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4. RHODIUM AND IRIDIUM

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CONTENTS

4.1 SCOPE AND ORGANISATION OF THE REVIEW

This review covers the coordination chemistry of rhodium and iridium published during the year 1979. For principal journals, coverage is of all parts of the journals which have 1979 as their date-line, whilst for those journals that were followed through Chemical Abstracts, abstracts that appeared in Volumes 90 and 91 {up to 91 (20)} have been reviewed.

Being a review of coordination chemistry, compounds which contain metal-to-carbon bonds have not been covered. However, in certain cases, compounds containing CO have been included where it was felt they were relevant to the subject under discussion (but coverage of them is by no means comprehensive). Similarly, subjects such as catalysis, kinetics and photochemistry have, in general, not been included, although some light-assisted reaction chemistry is reviewed along with related thermal reactions.

Since, for oxygen and nitrogen donor ligands very few of the complexes have the metal in an oxidation state other than (III), and since most phosphorus and Group IV donor complexes have the metal in oxidation state(I), all such complexes are reviewed by donor atom rather than by metal oxidation state. This approach has also been employed because, for example, many of the phosphine complexes of the metals in oxidation state (III) are formed by oxidative addition of small molecules to M^I complexes. The only exception to this general format is that carboxylate complexes of rhodium(II) are treated in a separate section.

4.2 MAJOR ADVANCES

The observation that $[Ru(bipy)_3]^{2+}$ is capable [1] of catalysing the photochemical cleavage of water has led to a general increase in activity in the area of transition metal bipyridine complexes. For iridium(III), the fact that some of the properties of the excited state are not substantially different [2] from those of $\{[Ru(bipy)_3]^{2+}\}^*$ has led to their chemistry being studied further, and the complex $[Ir(bipy)_3H_2O]^{3+}$, previously thought [3] to contain a monodentate bipy ligand, has been reformulated [4] as containing three chelate bipy groups but with H_2O added across an N=C bond. $[Rh(bipy)_3]^{3+}$ has been shown [5] to act as an electron transfer catalyst in the photochemical production of dihydrogen from water using $[Ru(bipy)_3]^{2+}$ as photosensitiser and triethanolamine as electron donor.

The phosphine chemistry of rhodium and iridium has been further explored, the main advances coming in developments of various methods for anchoring the phosphorus to solid supports for use in catalysis ($SnCl_3$ complexes have also been used for this) and in the identification of parameters that lead to optical induction during asymmetric catalysis. The carbon-centred cluster $[CHg_6\{Rh(PMe_3)_3\}_4]$ is also of great interest [6].

Finally, dispute over the order of the bond in adducts of $Rh_2(OAc)_4$ continues, but appears to be leaning in favour of their being a single σ bond, the bond being exactly nullified by occupation of a π^* orbital. The short Rh—Rh distance is then attributed to there being π electron density between the two rhodium atoms but deriving from the ligand framework.

4.3 COMPLEXES WITH GROUP III DONOR LIGANDS

Apart from several papers on carborane complexes of rhodium and iridium, which are considered to be beyond the scope of this review, only complexes of polyboranes have been reported [7,8].

Thus, reactions of $[Ir(dppe)_2]Cl$ with $[B_{10}H_{13}X]$ (X = H or 6-Cl) or of $[Ir(dppe)_2CO]Cl$ with $[NHEt_3][B_{10}H_{13}]$ give [7] ionic products, $[Ir(dppe)_2HCl][B_{10}H_{12}X]$ and $[IrCO(dppe)_2][B_{10}H_{13}]$, in the former of which the borane has protonated the Ir(I) centre. Isolation of small amounts of $[Ir(dppe)_2H_2][B_9H_{14}]$ from $[IrCO(dppe)_2]Cl$ and $[NHEt_3][B_{10}H_{13}]$ in methanol is attributed [7] to degradation of the decaborane by methanol

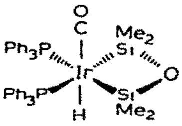
$$[B_{10}H_{13}]^- + MeOH \rightarrow [B_9H_{14}]^- + 2\ \{H\} + B(OMe)_3$$

The X-ray structure of the dihydride [7] shows the cation to have *cis* stereochemistry, although the nonaborate anion was too disordered for analysis.

In contrast to these ionic compounds, the octahydro-*nida*-pentaborate(—1) anion reacts [8] with $[Ir(CO)Cl(PPh_3)_2]$ to form a cage compound with the iridium atom assimilated into the cage, [$Ir(B_5H_8)(CO)(PPh_3)_2$]. One of the hydrogen atoms of the borane occupies the sixth site on iridium [8]. This type of coordination has only otherwise been described for the related [$Fe(CO)_3(B_5H_9)$] formed [9] from co-thermolysis of [$Fe(CO)_5$] and [B_5H_9], and its deprotonated form K[$Fe(CO)_3(B_5H_8)$].

4.4 COMPLEXES WITH GROUP IV DONOR LIGANDS

Vaska's compound reacts [10] with tetramethyldisiloxane to give the metallocyclic compound (1) whilst [$IrCO(PEt_3)_2X$]



(1)

(X = halide) oxidatively adds [11] [H_3MQ] (Q = H, Cl, Br or I, M = Si or Ge; Q = Me or SiH_3, M = Si) to give [$IrHX(MH_2Q)(CO)(PEt_3)_2$] in which the phosphines are mutually *trans*. For the germyl compounds the major products have H *trans* to X whilst for M = Si, the *trans* addition product is formed. For the silyl complexes, if X = Cl and Q = Br or I, halide exchange also occurs.

Apart from these compounds, all compounds of rhodium and iridium with Group IV ligands contain halotin ligands. Thus, HCl solutions of $RhCl_3$ [12] or K_3[$IrCl_6$] [13] and $SnCl_2$ afford Cs_3[$MCl_4(SnCl_3)_2$], with *cis*-$SnCl_3$ groups, on addition of CsCl. [Me_4N^+] gives [Me_4N]$_3$[$MCl_n(SnCl_3)_{6-n}$] (M = Ir, n = 1; M = Rh, n = 1, 2 or 3), which for M = Rh, n = 1 undergoes solvolysis [14] of the Sn—Cl bonds in ethanol containing dmso to give [Me_4N]$_2$[Rh{$SnCl_2$dmso}-($SnCl_3$)$_4$Cl] or [Rh{$SnCl_2$dmso}$_5$Cl]Cl_2, which can also be made from [$RhCl_3(dmso)_3$] and excess $SnCl_2$. [Rh(dmso){$SnCl_2$dmso}$_2$$Cl_3$] is formed from [$Me_4N$]$_3$[$Rh(SnCl_3)_2Cl_4$] by a similar method.

The insertion of $SnCl_2$ into M—Cl bonds has also been used in the formation [15] of [$Ir(PPh_3)_2L(SnCl_3)_3$] (L = CO or PPh_3) from [$Ir(PPh_3)_2LCl_3$] and of [$Rh(SnCl_3)(PPh_3)_3$] from [$RhCl(PPh_3)_3$] [16,17]. The last $SnCl_3$ compound has been employed [16,17] to make supported hydrogenation catalysts by reaction with silica which had previously been treated with a Grignard or alkyl lithium reagent.

Finally, the crystal structure of Cs_4[*cis*-$Rh(SnF_2H_2O)_2(Sn_4F_{15})$]4 H_2O shows [18] the rhodium to be coordinated by six tin atoms, and the four tin atoms of the tetradentate group to be bridged by fluorine atoms.

4.5 COMPLEXES WITH GROUP V DONOR LIGANDS

4.5.1 Nitrogen donors

Although the photochemical and kinetic properties of simple amine complexes of iridium and rhodium, both of which are considered to be beyond the scope of this review, have been extensively studied, little new coordination chemistry of these species has been reported. Photolysis of $[Rh(NH_3)_4(OH_2)H]^{2+}$ in the presence of oxygen forms [19] $[Rh(NH_3)_4]^{2+}$ which acts as a chain carrier and activates oxygen by coordination. The hydroperoxo species only slowly decomposes to give a coloured superoxo complex.

$[Rh(OH)(H_2O)(NH_3)_4][S_2O_6]$ forms [20] the hydroxo bridged dimer $[(NH_3)_4Rh(OH)]_2Br_4$ on heating to 120°C and precipitation with bromide ion. An analogous reaction is obtained if the ammonia ligands are replaced by two en ligands and both products are isomorphous with their Cr or Co analogues. A new high yield route to [*cis*-$Rh(en)_2X_2]^+$ (X = halide) from $RhCl_3$ and $[enH_2]Cl_2$ has been reported [21]. This involves reaction at pH 6.8 in the presence of NaOH, evaporation to dryness to give a *cis*/*trans* mixture and treatment with $NaBH_4$ in the presence of oxalate ion (ox) to give $[Rh(ox)(en)_2][ClO_4]$. Refluxing this product with 6 *M* HX gives [*cis*-$RhX_2(en)_2][ClO_4]$ in >60% isolated yield. The analogous *S*-bonded thiocyanate complex, $[Rh(SCN)_2(en)_2]SCN$ is obtained [22] along with $Na[Rh(SCN)_4(en)]$ on refluxing $Na_3[Rh(SCN)_6]$ with 3 moles of en in ethanenitrile.

A detailed IR and Raman study of the recently resolved [23] $\Lambda\delta\delta\delta$ tris-(1S,2S-cyclohexanediamine)iridium(III) chloride and its ND_2 analogue has allowed [24] fundamental vibrations to be assigned, although agreement between observed and calculated values in the far infrared region is not good.

A neutron diffraction study of *trans*-$[RhCl_2(py)_4][(NO_3)_2H]$ has been carried out [25], mainly on account of the hydrogen dinitrate ion, which contains two nitrate ions hydrogen bonded to a proton with the angle at hydrogen being 168°. This is somewhat similar to the $[(Pr_2SO)_2H]^+$ cation discussed [26] below. The cation seems to have the expected structure with the pyridine rings tilted out of the plane containing the rhodium atom and the four nitrogen atoms [25].

