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4. Iridium

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CONTENTS

INTRODUCTION

This chapter surveys the coordination chemistry of iridium reported during 1990. Complexes have been arranged according to the oxidation state of the iridium atom(s) and each section is subdivided with respect to the donor atom(s) of the ligand. Some overlap with complexes of rhodium is unavoidable and hence the reader will find cross references to associated work in the accompanying chapter which surveys the coordination chemistry of rhodium for 1990. The final section of this survey includes some homo– and heterometallic iridium clusters; it is not a comprehensive account, but rather highlights aspects of the cluster area. As usual, I am extremely grateful to the Cambridge Crystallographic Data Base for allowing access to coordinates for structural figures redrawn for this review. (Hydrogen atoms have been omitted from most figures for clarity).

Two reviews of general interest have appeared during the past year. For the present series of *Coordination Chemistry Reviews*, Constable [1] has surveyed complexes of iridium for the year 1984 (67 references). Steel [2] has reviewed transition metal (including Ir) complexes in which

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aromatic *N*-heterocycles serve as bridging ligands. The article (439 references) is sectionalised according to ligands: azines, azoles, bipyridyldiazines, 2,2'-bipyrimidines, ligands incorporating 2,2'-bipyridine units, tridentate chelates and mixed denticity ligands.

4.1 IRIDIUM(VI), IRIDIUM(V) AND IRIDIUM(IV)

The iridium(V) hydride IrH_5L_2 ($L = {}^iPr_3P$) reacts with $CF_3COOCH_2CF_3$ via an autocatalytic reaction to give $IrH_2L_2(OCH_2CF_3)$ and CF_3CH_2OH. A mechanism has been proposed

$$-d[IrH_5L_2]/dt = k\,[IrH_5L_2]^{1/2}[CF_3COOCH_2CF_3][IrH_2L_2(OCH_2CF_3)]^{1/2}[CF_3CH_2OH]^{-1/2} \qquad \text{(i)}$$

which is consistent with the rate law given in equ. (i) with $k = 1.25 \times 10^{-4}\ M^{-1/2}s^{-1}$. IrH_5L_2 is an effective catalyst precursor for transfer hydrogenation reactions, *e.g.* $CH_2{=}CHCMe_3 + Me_2CHOH \rightarrow MeCH_2CMe_3 + Me_2CO$. [3] Iridium(V) is also stabilised by the ligand $[C(Ph_2PO)_3]^-$ (L^-) in $LIrH_2(SiPh_2Me)_2$; complexes formed with L^- also include iridium(I) (see Section 4.4.4) and iridium(III) species and all are catalysts for the *anti*-addition of silanes to alkynes. [4]

Electronic absorption spectra have been recorded for a series of iridium(VI), iridium(V) and iridium(IV) hydroxy complexes; band half-widths and positions of peak maxima have been determined and assignments have been made. Rate constants for the reduction of Ir(VI) and Ir(V) hydroxy complexes have been determined spectrophotometrically at 25°C in 3M NaOH; $k = (2.57 \pm 0.09) \times 10^{-3}$ and $(1.53 \pm 0.05) \times 10^{-4}\ s^{-1}$ respectively. [5] Photoabsorption studies of the complexation of iridium(IV) with 1,3-$(OH)_2$-C_6H_3-4-R (R = 2-pyridylazo or 2-thiazolylazo) in the presence of $[C_5H_5NCH_2(CH_2)_{14}CH_3][Cl]$ have been reported. Addition of the pyridinium chloride results in the formation of more intensely coloured Ir(IV)-azo complexes. Interest in this area lies in applications to photometric analysis. [6]

Several studies of the kinetics of oxidations involving $[IrCl_6]^{2-}$ have been discussed. The oxidation of $[SO_3]^{2-}$ in aqueous solution at 25°C has been reinvestigated and new data show that, under anaerobic conditions, the sulphur containing product is exclusively the sulphate(VI) ion (equ. (ii)). The consumption ratio $\Delta[IrCl_6]^{2-}:\Delta[SO_3]^{2-}$ is 2.1 ± 0.8. [7] The kinetics of the reaction

$$2\,[IrCl_6]^{2-} + [SO_3]^{2-} + H_2O \rightarrow 2\,[IrCl_6]^{3-} + [SO_4]^{2-} + 2\,H^+ \qquad \text{(ii)}$$

between $[NO_2]^-$ and $[IrCl_6]^{2-}$ or $[IrCl_6]^{3-}$ have been studied under pseudo-first order conditions with respect to $[NO_2]^-$ over a temperature range 50–71°C. The proposed mechanism involves the formation of an intermediate complex between $[IrCl_6]^{3-}$ and HNO_2; rate of loss of hydrogen ion from this intermediate species with concomitant formation of iridium(III) nitro complexes controls the rates of subsequent pathways. [8] The hexachloroiridium(IV) dianion oxidises $[MW(O)_2(\mu\text{-}O)(\mu\text{-}X)(\mu\text{-edta-}N,N')]^{2-}$ (M = Mo, X = O; M = W, X = S) in aqueous perchlorate solution. The kinetics of the outer sphere process ($18 \leq T \leq 40$°C) are dependent upon M and X; when M = Mo and X = O, a straight forward second order rate law is obeyed, but for M = W and X = S, the one-electron oxidised intermediate is sufficiently stable with respect to decomposition that the rate law given in equ. (iii) is obeyed where k_1, k_{-1} and k_2 are defined in equs. (iv)-(vi). [9]

$$-d[\mathrm{Ir(IV)}]/dt = 2k_1k_2[\mathrm{W_2OS}][\mathrm{Ir(IV)}]/\{k_{-1}[\mathrm{Ir(III)}] + k_2\} \qquad \text{(iii)}$$

W_2OS represents $[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-edta-}N,N')]^{2-}$

$$\{\mathrm{W(V)_2}\} + \{\mathrm{Ir(IV)}\} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{\mathrm{W(V)W(VI)}\} + \mathrm{Ir(III)} \qquad \text{(iv)}$$

$$\{\mathrm{W(V)W(VI)}\} \xrightarrow{k_2} \{\mathrm{W(V),\ W(VI)}\} \qquad \text{(v)}$$

$$\{\mathrm{W(V)}\} + \{\mathrm{Ir(IV)}\} \xrightarrow{\text{fast}} \{\mathrm{W(VI)}\} + \{\mathrm{Ir(III)}\} \qquad \text{(vi)}$$

The iridium(IV) cationic complexes $[IrL_3]^+$ and $[IrL'_3]^+$ (L = *N*-R-*N*-R'dtc, L' = $Et_2NCSe_2^-$) have been produced electrochemically by the oxidation of the analogous Ir(III) complexes. Values of E°(IrL_3^+/IrL_3) are dependent upon R and R' and are compared with E°($IrL'_3{}^+/IrL'_3$) in Table 1. A comparison with data for the corresponding cobalt and rhodium complexes reveals the unexpected trend in values of E° of Rh>Co>Ir with the rhodium couple having the most positive E°. Bulk electrolysis allows the preparation of $[IrL_3]^+$ complexes which are stable on the synthetic timescale; in contrast, $[IrL'_3]^+$ dimerises with an associated redox reaction to give $[Ir_2L'_5]^+$. [10]

Table 1 Values of the reversible half wave potential ($E^r_{1/2}$ = E°) for $IrL_3 \rightleftharpoons [IrL_3]^+ + e^-$ or $IrL'_3 \rightleftharpoons [IrL'_3]^+ + e^-$.

