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5. RHODIUM AND IRIDIUM

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Introduction

RHODIUM

IRIDIUM

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INTRODUCTION

Whilst being essentially a continuation of the 1979 Review of rhodium and iridium, written by Dr. Cole-Hamilton and published in this journal in 1981, there has been an inevitable change in emphasis and style as a result of the change of author. The majority of the articles covered in this review were published in 1980, although many from 1979 are also included. The papers coincide, therefore, with Volumes 92 and 93 of Chemical Abstracts.

Although the review concentrates predominantly upon the coordination chemistry of rhodium and iridium, special emphasis has been placed upon the catalytic properties and uses of these metals.

RHODIUM

5.1 RHODIUM(V) and (IV)

Elemental rhodium reacts with a mixture of molecular fluorine and nitrosyl fluoride to give $[NO]_2[RhF_6]$. This material has also been produced from the reaction between $[O_2][RhF_6]$ and NOF at about 50 °C. $[NO][RhF_6]$ was isolated when a large excess of fluorine was used relative to nitrosyl fluoride, and this compound was also prepared by the direct oxidation of NO with $[RhF_6]$. Both $[NO][RhF_6]$ and $[NO]_2[RhF_6]$ have been characterised by Raman spectroscopy [1].

5.2 RHODIUM(III)

5.2.1 *Halide complexes*

The species $[RhF_{6-n}(H_2O)_n]^{n-3}$ (n = 0-6) are formed by reaction of $[RhF_6]^{3-}$ with aqueous HF solutions. In the presence of Cl^- ions, aquation of $[RhF_6]^{3-}$ occurred with the subsequent formation of aqua-chloro species, but no mixed chloro-fluoro species were observed by ^{19}F NMR or electronic spectroscopy [2]. XPES has revealed that the substitution of F^- by Cl^- in $K_3[RhF_6]$ leads to a decrease in the ionisation potential of all the molecular levels of the complex. This effect is less for substitution of Cl^- by Br^- [3].

Formation of $M_3[RhCl_6]$ (M = Na or K) by the thermal chlorination of rhodium (in the presence of NaCl or KCl) has been studied. Chlorination of rhodium in the presence of MCl_2 (M = Mg, Ca, Sr or Ba) results only in the formation of $RhCl_3$ [4]. Dehydration of $RhCl_3.3H_2O$ in air is complete at 230 °C ($RhCl_3.H_2O$ being stable up to 210 °C); anhydrous $RhCl_3$ is gradually transformed by atmospheric oxygen into Rh_2O_3 at 640-880 °C [5].

5.2.2 *Complexes with oxygen donor ligands*

5.2.2.1 *Oxides and aqueous chemistry*

The compounds $M[Rh_2O_4]$ (M = Mg, Zn or Cd) have been examined by electrical conductivity, X-ray diffraction and IR spectroscopy and shown to possess a cubic spinel-type structure [6]. The vibrational spectra of $Ln[RhO_3]$ (Ln = La, Pr, Gd or Lu) have been examined [7].

The acid dissociation constants have been determined for $[Rh(H_2O)_2(NO_2)_4]^-$, $[Rh(H_2O)(SO_4)(NO_2)_3]^{2-}$ and $[Rh(H_2O)(NO_2)_5]^{2-}$ [8]. The *cis*- and *trans*-isomers of $[Rh(NH_3)_4(H_2O)_2][ClO_4]_3$ have been synthesised and their acid dissociation constants have also been measured, along with those for other aquaamine complexes (Table 1) [9].

5.2.2.2 *Carbonate and nitrate complexes*

The new carbonate complexes, *trans*-$[Rh(en)_2(OCO_2)(OH_2)][ClO_4]$ and *trans*-$[Rh(en)_2(OCO_2)_2]^-$ have been prepared from *trans*-$[Rh(en)_2(OH)(OH_2)][ClO_4]_2$ and $[HCO_3]^-$ or $[CO_3]^{2-}$ and the rate parameters for acid-catalysed decarboxylation have been determined. *Trans*-$[Rh(en)_2(OH)(OH_2)]^{2+}$ and *trans*-$[Rh(en)_2(OCO_2)(OH)]$ take up CO_2 to produce the *trans* isomers of $[Rh(en)_2(OCO_2)(OH_2)]^+$ and $[Rh(en)_2(OCO_2)_2]^-$, respectively [10]. The kinetics of the acid-catalysed decarboxylation of $[Rh_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)(1,4,7\text{-triazacyclononane})_2]^{2+}$ [11] and the production and rates of decarboxylation of *trans*-$[Rh(en)_2(OCO_2)X]$, (X = Cl,

TABLE 1
Acid Dissociation Constants [9].

Complex	pK_a [a]
$[Rh(NH_3)_5(H_2O)]^{3+}$	6.93
cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	6.4(1), 8.32(2)
trans-$[Rh(NH_3)_4(H_2O)_2]^{3+}$	4.92(1), 8.26(2)
cis-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	7.84
trans-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$	6.75
cis-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	7.89
trans-$[Rh(NH_3)_4(H_2O)Br]^{2+}$	6.87

[a] Measured at 25 °C in 1.0 *M* $Na[ClO_4]$.

Br or I) have also been studied [12].

The molecular structures of the nitrate complexes, $[Rh(\eta^5-C_5Me_5)(NO_3)_2(PPh_3)]$ (1) and $[Rh(\eta^5-C_5Me_5)(NO_3)_2]$ (2) have been determined [13].

5.2.2.3 *Sulphoxide and ketone complexes*

Addition of dmso to rhodium halides gives $[RhX_{6-n}(dmso)_n]^{n-3}$ (n = 1–5, X = Cl; n = 2–5, X = Br) and $[Rh_2Br_8(dmso)]^{2-}$. Both oxygen and sulphur bonded isomers are said to co-exist in solution [14]. *Mer*-$[RhCl_3L_3]$ (L = dmso, tetramethylene sulphoxide, MeSOPh or (R)-Methyl-4-tolyl sulphoxide) and $[RhCl_4(R_2SO)_2]^-$ (R = Me or Pr) have also been obtained [15]. The cation in the dmso species *trans*-$[H(Me_2SO)_2][RhCl_4(Me_2SO)_2]$ was found to contain the hydrogen bonded entity $[Me_2SO....H....OSMe_2]$ [16].

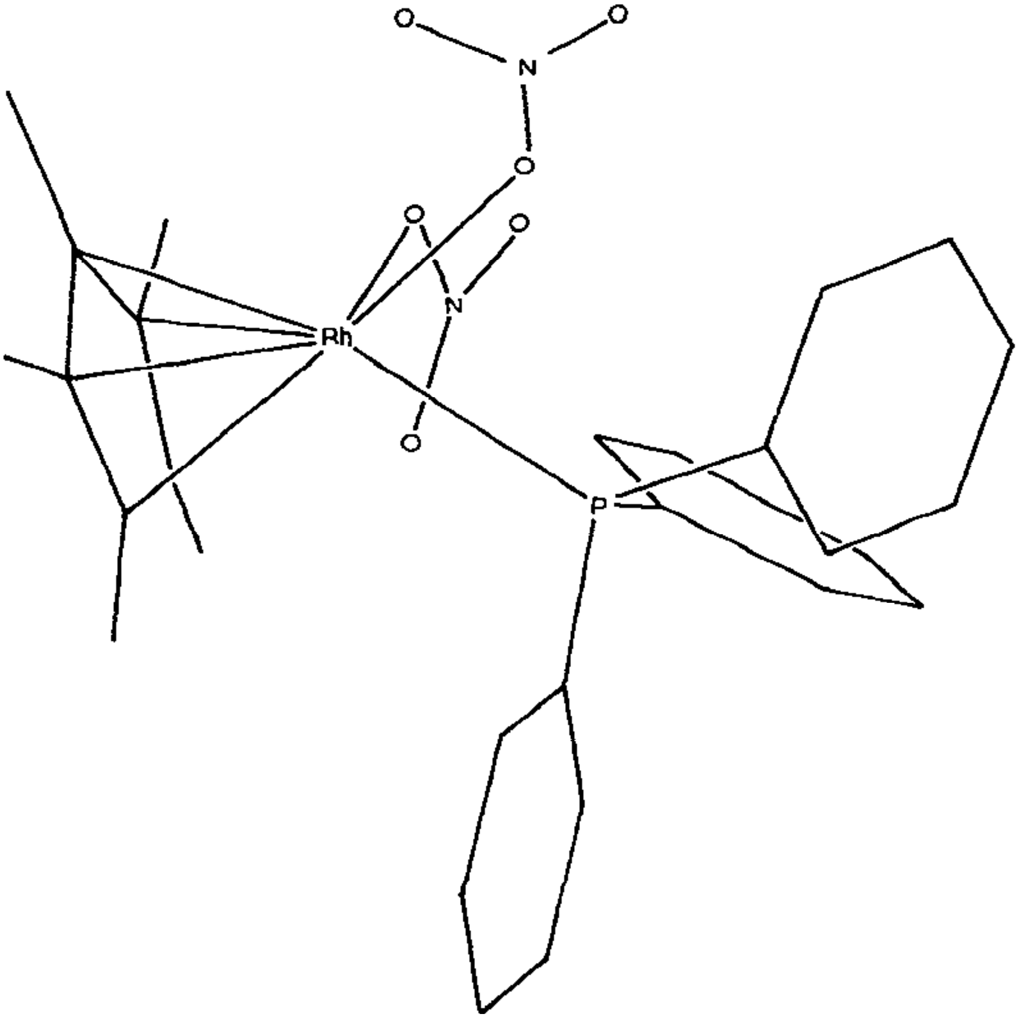
The compounds, $[RhL_3Cl_3].H_2O$, $[RhL_3Br_3].2H_2O$ and $[RhL_3I_3]$ (L = (3)), have been prepared and characterised and shown to involve the *meridional* configuration about the metal [17].

5.2.2.4 *Carboxylates*

Electronic absorption and CD spectra have been reported for the six-coordinate complexes, *trans*-(O_5)-$[Rh(edda)]^-$, *trans*-(O_5O_6)-$[Rh(edda)]^-$, and *trans*-(O_5)-$[Rh(S,S\text{-}edds)]^-$ (edda = ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate; S,S-EDDS = (S,S)-ethylenediamine-*N*,*N'*-disuccinate) [18]. Structures for $[Rh_3O(O_2CMe)_6(H_2O)_3][ClO_4].nH_2O$ (n = 1 or 2) have been determined and no evidence for direct metal-metal bonding has been found [19].

5.2.2.5 *Complexes with oxygen-nitrogen donor ligands*

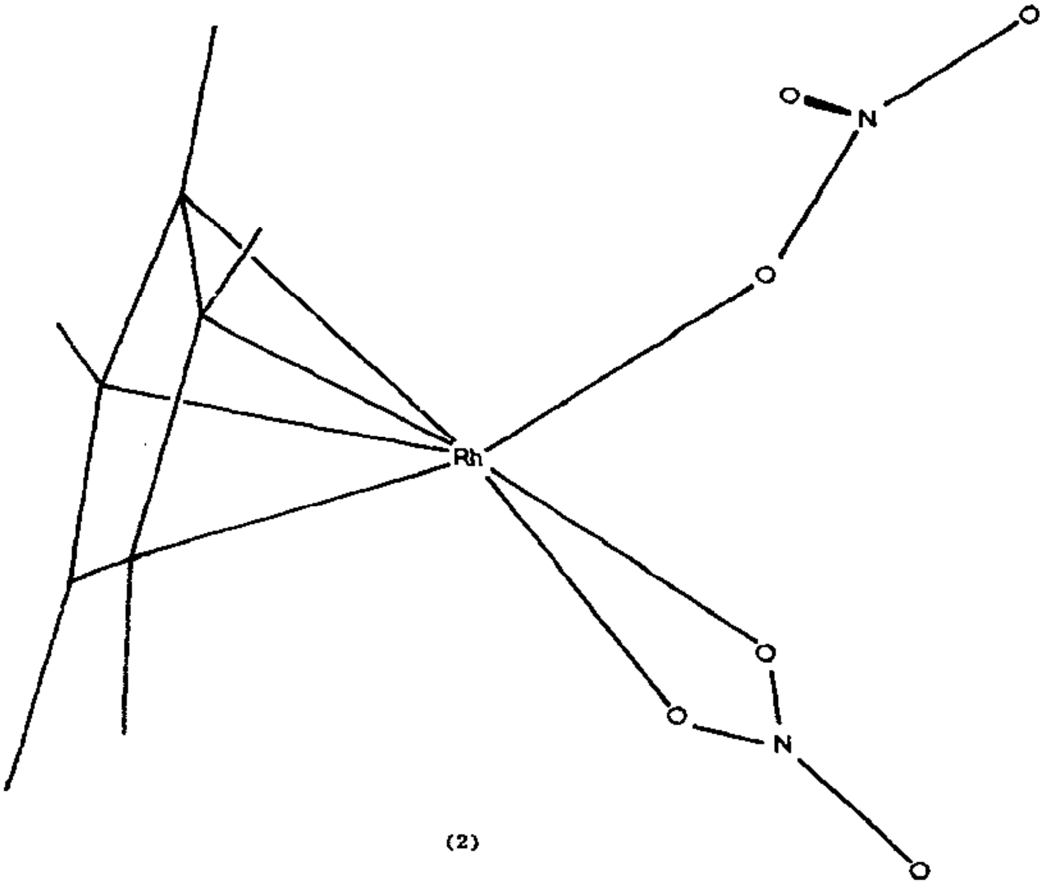
Hydrated $RhCl_3$ reacts with 3-aminopropanoic acid to form $[Rh(NH_2CH_2CH_2COO)_3].2H_2O$



(1)

in which the ligand is bidentately-coordinated through the N and O atoms. The complex reacts with HCl to give [Rh($NH_2CH_2CH_2COOH$)($NH_2CH_2CH_2COOH$)$_2$Cl].H_2O, [Rh($NH_2CH_2CH_2COOH$)$_2$($NH_2CH_2CH_2COO$)Cl_2].H_2O and [Rh($NH_2CH_2CH_2COOH$)$_3Cl_3$] [20].

A series of hydroxyimino-β-diketone complexes of the type [RhL_3] (L = R'COC=N(OH)COMe; R' = Me, OMe, OEt, PhNH or MeC_6H_4NH) have been examined and their structures assigned from IR and NMR spectroscopic studies. The ligands are coordinated to rhodium through the keto-oxygen and nitrogen atoms of the hydroxyimino groups [21].



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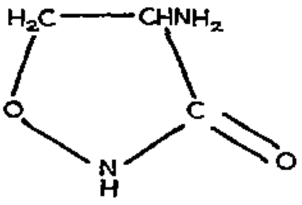

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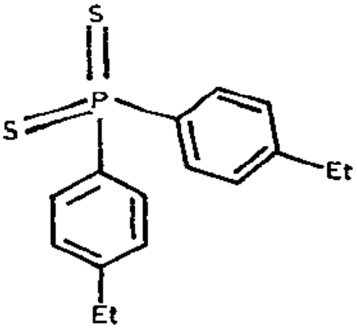
5.2.3 *Complexes with sulphur or sulphur-nitrogen donor ligands*

The octahedral complexes [RhL_3] {L = (4) or (5)} have been synthesised and characterised using magnetic measurements and IR and electronic spectroscopy. The placement of these ligands in the spectrochemical and nephelauxetic series



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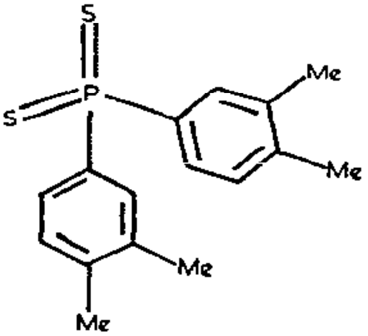
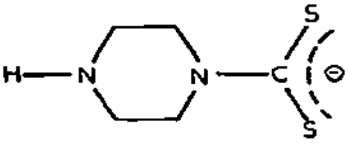


(5)

has been assessed [22].

The compounds $[RhL_2Cl].2H_2O$ and $[Rh_2Q_3]$ have been prepared from solutions containing piperazine dithiocarbamate (L = (6)) and piperazine bis(dithiocarbamate)



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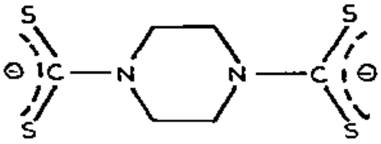
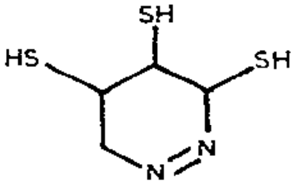


(7)

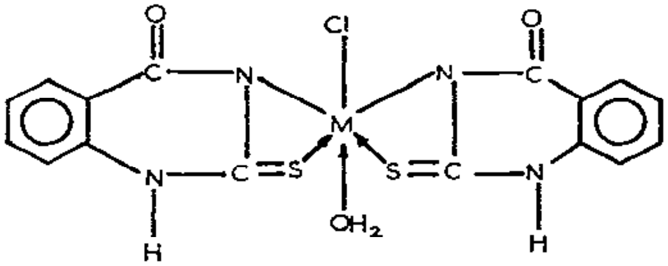
(Q = (7)), respectively [23]. IR, electronic spectroscopic and magnetic studies indicate that $[Rh_2(th)_3]$ {th = (8)} has an octahedral coordination about the



(8)

metal atom [24]. The He(I) excited photoelectron spectrum of $[Rh\{S_2P(OEt)_2\}_3]$ has been reported [25].

The trithiaveratrylene ("Vn_3S_3") rhodium complex $[Rh(NO_3)_3(Vn_3S_3)].3CH_3CON(CH_3)_2$ has been found to contain the expected octahedral coordination [26]. The complex $[Rh(Q)_2Cl(H_2O)].7H_2O$ (HQ = quinazoline-2-thione-4-one) has been prepared and its structure (9) tentatively assigned on the basis of spectroscopic and magnetic measurements [27]. $[Rh(1\text{-imino-3-thioisoindoline})_3]$ has been prepared [28] and a triazoline thione complex of rhodium(III) has been characterised spectroscopically [29].



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5.2.4 *Complexes with tellurium donor ligands*

The aryl telluride complexes of rhodium(III); $[(Ph_2Te)_3RhCl_3]$, $[(Ph_2Te)_2RhCl_3(CO)]$, $[(Ph_2Te)_2RhClBr_2(CO)]$, $[(Ph_2Te)_2RhClI_2(CO)]$, $[(Ph_2Te)_2RhCl(CNS)_2(CO)]$, $[(Ph_2Te)_2RhCl_2(TePh)]$, $[(Ph_2Te)_2RhCl(CO)(TePh)]$ and $[Rh(TePh)_3]$ have been prepared [30].

5.2.5 *Complexes with nitrogen donor ligands*

5.2.5.1 *Ammine, amine, diimine and isonitrile complexes*

$[Rh(NH_3)_5X][NO_3]_2$ (X = Cl, Br or NO_3) has been studied by simultaneous light emission and differential thermal analysis [31]. Ligand-field excitation of aqueous *cis*- or *trans*-$[Rh_2(en)_2XI]^{n+}$ (X = I, NH_3 or H_2O) leads in general to the formation of *trans*-$[Rh_2(en)_2(H_2O)I]^{2+}$. However, *cis*-$[Rh(en)_2(NH_3)I]^{2+}$ gives both *trans*- and *cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ as photoproducts [32]. The *cis/trans* and *trans/cis* photoisomerisation of some rhodium(III) tetraammine complexes (*e.g.* $[Rh(NH_3)_4(H_2O)_2]^{3+}$) has also been examined [33]. The photophysical and photochemical properties of $[Rh(NH_3)_5Cl]^{2+}$ in a variety of non-aqueous solvents have been reported. The identity of the ligand labilised from the ligand-field excited states is a function of the solvent medium: chloride ion substitution is prevalent in aqueous and formamide solution and ammonia substitution predominates in dmf, dmso and MeOH solutions [34]. The energy and electron-transfer processes of $[Rh(phen)_3]^{3+}$ have been investigated quantitatively [35] and the compounds *cis*-$[RhCl_2(bipy)_2]Cl$ and *cis*-$[RhBr_2(bipy)_2]Br$ have been studied by sub-picosecond laser spectroscopy [36].

$Na_3[RhCl_6]$ reacts with 3- or 4-nitroaniline to give $[RhL_2(H_2O)Cl_3]$ and $[RhL_3Cl_3]$ (L = nitroaniline). The IR spectra reveal that the 3-nitroaniline complex contains three facial groups whereas the 4-nitroaniline complex has the chloride groups in the *mer*-positions. Decomposition of $[4\text{-}NO_2C_6H_4NH_3]_3[RhCl_6]$ at 130 °C gives $[RhL_3Cl_3]$ [37]. Octahedral complexes of rhodium(III) with 12-, 13-, 14-, 15-, and 16-membered macrocyclic tetramines have been prepared containing Cl^- or $[PF_6]^-$ counter ions. The molecular geometries (*cis* or *trans*) of the complexes have been assigned on the basis of their UV–VIS absorption spectra and the values for 10 Dq have been estimated [38]. The reaction of $RhCl_3.3H_2O$ in dmso with 1,4,7-triazacyclononane (L) in MeOH gives $[RhL_2]^{3+}$ or $[RhLCl_3]$, depending upon the molar ratios used. Treatment of $[RhLCl_3]$ with $Ag[ClO_4]$ produces $[Rh_2L_2(OH)_4(\mu\text{-}OH)_2]^{4+}$, which at a higher pH forms $[Rh_2L_2(\mu\text{-}OH)_3]^{3+}$. $[Rh_2L_2(OH_2)_2(\mu\text{-}OH)_2]^{4+}$ reacts with $MeCO_2H$ to give $[Rh_2L_2(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)]^{3+}$ and, at pH>8.5, $[Rh_2L_2(OH)_2(\mu\text{-}OH)_2]^{2+}$ is produced which reacts with $[CO_3]^{2-}$ to form $[Rh_2L_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]^{2+}$ [39]. The crystal structures of *cis*- and *trans*-$[Rh(Cl_2)(en)_2][NO_3]$ have been reported [40].

The complexes $[HB(3,5\text{-}Me_2pzl)_3RhCl_2(MeOH)]$ and $[HB(pzl)_3RhCl_2]_2$ have been synthesised. These materials may be used as starting materials for a multitude of derivatives, since many neutral donor ligands displace the coordinated solvent molecules [41]. $[RhX_2(AsRPh_2)_3]$ (X = Cl or Br; R = Me, Et or Pr) react with 4-tolylisocyanide (L) to give $[RhX_3(AsRPh_2)_2L]$ [42].

5.2.5.2 *Thiosemicarbazide and thiosemicarbazone complexes*

A crystal structure determination of $[Rh(thios)_3]Cl_3$ (thios = thiosemicarbazide. $H_2NC{=}SNHNH_2$) has revealed that the metal atom is octahedrally coordinated in a *fac*-arrangement by three sulphur atoms and three hydrazinic nitrogen atoms of the thios ligands [43]. $[Rh(HL)_2]Cl$ ($H_2L = H_2NC{=}SNHN{=}CR_1R_2$; $R_1 = CH_2CH_2CO_2H$, $R_2 = CO_2H$) reacts with HBr to give $[Rh(HL)_2Br]$ and addition of $Na[O_2CMe]$ to $[Rh(HL)_2]Cl$ gives $[Rh(HL)L]$. $[Rh(HQ)_2]Cl$ ($H_2Q = PhNHC{=}SNHN{=}CR_1R_2$; $R_1 = CH_2CH_2CO_2H$, $R_2 = CO_2H$) has been produced from the reaction of $RhCl_3.3H_2O$ with H_2Q [44]. Complexes of the type $[RhQ_2X_2]X$ ($Q = H_2NNHC{=}SNHNHCO\text{-}3\text{-}py$ or $MeOC_6H_4CH{=}NNHC{=}SNHNHCOPh$; X = Br or Cl) have been characterised by IR and UV spectral and magnetic susceptibility data [45].