5-Substituted imidazoles (substituent = H or NO_2) (imid) react [27] with rhodium trichloride in HCl to give *mer*-$[RhCl_3(imid)_3]$ bound through the pyrrole nitrogen atom, although chlorobridged $[RhCl_3(imid)_2]_2$ is formed if the substituent is NH_2.

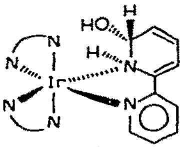
The pyrazolato bridged species, $[(Rh(CO)_2pzl)_2]$ has been prepared [28] by interaction of $[Rh(CO)_2Cl]_2$ with $[PPh_3Aupzl]$, whilst related complexes containing the pyrazolato ion bridging rhodium and boron are prepared [29] from $[Rh(CO)_2Cl]_2$ and zinc diethylbis(pyrazolyl)borate. Isocyanide analogues have also been prepared by exchange of the CO groups. Other bridged species include [30] $[(NC)_5FeLRh(NH_3)_5]$ where L is a linear bridging group such as pyrazine or 4,4′-bipyridyl.

Complexes of the tridentate diaminophenol and its 3-OR (R = Me or Et) (L) derivatives of the form $[RhLCl_3] \cdot 2\,H_2O$ have been synthesised [31] and tested for antimitogenic activity by studying their effect on DNA synthesis. In contrast to complexes of other metals, these non-toxic compounds enhance the rate of DNA production and it has been suggested that any antitumor activity of these complexes may be attributed to an increase of the host's immune response. Related to this, changes in the electronic spectra and viscosity of DNA in acetate buffer on addition of Rh^{3+}, as well as variations in melting point with ionic strength, imply [32] that binding is through phosphate groups as well as nitrogen bases.

In 8-alkylquinoline-2-carboxaldehyde-*N*-methylimine (qa) complexes of the form $[RhClL_2(qa)]$ (L = CO), the ligand binds [33] as an N—N chelate in a five coordinate complex. For L_2 = cod, however, binding is through the exocyclic nitrogen atom and the 3-H atom sits above the plane of the complex. On refluxing with $PCych_3$ metallation of the 3-C atom occurs to give $[RhHCl(qa\text{-}H^3)(PCych_3)_2]$. The iridium analogue is similarly prepared. A related metallation of the unsubstituted phenyl ring accounts [34] for the formation of $[(RhClL)_2]$ from (4-hydroxy-3,5-ditertiarybutylphenyl)phenyldiimine(LH) and rhodium trichloride.

Other work on chelate nitrogen donors has concentrated on M^{III} complexes of bipy and phen which have uses related to the photodecomposition of water. Thus, full details [5] and quantum yields [35] have appeared on the use of $[Rh(bipy)_3]^{3+}$ as an electron transfer catalyst for the production of dihydrogen from triethanolamine (teoa), $[Ru(bipy)_3]^{2+}$, $[Rh(bipy)_3]^{3+}$ and a redox catalyst such as colloidal platinum. The $[Rh(bipy)_3]^{2+}$ formed by electron transfer from $\{[Ru(bipy)_3]^{2+}\}^*$ decomposes to $[Rh(bipy)_2]^{2+}$, which receives an electron from teoa to give $[Rh(bipy)_2]^+$. Subsequent steps involve oxidative addition of water, protonation, loss of dihydrogen under the influence of the redox catalyst and coordination of bipy to regenerate $[Rh(bipy)_3]^{3+}$. The X-ray structure of the $[(-)Rh(3,3'\text{-dimethylbipy})_3]^{3+}$ shows [36] it to have the absolute configuration $\Lambda(\delta\lambda\lambda)$.

Reproducible syntheses of pure $[IrCl_2(L—L)_2]^+$, $[Ir(L—L)_3]^{3+}$, $[Ir(L—L)_3(OH)]^{2+}$ and $[Ir(L—L)_3(H_2O)]^{3+}$ (L—L = bipy or phen) have now been reported [37] although some of the procedures are somewhat involved. Purities and structures were determined on the basis of emission and ^{13}C and ^1H NMR spectra. These authors assume the original formulation [3] of $[Ir(L—L)_3X]^{n+}$ (X = OH, n = 2; X = H_2O, n = 3) as containing a monodentate L—L group and, although they do not interpret the ^1H NMR spectra, assign the ten ^{13}C resonances of $[Ir(bipy)_3(OH)]^{2+}$ as arising five from $2\frac{1}{2}$ coordinated bipyridine groups and five from the uncoordinated half of the monodentate bipy. In this case, it might be expected that the free pyridyl group should give a similar spectrum to that of bipy itself. It does not, but the small differences in chemical shift could be due to the different charge associated with the ring. On the basis of IR spectra $\{\nu(N—H)$ at 2650 $cm^{-1}\}$, lack of further protonation of $[Ir(bipy)_3(H_2O)]^{2+}$, which would be expected if there were a free nitrogen atom, and detailed analysis of the ^1H NMR spectrum, Gillard et al. suggest [4] that the complex is better formulated as having three bidentate bipy molecules but with addition of H_2O having occurred across an N=C bond of one bipy ligand (2). The basic form of this complex



(2)

is then identical except that the N—H hydrogen atom is removed. The ^{13}C spectrum [37] can then be assigned so that five resonances arise from the five "normal" pyridyl rings, whilst the other five resonances come from the ring to which the water has been added. It might be expected that the resonance from the sp^3 carbon atom should appear at higher field, but the electronegative hydroxide group would tend to cancel this effect. Some evidence that phototautomerism occurs in $[Ir(bipy)_3(H_2O)]^{3+}$ has been presented [38], but since this is based on the original formulation of the complex and is suggested to involve O → N hydrogen transfer, the exact significance of these results must be considered uncertain.

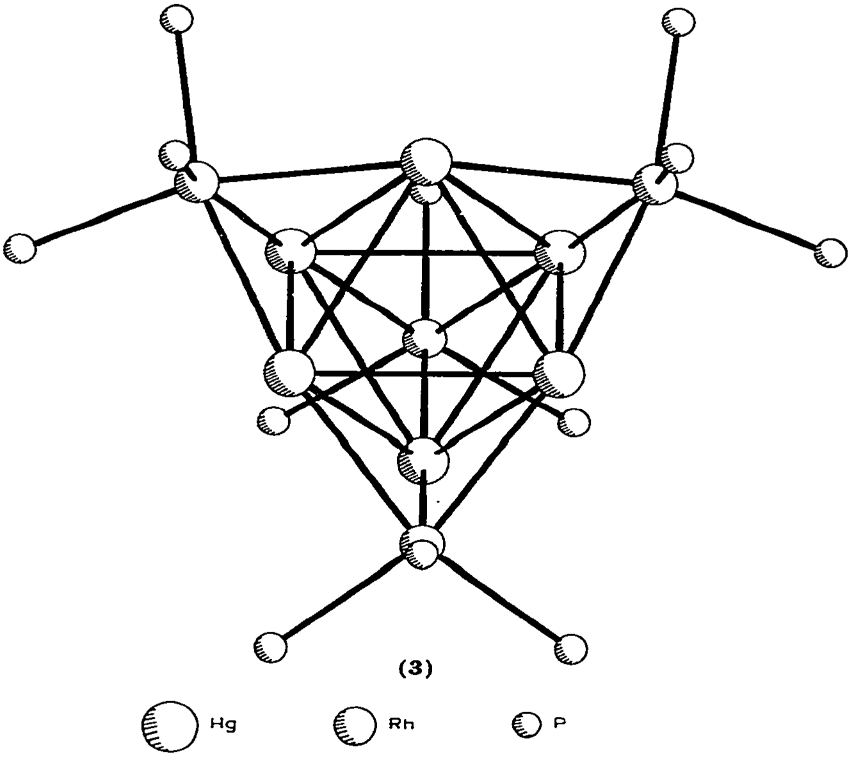
Electrochemical studies on $[Ir(phen)_2Cl_2]^+$ and $[Ir(5,6\text{-dimethylphen})_2Cl_2]^+$ have shown [39] that both 1e oxidation and reduction can occur but that the reduction product readily loses Cl^-. Further reduction to $[IrCl_2(phen)_2]^{n-}$ ($n = 1$ or 2) or $[Ir(phen)_2Cl]^{n-}$ ($n = 0$, 1 or 2) can occur, but $[Ir(phen)_2]$ forms on loss of Cl^- from $[Ir(phen)_2Cl]^-$. Apparently the Pt electrode interacts with the complexes via a π type interaction with the 5, 6 double bond of a phen group. For $[Ir(bipy)_3(OH)]^{2+}$, whose structure has been discussed above, five successive one-electron reductions occur [40] although the neutral $[Ir(bipy)_3(OH)]$ deposits. For $[Ir(bipy)_3]^{3+}$, all oxidation and reduction products, $[Ir(bipy)_3]^{n+}$ ($n = -3 \rightarrow +4$) are accessible [40], and once again neutral $[Ir(bipy)_3]$ deposits.

Finally, equilibrium constants for the protonation of [Rh(porphyrin)-(OH)], formed [41] by alkaline treatment of [RhCl(CO)(porphyrin)], and related complexes of other metals, show that these constants are independent of porphyrin substituents, but correlate well with the calculated effective charge along the z axis.

