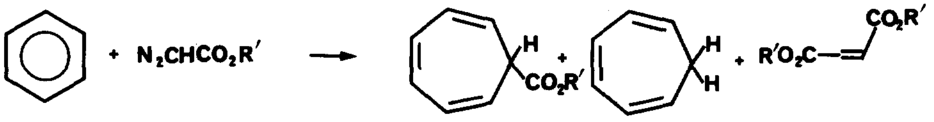


(103)

A typical reaction is the conversion of (104) to (105).

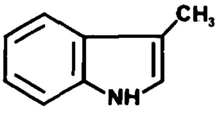
(104) (105)

$[Rh_2(tfa)_4]$ catalyses the addition of carbenes (generated from diazo esters) to aromatic compounds to give cycloheptatrienes (106) and (107) [352].



(106) (107)

Although supported rhodium catalysts (Rh/C or Rh/Al_2O_3) are effective in the conversion of 2-nitrostyrene into skatole (108) under hydroformylation conditions, the complexes, $[RhCl(PPh_3)_3]$ or $[RhCl(CO)(PPh_3)_2]$ lead only to a low conversion of the 2-nitrostyrene even under high pressures and at high temperatures. Clusters, such as $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ are found to be ineffective [353].



(108)

$[\{(-)\text{-diop}\}RhCl]$ catalyses the asymmetric addition of CCl_3Br to styrene to give (s)-(-)-$PhCHBrCH_2CCl_3$ [354].

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