5. RHODIUM AND IRIDIUM

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CONTENTS

Introduction

RHODIUM

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 $^\circ$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 $^\circ$C ($RhCl_3.H_2O$ being stable up to 210 $^\circ$C); anhydrous $RhCl_3$ is gradually transformed by atmospheric oxygen into Rh_2O_3 at 640–880 $^\circ$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 $[Rh_2(\mu-OH)_2(\mu-CO_3)(1,4,7-triazacyclononane)_2]^{2+}$ [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)-$[Rh(S,S$-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 $[Rh(NH_2CH_2CH_2COO)_3].2H_2O$
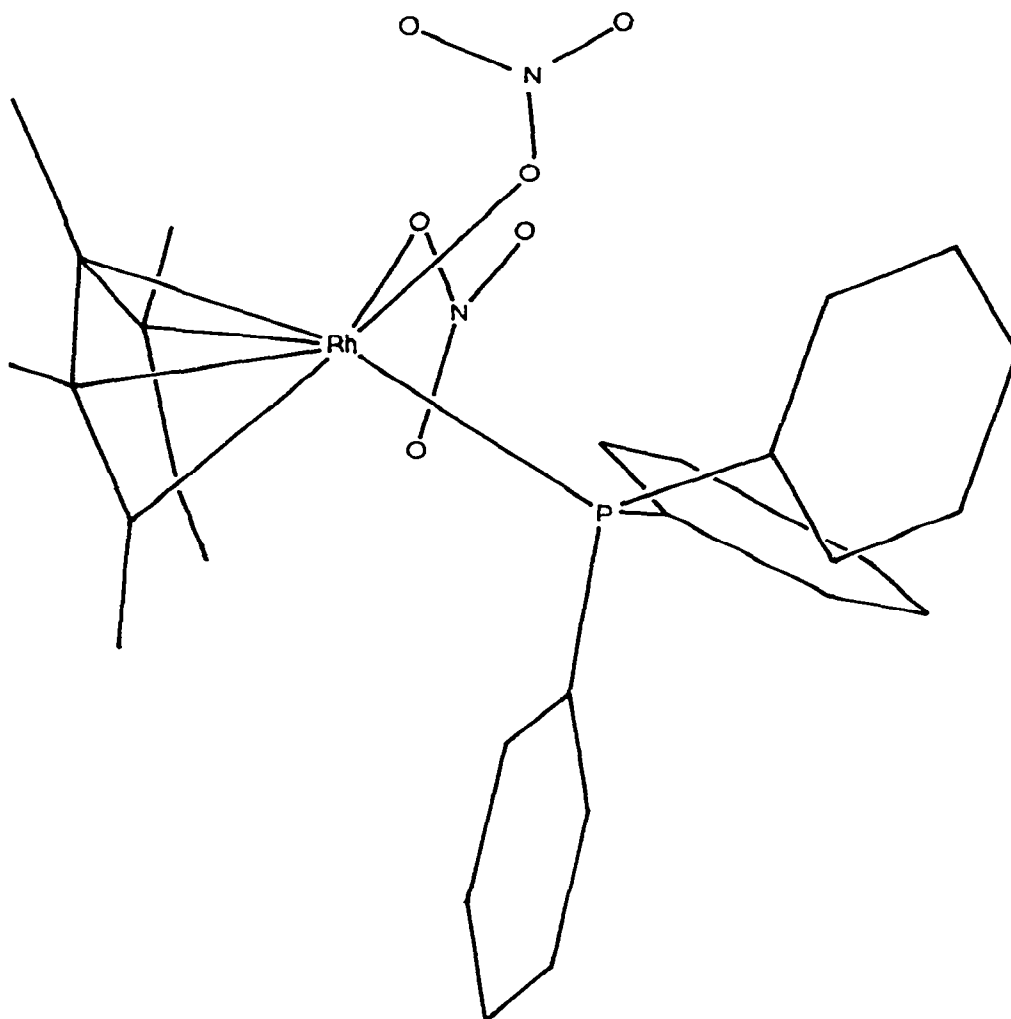
(1)

in which the ligand is bidentately-coordinated through the N and O atoms. The complex reacts with HCl to give [Rh(NH$_2$CH$_2$CH$_2$COOH)(NH$_2$CH$_2$CH$_2$COOH)$_2$Cl].H$_2$O, [Rh(NH$_2$CH$_2$CH$_2$COOH)$_2$(NH$_2$CH$_2$CH$_2$COO)Cl$_2$].H$_2$O and [Rh(NH$_2$CH$_2$CH$_2$COOH)$_3$Cl$_3$] [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$_6$H$_4$NH) 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].

(2)

(3)
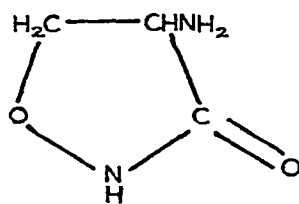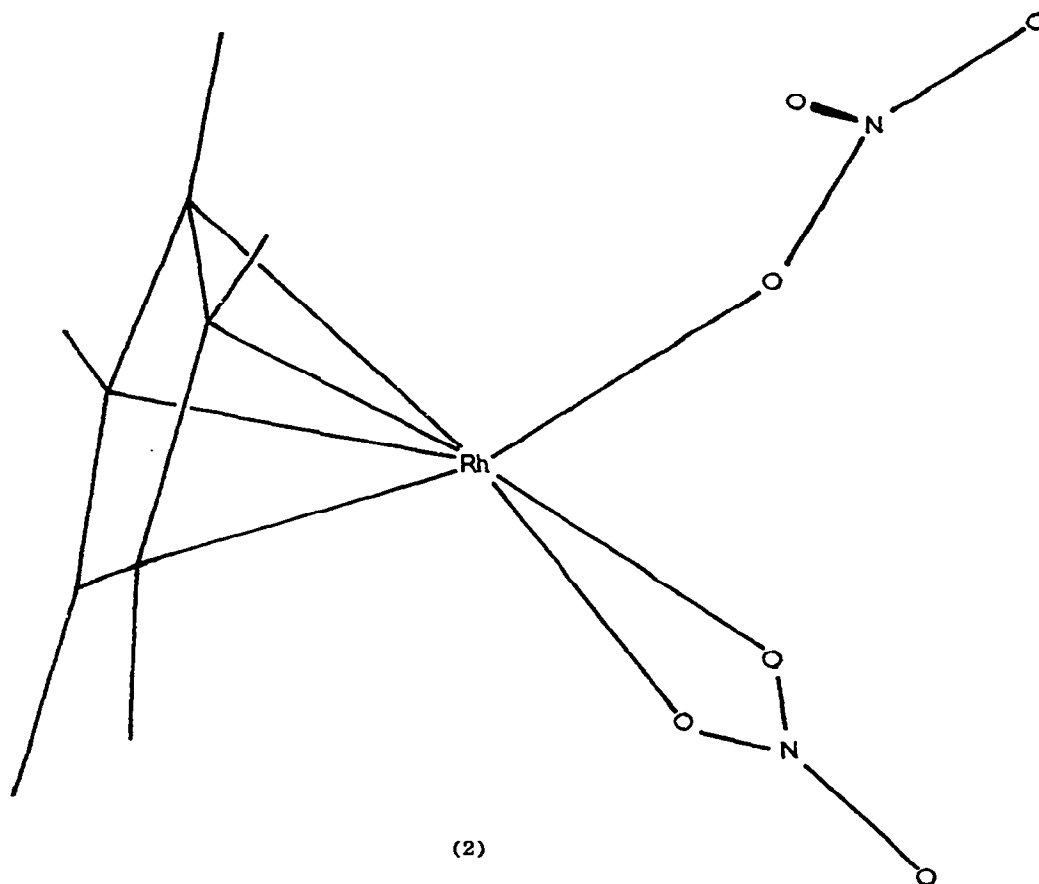
5.2.3 Complexes with sulphur or sulphur-nitrogen donor ligands

The octahedral complexes [RhL₃] {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
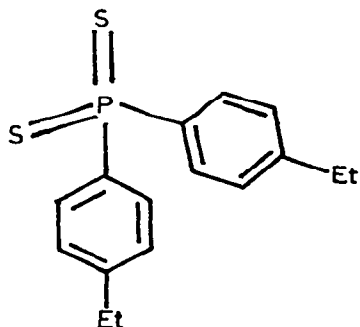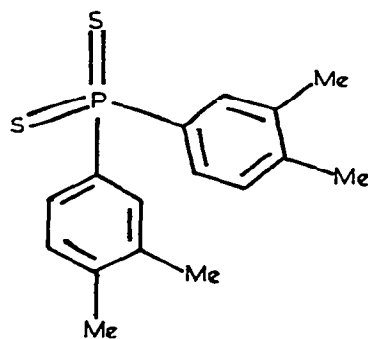
(4)   (5)

has been assessed [22].

The compounds [RhL₂Cl].2H₂O and [Rh₂Q₃] have been prepared from solutions containing piperazine dithiocarbamate (L = (6)) and piperazine bis(dithiocarbamate)
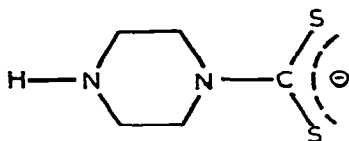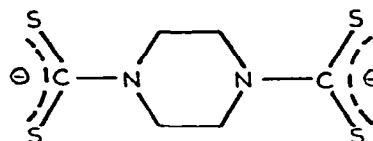
(6)   (7)

(Q = (7)), respectively [23]. IR, electronic spectroscopic and magnetic studies indicate that [Rh₂(th)₃] {th = (8)} has an octahedral coordination about the
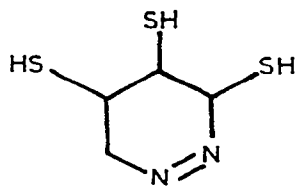
(8)

metal atom [24]. The He(I) excited photoelectron spectrum of [Rh{S₂P(OEt)₂}₃] has been reported [25].

The trithiaveratrylene ("Vn₃S₃") rhodium complex [Rh(NO₃)₃(Vn₃S₃)].3CH₃CON(CH₃)₂ has been found to contain the expected octahedral coordination [26]. The complex [Rh(Q)₂Cl(H₂O)].7H₂O (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-imino-3-thioisoindoline)₃] has been prepared [28] and a triazoline thione complex of rhodium(III) has been characterised spectroscopically [29].

(9)
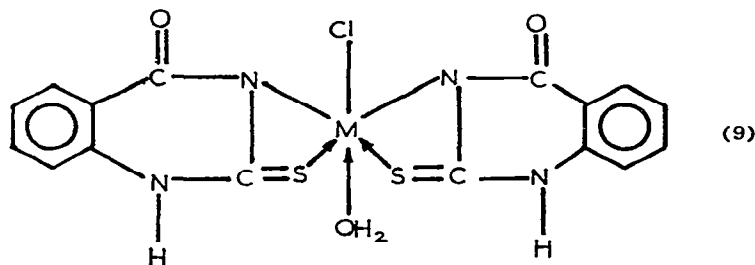
5.2.4 Complexes with tellurium donor ligands

The aryl telluride complexes of rhodium(III); [(Ph$_2$Te)$_3$RhCl$_3$],
[(Ph$_2$Te)$_2$RhCl$_3$(CO)], [(Ph$_2$Te)$_2$RhClBr$_2$(CO)], [(Ph$_2$Te)$_2$RhClI$_2$(CO)],
[(Ph$_2$Te)$_2$RhCl(CNS)$_2$(CO)], [(Ph$_2$Te)$_2$RhCl$_2$(TePh)], [(Ph$_2$Te)$_2$RhCl(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$_3$)$_5$X][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)$_2$XI]$^{n+}$ (X = I, NH$_3$ or H$_2$O) leads in general to
the formation of trans-[Rh$_2$(en)$_2$(H$_2$O)I]$^{2+}$. However, cis-[Rh(en)$_2$(NH$_3$)I]$^{2+}$
gives both trans- and cis-[Rh(en)$_2$(NH$_3$)(H$_2$O)]$^{3+}$ as photoproducts [32]. The
cis/trans and trans/cis photoisomerisation of some rhodium(III) tetraammine
complexes (e.g. [Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$) has also been examined [33]. The photo-
physical and photochemical properties of [Rh(NH$_3$)$_5$Cl]$^{2+}$ 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 bv sub-picosecond laser spectroscopy [36].

Na$_3$[RhCl$_6$] reacts with 3- or 4-nitroaniline to give [RhL$_2$(H$_2$O)Cl$_3$] and
[RhL$_3$Cl$_3$] (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-NO$_2$C$_6$H$_4$NH$_3$]$_3$[RhCl$_6$]
at 130 °C gives [RhL$_3$Cl$_3$] [37]. Octahedral complexes of rhodium(III) with 12-,
13-, 14-, 15-, and 16-membered macrocyclic tetramines have been prepared contain-
ing 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 $[Rh_2L_2(OH)_4(\mu-OH)_2]^{4+}$, which at a higher pH forms $[Rh_2L_2(\mu-OH)_3]^{3+}$. $[Rh_2L_2(OH_2)_2(\mu-OH)_2]^{4+}$ reacts with $MeCO_2H$ to give $[Rh_2L_2(\mu-OH)_2(\mu-O_2CMe)]^{3+}$ and, at pH>8.5, $[Rh_2L_2(OH)_2(\mu-OH)_2]^{2+}$ is produced which reacts with $[CO_3]^{2-}$ to form $[Rh_2L_2(\mu-OH)_2(\mu-CO_3)]^{2+}$ [39]. The crystal structures of cis- and trans-$[Rh(Cl_2)(en)_2][NO_3]$ have been reported [40].