4.5.2 Monotertiary phosphine, phosphite and arsine complexes

Although rhodium(I) complexes of monotertiary phosphines have been very extensively studied, those containing PMe_3 have only recently been prepared. Thus, reactions of $[RhCl(PPh_3)_3]$ [6] or of $[Rh(cod)Cl]_2$ [42] with excess PMe_3 afford the water soluble $[Rh(PMe_3)_4]Cl$ which can be converted into $[Rh(PMe_3)_3Cl]$ [6], the previously reported [43] synthesis of which apparently gives mixtures [6]. The structures of these two complexes are as expected, with square planar rhodium atoms, and they react [6] with dihydrogen to give the previously reported [44] $[RhH_2(PMe_3)_4]^+$. Fluxional $[Rh(PMe_3)_3]X$ ($X = [PF_6]$ or $[BPh_4]$), which does not contain a π-bonded $[BPh_4]^-$, is obtained [6] on addition of the appropriate anion to solutions of

[Rh(PMe_3)$_4$]Cl in polar solvents. Sodium [6] or thallium [42] cyclopentadienides give the highly nucleophilic [cpRh(PMe_3)$_2$], whose reactions with nucleophiles give [2] a range of products of general formula [cpRh(PMe_3)$_2$X]$^+$. Sodium amalgam reduction of [Rh(PMe_3)$_4$]Cl gives [6] a petroleum soluble cluster of probable formula [$CHg_6Rh_4(PMe_3)_{12}$], in which each rhodium atom is coordinated to three phosphines and bridges a triangular face of a carbon-centred octahedron of mercury atoms (3) [45], the rhodium atoms being at the corners of a tetrahedron. Being such a good scatterer of X-rays, the metal framework makes it difficult to tell whether a weak peak in the centre of the octahedron arises from a carbon atom or is a ghost peak *. A related cationic complex, [Rh{P(OPh)$_3$}$_4$][ClO$_4$] is obtained [43] from [RhCl{P(OPh)$_3$}$_3$], excess P(OPh)$_3$ and Ag[ClO$_4$], but if the reaction is carried out in the absence of excess P(OPh)$_3$ in benzene—dichloromethane, only 50% of this ionic product is formed. The other product is [(C_6H_6)Rh{P(OPh)$_3$}$_2$][ClO$_4$] which contains a π-bonded benzene ring. The latter complex is the only product from reaction of [RhCl(P(OPh)$_3$)$_2$]$_2$ with Ag[ClO$_4$] in the presence of benzene. The π-bonded mesitylene complex is similarly



(3)

Heavy atom positions for $Hg_6Rh_4(PMe_3)_{12}$, reproduced by kind permission of Prof. Sir Geoffrey Wilkinson and Dr. M.B. Hursthouse.

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* Note added in proof. Further refinement shows that there is no carbon atom in the centre of the cluster (G. Wilkinson, personal communication).

prepared, whilst $Na[BPh_4]$ in methanol gives [46] $[Rh\{P(OPh)_3\}_2\{BPh_4\}]$ containing a π-bonded BPh_4 group.

Calorimetric, as well as ^1H and ^{31}P NMR studies have shown [47] that the formation of $[RhCl\{P(OMe)_3\}_3]$ from $[RhCl(cod)]_2$ and excess phosphite is a stepwise process which occurs both by initial bridge cleavage and by initial replacement of cod, the respective intermediates being $[RhCl(cod)\{P(OMe)_3\}]$ and $[Rh_2Cl_2\{P(OMe)_3\}_2(cod)]$. Similar reactions occur for $[RhCl(CO)_2]_2$ although loss of CO is stepwise and the final product is $[Rh(CO)\{P(OMe)_3\}_4]Cl$.

A number of other simple phosphine containing complexes has been reported. Thus, MCl_3 (M = Ir, Rh) react [48] with $PCych_3$ in alcohols to give $[MCl(CO)(PCych_3)_2]$, which for M = Rh can also be obtained from $[RhCl(cod)]_2$ and $PCych_3$ in dichloromethane—methanol. In acetone, $RhCl_3$ and $PCych_3$ give $[RhHCl_2(PCych_3)_2]$ whilst the iridium analogue can be made either from $IrCl_4$ and $PCych_3$ in 2-methoxyethanol or from reaction of $[IrCl(cot)_2]_2$ in the presence of HCl. In the absence of HCl, this last reaction leads to a compound containing a metallated phosphine ligand, whilst under hydrogen $[IrH_2Cl(PCych_3)_2]$ is formed.

A similar complex to this last, $[RhH_2Cl\{P(4\text{-}ClC_6H_4)_3\}_2]$ is obtained [49] from oxidative addition of hydrogen to $[Rh(cod)\{P(4\text{-}ClC_6H_4)_3\}_2]X$, which in turn comes from reaction of $[Rh(cod)Cl]_2$ and the phosphine.

The structure of $[RhBr_3(PMe_2Ph)_3]$ has been reported [50] and is doubtless similar to those of $[MCl_3P_3]$ (M = Rh or Ir, P is one of a range of 1-phenyl phospholes, which is either unsubstituted (P′) or contains 3-methyl (MP) or 3,4-dimethyl (DMP) substituents) obtained [51] from reaction of $RhCl_3$ and P. Somewhat surprisingly only P′ causes reduction to iridium(I) giving $IrClP'_3$, whilst 1,2,5-triphenyl-phosphole (TPP) gives $[RhHCl_2(TPP)_2]$ on prolonged reflux with $RhCl_3$ in EtOH. The other rhodium(I) complexes can be isolated from the phosphole and $[RhCl(CO)_2]_2$ followed by heating in the presence of excess phosphole. A mixed rhodium(I), rhodium(III) dimer, $[Rh_2Cl_4P'_5]$ is formed by decarbonylation of the product obtained from $RhCl_3$ and P′ in ethanol under CO.

The desire to confer water or dilute acid solubility onto phosphine complexes of rhodium so that they may be more readily removed from homogeneous catalytic reaction mixtures has led to the synthesis of various phosphine complexes in which there are unbound amine nitrogen atoms. Thus, various rhodium complexes of tris-2-pyridylphosphine, $[RhCl(CO)(PPy_3)_2]$ and $[RhH(CO)(PPh_3)(PPy_3)_2]$, have been synthesised [52,53] and used for hydroformylation studies but catalyst recovery is low and problems with chelation (see below) can occur. Apparently greater success has been achieved [54] by using $P(CH_2CH_2CH_2NR_2)_3$ (R = Me or Et) and washing the catalyst from product aldehyde with dilute acid. The catalytically active species may then be recovered on addition of base.

XPES studies of various amino phosphine complexes, $[RhClCO\{PPh_{3-n}(NRR')_n\}_2]$ show [55] that whereas there is N → P π donation in the free ligand, this becomes P → N on complexing. The fact that there is a correlation between the product ratio during hydroformylation and the N 1s binding energy suggests that there is an electronic influence on selectivity, although in general the selectivity also appears to be greater the greater the size (cone angle) of the phosphine, so that steric effects may also be responsible for the observed changes in selectivity.

Phosphines have also been synthesized for supporting rhodium complexes on heterogeneous supports, again to circumvent the problems associated with separating homogeneous catalysts from products and solvents. $[\mathrm{RhL'_3Cl}]$, $[\mathrm{Rh_2L_4Cl_2}]$, and $[\mathrm{RhL_2(CO)Cl}]$ {where $\mathrm{L' = Cl_3Si(CH_2)_2PPh_2}$ and $\mathrm{L = L'}$ or $\mathrm{Cl_3Si(CH_2)_8PPh_2}$} have been synthesized [56] for supporting on silica, whilst related compounds containing $\mathrm{(Me_3SiO)_2MeSi(CH_2)_2PPh_2}$ can be polymerised to give insoluble resins. Reactions of these compounds with small molecules such as H_2, CO, and HCl are similar to those of the $\mathrm{PPh_3}$ analogues.

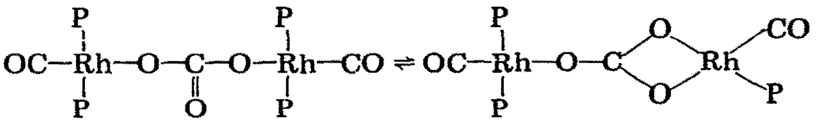
Related studies have demonstrated [57] that the type of species present when $\mathrm{PPh_3}$ complexes of rhodium(I) are reacted with polymer-bound $\mathrm{PPh_2}$ groups usually only contain one such group and are otherwise similar to their $\mathrm{PPh_3}$ analogues.

A low temperature re-examination [58] of the X-ray crystal structure of $[\mathrm{RhCl(N_2)\{P(CMe_2H)_3\}_2}]$, which had previously been thought [59] to contain a sideways bound N_2 group, the first example of such binding in a mononuclear complex, has shown that in this molecule, as in all analogous complexes with different phosphines, the N_2 molecule is in fact bound end on. The initial erroneous formulation is attributed to the high thermal motion of the chlorine atom, the extremities of which correspond precisely to the positions previously reported for the two nitrogen atoms. ^{15}N and ^{31}P NMR studies on the $^{15}N_2$ complex have also shown conclusively that only one nitrogen atom is bound to the rhodium in solution and that the activation energy for rotation of the N_2 molecule, which would require a sideways bound intermediate, is high.

Analogous iridium dinitrogen complexes, $[\mathrm{IrX(N_2)L_2}]$ ($\mathrm{L = PPh_3}$, X = NCO, F; $\mathrm{L = AsPh_3}$, X = NCO; L = P(4-tolyl)$_3$, X = Cl) have been prepared [60] from their CO analogues and furoyl azide. These and other iridium N_2 complexes, which could not be isolated, are generally less stable than the related rhodium species, although this instability may well be kinetic in origin, since in many cases low frequency $\nu(\mathrm{N{\equiv}N})$ suggest a strong Ir—N bond.

Some hydrido dinitrogen complexes of rhodium with bulky phosphines of the form $[\mathrm{RhH(N_2)P_2}]$ ($\mathrm{P = PPh(CMe_3)_2, P(CMe_3)_3}$) arise [61] from sodium amalgam reduction of $\mathrm{RhCl_3}$ in the presence of the phosphine under nitrogen in tetrahydrofuran. $\mathrm{P(CHMe_2)_3}$ gives $[\mathrm{RhHP_3}]$ whilst $\mathrm{PCych_3}$ gives a dimer $[\mathrm{\{RhHP_2\}_2(N_2)}]$ in which the nitrogen molecule forms a linear bridge between the two rhodium atoms. Similar dimers may also be prepared along with $[\mathrm{RhHP_2}]$ for $\mathrm{P = P(CHMe_2)_3}$ or $\mathrm{PPh_2(CMe_3)}$. For $\mathrm{P = P(CMe_3)_3}$ or $\mathrm{PCych_3}$, nitrogen is readily lost to give the structurally characterised [62], three coordinate $[RhHP_2]$.