5.2.5.3 *Oxime complexes*

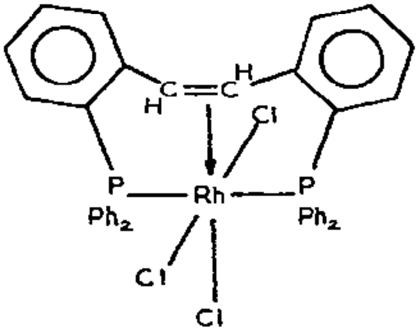
$[RhLCl_2(H_2O)_2]$ (HL = α-furilmonoxime or α-furildioxime) is formed by complexation of Rh(III) with oximes in the absence of ethanoate ion, but $[RhL_2(H_2O)(O_2CMe)]$ is formed in the presence of ethanoate ions [46].

5.2.6 *Complexes with phosphorus donor ligands*

5.2.6.1 *Phosphine and diphosphine complexes*

Benzoyl chloride reacts with $[Rh(dppp)_2]Cl$ to form the five-coordinate complex, $[RhCl_2(COPH)(dppp)]$, containing a square pyramidal structure with the PhCO group occupying the apex [47]. The structure of $[RhCl_3(bdpps)]$ (10) has been evaluated [48] and large-ring and cyclometallate complexes of Rh(III) with α,ω-diphosphines have been reported [50].

It has been observed that the $Rh(PPh_3)_2$ fragment can be readily transferred

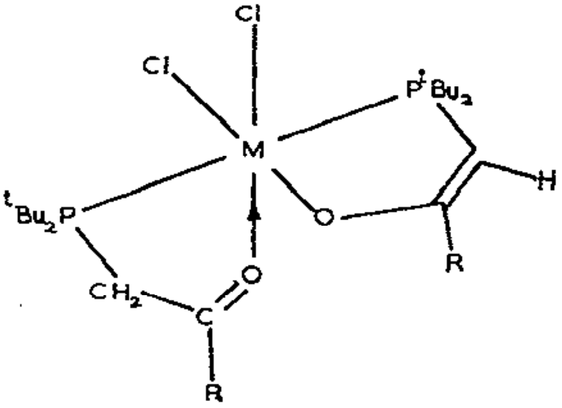


(10)

between carbaborane cages [49].

5.2.6.2 Complexes with phophorus-oxygen or phosphorus-sulphur donor ligands

$RhCl_3.3H_2O$ combines with the β-ketophosphine, $P(CMe_3)_2(CH_2COPh)$, to give $[RhCl_2\{(CMe_3)_2PCH{=}C(O)Ph\}\{P(CMe_3)_2(CH_2COPh)\}]$ (11) in which both phosphine



(11)

ligands are bidentate and the keto-group is strongly coordinated, the latter not being displaced by treatment with carbon monoxide [51].

The reaction of $[RhCl(PPh_3)_3]$ with $Ph_2PSC(NC_6H_4\text{-}4\text{-}Me)(NHC_6H_4\text{-}4\text{-}Me)$ or $Ph_2PSCONHPh$ in the presence of base produces $[Rh(PPh_3)_2(SPPh_2)]$ which contains a side-on coordinated η^2-Ph_2PS grouping. This compound may also be prepared from interaction of $[RhCl(PPh_3)_3]$ and Ph_2PSH. $[Rh(PPh_3)_2(SPPh_2)]$ reacts with PhNCS to give $[Rh(PPh_3)(PhNC)(PhNCS_2)(Ph_2PSCSNPh)]$ [52].

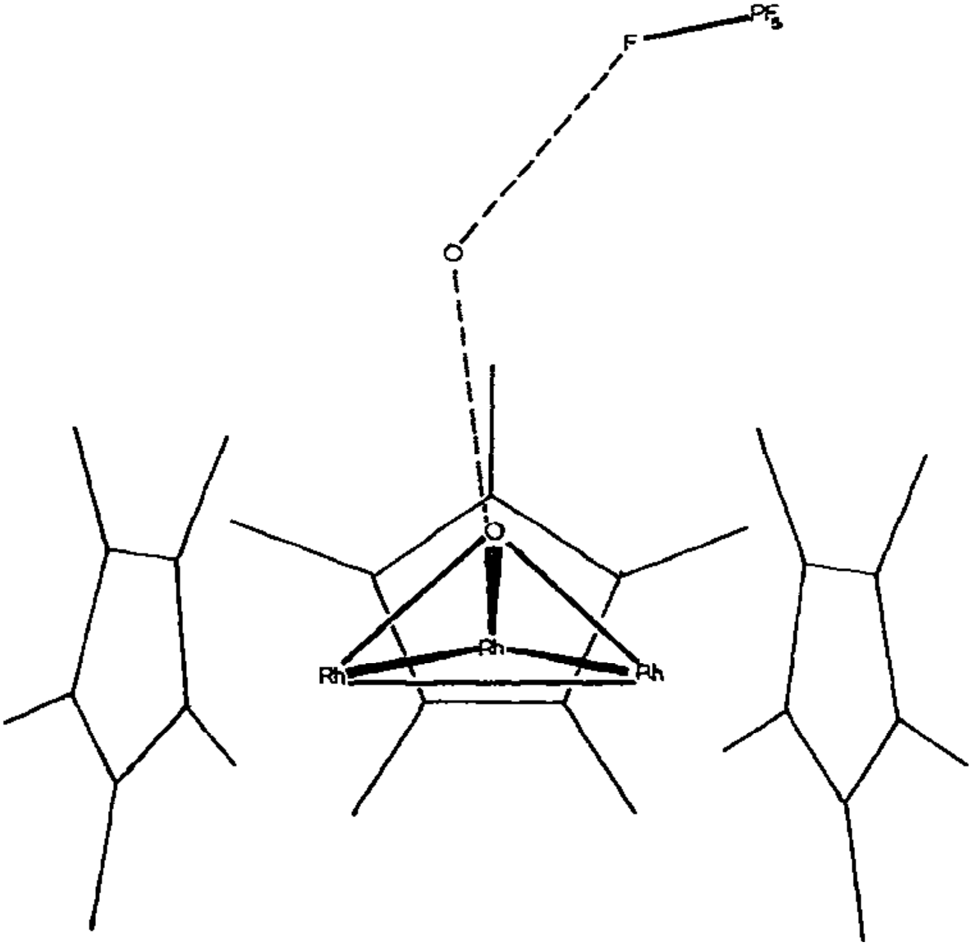
5.2.7 Complexes with Group IV donor ligands

5.2.7.1 Complexes with carbon donor ligands

Reaction of $[Rh(cp)(C_2H_5)(PMe_3)_2]X$ with $[Ph_3C]X$ ($X = [PF_6]$ or $[BF_4]$) gives $[Rh(cp)(C_2H_4)(PMe_3)_2]X_2$. The ethylene ligand is easily attacked by nucleophiles, *N*, to give complexes containing Rh–C_2H_4*N* moieties [53]. The rates of hydrogenation of the coordinated olefin (acrylonitrile or styrene) in $[Rh(H_2)X(olefin)(PPh_3)_2]$ (X = Cl, Br or I) have been measured [54]. The crystal structure of $[Rh_2(\mu\text{-}I)_2(I)_2(\eta^5\text{-}C_5Me_4Et)_2]$ has been determined [55].

5.2.7.2 Complexes with tin donor ligands

The crystal structure of $Cs_4[Rh\{SnF_2(H_2O)_2\}_2\{Sn_4F_{15}\}].4H_2O$ has been determined; these rhodium atoms have been found to be octahedrally coordinated to six tin



(12)

atoms, with the $SnF_2(H_2O)_2$ groups *cis* to each other and the $\{Sn_4F_{15}\}^{7-}$ ion is fluorine bridged with the formula, $[F_3Sn(\mu\text{-}F)SnF_4(\mu\text{-}F)SnF_4(\mu\text{-}F)SnF_3]^{7-}$ [56]. $[NMe_4]_3[RhCl_4(SnCl_3)_2]$ has been prepared by the reaction of $RhCl_3.3H_2O$ with $SnCl_2.2H_2O$ and $[NMe_4]Cl$ and similar complexes containing the anions; $[RhCl_3(SnCl_3)_3]^{3-}$, $[RhBr_3(SnCl_3)_3]^{3-}$, $[RhCl_2(SnCl_3)_4]^{3-}$, $[RhSn_5Cl_5]^{3-}$ and $[RhSn_6Cl_{22}]^{3-}$ have been prepared and isolated with a variety of cations [57].

5.2.8 Hydride complexes

The trinuclear complex $[Rh_3H_3(\eta^5\text{-}C_5Me_5)_3O][PF_6].H_2O$ (12) has been prepared and its geometry established by X-ray diffraction. A difference Fourier synthesis shows the presence of hydride ligands bridging the metal atoms on the side opposite to the capping oxygen atom [58]. The proton NMR spectrum shows the molecule to be non-fluxional and unusually rigid.

5.3 RHODIUM(II)

The chemistry of this oxidation state is dominated at present by the substitution chemistry of Rh_2^{4+} centres.

5.3.1 Complexes with oxygen donor ligands

5.3.1.1 Sulphate and phosphate complexes

$[Rh_2(RCO_2)_4].H_2O$ (R = H or Me) reacts with $Cs_2[SO_4]$ in the presence of H_2SO_4 to give $Cs_4[Rh_2(SO_4)_4(H_2O)_2].2H_2O$ which contains a Rh-Rh bond and bridging sulphate groups. $Rh_2O_3.nH_2O$ reacts with H_2SO_4 in the presence of M^+ to form $M_4[Rh_2(SO_4)_4(H_2O)_2]$ (M = Cs or H_3O) [59]. $[Rh_2(O_2CMe)_4]$ reacts with H_3PO_4 to form $[Rh_2(H_2PO_4)_4(H_2O)_2]$, which is diamagnetic and possesses a dimeric structure with a Rh-Rh bond and bridging phosphate groups. Further reaction with pyridine produces $[pyH]_4[Rh_2(HPO_4)_4(py)_2]$ [60].

5.3.1.2 Carbonate and carboxylate complexes

X-ray crystallography has been used to confirm the presence of the $[Rh_2(CO_3)_4]^{4-}$ dinuclear grouping in the complexes $Cs_4[Rh_2(CO_3)_4(H_2O)_2].6H_2O$ and $Cs_4Na_2[Rh_2(CO_3)_4Cl_2].8H_2O$ [61].

The binuclear, carboxylato-bridged species $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$, $[Rh_2(O_2CMe)_4(\text{tetrahydrothiophene})_2]$, $[Rh_2(O_2CMe)_4(\text{dmso})_2]$ [62] and $[Rh_2(O_2CMe)_4(H_2O)_2][ClO_4]$ [63] have been examined by X-ray crystallography; the last complex is reported to contain a multiple Rh(II)-Rh(III) bond. The XPES of $[Rh_2(O_2CMe)_4]$, $[Rh_2(O_2CMe)_4][ClO_4]$, $[Rh_2(O_2CMe)_4(\text{4-cyanopyridine})]$ and $[Rh_2(O_2CR)_4L_2]$ (R = H, Me, Ph, CCl_3, CF_3, *etc.*); L = H_2O, py, dmso, tu, MeCN, dmf, *etc.*) have been recorded [64,65] and the complexes $[Rh_2(O_2CR)_4L_2]$ (R = H, Me or CF_3; L = H_2O, py, NH_3, urea, tu, dmso, $MeNH_2$, EtOH or PPh_3) and $M_2[Rh_2(O_2CR)_4X_2]$ (M = Na, K or guanidinium; X = Cl, Br, I or NO_2) have been examined by IR spectroscopy [66]. Rhodium(II) carboxylates are reported to coordinate with dmso to produce compounds having the general formula $[Rh_2(O_2CR)_4(dmso)_2]$ (R = C_2H_5 or CF_3); when R = C_2H_5, coordination is *via* the sulphur atom of dmso but when R = CF_3, coordination is *via* the oxygen atom [67].

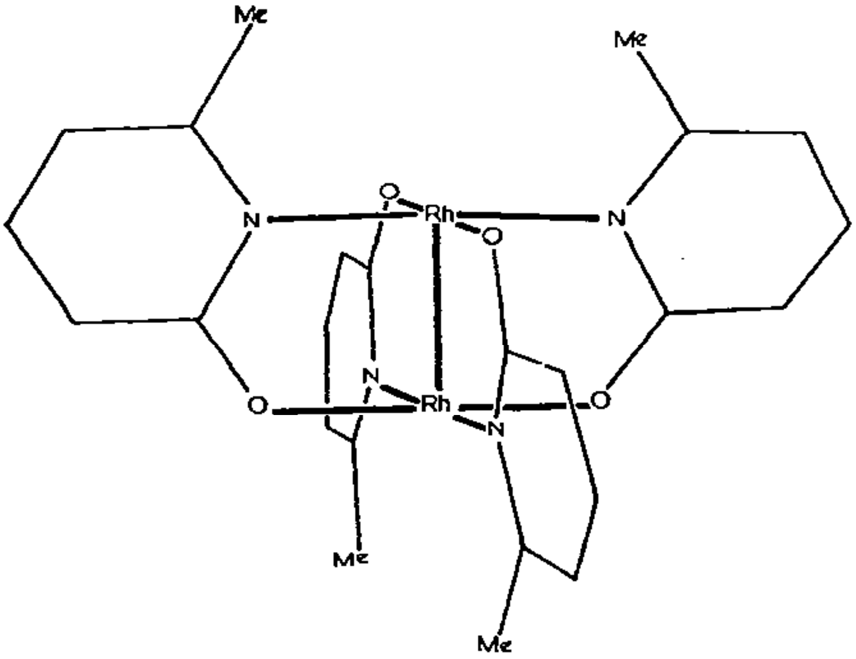
Complexes of general formula, $H_4[Rh_2L_4Q_2]$ (H_2L = salicylic acid; Q = NH_3, py, $PhNH_2$, en, urea, $MeCSNH_2$ or $\frac{1}{2}N_2H_4$) have been examined. Their structures are considered to be analogous to those of the corresponding ethanoate or methanoate dimeric complexes [68].

5.3.1.3 Complexes with oxygen-sulphur donor ligands

The thiocarboxylate complexes; $[Rh_2(RCOS)_4L_2]$ (R = H, Me, Ph, CCl_3, CF_3, *etc.*; L = H_2O, py, dmso, tu, MeCN, dmf, *etc.*) have been examined by XPES [65].

5.3.1.4 Complexes with oxygen-nitrogen donor ligands

[Rh$_2$(6-methyl-2-oxypyridine)$_4$] (13) has been synthesised and its structure established by X-ray crystallography; He-I and He-II UVPES indicate the presence of a metal-metal single bond [69].



(13)

5.3.1.5 *Complexes with oxygen-phosphorus donor ligands*

Treatment of the six-coordinate rhodium(III) complex, $[RhCl_2\{(CMe_3)_2PCH{=}C(O)Ph\}\{P(CMe_3)_2(CH_2COPh)\}]$ with sodium methoxide proceeds rapidly to produce an intense blue coloured material which appears to be the rhodium(II) complex, *trans*-$[Rh\{(CMe_3)_2PCH{=}C(O)Ph\}_2]$ [51].

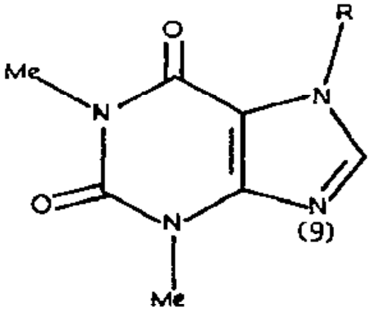
5.3.2 *Complexes with nitrogen donor ligands*

5.3.2.1 *Amine complexes*

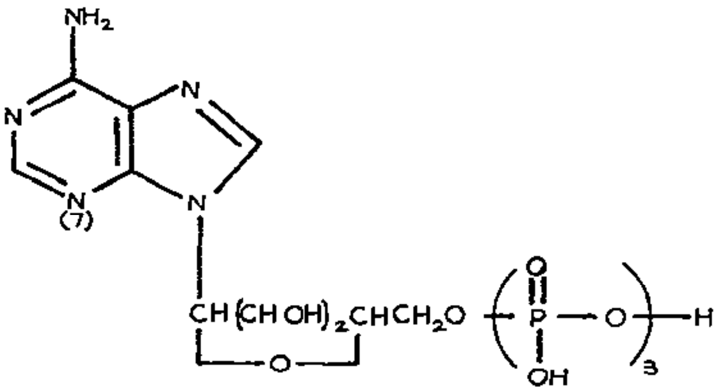
The crystal structure of $[Rh_2(\beta\text{-alanine})_4(H_2O)_2][ClO_4]_4.2H_2O$ has been determined [70].

5.3.2.2 *Complexes with nitrogen-containing heterocycles*

The crystal structures of $[Rh_2(O_2CMe)_4(\text{theophylline})_2]$ and $[Rh_2(O_2CMe)_4(\text{caffeine})_2]$ have been determined [71]. Both of the bases are coordinated *via* N(9) {see (14)}



(14; R = H, theophylline; R = Me, caffeine)



(15)

to the dirhodium tetraethanoate nucleus at the axial positions.

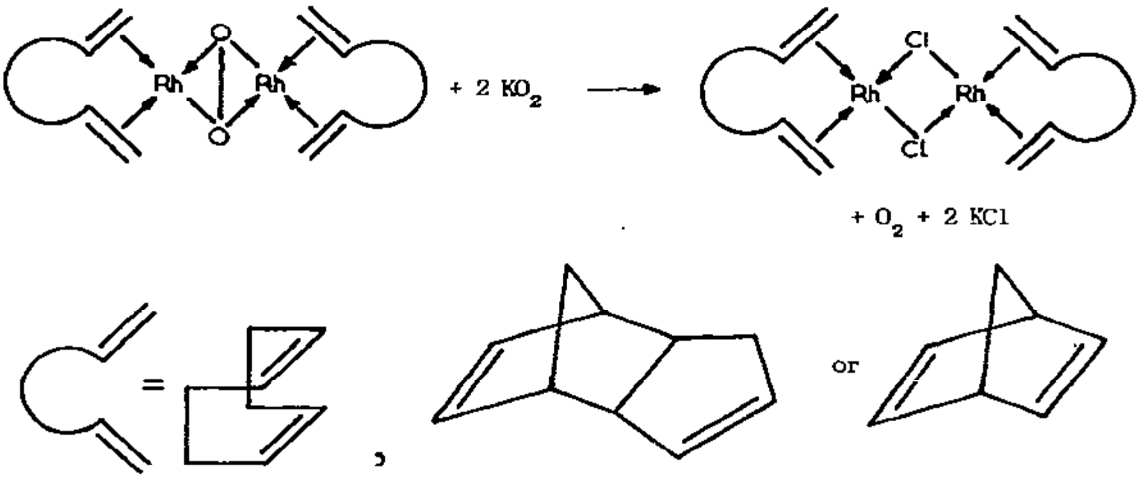
The preparation of the adenosine triphosphate complexes, $[Rh(H_3ATP)(H_2O)_4]Cl_2$ and $[Rh(H_4ATP)(NH_3)_5].xH_2O$ have been reported [72]; the purine ring is bound to the metal by the N(7) atom (15). The interactions of the rhodium(II) ethanoate dimer with the monophosphate nucleotides of guanine, cytosine, adenosine and uracil have been studied by Raman difference spectroscopy [73].

5.4 RHODIUM(I)

5.4.1 Complexes with Group VI donor ligands

5.4.1.1 Complexes with oxygen donor ligands

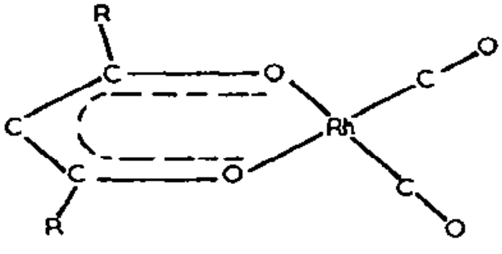
New dioxygen complexes of rhodium have been prepared by the reaction illustrated in Scheme I [74].



SCHEME I: Preparation of rhodium dioxygen complexes.

Carbon dioxide interacts with coordinately unsaturated rhodium(I) complexes containing dppe. Thus, CO_2 and $[Rh(C_6H_5)(dppe)]$ in acetone solution at 90 °C yield the benzoate complex, $[Rh(OOCC_6H_5)(dppe)]$. This material was also prepared from the reaction of $[Rh(dppe)(\eta^6\text{-}BPh_4)]$ with CO_2 [75]. The dimeric nature of $[Rh_2(OOCH)_2(CO)_4]$ has been indicated by its mass spectrum and the monomer-dimer equilibrium has been studied in methanol-benzene solutions [76]. Amino acid complexes of the type $[(XY)Rh(CO)_2]$ (XYH = amino acid) have been prepared from $[Rh(O_2CMe)(cod)_2]$ by carboxylate ligand exchange and treatment with carbon monoxide. The complexes have square-planar geometry with *cis*-carbonyl groups [77].

The He-I and He-II photoelectron spectra of a series of square-planar Rh(I) complexes have been published [78]. The spectra of the complexes (16) and (17)



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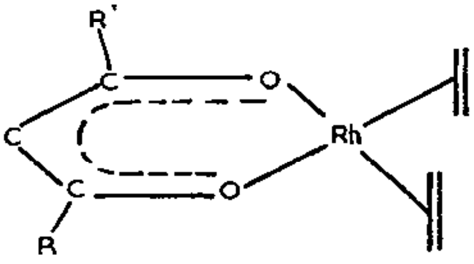
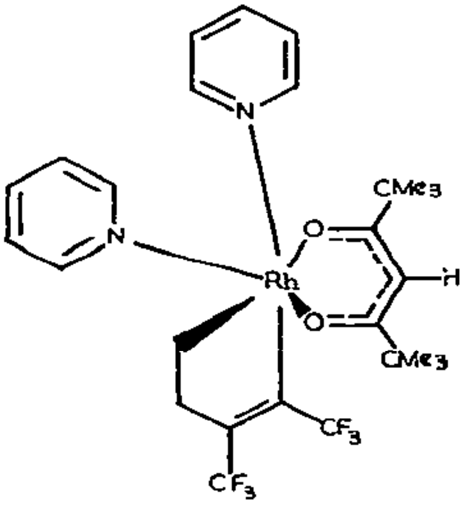


(17)

(R,R' = Me,Me; CF_3,Me; CF_3,CF_3; CMe_3,CMe_3)

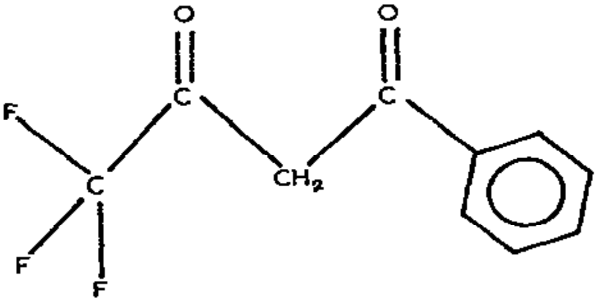
have been assigned on the basis of the intensity differences of the bands derived from the two energy sources, from MO calculations, and by comparison with the corresponding spectra of related compounds.

The complex (18) has been characterised from single crystal X-ray diffraction studies [79].



(18)

The compounds $[RhCl(Ph_2SO)(C_8H_{14}]_2$, $[RhCl(dmso)_2]_2$ and $[RhCl(dios)_2]_2$ (dios = (2R,3R)-2,3-isopropylidene-2,3-dihydroxy-1,4-bis(methylsulphinyl)butane) have been synthesised from $[RhCl(C_8H_{14})_2]$ [15]. The structure of [Rh(tfba)(cod)] {tfba = (19)} has been determined by X-ray crystallography; the geometry about the rhodium atom is essentially square planar and the bond lengths obtained indicate that the oxygen atom nearest to the phenyl ring has the largest static

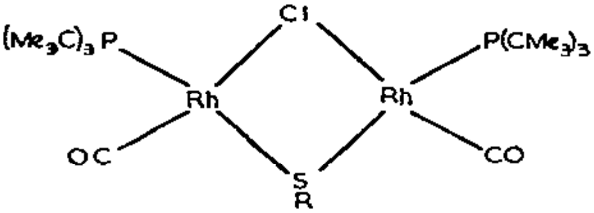


(19)

trans-effect [80].