The complexes $[HB(3,5-Me_2pzl)_3RhCl_2(MeOH)]$ 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 = $H_2NNHC=SNHNHCO$-3-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)
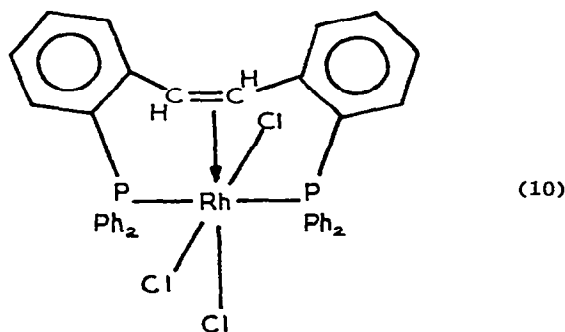
between carbaborane cages [49].

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

RhCl$_3$.3H$_2$O combines with the β-ketophosphine, P(CMe$_3$)$_2$(CH$_2$COPh), to give [RhCl$_2${(CMe$_3$)$_2$PCH=C(O)Ph}{P(CMe$_3$)$_2$(CH$_2$COPh)}] (11) in which both phosphine

(11)
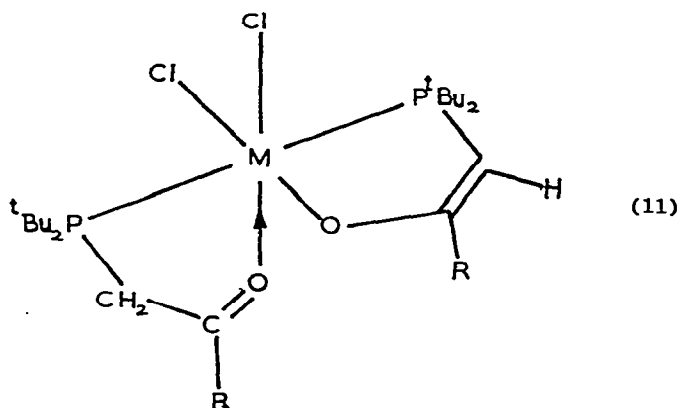
ligands are bidentate and the keto-group is strongly coordinated, the latter not being displaced by treatment with carbon monoxide [51].

The reaction of [RhCl(PPh$_3$)$_3$] with Ph$_2$PSC(NC$_6$H$_4$-4-Me)(NHC$_6$H$_4$-4-Me) or Ph$_2$PSCONHPh in the presence of base produces [Rh(PPh$_3$)$_2$(SPPh$_2$)] which contains a side-on coordinated η^2-Ph$_2$PS grouping. This compound may also be prepared from interaction of [RhCl(PPh$_3$)$_3$] and Ph$_2$PSH. [Rh(PPh$_3$)$_2$(SPPh$_2$)] reacts with PhNCS to give [Rh(PPh$_3$)(PhNC)(PhNCS$_2$)(Ph$_2$PSCSNPh)] [52].

5.2.7 Complexes with Group IV donor ligands

5.2.7.1 Complexes with carbon donor ligands

Reaction of [Rh(cp)(C$_2$H$_5$)(PMe$_3$)$_2$]X with [Ph$_3$C]X (X = [PF$_6$] or [BF$_4$]) gives [Rh(cp)(C$_2$H$_4$)(PMe$_3$)$_2$]X$_2$. The ethylene ligand is easily attacked by nucleophiles, N, to give complexes containing Rh-C$_2$H$_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$_2$(μ-I)$_2$(I)$_2$(η^5-C$_5$Me$_4$Et)$_2$] has been determined [55].

5.2.7.2 Complexes with tin donor ligands

The crystal structure of Cs$_4$[Rh{SnF$_2$(H$_2$O)$_2$}$_2${Sn$_4$F$_{15}$}].4H$_2$O 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, $[F_3Sn(\mu-F)SnF_4(\mu-F)SnF_4(\mu-F)SnF_3]^{7-}$ [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 $[Rh_3H_3(\eta^5-C_5Me_5)_3O][PF_6].H_2O$ (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 $[Rh_2(O_2CCMe_3)_4(H_2O)_2]$, $[Rh_2(O_2CMe)_4(tetrahydrothiophene)_2]$, $[Rh_2(O_2CMe)_4(dmso)_2]$ [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 $[Rh_2(O_2CMe)_4]$, $[Rh_2(O_2CMe)_4][ClO_4]$, $[Rh_2(O_2CMe)_4(4-cyanopyridine)]$ 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$_2$CR)$_4$L$_2$] (R = H, Me or CF$_3$; L = H$_2$O, py, NH$_3$, urea, tu, dmso, MeNH$_2$, EtOH or PPh$_3$) and M$_2$[Rh$_2$(O$_2$CR)$_4$X$_2$] (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$_2$CR)$_4$(dmso)$_2$] (R = C$_2$H$_5$ or CF$_3$); when R = C$_2$H$_5$, 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$_2$L$_4$Q$_2$] (H$_2$L = salicylic acid; Q = NH$_3$, py, PhNH$_2$, en, urea, MeCSNH$_2$ or ½N$_2$H$_4$) 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)$_4$L$_2$] (R = H, Me, Ph, CCl$_3$, CF$_3$, *etc*.; L = H$_2$O, 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$_3$)$_2$PCH=C(O)Ph}{P(CMe$_3$)$_2$(CH$_2$COPh)} with sodium methoxide proceeds rapidly to produce an intense blue coloured material which appears to be the rhodium(II) complex, trans-[Rh{(CMe$_3$)$_2$PCH=C(O)Ph}$_2$] [51].

5.3.2 Complexes with nitrogen donor ligands

5.3.2.1 Amine complexes

The crystal structure of [Rh$_2$(β-alanine)$_4$(H$_2$O)$_2$][ClO$_4$]$_4$.2H$_2$O has been determined [70].

5.3.2.2 Complexes with nitrogen-containing heterocycles

The crystal structures of [Rh$_2$(O$_2$CMe)$_4$(theophylline)$_2$] and [Rh$_2$(O$_2$CMe)$_4$(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 $[Rh(dppe)(\eta^6-BPh_4)]$ 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)

(16)   (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(Ph2SO)(C8H14]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(C8H14)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(R₂SO)₂] (X = Cl or Br; R = Me, Pr or Bu) and sulphides of the type, [Rh(CO)X(R₂S)] (X = Cl or Br; R = Me, Et or CHMe₂) 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 = Me₂CH, Bu, Me₃C, Ph, 4-tolyl or 4-ClC₆H₄) have been synthesised by replacing the SR group for the bridging

(20)

chloride in the corresponding di-μ-chloro compound [82]. [RhCl(Ph₂SO)₂]₂ has also been prepared and shown to involve coordination *via* the sulphur atoms [15].

Reaction of CS₂ with [Rh(cp)(C₂H₄)(PR₃)] (PR₃ = PMe₃ or PMe₂Ph) produces the complex [Rh(cp)(PR₃)(CS₂)] in which the CS₂ ligand is η²-bonded. [Rh(cp)(PMe₃)(CS₂)] reacts with [Cr(CO)₅(thf)] and [Mn(cp)(CO)₂(thf)] to give [Rh(cp)(PMe₃)(SCS)Cr(CO)₅] and [Rh(cp)(PMe₃)(SCS)Mn(CO)₂(cp)], respectively; the CS₂ molecule bridges the two metal atoms in these complexes. The reaction of [Rh(cp)(C₂H₄)(PMe₃)] with CS₂ can also give another product, [Rh(cp)(PMe₃)(C₂S₄)], which contains a five-membered RhSCSC heterocyclic ring [83].

[Rh(th₃)₃Cl] (th₃ = (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, [(Ph₂Te)₂Rh(CO)Cl], [(Ph₂Te)Rh(CO)(CNS)], [(Ph₂Te)₃RhCl] and [(Ph₂Te)₂RhCl]₂, have been synthesised and characterised by IR spectroscopy, thermal analysis and molecular mass

measurements [30].

The compounds [Rh{X-C(Z)-Y}(PPh$_3$)$_2$] ({X-C(Z)-Y} = (21)) react with an excess

(21)

of CS$_2$ to give the thiocarbonyl complexes [Rh{X-C(Z)-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(η^2-CS$_2$)(PPh$_3$)(py)$_2$] (22) can be formed by

(22)

(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$_3$P)$_2$Rh(CO)Cl] reacts with (Me$_2$NCS)$_2$S to give the kinetically-stable product, [(Ph$_3$P)Rh(η^2-CSNMe$_2$)(S$_2$CNMe$_2$)(CO)]X (X = Cl or [PF$_6$]). This complex in solution slowly transforms into the thermo-dynamically stable product [(Ph$_3$P)Rh(η^2-CSNMe$_2$)(S$_2$CNMe$_2$)Cl] (23) [85]. The reaction of [Rh(cp)(PMe$_3$)(C$_2$H$_4$)] and CSSe gives [Rh(cp)(PMe$_3$)(η^2-CSSe)], which undergoes reaction with Ph$_3$P 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-L)] (L-L = salicylaldoxime, 2-OHC$_6$H$_5$CH(=NOH), α-benzoin oxime, C$_6$H$_5$CH(OH)C(=NOH)C$_6$H$_5$, α-furil dioxime, C$_4$H$_4$C(=NOH)C$_4$H$_4$C(=NOH), α-benzil dioxime, C$_6$H$_5$C(=NOH)C$_6$H$_5$C(=NOH), dimethylglyoxime, CH$_3$C(=NOH)CH$_3$C(=NOH) or cupferron, C$_6$H$_5$N(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$_2$Rh(dmg)$_2$(PPh$_3$)]$_2$. The degree of oxidation in this complex and in [(PPh$_3$)Rh(dmg)$_2$], [(OPPh$_3$)Rh(dmg)$_2$]$_2$O$_2$, H[Rh(dmg)Cl$_2$], [HRh(dmg)$_2$] and [PhNHCH$_2$Rh(dmg)$_2$] has been examined by XPES [88]. Rb[RhCl$_2$(dmg)$_2$].H$_2$O 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$_2$O$_3$ 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$_2$O$_3$ in dichloromethane to give [Rh(NO)$_2$(NO$_2$)(AsPh$_3$)$_2$].1.5CH$_2$Cl$_2$ and [Rh(NO)$_2$(NO$_2$)(PPh$_3$)$_2$].0.5CH$_2$Cl$_2$, respectively. The reaction of [Rh(CO)(O$_2$CMe)(PPh$_3$)$_2$] with N$_2$O$_3$ produces [Rh(NO)(NO$_2$)$_2$(PPh$_3$)$_2$]. N$_2$O$_3$ combines with RhCl$_3$.3H$_2$O 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-L)]$^+$ (L-L = phen or bipy) reacts with [IrX$_2$(CO)$_2$]$^-$ to give [Rh(CO)$_3$(L-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$_3$COCH$_3$)][ClO$_4$] produces complexes of general formula [Rh(CO)(PPh$_3$)$_2$L][ClO$_4$]. Monodentate coordination is favoured by replacing triphenylphosphine with P(C$_6$H$_{11}$)$_3$ and bidentate linkage is favoured by using AsPh$_3$ or PMe$_2$Ph. 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-FC_6H_4 or CMe_3) have been generated as short lived intermediates [94]. The bidentate, diazadiene ligand, $(CHMe_2)CH-N=CH-CH=N-CH(CHMe_2)$ = 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, $H_3[Rh_4(1,3-diisocyanopropane)_8Cl][CoCl_4]_4.nH_2O$, 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 $[Rh_2(1,3-diisocyanopropane)_4][BPh_4]_2 \cdot MeCN$
and $[Rh_2(2,5-dimethyl-2,5-diisocyanohexane)_4][PF_6]_2 \cdot 2MeCN$; both compounds are
found to contain ligand-bridged, binuclear cations and the coordination geometry
about the metal atoms is approximately square-planar [100].

Irradiation ($\lambda > 520$ 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.

(25)

(26)

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 $^\circ$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 190 $^\circ$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

(27)

(28)

[RhPd(Ph₂Ppy)₂(CO)Cl₃] (28) have been described [107].

Reaction of [Rh(C₂H₄)₂Cl]₂ with 2-allylaniline (L = (29)) gives the dimer

(29)

(30)

[RhLCl]₂, in which the ligand is coordinated to the metal through both the nitrogen atom and the alkene group. Reaction of [Rh(C₂H₄)₂Cl]₂ with N-allylaniline = Y = (30) produces [Rh₂Cl₂Y₃] [108].

5.4.3 Complexes with phosphorus and arsenic donor ligands

5.4.3.1 Phosphine complexes

[RhCl(PPh₃)₃] decomposes above 140 °C in both the solid state and in solution to yield biphenyl; rhodium complexes with 4-substituted PPh₃ ligands form 4,4'-disubstituted biphenyls. The mechanism of these ring connections is believed to occur by dissociation of [RhCl(PPh₃)] into PPh₃ and solvated [RhCl(PPh₃)₂], followed by the oxidative addition of PPh₃ to the latter to form a phenyl-rhodium intermediate [109]. The high-resolution, solid state ³¹P NMR spectrum of RhCl(PPh₃)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)(PPh₃)₂] has been resolved [111].

The preparation and characterisation of the following trimethylphosphine complexes have been described; [Rh(PMe₃)₄Cl], [RhCl(PMe₃)₃], [Rh(PMe₃)₃]X (X = [PF₆], [BPh₄]), [RhH₂(PMe₃)₄]Cl, [RhCl(CO)(PMe₃)₂] and [Rh(PMe₃)₃(CH₂Cl₂)]Cl. Crystal structures determined for [Rh(PMe₃)₄]Cl and [RhCl(PMe₃)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(CHMe₂)}₃] has been determined and it possesses a strictly planar coordination about the metal. The fluxional behaviour of this compound and of [RhH(PEt₃)₃] and [RhH(PEt₃)₄] have been reported [113]. [RhH{P(CHMe₂)₃}₃] and [Rh₂(H₂)(µ-N₂){P(cych)₃}₄] undergo oxidative additon of H₂O. The preparation of [Rh(H)₂(py)₂{P(CHMe₂)₃}₃]X (X = OH or [BPh₄]), [Rh(H₂)(py)₂{P(cych)₃}₂][BPh₄], [Rh₂(C₆F₅)₂(N₂){P(cych)₃}₄].2PhMe, [Rh(C₆F₅(CO){P(cych)₃}₂] and [Rh(C₆F₅(PhCN){P(cych)₃}₂] have been reported [114].