Many of these complexes react [63] with CO_2 and water to give $[RhH_2P_2(O_2COH)]$ with *cis* hydrides and *trans* phosphines, which react further with CO_2 or CO to give $[Rh(CO)P_2(O_2COH)]$. For $P = P(CHMe_2)_3$, this complex dimerises via a bridging carboxylate group to $[Rh_2(CO)_2P_4(CO_3)]$ (4) which reversibly loses phosphine.



(4)

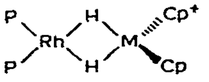
Formic acid and $[RhH\{P(CHMe_2)_3\}_3]$, on the other hand, give [63] first $[RhH_2P_2(O_2CH)]$ and then $[Rh(O_2CH)P_2(CO)]$.

Attempts to react CO_2 with iridium(III) hydrides containing PPh_2Et or dppe or with $[IrHCO(PPh_3)_3]$ have been unsuccessful [64], but adduct formation occurs with other iridium(I) complexes such as $[Ir(OH)(CO)(PPh_3)_2]$, $[IrCl(R_2PCH_2CH_2PR_2)_2]$ (R = Me or Et) and $[IrCl(cot)(PMe_3)_3]$, for the last of which the initially formed $[IrCl(CO_2)(PMe_3)_3]$ gives $[IrCl(C_2O_4)(PMe_3)_3]$, the nature of which has not been described but which presumably contains an oxalate group. A review of CO_2 fixation by metal complexes including those of rhodium and iridium has appeared [65].

All the above mentioned hydrido N_2 containing complexes also react [61] with hydrogen to give $[RhH_3P_2]$ which is similar to $[RhH_3P_3]$ ($P = P(OR)_3$), one of the products [66] from hydrogenolysis of $[Rh(allyl)P_n]$ ($n = 2$ or 3). Other products from these hydrogenolyses are $[HRhP_4]$ and the unusual clusters $[HRh\{P(OR)_3\}_2]_n$ (R = Me or Et, $n = 3$; R = $CHMe_2$, $n = 2$). Addition of hydrogen to these clusters, which are catalysts for the hydrogenation of alkenes and in some cases arenes, affords the triply bridged $[H\{P(OCHMe_2)_3\}_2RhH_3Rh\{P(OCHMe_2)_3\}_2]$ or $[H_5Rh_3\{P(OMe)_3\}_6]$, both of which are fluxional.

Product studies [67] on the oxidative addition of H_2 to $[IrD(CO)(PPh_3)_3]$ or of D_2 to $[IrH(CO)(PPh_3)_3]$ show that the final products have the elements of the added molecule either mutually *cis* or mutually *trans* so that *cis* and *trans* addition is thought to be occurring. However, the fact that the products are obtained in approximately the equilibrium ratio and that intramolecular exchange is rapid (although not on the NMR time scale at −20°C) makes it more likely that the addition occurs stereospecifically *cis*, by the normally accepted three centred transition state, which for $[RhCl(PPh_3)_3]$ and H_2 has been calculated [68] to be a low energy process. H—D exchange would then occur in a subsequent step. Enthalpies of oxidative addition of various molecules to $[M(CO)XL_2]$ (L = a wide range of tertiary phosphines and arsines, M = Rh or Ir) have been measured and shown [69] somewhat predictably to be dependent on both steric and electronic factors.

Reaction [70] of $[RhH_2(PPh_3)_2(acetone)_2]^+$ with $[cp_2MH_2]$ (M = W or Mo) gives the interesting mixed metal complex with bridging hydrides (5)



P = PPh_3

(5)

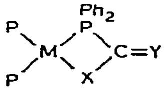
Exchange of the hydrido and cp hydrogens with deuterium is thought to involve oxidative addition of the cp C—H bonds across rhodium.

Low spin rhodium(II) hydrides are thought [71] on the basis of EPR measurements, to be present in UV irradiated single crystals of LiH doped with rhodium.

A wide range of phosphine or arsine nitrosyl containing complexes of rhodium has been made [72] by action of $NOBr_3$ on various rhodium complexes. In general, bromide is also incorporated into the final products giving such complexes as *all trans*-$[Rh(CO)(NO)Br_2(PPh_3)_2]$ (containing bent NO) and $[Rh(NO)ClBr(AsPh_3)_3]$. On occasions oxidation to nitrite occurs as in $[Rh(NO_2)Br_2(PPh_3)_2]$ whilst NOBr is sometimes present intact *viz* $RhBr_3AsPh_3 \cdot 0.5\ NOBr$ and $RhBr_3(OPPh_3)_2NOBr$. Finally, infrared studies suggest that the hyponitrite ion is present in $[RhBr_2(PPh_3)_2]_2[N_2O_2]$ obtained either from $RhCl_3$, $NOBr_3$ and PPh_3 or from $[RhHCO(PPh_3)_3]$ and $NOBr_3$.

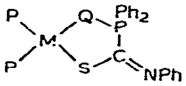
$[RhNO(PPh_3)_3]$ acts [73] as an NO transfer agent to such acceptors as $[NiCl_2(PPh_3)_2]$, $[CoCl(PPh_3)_3]$, $[CoCl_2(PPh_3)_2]$, $[Co(dppe)_2]^+$ or $[FeCl_2(dppe)]$. In the absence of an acceptor, trityl or silver ions promote the self transfer of NO to give $[Rh(PPh_3)_2(acetone)_2]^+$ and $[Rh(NO)_2(PPh_3)_2]^+$. Molecular orbital calculations have been carried out [74] on the related $[Ir(NO)_2(PH_3)_2]^+$. NO can also be lost in reactions of $[IrNO(MeCN)_2(PPh_3)_2]^{2+}$ with aminophenols such as 2-aminophenol, 2-amino-4-nitrophenol, 2-amino-5-methylphenol, 2-aminonaphthol or 2-amino-4-methylphenol (apH) to give [75] $[Ir(ap)(PPh_3)_3]^+$ in which hydrogen atom transfer from a chelating aminophenoxo species is thought to give HNO and the iminophenoxo product. Other products of these reactions are $[Ir(NO)(apH)(PPh_3)]$ and $[IrNO(PPh_3)_3]$.

Pseudo allyl complexes may be prepared [76] from $[RhCl(PPh_3)_3]$ or $[Ir(cot)_2Cl]_2$ in the presence of PPh_3 and $[Ph_2PC(X)(Y)]^-$ or $[Ph_2P(Q)C(X)(Y)]^-$. The compounds containing phosphorus(III) give 4 membered rings (6) whilst five membered rings are obtained if P(V) is present (7).



(6)

Y = X = S or N(4-tolyl)
Y = O, X = NPh
Y = NPh, X = S

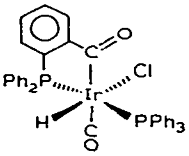


(7)

Q = S or O

A number of reactions of these compounds has been reported [76,77] RNCS (R = Me or Ph) gives $[Rh(PPh_3)\{Ph_2PC(S)NPh\}(PhNCS_2)(PhNC)]$, for which spectroscopic data suggest the presence of a phenyl isocyanide and a phenyl dithiocarbimate ligand. Similar results are obtained with CS_2. The loss of PhNCO from (7) (Q = S) to give [76] $[Rh(S\text{-}PPh_2)(PPh_3)_2]_2$ is somewhat reminiscent of the formation [78] of $[Ir(NCS)(CO)(PPh_3)_2]$ from $[Ir(N_3)(CS)(PPh_3)_2]$ and CO, and of the formation [79] of $[RhCl\{P(CHMe_2)_3\}_2SO_2]$ by hydrolysis of $[RhCl(P(CHMe_2)_3)_2\{OSNH(4\text{-tolyl})\}]$, for which X-ray structural data show an *S*-bonded ligand. Syntheses of the related dimeric $[RhCl(PPh_3)_2SO_2]_2$, $[RhCl(PMePh_2)_3SO_2]$ and $[Ir(SPh)(CO)(PPh_3)_2SO_2]$ have been reported [80], the last of which contains pyramidal *S*-bonded SO_2, as does $[IrCl(CO)(PPh_3)_2(SO_2)]$ for which enthalpies of formation have recently been measured [81,82]. All of these complexes give sulphates on reaction with oxygen and correlations between mode and reversibility of binding have been devised [80].

Metallation of $(CMe_3)_2PCH(R)OCH_3$ (R = Me or H)(P) by $[IrCl(cot)_2]_2$ to give $[IrHCl\{(CMe_3)_2PCH(R)OCH_2\}P]$ is so rapid that non-metallated products cannot be isolated [83]. This contrasts with similar reaction on platinum(II) but probably arises because electrophilic attack is implicated [84] for this and related metallation on iridium(I) whilst metallation by Pd(II) and probably Pt(II) involves nucleophilic attack. A similar metallation occurs [85] on treating $[IrCl(CO)(PPh_3)_2]$ with $Ph_2P(C_6H_4CHO)$ to give (8)

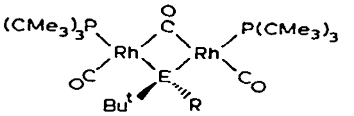


(8)

but this loses CO on heating, by an analogous mechanism to that proposed for decarbonylation of aldehydes, to regenerate the starting complex.

A related metallation of 2-vinyl-pyridine occurs [86] in its reaction with $[Rh_2X_6(PBu_3)_4]$ to give $[Rh(CHCHC_6H_4N)X_2(PBu_3)_2]$ (X = Cl or Br). Simple metathesis of chloride for bromide occurs on shaking the complex (X = Cl) with LiBr, but reaction with bromine affords $[Rh\{CHC(Br)C_6H_4N\}Br_2(PBu_3)_2]$.

Finally, reaction of $[RhCl(PPh_3)_3]$ with $Li[N(SiMe)_2]$ gives [87] the three-coordinate $[Rh\{N(SiMe_3)_2\}(PPh_3)_2]$, presumably on account of the bulk of the amide ligand; and phosphido bridged species (9) are obtained [88] on treatment of $[RhCl(CO)(PBu_3)_2]$ with $[(CMe_3)(SiMe_3)RE]$ (R = CME_3 or $SiMe_3$; E = As or P).