5.4.1.2 *Complexes with sulphur or tellurium donor ligands*

Sulphoxides of the type, $[Rh(CO)X(R_2SO)_2]$ (X = Cl or Br; R = Me, Pr or Bu) and sulphides of the type, $[Rh(CO)X(R_2S)]$ (X = Cl or Br; R = Me, Et or $CHMe_2$) have been prepared. The IR stretching frequencies of the S-O bond in the sulphoxide complexes indicate that coordination is through the sulphur atom [81]. The thio-bridged complexes (20) (R = Me_2CH, Bu, Me_3C, Ph, 4-tolyl or 4-ClC_6H_4) have been synthesised by replacing the SR group for the bridging chloride in the corresponding di-μ-chloro compound [82]. $[RhCl(Ph_2SO)_2]_2$ has also been prepared and shown to involve coordination *via* the sulphur atoms [15].



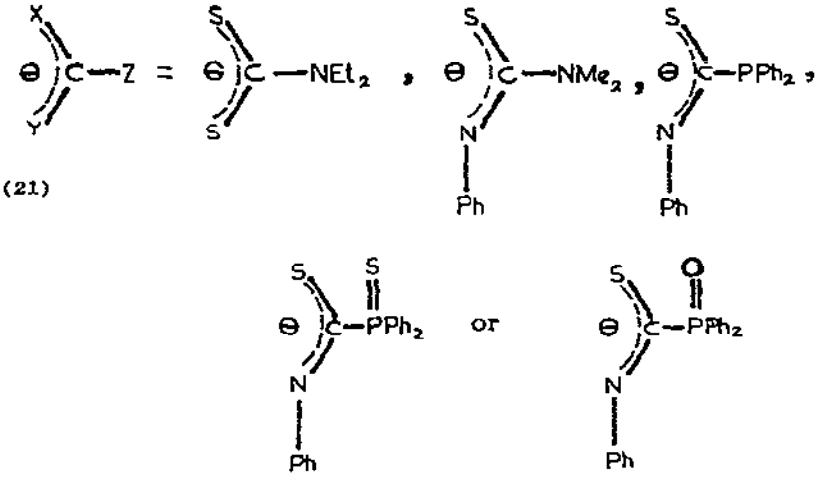
(20)

Reaction of CS_2 with $[Rh(cp)(C_2H_4)(PR_3)]$ (PR_3 = PMe_3 or PMe_2Ph) produces the complex $[Rh(cp)(PR_3)(CS_2)]$ in which the CS_2 ligand is η^2-bonded. $[Rh(cp)(PMe_3)(CS_2)]$ reacts with $[Cr(CO)_5(thf)]$ and $[Mn(cp)(CO)_2(thf)]$ to give $[Rh(cp)(PMe_3)(SCS)Cr(CO)_5]$ and $[Rh(cp)(PMe_3)(SCS)Mn(CO)_2(cp)]$, respectively; the CS_2 molecule bridges the two metal atoms in these complexes. The reaction of $[Rh(cp)(C_2H_4)(PMe_3)]$ with CS_2 can also give another product, $[Rh(cp)(PMe_3)(C_2S_4)]$, which contains a five-membered RhSCSC heterocyclic ring [83].

$[Rh(th_3)_3Cl]$ (th_3 = (8)) has been tentatively postulated to possess a square planar geometry on the basis of IR and UV-VIS spectral and magnetic studies [24].

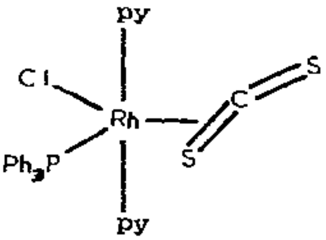
The tellurium-rhodium(I) bonded complexes, $[(Ph_2Te)_2Rh(CO)Cl]$, $[(Ph_2Te)Rh(CO)(CNS)]$, $[(Ph_2Te)_3RhCl]$ and $[(Ph_2Te)_2RhCl]_2$, have been synthesised and characterised by IR spectroscopy, thermal analysis and molecular mass measurements [30].

The compounds $[Rh\{X\text{-}C(Z)\text{-}Y\}(PPh_3)_2]$ ($\{X\text{-}C(Z)\text{-}Y\}$ = (21)) react with an excess



(21)

of CS_2 to give the thiocarbonyl complexes $[Rh\{X\text{-}C(Z)\text{-}Y\}(CS)(PPh_3)]$. The initial step in the reaction is believed to be side-on coordination of CS_2 through one of the C=S double bonds. $[RhCl(\eta^2\text{-}CS_2)(PPh_3)(py)_2]$ (22) can be formed by



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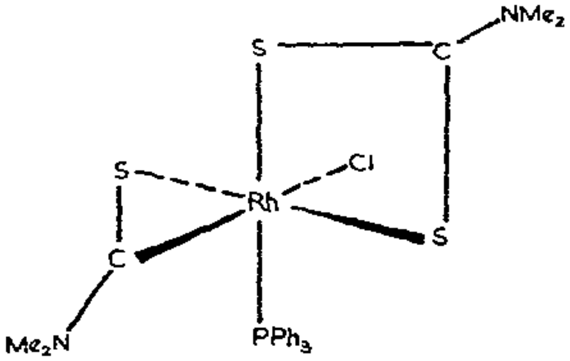


(23)

addition of pyridine to a solution of $[RhCl(PPh_3)_2]$ in benzene that has been treated with CS_2. In the absence of pyridine and with an excess of PPh_3, $[RhCl(CS)(PPh_3)_2]$ is formed [84]. $[(Ph_3P)_2Rh(CO)Cl]$ reacts with $(Me_2NCS)_2S$ to give the kinetically-stable product, $[(Ph_3P)Rh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)(CO)]X$ (X = Cl or $[PF_6]$). This complex in solution slowly transforms into the thermodynamically stable product $[(Ph_3P)Rh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)Cl]$ (23) [85]. The reaction of $[Rh(cp)(PMe_3)(C_2H_4)]$ and CSSe gives $[Rh(cp)(PMe_3)(\eta^2\text{-}CSSe)]$, which undergoes reaction with Ph_3P to give $[Rh(cp)(CS)PMe_3)]$ [86].

5.4.2 *Complexes with nitrogen donor ligands*

5.4.2.1 *Oxime and nitric oxide complexes*

The neutral, square-planar compounds, $[Rh(CO)_2(L\text{-}L)]$ (L-L = salicylaldoxime, $2\text{-}OHC_6H_5CH(=NOH)$, α-benzoin oxime, $C_6H_5CH(OH)C(=NOH)C_6H_5$, α-furil dioxime, $C_4H_4C(=NOH)C_4H_4C(=NOH)$, α-benzil dioxime, $C_6H_5C(=NOH)C_6H_5C(=NOH)$, dimethylglyoxime, $CH_3C(=NOH)CH_3C(=NOH)$ or cupferron, $C_6H_5N(NO)ONH_4$) have been prepared. These dicarbonyls react with PPh_3, $AsPh_3$ and $SbPh_3$ to give monocarbonyl derivatives which form 1:1 adducts with tcne [87]. Reduction of $[RhCl(dmg)(PPh_3)]$ with an excess of $Na[BH_4]$ gives $[BH_2Rh(dmg)_2(PPh_3)]_2$. The degree of oxidation in this complex and in $[(PPh_3)Rh(dmg)_2]$, $[(OPPh_3)Rh(dmg)_2]_2O_2$, $H[Rh(dmg)Cl_2]$, $[HRh(dmg)_2]$ and $[PhNHCH_2Rh(dmg)_2]$ has been examined by XPES [88]. $Rb[RhCl_2(dmg)_2].H_2O$ has octahedral coordination about the rhodium atom with two dmg ligands in the equatorial plane [89].

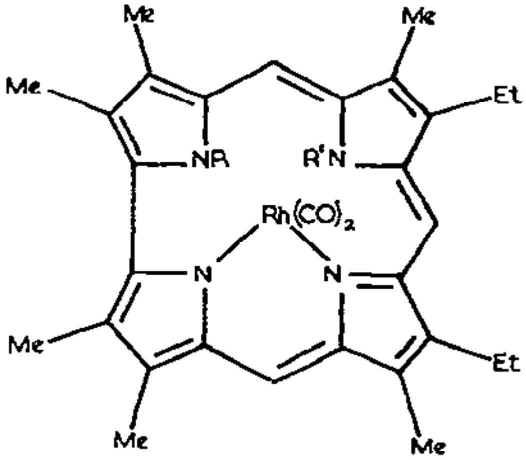
$[RhCl(PPh_3)_3]$ and $[Rh(CO)Cl(PPh_3)_2]$ react with N_2O_3 in dichloromethane to produce solvated $[Rh(NO)(NO_2)Cl(PPh_3)_2]$. $[Rh(CO)Cl(AsPh_3)_2]$ and $[RhH(CO)(PPh_3)_3]$ combine with N_2O_3 in dichloromethane to give $[Rh(NO)_2(NO_2)(AsPh_3)_2].1.5CH_2Cl_2$ and $[Rh(NO)_2(NO_2)(PPh_3)_2].0.5CH_2Cl_2$, respectively. The reaction of $[Rh(CO)(O_2CMe)(PPh_3)_2]$ with N_2O_3 produces $[Rh(NO)(NO_2)_2(PPh_3)_2]$. N_2O_3 combines with $RhCl_3.3H_2O$ to give $[Rh(NO)Cl_2(PPh_3)_2]$, in the presence of triphenylphosphine and $[Rh(NO)Cl_2(AsPh_3)_2)]$, in the presence of triphenylarsine. The IR spectra of these complexes indicates that the nitric oxide is coordinated as NO^- [90].

5.4.2.2 *Diimine complexes*

$[Rh(cod)(L\text{-}L)]^+$ (L-L = phen or bipy) reacts with $[IrX_2(CO)_2]^-$ to give $[Rh(CO)_3(L\text{-}L)][IrX_2(CO)_2]$ which has been characterised by IR and diffuse reflectance spectroscopy [91]. Addition of a monodentate (*e.g.* 8-methylquinoline) or bidentate (*e.g.* phen) ligand, L, to $[Rh(CO)(PPh_3)_2(CH_3COCH_3)][ClO_4]$ produces complexes of general formula $[Rh(CO)(PPh_3)_2L][ClO_4]$. Monodentate coordination is favoured by replacing triphenylphosphine with $P(C_6H_{11})_3$ and bidentate linkage is favoured by using $AsPh_3$ or PMe_2Ph. By increasing the size of the 8-substituent and, especially, by the further introduction of a 2-methyl group, the equilibrium constants for cleavage of $[Rh(CO)_2Cl]_2$ by substituted quinolines are reduced in the reaction [92]:

$$[Rh_2Cl_2(CO)_4] + 2L \longrightarrow 2[RhCl(CO)_2L]$$

The structure of the polypyrrole macrocycle (24) has been determined (R = Me, R' = H; R = H, R' = Me) [93].



(24)

5.4.2.3 *Diazenide complexes*

The four coordinate rhodium complexes, $[RhCl(N_2C_5X_4)(PR_3)_2]$ (X = Cl or Br; R = Ph, CMe_2H, $4\text{-}FC_6H_4$ or CMe_3) have been generated as short lived intermediates [94]. The bidentate, diazadiene ligand, $(CHMe_2)CH\text{-}N\text{=}CH\text{-}CH\text{=}N\text{-}CH(CHMe_2)$ = dad, combines with $[Rh_2(CO)_4Cl_2]$ to give $[Rh_2(dad)(CO)_4Cl_2]$. An X-ray crystal structure of this material reveals that it should be formulated as $[Rh(dad)(CO)_4]^+$ $[Rh(CO)_2Cl_2]^-$; both cation and anion contain four-coordinate, square-planar geometries [95].

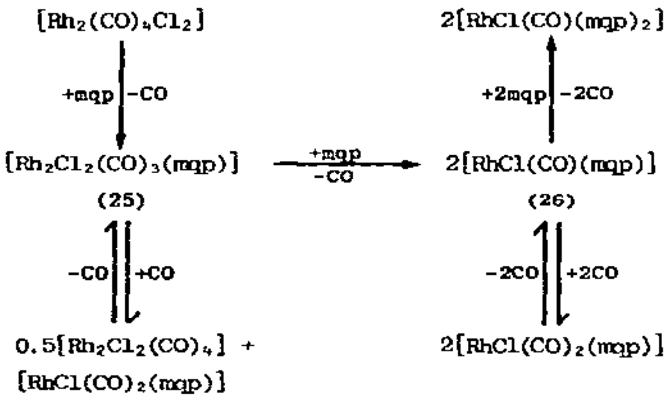
5.4.2.4 *Isonitrile complexes*

Planar, four-coordinate polymers containing rhodium(I) are produced from the reaction between the bridging ligands, 1,4- or 1,5-diisocyanonaphthalene (= bridge) with $[Rh(CO)_2Cl]_2$; these polycrystalline solids analyse as $\{[Rh(bridge)_2]Cl\}_n$ [96]. Similarly, coordination polymers containing 1,4-diisocyanobenzene or 4,4'-diisocyanobiphenyl bridging ligands have been produced [97] and polymeric complexes of the type, $[RhL_2Cl.xH_2O]_n$ (x = 0-8), with L = 1,3-diisocyanobenzene, 2,4-diisocyanotoluene or 4,4'-diisocyanodiphenylmethane, have been synthesised [98]. An X-ray crystallographic analysis of the salt, $H_3[Rh_4(1,3\text{-diisocyanopropane})_8Cl][CoCl_4]_4.nH_2O$, has been obtained. The cation consists of two $[Rh_2(bridge)_4]^{3+}$ units linked by a Rh–Rh bond, the chloride ion bridging these $[Rh_4(bridge)_8]^{6+}$ units to form an infinite polymer chain. The oxidation state of rhodium in this material is formally 1.5 [99]. Crystal structure analyses have been carried out on $[Rh_2(1,3\text{-diisocyanopropane})_4][BPh_4]_2.MeCN$ and $[Rh_2(2,5\text{-dimethyl-2,5-diisocyanohexane})_4][PF_6]_2.2MeCN$; both compounds are found to contain ligand-bridged, binuclear cations and the coordination geometry about the metal atoms is approximately square-planar [100].

Irradiation (λ>520 nm) of $[\{Rh_2(bridge)_4\}_2]^{6+}$ (bridge = 1,3-diisocyanopropane) in concentrated HCl solutions at room temperature produces $[Rh_2(bridge)_4Cl_2]^{2+}$ with the evolution of dihydrogen. Controlled reduction of $[\{Rh_2(bridge)_4\}_2]^{6+}$ in sulphuric acid solution produces the hexanuclear cation, $[\{Rh_2(bridge)_4\}_3]^{8+}$ (which can dimerise) and the octanuclear species, $[\{Rh_2(bridge)_4\}_4]^{10+}$. In 6 *M* hydrochloric acid solutions photogenerated $[Rh_2(bridge)_4]^{2+}$ is trapped by $[\{Rh_2(bridge)_4\}_2]^{6+}$ to give $[\{Rh_2(bridge)_4\}_3]^{8+}$; in 12 *M* solutions, $[Rh_2(bridge)_4]^{2+}$ reacts with the HCl to produce dihydrogen [101,102]. The energy-transfer and electron-transfer processes involved in the $^3A_{2u}$ excited states of $[Rh_2(bridge)_4]^{2+}$ complexes have been examined (bridge = 1,3-diisocyanopropane or 2,5-dimethyl-2,5-diisocyanohexane [103].

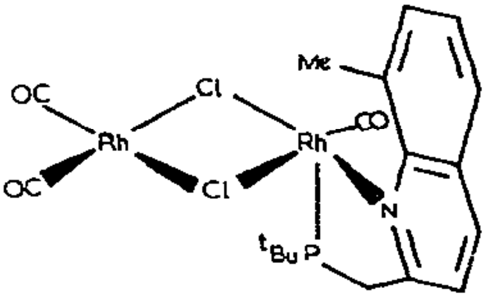
5.4.2.5 Complexes with nitrogen and other donor atom ligands

The reactions of $[\{Rh(CO)_2Cl\}_2]$ with the ligand (8-methyl-2-quinolylmethyl)di-*t*-butylphosphine (mqp) are described in Scheme II [104].



SCHEME II: Preparation and reactions of complexes containing mqp.

Complexes containing the tris(2-pyridyl)phosphine ligand, such as $[RhCl(CO)\{P(py)_3\}_2]$ and $[RhCl(cod)\{P(py)_3\}]$, have been described. In certain cases, as in $[RhCl\{P(py)_3\}_2]$, the nitrogen atom of one of the pyridyl groups is believed to be able to act as a donor to produce a phosphorus-nitrogen chelate.



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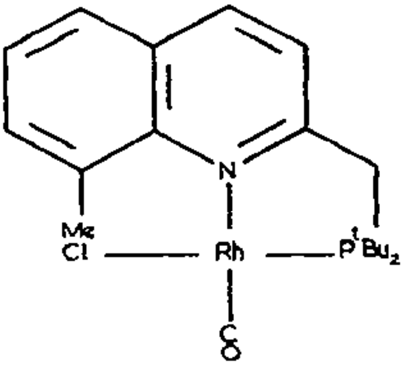

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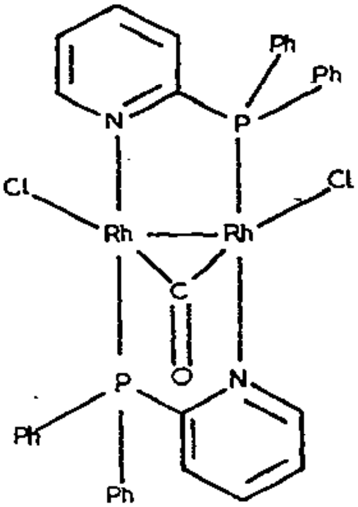
The diphenyl-2-pyridylphosphine compound, [RhH(CO){PPh$_2$(py)}$_3$] has also been prepared [105]. During the thermal decomposition of [Rh(CO)L$_2$Cl] (L = 2-[2-(diphenylphosphino)ethyl]pyridine) in air at temperatures below 170 °C, the phosphine ligand is oxidised to the phosphine oxide, L', and [Rh(CO)L$'_2$Cl] is formed, the coordination being through the nitrogen of pyridine rather than the phosphorus atom. At 180 °C, CO is eliminated and [Rh$_2$L'$_4$Cl$_2$] is produced which is chloride bridged. When [Rh(CO)L$_2$Cl] is decomposed in helium, however, CO is evolved with the resulting formation of [RhL$_2$Cl], in which L is now bidentate and coordinated through both the phosphorus and nitrogen atoms [106]. The synthesis and structures of [Rh$_2$(Ph$_2$Ppy)$_2$(μ-CO)Cl$_2$] (27) and



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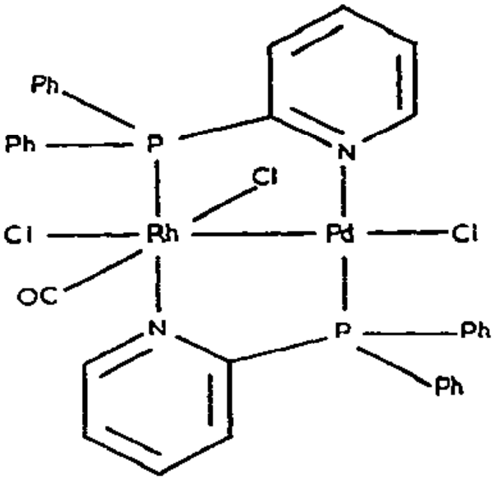
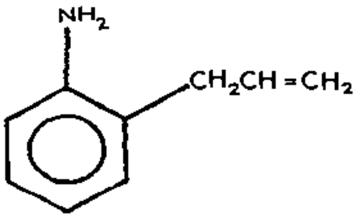


(28)

$[RhPd(Ph_2Ppy)_2(CO)Cl_3]$ (28) have been described [107].

Reaction of $[Rh(C_2H_4)_2Cl]_2$ with 2-allylaniline (L = (29)) gives the dimer



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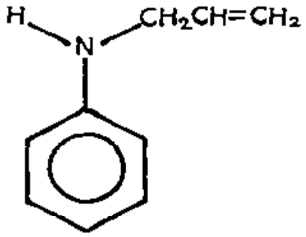


(30)

$[RhLCl]_2$, in which the ligand is coordinated to the metal through both the nitrogen atom and the alkene group. Reaction of $[Rh(C_2H_4)_2Cl]_2$ with *N*-allyaniline = Y = (30) produces $[Rh_2Cl_2Y_3]$ [108].

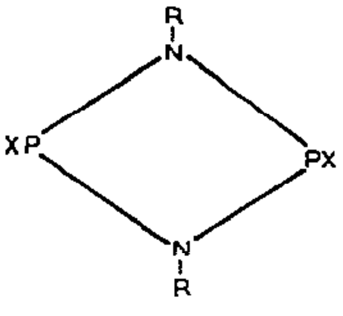
5.4.3 Complexes with phosphorus and arsenic donor ligands

5.4.3.1 Phosphine complexes

$[RhCl(PPh_3)_3]$ decomposes above 140 °C in both the solid state and in solution to yield biphenyl; rhodium complexes with 4-substituted PPh_3 ligands form 4,4'-disubstituted biphenyls. The mechanism of these ring connections is believed to occur by dissociation of $[RhCl(PPh_3)]$ into PPh_3 and solvated $[RhCl(PPh_3)_2]$, followed by the oxidative addition of PPh_3 to the latter to form a phenylrhodium intermediate [109]. The high-resolution, solid state ^{31}P NMR spectrum of $RhCl(PPh_3)_3$ has been recorded. The parameters found for the solid complex are in reasonable agreement with those derived from the solution spectrum in dichloromethane [110]. The crystal structure of square-planar *trans*-$[RhCl(CO)(PPh_3)_2]$ has been resolved [111].

The preparation and characterisation of the following trimethylphosphine complexes have been described; $[Rh(PMe_3)_4Cl]$, $[RhCl(PMe_3)_3]$, $[Rh(PMe_3)_3]X$ (X = $[PF_6]$, $[BPh_4]$), $[RhH_2(PMe_3)_4]Cl$, $[RhCl(CO)(PMe_3)_2]$ and $[Rh(PMe_3)_3(CH_2Cl_2)]Cl$. Crystal structures determined for $[Rh(PMe_3)_4]Cl$ and $[RhCl(PMe_3)_3]$ demonstrate that the metal is in an environment which is approximately square planar but is significantly distorted towards a tetrahedral geometry [112]. The X-ray structure of the sterically-crowded complex $[RhH\{P(CHMe_2)\}_3]$ has been determined and it possesses a strictly planar coordination about the metal. The fluxional behaviour of this compound and of $[RhH(PEt_3)_3]$ and $[RhH(PEt_3)_4]$ have been reported [113]. $[RhH\{P(CHMe_2)_3\}_3]$ and $[Rh_2(H_2)(\mu\text{-}N_2)\{P(cych)_3\}_4]$ undergo oxidative additon of H_2O. The preparation of $[Rh(H)_2(py)_2\{P(CHMe_2)_3\}_3]X$ (X = OH or $[BPh_4]$), $[Rh(H_2)(py)_2\{P(cych)_3\}_2][BPh_4]$, $[Rh_2(C_6F_5)_2(N_2)\{P(cych)_3\}_4].2PhMe$, $[Rh(C_6F_5(CO)\{P(cych)_3\}_2]$ and $[Rh(C_6F_5(PhCN)\{P(cych)_3\}_2]$ have been reported [114].