L or L'	Et_2dtc	$^iPr_2dtc$	morphdtc	pyrrdtc	$Et_2NCSe_2^-$
$E^r_{1/2}$ / V vs. Ag/AgCl	+0.79	+0.68	+0.92	+0.81	+0.56

The mixed Ir(IV)Ir(III) complex $K_7H[Ir_3O(SO_4)_{8.5}(H_2O)_{0.5}].1.5H_2O$ has been prepared along with related species (see Section 4.2.4) via the reaction of $K_2[IrCl_4]$ with H_2SO_4 in aqueous solution in the presence of $SC(NH_2)_2$. Atomic radial distribution data have been used to structurally characterise the former complex. The core consists of an Ir_3-triangular array, capped by a μ_3-O atom and edge bridged by six sulphato groups, two per Ir-Ir edge; Ir-Ir = 3.30 Å. [11]

4.2 *IRIDIUM(III)*

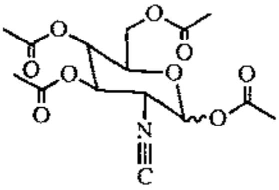
4.2.1 *Complexes with halide, pseudohalide and hydride ligands*

Electron transfer from $[IrCl_6]^{3-}$ to ozone has been investigated. The rate determining step of the reaction given in equ. (vii) appears to occur via an outer sphere electron transfer from the iridium halide to ozone; the $[O_3]^-$ ion is then protonated and the product subsequently oxidises a second equivalent of $[IrCl_6]^{3-}$. In the rate equation, equ. (viii), $k = 1.7 \times 10^4\ M^{-1}s^{-1}$ at 25°C. [12]

$$O_3 + 2[IrCl_6]^{3-} + 2[H]^+ \rightleftharpoons O_2 + 2[IrCl_6]^{2-} + H_2O \qquad \text{(vii)}$$

$$d[IrCl_6]^{2-}/dt = 2k[O_3][IrCl_6{}^{3-}] \qquad \text{(viii)}$$

The isocyanide complex $Cp^*Ir(CNR)Cl_2$ (α-anomer of CNR = (**1**)) has been synthesised and characterised by IR and NMR spectroscopy and X-ray crystallography. (Other related transition metal complexes are also reported). In the IR spectrum, the complexes incorporating the α- and β-anomers of (**1**) are separately characterised by absorptions at ν_{NC} = 2181 and 2159 cm^{-1} respectively and ν_{IrCl} = 295, 269 and 286, 263 cm^{-1} respectively. Pertinent distances for the molecular structure of $Cp^*Ir(CNR)Cl_2$ are $Ir\text{-}C_{CNR}$ = 1.967 (25), Ir-Cl = 2.389 (6), 2.391 (5), CN_{CNR} = 1.130 (28) Å. [13]



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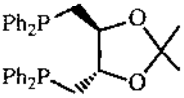

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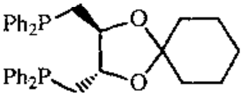

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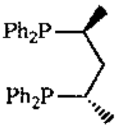

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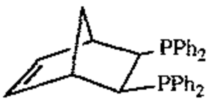

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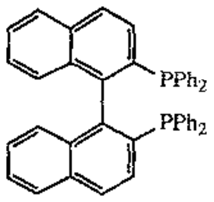


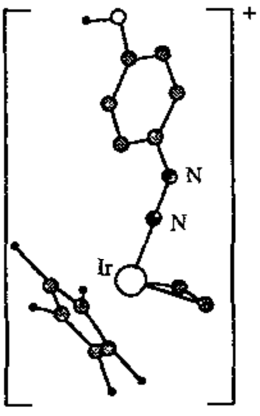
(**6**)

Reaction of $IrCl_3.3H_2O$ with ${}^iPr_3P$ and $NaC_{10}H_8$ in the presence of H_2 in thf at 25°C leads to the complex $Ir(H)_2Cl(\eta^2\text{-}H_2)({}^iPr_3P)_2$ which lies in equilibrium with $\{H_2 + Ir(H)_2Cl({}^iPr_3P)_2\}$. The ^1H NMR spectrum of the complex is dependent upon the pressure of H_2 and the iridium-bound dihydrogen ligand is observed to exchange rapidly with free H_2. An X-ray diffraction study of $Ir(H)_2Cl(\eta^2\text{-}H_2)(^iPr_3P)_2$ (in which H atoms were not located) illustrates a trigonal arrangement of P-donors around the Ir(III) centre; Ir-P = 2.303 (1) and 2.307 (1) Å and Ir-Cl = 2.427 (2) Å. [14]

Reduction of IrH_5L_2 ($L = P(c\text{-}C_6H_{11})_3$) with dppm or dppe (L-L) leads to the nonfluxional complexes *trans-mer*-IrH_3L_2(L-L-*P*) in which the bis-phosphine ligand exhibits a monodentate mode. Spectroscopic characterisation is reported for the Ir(III) complexes; $J_{PHtrans} = 122.3$ Hz, $J_{PHcis} = 22.6$ Hz and $J_{PHtrans} = 117.2$ Hz, $J_{PHcis} = 23.5$ Hz for L-L = dppm and dppe respectively. Related Os and Re complexes are also reported. [15] Dinuclear complexes $[(L\text{-}L)Ir(H)_2(\mu\text{-}I)]_2$ in which L-L= ligands (2)–(6). Both *transoid and cisoid* complexes have been characterised and have been tested as catalysts for enantioselective hydrogenation of selected imines. [16]