(9)

4.5.3 Ditertiary phosphine and related complexes

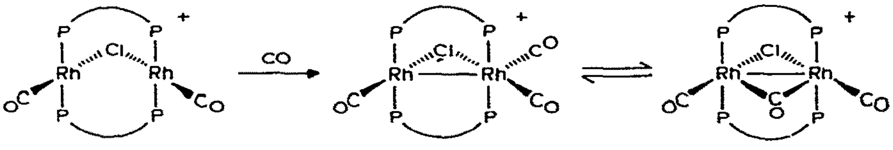
Interaction of $[(\mathrm{cod})\mathrm{RhCl}]_2$ with diphosphine ligands (P—P = $\mathrm{Ph_2P(CH_2)_nPPh_2}$; n = 1—4, or (+)diop) in benzene gives [89] compounds of general formula $[\mathrm{Rh(P—P)_2Cl}]$. For n = 3, the same compound is obtained [90] from $[\mathrm{RhCl(C_2H_4)_2}]_2$ and dppp in methanol. In polar solvents, all of the complexes are ionic but variations in the ^{31}P NMR chemical shift of the phosphorus atoms in $[\mathrm{Rh(dppm)_2Cl}]$ suggest [89] that it is five coordinate in non-polar solvents. Similarly, for n = 4 and for (+)diop, the chloro complexes show complicated ^{31}P NMR spectra, which are thought to arise from there being both ionic and 5-coordinate species in solution, although the presence of multinuclear species with bridging diphosphines cannot be ruled out. These three complexes (n = 2, n = 4 and (+)diop) are also thought to be 5-coordinate in the solid state. The free cations $[\mathrm{Rh(P—P)_2}]^+$ for all the complexes are obtained on addition of the silver salt of a non-complexing ion ($[\mathrm{PF_6}]^-$, $[\mathrm{AsF_6}]^-$ or $[\mathrm{SbF_6}]^-$). Many of the ionic species are active hydrogenation catalysts although with chloride present very low activities are observed [89]. $[\mathrm{Rh(dppp)_2}]^+$ [90] and $[\mathrm{Rh(P—P)(cod)}]^+$ [91] oxidatively add hydrogen to give *cis*-$[\mathrm{RhH_2(dppp)_2}]^+$ and $[\mathrm{Rh(P—P)(MeOH)H_2}]^+$ in the last of which the phosphine is coordinated by both phosphorus atoms and the 3-O atom of the (2R,4R)-bis(diphenylphosphinomethyl)dioxolan ligand (P—P).

Somewhat surprisingly, similar reactions starting from $[\mathrm{RhCl(C_2H_4)_2}]_2$ and (+)diop or dppp [90] or from $[(\mathrm{diene})\mathrm{RhCl}]_2$ (diene = cod or nbd) and etdp [92] in non-polar solvents do not give these ionic products but lead to stepwise displacement of ethylene to give $[\mathrm{(P—P)RhCl_2Rh(C_2H_4)_2}]$ and $[\mathrm{(P—P)_2RhCl}]_2$, retaining the dimeric structure, although ionic compounds are formed in methanol in the presence of non-coordinating ions.

Addition of $\mathrm{Na[BH_4]}$ to $[\mathrm{RhCl(P—P)_2}]$ (P—P = $\mathrm{Ph_2P(CH_2)_nPPh_2}$, n = 2 or 3, or (+)diop) affords [89] $[\mathrm{RhH(P—P)_2}]$ which, for n = 2 has also been prepared [93] electrochemically from $[\mathrm{Rh(dppe)_2Cl}]$, the hydride being abstracted from solvents such as ethanenitrile. The presence of the radical intermediate $\mathrm{Rh^0(dppe)_2}$ is inferred from the identification of cyclohexene, cyclohexane, bicyclohexyl and di(cyclohexyl)mercury, the mercury in the latter coming from the electrode, when the reduction was carried out in the presence of cyclohexylchloride.

The chelate coordination [89] of dppm to rhodium(I) in $[\mathrm{Rh(dppm)_2}]^+$ is somewhat unusual since, in general, dimeric A-frame type complexes are formed but it is interesting to note that a rhodium(III) complex, *trans*-$[\mathrm{RhHCl(dppm)_2}][\mathrm{BPh_4}]$ is formed [94] on reaction of $[\mathrm{Rh(CO)_2Cl_2}]^-$ with 2 moles of dppm whilst 1 : 1 ratios give the usual A-frame type complex $[\mathrm{Rh_2(CO)_2}(\mu\text{-Cl})(\mathrm{dppm})_2]^+$. Similar Rh(III) complexes, $[\mathrm{RhCl_2(L—L)_2}]\mathrm{Cl}$ (L—L = dppe or dpae) are obtained [95] from $[\mathrm{RhCl_4(H_2O)}]^-$ and L—L. The chelate nature of dppm in $[\mathrm{RhHCl(dppm)_2}][\mathrm{BPh_4}]$ has been confirmed by X-ray studies [94]. The diphosphite etdp can also act as either a bridging or chelate ligand for Rh(I). Apart from those chelate complexes described above, others include, $[Rh(etdp)_2XBr]^+$ (X = H or Br), obtained [92] from oxidative addition of XBr to $[Rh(etdp)_2]^+$ and $[Rh(diene)(etdp)]^+$ which is formed on addition of etdp to $[Rh(diene)S_2]^+$ (diene = cod or nbd). Both $[Rh(etdp)_2]^+$ and $[Rh(diene)(etdp)]^+$ are reversible CO carriers in solution. As a bridging ligand, etdp forms [95] $[Rh_2(CO)Cl_2(etdp)_2]$ after recrystallisation of the product obtained either from $[Rh(CO)_2Cl]_2$ and etdp or from $[Rh(etdp)Cl]_2$ and CO from first benzene and then $CHCl_3$/petroleum. The crystal structure of this compound shows it to have bridging etdp ligands with one Rh atom having two terminal Cl groups making up a trigonal bipyramid and the other a single terminal CO group *trans* to the Rh—Rh bond in a square planar configuration [96]. A similar type of structure has recently been observed for $[Pt_2(Me)_3(\mu\text{-dppm})_2][PF_6]$ [97].

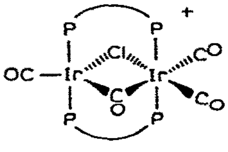
As mentioned above, $[Rh(CO)_2Cl]_2$ reacts with 1 mole of dppm or dpam to give the A-frame complexes $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ [94,98] for which the crystal structure of the $[BF_4]$ salt shows [99] a non-bonded Rh—Rh distance of 3.152 Å, and square planar geometry about each rhodium atom, with terminal CO *trans* to bridging Cl. The other possible bridging site is apparently less blocked by phenyl rings than it is when SO_2 or S are adducted. The SO_2 adduct is formed by simply passing SO_2 through a solution of the cation [100]. A number of workers have studied $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-L—L})_2]^+$ (L—L = dppm or dpam), which is formed [98,101] by bubbling CO through a solution of $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-L—L})_2]^+$ or by reaction [100] of L—L with $[Rh(CO)_2Cl_2]^-$ in the presence of CO. Two X-ray structures for L—L = dppm [98,101] have shown that the extra CO molecule occupies the vacant bridging site and that the Rh—Rh interaction is considerably shorter (2.84 Å) than in the non-adducted dimer, and probably represents an Rh—Rh single bond. The slight differences in parameters for the two determinations are probably a result of different packing forces owing to the presence of different anions. For the bridging CO group, $\nu(C{=}O)$ is at 1863 cm^{-1} [98,100,101], considerably higher than for related Pt and Pd complexes where no M—M bond is present [102,103]. Interestingly, use of ^{13}CO for the formation of the adduct leads [100] to a product containing ^{13}CO both in the bridging and/or the terminal position, suggesting that initial coordination is to one Rh atom and bridging then occurs, or that facile bridge terminal exchange, again via an intermediate containing three terminally bound CO groups (**10**), occurs, or both.



(**10**)

The iridium analogue, $[Ir_2(CO)_2(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, prepared from $[IrCl(C_8H_{12})]_2$, CO and dppm adds [100] more CO to give $[Ir_2(CO)_3(\mu\text{-CO})$-

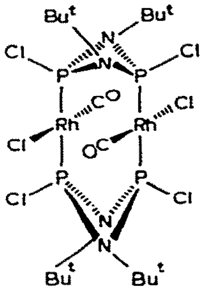
$(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, presumably with no Ir—Ir bond (**11**).



(**11**)

Similar compounds, which do not contain bridges, are formed [104] from $[(cod)RhCl]_2$, L—L (L—L = dppm or dpam) and organoisocyanides but these are considered to be beyond the scope of this review.

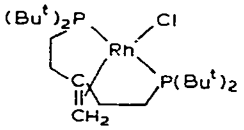
One neutral complex of this type has been reported [105] $[RhCl(CO)(ClPN(CMe_3))_2]_2$, prepared by the action of the phosphetidine on $[RhCl(CO)_2]_2$. The phosphetidine ligands bridge the two Rh atoms with binding through phosphorus and the CO and Cl groups occupy mutually *trans* positions in the square planar coordination sphere (**12**).



(**12**)

Diphosphines that can span *trans* positions are becoming of great interest and crystal structures [106,107] of $[IrCl_n(dpphe)]$ (n = 1 or 3) both show that the phosphine acts as a *meridional* tridentate ligand, the olefin being *trans* substituted. Oxidative additions of Cl_2 and Br_2 to [RhCl(dpphe)], or of Cl_2, H_2, MeI or HCl to the Ir analogue, are rapid and give rise in general to *cis* addition products [107]. The ^{13}C NMR spectra of these complexes have been reported and analysed [108].