The structure and properties of *trans*-$[RhCl(CO)\{P(2\text{-}C_5H_4N)_3\}_2]$ have been described [115] and the He-I and He-II UVPES of $[Rh_2Cl_2(PF_3)_4]$ have been recorded [116]. Displacement of ethene from $[Rh(cp)(C_2H_4)_2]$ by $(PXNR)_2 = \{L = (31)\}$ gives



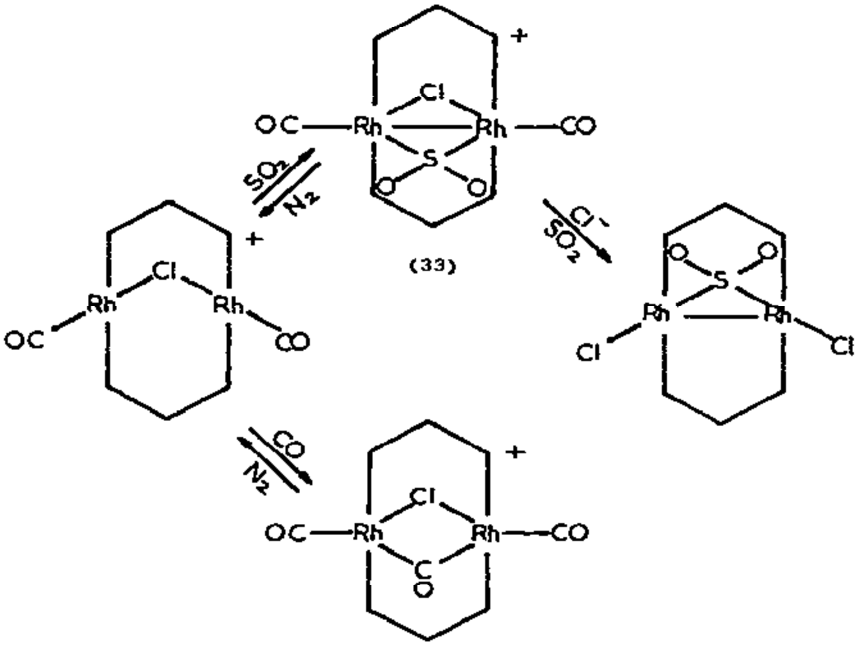
(31)

the complexes $[Rh(L)\{(PFNR)_2\}_2]$ ($R = CHMe_2$ or CMe_3). Displacement of ethene from $[RhCl(C_2H_4)_2]_2$ by L ($R = CMe_3$, $X = F$ or Cl; $R = CHMe_2$, $X = Cl$) gives $[RhCl(PXNR)_2]_n$; $[RhCl\{[PClN(CMe_3)]_2\}_2]_x$ can be isolated from the analogous cod or butadiene precursors. The intermediate complex, $[RhCl(\eta\text{-}C_8H_{12})\{PClN(CMe_3)\}_2]$ was characterised by ^{31}P NMR spectroscopy. $[RhCl(PXNR)_2]_n$ ($X = F$, $R = CMe_3$) reacts with CO to give $[RhCl(CO)\{PFN(CMe_3)\}_2]$ and ring displacement occurs with dppe to give $[RhCl(dppe)_2]$ [117]. Polymer-bound complexes of rhodium(I) have also been studied by ^{31}P NMR spectroscopy [118].

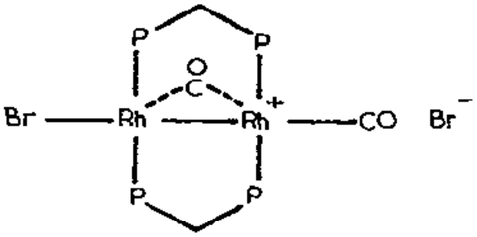
Treatment of $[Rh(CO)_2Cl]_2$ with $P(CMe_3)_2(CH_2COR)$ ($R = Ph$ or CMe_3) gives *trans*-$[RhCl(CO)\{P(CMe_3)_2(CH_2COR)\}_2]$. Reaction of these products with sodium methoxide gives $[\overline{Rh(CO)\{(CMe_3)_2PCH{=}C(O})R\}\{P(CMe_3)_2(CH_2COR)\}]$ [51].

5.4.3.2 *Diphosphine and related complexes*

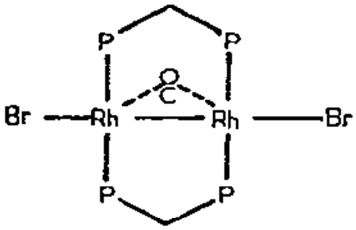
The "A-frame" complex, $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][BPh_4]$ (32) undergoes reaction with sulphur dioxide to produce (33). Treatment of (33) with excess of sulphur dioxide in the presence of chloride ion generates (34) and reaction of (32) with carbon monoxide produces (35) [119]. The X-ray crystal structure of (34) has been determined. The asymmetric species $[Rh_2Br(\mu\text{-}CO)(CO)(\mu\text{-}dppm)_2]Br$ (36) has been produced from the reaction of *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$ with sodium bromide. The former species loses carbon monoxide in solution to give the "A-frame" complex, $[Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (37). When KI is used in place of NaBr, $[Rh_2I(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ is formed. Both the bromo- and iodo- species react with CO and with SO_2 to give $[Rh_2(CO)_2(\mu\text{-}L)(\mu\text{-}X)(\mu\text{-}dppm)_2]X$ ($L = CO$ or SO_2; $X = Br$ or I). $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ is prepared by heating *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$ under reflux in toluene. Excess of CO combines with the chloro- and bromo-monocarbonyl species to give $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}X)(\mu\text{-}dppm)_2]X$ ($X = Cl$ or Br), whereas SO_2 produces equimolar amounts of $[Rh_2X_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2]$ and $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}X)(\mu\text{-}dppm)_2]X$ [120]. (37) is found to have an unusually



(32) (33) (34) (35)



(36)



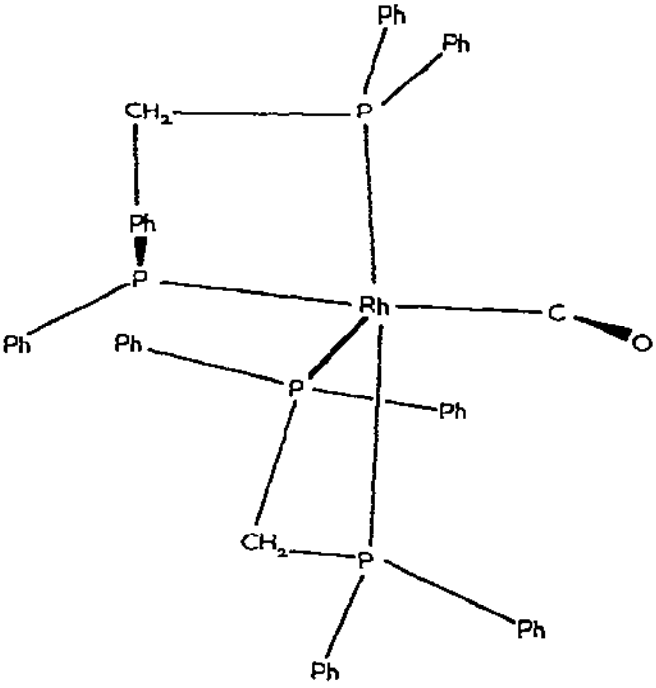
(37)

low carbonyl stretching frequency (1745 cm^{-1}), a low-field ^{13}C chemical shift (227.5 ppm), and a short rhodium-carbonyl distance. This information suggests a high degree of back-donation from the metals to the CO ligand [121].

Dioxygen combines with $[Rh(L-L)_2]^+$ (L-L = dppm, dppe or dppp) to yield *cis*-$[Rh(L-L)_2O_2]^+$ and the binding is reversible for dppe. Dihydrogen reacts with $[Rh(L-L)_2]^+$ to give *cis*-$[H_2Rh(L-L)]^+$ (L-L = dppp or diop). Addition of gaseous HCl to [Rh(L-L)Cl] (L-L = dppm, dppe or dppp) gives $[HRh(L-L)Cl_2]$ [122]. The new complexes $[Rh_2(\mu-Y)(CO)_2(\mu-dppm)_2]^{(2-n)+}$ are formed from the reaction of $[Rh_2Cl_2(CO)_2(\mu-dppm)_2]$ with $Y^{n-} = S^{2-}$, Se^{2-} or $PH(cych)^-$. The sulphide species has an "A-frame" structure and reacts with SO_2 to yield $[Rh_2(\mu-S)(\mu-SO_2)(CO)_2(\mu-dppm)_2]$ and with MeNC to give $[Rh_2(\mu-S)(CNMe)_2(\mu-dppm)_2]$ [123].

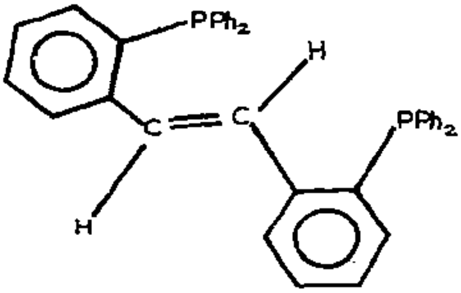
The reaction of CO with $[Rh(dppb)_2]^+$ gives the dimeric products $[Rh_2(dppb)_3(CO)_x]$

(x = 2, 3 or 4). The chemical and ^{31}P NMR properties of $[Rh(dppm)_2(CO)]^+$ and $[Rh(dppp)_2(CO)]^+$ and the crystal structure of $[Rh(dppm)_2(CO)][BF_4]$ (38) have been reported [124].



(38)

The complex, $[(bdpps)RhCl].CH_2Cl_2$, containing the tridentate chelating ligand bdpps, (39), has been prepared and its structure determined. The geometry of the



(39)

complex was found to be approximately square planar with the phosphorus groups occupying *trans* sites [48].

Rhodium complexes of $Ph_2PNHPPh_2$ (L–L) have been prepared (Scheme III) and characterised by IR, Raman and NMR spectroscopy [125].

$$\begin{tikzcd}{[Rh_2(C_2H_4)_4Cl_2]} \arrow[r, "L-L"] & {[Rh(L-L)_2]Cl} \arrow[r, "CS_2"] \arrow[d, "{[NH_4][PF_6]}"] & {[Rh(\eta^2-CS_2)(L-L)_2]Cl} \\ & {[Rh(L-L)_2][PF_6]} & \end{tikzcd}$$

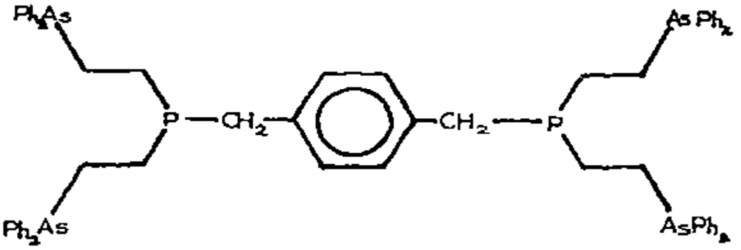
$$\underset{(X = Cl \text{ or } [PF_6])}{[Rh(L-L)_2]X} \xrightarrow{Q} \underset{(Q = CO,\ O_2 \text{ or } S_2)}{[RhQ(L-L)_2]X}$$

$$[RhQ(L-L)_2][PF_6] \xrightarrow{SO_2} [Rh(\eta^2-SO_4)(L-L)_2][PF_6]$$

$$[Rh(CO)(L-L)_2Cl] \xrightarrow{MeOH} [Rh_2Cl_2(\mu-CO)\{\mu-(L-L)\}_2]$$

SCHEME III: Preparative routes to $Ph_2PNHPPh_2$(L-L) complexes of rhodium(I).

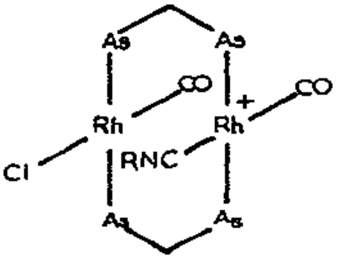
The ligand, tdadx (40) reacts with $[RhCl(CO)(PPh_3)_2]$ in benzene solution to give $[Rh_2Cl_2(tdadx)]$, which combines with dioxygen to form $[Rh_2Cl_2(tdadx)(O_2)_2]$ and with carbon monoxide to form $[Rh_2Cl_2(tdadx)(CO)_4]$. The ligand tddx



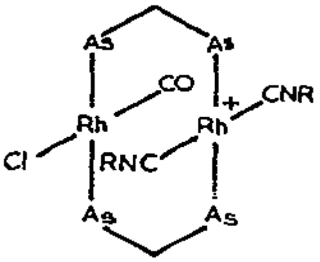
(40)

(phosphorus substituted for the arsenic atoms of tdadx) behaves similarly: $[Rh_2Cl_2(tddx)]$ giving $[Rh_2Cl_2(tddx)(O_2)_2]$ and $[Rh_2Cl_2(tddx)(CO)_4]$ with dioxygen and carbon monoxide, respectively [126].

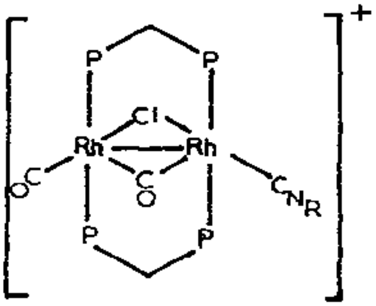
CMe_3NC (RNC) reacts with $[Rh_2(CO)_2Cl\{\mu-(L-L)\}_2]X$ (L-L = dppm or dpam; X = $[B(C_6H_5)_4]$ or $[PF_6]$) to give (41), (42), (43) or (44), depending upon the



(41)



(42)



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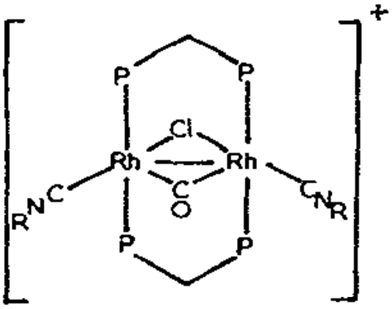
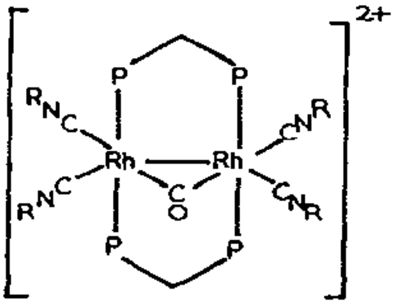
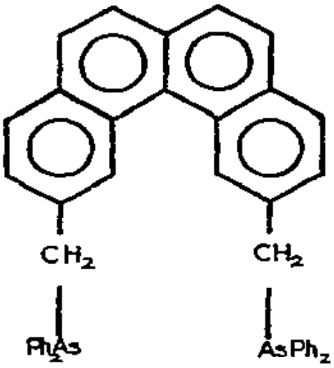




(44)

(45)

relative amounts of isonitrile used. The use of an excess of the isonitrile and $\mathrm{Na[BPh_4]}$ gives (45), which combines with CO or with $\mathrm{SO_2}$ to give $\mathrm{[Rh_2(\mu\text{-}L)(CMe_3NC)_4(L\text{-}L)_2][BPh_4]}$ (L = CO or $\mathrm{SO_2}$) [127]. The square-planar complex, *trans*-[RhCl(CO)(L'-L')] {L'-L' = (46)} has been prepared and characterised [128].

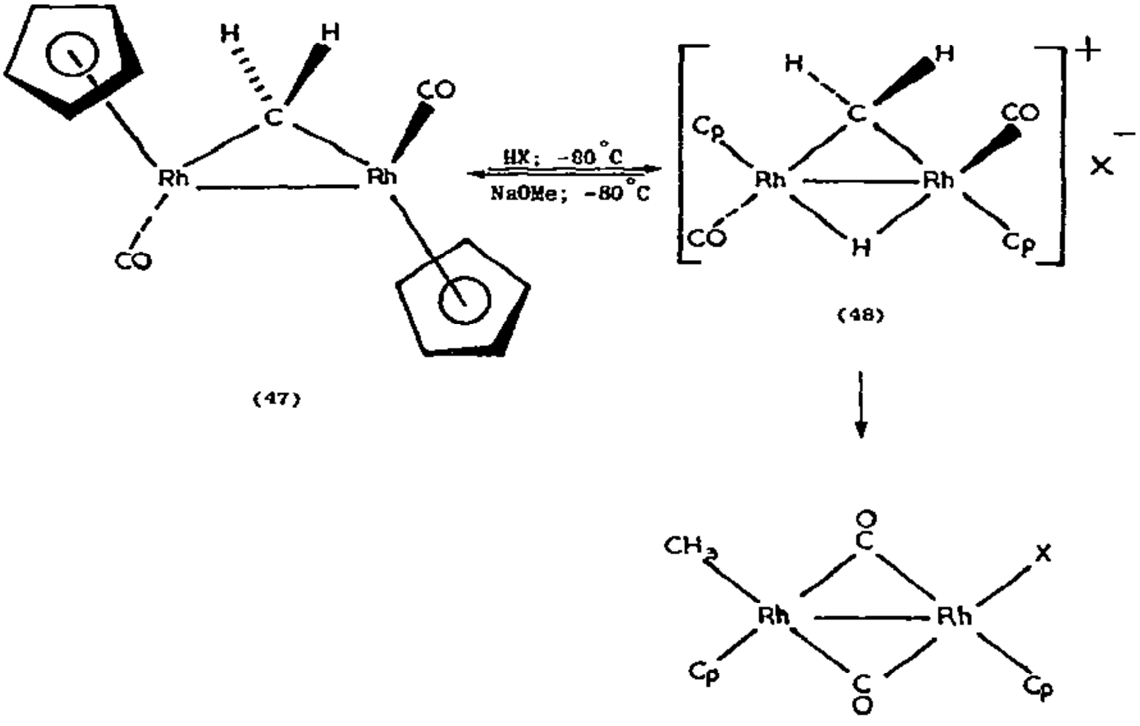


(46)

5.4.4 Complexes with Group IV donor ligands

5.4.4.1 Complexes with carbon donor ligands

The methylene-bridging complex (47) reacts with dry HCl or HBr to produce near quantitative amounts of the halo(methyl) complex (49) *via* (48) [129].



(47)

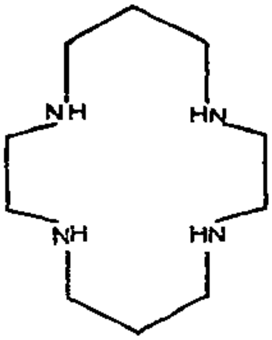
(48)

(49)

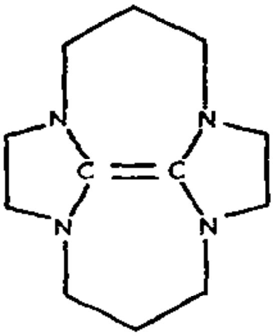
Reaction of the macrocyclic tetraamine (50) with $HC(OMe)_2NMe_2$ gives (51). Treatment of (51) with $[Rh_2Cl_2(cod)_2]$ gives (52) or (53) upon oxidation. Reaction between (52) and carbon monoxide gives the chelating dicarbene species (54) [130]. The IR and Raman spectra of $[Rh_2Cl_2(cod)_2]$ [131] and $[Rh_2Cl_2(nbd)_2]$ [132] have been recorded and an improved synthesis of $[Rh_2Cl_2(CO)_4]$ has been developed by passage of CO through saturated solutions of $[Rh_2Cl_2(cod)_2]$ or $[Rh_2Cl_2(nbd)_2]$ in *n*-hexane [133]. The He-I and He-II UVPES of $[Rh_2Cl_2(CO)_4]$ have been recorded [134].

^{103}Rh NMR chemical shifts for $[Rh(MeCN)_2(CO)_2][BF_4]$, $[Rh(acac)(CO)_2]$, $[NBu_4][RhCl_2(CO)_2]$, $[Rh_2Cl_2(CO)_4]$, $[NBu_4][RhBr_2(CO)_2]$ and $[Rh_2Br_2(CO)_4]$ have been measured by employing a double-resonance ^{13}C-^{103}Rh technique [135].

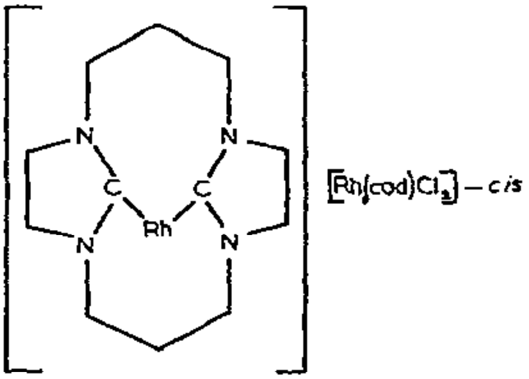
The complexes, *trans*-$[Rh(CO)X(L)_2]$ (X = F, Cl, Br, I, CN, SCN, SeCN, NO_2, NO_3 or ClO_4; L = $AsPh_3$ or $SbPh_3$) and their adducts with SO_2 and tcne were


NH
HN
NH
HN

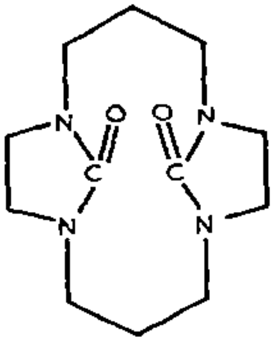
(50)


N
N
C
C
N
N

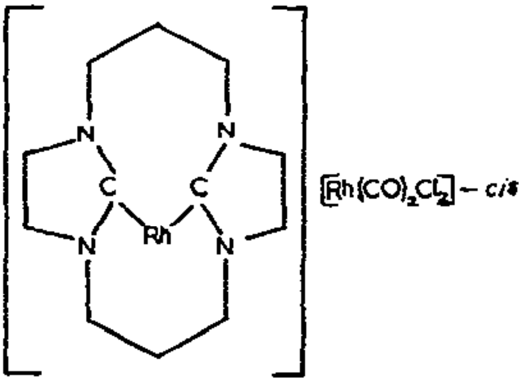
(51)


N
N
C
C
Rh
N
N
[Rh(cod)Cl2]− cis

(52)


N
O
O
N
C
C
N
N

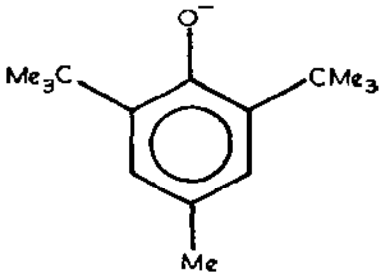
(53)


N
N
C
C
Rh
N
N
[Rh(CO)2Cl2]− cis

(54)

prepared and the ligand influence on the carbonyl stretching frequency was determined [136]. $[Rh(CO)Cl(SPPh_3)_2]$, $[Rh(CO)Cl(PPh_3)_2]$, $[Rh(CO)Cl(PPh_3)_2(SPPh_3)]$, $[Rh(CO)Cl(AsPh_3)_2(SAsPh_3)]$, $[Rh_2(CO)_2Cl_2(SAsPPh_3)_2]$, $[Rh(CO)(CS)Cl(PPh_3)_2]$ and $[Rh_2(COS)_2Cl_2(SbPh_3)_2]$ have been prepared by the reaction of one of a variety of rhodium compounds with carbonyl sulphide in the presence of PPh_3, $AsPh_3$ or $SbPh_3$. In most cases it can be seen that COS acts as a carbonylating agent, although some $SPPh_3$ and $SAsPh_3$ complexes (such as $[Rh_2Cl_2(SPPh_3)_4]$ and $[RhCl_3(AsPh_3)(SAsPh_3)]$) have also been produced [137]. $[Rh(CO)_2(R_2PCH_2)_3CR'][PF_6]$ ($R = Ph$; $R' = MeCH_2PR_2$) reacts with liquid ammonia at room temperature to give $[Rh(CO)(CONH_2)(R_2PCH_2)_3CR']$ which, at 100 °C in liquid ammonia, forms $[(\mu\text{-}CO)_2Rh(R_2PCH_2)_3CR']_2$. $[Rh(CO)(CONH_2)(R_2PCH_2)_3CR']$ reacts with MeOH to give $[Rh(CO)(CO_2Me)(R_2PCH_2)_3CR']$ [138]. The platinum compound $[(Ph_3P)(4\text{-tolylNC})Pt\{C(OMe){=}N\}(4\text{-tolyl})_2]$ (= L) acts as a bidentate ligand in the complex $[Rh(CO)_2ClL]$ [139].