The structure and properties of trans-[RhCl(CO){P(2-C$_5$H$_4$N)$_3$}$_2$] have been described [115] and the He–I and He–II UVPES of [Rh$_2$Cl$_2$(PF$_3$)$_4$] have been recorded [116]. Displacement of ethene from [Rh(cp)(C$_2$H$_4$)$_2$] 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$_2$H$_4$)$_2$]$_2$ 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(η-C$_8$H$_{12}$){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)$_2$Cl]$_2$ with P(CMe$_3$)$_2$(CH$_2$COR) (R = Ph or CMe$_3$) gives trans-[RhCl(CO){P(CMe$_3$)$_2$(CH$_2$COR)}$_2$]. Reaction of these products with sodium methoxide gives [Rh(CO){(CMe$_3$)$_2$PCH=C(O)R}{P(CMe$_3$)$_2$(CH$_2$COR)}] [51].

5.4.3.2 Diphosphine and related complexes

The "A-frame" complex, [Rh$_2$(CO)$_2$(μ-Cl)(μ-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$_2$Br(μ-CO)(CO)(μ-dppm)$_2$]Br (36) has been produced from the reaction of trans-[Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$] with sodium bromide. The former species loses carbon monoxide in solution to give the "A-frame" complex, [Rh$_2$Br$_2$(μ-CO)(μ-dppm)$_2$] (37). When KI is used in place of NaBr, [Rh$_2$I(CO)(μ-CO)(μ-dppm)$_2$] is formed. Both the bromo- and iodo- species react with CO and with SO$_2$ to give [Rh$_2$(CO)$_2$(μ-L)(μ-X)(μ-dppm)$_2$]X (L = CO or SO$_2$; X = Br or I). [Rh$_2$Cl$_2$(μ-CO)(μ-dppm)$_2$] is prepared by heating trans-[Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$] under reflux in toluene. Excess of CO combines with the chloro- and bromo-monocarbonyl species to give [Rh$_2$(CO)$_2$(μ-CO)(μ-X)(μ-dppm)$_2$]X (X = Cl or Br), whereas SO$_2$ produces equimolar amounts of [Rh$_2$X$_2$(μ-SO$_2$)(μ-dppm)$_2$] and [Rh$_2$(CO)$_2$(μ-SO$_2$)(μ-X)(μ-dppm)$_2$]X [120]. (37) is found to have an unusually

(33)

(32)

(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$_2$Cl$_2$, 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$_2$PNHPPh$_2$ (L–L) have been prepared (Scheme III) and characterised by IR, Raman and NMR spectroscopy [125].

$$[Rh_2(C_2H_4)_4Cl_2] \xrightarrow{\text{L-L}} [Rh(L-L)_2]Cl \xrightarrow{\text{CS}_2} [Rh(\eta^2\text{-}CS_2)(L-L)_2]Cl$$

$$\Big\downarrow [NH_4][PF_6]$$

$$[Rh(L-L)_2][PF_6]$$

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

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

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

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 $[Rh_2(CO)_2Cl\{\mu\text{-}(L-L)\}_2]X$ (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)

278

(43)

(44)

(45)

relative amounts of isonitrile used. The use of an excess of the isonitrile
and Na[BPh$_4$] gives (45), which combines with CO or with SO$_2$ to give
[Rh$_2$(μ-L)(CMe$_3$NC)$_4$(L-L)$_2$][BPh$_4$] (L = CO or 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].

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, NO₂, NO₃ or ClO₄; L = AsPh₃ or SbPh₃) and their adducts with SO₂ and tcne were

(50)

(51)

$[Rh(cod)Cl_2] - cis$

(52)

(53)

$[Rh(CO)_2Cl_2] - cis$

(54)

prepared and the ligand influence on the carbonyl stretching frequency was
determined [136]. [Rh(CO)Cl(SPPh₃)₂], [Rh(CO)Cl(PPh₃)₂], [Rh(CO)Cl(PPh₃)₂(SPPh₃)],
[Rh(CO)Cl(AsPh₃)₂(SAsPh₃)], [Rh₂(CO)₂Cl₂(SAsPPh₃)₂], [Rh(CO)(CS)Cl(PPh₃)₂] and
[Rh₂(COS)₂Cl₂(SbPh₃)₂] have been prepared by the reaction of one of a variety of
rhodium compounds with carbonyl sulphide in the presence of PPh₃, AsPh₃ or
SbPh₃. In most cases it can be seen that COS acts as a carbonylating agent,
although some SPPh₃ and SAsPh₃ complexes (such as [Rh₂Cl₂(SPPh₃)₄] and
[RhCl₃(AsPh₃)(SAsPh₃)]) have also been produced [137]. [Rh(CO)₂(R₂PCH₂)₃CR'][PF₆]
(R = Ph; R' = MeCH₂PR₂) reacts with liquid ammonia at room temperature to give
[Rh(CO)(CONH₂)(R₂PCH₂)₃CR'] which, at 100 °C in liquid ammonia, forms
[(μ-CO)₂Rh(R₂PCH₂)₃CR']₂. [Rh(CO)(CONH₂)(R₂PCH₂)₃CR'] reacts with MeOH to give
[Rh(CO)(CO₂Me)(R₂PCH₂)₃CR'] [138]. The platinum compound
[(Ph₃P)(4-tolylNC)Pt{C(OMe)=N}(4-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-η⁵)(PPh₃)₂] has been determined; ArO = (55) and bonds to the metal in

(55)

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)(PPh₃)(NO₃)] has been
examined by thermogravimetry [141].

Mechanistic studies using spin-trapping species have been carried out on
several rhodium(I)-alkyl halide oxidative additions [142]. The *closo*-
hydridorhodacarborane, 3,3-(Et₃P)₂-3-H-3,1,2-RhC₂B₉H₁₁ , has been prepared
in situ from the PPh₃ analogue and investigated by ¹¹B NMR spectroscopy [143].

5.4.4.2 Complexes with tin donor ligands

Ph₃SnX (X = Cl or Br) adds oxidatively to [Rh(Me₃CNC)₄][ClO₄] to give *cis*-
[Rh(Ph₃Sn)X(Me₃CNC)₄][ClO₄] [144]. The preparation and properties of the
five coordinate complexes, [Rh(SnCl₃)(diolefin)(L)₂] (diolefin = cod or nbd;
L = PPh$_x$Et$_{3-x}$) and [Rh(SnCl₃)(diolefin)(L-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$_2$L$_2$Cl$_2$] (L = cp or nbd) with Hg[R(NC)YNR']$_2$ (Y = H; R = R' = CHMe$_2$; R = Me, CHMe$_2$ or 4-MeC$_6$H$_4$; R' = 4-MeC$_6$H$_4$ and Y = Me, R = R' = 4-MeC$_6$H$_4$) gives the complexes of general formula [L{R(NC)YNR'}$_2$RhHgCl], 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 [(μ-CO){(Rh(cp)(CO)}$_2$] with [HBF$_4$].Et$_2$O gives [(μ-CO)(μ-H){Rh(cp)(CO)$_2$}][BF$_4$] in quantitative yield. Deprotonation of this complex is effected by [MeO]Na. Reaction of [(μ-CO){Rh(cp)(CO)}$_2$] with [HBF$_4$].H$_2$O 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

(56)   (57)

-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].

X-ray and neutron diffraction data have revealed definitive structures for [H$_2$Rh$_2${P(OCHMe$_2$)$_3$}$_4$] and [H$_3$Rh$_3${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)$_2$(μ-dppm)$_2$] (58) has been generated by reduction of [Rh$_2$Cl$_2$(CO)$_2$(μ-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

OC——Rh —— Rh——CO

(58)

CO

H [PF$_6$]

−H$_2$

O
C
Rh   Rh
OC   CO

(59)

H[PF$_6$]

−H$_2$

H
Rh   Rh$^+$ [PF$_6$]$^-$
OC   CO

(61)

−CO

CO

H
Rh —— Rh$^+$ [PF$_6$]$^-$
C
O
OC   CO

(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$_2$O ——► 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 tetra-hedral 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 $[\delta(^{103}Rh) = -644 \text{ ppm}]$ 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, $[FeRhW(\mu_3-CC_6H_4Me-4)(\mu_2-CO)(CO)_5(\eta^5-C_5H_5)-(\eta^9-C_9H_7)]$, 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 $[Rh_3(\mu-PPh_2)_3(CO)_3(PPh_3)_2]$ [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, $[Rh_4(CO)_5(\mu-PPh_2)_5]$, 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 $-(CH_2)_3NH(CH_2)_2NH_2$ 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 $[Rh(CO)_4]^-$:

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

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. $[Rh_5(CO)_{10}(\mu_2-CO)_5]$ 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 $[Rh_{14}(\mu-CO)_{15}(CO)_{11}]^{2-}$ [168] and $[Rh_{14}H(\mu-CO)_{15}(CO)_{10}]^{3-}$ [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, $[Rh_{22}(\mu_3-CO)_7(\mu-CO)_{18}(CO)_{12}]^{4-}$, 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 nitro-
benzene 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-CO$_2$Me, 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$_2$Me 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–L)(CO)(MeCN)][PF$_6$], [RhCl(C$_2$H$_4$)(L–L)] and [Rh(L–L)$_2$Cl], 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$_2$(μ-H)(μ-CO)(CO)$_2$(dppm)$_2$][PF$_6$] have been mentioned briefly in Section 5.5.

$$[HRh(CO)_2I_3]^- \xrightarrow{\begin{array}{c}HI \quad H_2\end{array}} [Rh(CO)_2I_4]^- \rightleftharpoons [Rh(CO)I_5]^{2-}$$

$$HI \updownarrow \qquad\qquad\qquad \updownarrow \begin{array}{c}CO\\ \\I^-\end{array}$$

$$[Rh(CO)_2I_2]^-$$

$$\downarrow -CO_2$$

$$[Rh(CO)_2I_3(COOH)] \rightleftharpoons [Rh(CO)_3I_3]$$

$$\xrightarrow{\begin{array}{cc}H^+ & H_2O\end{array}}$$

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]. $[Rh\{(2R,3R)-Ph_2PCHMeCHMePPh_2\}(nbd)][ClO_4]$ 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

(65)

(66)

(67)

$\left[ClO_4 \right]^-$

(68; S = MeOH or MeCN)

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

The complexes, [(cod)Rh(ppfa)]X (X = [ClO₄], [BF₄] or [BPh₄]),
[(nbd)Rh(ppfa)][ClO₄] and [Rh(CO)Cl(ppfa)] (ppfa = (69)) have been found to

(69)

catalyse the asymmetric hydrogenation of PhCH=C(COOH)(NHCOR) and
CH₂=C(COOH)(NHCOR). The X-ray structure of [(nbd)Rh(ppfa)][PF₆] 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;
[RhClL₂], [H₂RhClL₃], [H₂RhClL₂], [H₂RhClL₂(C₂H₄)] and [HRhClL₂(C₂H₅)] (L =
Ph₃), which are possible intermediates involved in the hydrogenation of alkenes
catalysed by Wilkinson's catalyst [196]. [Rh(py)₄Cl₂]Cl with en or 1,3-pn were
effective for the Na[BH₄] 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, $(3,3-(PPh_3)_2-4-C_5H_5N-3,1,2-RhC_2B_9H_{10})$, 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

(CO₂)

R₃P — Rh — PR₃

R₃P   Cl

C O₂

R₃P   PR₃
    Rh
R₃P   Cl

O P R₃

PR₃

OPR₃   PR₃
    Rh
R₃P   Cl

CO

R₃PO   CO   PR₃
      Rh
R₃P   Cl

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$_2$(η^5-C$_5$Me$_5$)$_2$(OH)$_3$]Cl and [Rh$_2$(η^5-C$_5$Me$_5$)$_2$Cl$_4$] 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, $BuNH_2$ + $EtCO_2R$ ⟶ $BuNHCOEt$ + 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. $R_3'SiOH$ + R_2SiH_2 ⟶ $R_2HSiOSiR_3'$ + H_2

(R_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. $\quad$ HO[Me$_2$SiO]$_n$H + H$_2$SiR$_2$ $\longrightarrow$ HO[Me$_2$SiO]$_n$SiR$_2$H $\xrightarrow{\;-H_2\;}$ [Me$_2$SiO]$_n$[R$_2$SiO]

$$\text{(R}_2 = \text{Et}_2, \text{ Pr}_2 \text{ or MePh; } n = 2, 3 \text{ or 4)}$$

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$_2$O)]$^-$, [IrCl$_4$(H$_2$O)$_2$] 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

$$6[\text{IrCl}_6]^{2-} + 4\text{H}_2\text{O} + [\text{SCN}]^- \longrightarrow 6[\text{IrCl}_6]^{3-} + [\text{SO}_4]^{2-} + [\text{CN}]^- + 8\text{H}^+ \text{ and}$$

$$2[\text{IrBr}_6]^{2-} + 2\text{I}^- \longrightarrow 2[\text{IrBr}_6]^{3-} + \text{I}_2 \text{ have been evaluated for aqueous solution}$$
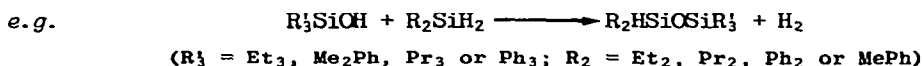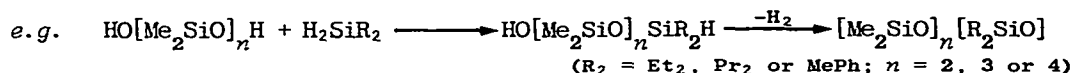
[221].