A similar type of metallation reaction to that which is thought to give the above dpphe complexes from $Ph_2P(CH_2)_6PPh_2$ has been reported [109] for $(CMe_3)_2P(CH_2)_5P(CMe_3)_2$(P—P). Thus, treatment of $[Rh_2H_2Cl_4(P\text{—}P)_2]$ with 2-methylpyridine breaks down the dimer and gives the metallated complex $[RhHCl\{(CMe_3)_2PCH_2CH_2CHCH_2CH_2P(CMe_3)_2\}]$ for which an X-ray structure again shows meridional coordination for the tridentate ligand. The hydride, which exchanges rapidly on the NMR time scale with the methyne proton, is at the apex of a square pyramid. $(CMe_3)_2PCH_2CH_2MeCH_2CH_2P(CMe_3)_2$ gives the analogous complex hydride which is not fluxional (there being no methyne proton available for exchange) but which loses H_2 to give an olefin complex (13) in refluxing propan-2-ol.



(13)

As part of their interesting studies on compounds containing the P_3 ring, Bianchini et al. have synthesised [110] [M(triphos)P_3] (M = Ir or Rh) from [$RhL_2Cl]_2$ (L = CO or C_2H_4) or [IrClCO($PPh_3)_2$], white phosphorus and triphos. The P_3 ligand is coordinated as a planar cyclic group. Other triphosphine-containing complexes [RhLCl], where L = [$Ph_2P(CH_2)_3]_2PPh$ have also been synthesised [111] and their NMR spectra used to derive a qualitative *trans* influence series which is somewhat different from that found in complexes of Pt(II). Other rhodium triphosphine complexes have been synthesised and abstracted [112].

The phosphonium cation, [$Ph_2P(CH_2)_2PPh_2Bz]^+$ (P—P$^+$) has been used [113] to anchor catalytically active rhodium complexes to insoluble supports such as hectorite by forming such complexes as [RhCl(PPh_3)(P—P$^+$)] and [RhCl(cod)(P—P$^+$)] [$BF_4]^-$. [RhCl(P—P$^+)_n$] (n = 2 or 3) prepared from [RhCl(cod)]$_2$ and two or three moles of P—P$^+$ are not catalytically active, suggesting that this ligand is less labile than PPh_3.

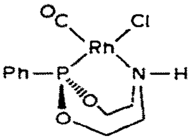
Water soluble complexes of the general formula [Rh(P—P)nbd]$^+$ where the diphosphine is derived from bis(2-diphenylphosphinoethyl)amine via coupling at nitrogen with a sulphonated group, a polyhydroxo species or a polyether have been reported [114] and used for hydrogenation. A similar complex where the diphosphine is derived from [115] a sugar has been used for asymmetric silylation of alkenes. Other workers from several groups [90,91,116—120] have used ^{31}P NMR and ^{13}C NMR studies [121] to show that only certain possible isomers are present when such ligands as α-acetamido cinnamic acid are coordinated to a rhodium atom which is coordinated by a chiral diphosphine, and have correlated this behaviour with the complexes' ability to induce asymmetric hydrogenation.

Finally in this section, chelate ligands containing only one phosphorus or arsenic atom will be considered. [Rh(cod)Cl]$_2$ reacts [52] with tris-(2-pyridyl)phosphine (PPy_3) to give [RhCl($PPy_3)_2$] in which one of the phosphine groups is bound by a nitrogen atom as well as the phosphorus atom. In contrast, [RhH(CO)(PPh_3)($PPy_3)_2$] and [RhCl(CO)($PPy_3)_2$] do not appear to have such an interaction. For the latter complex, this has been confirmed crystallographically [53].

8-Diphenylphosphinoquinoline (P—N) reduces [122] $RhCl_3$ to the paramagnetic square planar [$RhCl_2$(P—N)$_2$] whilst dimeric [$RhCl_3$(As—N)]$_2$ is obtained from 8-diphenylarsinoquinoline (As—N). Both of these ligands give dimeric chloride bridged dimers, [$RhCl_2$(CO)(N—X)]$_2$, on reaction with [$RhCl_2(CO)_2]^-$. The lack of an Rh—Rh bond in these Rh(II) dimers is evidenced by their magnetic moments of ca. 2.3 μ_B. For the related *trans*-

$[RhCl_2(Me_2AsC_6H_4NMe_2)]^+$, it has been shown that treatment with either a 2-electron donor (e.g. NR_3) [123] or an anionic ligand (e.g. X^-) [124] causes rupture of the Rh—N bond and formation of $[RhCl_2(As\text{—}N)_2Y]^{n+}$ ($Y = NR_3$, $n = 1$; $Y = X$, $n = 0$). The kinetics of these reactions have been discussed.

An interesting series of ligands, based on $PhP(OCH_2CH_2)_2NH$ (P—N) has been used [125,126] to form complexes of rhodium, [RhClCO(P—N)] from $[RhCl(CO)_2]_2$ or $[Rh(P\text{—}N)_2]^+$ from $[RhCl(C_2H_4)_2]_2$. In all the complexes, the rhodium atom sits above the cradle formed by the ligand (14)



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4.6 COMPLEXES WITH GROUP VI DONOR LIGANDS

4.6.1 Oxygen donors

Action of acetic anhydride on dmf solutions of $[Rh(NH_3)_5H_2O][CF_3SO_3]_3$ gives [127] the previously reported [128] $[Rh(NH_3)_5(OAc)][CF_3SO_3]_2$ in 81% yield, whilst the only other carboxylate complexes reported are those from edta and related sequestering ligands. Equilibrium constants have been measured [129] for the formation of $[RhLCl_2]^{3-}$, $[RhLClOH]^{3-}$ and $[RhL(OH)_2]^{3-}$ (H_4L = edta) from $[RhCl_5]^{2-}$ and for the interconversions between these species. X-ray structural determinations [130] on the related $K[Ir(H_2L)Cl_2]$ and (+)-K[Ir(HL)Cl] · H_2O show that in the former H_2L is bound as a tetradentate ligand with the chlorides *trans* to the two nitrogen atoms, whilst the latter, which has absolute configuration ΛΔΛ*, contains a pentadentate HL ligand with Cl again *trans* to a nitrogen atom. K[Ir(HL)Cl] has also been prepared [131,132] for L = *trans*-1,2-cyclohexanediaminotetraacetate, by refluxing the dipotassium salt with solutions of $K_3[IrCl_6]$ · 3 H_2O. Addition of MCl to K[Ir(HL)Cl] affords $M[Ir(H_2L)Cl_2]$ (M = H or K). The structures of these compounds are analogous to their edta counterparts (see above) and related rhodium(III) complexes have been prepared [132].

Coefficients for the partition of $Rh(acac)_3$ between heptane and water-dmso have been measured [133] and discussed in terms of the extended McDevit and Long theory.

Vapour pressure measurements have been carried out [134] on $[M(tfa)_3]$ (M = Co, Rh or Ir) and the thermal stability shown to increase on going down the group. Photochemically, $[Rh(tfa)_3]$ decomposes [135,136] to a rhodium(II) complex, *trans*-$[Rh(tfa)_2(SH)_2]$ in the presence of hydrogen donors (SH) such as propan-2-ol. In the absence of such donors, the initially formed charge transfer excited state decays to the starting material, although isomerisation, either by a Bailar twist or via partial dissociation of a tfa ligand, can occur [135].

The ^1H NMR spectrum of [Rh(3-mesitylacac)$_3$] has been analysed [137] and the fact that the chemical shift of the *ortho* and *para* methyl groups are so similar used to show that there is little anisotropy in the aromatic ring.

It has been shown [138], on the basis of M—O bond lengths in [Rh(acac)(CO)(PPh$_3$)], that PPh$_3$ has a higher *trans* influence (the term *trans* effect is used in the paper to describe both the thermodynamic parameter normally referred to as *trans* influence [139] and the kinetic parameter correctly termed *trans* effect) than CO in these complexes as in those of Pt(II). For the unsymmetrical complex, [Rh(tta)(CO)$_2$] (1), reaction with PPh$_3$ displaces the CO *trans* to the trifluoroacetyl group, suggesting that this group has a higher *trans* effect than the thenoyl moiety. Small differences in the Rh—C distances in [RhL(CO)(PPh$_3$)] (L = tta or acac) suggest that the acetyl group has a higher *trans* influence than its perfluorinated analogue. Discussion based on the reaction of [Rh(acac)(CO)(PPh$_3$)] with tta which gives the product with CO *trans* to the trifluoroacetyl group confuse *trans* influence and *trans* effect, which are often not the same in square planar complexes, since associative exchange mechanisms generally operate [140].

A qualitative *trans* effect (termed *trans* influence by the authors) series for the halide ions, $I^- > Br^- > Cl^-$, has been derived [141] from reactions of H[RhX^{1}X^2(dmg)$_2$] (X^1, X^2 are halide ions). Thus, on reaction with another halide the lighter one is replaced before the heavier and with thiourea only the lighter halide is replaced. With pyridine or aniline (N) H[RhClBr(dmg)$_2$] gives a mixture of [RhCl(dmg)$_2$N] and [RhBr(dmg)$_2$N] in which the latter predominates. The electrochemistry of these and related species has been studied [142] as a means of identifying the catalytically active species produced by reduction of rhodoximes with Na[BH$_4$]. An initial two electron reduction of H[Rh(dmg)$_2$Cl$_2$] forms [Rh(dmg)$_2$]$^-$ which then reacts with unchanged starting complex to give [Rh^{II}(dmg)$_2$]$_2$. This compound gives [Rh^{III}(dmg)$_2$H] with hydrogen and the hydride reacts with oxygen to give [Rh(dmg)$_2$]$^+$ which in turn regenerates the rhodium(III) hydride on reaction with hydrogen. It is this rhodium(III) hydride which is thought to be the active hydrogenation catalyst. α-Piperidineacetophenone also forms [143] a rhodium complex which is active for hydrogenation.

Other Schiff base complexes, [Rh(Sal=NR)(C$_2$H$_4$)$_2$] have been prepared [144] from [RhCl(C$_2$H$_4$)$_2$]$_2$ and Tl(Sal=NR) [Sal=NR = N-4-tolylsalicylaldimine (R = 4-tol) or N-methylsalicylaldimine (R = Me)]. These complexes react with phosphines or arsines to give [Rh(Sal=NR)(C$_2$H$_4$)L] (L = PPh$_3$ or AsPh$_3$) or [Rh(Sal=NR)L$_2$] (L = PPh$_3$, PMePh$_2$; R = Me). The latter products are also obtained from ditertiary phosphines or arsines (L$_2$ = dpae, (Ph$_2$AsCH)$_2$ or (Ph$_2$PCH)$_2$, R = Me or 4-tol). [Rh(Sal=NR)L$_2$] add methyl iodide to give [RhMeI(Sal=NR)L$_2$] (L = PPh$_3$ or PMePh$_2$) whilst [Rh(Sal=NR)(dpae)] gives 5-coordinate [Rh(Sal=NR)(dpae)C$_4$F$_6$] with hexafluorobut-2-yne.