4.2.2 Complexes with nitrogen donor ligands

The salt $[NH_4]_2Na[Ir\{NO_2\}_6]$ has been prepared from the trisodium analogue and has been structurally characterised. The octahedral coordination sphere of the Ir(III) ion has contacts Ir-N = 2.060 (8) Å. [17] A series of ammine complexes has been synthesised and characterised: *mer*-$Ir(NH_3)_3Cl_3$, *cis*-$[Ir(NH_3)_4Cl_2]Cl.0.5H_2O$, *trans*-$[Ir(NH_3)_4Cl_2]Cl.H_2O$, $[Ir(NH_3)_5Cl]Cl_2$, *trans*-$[Ir(NH_3)_4Cl(OOCMe)][CF_3SO_3]$ and $[Ir(NH_3)_5(OOCMe)][ClO_4]_2$. A routine method for the high yield (84%) preparation of $Ir(NH_3)_3Cl_3$ from $IrCl_3.xH_2O$ with 12M NH_3 in an autoclave at 150°C for 96 hr is given. The paper includes a discussion of the electronic spectral data for these Ir(III) complexes. [18]



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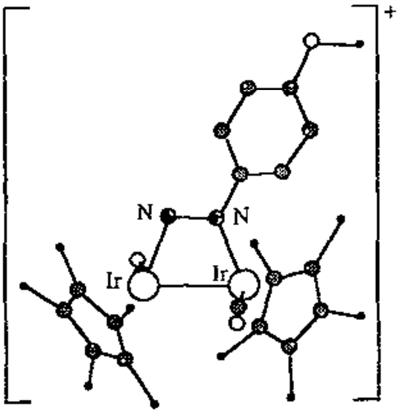
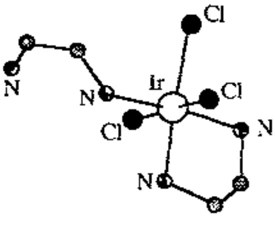


(8)

Treatment of $Cp^*Ir(C_2H_4)_2$ with $[MeO\text{-}C_6H_4\text{-}4\text{-}N_2][BF_4]$ in acetone solution at –78°C leads to the red crystalline mononuclear complex (7) in which one ethylene moiety is retained; selected structural data for (7) are Ir-N = 1.811 (7) Å and N-N = 1.205 (9) Å, ∠IrNN = 176.2 (6)° and ∠120.4 (6)°. The coordinated olefin is removed in further reaction with $Cp^*Ir(CO)_2$ and the diiridium complex (**8**) is produced in which the diazenide ligand adopts a μ_2-η^2-*N,N'*-mode. The central Ir_2N_2-unit is planar with ∠IrNN = 106.2 (24) and 115.1 (25)°, ∠NIrN = 70.7 (10) and 68.0 (10)° and Ir-Ir = 2.723 (4) Å, Ir-N = 2.02 (2) and 2.06 (2) Å and N-N = 1.29 (2) Å. [19] The tris(azenido) iridium(III) complexes $Ir(ArNNNAr)_3$ (Ar = 4-X-C_6H_4; X = H, Me, Cl) have been prepared from $[NH_4]_2[IrCl_6]$ with excess 1,3-diaryltriazene and Et_3N in aqueous ethanol. (Related Rh(III) complexes have been reported; see accompanying Chapter). Spectroscopic data for $Ir(ArNNNAr)_3$ indicate that the tris(azenido) ligands chelate to the metal centre. [20]

Crystallographic characterisation of the neutral complex *mer*-$Ir(en)_2Cl_3$, (**9**), shows that one en ligand is coordinated terminally via a single Ir-N interaction; Ir-$N_{monodentate}$ = 2.103 (4) Å, Ir-$N_{chelate}$ = 2.066 (4) and 2.060 (4) Å. Complex (**9**) has been prepared from the protonated analogue *mer*-$[Ir(en)(enH)Cl_3]^+$, (**10**). Interestingly, the conformation of the monodentate $[enH]^+$ ligand does not mimic that of the corresponding en ligand in (**9**). In (**9**), it adopts a *sym-cis*-conformation whereas in the cation (**10**), it exhibits a *sym-trans*-conformation. Pertinent distances in (**10**) are Ir-N_{en} = 2.088 (9) and 2.068 (9) Å, Ir-N_{enH} = 2.101 (10) Å. [21]



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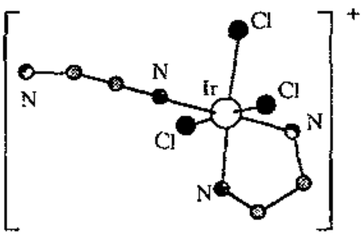
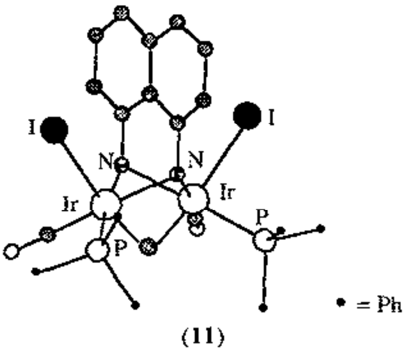


(**10**)

Reactions of $MCl_3(tht)_3$ (M = Rh or Ir) with MeLi in Et_2O in the presence of tmed give the air stable complexes $[Li(tmed)_3][MMe_6]$ which have been successfully used as precursors to a group of rhodium(III) (see Chapter 5) and iridium(III) complexes. One such is *fac*-$IrMe_3(CO)(tmed)$. [22]

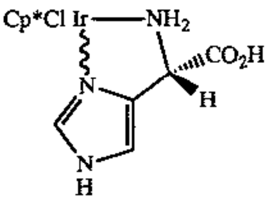


(**11**)

A series of three diiridium(II) complexes containing the bridging diamido ligand, L (H_2L = 1,8-$(H_2N)_2$-$C_{10}H_6$) have been prepared via oxidative addition of I_2, MeI or CH_2I_2 respectively to

$Ir_2(\mu\text{-}L)(CO)_2(PPh_3)_2$. One of the products, $Ir_2(\mu\text{-}L)(CH_2I)(I)(CO)_2(PPh_3)_2$ undergoes thermal oxidative isomerisation to generate the diiridium(III) complex (**11**). Each iridium(III) centre is essentially octahedrally disposed; the triply bridged Ir-----Ir separation is 3.0306 (4) Å and Ir-N distances are 2.158 (6) and 2.158 (5) Å. [23]

The dinuclear complexes $Cp^*MCl(\mu\text{-}Cl)_2MClCp^*$ (M = Rh or Ir) or $(cod)Ir(\mu\text{-}Cl)_2Ir(cod)$ have been used as precursors to a series of half-sandwich compounds involving biologically significant α-amino acid anionic ligands, (see also Section 4.2.6). Cp^*IrCl(L-his), (**12**), has been crystallographically characterised and in solution, diastereomers of (**12**) have been detected by ^1H NMR spectroscopy. [24]