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$_2$O$_5$ [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-C$_6$H$_4$(SR)$_2$; R = Me or Ph; n = 2 or 3), *cis-* and *trans-*[Ir(SMe$_2$)$_2$Cl$_4$]$^-$, [Ir(SPh$_2$)$_2$Cl$_4$]$^-$ 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 ^{1}H 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$_3$X$_3$] (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]

(70)   (71)
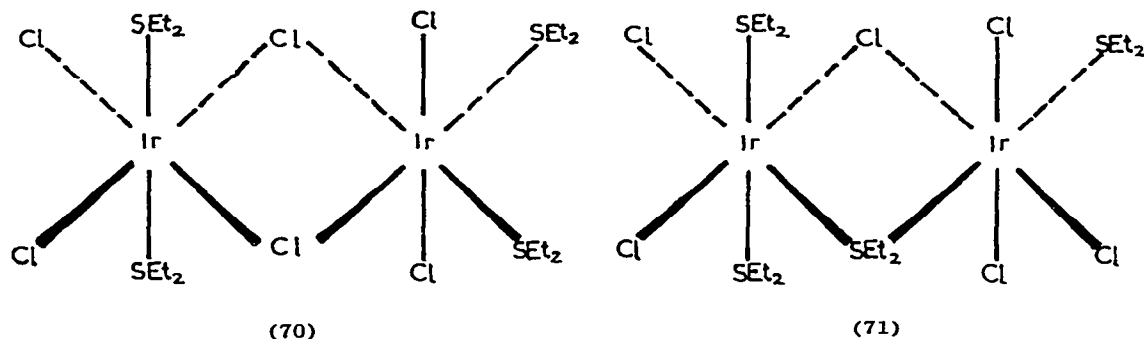
have been determined and the photolysis of mer-$[IrCl_3(SEt_2)_3]$ in benzene or toluene solution gives rise to a mixture of $[Ir_2(\mu\text{-}Cl)_2Cl_4(Et_2S)_4]$ and $[Ir_2Cl_5(\mu\text{-}Cl)(\mu\text{-}Et_2S)(Et_2S)_3]$ [227].

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$_2$O, 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$_2$O, 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-Me$_2$pzl)$_3$ 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$_2$CCF$_3$, respectively [41].

5.11.2.2 Complexes with nitrogen-phosphorus donor ligands

A mixture of $[Ir_2Cl_2(C_8H_{14})_4]$ (C$_8$H$_{14}$ = cyclooctene), mqpH (72), and pyridine-d_5 in hexane produces the complex $[IrClH(mqp)(NC_5D_5)_2]$. Although the metal-hydride

(72)
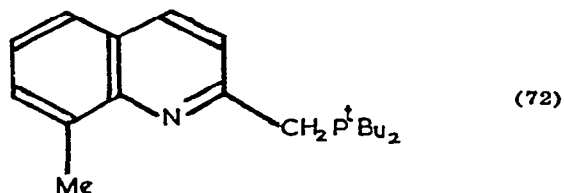
stretch can be easily identified in the IR spectrum at 2180 cm^{-1} and the NMR spectrum indicates that the pyridine ligands are mutually *cis*, it is not clear to which of the remaining possible six-coordinate isomers the structure belongs [104].

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 $[IrCl(2-thpy)_2]_2$ (73). This material combines readily with L (L = PBu_3,
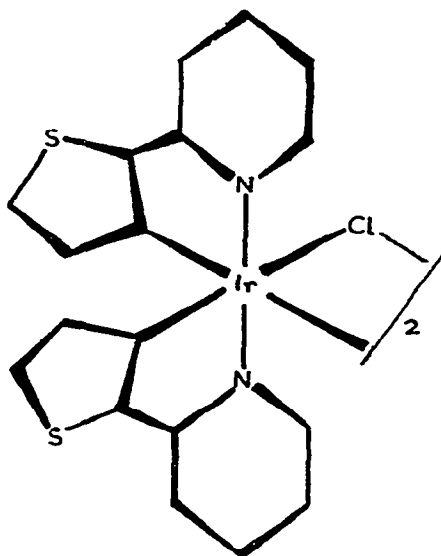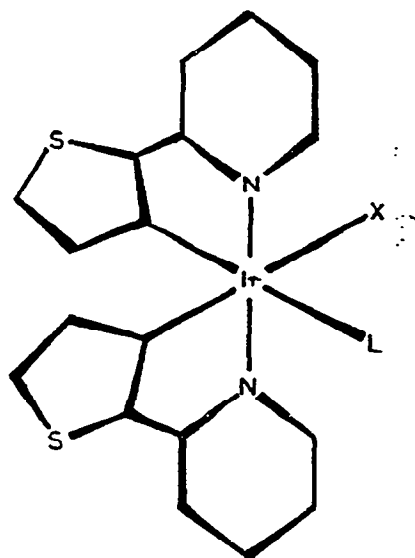
(73)   (74; L = PBu_3, py or dmso)

py or dmso) to give $[IrCl(L)(2-thpy)_2]$. The spectroscopic properties of these complexes are consistent with structure (74) [231]. The bromide and iodide analogues of $[IrCl(PBu_3)(2-thpy)_2]$ were prepared by halide exchange reactions.

5.11.3 Complexes with phosphorus donor ligands

5.11.3.1 Phosphine and diphosphine complexes

[Ir(cod)Cl]$_2$ reacts with PMe$_2$Ph in MeCN to give the red species [Ir(PMe$_2$Ph)$_4$]$^+$, which will react with dihydrogen to give cis-[IrH$_2$(PMe$_2$Ph)$_4$]$^+$. In the absence of dihydrogen and after prolonged heating under reflux, the cyclometallated complex, fac-[IrH(PMe$_2$C$_6$H$_4$)(PMe$_2$Ph)]$^+$ is produced [232]. The complex (75) has a
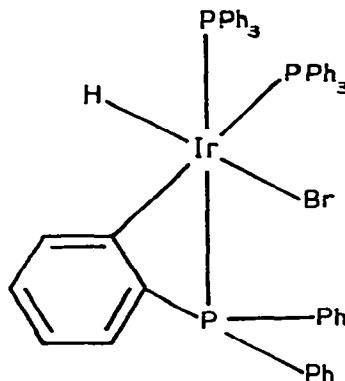
(75)

distorted octahedral coordination geometry about the central iridium atom [233].

The mixed-metal complex [(Ph$_3$P)$_2$Pt(μ-Cl)$_2$Ir(PMe$_2$Ph)Cl$_2$]$^+$ [IrCl$_4$(PMe$_2$Ph)$_2$]$^-$ has been synthesised [234]. [(bdpps)Cl$_3$Ir] (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$_2$COR) (R = Ph or CMe$_3$) gives [IrCl$_2${(CMe$_3$)$_2$PCH=C(O)R}{P(CMe$_3$)(CH$_2$COR)}]. 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$_6$],
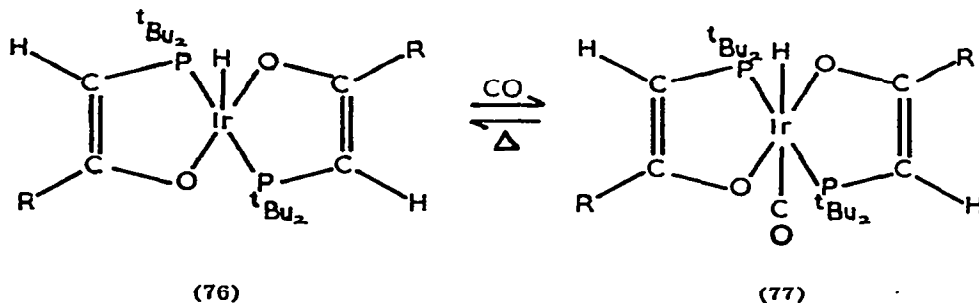
(76)   (77)

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].

5.11.4 Complexes with Group IV donor ligands

5.11.4.1 Complexes with carbon donor ligands

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

(78)
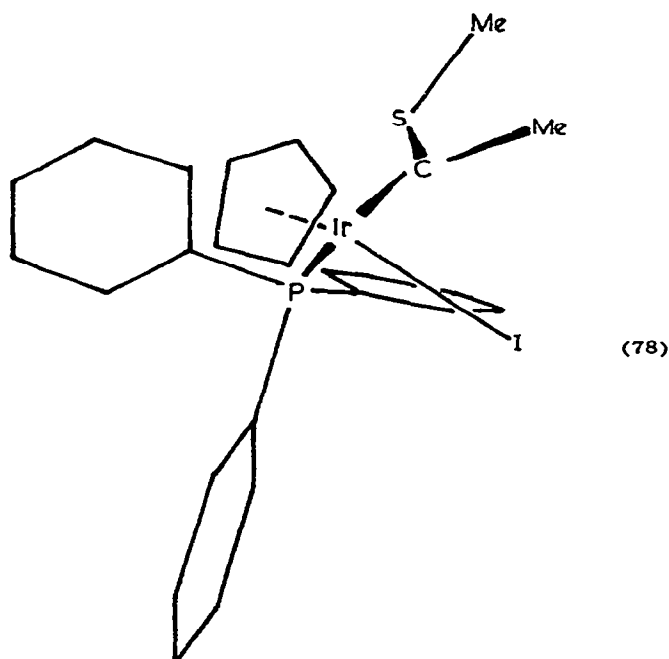
contains the methyl(methylthio)carbene ligand. The bonding of the C(Me)SMe group indicates that the complex should be formulated as a C(Me)=SMe complex of iridium(III) [235].

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 $[IrH(CHO)(PMe_3)_4]$ 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)
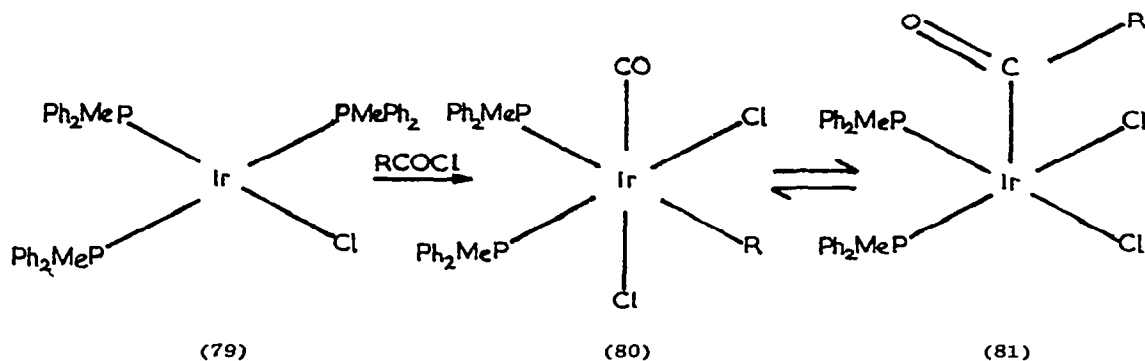
coordinate alkyliridium complexes, cis-[IrCl$_2$R(CO)(PMePh$_2$)$_2$] (80). Solutions of these complexes equilibriate rapidly with the five-coordinate species (81). Species (80) is reported to isomerise at room temperature into the $trans$-isomer (with respect to the phosphine ligands) [237].

The carbon dioxide complex [Ir(dmpe)$_2$Cl(CO$_2$)] reacts with MeFSO$_3$ to give the methoxycarbonyl species, [IrCl(CO$_2$Me)(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$_2$B$_9$H$_{10}$ - and C$_2$B$_9$H$_{11}$ -anions are discussed in Section 5.15.2.

5.11.4.3 Complexes with tin donor ligands

On addition of [Me$_4$N]Br, K$_2$[IrBr$_6$] reacts with SnBr$_2$ in aqueous solutions containing HBr to give [Me$_4$N]$_3$[IrBr$_4$(SnBr$_3$)$_2$].[Me$_4$N]$_3$[IrBr(SnBr$_3$)$_5$] is reported to hydrolyse to give H$_3$[Ir{Sn(OH)$_3$}$_5$Br].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

(82)   (83)
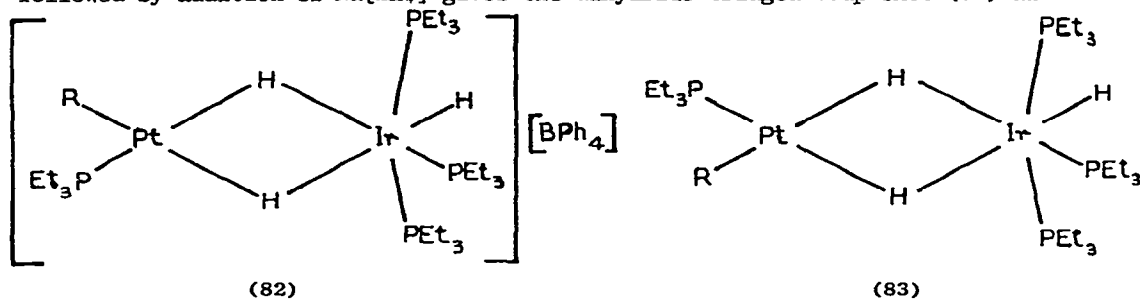
(83) which were characterised by NMR spectroscopy [242]. X-ray and molecular structures of [Ir₂H₅(dppp)][BF₄] and [Ir₃H₇(dppp)][BF₄]₂ have been reported, along with their dynamic NMR properties [243].