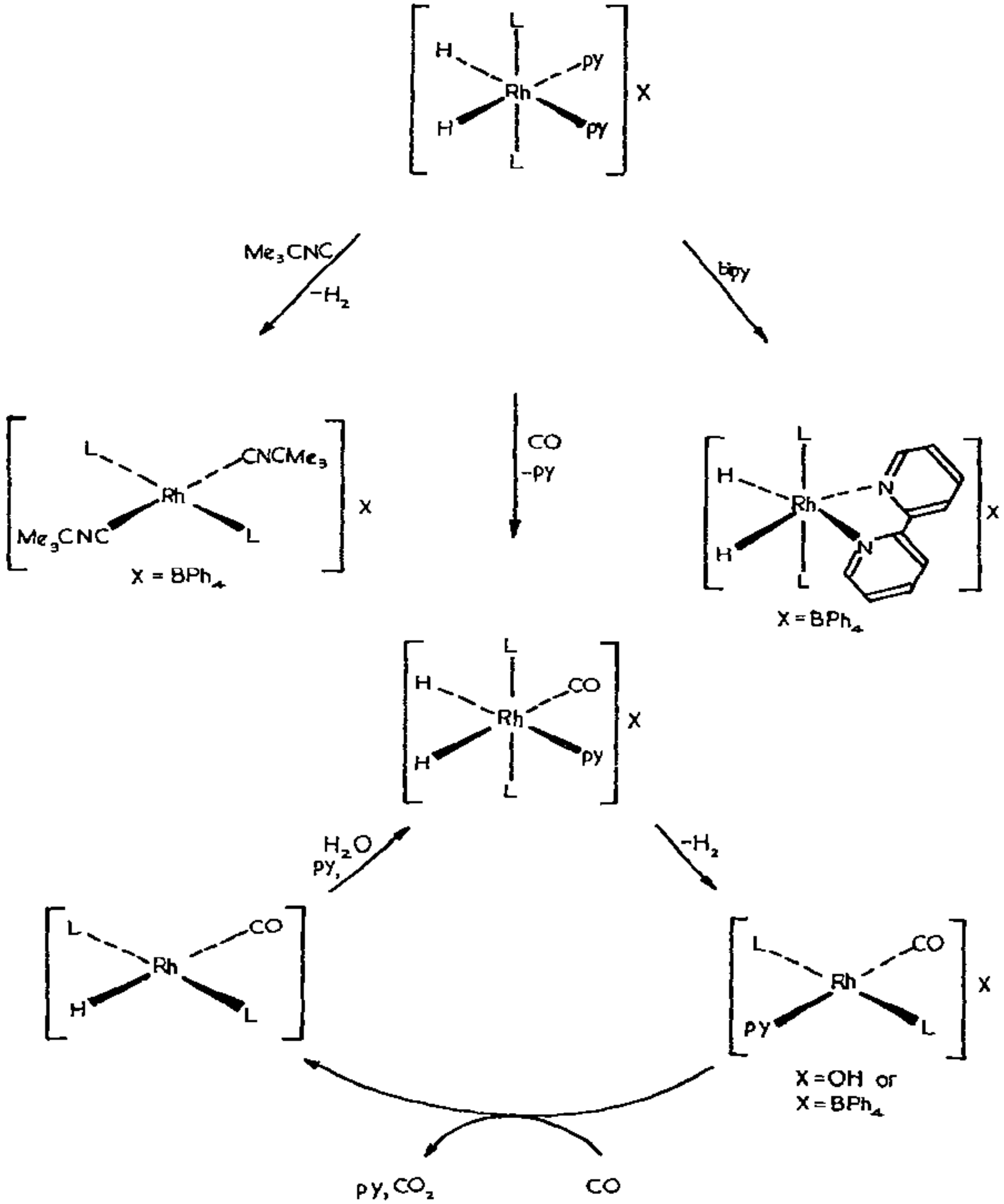
The crystal and molecular structure of the 18-electron, d^8 complex, $[Rh(ArO\text{-}\eta^5)(PPh_3)_2]$ has been determined; ArO = (55) and bonds to the metal in this molecule *via* the aromatic ring and not through the oxygen atom (as occurs in $[Ti(ArO)(cp)_2]$) [140]. The decomposition of $[Rh(CO)(PPh_3)(NO_3)]$ has been examined by thermogravimetry [141].


(55)

Mechanistic studies using spin-trapping species have been carried out on several rhodium(I)-alkyl halide oxidative additions [142]. The *closo*-hydridorhodacarborane, $3,3\text{-}(Et_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11}$, has been prepared *in situ* from the PPh_3 analogue and investigated by ^{11}B NMR spectroscopy [143].

5.4.4.2 Complexes with tin donor ligands

Ph_3SnX ($X = Cl$ or Br) adds oxidatively to $[Rh(Me_3CNC)_4][ClO_4]$ to give *cis*-$[Rh(Ph_3Sn)X(Me_3CNC)_4][ClO_4]$ [144]. The preparation and properties of the five coordinate complexes, $[Rh(SnCl_3)(diolefin)(L)_2]$ (diolefin = cod or nbd; $L = PPh_xEt_{3-x}$) and $[Rh(SnCl_3)(diolefin)(L\text{-}L)]$ (L-L = dppe, dppp, dppb, diop or a similar bidentate ligand have been described [145].



SCHEME IV: Decomposition of hydride complexes.

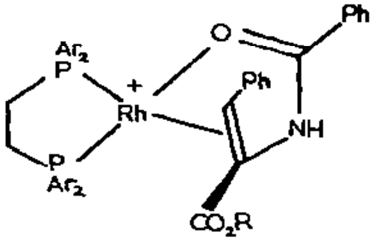
5.4.5 *Complexes with mercury donor ligands*

Reaction of $[Rh_2L_2Cl_2]$ (L = cp or nbd) with $Hg[R(NC)YNR']_2$ (Y = H; R = R' = $CHMe_2$; R = Me, $CHMe_2$ or 4-MeC_6H_4; R' = 4-MeC_6H_4 and Y = Me, R = R' = 4-MeC_6H_4) gives the complexes of general formula $[L\{R(NC)YNR'\}_2RhHgCl]$, which are monomers in solution and dimers in the solid state. The complexes contain a rhodium-mercury bond [146].

5.4.6 *Hydride complexes*

Protonation of the metal-metal bond in $[(\mu\text{-}CO)\{(Rh(cp)(CO)\}_2]$ with $[HBF_4].Et_2O$ gives $[(\mu\text{-}CO)(\mu\text{-}H)\{Rh(cp)(CO)_2\}][BF_4]$ in quantitative yield. Deprotonation of this complex is effected by [MeO]Na. Reaction of $[(\mu\text{-}CO)\{Rh(cp)(CO)\}_2]$ with $[HBF_4].H_2O$ in thf produces the complex $[Rh_3(cp)_3(CO)_3]$ which has molecular C_{3v} symmetry [147].

If the enamide complex (56) is prepared under a dihydrogen atmosphere at −78 °C and then allowed to warm slowly by 25 °C, the new species (57) is formed which has been characterised by ^{13}C and ^{31}P NMR spectroscopy (R = H or Me) [148]. Stoicheiometric dihydrogen evolution occurs as indicated in Scheme IV (L = $P(CHMe_2)_3$; X = $[BPh_4]$ or OH) [149].



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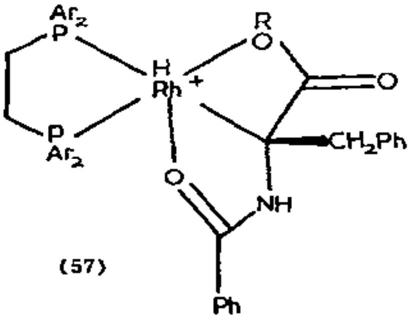
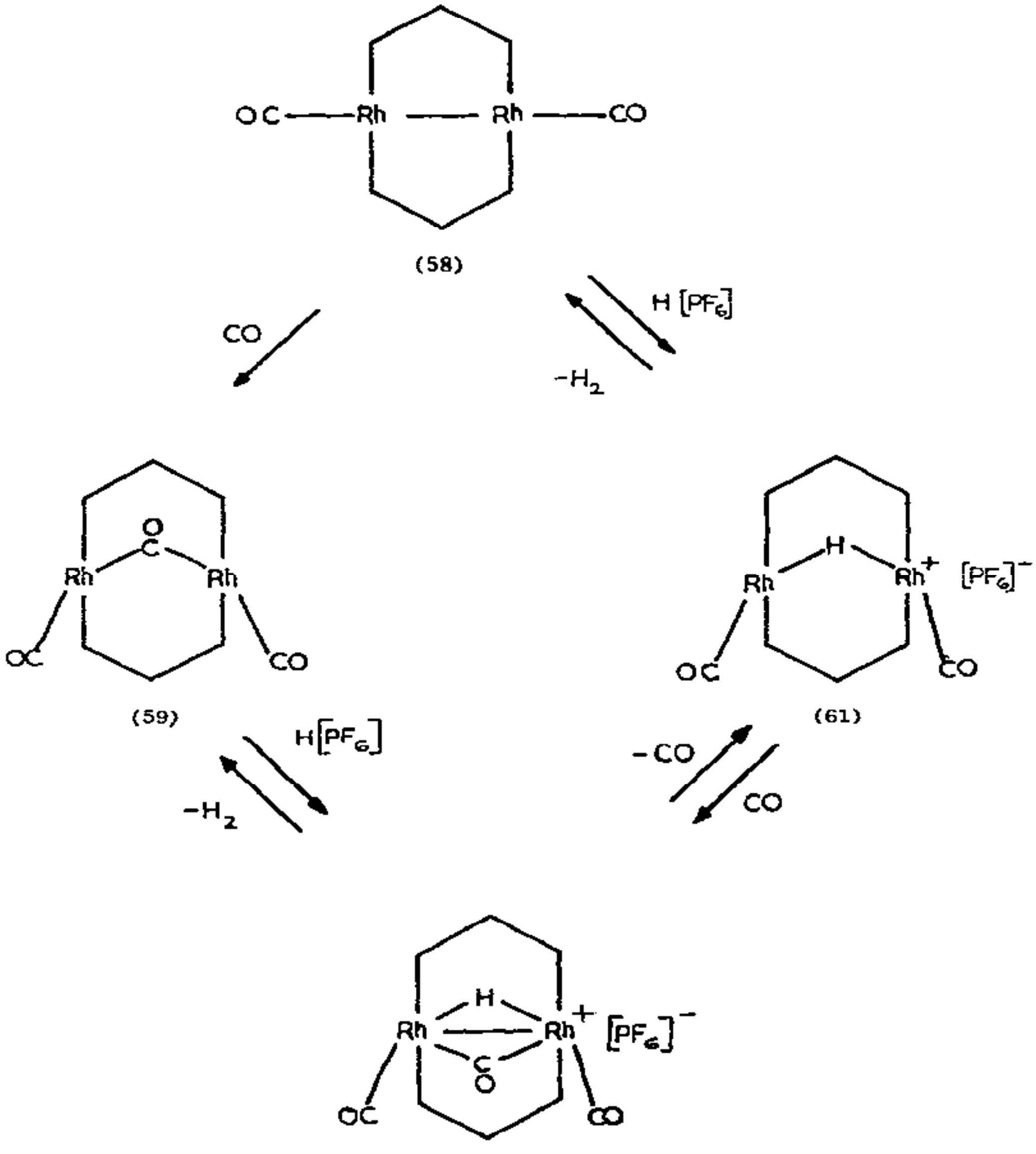


(57)

X-ray and neutron diffraction data have revealed definitive structures for $[H_2Rh_2\{P(OCHMe_2)_3\}_4]$ and $[H_3Rh_3\{P(OMe)_3\}_6]$ [150,151]; the latter is reported to consist of a triangle of rhodium atoms each bonded to two $P(OMe)_3$ groups and two bridging hydride ligands.

5.5 RHODIUM(0)

The rhodium(0) species, $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ (58) has been generated by reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$ with $Na[BH_4]$ and its IR spectrum was found to contain a single carbonyl stretching band at 1915 cm^{-1}. Some reactions of



(60)

this compound are illustrated by the formation of (59, 60 and 61). The structure of the cation contained in (60) has been determined by X-ray crystallography [123] and this compound is reported to be a strikingly active catalyst for the water gas-shift reaction ($CO + H_2O \longrightarrow CO_2 + H_2$). Also solutions of (58) in toluene are reported to catalyse the hydrogenation of ethyne to ethane. $[Rh(dppe)_2]$ activates bonds between hydrogen and a tetrahedral carbon atom by hydrogen atom-abstraction forming $[RhH(dppe)_2]$ [152].

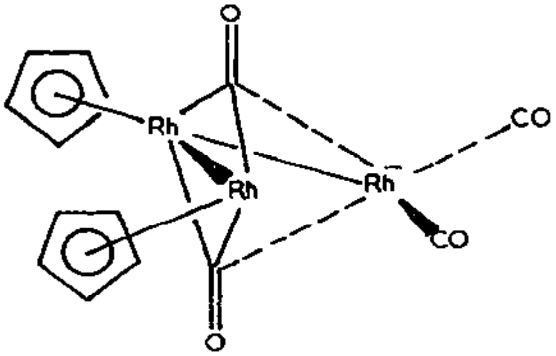
5.6 RHODIUM(-I)

The rhodium(-I) complex, $[Rh(CO)_4]^-$, has been examined by $^{13}C-^{103}Rh$ double resonance spectroscopy. The very high field shift obtained [$\delta(^{103}Rh) = -644$ ppm] is consistent with the rhodium in the anion having a low formal oxidation state [135].

5.7 RHODIUM CARBONYL CLUSTERS

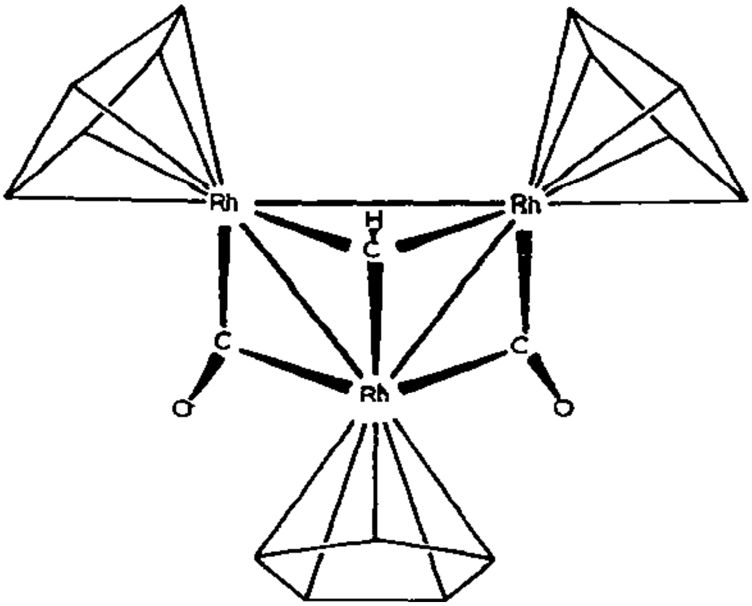
It is often envisaged that carbonyl metal clusters should possess potential catalytic properties that are intermediate between those of the mononuclear complexes and those of metal surfaces. It should be possible, therefore, to take advantage of the systems' metal-like qualities (such as multiple bonding of reactants through more than one metal centre) and its complex-like properties (such as modification of reactivity by choice of ligands). Although many of the reported examples of catalysis involving metal clusters are questionable, a few conclusive examples are known, one of the most important of which is the high-pressure conversion of synthesis gas into ethane-1,2-diol using $[Rh_{12}(CO)_{30}]^{2-}$ [153]. A few examples of catalysis using rhodium carbonyl clusters are discussed in Section 5.8 but most of the current work on these compounds is concerned with the elucidation of their structure and fluxional behaviour.

The mixed-metal cluster complex, $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}CO)(CO)_5(\eta^5\text{-}C_5H_5)(\eta^9\text{-}C_9H_7)]$, has been synthesised and its structure confirmed by X-ray diffraction methods [154]. $[RhFe_4C(CO)_{14}]^-$ contains a nearly-square pyramidal arrangement of metal atoms with the rhodium atom in the basal plane; a CO ligand bridges the rhodium and one of the basal iron atoms. The carbide carbon is displaced by 19 pm from the basal plane away from the iron atom that occupies the apical position [155]. The mixed-metal trimethylphosphite clusters,



(62)

$[Co_3Rh(CO)_{12-n}\{P(OMe)_3\}_n]$ and $[Co_2Rh_2(CO)_{12-n}\{P(OMe)_3\}_n]$ (n = 1-3) have been prepared [156]. Thermal decomposition of $[RhH(CO)(PPh_3)_3]$ in nonane at 120 °C gives the triangular cluster $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ [157]. The bonding in the trinuclear complex (62) has been examined [158] and the crystal structure of the cation alkylidyne-trirhodium cluster complex (63) has been determined [159].



(63)

Variable-temperature NMR studies of $[Rh_4(CO)_8\{P(OPh)_3\}_4]$ have shown that the same structure persists in solution as in the solid state at low temperature. At higher temperatures the CO ligands are found to exhibit fluxional behaviour [160]. The phosphide-bridged tetrarhodium cluster, $[Rh_4(CO)_5(\mu\text{-}PPh_2)_5]$, has been prepared and found to possess an *arachno* structure with PPh_2^- groups as the only bridging ligands [161].

The mixed-metal carbido carbonyl cluster, $[Cu_2Rh_6C(CO)_{15}(NCMe)_2].0.5MeOH$, prepared by the reaction of $K_2[Rh_6C(CO)_{15}].3thf$ with $[Cu(NCMe)_4][BF_4]$ in methanol solution, is composed of a prism of rhodium atoms that is capped on each triangular face with linear Cu(NCMe) portions, the carbonyl ligands having the same geometry as found in the parent anion. The idealised symmetry of the unsolvated molecule is D_{3h} and the Cu-Rh, Rh-Rh and Rh-carbide mean distances are 266, 278 and 213 pm, respectively [162]. $[Rh_6(CO)_{16}]$, supported on a zeolite, may be decarbonylated by dioxygen, or *in vacuo* at 100 °C, without appreciable loss of the cluster structure. These results suggest that zeolite is a suitable support to stabilise small clusters. By contrast, on alumina, $[Rh_6(CO)_{16}]$ is readily fragmented, the zerovalent rhodium being oxidised by O_2

and H_2O to give Rh(I) which, upon carbonylation, gives Rh(I) dicarbonyl complexes [163]. Similarly, IR spectroscopy has revealed that catalysts prepared by chemisorption of $[Rh_6(CO)_{16}]$ onto ligand-modified SiO_2 do not contain Rh_6 clusters but only mononuclear surface species, such as $L_nRh(CO)_2$ and $L_mRh(CO)$, where L represents surface-attached ligands such as $\text{-}(CH_2)_3NH(CH_2)_2NH_2$ and the values of n and m are unknown [164].

A ^{103}Rh NMR study of $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_{17}S_2(CO)_{32}]^{3-}$ provides evidence for charge separation and rhodium atom fluxionality in this class of molecules [165]. The species $[Rh_{12}(CO)_{\sim 34}]^{2-}$ has been reformulated as $[Rh_5(CO)_{15}]^-$ and can be prepared from $[Rh_4(CO)_{12}]$ and $[Rh(CO)_4]^-$:

$$[Rh_4(CO)_{12}] + [Rh(CO)_4]^- \xrightarrow{thf} [Rh_5(CO)_{15}]^- + CO$$

The metal atoms of the $[Rh_5(CO)_{15}]^-$ anion in the crystalline state form a trigonal-bipyramidal structure containing ten terminal CO ligands and five μ_2-bridging CO ligands. $[Rh_5(CO)_{10}(\mu_2\text{-}CO)_5]$ slowly decomposes in thf solutions under dinitrogen and gives the equilibrium [166]:

$$6[Rh_5(CO)_{15}]^- \underset{CO}{\overset{N_2}{\rightleftharpoons}} 2[Rh_{12}(CO)_{30}]^{2-} + [Rh_6(CO)_{15}]^{2-} + 15CO$$

The structure of $[Rh_{12}(CO)_{30}]^{2-}$ in solution, studied by ^{13}C and ^{103}Rh NMR spectroscopy, has been found to be consistent with that found in the solid state [167].

The X-ray crystal structures of $[Rh_{14}(\mu\text{-}CO)_{15}(CO)_{11}]^{2-}$ [168] and $[Rh_{14}H(\mu\text{-}CO)_{15}(CO)_{16}]^{3-}$ [169] have been determined and fluxional behaviour has been observed in the tetradeca-nuclear species, $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{14}(CO)_{25}H]^{3-}$ [170]. The synthesis and X-ray characterisation of the anion, $[Rh_{22}(\mu_3\text{-}CO)_7(\mu\text{-}CO)_{18}(CO)_{12}]^{4-}$, in the $[NEt_3Pr]^+$ salt has been reported [171].

5.8 RHODIUM NITROSYLS

The reaction of NOCl and PPh_3 with $RhCl_3.3H_2O$ gives $[Rh(NO)_2Cl(PPh_3)_2]$ which undergoes thermal decomposition to produce $[Rh(NO)Cl_2(PPh_3)_2]$. The corresponding reaction with $AsPh_3$ produces $[Rh_2(NO)_3Cl_5(AsPh_3)_4]$ and $[Rh(NO)Cl_2(AsPh_3)_2].CH_2Cl_2$ and the reaction of NOBr and L (L = $AsPh_3$ or PPh_3) with $RhCl_3.3H_2O$ gives $[Rh(NO)ClBrL_2]$ [172].

5.9 RHODIUM CATALYSTS

5.9.1 Synthesis Gas Chemistry

5.9.1.1 Carbon monoxide hydrogenation

CO hydrogenation is currently one of the most important aspects of catalytic research. Apart from the well-established hydrogenation of carbon monoxide to methanol and the continuing research on Fischer-Tropsch chemistry in which CO is converted to hydrocarbons, the selective hydrogenation of CO to ethane-1,2-diol, ethanol and vinyl acetate also have potential technological importance. The carbonyl complexes; $[Rh_4(CO)_{12}]$, $[Rh(CO)_2Cl]_2$, and $Na_2[Rh_{12}(CO)_{30}]$, in conjunction with aluminium and aluminium bromide, catalyse the reaction of CO with dihydrogen to give aliphatic hydrocarbons [173]. The catalytic activity for hydrogenation of CO to alcohols using $[Rh(CO)_2(acac)]$, $[Rh_6C(CO)_{15}]^{2-}$, $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_{17}S_2(CO)_{21}]^{3-}$ has been assessed. It is believed that the encapsulated heteroatoms enhance the catalytic effectiveness of the complexes. The high pressure infrared spectra of these complexes has been described [174].

An IR spectroscopic study of rhodium carbonyl complexes, involved in the synthesis of ethane-1,2-diol and derivatives, has been undertaken at high pressure and at temperatures below that required for optimum catalytic activity. Under these milder conditions, starting from $[Rh(CO)_2(acac)]$, the only detectable species appear to consist of the $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ anions [175].

5.9.1.2 Nitrobenzene reduction

Synthesis gas may be used as the reducing agent for the conversion of nitrobenzene to aniline, in the presence of $[Rh_6(CO)_{16}]$ as catalyst, according to the reaction $PhNO_2 + 2CO + H_2 \longrightarrow PhNH_2 + 2CO_2$ [176].

5.9.1.3 Carbonylation of aromatic nitro compounds

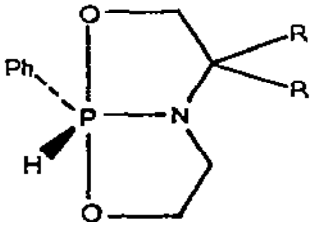
The conversion of aromatic nitro compounds into their corresponding isocyanates has been carried out traditionally by hydrogen reduction to the amine, followed by phosgenation of the amine to the isocyanate accompanied by the resulting loss of hydrogen chloride. A variety of rhodium catalysts have been found to catalyse the direct reductive carbonylation of aromatic nitro compounds, as $ArNO_2 + 3CO \longrightarrow ArNCO + 2CO_2$. $[RhH(CO)(PPh_3)_3]$ catalyses this reaction at 25 °C and 80 atmospheres pressure, in the presence of $MoCl_5$ as a co-catalyst. Selectivities were found to be in the range 92–100% and conversions of reactant (Ar = Ph, 2-, 3-, or 4-tolyl) were 15-100% [177]. The carbonylation of $PhNO_2$ to PhNCO has also been examined using $[Rh(CO)_2Cl]_2$ [178] and in the presence of py-HCl as a co-catalyst. $[pyH][Rh(CO)_2Cl_2]$ and $[(py)Rh(CO)_2Cl]$ were also examined in this system [179]. In the presence of $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$, nitroarenes, CO and C_6H_6 combine to give RC_6H_4NHBz (R = 4-OMe, 4-Cl, 4-Me, H, 4-NC, 4-C(OMe), $4\text{-}CO_2Me$, 3-Me or 2-Me), *via* the reductive carbonylation of nitroarenes and subsequent addition of C_6H_6 to the aryl isocyanate [180].