Finally, a number of complexes of rhodium with oxygen anions has been reported. Thus, rhodium trichloride reacts [145,146] with $[NH_4]_6Mo_7O_{24}$ to give $[NH_4]_3[RhMo_6O_{18}(OH)_6] \cdot 7\ H_2O$ and the analogous potassium salt arises from reaction of K_3RhCl_6 with K_2MoO_4. The related tungstophosphate, $[(nbd)_2RhSnW_{11}PO_{39}]^{4-}$ is formed [147] on interaction of $[(nbd)_2Rh(SnCl_3)]$ with $[W_{11}PO_{39}]^{7-}$, a reaction which is related to the supporting of such rhodium complexes on inorganic oxide supports. Sodium triphosphate gives [148] the polyanionic $[Rh(HP_3O_{10})_2]^{5-}$ and $[Rh(P_3O_{10})_2]^{7-}$ on reaction with $RhCl_3$.

Various studies of Ir(III) [149] and Ir(IV) [150] species present in mineral acid solutions (H_2SO_4, $HClO_4$ or H_3PO_4) have been carried out and the extraction of rhodium from sulphuric acid solutions has been shown [151,152] to be most efficient when the surfactant octylaniline cation is added, although dependence on the anion of the extracting species, $Br^- > Cl^- > SCN^-$ has also been noted [152]. The rhodium species present in these solutions are evidently $Rh_2(SO_4)_3$ and $Cs_2H_4[RhO(SO_4)_4(HSO_4)_2]$ [152].

4.6.2 Rhodium(II) carboxylates

Although most of the work carried out on the dinuclear carboxylates of Rh(II), $[Rh_2(O_2CR)_4]$, has been spectroscopic and aimed at elucidating the nature of the M—M interaction, some reaction chemistry has also been reported.

Reactions of $[Rh_2(OAc)_4]$ with HX (X = Cl, Br) in ethanol or acetone lead [94] to destruction of the dimer and formation of $[RhCl_4(H_2O)]^-$, which can be precipitated with $[Ph_4As]Cl$ and whose reaction chemistry is discussed elsewhere in this review.

Adenine based nucleosides or nucleotides in general form 1 : 1 adducts with $[Rh_2(OAc)_4]$ which are believed to be polymeric, the adenine acting as a bridge between two dinuclear rhodium moieties, coordination being via the N_1 and N_7 atoms [153] of the purine ring. The only exception to this general rule occurs for tetra acetyl adenosine which forms 1 : 2 adducts because coordination of N_1 is precluded by the steric hindrance of the adjacent bulky acetyl group. Although this last observation would appear to suggest that bonding of similar nucleosides to $[Rh_2(OAc)_4]$ can occur through only one nitrogen atom, guanosine, inosine and cytodine do not form adducts. Substituted guanidines ($NH_2C(=NH)NHR'$; R' = H, CN or NH_2) form [154] 1 : 2 adducts with $[Rh_2(O_2CR)_4]$ (R = H, CH_3 or Et) but, for the more electron-withdrawing cyano groups, the lower availability of the N-lone pair leads to the isolation of 1 : 1 adducts for R = Me or Et. A similar explanation accounts for the lack of adduct formation when R' = NO_2. In the presence of HCl, these adducts do not form but chloride ion adds to give $[GuH]_2[Rh_2(O_2CR)_4Cl_2]$ (Gu = $NH_2C(=NH)NHR'$). Finally, replacement of O_2CR by carbonate occurs on reaction with guanidine carbonate [154].

X-ray structures of a number of adducts of $[Rh_2(O_2CR)_4]$ have been measured. These include $[Rh_2(O_2C(CH_2)_2NH_3^+)_4(H_2O)_2][ClO_4]_4$, obtained [155] from the action of perchloric acid on the product of reaction of $RhCl_3 \cdot 3 H_2O$ and t-butyloxycarbonyl-β-alanine, and $[Rh_2(O_2CCF_3)_4(EtOH)_2]$ which shows extensive hydrogen bonding between EtOH groups of adjacent dimers [156].

Comparison of the Rh—Rh bond lengths in $[Rh_2(OAc)_4X_2]$, ($X = H_2O$, py, $NHEt_2$, CO, $P(OPh)_3$, PF_3 or $P(OMe)_3$) shows [157,158] that it increases from 2.3955 to 2.4555 Å along the series and, as expected, varies with the *trans* influence of the adduct ligand provided that both σ and π interactions are taken into account [157]. A more recent publication [159] has suggested that σ factors alone are responsible for these differences in Rh—Rh bond lengths, the apparent higher σ donor capability of CO and PR_3 than of the other donors arising from better overlap of the more diffuse lone pairs of CO and PR_3 with the Rh—Rh σ^* orbitals.

Controversy surrounds [157,159] the exact extent and nature of the π interaction between $[Rh_2(OAc)_4]$ and CO or PR_3. Although both groups of workers agree that there is a π interaction, Cristoph and Koh [157] suggest that the donor orbital is π bonding with respect to the Rh—Rh bond, whilst Norman et al. [159] maintain it is π^*. Enthalpy studies [160] on the formation of adducts of $[Rh_2(O_2CPr)_4]$ suggest that the π donor capability of this complex is high and support the view that the donor orbital is π^* with respect to the Rh—Rh bond. These conclusions are further supported by electrochemical studies on adducted and base free $[Rh_2(O_2CPr)_4]$ [160].

The measured Rh—Rh distances of all the above adducts [157] are considerably less than those expected for a Rh—Rh single bond (2.7 Å) and might be considered more consistent with there being a triple bond, particularly since comparison [158] of the M—M bond lengths and O—C—O and O—M—M angles with those in related complexes suggest that the Rh—Rh distance is not constrained by the ligand framework to be as short as it is. However, detailed MO calculations [157] suggest that the Rh—Rh bond may still be single and purely σ in character but of exceptional strength due largely to π bonding effects of the carboxylate framework, which provides substantial π electron density (formally ligand in origin) in the metal bonding region. A similar conclusion has been reached using [159,161] SCF-Xα-SW calculations and more readily rationalises the UV visible spectral bands both in solution and in the single crystal [162]. The strong band with vibrational structure in the $\perp^b$ polarization at 17 300 cm^{-1} has been assigned as Rh—Rh $\pi^* \rightarrow \sigma^*$ [162], whilst a weaker band at 22 000 cm^{-1} is assigned as a Rh—O $\pi^* \rightarrow \sigma^*$ transition. Both of these bands exhibit weaker low energy shoulders assigned [159] to forbidden $\delta^* \rightarrow \sigma^*$ transitions on the basis of their low intensity and the small energy separation of the π^* and δ^* orbitals. A similar interpretation has been placed [159] on the spectrum of $[Rh_2(OAc)_4(H_2O)_2]^+$, although the bands are shifted to higher energy. An absorption in the spectrum of the cation at 13 000 cm^{-1} which is absent in that of the neutral species has been tentatively assigned [159] to a $\delta \rightarrow \delta^*$ transition.

Attempts further to elucidate the order of the Rh—Rh bond in these complexes have been made by observing [163] the EPR spectrum of $[Rh_2(OAc)_4(PPh_3)_2]^+$ generated either radiochemically or electrochemically. These studies suggest that the unpaired electron is in a phosphine lone pair orbital which is delocalised over the whole molecule. Once again, this does not unequivocally distinguish between the single bond or triple bond models, but on balance, given the better agreement of calculated and observed electronic spectra using the single σ-bonded model, with the π bonding interaction being exactly cancelled by a π antibonding interaction, the latter appears to have the upper hand at present.

The stability of the dimer adduct interaction appears to depend both on the σ donor [158,164] and π acceptor [164] properties of the base. Thus, enthalpy studies [164] show that the stabilities of 1 : 1 adducts of $[Rh_2(O_2CR)_4]$ (R = Me or $MeOCH_2$) with isonicotinic acid, pyridine, nyacin and picolinic acid are related to their π acceptor properties. Once one ligand has been added, the π donor orbitals on the metal are less available for donation to a second ligand and hence the stabilities of the 1 : 2 adducts depend more on the σ donor properties of the adding base. Consistent with this, $K_2 << K_1$.

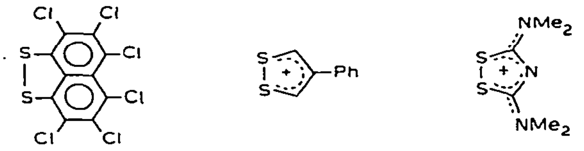
Finally, a full normal coordinate analysis of all the vibrations of the $[Rh_2(OYCCX_3)_4]$ (X = H or D, Y = O or S) moiety has appeared [165]. This allows detailed interpretation of the IR spectra of $[Rh_2(SOCCX_3)_4]$ and assignment of many of the vibrations. The infrared spectra of the dinuclear $[Rh_2(O_2CR)_2(N—N)_2X_2]$ (R = H or Me; N—N = bipy or phen; X = Cl or Br) have also been reported [166] and the low value of Rh—X taken as indication of a weak Rh—X interaction in these species, which contain carboxylate bridges, chelating nitrogen ligands and apical halides. The compounds are prepared from $[Rh_2X_2(allyl)_4]$, nitrogen ligand (1 : 2) and carboxylic acid in ethanol. The X^- ligands are readily solvolysed in water.

4.6.3 Sulphur donors

Simple metal polysulphides have been used [167] for the extraction of rhodium and iridium from such ores as magnetite and pyrrhotite. Sulphur—sulphide concentrates of the ores were digested with alkali and 60—80% of the metal was extracted as an alkali stable polysulphide. The role of sulphur and selenium in the formation of cluster complexes of rhodium(III) has also been discussed [168].