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, PMe₂Ph or PMe₃)

(84)   (85)
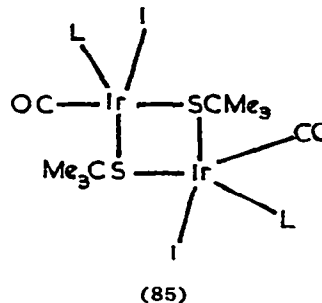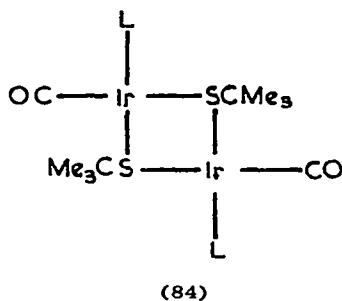
gives (85) [245].

5.12.2 Alkyl thiol complexes

[Ir(μ-SCMe₃)(CO)₂]₂ combines with hexafluorobut-2-yne to give [Ir₃(μ—SCMe₃)₃(CO)₆(μ-C₄F₆)]. 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 [Ir₃(μ—SCMe₃)₃(μ-C₂(CO₂Me)₂(CO)₆)]. However, [Ir(μ-SCMe₃)₂(CO){P(OMe)₃}₃]₂ reacts with hexafluorobut-2-yne to produce the dinuclear [Ir₂(μ-SCMe₃)₂(μ-C₄F₆)(CO)₂{P(OMe)₃}₃]₂, with C₂(CO₂Me)₂ to produce the tetranuclear [Ir₂(μ-SCMe₃)₂(μ-C₄F₆)(CO)₂{P(OMe)₃}₃]₂, and with C₂(CO₂Me)₂ to produce [Ir₂(μ-SCMe₃)₂{(μ-C₂(CO₂Me)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(PPh₃)₂L] complexes, (L = CO, CS, N₂, C₂H₄, PPh₃, NO⁺, N₂Ar⁺, Me₃CNC, N₂C₅Cl₄ or N₂C₅Br₄) have been correlated in order to assess the *trans*-influence of the ligands L [247].

Oxidation of [(4-CH₃C₆H₄NH₂)Ir(CO)₂Cl], with an excess of I₂ in dichloromethane, produces the six-coordinate complex, [(4-CH₃C₆H₄NH₂)Ir(CO)₂ClI₂]. The electronic spectrum of a mixture of these two complexes in CH₂Cl₂ reveals an absorption band at 490 nm that is not present in the spectra of the individual components. The adduct [(4-CH₃C₆H₄NH₂)₂Ir₂(CO)₄Cl₂I₂], 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, CH₃CO, Pr, Et, CHMe₂ or C₆H₅CH₂) to *trans*-[IrCl(CO)(PMe₃)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)L₂] (L = tertiary phosphine), have been examined by NMR spectroscopy [250]. Spin-trapping experiments for the oxidative addition of MeI, PhCH₂Br and Ph₂CHBr on *trans*-[Ir(CO)Cl(PPh₃)₂] have been monitored by EPR spectroscopy [251].

(86)
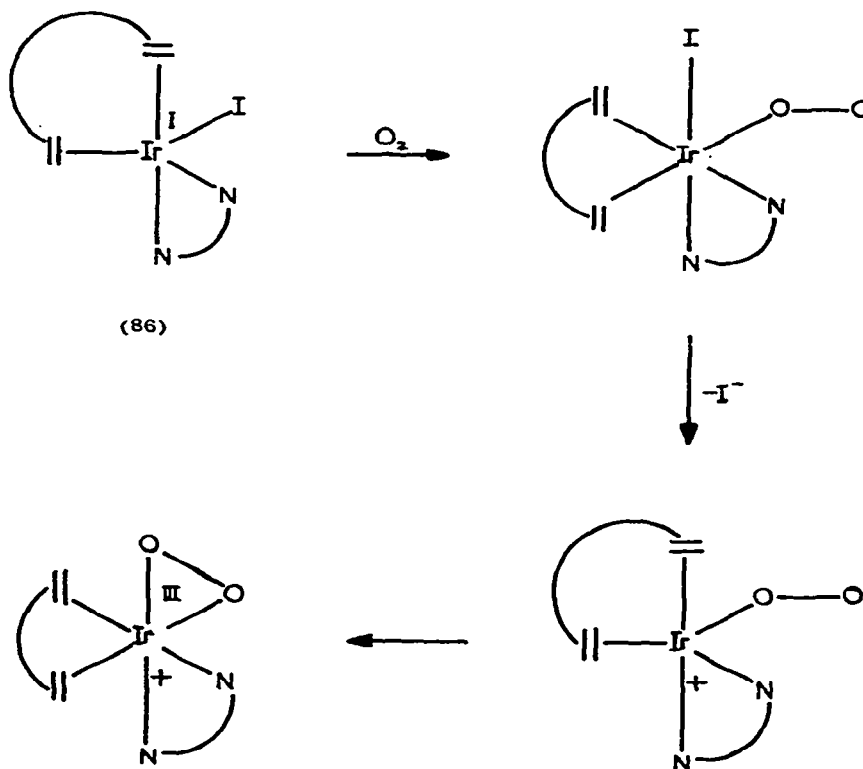
SCHEME VII: Preparation and Reactions of Iridium-peroxo complexes.

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$\frac{1}{2}$] (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$_3$)$_2$(μ–SO$_2$)$_2$] with para–substituted aryldiazonium salts gives [Ir$_2$(CO)$_4$(PPh$_3$)$_2$(μ–N$_2$C$_6$H$_4$R)(μ–SO$_2$)][BF$_4$]. Treatment of the substituted diazo complex with H[BF$_4$] gives the protonated species [Ir$_2$(CO)$_4$(PPh$_3$)$_2$(μ–N=NHC$_6$H$_4$R)(μ–SO$_2$)][BF$_4$] and alkyl halides give the halogen–bridging [Ir$_2$(CO)$_2$(PPh$_3$)$_2$(μ–X)(μ–N$_2$C$_6$H$_4$R)(μ–SO$_2$)] [253]. Addition of PR$_3$ (PMe$_3$, PMe$_2$Ph, P(NMe$_2$)$_3$, PPh$_3$ or P(OMe)$_3$) to [Ir$_2$(μ–SCMe$_3$)$_2$(CO)$_4$] gives [Ir$_2$(μ–SCMe$_3$)$_2$(CO)$_2$(PR$_3$)$_2$] [254]. (Me$_2$NCS)$_2$S reacts with [(Ph$_3$P)Ir(CO)Cl] to give [(Ph$_3$P)Ir(η^2–CSNMe$_2$)(S$_2$CNMe$_2$)(CO)]X (X = Cl or [PF$_6$]) [85]. [Ir$_2$(μ–S)(CO)$_2$(μ–dppm)$_2$] is formed from [Ir$_2$Cl(CO)$_4$(μ–dppm)$_2$]$^+$ [IrCl$_2$(CO)$_2$]$^-$ and sulphide and reacts with CO to form (87), containing the CO molecule in the *endo*-pocket.

(87)
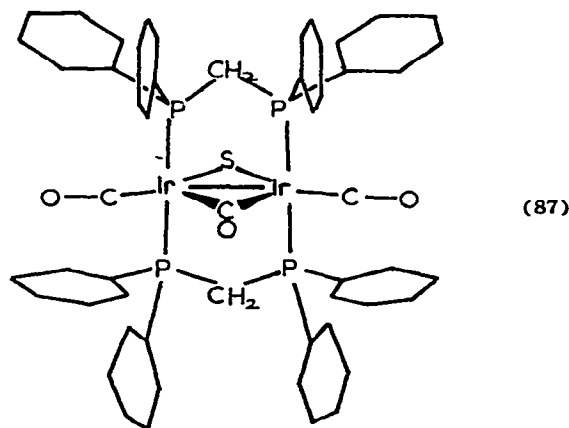
Oxidative addition of H$_2$ to [Ir$_2$(μ–S)(CO)$_2$(μ–dppm$_2$)] gives [Ir$_2$H$_2$(μ–S)(CO)$_2$(μ–dppm)$_2$] [255]. [Ir(S$_2$CPPh$_3$)(CO)(PPh$_3$)$_2$][BF$_4$] consists of a distorted trigonal–bipyramid of donor atoms about the metal, containing the

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 $4-CH_3C_6H_4N_2=NC_6H_4CH_3-4$ (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:
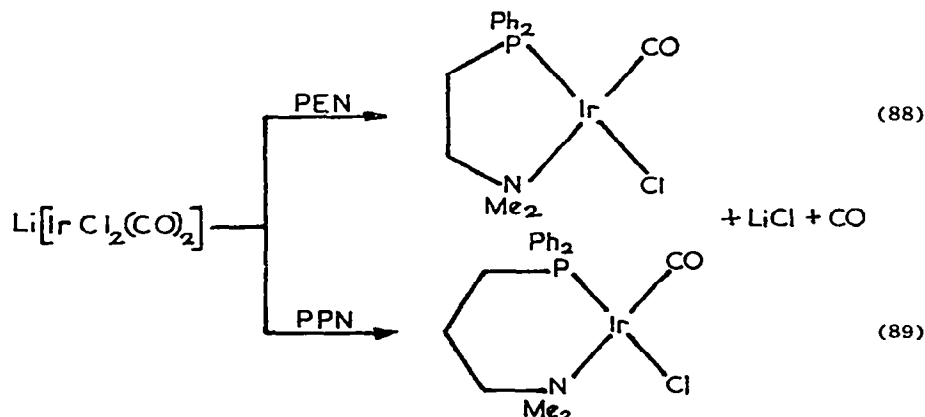
The crystal structure of the complex (90) has been determined and the IR and ^{31}P NMR spectral data suggest that all three complexes (88, 89 and 90) possess the same stereochemistry [261].

(90)
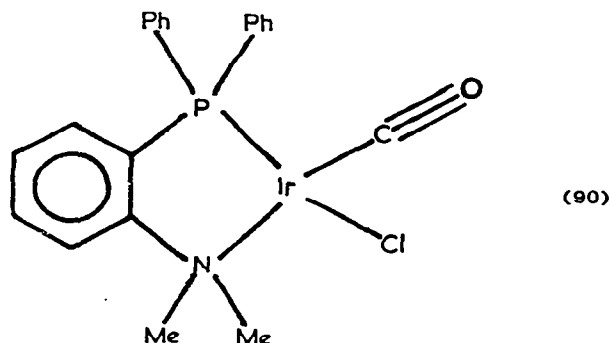
5.13.3.3 Complexes with phosphorus, arsenic or phosphorus-arsenic donor ligands

R_2PNHPR_2 (R = Ph) reacts with [(μ-Cl)$_2$Ir$_2$(C$_8$H$_{12}$)$_2$] to give [Ir(R$_2$PNHPR$_2$)$_2$]Cl, which reacts with CO to produce [Ir(CO)(R$_2$PNHPR$_2$)$_2$]Cl and which is also formed from the combination of [Ir(CO)(PPh$_3$)$_2$Cl] and [Ir(CO)$_2$(4–H$_2$NC$_6$H$_4$CH$_3$)Cl] with R$_2$PNHPR$_2$. Oxidative addition of O$_2$, CS$_2$, I$_2$ or (SCN)$_2$ to [Ir(R$_2$PNHPR$_2$)]Cl yields [Ir(O$_2$)(R$_2$PNHPR$_2$)$_2$]Cl, [Ir(η^2–CS$_2$)(R$_2$PNHPR$_2$)]Cl, [Ir(I$_2$)(R$_2$PNHPR$_2$)$_2$]Cl or [Ir(SCN)$_2$(R$_2$PNHPR$_2$)$_2$]Cl, respectively [262].

Trans-[IrCl(CO)(L–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$_2$Cl$_2$(tddx)] combines with dihydrogen to produce [Ir$_2$Cl$_2$(tddx)H$_4$], with dioxygen to produce [Ir$_2$Cl$_2$(tddx)(O$_2$)$_2$], with CO to give [Ir$_2$Cl$_2$(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(μ–SCMe$_3$)(CO)(PR$_3$)]$_2$ (R = Me, Ph or OMe) to give the π-bonded 1:1 adducts, [Ir(μ–SCMe$_3$)(CO)(PR$_3$)(tcne)]$_2$ [263]. [Ir(nbd)$_3$Cl]$_x$, obtained from the reaction of [Ir$_2$(cod)$_2$Cl$_2$] with an excess of nbd, undergoes the reactions shown in Scheme VIII [264].

The crystal structure of [Ir(CO)$_3$Cl] has been determined [265]. The reactions

$[Ir(C_7H_8)_3(PMe_3)Cl]$ $[Ir(nbd)_3(acac)]$

PMe$_3$ $(CH_3CO)_2CH_2/Na_2CO_3$

$[Ir(nbd)_3Cl]_x$

CO/PPh$_3$ PPhMe$_2$

$[Ir(nbd)_3(CO)_2(PPh_3)Cl]$ $[Ir(nbd)_3(PPhMe_2)Cl]$
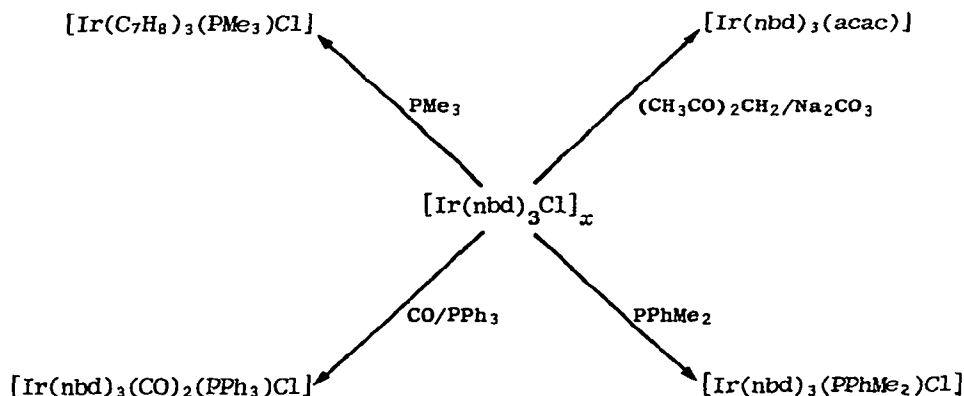
SCHEME VIII: Some reactions of $[Ir(nbd)_3Cl]_x$.