5.9.1.4 Decarbonylation of aldehydes

Rhodium(I) complexes containing chelating diphosphine ligands have been studied as catalysts for the decarbonylation of aldehydes. The catalytic activity is found to be a function of n, the number of CH_2 groups, in the ligand $Ph_2P(CH_2)_nPPh_2$, and to be a maximum for $n = 3$ [181].

5.9.1.5 Hydroformylation

Vapour-phase hydroformylation of ethene and propene has been found to proceed at 25-180 °C and atmospheric pressure over the metal oxide supported complexes $[Rh_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$, $[Rh_2Co_2(CO)_{12}]$ and $[RhCo_3(CO)_{12}]$ [182]. The hydroformylation of $CH_2{=}CMeCO_2Me$ has been studied in the presence of $[RhH(CO)(PPh_3)_3]$ and its polymer anchored analogue [183]. This catalyst, in the presence of chiral phosphines, has also been used to convert *N*-vinylsuccinimide and *N*-vinylphthalimide into optically active aminoaldehydes [184]. $[RhH(CO)(PPh_3)\{P(py)_3\}_2]$ acts as a selective catalyst for the hydroformylation of hex-1-ene to heptanal [105] and $[Rh(CO)_2(cp)]$, supported upon a highly cross-linked styrene-divinylbenzene copolymer, catalyses the hydroformylation of pent-1-ene to hexanal at 50 °C [185]. The complexes, [RhCl(CO)(L-L)], $[Rh(L\text{-}L)(CO)(MeCN)][PF_6]$, $[RhCl(C_2H_4)(L\text{-}L)]$ and $[Rh(L\text{-}L)_2Cl]$, containing the bidentate ligand L-L = (64), have been examined for their activity as alkene hydroformylation catalysts [186].

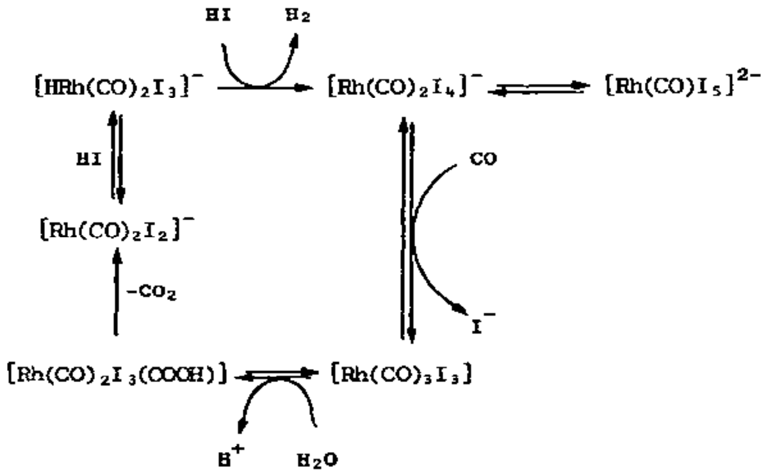


(64)

5.9.1.6 Water gas-shift reaction

A catalyst system based on rhodium carbonyl-iodide complexes is effective in the water gas-shift reaction ($H_2O + CO \longrightarrow H_2 + CO_2$) at low temperatures and pressures [187]. The proposed mechanisms are outlined in Scheme V.

The catalytic properties of the complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2][PF_6]$ have been mentioned briefly in Section 5.5.



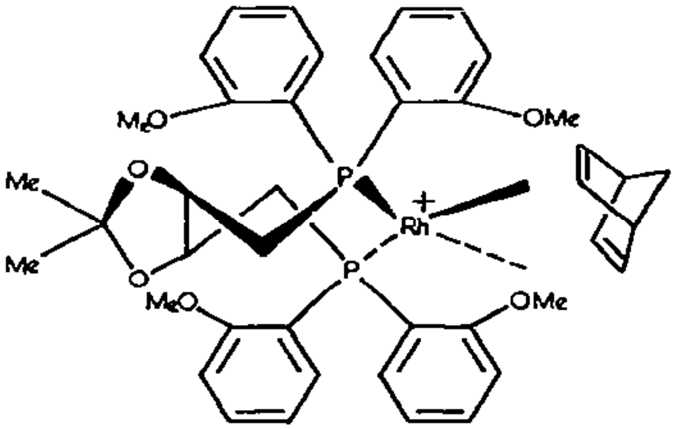
SCHEME V: Proposed mechanisms for the water gas-shift reaction using rhodium carbonyl iodide catalysts.

5.9.2 *Reactions of Alkenes*

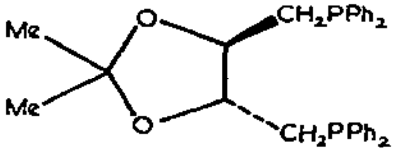
5.9.2.1 *Hydrogenation*

The compounds $[HRh\{P(OCHMe_2)_3\}_2]_2$, $[HRh\{P(OMe)_3\}_2]_3$, $[H_4Rh_2P(OCHMe_3)_4]$, and $[H_5Rh_3\{P(OMe)_3\}]$ [188], $[RhCl(CO)(L{-}L)]$, $[Rh(L{-}L)(CO)(MeCN)][PF_6]$, $[RhCl(C_2H_4)(L{-}L)]$ and $[Rh(L{-}L)_2Cl]$ (L–L = (64)) [186] and $[Rh_2Cl(CO)_2(\mu\text{-dppm})_2]^+$ [189] have been examined for catalytic activity in alkene hydrogenation. $[Rh(cp)(CO)_2]$, supported on a styrene-divinylbenzene copolymer, has been found to catalyse the hydrogenation of cyclohexane [185]. Attempts to hydrogenate alkenes using $[RhCl\{P(py)_3\}_2]$ and $[Rh(cod)\{P(py)_3\}_2][PF_6]$ were not successful [105]. $[Rh\{(2R,3R)\text{-}Ph_2PCHMeCHMePPh_2\}(nbd)][ClO_4]$ has been found to catalyse the asymmetric hydrogenation of $RCH{=}C(NHCOR')CO_2H$ (R = H, Ph, Me_2CH, $4\text{-}C_6H_4(OH)_2$, or $3,4\text{-}(MeO)(AcO)C_6H_3$, R' = Me; R = Ph, $3,4\text{-}(MeO)(OH)C_6H_3$, R' = Ph) to give $(S)\text{-}RCH_2CH(NHCOR')CO_2H$ [190]. The rhodium anisylphosphine complex (65) has been found to catalyse the asymmetric hydrogenation of enamides and $MeO_2CC({=}CH_2)CH_2CO_2Me$, with the production of different optical isomers as compared to those produced by using rhodium complexes of the phosphine ligand (66) [191]. The rhodium(I) complex (67) is said to be an excellent catalyst for the asymmetric hydrogenation of prochiral α-(acylamino) acrylic acids or esters [192].

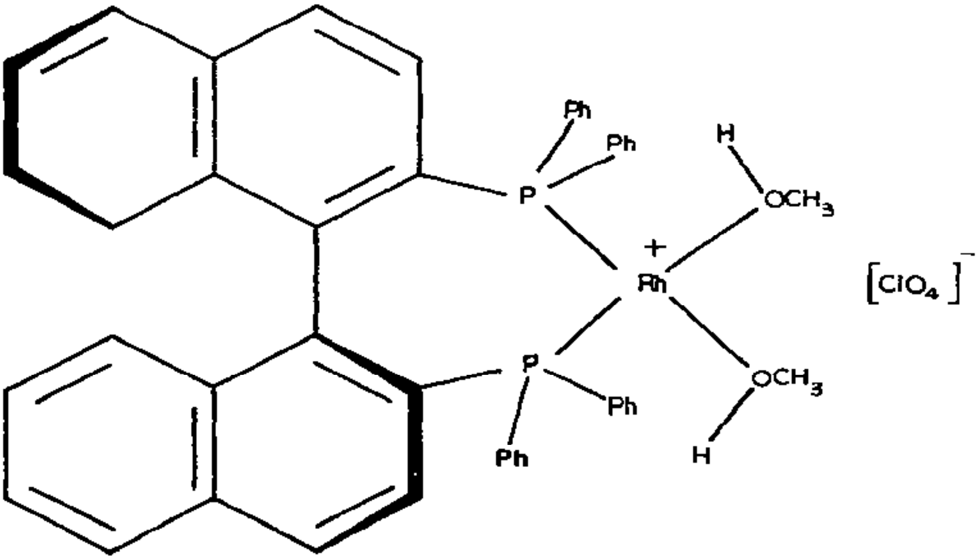
The mechanism of the asymmetric homogeneous hydrogenation of dehydroamino acids by cationic rhodium complexes containing chiral biphosphines related to dppe, has been examined by ^{31}P and ^{13}C NMR spectroscopy [193]. The hydridoalkyl rhodium(III) intermediate (68) has been detected during the homogeneous catalytic


MeO
OMe
MeO
OMe
Me
Me
O
O
P
P
Rh
+

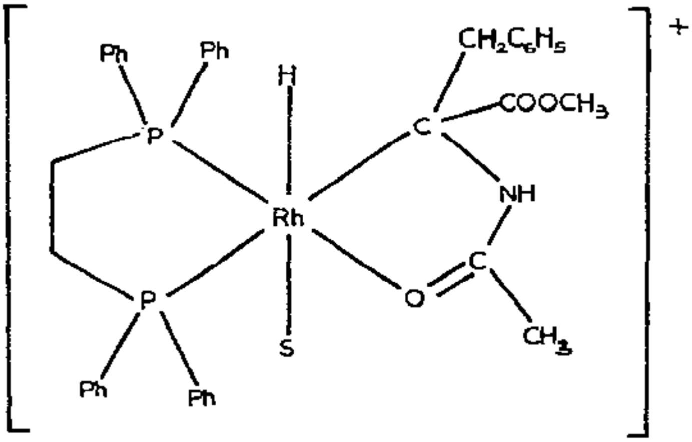
(65)


Me
Me
O
O
CH₂PPh₂
CH₂PPh₂

(66)


Ph
Ph
P
Rh
+
H
OCH₃
OCH₃
H
P
Ph
Ph
[ClO₄]⁻

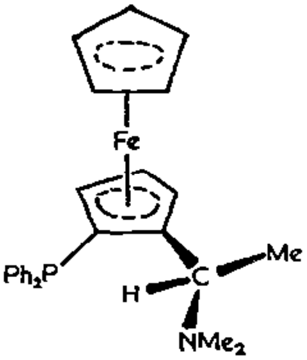
(67)



(68; S = MeOH or MeCN)

hydrogenation reaction of PhCH=C(NHCOMe)(COOMe) [194].

The complexes, [(cod)Rh(ppfa)]X (X = [ClO_4], [BF_4] or [BPh_4]), [(nbd)Rh(ppfa)][ClO_4] and [Rh(CO)Cl(ppfa)] (ppfa = (69)) have been found to



(69)

catalyse the asymmetric hydrogenation of PhCH=C(COOH)(NHCOR) and CH_2=C(COOH)(NHCOR). The X-ray structure of [(nbd)Rh(ppfa)][PF_6] has been determined and indicates that (69) is bidentately coordinated to rhodium through both the phosphorus and nitrogen atoms of the ligand [195].

Ab initio LCAO-MO-SCF calculations have been performed on the complexes; [$RhClL_2$], [H_2RhClL_3], [H_2RhClL_2], [$H_2RhClL_2(C_2H_4)$] and [$HRhClL_2(C_2H_5)$] (L = Ph_3), which are possible intermediates involved in the hydrogenation of alkenes catalysed by Wilkinson's catalyst [196]. [$Rh(py)_4Cl_2$]Cl with en or 1,3-pn were effective for the Na[BH_4] reduction of 1,3-cyclohexadiene, cyclohexene and

1-hexene [197].

5.9.2.2 *Isomerisation*

$[Rh(CO)_2Cl]_2$ is catalytically effective for the isomerisation of allyl alcohols to carbonyl compounds; for example, treatment of a solution of $CH_2{=}CHCH(OH)C_3H_7$ in dichloromethane at room temperature results in the formation of high yields of $C_2H_5COC_3H_7$ [198].

Complexes of the type $[RhClL_n]$, where L represents a tertiary phosphine ligand, were prepared *in situ* from $[RhCl(C_8H_{14})_2]_n$ and used to catalyse the hydroacylation of 4,5-unsaturated aldehydes to the corresponding cyclopentanones [199]. The mechanism involved in the $[RhCl(PPh_3)_3]$-catalysed cyclisation of 4-hexenal to 2-methylpentanone have been investigated by using deuterium labelling [200].

Rhodium(II) carboxylates (*e.g.* $[Rh_2(CH_3COO)_4]$) have been found to be efficient catalysts for the cyclopropanation of alkenes by diazo esters [201].

5.9.2.3 *Oligomerisation*

$[Rh(SnCl_3)_2Cl_4]^{3-}$, immobilised on an anion-exchange resin (AV-17-8) is found to be a highly active catalyst for the formation of *cis*- and *trans*-but-2-ene from ethene [202].

5.9.2.4 *Hydrosilylation*

The rhodium carborane complex, $(3,3\text{-}(PPh_3)_2\text{-}4\text{-}C_5H_5N\text{-}3,1,2\text{-}RhC_2B_9H_{10})$, in thf solutions, has been found to catalyse the hydrosilylation of styrene with $PhSiMe_2H$, to give $PhCHMeSiMe_2Ph$-$PhCH_2CH_2SiMe_2Ph$. Under similar conditions $PhC{\equiv}CH$ gives *cis*- and *trans*-$PhCH{=}CHSiMe_2Ph$ [203].

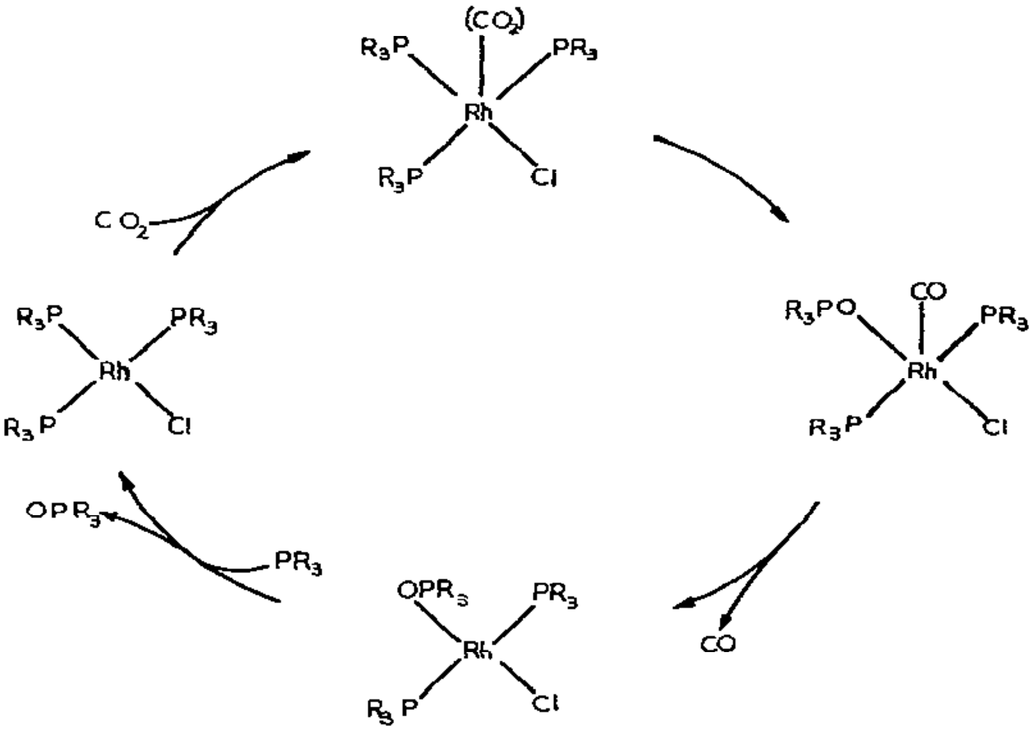
5.9.2.5 *Benzene-ethene coupling*

$[Rh_4(CO)_{12}]$, under carbon monoxide, catalyses the reaction $C_6H_6 + 3CH_2{=}CH_2 + CO \longrightarrow C_6H_5CH{=}CH_2 + CH_3CH_2COCH_2CH_3$ between ethene and benzene to produce styrene and pentan-3-one. The reaction was carried out at 220 °C for 7 hr. to give a yield of styrene (based on a rhodium atom) of 91.7%. $[Rh_6(CO)_{16}]$ showed a similar degree of catalytic activity in this reaction but $[Rh_2(CO)_4Cl_2]$ showed lesser activity [204].

5.9.3 *Oxidation*

$[RhCl(PPh_3)_3]$ and $[Rh_2Cl_2(cyclooctene)_4]$ have been found to catalyse the oxidation of phosphines by CO_2 according to Scheme VI (R = Ph, $BuPh_2$ or Et) [205].

The molecular dioxygen complexes $[RhO_2L_4][A]$ (L = $AsPh_3$ or $AsPhMe_2$; A = ClO_4 or PF_6) oxidise terminal alkenes to the corresponding methylalkyl ketone



SCHEME VI: Catalytic oxidation of phosphines.

under air-free conditions. ^{18}O-labelling experiments indicate that the ketonic oxygen is derived from the complexes. Reaction of O_2 with [Rh(1,7-octadiene)$_2$][A] gives 1-octen-7-one catalytically [206]. The yield of carboxylic acid produced by the [$Rh_6(CO)_{16}$]-catalysed oxidation of cyclohexanone with dioxygen is found to increase with increasing partial pressure of CO [207]. Apart from being an effective catalyst for converting ketones to the corresponding acids, [$Rh_6(CO)_{16}$] can catalyse the oxidation of cyclic alcohols to carboxylic acids using dioxygen: thus, cyclohexanol was oxidised to hexanedioic acid *via* cyclohexanone [208].

5.9.4 Reactions of aldehyde and ketones

The half-sandwich complexes, [$Rh_2(\eta^5$-$C_5Me_5)_2(OH)_3$]Cl and [$Rh_2(\eta^5$-$C_5Me_5)_2Cl_4$] are found to catalyse the disproportionation of ethanol into ethanoic acid and ethanol, according to $2CH_3CHO + H_2O \longrightarrow CH_3CH_2OH + CH_3COOH$. Other aldehydes are found to behave in a similar way [209].

Reaction of benzothiazole (C_7H_5SN) with [Rh_2(cod)$_2Cl_2$] and [$Rh_2(C_2H_4)_2Cl_2$] gives [Rh_2(cod)$_2(C_7H_5SN)_2Cl_2$] and [$Rh_2(C_7H_5SN)_2Cl_2$], respectively. The former complex was found to catalyse the hydrogenation of Me_2CO to Me_2CHOH and the latter complex was found to promote the dimerisation of Me_2CO to diacetone alcohol and mesityl oxide, $Me_2C{=}CHCOMe$ [210].

5.9.5 Reactions of nitrogen-containing compounds

Various rhodium(I) complexes; $RhCl_3.3H_2O$, [$RhCl(PPh_3)_2]_2$,[$RhCl(C_2H_4)_2]_2$, [RhCl(cod)]$_2$, [$RhCl(PPh_3)_3$], [RhCl(cod)(PPh_3)] or [$RhCl(CO)(PPh_3)_2$], have been found to catalyse the reaction of amines with anthraquinone to give the 1-alkylaminoanthraquinones and small amounts of the 1,4-alkylamino-derivatives [211]. Catalytic amounts of $RhCl_3.3H_2O$ are reported to accelerate the reaction between certain amines and esters (for example, $BuNH_2 + EtCO_2R \longrightarrow BuNHCOEt + ROH$) [212]. The reductive amination of cyclohexanone has been examined over H[Rh(dmg)$_2Cl_2$] in the presence of Na[BH_4] [213]. [$RhCl(PPh_3)$] was found to catalyse the reduction of azobenzene by Me_2CHOH to give aniline [214].

5.9.6 Hydride transfer

[$RhCl(PPh_3)_3$] has been found to catalyse hydrogen transfer from Me_2CHOH to PhNHNHPh to give Me_2CO and $PhNH_2$ [215].

5.9.7 Photocatalytic dihydrogen production

Under the influence of UV radiation at room temperature, [$RhCl(PPh_3)_3$] has been employed as a catalyst for hydrogen production from methanol and water as, $CH_3OH + H_2O \xrightarrow{h\nu,\ catalyst} CO_2 + 3H_2$ [216].

5.9.8 Reactions of silicon hydrides with silanols

Solutions of the rhodium(I) complexes; [$RhCl(PPh_3)_3$], [$RhH(CO)(PPh_3)_3$] and [$RhCl(CO)(PPh_3)_2$], and their silica-supported analogues have been found to be very effective and selective catalysts for the reaction of simple silanes with organosilanols:

e.g. $$R^1_3SiOH + R_2SiH_2 \longrightarrow R_2HSiOSiR^1_3 + H_2$$

(R^1_3 = Et_3, Me_2Ph, Pr_3 or Ph_3; R_2 = Et_2, Pr_2, Ph_2 or MePh)

and for the reaction of oligomeric hydridosiloxanes with organosiloxanediols [217]:

e.g. $$\mathrm{HO[Me_2SiO]}_n\mathrm{H} + \mathrm{H_2SiR_2} \longrightarrow \mathrm{HO[Me_2SiO]}_n\mathrm{SiR_2H} \xrightarrow{-\mathrm{H_2}} \mathrm{[Me_2SiO]}_n\mathrm{[R_2SiO]}$$

(R_2 = Et_2, Pr_2 or MePh; n = 2, 3 or 4)

IRIDIUM

5.10 IRIDIUM(IV)

5.10.1 Halide complexes

$[NO]_2[IrF_6]$ has been prepared from the action of nitrosyl fluoride and fluorine on metallic iridium [1]. This complex was characterised by Raman spectroscopy, and the resonance Raman spectrum of $[NBu_4]_2[IrCl_6]$ has also been measured [218]. The kinetics of the oxidation of hydrazine by $[IrCl_6]^{2-}$, $[IrCl_5(H_2O)]^-$, $[IrCl_4(H_2O)_2]$ and $[IrBr_6]^{2-}$ have been examined in acidic aqueous perchlorate solution [219] and the reduction of $[IrX_6]^{2-}$ (X = Cl or Br) by 2-thiopyrimidine and 2-thiouracil has also been investigated [220]. The kinetics of reactions $6[IrCl_6]^{2-} + 4H_2O + [SCN]^- \longrightarrow 6[IrCl_6]^{3-} + [SO_4]^{2-} + [CN]^- + 8H^+$ and $2[IrBr_6]^{2-} + 2I^- \longrightarrow 2[IrBr_6]^{3-} + I_2$ have been evaluated for aqueous solution [221].

5.10.2 Complexes with Group VI donor ligands

A detailed account of the syntheses and some properties of the salts $[M_2[Ir(NO_3)_6]$ (M = K, Rb or Cs) has been reported; these complexes were prepared by the reaction of the corresponding $[IrBr_6]^{2-}$ compounds with N_2O_5 [222]. $Ba[Ir(OH)_6]$ has also been prepared [223].