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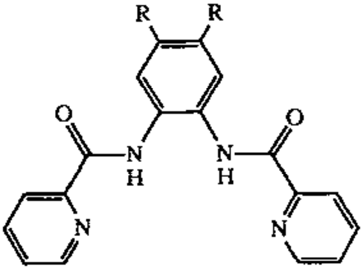
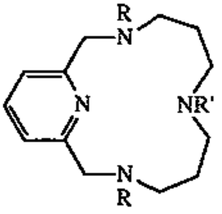


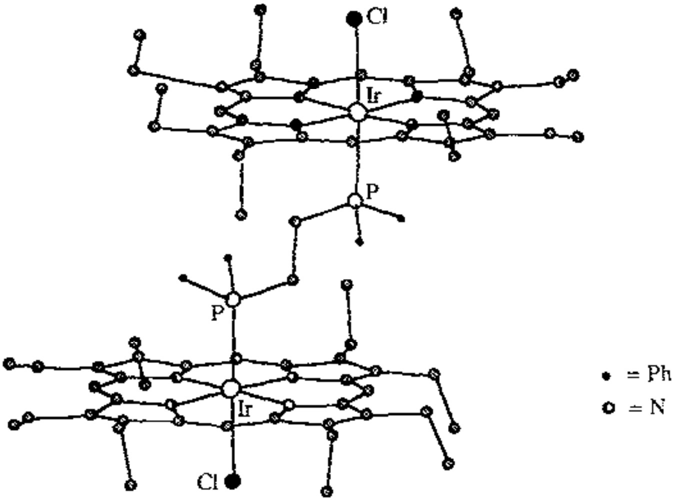
(**13**) R = H
(**14**) R = Cl

The preparations of ligands (**13**) and (**14**) have been detailed in addition to their complexation to rhodium(III) and iridium(III). The complexes $Na[IrLCl_2]$ (H_2L = (**13**) or (**14**)) have been isolated and characterised by IR, electronic absorption and ^1H NMR spectroscopy. The crystallographically determined structure of the related Rh(III) complex $[RhL(py)_2][ClO_4]$ (H_2L = (**13**)) shows that the ligand L^{2-} is tetradentate and occupies the equatorial plane of an octahedral array of donor atoms, (see Chapter 5). [25] The macrocycles (**15**) to (**17**) coordinate to Ir(III) in a similar manner and an X-ray diffraction study of [IrCl(Et)L] for L = (**15**) shows an octahedral coordination sphere with the N_4-donor set lying in the equatorial plane; Ir-N = 1.950 (7), 2.147 (8), 2.131 (8) and 2.139 (8) Å. Significant lengthening of the Ir-Cl bond is observed (2.536 (3) Å) due to the *trans*-influence of the ethyl group. [26]



(**15**) R = R' = Me
(**16**) R = H, R' = Me
(**17**) R = R' = H

The dppe bridged iridaporphyrin complex [Ir(OEP)Cl]$_2$(μ-dppe), (**18**), has been prepared from Ir(OEP)(C_3H_7) and dppe in CH_2Cl_2. The reaction is solvent dependent and, for example, in benzene a mononuclear species persists. Complex (**18**) exhibits a beautiful molecular structure with the two porphyrin moieties stacked above one another and mutually offset. The molecule has C_i symmetry and each Ir(III) atom is displaced 0.065 Å out of the plane of the N_4-donor set and towards the phosphorus atom; Ir-N = 2.059 (15), 2.059 (13), 2.034 (14), 2.029 (14) Å and Ir-P = 2.268 (5) Å. The electrochemical behaviour of (**18**) has been studied; two reversible oxidations and one irreversible reduction (an ECE mechanism) are observed. The first oxidation process is a 2 electron transfer in which one electron is removed from each OEP ligand. The resulting biradical has been characterised by ESR spectroscopy. [27]

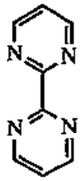


(**18**)

The oxidative addition of an N-H bond to Ir(I) is the method employed to produce the Ir(III) complex $(Me_3P)_3Ir(H)ClL$ where HL = pyrrole, indole, 3-methyl-indole or 7-azaindole. Complexes have been characterised by IR and ^{13}C, ^1H and ^{31}P NMR spectroscopy and a *fac*-isomer for $(Me_3P)_3Ir(H)ClL$ (HL = indole) has been confirmed crystallographically including hydride location *trans*-to the chloride ligand; Ir-N = 2.131 (4) Å and Ir-H = 1.489 (49) Å. [28]

The pyrazolate ligand, L^-, bridges iridium(III) and rhodium(III) atoms in the complex Cp*Ir(μ-I)$_2$(μ-L)RhI(CO)(COOMe). Each transition metal atom is in an octahedral environment (Ir is pseudo-octahedral); for the Ir-(μ-L)-Rh unit distances are Ir-N = 2.095 (8) and Rh-N = 2.081 (9) Å. IR and ^1H NMR spectroscopic data for Cp*Ir(μ-I)$_2$(μ-L)RhI(CO)(COOMe) have been reported. [29]

The synthesis and spectroscopic characterisation of the orthometallated iridium(III) complex [{Ir(bipy-C^3,N')(bipy-N,N')Cl}$_2$]$^{2+}$. Data including ^1H-^{13}C heteronuclear correlation spectra support D_2 molecular symmetry. The dication is prepared from a mixture of $K_2[IrCl_6]$ and $K_3[IrCl_6]$ with 2,2'-bipy in aqueous ethanol; the presence of Ir(IV) facilitates the orthometallation process. [30]



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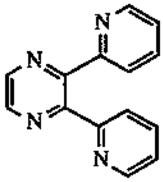

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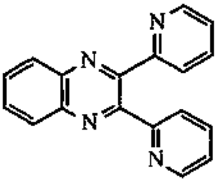

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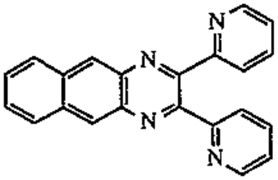
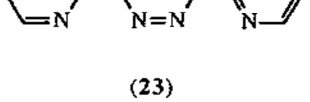


(22)