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 $[Ir_2(CO)_3(Me_3NC)Cl(L_2)_2]X$, $[Ir_2(CO)_2(Me_3NC)_2Cl(L-L)_2]X$ (L-L = dppm, X = [BPh$_4$]; L-L = dpam, X = [BF$_4$]) and $[Ir_2(CO)(Me_3NC)_4(L-L)_2][BPh_4]_2$ have been obtained from the reactions of Me$_3$NC with the A-frame complexes, $[Ir_2(CO)_3Cl(L-L)_2]X$ [267]. $[Ir(cp)(CO)_2]$ combines with CF$_3$C≡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$_3$C≡CCH$_3$ produces (91) and a small quantity of C$_6$Me$_6$ [268].

(91)
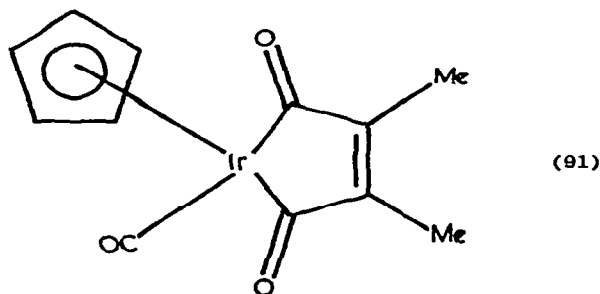
5.13.4.2 Carborane complexes

The oxidative addition of HCl, HBr, HI, Cl$_2$ and Br$_2$ to square-planar d^8 carborane-iridium(I) complexes, trans-$[Ir(σ-carborane)(CO)L_2]$ (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, $[IrHX(σ-carborane)(CO)L_2]$, undergo reductive elimination of the carborane [269]. Reactions of

[Ir(cod)(PR₃)₂][*nido*-7,8-C₂B₉H₁₂] are discussed in Section 5.15.2.

5.13.5 Mercury complexes

The formation of complexes of the type $[\{Ir(CO)Cl(PPh_3)_2\}_n Hg][ClO_4]_2$ ($n =$ 1-3) and $[\{Ir(CO)Cl(PPh_3)_2\}_3 Hg(ClO_4)_x][ClO_4]_{2-x}$ has been observed spectro-scopically and polarographically. $[\{Ir(CO)Cl(PPh_3)_2\}_4 Hg][ClO_4]_2$ 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

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

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)$_3$I], 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)$_2$I$_2$]. The minor product {ν(CO) = 2125, 2090 and 1710 cm^{-1}} has been tentatively formulated as [{Ir(COMe)(CO)$_2$I$_2$}$_n$] (n = 1 or 2) [272].

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$_2$(μ-S)(CO)$_2$(μ-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$_2$Cl(CO)$_3$(μ-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$_2$B$_9$H$_{11}$, has been prepared [274]. The complex and related materials may be prepared as shown in Scheme X.

nido-3,9-[(H)$_2$(PR$_3$)$_2$Ir]-3,9-μ-(H)$_2$-7,8-C$_2$B$_9$H$_{10}$

[Ir(cod)(PR$_3$)$_2$][nido-7,8-C$_2$B$_9$H$_{12}$] ———— H$_2$ ————

Δ

closo-3,3-(PR$_3$)$_2$-3-H-3,1,2-IrC$_2$B$_9$H$_{11}$

(R = Ph or p-tolyl)
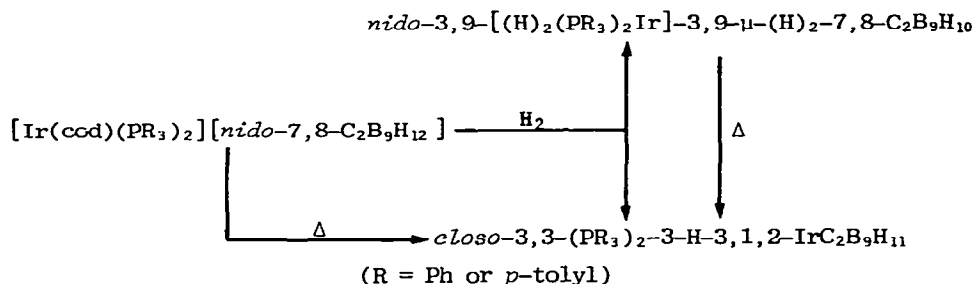
SCHEME X: Preparation of iridium-carboborane catalysts.

[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$_2$O ————→RCH$_2$OH + RCO$_2$H, is catalysed by [Ir$_2$(C$_5$Me$_5$)$_2$Cl$_4$] [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$_2$PCH$_2$CH$_2$CH$_2$- 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].

REFERENCES

1 W.A. Sunder, A.L. Wayda, D. Distefano, W.E. Falconer and J.E. Griffiths, *J. Fluorine Chem.*, 14 (1979) 299.

2 V.A. Shipachev, S.V. Zemskov and S.V. Tkachev, *Koord. Khim.*, 6 (1980) 1237.

3 B.I. Peshchevitskii, S.V. Zemskov, A.P. Sadovskii, E.A. Kravtsova and V.N. Mit'kin, *Koord. Khim.*, 5 (1979) 1838.

4 M. Walewski and J. Dobrowolski, *Zesz. Nauk Politech. Slask., Chem.*, 88 (1979) 5.

5 M. Walewski, H. Warachim and J. Dobrowolski, *Zesz. Nauk Politech. Slask., Chem.*, 639 (1980) 67.

6 I.S. Shaplygin and V.B. Lazarev, *Zh. Neorg. Khim.*, 25 (1980) 906.

7 L.L. Kochergina, V.V. Fomichev, O.I. Kondratov, I.S. Shaplygin and K.I. Petrov, *Zh. Neorg. Khim.*, 25 (1980) 2082.

8 Yu.N. Kukushkin and O.V. Stefanova, *Koord. Khim.*, 5 (1979) 1379.

9 L.H. Skibsted and P.C. Ford, *Acta Chem. Scand. A*, 34 (1980) 109.

10 R. van Eldik, D.A. Palmer and G.M. Harris, *Inorg. Chem.*, 19 (1980) 3673.

11 K. Wieghardt, W. Schmidt, R. van Eldik, B. Nuber and J. Weiss, *Inorg. Chem.*, 19 (1980) 2922.

12 R. van Eldik, D.A. Palmer, H. Kelm and G.M. Harris, *Inorg. Chem.*, 19 (1980) 3679.

13 M.B. Hursthouse, K.M. Abdul Malik, D.M.P. Mingos and S.D. Willoughby, *J. Organomet. Chem.*, 192 (1980) 235.

14 J.R. Barnes, P.L. Goggin and R.J. Goodfellow, *J. Chem. Res. Synop.*, 4 (1979) 118.

15 B.R. James and R.H. Morris, *Can. J. Chem.*, 58 (1980) 399.

16 B.R. James, R.H. Morris, F.W.B. Einsten and A. Willis, *J. Chem. Soc., Chem. Commun.*, (1980) 31.

17 C. Preti and G. Tosi, *Aust. J. Chem.*, 33 (1980) 57.

18 D.J. Radanovic, K.D. Gailey, M.I. Djuran and B.E. Douglas, *J. Coord. Chem.*, 10 (1980) 115.

19 T. Glowiak, M. Kubiak, T. Szymanska-Buzar and B. Jezowska-Trzebiatowska, *Int. Semin. Cryst. Chem. Coord. Organomet. Compd. (Proc.)*, 3rd (1977) 211.

20 A.E. Bukanova, I.V. Prokof'eva and L.K. Shubochkin, *Zh. Neorg. Khim.*, 25 (1980) 1575.

21 V. Balasubramanian, N.S. Dixit and C.C. Patel, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 152.

22 R.N. Mukherjee and P.K. Gogoi, *Indian J. Chem. Sect. A*, 19 (1980) 455.

23 K.S. Siddiqi, P. Khan, N. Singhal and S.A.A. Zaidi, *Indian J. Chem. Sect. A*, 19 (1980) 265.

24 J.S. Dwivedi and U. Agarwala, *Indian J. Chem. Sect. A*, 17 (1979) 276.

25 E. Ciliberto, L.L. Constanzo, I. Fragala and G. Grannozzi, *Inorg. Chim. Acta*, 44 (1980) L25.

26 J. Kopf, K. von Deuten and G. Klar, *Cryst. Struct. Commun.*, 8 (1979) 1011.

27 B. Singh, M.M.P. Bukhaiyar, R.K. Mehra and R.J. Sinha, *Indian J. Chem. Sect. A*, 17 (1979) 520.

28 A.K. Nigam and G.D. Tiwari, *J. Indian Chem. Soc.*, 57 (1980) 223.

29 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.*, 10 (1980) 269.

30 S.A. Gardner, *J. Organomet. Chem.*, 190 (1980) 289.

31 W.W. Wendlandt, *Thermochim. Acta*, 39 (1980) 313.

32 S.F. Clark and J.D. Petersen, *Inorg. Chem.*, 19 (1980) 2917.

33 L.H. Skibsted and P.C. Ford, *Inorg. Chem.*, 19 (1980) 1828.

34 M.A. Bergkamp, R.J. Watts and P.C. Ford, *J. Am. Chem. Soc.*, 102 (1980) 2627.

35   R. Ballardini and G. Verani, *J. Am. Chem. Soc.*, 102 (1980) 1719.

36   T. Kabayashi, C.V. Shank and Y. Ohhashi, *Kosoku Hanno Toronkai Koen Yokoshu*, 14th (1979) 1.

37   Yu.N. Kukushkin, G.N. Portnov, T.O. Blyumental and S.A. Simanova, *Zh. Obshch. Khim.*, 50 (1980) 1108.

38   P.K. Bhattacharya, *J. Chem. Soc., Dalton Trans.*, (1980) 810.

39   K. Wieghardt, W. Schmidt, B. Nuber, B. Prikner and J. Weiss, *Chem. Ber.*, 113 (1980) 36.

40   I.A. Baidana, N.V. Podeberezskaya, A.V. Belyaev and V.V. Bakakin, *Zh. Struct. Khim.*, 20 (1979) 1096.

41   S. May, P. Reinsalu and J. Powell, *Inorg. Chem.*, 17 (1980) 1582.

42   K.G. Srinivasamurthy, N.M.N. Gowda and G.K.N. Reddy, *Indian J. Chem. Sect. A*, 18 (1979) 322.

43   M.E. Rusanovskii, I.D. Samus, I.N. Kiselava and N.V. Belov, *Dokl. Akad. Nauk S.S.S.R.*, 250 (1980) 361.

44   N.I. Belichuk and O.A. Bologa, *Zh. Neorg. Khim.*, 24 (1979) 3060.

45   S.K. Sahni, P.C. Jain and V.B. Rana, *Indian J. Chem. Sect. A*, 18 (1979) 161.

46   K.M. Savostina, O.A. Shpigun and T.V. Chebrikova, *Zh. Neqrg. Khim.*, 24 (1979) 2723.

47   M.F. McGuiggan, D.H. Doughty and L.H. Pignolet, *J. Organomet. Chem.*, 185 (1980) 241.

48   G.B. Robertson, P.A. Tucker and P.O. Whimp, *Inorg. Chem.*, 19 (1980) 2307.

49   C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell and B.L. Shaw, *J. Am. Chem. Soc.*, 102 (1980) 4373.

50   T.B. Marder, J.A. Long and M.F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, (1980) 677.

51   H.D. Empsall, S. Johnson and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1980) 302.

52   D.H.M.W. Thewissen, *J. Organomet. Chem.*, 192 (1980) 115.

53   H. Werner, R. Feser and R. Werner, *J. Organomet. Chem.*, 181 (1979) C7.

54   Y. Ohtani, A. Yamagishi and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3747.

55   I.W. Nowell, G. Fairhurst and C. White, *Inorg. Chim. Acta*, 41 (1980) 61.

56   T.S. Khodashova and M.A. Porai-Koshits, *Int. Semin. Cryst. Chem. Coord. Organomet. Compd. (Proc.)*, 3rd (1977) 142.

57   T. Kimura, *Sci. Pap. Inst. Phys. Chem. Res. Jpn.*, 73 (1979) 31.

58   A. Nutton, P.M. Bailey, M.C. Braund, R.J. Goodfellow, R.S. Thompson and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1980) 631.

59   I.B. Baronovskii, N.N. Chalisova and G.Ya. Mazo, *Zh. Neorg. Khim.*, 24 (1979) 3395.

60   I.B. Baronovskii, S.S. Abdullaev and R.N. Shchelokov, *Zh. Neorg. Khim.*, 24 (1979) 3149.

61   F.A. Cotton and T.R. Felthouse, *Inorg. Chem.*, 19 (1980) 320.

62   F.A. Cotton and T.R. Felthouse, *Inorg. Chem.*, 19 (1980) 323.

63   M. Moszner, T. Glowiak and J.J. Ziolkowski, *Int. Semin. Cryst. Chem. Coord. Organomet. Compd. (Proc.)*, 3rd (1977) 235.