The iridium(III) anions, $[Ir(L)Cl_4]^-$ (L = $RS(CH_2)_n SR$, RSCH=CHSR or $1,2\text{-}C_6H_4(SR)_2$; R = Me or Ph; n = 2 or 3), *cis*- and *trans*-$[Ir(SMe_2)_2Cl_4]^-$, $[Ir(SPh_2)_2Cl_4]^-$ and $[Ir(SPh_2)Cl_5]^{2-}$ are oxidised by chlorine to the corresponding iridium(IV) complexes. The isolated compounds were characterised by IR, UV-VIS and ^1H NMR spectroscopy. The magnetic moments of the solids were around the spin-only value of 1.7 μ_B, consistent with the presence of low-spin d^5 iridium(IV) [224].

5.11 IRIDIUM(III)

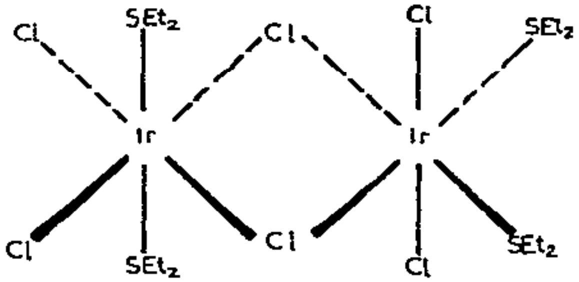
5.11.1 Complexes with Group VI donor ligands

5.11.1.1 Complexes with oxygen donor ligands

Octahedral complexes of the type $[IrL_3X_3]$ (X = Cl, Br or I; L = (**3**)) have been prepared and characterised. Ligand-field parameters have been assigned on the basis of the solid-state electronic spectra, and the far IR spectra of the complexes are consistent with *mer*-geometry [17].

5.11.1.2 Sulphide complexes

The structures of the diethyl sulphide complexes (70) [225] and (71) [226]



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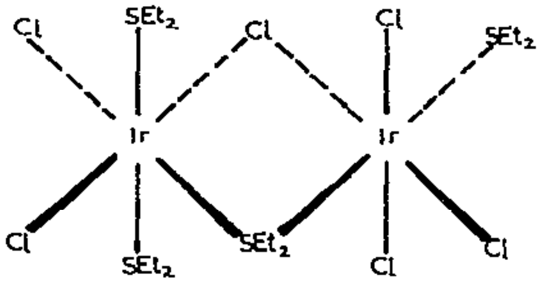


(71)

have been determined and the photolysis of *mer*-$[IrCl_3(SEt_2)_3]$ in benzene or toluene solution gives rise to a mixture of $[Ir_2(\mu\text{-}Cl)_2Cl_4(Et_2S)_4]$ and $[Ir_2Cl_5(\mu\text{-}Cl)(\mu\text{-}Et_2S)(Et_2S)_3]$ [227].

5.11.2 Complexes with nitrogen donor ligands

5.11.2.1 Ammine, amine, diimine and isonitrile complexes

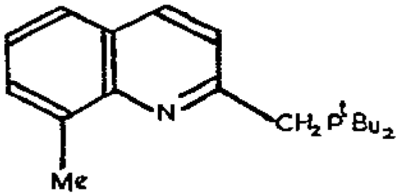
The photochemical properties of $[Ir(NH_3)_5X]^{2+}$ ($X = Cl^-$, Br^- or I^-), $[Ir(NH_3)_5L]^{3+}$ ($L = NH_3$, H_2O, MeCN or PhCN), *trans*-$[Ir(NH_3)_4I_2]^+$ and *trans*-$[Ir(NH_3)_4(H_2O)I]^{2+}$ have been investigated in aqueous solution [228], as has the photochemistry of *cis*- and *trans*-$[Ir(en)_2XY]^+$ ($X = Y = Cl^-$, Br^- or I^-; $X = OH^-$, $Y = Cl^-$ [229]. The solvent dependence of the rate of chloride substitution, by H_2O, MeOH, dmf or MeCN, has been determined for the excited states of $[IrCl_2(bipy)_2]^+$ [230] and *cis*-$[IrCl_2(phen)_2]Cl$ by sub-picosecond laser spectroscopy [36].

$[Ir(H_3ATP)(H_2O)_4]Cl_2$ has been prepared. Bonding of the metal to the purine ring of the ATP molecule is through the N(7) atom (14) [72].

Complexes containing the ligand LH = $HB(3,5\text{-}Me_2pzl)_3$ have been prepared; $[LIrCl_2AsPh(Me)_2]$, $[LIrCl(acac)]$ and $[LIr(CF_3CO_2)_2(H_2O)]$ are formed from the reaction of $[LIrCl_2]_2$ with $AsPhMe_2$, acac and AgO_2CCF_3, respectively [41].

5.11.2.2 Complexes with nitrogen-phosphorus donor ligands

A mixture of $[Ir_2Cl_2(C_8H_{14})_4]$ (C_8H_{14} = cyclooctene), mqpH (72), and pyridine-d_5 in hexane produces the complex $[IrClH(mqp)(NC_5D_5)_2]$. Although the metal-hydride

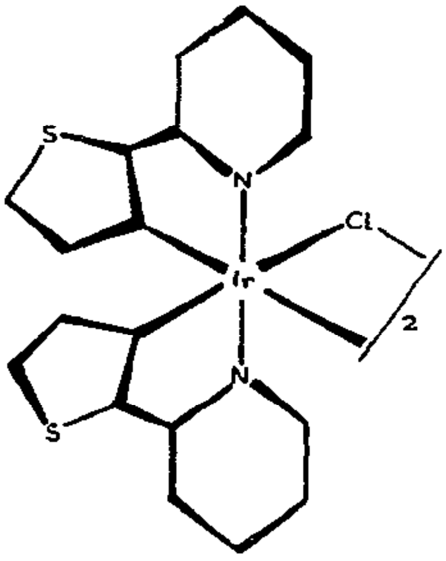


(72)

stretch can be easily identified in the IR spectrum at 2180 cm^{-1} and the NMR spectrum indicates that the pyridine ligands are mutually *cis*, it is not clear to which of the remaining possible six-coordinate isomers the structure belongs [104].

5.11.2.3 Complexes with nitrogen-carbon donor ligands

2-(2-thienyl)pyridine (2-thpyH) reacts with hydrated $IrCl_3$ to give the orange complex $[IrCl(2\text{-thpy})_2]_2$ (73). This material combines readily with L (L = PBu_3, py or dmso) to give $[IrCl(L)(2\text{-thpy})_2]$. The spectroscopic properties of these complexes are consistent with structure (74) [231]. The bromide and iodide analogues of $[IrCl(PBu_3)(2\text{-thpy})_2]$ were prepared by halide exchange reactions.



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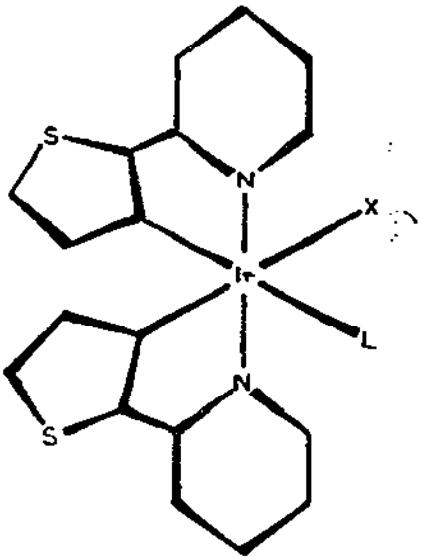
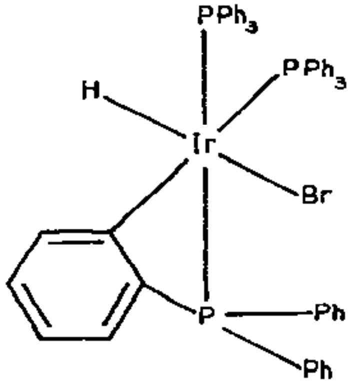


(74; L = PBu_3, py or dmso)

5.11.3 Complexes with phosphorus donor ligands

5.11.3.1 Phosphine and diphosphine complexes

$[Ir(cod)Cl]_2$ reacts with PMe_2Ph in MeCN to give the red species $[Ir(PMe_2Ph)_4]^+$, which will react with dihydrogen to give *cis*-$[IrH_2(PMe_2Ph)_4]^+$. In the absence of dihydrogen and after prolonged heating under reflux, the cyclometallated complex, *fac*-$[IrH(PMe_2C_6H_4)(PMe_2Ph)]^+$ is produced [232]. The complex (75) has a distorted octahedral coordination geometry about the central iridium atom [233].

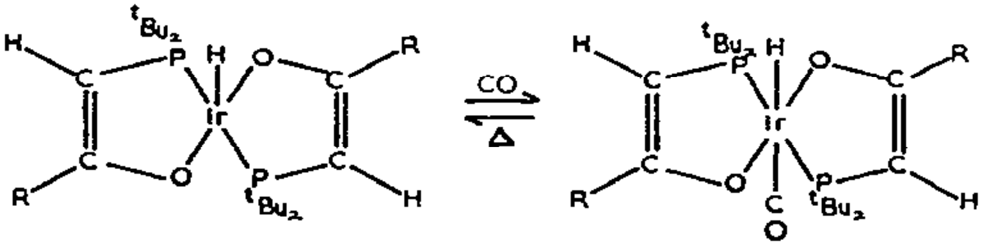


(75)

The mixed-metal complex $[(Ph_3P)_2Pt(\mu\text{-}Cl)_2Ir(PMe_2Ph)Cl_2]^+$ $[IrCl_4(PMe_2Ph)_2]^-$ has been synthesised [234]. $[(bdpps)Cl_3Ir]$ (bdpps = (39)) has a similar structure to its rhodium analogue [48].

5.11.3.2 Complexes with phosphorus-oxygen donor ligands

The reaction between iridium(III) chloride and $(CMe_3)_2(CH_2COR)$ (R = Ph or CMe_3) gives $[IrCl_2\{(CMe_3)_2PCH{=}C(O)R\}\{P(CMe_3)(CH_2COR)\}]$. These complexes react with sodium ethoxide to produce purple, five coordinate hydrides, possessing the square-pyramidal geometry (76), which take up carbon monoxide reversibly to give colourless hydridocarbonyls (77) [51]. Carbonylation of $Na_2[IrCl_6]$,



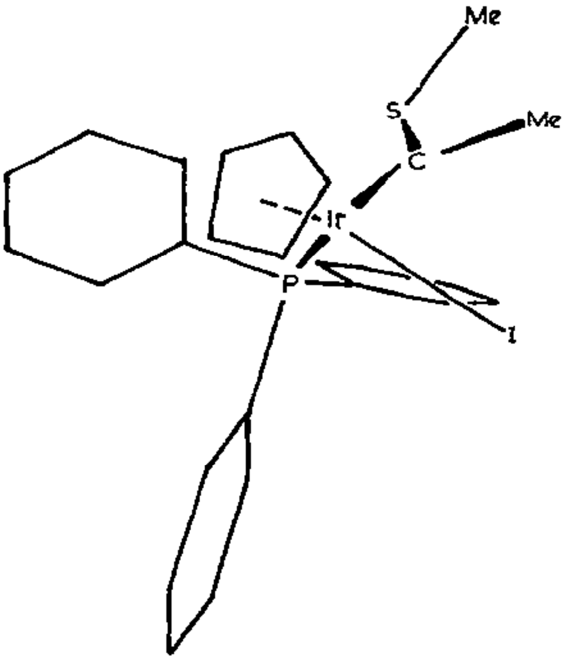
(76) (77)

followed by addition of $(CMe_3)_2(CH_2COPh)$ gives $[IrH(Cl)(CO)\{(CMe_3)_2PCH{=}C(O)Ph\}\{P(CMe_3)_2(CH_2COPh)\}]$, in which one of the keto groups is uncoordinated. Addition of sodium methoxide gives a mixture of (77) (R = Ph) and *trans*-$[IrCl(CO)\{P(CMe_3)_2(CH_2COPh)\}_2]$. Similarly, addition of $P(CMe_3)_2(CH_2COCMe_3)$ to a carbonylated solution of $[IrCl_6]^{2-}$ yields the six-coordinate compound $[IrHCl_2(CO)\{P(CMe_3)_2CH_2COCMe_3\}_2]$, containing monodentate phosphine ligands [51].

5.11.6 Complexes with Group IV donor ligands

5.11.6.1 Complexes with carbon donor ligands

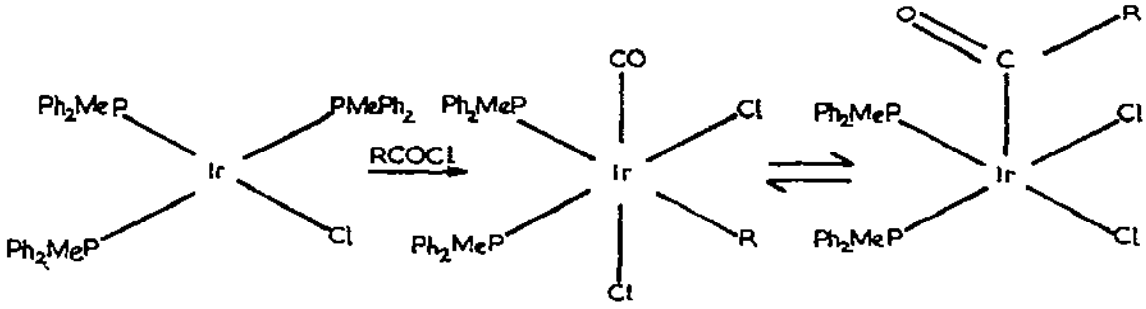
$[IrI\{C(Me)SMe\}(PPh_3)(cp)]$ (78) has an approximately tetrahedral geometry and



(78)

contains the methyl(methylthio)carbene ligand. The bonding of the C(Me)SMe group indicates that the complex should be formulated as a $C(Me){=}SMe$ complex of iridium(III) [235].

Reaction between paraformaldehyde, $(CH_2O)_n$, and $[Ir(PMe_3)_4][PF_6]$ in thf at room temperature produces the new cationic formyl complex, $[IrH(CHO)(PMe_3)_4][PF_6]$. Similarly, $[IrClH(CHO)(PMe_3)_3]$ and $[IrH(Me)(CHO)(PMe_3)_3]$ can be prepared from paraformaldehyde solutions in thf with $[IrCl(C_8H_{14})(PMe_3)_3]$ and $[Ir(Me)(PMe_3)_4]$, respectively. The formyl grouping in the $[IrH(CHOO)(PMe_3)_4]$ cation may be reduced to methyl with, for example, borane [236]. RCOCl (R = Me, Et or Pr) reacts with $[IrCl(PMePh_2)_3]$ (79) (or $[Ir_2Cl_2(C_8H_{14})_4]$ + $PMePh_2$) to produce six-



(79) (80) (81)

coordinate alkyliridium complexes, *cis*-[$IrCl_2R(CO)(PMePh_2)_2$] (80). Solutions of these complexes equilibriate rapidly with the five-coordinate species (81). Species (80) is reported to isomerise at room temperature into the *trans*-isomer (with respect to the phosphine ligands) [237].

The carbon dioxide complex [$Ir(dmpe)_2Cl(CO_2)$] reacts with $MeFSO_3$ to give the methoxycarbonyl species, [$IrCl(CO_2Me)(dmpe)_2$][FSO_3]; its structure has been confirmed crystallographically [238]. The single crystal absorption spectrum of [$Co(NH_3)_6$][$Ir(CN)_6$] has been examined [239].

5.11.4.2 Carborane complexes

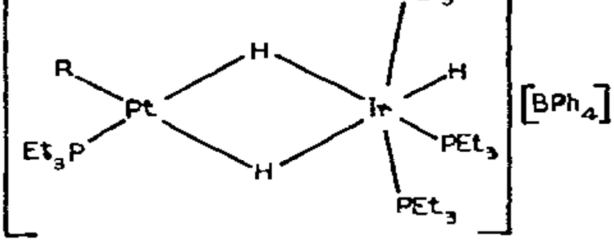
Several eighteen-electron, iridium(III)-carborane complexes have been produced [240] and carborane complexes containing the $C_2B_9H_{10}$- and $C_2B_9H_{11}$-anions are discussed in Section 5.15.2.

5.11.4.3 Complexes with tin donor ligands

On addition of [Me_4N]Br, K_2[$IrBr_6$] reacts with $SnBr_2$ in aqueous solutions containing HBr to give [Me_4N]$_3$[$IrBr_4(SnBr_3)_2$].[Me_4N]$_3$[$IrBr(SnBr_3)_5$] is reported to hydrolyse to give H_3[$Ir\{Sn(OH)_3\}_5Br$].HBr [241].

5.11.5 Hydride complexes

Reaction of *trans*-[$PtR(MeOH)(PEt_3)_2$]$^+$ (R = Ph, H) with [$IrH_5(PEt_3)_2$], followed by addition of Na[BH_4] gives the dihydrido-bridged complexes (82) and



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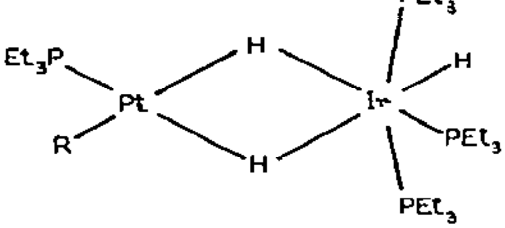


(83)

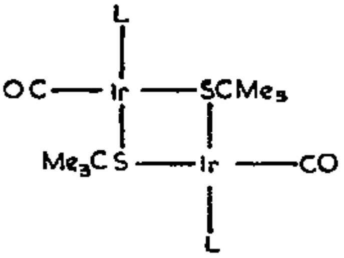
(83) which were characterised by NMR spectroscopy [242]. X-ray and molecular structures of $[Ir_2H_5(dppp)][BF_4]$ and $[Ir_3H_7(dppp)][BF_4]_2$ have been reported, along with their dynamic NMR properties [243].

5.12 IRIDIUM(II)

5.12.1 *Halide complexes*

The electron irradiation of $[IrCl_6]^{3-}$ in a NaCl matrix produces a paramagnetic species assignable to $[IrCl_6]^{4-}$, on the basis of EPR measurements [249].

Oxidative addition of I_2 to (84) (where L = CO, $P(OMe)_3$, PMe_2Ph or PMe_3)



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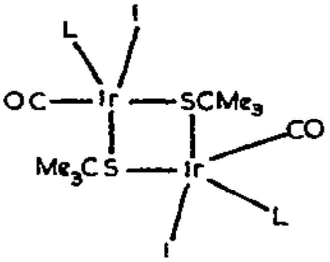


(85)

gives (85) [245].

5.12.2 *Alkyl thiol complexes*

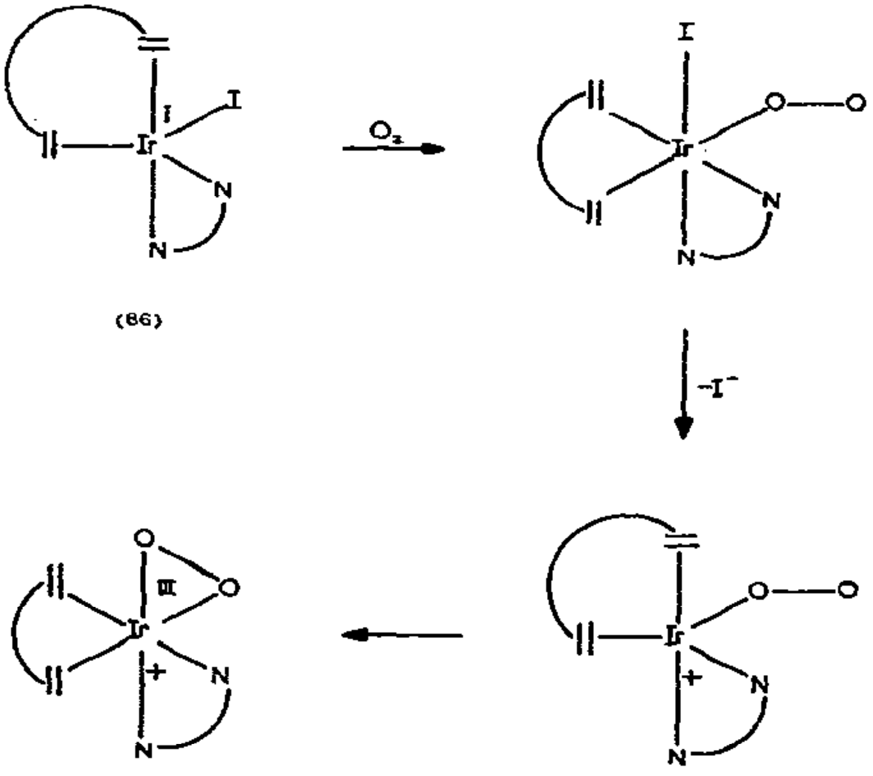
$[Ir(\mu\text{-}SCMe_3)(CO)_2]_2$ combines with hexafluorobut-2-yne to give $[Ir_3(\mu\text{-}SCMe_3)_3(CO)_6(\mu\text{-}C_4F_6)]$. In this complex two of the iridium atoms are considered to be in the +II oxidation state and the remaining iridium atom in the +I state. Dimethylacetylene dicarboxylate reacts similarly to give $[Ir_3(\mu\text{-}SCMe_3)_3(\mu\text{-}C_2(CO_2Me)_2(CO)_6)]$. However, $[Ir(\mu\text{-}SCMe_3)_2(CO)\{P(OMe)_3\}_3]_2$ reacts with hexafluorobut-2-yne to produce the dinuclear $[Ir_2(\mu\text{-}SCMe_3)_2(\mu\text{-}C_4F_6)(CO)_2\{P(OMe)_3\}_3]_2$, with $C_2(CO_2Me)_2$ to produce the tetranuclear $[Ir_2(\mu\text{-}SCMe_3)_2(\mu\text{-}C_4F_6)(CO)_2\{P(OMe)_3\}_3]_2$, and with $C_2(CO_2Me)_2$ to produce $[Ir_2(\mu\text{-}SCMe_3)_2\{(\mu\text{-}C_2(CO_2Me)_2\}(CO)_2\{P(OMe)_3\}_2]$. The structure of the trinuclear fluorobutyne species has been determined and is described as possessing a crown-like structure [246].

5.13 IRIDIUM(I)

5.13.1 *Halide complexes*

The ν(Ir–Cl) stretching frequencies, along with the ^{31}P chemical shifts, in *trans*-[IrCl(PPh$_3$)$_2$L] complexes, (L = CO, CS, N$_2$, C$_2$H$_4$, PPh$_3$, NO$^+$, N$_2$Ar$^+$, Me$_3$CNC, N$_2$C$_5$Cl$_4$ or N$_2$C$_5$Br$_4$) have been correlated in order to assess the *trans*-influence of the ligands L [247].

Oxidation of [(4-CH$_3$C$_6$H$_4$NH$_2$)Ir(CO)$_2$Cl], with an excess of I$_2$ in dichloromethane, produces the six-coordinate complex, [(4-CH$_3$C$_6$H$_4$NH$_2$)Ir(CO)$_2$ClI$_2$]. The electronic spectrum of a mixture of these two complexes in CH$_2$Cl$_2$ reveals an absorption band at 490 nm that is not present in the spectra of the individual components. The adduct [(4-CH$_3$C$_6$H$_4$NH$_2$)$_2$Ir$_2$(CO)$_4$Cl$_2$I$_2$], containing Ir(I) and Ir(III) atoms is said to be formed, and has been isolated as diamagnetic green crystals from solutions containing equimolar quantities of both complexes [248]. Enthalpy changes in the oxidative addition of RI (R = H, Me, I, CH$_3$CO, Pr, Et, CHMe$_2$ or C$_6$H$_5$CH$_2$) to *trans*-[IrCl(CO)(PMe$_3$)$_2$] were measured in 1,2-dichloroethane [249] and the changes in stereochemistry, which occur at carbon during oxidative addition of an alkyl halide to [IrCl(CO)L$_2$] (L = tertiary phosphine), have been examined by NMR spectroscopy [250]. Spin-trapping experiments for the oxidative addition of MeI, PhCH$_2$Br and Ph$_2$CHBr on *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] have been monitored by EPR spectroscopy [251].



SCHEME VII: Preparation and Reactions of Iridium-peroxo complexes.