Complexation of iridium(III) and rhodium(III) (see Chapter 5) ions with bipy and ligands (**19**) to (**22**) occurs to give complex cations $[ML_2X_2]^+$ (M = Ir, X = Cl; M = Rh, X = Br). The molecular structure of free (**21**) has been determined. Electronic spectra for $[IrL_2Cl_2]^+$ exhibit intense ligand-based absorptions in the UV region and CT absorptions in the visible region. [31] The luminescent properties of the excited states of the complexes $[Ir(phen)_3]^{3+}$ and $[Ir(terpy)_2]^{3+}$ have been investigated; emissions are assigned predominantly to π-π^* transitions. Significantly, it has been noted that, despite its usual role as a quenching agent, $HgCl_2$ enhances the lifetimes and luminescence efficiencies of $[Ir(phen)_3]^{3+}$ and $[Ir(terpy)_2]^{3+}$ with the formation of novel excited state complexes. [32]

Ligand L, (**23**), is ideally suited to bring together two metal ions, chelating to each metal and bridging between them. Reactions of $[Ir(NO)L(PPh_3)_2]^{2+}$ or $[Ir(NO)L(PPh_3)_2Cl]^+$ with $PdCl_2(NCPh)_2$ produce $[(Ph_3P)_2(NO)Ir(\mu\text{-}L)(\mu\text{-}Cl)PdCl]^{2+}$ or $[(Ph_3P)Cl_2Ir(\mu\text{-}L)(\mu\text{-}NO)PdCl]^+$ respectively. In the former complex dication, the terminal nitrosyl ligand is bent ($\angle$IrNO = 123(3)°) and the Ir----Pd separation is 3.681 (4) Å. In going to the monocationic complex, the replacement of the bridging chloride by nitrosyl group reduces the Ir----Pd separation to 3.327 (2) Å. [33] The linearly bound nitrosyl ligand in $[Ir(NO)L(PPh_3)_2]^{2+}$ alters its mode becoming bent upon treatment of the complex cation with chloride or iodide ion. Following a similar synthetic route to that described above, $[(Ph_3P)X_2Ir(\mu\text{-}L)(\mu\text{-}NO)PdR]^+$ has been prepared where X = Cl, R = Me or X = I, R = Me or Ph. The cationic complexes have been characterised spectroscopically. [34]



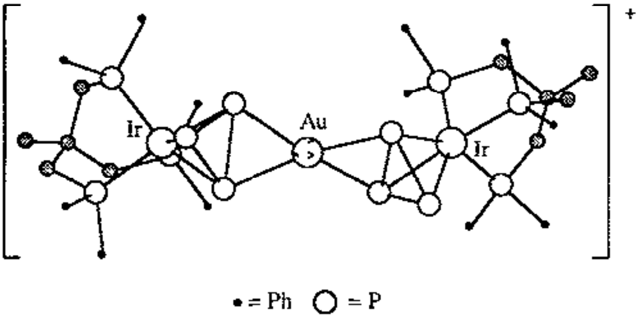
(23)

4.2.3 *Complexes with phosphorus donor ligands*

The iridium(III) complex *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$ has been the subject of a neutron diffraction study at 20 K; Ir-P bond distances are 2.338 (4), 2.364 (6), and 2.265 (6) Å. The most significant feature of the structure is the formation of an intramolecular $H(\delta^+)$----$H(\delta^-)$ interaction between the hydroxy and hydride ligands. The H---H separation is 2.40 (1) Å; other distances are Ir-H = 1.617 (9), Ir-O = 2.119 (5) and O-H = 0.93 (1) Å. [35] Reaction of $Me_3Ir(PMe_2Ph)_3$ with $HBF_4.OEt_2$ leads to $Me_2Ir(PMe_2Ph)_3(FBF_3)$ with associated methane elimination. An X-ray diffraction study of the product reveals that the tetrafluoroborate anion is coordinated to the iridium(III) centre (Ir-F = 2.389 (7) Å and Ir-P = 2.342 (3), 2.348 (3) and 2.332 (4) Å). This and the analogous rhodium(III) complex have been characterised by ^1H, ^{31}P, ^{11}B and ^{19}F NMR spectroscopy. In $Me_2Ir(PMe_2Ph)_3(FBF_3)$, the $[BF_4]^-$ ion may be replaced by ethylene or carbon monoxide to give cationic complexes. [36]

The synthesis of the amide iridium(III) complex $Cp^*Ir(Me)(NHPh)(PPh_3)$ has been reported. This complex reacts with dppe to give $Cp^*Ir(Me)(NHPh)(dppe\text{-}P)$ within 1 hr (monitored by ^{31}P NMR spectroscopy). After 24hr, both the starting complex and $Cp^*Ir(Me)(NHPh)(dppe\text{-}P)$ are consumed; the amide ligand is lost as $PhNH_2$ via internal deprotonation of the Cp* ligand to give the tetramethylfulvene complex $(\eta^4\text{-}C_5Me_4CH_2)Ir(dppe\text{-}P,P')(Me)$ which has been structurally characterised. [37]

The novel complex cations $[\{LM(P_3)\}_2Au]^+$ (M = Co, Rh, Ir; L = 1,1,1-tris(diphenyl phosphinomethyl)ethane) have been prepared from $LM(P_3)$ and R_3PAuCl (R = Me, Ph) and have been structurally characterised. In each member of the series, the Au(I) atom fuses together two $\{LM(P_3)\}$-units via P-Au-P bridge interactions. In the iridium(III) complex, (**24**), each Ir atom is in an octahedral environment: $Ir\text{-}P_{(P_3)}$ = 2.372 (9)–2.463 (8) Å and $Ir\text{-}P_{(phosphine)}$ = 2.265 (8)–2.289 (8) Å. [38]