64   A.M. Dennis, R.A. Howard, K.M. Kadish, J.L. Bear, J. Brace and N. Winograd, *Inorg. Chim. Acta*, 44 (1980) L139.

65   V.I. Nefedov, Ya.V. Salyn and I.B. Baranovskii, *Zh. Neorg. Khim.*, 25 (1980) 216.

66   G.Ya. Mazo, I.B. Baranovskii and R.N. Shchelokov, *Zh. Neorg. Khim.*, 24 (1979) 3330.

67   F.A. Cotton and T.R. Felthouse, *Inorg. Chem.*, 19 (1980) 2347.

68   R.N. Shchelokov, A.G. Maiorova, G.N. Kuznetsova, I.F. Golovaneva and O.N. Evstafeva, *Zh. Neorg. Khim.*, 25 (1980) 1891.

69   M. Berry, C.D. Garner, I.H. Hillier, A.A. MacDowell and W. Clegg, *J. Chem. Soc., Chem. Commun.*, (1980) 494.

70   A.M. Dennis, R.A. Howard, J.L. Bear, J.D. Korp and I. Bernal, *Inorg. Chim. Acta*, 37 (1979) L561.

71   K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, (1980) 186.

72   B.T. Khan, M.R. Somayajula and M.M. Taqui, *Indian J. Chem. Sect. A*, 17

(1979) 359.

73 M.R. Moller, M.A. Bruck, T. O'Connor, F.J. Armatis, E.A. Knolinskii, N. Kottmair and R.S. Tobias, *J. Am. Chem. Soc.*, 102 (1980) 4589.

74 F. Sakurai, H. Suzuki, Y. Moro-oka and T. Ikawa, *J. Am. Chem. Soc.*, 102 (1980) 1749.

75 P. Albano, M. Aresta and M. Manassero, *Inorg. Chem.*, 19 (1980) 1069.

76 F. Pruchnik and K. Wajda, *Inorg. Chim. Acta*, 40 (1980) 203.

77 Z. Nagy-Magos, P. Kvintovics and L. Marko, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 186.

78 H. van Dam, A. Terpstra, D.J. Stufkens and A. Oskam, *Inorg. Chem.*, 19 (1980) 3448.

79 C.E. Dean, R.D.W. Kemmitt, D.R. Russell and M.D. Schilling, *J. Organomet. Chem.*, 187 (1980) C1.

80 J.G. Leipoldt, S.S. Basson, G.J. Lamprecht, L.D.C. Bok, J.J.J. Schlebusch, *Inorg. Chim. Acta*, 40 (1980) 43.

81 D.K. Dutta and M.M. Singh, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 244.

82 H. Schumann, G. Cielusek, J. Pickardt, *Angew. Chem.*, 92 (1980) 60.

83 H. Werner, O. Kolb, R. Feser and U. Schubert, *J. Organomet. Chem.*, 191 (1980) 283.

84 D.H.M.W. Thewissen, *J. Organomet. Chem.*, 188 (1980) 211.

85 W.K. Dean, *J. Organomet. Chem.*, 190 (1980) 353.

86 H. Werner and O. Kolb, *Angew. Chem.*, 91 (1979) 930.

87 K. Goswami and M.M. Singh, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 83.

88 M.V. Klyuev, B.G. Rogachev, Yu.M. Shul'ga and M.L. Khidekel, *Izv. Akad. Nauk S.S.S.R, Ser. Khim.*, 8 (1979) 1869.

89 Yu.A. Simanov, L.A. Nemchinova and O.A. Bologa, *Kristallografiya*, 24 (1979) 829.

90 K.K. Pandey and U.C. Agarwala, *Z. Anorg. Allg. Chem.*, 457 (1979) 235.

91 P.N.A. Seth, A.E. Underhill and D.M. Watkins, *J. Inorg. Nucl. Chem. Lett.*, 16 (1980) 1.

92 A.J. Deeming and I.P. Rothwell, *J. Chem. Soc., Dalton Trans.*, (1980) 1259.

93 A.M. Abeysekera, R. Grigg, J. Trocha-Grimshaw and T.J. King, *J. Chem. Soc Soc., Perkin Trans. 1*, 9 (1979) 2184.

94 K.D. Schramm and J.A. Ibers, *Inorg. Chem.*, 19 (1980) 2435.

95 J. Kopf, J. Klaus and H. Tom Dieck, *Cryst. Struct. Commun.*, 9 (1980) 783.

96 A. Efraty, I. Feinstein, F. Frolow and A. Goldman, *J. Chem. Soc., Chem. Commun.*, (1980) 864.

97 A. Efraty, I. Feinstein, F. Frolow and L. Wackerle, *J. Am. Chem. Soc.*, 102 (1980) 6343.

98 A. Efraty, I. Feinstein, L. Wackerle and F. Frolow, *Angew. Chem.*, 92 (1980) 649.

99 K.R. Mann, M.J. DiPierro and T.P. Gill, *J. Am. Chem. Soc.*, 102 (1980) 3965.

100 K.R. Mann, J.A. Thich, R.A. Bell, C.L. Coyle and H.B. Gray, *Inorg. Chem.*, 19 (1980) 2462.

101 I.S. Sigal, K.R. Mann and H.B. Gray, *J. Am. Chem. Soc.*, 102 (1980) 7252.

102 H.B. Gray, V.M. Miskowski, S.J. Milder, T.P. Smith, A.W. Maverick, J.D. Buhr, W.L. Gladfelter, J.S. Sigal and K.R. Mann, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 819.

103 S.J. Milder, R.A. Goldbeck, D.S. Kliger and H.B. Gray, *J. Am. Chem. Soc.*, 102 (1980) 6761.

104 A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 1974.

105 K. Kurtev, D. Ribola, R.A. Jones, D.J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1980) 55.

106 Yu.N. Kukushkin, A.I. Osokin, L.I. Danilina and V.P. Kotel'nikov, *Zh. Neorg. Khim.*, 24 (1979) 2180.

107 J.P. Farr, M.O. Olmstead and A.L. Balch, *J. Am. Chem. Soc.*, 102 (1980) 6654.

108 M. Aresta and M. De Fazio, *J. Organomet. Chem.*, 186 (1980) 109.

314

109 M. Lewin, Z. Aizenshtat and J. Blum, *J. Organomet. Chem.*, 184 (1980) 255.
110 J.W. Diesveld, E.M. Menger, H.T. Edzes and W.S. Veeman, *J. Am. Chem. Soc.*, 102 (1980) 7935.
111 A. Del Pra, G. Zanotti and P. Segala, *Cryst. Struct. Commun.*, 8 (1979) 959.
112 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem. Soc., Dalton Trans.*, (1980) 511.
113 T. Yoshida, D.L. Thorn, T. Okano, S. Otsuka and J.A. Ibers, *J. Am. Chem. Soc.*, 102 (1980) 6451.
114 T. Yoshida, T. Okana, K. Saito and S. Otsuka, *Inorg. Chim. Acta*, 44 (1980) L135.
115 F. Pruchnik and T. Lis, *Inorg. Chim. Acta*, 40 (1980) 207.
116 J.F. Nixon, R.J. Suffolk, M.J. Taylor, J.G. Norman, D.E. Hoskins and D.J. Gmur, *Inorg. Chem.*, 19 (1980) 810.
117 J.C.T.R. Burckett St. Laurent, H.E. Hosseini, J. Sinclair and J.F. Nixon, *Inorg. Chim. Acta*, 44 (1980) L17.
118 A.J. Naaktgeboren, R.J.M. Nolte and W. Drenth, *J. Am. Chem. Soc.*, 102 (1980) 3350.
119 M. Cowie and S.K. Dwight, *Inorg. Chem.*, 19 (1980) 209.
120 M. Cowie and S.K. Dwight, *Inorg. Chem.*, 19 (1980) 2500.
121 M. Cowie and S.K. Dwight, *Inorg. Chem.*, 19 (1980) 2508.
122 B.R. James and D. Mahajan, *Can. J. Chem.*, 58 (1980) 996.
123 C.P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 102 (1980) 3637.
124 L.H. Pignolet, D.H. Doughty, S.C. Nowicki and A.L. Casalnuovo, *Inorg. Chem.*, 19 (1980) 2172.
125 J. Ellerman, E.F. Hohenberger, W. Kehr, A. Puerzer and G. Thiele, *Z. Anorg. Allg. Chem.*, 464 (1980) 45.
126 M.M. Taquikhan, R. Mohiuddin, M. Ahmed and A.E. Martell, *J. Coord. Chem.*, 10 (1980) 1.
127 J.T. Mague and S.H. De Vries, *Inorg. Chem.*, 19 (1980) 3743.
128 G. Balimann, L.M. Venanzi, F. Bachechi and L. Zambonelli, *Helv. Chim. Acta*, 63 (1980) 420.
129 W.A. Herrmann, J. Plank, M.L. Ziegler and B. Balbach, *J. Am. Chem. Soc.*, 102 (1980) 5906.
130 P.B. Hitchcock, M.F. Lappert, P. Terreros and K.P. Wainwright, *J. Chem. Soc., Chem. Commun.*, (1980) 1180.
131 D.W. Wertz and M.A. Moseley, *Inorg. Chem.*, 19 (1980) 705.
132 D.W. Wertz and M.A. Moseley, *Spectrochim. Acta, Sect. A*, 36 (1980) 467.
133 M.Z. Iqbal, *Arabian J. Sci. Eng.*, 5 (1980) 121.
134 J.F. Nixon, R.J. Suffolk, M.J. Taylor, J.G. Norman, Jr., D.E. Hoskins and D.J. Gmur, *Inorg. Chem.*, 19 (1980) 810.
135 C. Brown, B.T. Heaton, L. Longhetti, W.T. Povey and D.O. Smith, *J. Organomet. Chem.*, 192 (1980) 93.
136 K. Goswami and M.M. Singh, *J. Indian Chem. Soc.*, 56 (1979) 477.
137 S. Datta, K.K. Pandey and U.C. Agarwala, *Inorg. Chim. Acta*, 40 (1980) 65.
138 H. Behrens, J. Ellerman and E.F. Hohenberger, *Z. Naturforsch., Sect. B*, 35 (1980) 661.
139 G. Banditelli, A.L. Bandini, G. Minghetti and F. Bonati, *Synth. React. Inorg. Met.-Org. Chem.*, 9 (1979) 539.
140 B. Cetinkaya, P.B. Hitchcock, M.F. Lappert, S. Torroni, J.L. Atwood, W.E. Hunter and M.J. Zaworotko, *J. Organomet. Chem.*, 188 (1980) C31.
141 Yu.N. Kukushkin, N.P. Fedyanin and A.I. Mokhov, *Zh. Neorg. Khim.*, 25 (1980) 784.
142 T.L. Hall, M.F. Lappert and P.W. Lednor, *J. Chem. Soc., Dalton Trans.*, (1980) 1448.
143 W.C. Kalb, C.W. Kreimendahl, D.C. Busby and M.F. Hawthorne, *Inorg. Chem.*, 19 (1980) 1590.
144 R. Kuwae and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 53 (1980) 118.
145 R. Uson, L.A. Oro, M.R. Pinillos, A. Arruebo, K.A.O. Starzewski and P.S. Pregosin, *J. Organomet. Chem.*, 192 (1980) 227.
146 P.I. van Vliet, G. van Koten and K. Vrieze, *J. Organomet. Chem.*, 188 (1980) 301.

147   W.A. Herrmann, J. Plank and D. Riedel, *J. Organomet. Chem.*, 190 (1980) C47.
148   J.M. Brown and P.A. Chaloner, *J. Chem. Soc., Chem. Commun.*, (1980) 344.
149   T. Yoshida, T. Okano and S. Otsuka, *J. Am. Chem. Soc.*, 102 (1980) 5966.
150   R.K. Brown, J.M. Williams, M.F. Fredrich, V.W. Day, A.J. Sivak and E.L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, 76 (1979) 2099.
151   R.K. Brown, J.M. Williams, A.J. Sivak and E.L. Muetterties, *Inorg. Chem.*, 19 (1980) 370.
152   J.A. Sofranko, R. Eisenberg and J.A. Kampmeier, *J. Am. Chem. Soc.*, 102 (1980) 1163.
153   R.L. Pruett, *Ann. N.Y. Acad. Sci.*, 295 (1977) 329.
154   M. Chetcuti, M. Green, J.A.K. Howard, J.C. Jeffery, R.M. Mills, G.N. Pain, S.J. Porter, F.G.A. Stone, A.A. Wilson and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1980) 1057.
155   M. Tachikawa, A.C. Sievert, E.L. Muetterties, M.R. Thompson, C.S. Day and V.W. Day, *J. Am. Chem. Soc.*, 102 (1980) 1725.
156   D. Labroue, R. Queau and R. Poilblanc, *J. Organomet. Chem.*, 186 (1980) 101.
157   E. Billig, J.D. Jamerson and R.L. Pruett, *J. Organomet. Chem.*, 192 (1980) C49.
158   A.R. Pinhas, T.A. Albright, P. Hoffmann and R. Hoffman, *Helv. Chim. Acta*, 63 (1980) 29.
159   P.A. Dimas, E.N. Duesler, R.J. Lawson and J.R. Shapby, *J. Am. Chem. Soc.*, 102 (1980) 7787.
160   B.T. Heaton, L. Longhetti, L. Garleschelli and U. Sartor, *J. Organomet. Chem.*, 192 (1980) 431.
161   P.E. Kreter, D.W. Meek and G.G. Cristoph, *J. Organomet. Chem.*, 188 (1980) C27.
162   V.G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, (1980) 52.
163   P. Gelin, Y.B. Taarit and C. Naccache, *J. Catal.*, 59 (1979) 357.
164   H. Knoezinger, E.W. Thornton and M. Wolf, *J. Chem. Soc., Faraday Trans. 1*, 75 (1979) 1888.
165   O.A. Gansow, D.S. Gill, F.J. Bennis, J.R. Hutchison, J.L. Vidal and R.C. Schoening, *J. Am. Chem. Soc.*, 102 (1980) 2449.
166   A. Fumagalli, T.F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo and B.T. Heaton, *J. Am. Chem. Soc.*, 102 (1980) 1740.
167   B.T. Heaton, L. Strona, S. Martinengo and P. Chini, *J. Organomet. Chem.*, 194 (1980) C29.
168   S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, (1980) 1140.
169   G. Ciani, A. Sironi and S. Martinengo, *J. Organomet. Chem.*, 192 (1980) C42.
170   B.T. Heaton, C. Brown, D.O. Smith, L. Strona, R.J. Goodfellow, P. Chini and S. Martinengo, *J. Am. Chem. Soc.*, 102 (1980) 6175.
171   S. Martinengo, G. Ciani and A. Sironi, *J. Am. Chem. Soc.*, 102 (1980) 7564.
172   K.K. Pandey and U.C. Agarwala, *J. Inorg. Nucl. Chem.*, 42 (1980) 293.
173   A.L. Lapidus and M.M. Savel'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2 (1980) 335.
174   J.L. Vidal, W.E. Walker, R.L. Pruett, R.C. Schoening and R.A. Fiato, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 499.
175   J.L. Vidal and W.E. Walker, *Inorg. Chem.*, 19 (1980) 896.
176   T. Cole, R. Ramage, K. Cann and R. Petit, *J. Am. Chem. Soc.*, 102 (1980) 6182.
177   L.V. Gorbunova, I.L. Knyazeva and E.A. Davydova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5 (1980) 1054.
178   K. Unverferth, R. Hoentsch and K. Schwetlick, *J. Prakt. Chem.*, 321 (1979) 928.
179   S.S. Novikov, V.I. Manov-Yuvenskii and A.V. Smetanin, *Dokl. Acad. Nauk SSSR*, 251 (1980) 371.
180   T. Mise, P. Hong and H. Yamazaki, *Chem. Lett.*, 4 (1980) 439.
181   D.H. Doughty, M.F. McGuiggan, H. Wang and L.H. Pignolet, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 909.
182   M. Ichikawa, *J. Catal.*, 59 (1979) 67.