5.13.2 *Complexes with Group VI donor ligands*

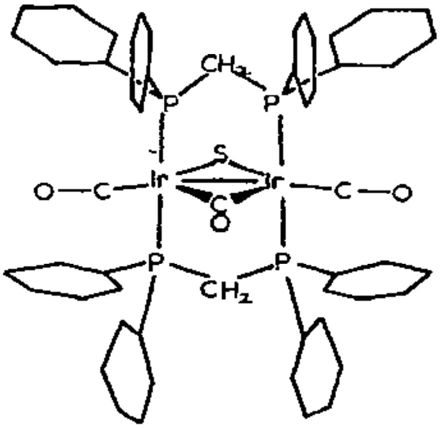
5.13.2.1 *Complexes with oxygen donor ligands*

Dioxygen reacts faster with the five-coordinate complex [(cod)Ir(phen)I] (86), than with the four-coordinate complex [(cod)Ir(phen)]Cl, to form the Ir(III) peroxide species [(cod)Ir(phen)(O_2)]X (X = Cl or I) [252]. The oxygenation of (86) may occur *via* the mechanism shown in Scheme VII.

Square planar Ir(I) complexes of general formula [(LL)IrL$'_2$] (LL = β-diketonate derivative, L$'$ = CO or ethene) have been examined by UVPES [78]. The study was made in conjunction with that on a similar series of rhodium complexes discussed earlier in this review (Section 5.4.1.1).

5.13.2.2 *Complexes with sulphur donor ligands*

Reaction of [$Ir_2(CO)_4(PPh_3)_2(\mu\text{-}SO_2)_2$] with para-substituted aryldiazonium salts gives [$Ir_2(CO)_4(PPh_3)_2(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)$][$BF_4$]. Treatment of the substituted diazo complex with H[BF_4] gives the protonated species [$Ir_2(CO)_4(PPh_3)_2(\mu\text{-}N{=}NHC_6H_4R)(\mu\text{-}SO_2)$][$BF_4$] and alkyl halides give the halogen-bridging [$Ir_2(CO)_2(PPh_3)_2(\mu\text{-}X)(\mu\text{-}N_2C_6H_4R)(\mu\text{-}SO_2)$] [253]. Addition of PR_3 (PMe_3, PMe_2Ph, $P(NMe_2)_3$, PPh_3 or $P(OMe)_3$) to [$Ir_2(\mu\text{-}SCMe_3)_2(CO)_4$] gives [$Ir_2(\mu\text{-}SCMe_3)_2(CO)_2(PR_3)_2$] [254]. ($(Me_2NCS)_2S$) reacts with [($Ph_3P$)Ir(CO)Cl] to give [($Ph_3P$)Ir($\eta^2$-$CSNMe_2$)($S_2CNMe_2$)(CO)]X (X = Cl or [$PF_6$]) [85]. [$Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2$] is formed from [$Ir_2Cl(CO)_4(\mu\text{-}dppm)_2$]$^+$ [$IrCl_2(CO)_2$]$^-$ and sulphide and reacts with CO to form (87), containing the CO molecule in the *endo*-pocket.



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Oxidative addition of H_2 to [$Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm_2)$] gives [$Ir_2H_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2$] [255]. [$Ir(S_2CPPh_3)(CO)(PPh_3)_2$][$BF_4$] consists of a distorted trigonal-bipyramid of donor atoms about the metal, containing the bidentate zwitterion $Ph_3P^+CS_2^-$, the sulphur atoms of which occupy an axial and an equatorial position; the CO ligand occupies the remaining axial position and the two phosphine groups the remaining equatorial positions [256].

5.13.3 Complexes with Group V donor ligands

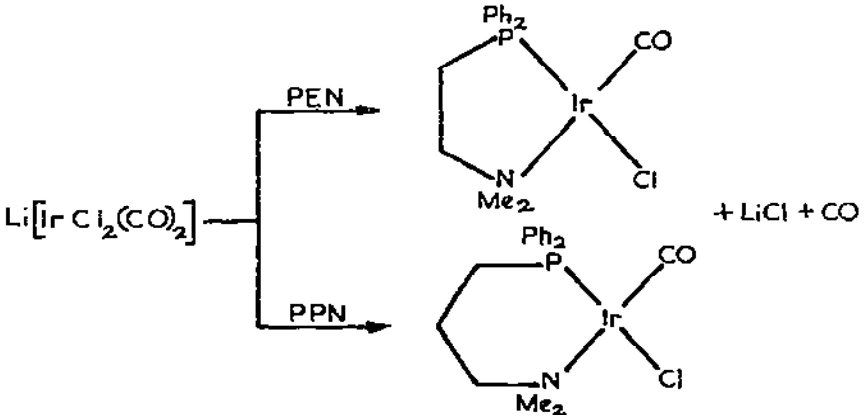
5.13.3.1 Complexes with nitrogen donor ligands

$[Ir(NO)(phen)(PPh_3)_2][PF_6]_2$ contains the metal atom in a trigonal-bipyramidal environment with the NO and phen ligands occupying the equatorial positions; NO is present as $[NO]^+$ [257]. The six-coordinate cation in $[Ir(NCMe)_3(NO)(PPh_3)_2][PF_6]_2$ contains a loosely-bound MeCN ligand (*trans*- to the NO group) relative to the other two ethanenitrile molecules [258].

The square-planar, tetrahalodiazocyclopentadiene complexes, $[IrCl(N_2C_5X_4)(PR_3)_2]$ (X = Cl or Br; R = phenyl, 4-fluorophenyl or 4-tolyl) have been prepared and characterised by IR, Raman, ^1H and ^{31}P NMR spectroscopy. $[IrCl(N_2C_5Cl_4)(PPh_3)_2]$ reacts with PMe_3, PMe_2Ph, $PMePh_2$, Me_3CNC or NO^+ to form a five-coordinate complex, and combines with HCl to form an oxidative addition product [94]. $[IrCl(N_2C_5Cl_4)(PPh_3)_2].C_7H_8$ has been shown to possess a square-planar geometry with *trans* PPh_3 ligands [259]. Similarly, the 1,3-diaryltriazenido anion $4\text{-}CH_3C_6H_4N_2{=}NC_6H_4CH_3\text{-}4$ (dtt) has been shown to be monodentate and *trans* to the carbonyl group, in the square-planar complex $[Ir(CO)(dtt)(PPh_3)_2]$ [260].

5.13.3.2 Complexes with nitrogen-phosphorus donor ligands

The new complexes (88) and (89) have been prepared:



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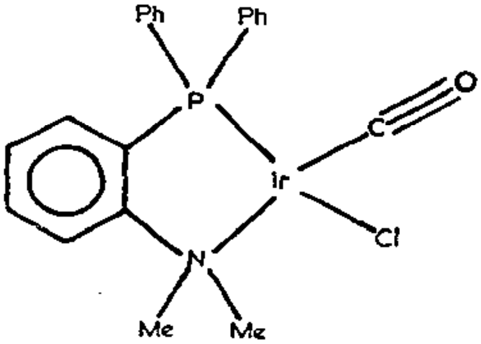
(89)

The crystal structure of the complex (90) has been determined and the IR and ^{31}P NMR spectral data suggest that all three complexes (88, 89 and 90) possess the same stereochemistry [261].



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5.13.3.3 *Complexes with phosphorus, arsenic or phosphorus-arsenic donor ligands*

R_2PNHPR_2 (R = Ph) reacts with $[(\mu\text{-}Cl)_2Ir_2(C_8H_{12})_2]$ to give $[Ir(R_2PNHPR_2)_2]Cl$, which reacts with CO to produce $[Ir(CO)(R_2PNHPR_2)_2]Cl$ and which is also formed from the combination of $[Ir(CO)(PPh_3)_2Cl]$ and $[Ir(CO)_2(4\text{-}H_2NC_6H_4CH_3)Cl]$ with R_2PNHPR_2. Oxidative addition of O_2, CS_2, I_2 or $(SCN)_2$ to $[Ir(R_2PNHPR_2)]Cl$ yields $[Ir(O_2)(R_2PNHPR_2)_2]Cl$, $[Ir(\eta^2\text{-}CS_2)(R_2PNHPR_2)]Cl$, $[Ir(I_2)(R_2PNHPR_2)_2]Cl$ or $[Ir(SCN)_2(R_2PNHPR_2)_2]Cl$, respectively [262].

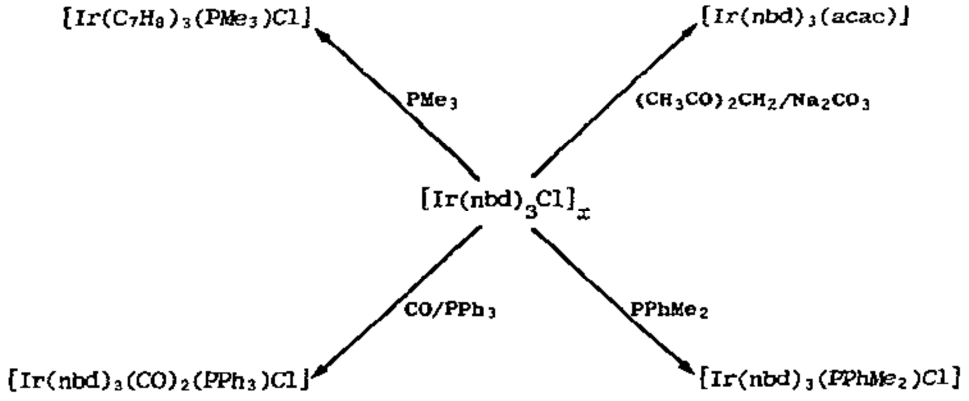
Trans-$[IrCl(CO)(L\text{-}L)]$ has a square-planar geometry and contains the *trans*-spanning ligand L-L (46) [128]. $[IrCl(CO)(PPh_3)_2]$ reacts with sexadentate tdadx (40) to produce $[Ir(tdadx)]Cl$, which reacts with dihydrogen to form $[IrH_2(tdadx)]Cl$ and with carbon monoxide to form $[Ir(CO)(tdadx)]Cl$. Reaction of $[Ir(tdadx)]Cl$ with nitric oxide gives the nitrosyl complex $[Ir(tdadx)(NO)]Cl_2$, in which the nitrosyl ligand has been formally assigned as $[NO]^-$, on the basis that the IR spectrum is similar to those of other iridium(III) complexes containing the $[NO]^-$ group. The analogous ligand, tddx (which contains phosphorus atoms in place of the arsenic atoms of (40), has also been studied. $[Ir_2Cl_2(tddx)]$ combines with dihydrogen to produce $[Ir_2Cl_2(tddx)H_4]$, with dioxygen to produce $[Ir_2Cl_2(tddx)(O_2)_2]$, with CO to give $[Ir_2Cl_2(tddx)(CO)_4]$ and with NO to give $[Ir_2(tddx)(NO)_2]Cl_4$ [126].

5.13.4 *Complexes with Group IV donor ligands*

5.13.4.1 *Complexes with carbon donor ligands*

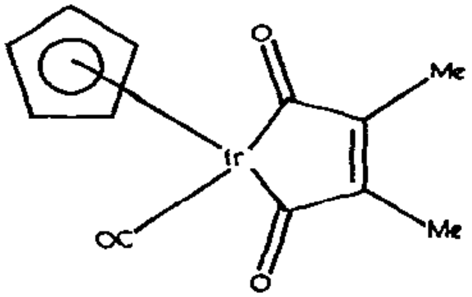
Tcne reacts with $[Ir(\mu\text{-}SCMe_3)(CO)(PR_3)]_2$ (R = Me, Ph or OMe) to give the π-bonded 1:1 adducts, $[Ir(\mu\text{-}SCMe_3)(CO)(PR_3)(tcne)]_2$ [263]. $[Ir(nbd)_3Cl]_x$, obtained from the reaction of $[Ir_2(cod)_2Cl_2]$ with an excess of nbd, undergoes the reactions shown in Scheme VIII [264].

The crystal structure of $[Ir(CO)_3Cl]$ has been determined [265]. The reactions



SCHEME VIII: Some reactions of $[Ir(nbd)_3Cl]_x$.

of $[Ir(CO)_3I]$ are discussed in Section 5.15.1. The pentacoordinated complexes $[Ir(SnCl_3)(cod)(L)_2]$ ($L = PR_3$) undergo carbonylation to give $[Ir(SnCl_3)(CO)_2(L)_2]$ [266]. The complexes $[Ir_2(CO)_3(Me_3NC)Cl(L_2)_2]X$, $[Ir_2(CO)_2(Me_3NC)_2Cl(L\text{-}L)_2]X$ ($L\text{-}L$ = dppm, $X = [BPh_4]$; $L\text{-}L$ = dpam, $X = [BF_4]$) and $[Ir_2(CO)(Me_3NC)_4(L\text{-}L)_2][BPh_4]_2$ have been obtained from the reactions of Me_3NC with the A-frame complexes, $[Ir_2(CO)_3Cl(L\text{-}L)_2]X$ [267]. $[Ir(cp)(CO)_2]$ combines with $CF_3C{\equiv}CCF_3$ to produce both *cis*- and *trans*-isomers of the σ-bridging alkyne complex, $[Ir_2(cp)_2(CO)_2(CF_3C_2CF_3)]$. Other, less well-characterised, complexes were also produced from this reaction. The reaction between $[Ir(cp)(CO)_2]$ and $CH_3C{\equiv}CCH_3$ produces (91) and a small quantity of C_6Me_6 [268].



(91)

5.13.4.2 *Carborane complexes*

The oxidative addition of HCl, HBr, HI, Cl_2 and Br_2 to square-planar d^8 carborane-iridium(I) complexes, *trans*-$[Ir(\sigma\text{-carborane})(CO)L_2]$ ($L = PPh_3$ or $PMePh_2$) has been investigated in the solid state and in solution; six-coordinate compounds were obtained. The HCl, HBr and HI adducts, $[IrHX(\sigma\text{-carborane})(CO)L_2]$, undergo reductive elimination of the carborane [269]. Reactions of

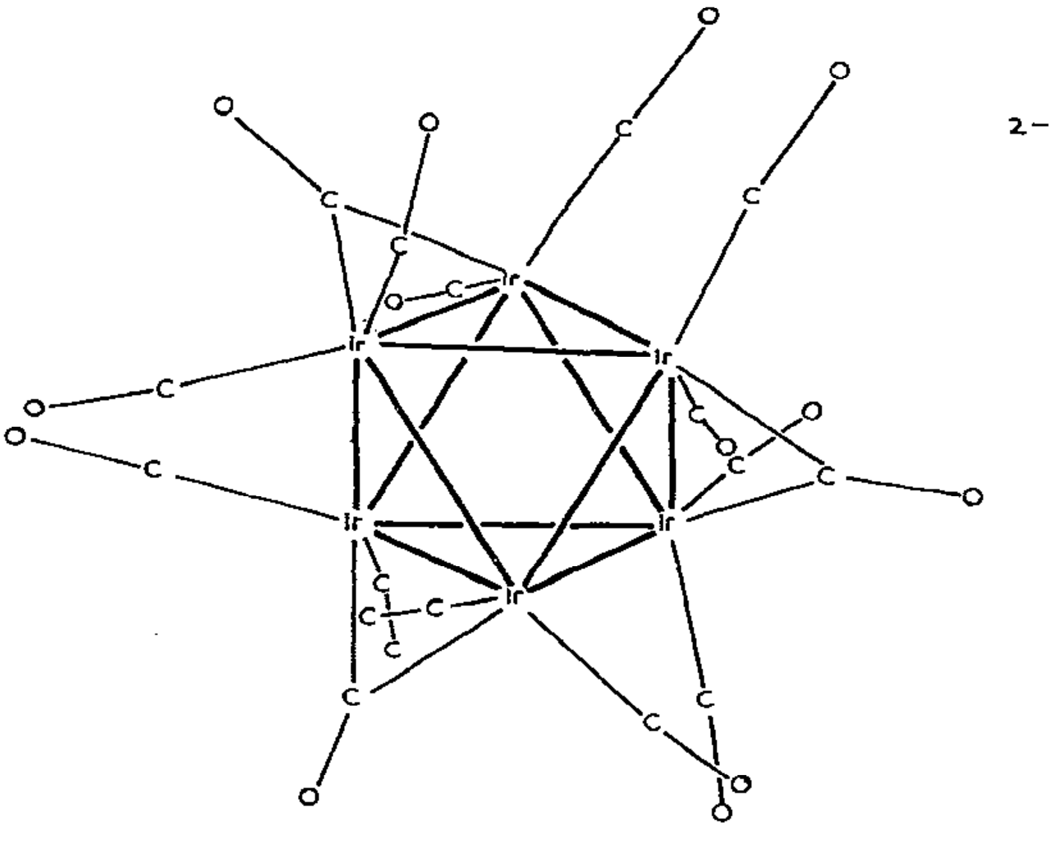
$[Ir(cod)(PR_3)_2][$*nido*$-7,8-C_2B_9H_{12}]$ are discussed in Section 5.15.2.

5.13.5 Mercury complexes

The formation of complexes of the type $[\{Ir(CO)Cl(PPh_3)_2\}_nHg][ClO_4]_2$ (n = 1–3) and $[\{Ir(CO)Cl(PPh_3)_2\}_3Hg(ClO_4)_x][ClO_4]_{2-x}$ has been observed spectroscopically and polarographically. $[\{Ir(CO)Cl(PPh_3)_2\}_4Hg][ClO_4]_2$ has also been identified [270].

5.14 IRIDIUM CARBONYL CLUSTERS

An improved synthesis and the X-ray crystal structure of $[Me_3CH_2Ph]_2[Ir_6(CO)_{15}]$ (92) has been obtained [271]. The carbonyl clusters $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1–3) are discussed in Section 5.15.1.



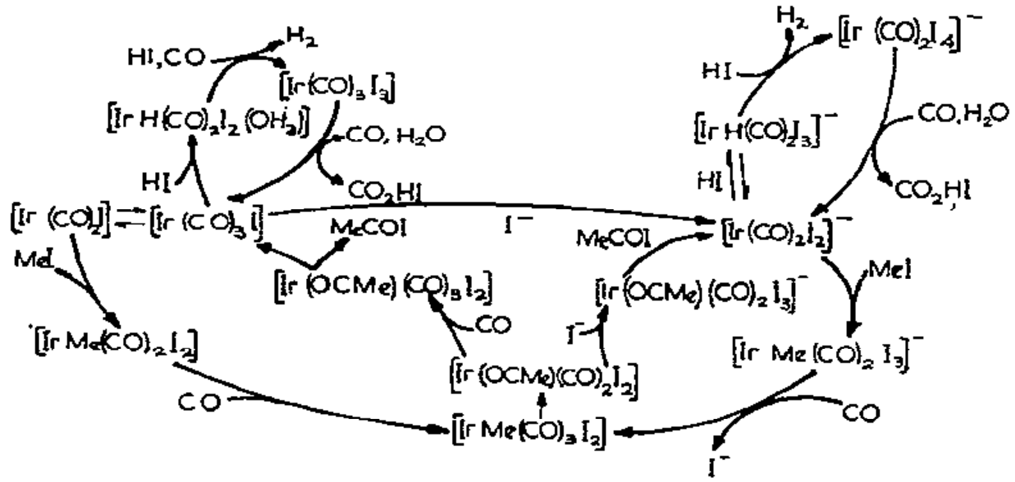
(92)

5.15 IRIDIUM CATALYSTS

5.15.1 Carbonylation Catalysis

The homogeneous, rhodium-based, process for the carbonylation of methanol is employed on a large scale commercially for the production of ethanoic acid. Although iridium compounds are also known to act as efficient catalysts for this system, the reactions are believed to involve more complicated mechanisms than those displayed in the rhodium-catalysed process.

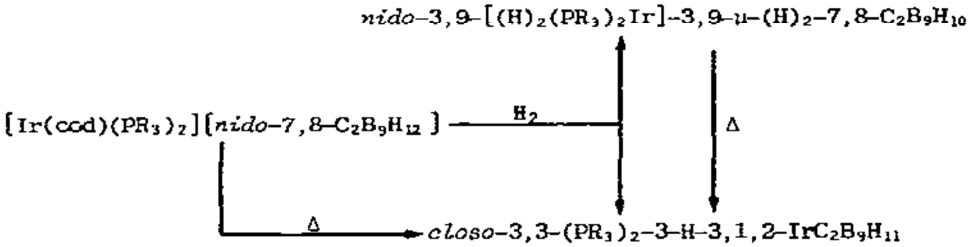
A mechanistic scheme, Scheme IX, has been described for methanol carbonylation using iridium halide precursors, in the presence of a methyl iodide promotor [272]. Two main cycles are in operation, involving either neutral or anionic complexes, and both lead to the reductive elimination of ethanoyl iodide, the hydrolysis of which is known to be rapid. $[Ir(CO)_3I]$, which is featured in the reaction scheme, has been generated *in situ* in dichloromethane and is found to react slowly with methyl iodide at room temperature to produce two new species that are considered to be intermediates in the iridium-catalysed carbonylation of methanol. The major product has two strong carbonyl stretching bands at 2118 and 2077 cm^{-1} and is formulated as $[IrMe(CO)_2I_2]$. The minor product $\{\nu(CO) = 2125, 2090$ and $1710\ cm^{-1}\}$ has been tentatively formulated as $[\{Ir(COMe)(CO)_2I_2\}_n]$ (n = 1 or 2) [272].



SCHEME IX: Mechanistic scheme for the iridium-catalysed carbonylation of methanol.

5.15.2 Hydrogenation Catalysis

$[Ir(cod)\{P(CHMe_2)_3\}(py)][PF_6]$, $[Ir(cod)(PMePh_2)_2][PF_6]$ and $[Ir(cod)(PPh_3)_2][PF_6]$ exhibit high activity in alkene hydrogenation [273]. $[Ir(SnCl_3)(CO)_2(L)]$ (L = phosphine derivatives) undergo hydrogenation to give $[Ir(SnCl_3)(H)_2(L_2)]$, which catalyses the hydrogenation (and isomerisation) of hept-1-ene; the rates of the reactions fall with decrease in the basicity of the phosphine ligand [266]. The A-frame complex, $[Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2]$, in the presence of dihydrogen, catalyses the reduction of ethyne, ethene and propene to the corresponding saturated hydrocarbon. The iridium species shows a greater activity towards hydrogenation than its rhodium analogue [255]. The cationic catalyst, $[Ir_2Cl(CO)_3(\mu\text{-}dppm)_2]^+$, was also found to be active in the hydrogenation of alkynes and alkenes [189]. The iridium analogue of the alkene hydrogenation and isomerisation catalyst, *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, has been prepared [274]. The complex and related materials may be prepared as shown in Scheme X.



(R = Ph or *p*-tolyl)

SCHEME X: Preparation of iridium-carboborane catalysts.

$[Ir_4(CO)_{12}]$ has been used as a catalyst in the synthesis gas reduction of nitrobenzene to aniline [176]. The "hydrogenation" of ethanal to ethanol in the disproportionation reaction $2RCHO + H_2O \longrightarrow RCH_2OH + RCO_2H$, is catalysed by $[Ir_2(C_5Me_5)_2Cl_4]$ [209]; other aldehydes (R = H, Et, Ph or MeCH=CH) behave similarly.

5.15.3 Heterogenised catalysts

Clusters analogous to $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1–3) have been anchored to phosphine-functionalised poly(styrene-divinylbenzene) and their catalytic activity for ethene and cyclohexene hydrogenation has been examined in a flow system [275]. Silica-anchored, tetranuclear iridium clusters, analogous to $[Ir_4(CO)_{12-x}(PPh_3)_x]$, have also been prepared by adding chlorobenzene solutions of $[Ir_4(CO)_{11}(PPh_3)]$ or $[Ir_4(CO)_{10}(PPh_3)_2]$ to silica containing attached $Ph_2PCH_2CH_2CH_2$– groups. The attached clusters were identified as

$[Ir_4(CO)_{10}(PPh_3)(Ph_2PCH_2CH_2CH_2-)]$ and $[Ir_4(CO)_9(PPh_3)_2(Ph_2PCH_2CH_2CH_2)]$, respectively, by their carbonyl IR spectra [276].

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