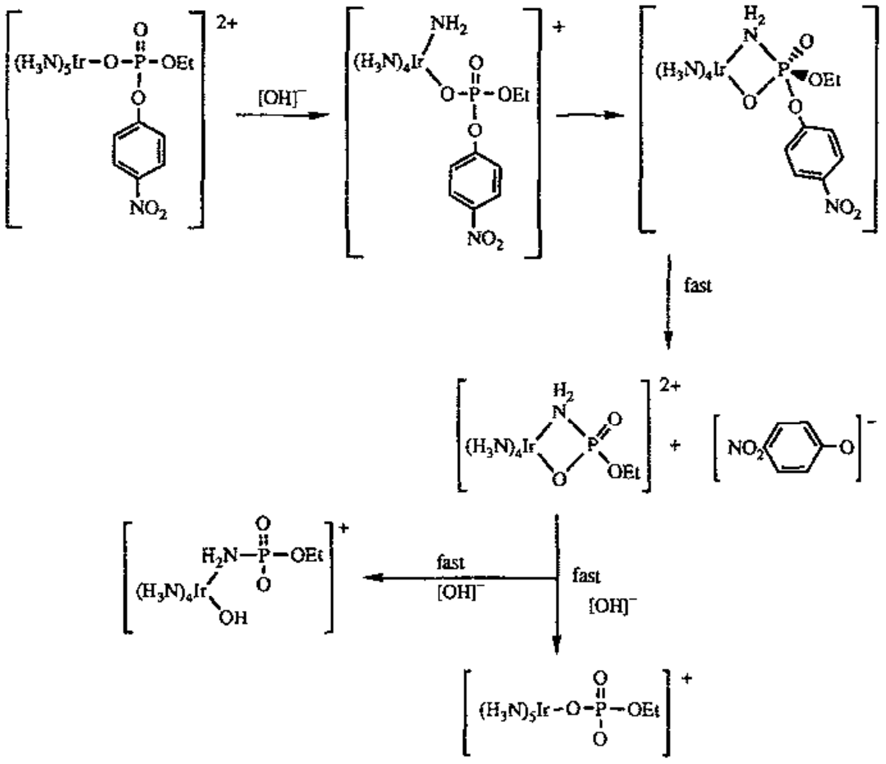
(**24**)

4.2.4 *Complexes with oxygen donor ligands*

Three closely related iridium(III) sulphate systems have been synthesised and characterised, two structurally by use of atomic radial distribution data (see Section 4.1). In the presence of $SC(NH_2)_2$, reaction between $K_2[IrCl_4]$ and H_2SO_4 in aqueous solution gives an amorphous sample $K_{2.6}H_{3.4}[Ir_3O(SO_4)_{6.5}(H_2I)_{2.3}].2.3H_2O$ or $K_{2.6}H_{1.4}[Ir_3O(SO_4)_{6.5}(H_2I)_{2.3}].2.3H_2O$. The three Ir atoms in each complex are capped by a μ_3-O atom. All iridium atoms are designated as Ir(III) and Ir-Ir distances lie in the range 3.75-3.80Å. [11]

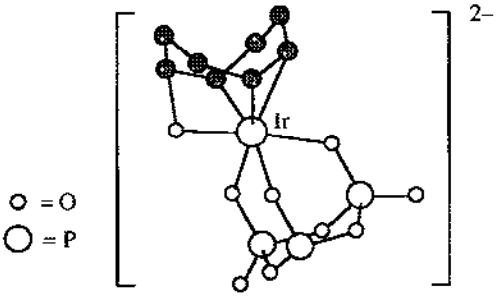
In the complexes $Cp^{*}MLCl$ (M = Ir or Rh; HL = $CpNi\{P(O)(OMe)_2\}_2H$), the ligand, L^-, introduced as TlL, acts as an O–O chelate to the iridium(III) centre. [39]

The phosphodiester complexes (ethyl-4-nitrophenylphosphato)pentaammineiridium(III) and bis(4-nitrophenylphosphato)pentaammineiridium(III) have been reported and the behaviour of these complex cations under basic conditions has been investigated. After deprotonation of a coordinated ammonia ligand, intramolecular attack occurs resulting in loss of 4-nitrophenylate ion. Scheme 1 illustrates the proposed mechanism for hydroxide attack on (ethyl-4-nitrophenylphosphato)pentaammineiridium(III). The kinetics of the reaction have been detailed. [40]



Scheme 1

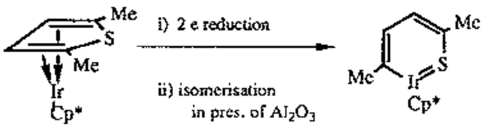
As part of a study of polyoxoanion-supported noble metal olefin complexes, the aim of which is to increase our understanding of the mechanism of O_2 activation and hydrocarbon oxidation, the iridium(I) complex $[(cod)IrP_3O_9]^{2-}$ has been prepared from $[(cod)Ir(NCMe)_2]^+$ and $[P_3O_9]^{3-}$. Details of the structure of this complex are given in Section 4.4.3. Oxidation by O_2 of $[(cod)IrP_3O_9]^{2-}$leads to $[(cod)Ir(P_3O_9)(\sigma\text{-}O_2)]^{2-}$ which reacts further with $[(cod)IrP_3O_9]^{2-}$ to give $[(cod)Ir(P_3O_9)(\mu\text{-}O_2)(P_3O_9)Ir(cod)]^{4-}$ followed by $[(cod)Ir(P_3O_9)(\mu\text{-}O)_2(P_3O_9)Ir(cod)]^{4-}$. These species have been detected in the ^{31}P NMR spectrum. The tetraanion breaks down to form (**25**) in which a C-O-Ir σ-bonded interaction is observed, the organic ligand now being both π- and σ-bonded to the iridium(III) atom. Further rearrangement of the dianion occurs to give (η^3-5-hydroxycyclo-octadien-6-yl)(hexaoxo-trioxatriphosphane-*O,O',O''*) iridium(III), the molecular structure of which has also been determined. [41]



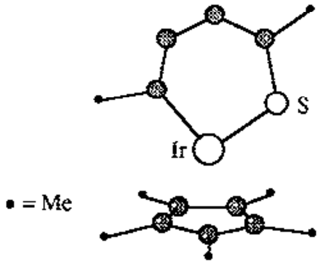
(25)

4.2.5 *Complexes with sulphur donor ligands*

The reduction of the dimethylthiophene iridium(I) complex shown in Scheme 2 by $Na[H_2Al(OCH_2CH_2OMe)_2]$ followed by isomerisation of the product leads to "iridathiabenzene" **(26)** which has been structurally characterised. In **(26)**, the planes of the metallacycle and the C_5-ring are essentially orthogonal (∠89.7 (2)°); the Ir-S distance is 2.203 (2) Å. [42] Adducts of **(26)** with PPh_3, PMe_3, PMe_2Ph, $PMePh_2$, $P(PhO)_3$ and CO have been formed and the structures of the complexes $Cp^*LIr\{SC_4H_2Me_2\}$ for L = PMe_2Ph and $PMePh_2$ have been determined. In the former, Ir-S = 2.348 (1), Ir-P = 2.252 (1) Å whilst in the latter, Ir-S = 2.346 (3), Ir-P = 2.255 (3) Å. The oxidative addition of H_2 to **(26)** has also been reported. The complexes in this family are of interest with regard to generating model compounds for studying the reactions of thiophene on hydrodesulphurisation catalysts. [43]