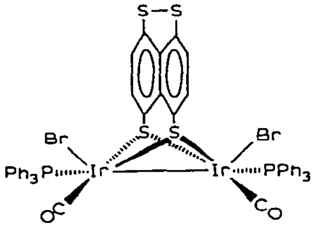
Simple alkyl sulphide or selenide complexes have been prepared from Bz_2X (X = S or Se) which give [169] *mer*-$[RhCl_3(XBz_2)_3]$ on reaction with $RhCl_3$; and from C_6F_5SH which apparently gives [170] sublimable $[Rh(SC_6F_5)_3]$ on refluxing with $RhCl_3$. This compound, surprisingly, does not form adducts with such bases as pyridine or bipy. Related thiosemicarbazide (LH) complexes of iridium(III) [171] and rhodium(III) [172] have also been reported. For the iridium complexes, reaction of $K_3[IrCl_6]$ with LH in HCl in the presence or absence of sodium ethanoate produces a series of complexes in which the thiosemicarbazide is not deprotonated and acts as a bidentate (N, S) ligand. These include $[IrHLCl_3] \cdot 1.5\ H_2O$ and $[Ir(HL)_2Cl_2]Cl \cdot H_2O$ whilst in other complexes a proton is lost from the hydrazine NH_2 group to give $[Ir(HL)LCl_2] \cdot 2\ H_2O$ or $[Ir(HL)L(H_2O)Cl]Cl \cdot 2\ H_2O$. For the rhodium(III) complexes, 1-salicylidene-4-phenylacetamidothiosemicarbazide forms [172] a diamagnetic octahedral complex with the thiosemicarbazide as a bidentate (*N*, *S*) ligand, whilst 1-(α-furfurylidene)-4-phenylacetamidothiosemicarbazide binds as a tridentate (*O*, *N*, *S*) ligand to give a complex of D_{4h} symmetry. These arguments are based on IR and UV/visible spectral data.

Some other sulphido species have been obtained by oxidative addition of alkyldisulphides to M^I (M = Ir or Rh) species. Thus, $[RhCl(PPh_3)_3]$ reacts [173] with cyclic disulphides, (**15**) (S—S)



(15)

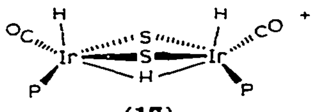
to give compounds in which the metal inserts into the S—S bond. All the products are neutral complexes of rhodium(III) of the general form $[RhCl_n\text{-}(S{-}S)(PPh_3)_2]$ where $n = 1$ for the neutral disulphide or 2 for the cationic disulphides. Interestingly, the similar tetrathionaphthalene does not add to iridium(I) to give an iridium(III) complex, but rather gives [174] the iridium(II) dimer (**16**) on reaction with $[IrBr(CO)(PPh_3)_2]$.



(S = $SCMe_3$)

(16)

The related iridium(I) dimer, $[Ir(SCMe_3)CO(PPh_3)]_2$ has been shown [175] to react with hydrogen to give a product, $[IrH(SCMe_3)CO(PPh_3)]_2$ which could be formed by addition of hydrogen across the double bond. However, it is believed [175] that activation of hydrogen occurs at one iridium atom and that this is followed by intramolecular hydrogen transfer. Protonation [176] of the dihydride gives (**17**).

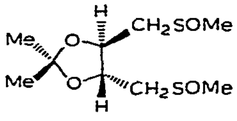


(17)

The electrochemistry of $[Rh(mnt)_2]^{2-}$ shows [176] that it will undergo reversible one electron oxidation or reduction at −0.73 and −1.37 V, respectively, but that on standing, the rhodium(III) species $[Rh(mnt)_2]^-$ forms a polymer which is not readily reduced. Both the rhodium(I) and rhodium(III) products are diamagnetic and they can be generated, respectively, with $Li[AlH_4]$ in thf or with iodine or tcne. Other work on mnt complexes has shown that in $[Rh(COR)(mnt)P_2]$ (P = PPh_3 or PEt_3; R = alkyl), generated [177] from [Rh(CO)(mnt)P] and alkyl halide, reversible migration of the alkyl group onto a sulphur atom can occur [178]. The structure of $[Rh(CO)(mnt-Et)(PPh_3)]$, shows [178] it to be a square planar complex of rhodium(I) with CO *trans* to the non-alkylated S atom.

For the 1,1-dithiolates, electronic spectra suggest [179] that six coordinate *tris* chelate complexes $[M(S—S)_3]$ (M = Rh or Ir) are formed with the 3-indoledithiocarboxylate ion, and detailed IR and electronic spectroscopic studies have shown [180] a high degree of covalency in the Rh—S bonds of $[Rh(S_2CMe)_3]$.

As part of their studies on the asymmetric hydrogenation of prochiral alkenes, James and co-workers have synthesised [26,181] a number of sulphoxide complexes of rhodium(I) and rhodium(III). Thus, wet isopropanol solutions of $RhCl_3$ give *mer*-$[RhCl_3(R_1R_2SO)_2(R_1R_2SO)]$ {$R_1 = R_2$ = Me or CD_3; R_1 = (R)-(+)-menthyl, R_2 = 4-tolyl; R_1 = Me, R_2 = Ph; $R_1R_2 = (CH_2)_4$; *S* and *O* refer to sulphur or oxygen bound sulphoxide, respectively} from which the *O*-bonded sulphoxide is readily replaced by other *O*-donors. If pyridine-*N*-oxide is used as donor, one or two moles of dmso may be replaced according to the stoicheiometry of the reaction [182]. The sulphoxide complexes react [26] with hydrogen in the presence of base to give rhodium(I) species but hydrido intermediates have not been isolated. For $R_1 = R_2$ = Ph or Pr direct reduction to $[RhCl(Ph_2SO)_2]_2$ occurs, although dipropylsulphoxide also gives $[(Pr_2SO)_2H][RhCl_4(Pr_2SO)_2]$, the hydrogen bonded cation of which is related to the above mentioned $[H(NO_3)_2]^-$ anion [25]. Other rhodium(I) species such as $[RhCl(Me_2SO)_2]_2$, $[RhCl(dios)_n]_2$ (n = 1 or 2, dios = (18)) have been prepared from $[RhCl(cot)_2]_2$, and cationic $[Rh(dtho)_2]^+$ (dtho = 2,5-dithiahexaneoxide) is also known.



(18)

Many of these complexes are active hydrogenation catalysts, but asymmetric induction has not been observed.

Detailed ^1H NMR studies on these and other dmso complexes of general formula $[Rh(dmso)_nX_{6-n}]^{(n-3)+}$ (X = Cl or Br, n = 1—5) have furnished [183] various systematics. Thus, coupling to rhodium is observed for *S*-bonded dmso but larger δ values occur for *O* bonding. On this basis, the structures of these complexes have been assigned. For all the complexes with the exception of one isomer of [$RhX(dmso)_5$]$^{3-}$, which has only one *S*-bonded dmso *cis* to the halide, and one isomer of *mer*-[$RhX_3(dmso)_3$] which has three *S*-bonded dmso groups, two dmso molecules are *S* bonded and the remainder are bonded through oxygen. In general the two *S*-bonded ligands are mutually *cis* although they can be *trans* in [$RhX_4(dmso)_2$]$^-$ or in *mer*-[$RhX_3(dmso)_3$]. IR studies and force-constant calculations on the last mentioned and related complexes show [184] that for the *O*-bonded dmso ligands there is a decrease in S=O double bond character as the M—O bond strength increases. Finally, [$RhCl_3\{(CD_3)_2SO\}_3$] reacts [185] with cyclo-L-methionylthionine to give a complex in which the peptide is coordinated through the sulphur atom, unlike methionine itself for which chelate *N, O* bonding has been proposed [186].

4.7 HALO COMPLEXES

A series of papers [187—190] on the IR and Raman spectra of IrF_6 in both neat [187,188] and mixed [188] single crystals concludes that there is non-vanishing Jahn—Teller interaction in the ground state [188]. Good fits of experimental and calculated data were found for all vibrational modes [188] provided that the Hamiltonian included quadratic terms in various vibrational coordinates [187,189,190]. IrF_6 has also been used [191] to oxidise chlorine, initially via Cl_2IrF_6. This complex then gives a range of products of which [Cl_3] [IrF_6], [Cl_3] [Ir_2F_{11}], Ir_4F_2O and Cl_3F have been identified.

The inertness of [$IrCl_6$]$^{2-}$, for which resonance Raman spectra have been reported and assigned [192], has made it possible to carry out [193] detailed studies on its various equilibria set up in water, and to identify all intermediates present in the hydrolysis. Under electrophoresis conditions in Na[ClO_4], [$IrCl_6$]$^{2-}$ is reduced [194] to [$IrCl_6$]$^{3-}$, which is the migrating species. K^+ and [NH_4]$^+$ suppress the reduction by the formation of outer sphere complexes.

Proton tunnelling has been observed [195] in [NH_4]$_2$ [$IrCl_6$] and tetraoctylammonium salts have been used [196] to extract [$IrBr_6$]$^{2-}$ or [IrF_6]$^{2-}$ into dichloroethane. Significantly, tridodecylammonium fluoride can be employed [197] as a phase transfer agent for halide exchange in [IrX_6]$^{2-}$ to give [MF_nX_{6-n}]$^{2-}$. [$IrCl_6$]$^{2-}$ has also been used [198] for the oxidation of organobis(dimethylglyoximato)cobalt complexes initially to give cation radicals, [$Co(dmg)_2R(H_2O)$]$^+$.

In contrast, [$IrCl_6$]$^{3-}$ can reduce [199] copper(III) peptides, despite the fact that the reaction is thermodynamically uphill. Acid hydrolysis of the formed copper(II) peptide, which is much more rapid than that of the copper(III) complex, disturbs the equilibrium in the desired direction. Electron transfer does not occur between [$IrCl_6$]$^{3-}$ and $InCl_3$ although potentiometric studies [200] suggest that $IrInCl_6$ may be produced.

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