183 C.U. Pittman, W.D. Honnick and J.J. Yang, *J. Org. Chem.*, 45 (1980) 684.

184 Y. Becker, A. Eisenstadt and J.K. Stille, *J. Org. Chem.*, 45 (1980) 2145.

185 G. Gubitosa and H.H. Brintzinger, *Colloq. Int. C.N.R.S., Relat. Catal. Homogeneous Catal. Heterogene*, 281 (1978) 173.

186 D. Bondoux, D. Houalla, C. Pradat, J.G. Riess, I. Tkatchenko and R. Wolf, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 969.

187 E.C. Baker, D.E. Hendrikson and R. Eisenberg, *J. Am. Chem. Soc.*, 102 (1980) 1020.

188 E.L. Muetterties, A.J. Sivak, R.K. Brown, J.W. Williams and M.F. Fredrich, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 487.

189 A.R. Sanger, *Prepr.-Can. Symp. Catal.*, 6 (1979) 37.

190 J. Koettner and G. Greber, *Chem. Ber.*, 113 (1980) 2323.

191 J.M. Brown and B.A. Murrer, *Tetrahedron Lett.*, 21 (1980) 581.

192 A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi and R. Noyori, *J. Am. Chem. Soc.*, 102 (1980) 7932.

193 J.M. Brown and P.A. Chaloner, *J. Am. Chem. Soc.*, 102 (1980) 3040.

194 A.S.C. Chan and J. Halpern, *J. Am. Chem. Soc.*, 102 (1980) 838.

195 W.R. Cullen, F.W.B. Einstein, C.-H. Huang, A.C. Willis and E.-S. Yeh, *J. Am. Chem. Soc.*, 102 (1980) 988.

196 A. Dedieu, *Inorg. Chem.*, 19 (1980) 375.

197 S.Z. Bernadyuk, G.V. Kudryavtsev and G.V. Lisichkin, *Koord. Khim.*, 5 (1979) 1834.

198 H. Alper and K. Hachem, *J. Org. Chem.*, 45 (1980) 2269.

199 R.C. Larock, K. Oertle and G.F. Potter, *J. Am. Chem. Soc.*, 102 (1980) 190.

200 R.E. Campbell, C.F. Lochow, K.P. Vora and R.G. Miller, *J. Am. Chem. Soc.*, 102 (1980) 5824.

201 A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot and P. Teyssie, *J. Org. Chem.*, 45 (1980) 695.

202 P.G. Antonov, N.V. Borunova, V.I. Anufriev and V.M. Ignatov, *Izv. Vysch. Uchebn; Zaved. Khim., Tekhnol.*, 22 (1979) 952.

203 L.I. Zakharkin and T.B. Agakhanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5 (1980) 1208.

204 P. Hong and H. Yamazaki, *Chem. Lett.*, 11 (1979) 1335.

205 K.M. Nicholas, *J. Organomet. Chem.*, 188 (1980) C10.

206 F. Igersheim and H. Mimoun, *Nouv. J. Chim.*, 4 (1980) 161.

207 M.K. Dickson, B.P. Sudha and D.M. Roundhill, *J. Organomet. Chem.*, 190 (1980) C43.

208 D.M. Roundhill, M.K. Dickson, N.S. Dixit and B.P. Sudah-Dixit, *J. Am. Chem. Soc.*, 102 (1980) 5538.

209 J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1980) 144.

210 M. Aresta, *Inorg. Chim. Acta*, 44 (1980) L3.

211 K. Mita, T. Yamagishi and M. Hida, *J. Chem. Soc., Chem. Commun.*, (1980) 1036.

212 Y. Yamamoto, H. Yatagai and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, (1980) 835.

213 M.V. Klyuev and M.L. Khidekel, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 134.

214 V.Z. Sharf, B.M. Savchenko, V.N. Krutii and L.Kh. Freidlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2 (1980) 456.

215 B.M. Savchenko, V.Z. Sharf, V.N. Krutii and L.Kh. Freidlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 11 (1979) 2632.

216 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, (1980) 694.

217 Z.M. Michalska, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 125.

218 E.D. Schmid, R.S. Krishnan and W.H. Kiefer, *Proc. Int. Conf. Raman Spectrosc.*, 6th, 2 (1978) 128.

219 D.F.C. Morris and T.J. Ritter, *J. Chem. Soc., Dalton Trans.*, (1980) 216.

220 H.N. Po, C.-F. Lo, N. Jones and R.W. Lee, *Inorg. Chim. Acta*, 46 (1980) 185.

221 D.M. Stanbury, W.K. Wilmarth, S. Khalaf, H.N. Po and J.E. Byrd, *Inorg.*

Chem., 19 (1980) 2715.

222   B. Harrison, N. Logan and A.D. Harris, *J. Chem. Soc., Dalton Trans.*, (1980) 2382.

223   B.L. Chamberland and S. Silverman, *J. Less-Common Met.*, 65 (1979) 41.

224   D.J. Gulliver, W. Levason, K.G. Smith and M.J. Selwood, *J. Chem. Soc., Dalton Trans.*, (1980) 1872.

225   A.F. Williams, H.D. Flack and M.G. Vincent, *Acta Crystallogr., Sect. B*, 36 (1980) 1204.

226   A.F. Williams, H.D. Flack and M.G. Vincent, *Acta Crystallogr., Sect. B*, 36 (1980) 1206.

227   G.B. Kauffman, J. Hua-San Tsai, M.H. Gubelmann and A.F. Williams, *J. Chem. Soc., Dalton Trans.*, (1980) 1791.

228   M. Talebinasab-Sarvari, A.V. Zanella and P.C. Ford, *Inorg. Chem.*, 19 (1980) 1835.

229   M. Talebinasab-Sarvari and P.C. Ford, *Inorg. Chem.*, 19 (1980) 2640.

230   B. Divisia, P.C. Ford and R.J. Watts, *J. Am. Chem. Soc.*, 102 (1980) 7264.

231   N. Nonoyama, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3749.

232   R.H. Crabtree, J.M. Quirk, H. Felkin, T. Fillebeen-Khan and C. Pascard, *J. Organomet. Chem.*, 187 (1980) C32.

233   K. von Deuten and L. Dahlenburg, *Cryst. Struct. Commun.*, 9 (1980) 421.

234   D.M.P. Mingos and C.T. Webber, *Nouv. J. Chim.*, 4 (1980) 77.

235   G. Bombieri, F. Faraone, G. Bruno and G. Faraone, *J. Organomet. Chem.*, 188 (1980) 379.

236   D.L. Thorn, *J. Am. Chem. Soc.*, 102 (1980) 7109.

237   M.A. Bennett and J.C. Jeffery, *Inorg. Chem.*, 19 (1980) 3763.

238   R.L. Harlow, J.B. Kinney and T. Herskovitz, *J. Chem. Soc., Chem. Commun.*, (1980) 813.

239   Y. Komi and A. Urushiyama, *Bull. Chem. Soc. Jpn.*, 53 (1980) 980.

240   C.W. Jung and M.F. Hawthorne, *J. Am. Chem. Soc.*, 102 (1980) 3024.

241   P.G. Antonov, Yu.N. Kukushkin, V.F. Shkredov and A.Sh. Bakhtiyarov, *Koord. Khim.*, 6 (1980) 599.

242   A. Immirzi, A. Musco, P.S. Pregosin and L.M. Venanzi, *Angew. Chem.*, 92 (1980) 744.

243   H.H. Wang and L.H. Pignolet, *Inorg. Chem.*, 19 (1980) 1470.

244   N.V. Vugman and N.M. Pinhal, *Mol. Phys.*, 38 (1979) 1999.

245   J.-J. Bonnet, P. Kalek and R. Poilblanc, *Angew. Chem.*, 92 (1980) 572.

246   J. Devillers, J.-J. Bonnet, D. de Montauzon, J. Galy and R. Poilblanc, *Inorg. Chem.*, 19 (1980) 154.

247   K.D. Schramm, T.H. Tulip and J.A. Ibers, *Inorg. Chem.*, 19 (1980) 3183.

248   A.L. Balch and J.R. Yow, *J. Am. Chem. Soc.*, 102 (1980) 1448.

249   G. Yoneda and D.M. Blake, *J. Organomet. Chem.*, 190 (1980) C71.

250   J.A. Labinger and J. Osborn, *Inorg. Chem.*, 19 (1980) 3230.

251   T.L. Hall, M.F. Lappert and P.W. Lednor, *J. Chem. Soc., Dalton Trans.*, (1980) 1448.

252   W.J. Louw, T.L.A. Gerber and D.J.A. de Waal, *J. Chem. Soc., Chem. Commun.*, (1980) 760.

253   M. Angoletta and G. Caglio, *J. Organomet. Chem.*, 185 (1980) 105.

254   D. de Montauzon, P. Kalck and R. Poilblanc, *J. Organomet. Chem.*, 186 (1980) 121.

255   C.P. Kubiak, C. Woodcock and R. Eisenberg, *Inorg. Chem.*, 19 (1980) 2733.

256   S.M. Boniface and G.R. Clark, *J. Organomet. Chem.*, 188 (1980) 263.

257   A. Tiripicchio, C.M. Tiripicchio, M. Ghedini and G. Dolcetti, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 102.

258   M. Lanfranchi, A. Tiripicchio, G. Dolcetti and M. Ghedini, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 21.

259   K.D. Schramm and J.A. Ibers, *Inorg. Chem.*, 19 (1980) 1231.

260   A. Immirzi, W. Porzio, G. Bombieri and L. Toniolo, *J. Chem. Soc., Dalton Trans.*, (1980) 1098.

261   D.M. Roundhill, R.A. Bechtold and S.G.N. Roundhill, *Inorg. Chem.*, 19 (1980) 284.

262   J. Ellermann and L. Mader, *Z. Naturforsch. Sect. B*, 35 (1980) 307.

318

263 A. Maisonnat, J.-J. Bonnet and R. Poilblanc, *Inorg. Chem.*, 19 (1980) 3168.
264 S.A. Bezman, P.H. Bird, A.R. Fraser and J.A. Osborn, *Inorg. Chem.*, 19 (1980) 3755.
265 A.H. Reis and S.W. Peterson, *Ann. N.Y. Acad. Sci.*, 313 (1978) 560.
266 R. Uson, L.A. Oro, M.J. Fernandez and M.T. Pinillos, *Inorg. Chem. Acta*, 39 (1980) 57.
267 J.T. Mague and S.H. De Vries, *Inorg. Chem.*, 19 (1980) 3743.
268 P.A. Corrigan and R.S. Dickson, *Aust. J. Chem.*, 32 (1979) 2147.
269 B. Longato, F. Morandini and S. Bresadola, *Inorg. Chim. Acta*, 39 (1980) 27.
270 J. Vecernik, J. Masek and A.A. Vlcek, *Collect. Czech. Chem. Commun.*, 45 (1980) 1468.
271 F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, (1980) 903.
272 D. Forster, *J. Chem. Soc., Dalton Trans.*, (1979) 1639.
273 R.H. Crabtree, D.F. Chodosh, J.M. Quirk, H. Felkin, T. Khan-Fellebeen and G.E. Morris, *Fundam. Res. Homogeneous Catal.*, 3 (1979) 475.
274 J.A. Doi, R.G. Teller and M.F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, (1980) 80.
275 J. Lieto, J.J. Rafalko and B.C. Gates, *J. Catal.*, 62 (1980) 149.
276 T. Castrillo, H. Knoezinger, J. Lieto and M. Wolf, *Inorg. Chim. Acta*, 44 (1980) L239.