Scheme 2

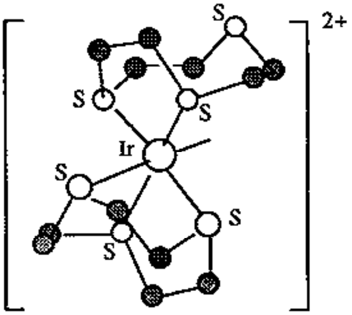


(26)

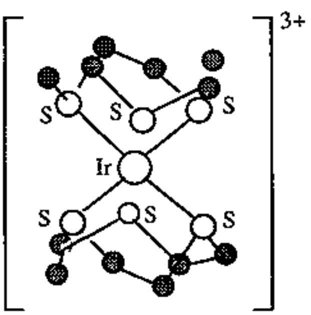
The preparation and reactivity of some bis(thiolate) and thiolate hydride complexes of iridium(III) have been described. In ethanol, $Cp^*IrCl_2(PMe_3)$ reacts with NaSH and H_2S to give

$Cp^*Ir(PMe_3)(SH)_2$, the molecular structure of which has been determined. The Ir(III) atom is tetrahedrally disposed with Ir-S = 2.370 (2) and 2.380 (2) Å and ∠SIrS = 88.74 (7) Å. Treatment of this complex with Me_2CO in the presence of HCl or $PhNH_3Cl$ leads to $Cp^*Ir(PMe_3)(S_2CMe_2)$ for which X-ray diffraction data are available. The molecule is the first example of a 2,4-dithiametallacyclobutane complex. The ^{t}butylthiolato derivative $Cp^*Ir(H)(PMe_3)(S^tBu)$ is produced in 88% yield by ligand exchange from $Cp^*Ir(H)(PMe_3)(OEt)$, itself formed by treating $Cp^*IrCl_2(PMe_3)$ with NaOEt in ethanol. As expected, the iridium(III) atom resides in a tetrahedral environment as confirmed crystallographically. [44]

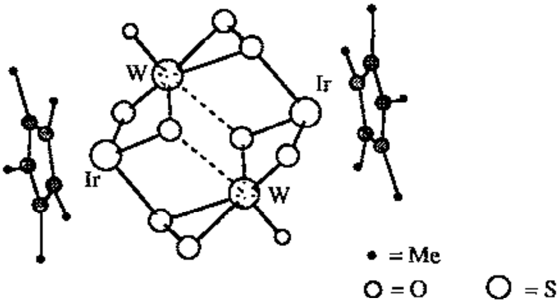
Complexation of the macrocyclic thioether 1,4,7-trithiacyclononane, L, to iridium(III) occurs on reacting $[(C_8H_{14})_2IrCl]_2$ with L in the presence of HBF_4. The product is $[Ir(H)L_2]^{2+}$, (**27**), and this dication has been isolated and crystallographically characterised as the hexafluorophosphate salt. The presence of the hydride ligand prevents each thioether macrocycle from being tridentate and thus, one sulphur donor atom is free: Ir-$S_{cis\text{-hydride}}$ = 2.344 (5), 2.319 (5), 2.298 (5) and 2.231 (5) Å, Ir-$S_{trans\text{-hydride}}$ = 2.476 (5) Å, Ir-H = 1.58 (6) Å. This contrasts with the centrosymmetric nature of $[IrL_2]^{3+}$, (**28**), in which Ir-S = 2.342 (3), 2.341 (3) and 2.338 (3) Å. The redox properties of (**28**) have been studied and compared with those of the Rh(III) congener. [45]



(**27**)



(**28**)

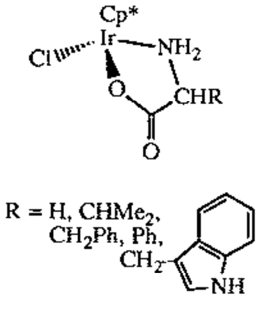


(**29**)

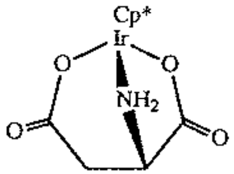
A fascinating double, but incomplete, cubane structure is exhibited by $[Cp^*IrW(O)(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$, **(29)**. Complex **(29)** has been prepared by the reaction of $[NH_4]_2[WS_4]$ with $NaBH_4$ followed by the addition of $[Cp^*IrCl_2]_2$; the assignment of Ir(III) and W(VI) oxidation states has been confirmed by X-ray PE spectra. Pertinent distances determined crystallographically for **(29)** are $Ir\text{-}S_{(\mu\text{-}S2)}$ = 2.378 (3) Å, $Ir\text{-}S_{(\mu\text{-}S)}$ = 2.401 (3) Å, $Ir\text{-}S_{(\text{"}\mu_3\text{"-}S)}$ = 2.349 (3) Å and $W\text{-}S_{(\text{"}\mu_3\text{"-}S)}$ = 2.906 (3) Å. The W----Ir separation is 2.816 (1) Å and is considered to be nonbonding. The rhodium(III) analogue of **(29)** has also been reported. [46]

4.2.6 *Complexes with mixed donor atom ligands*

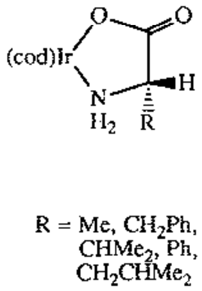
The complexation of several α-amino acid anionic ligands to Ir(III) has been described in Section 4.2.2 (see structure **(12)**). Further members of this series of complexes are represented in structures **(30)** to **(32)**. A crystallographic study of Cp*IrCl(L-Pro) has been carried out. [24] Independent work has also reported the molecular structure of Cp*IrCl(L-Pro); here, two independent molecules in the unit cell differ in the configuration of the ligand at the iridium(III) centre. In molecule *A*, the configuration is $R_{Ir}S_CS_N$ while in molecule *B*, it is $S_{Ir}S_CS_N$. The iridium atom is in a pseudo-octahedral environment with distances being Ir-O = 2.093 (6), Ir-N = 2.140 (8) Å in molecule *A*, and Ir-O = 2.078 (6), Ir-N = 2.132 (7) Å in molecule *B*. The chloro-derivatives Cp*IrLCl (HL = L-proline or L-alanine) do not epimerise when a $CDCl_3$ solution is left to stand at room temperature for 3 days. On the other hand, the related complex cations, $[Cp^*IrL(PPh_3)]^+$ epimerise rapidly in solution on the ^1H NMR timescale. [47]



(30)



(31)



(32)

The reaction of $H_3[MCl_6]$ (M = Ir or Rh) with cysteine (H_2L) leads to the formation of a range of complexes of which the iridium containing ones are Ir(HL-*O*,*S*)(HL-*N*,*S*)Cl(H_2O).H_2O, Ir(HL-*N*,*S*)Cl(H_2O)(OH), [Ir(HL-*O*,*S*)(HL-*N*,*S*)(μ-Cl)]$_2$.nH_2O (n = 2-4). The complexes have been characterised by XPS, IR spectroscopy and TGA. It is concluded that when $[HL]^-$ coordinates via an *N*,*S*-mode, it is in the betain form. [48]

4.3 IRIDIUM(II)

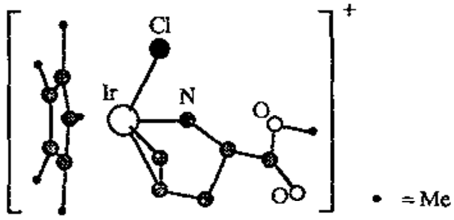
Oxidative addition of I_2, MeI or CH_2I_2 to $Ir_2(\mu\text{-}L)(CO)_2(PPh_3)_2$, L ($H_2L$ = 1,8-$(H_2N)_2$-$C_{10}H_6$), leads to diiridium(II) complexes in which L^{2-} bridges the two Ir atoms; (see Section 4.2.2). [23] The successful oxidation of $[Ir(\eta^5\text{-}C_5H_4PPh_2)(CO)]_2$ to the corresponding dication illustrates the flexible nature of the $C_5H_4PPh_2$ ligand which supports the dimetal framework. In the related Rh(II) complexes $[Rh(\eta^5\text{-}C_5H_4PPh_2)(py)]_2$ and $[\{Rh(\eta^5\text{-}C_5H_4PPh_2)(py)\}_2]^{2+}$, the metal-metal separation decreases from 4.3029 (6) to 2.7796 (9) Å upon oxidation (see Chapter 5). [49] The complex $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ oxidises on exposure to air or O_2 to give the peroxo-bridged $[Ir_2I_2(CO)_2(\mu\text{-}O_2)(dppm)_2]$. A crystallographic study of the complex shows that the peroxo group is skewed with respect to the Ir-Ir vector and the O-O bond is significantly lengthened upon interaction with the dimetal framework: O-O = 1.58 (2), Ir-O = 2.04 (1) and Ir-Ir = 2.705 (1) Å. The weak O-O bond is, as expected, readily cleaved in reactions with NO_2, SO_2 (both insertion reactions) and HCl (H_2O_2 is generated). [50]

The reaction of $[(cod)Ir(PPh_3)_2][SbF_6]$ in thf at 0°C with 1 atm H_2 leads to $[Ir(H)_2(thf)_2(PPh_3)_2][SbF_6]$ which, on recrystallisation from moist thf/hexane gives $[Ir(H)_2(thf)(H_2O)(PPh_3)_2][SbF_6]$ which has been structurally characterised. The complex provides an unusual example of thf and water coordinating to a late transition metal atom. The PPh_3 ligands are mutually *trans*; Ir-P = 2.297 (3) and 2.300 (3) Å, Ir-O_{thf} = 2.308 (8) and Ir-O_{water} = 2.258 (9) Å. There is significant cation-anion interaction via hydrogen bond formation with O_{water}---F_{anion} = 2.92 (1) Å. [51]

4.4 IRIDIUM(I)

4.4.1 Complexes with nitrogen donor ligands

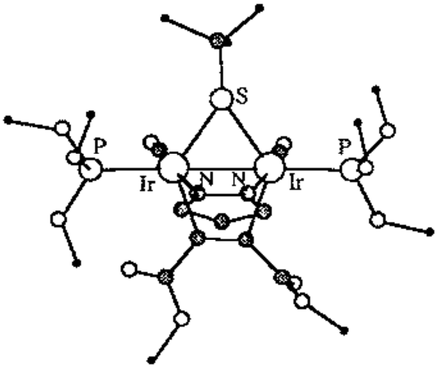
Reactions of *C*-allylglycine esters with $[Cp^*IrCl_2]_2$ or $[Rh(CO)_2Cl]_2$ leads to *N*-bonded *C*-allyl glycine ester complexes. The structure of the tetrafluoroborate salt of $[Cp^*IrCl(\eta^2,\sigma\text{-}CH_2{=}CHCH_2CH(CO_2Me)NH_2\text{-}N)]^+$, (33), has been determined; Ir-N = 2.124 (8) Å. [52] (Related rhodium complexes are discussed in Chapter 5).



(33)

The molecular structure of the pyridine containing complex [(cod)Ir(py){P(2-MeO-C_6H_4)$_3$}][PF$_6$] has been reported; Ir-N = 2.04 (2) Å, Ir-P = 2.345 (7) Å and ∠NIrP = 93.0 (6)°. The complex is a hydrogen catalyst. [53] The monolithiated derivative of 2,6-Me$_2$-py reacts with [(cod)IrCl]$_2$ to give a *C,N*-bridged diiridium complex (Ir----Ir = 3.5889 (3) Å and Ir-N = 2.103 (6) and 2.104 (5) Å) which cleaves with PPh$_2$Et to give (cod)Ir(PPh$_2$Et)$_2$(CH$_2$-py-6-Me) which has been characterised by X-ray diffraction. During the cleavage, the *N*-coordination is lost. Related Rh(I) complexes have also been reported. [54]

The preparation and properties of Ir$_2$(μ-pz)(μ-S^{t}Bu)(cod)$_2$ and Ir$_2$(μ-pz)(μ-S^{t}Bu)(CO)$_2$ {P(OMe)$_3$}$_2$ have been described. The stepwise addition of I_2 to Ir$_2$(μ-pz)(μ-S^{t}Bu)(CO)$_2$ {P(OMe)$_3$}$_2$ leads to Ir$_2$(μ-pz)(μ-S^{t}Bu)I$_n$(CO)$_2${P(OMe)$_3$}$_2$ (n = 2 or 4) and reaction of the diiridium complex with MeO$_2$CC≡CCO$_2$Me leads to **(34)** in which the pyrazine, thiolate and alkyne ligands support the Ir-Ir framework. Pertinent distances for **(34)** are Ir-N = 2.095 (11) and 2.087 (11) Å, Ir-S = 2.471 (4) and 2.459 (4) Å and Ir-Ir = 2.614 (2) Å. Oxidative addition of I_2 to complex **(34)** occurs to give **(35)**. In going from **(34)** to **(35)** the flexibility of the triply bridged diiridium unit is tested with a significant increase in the Ir----Ir separation being tolerated; in (35) Ir---Ir = 3.626 (2) Å. [55]



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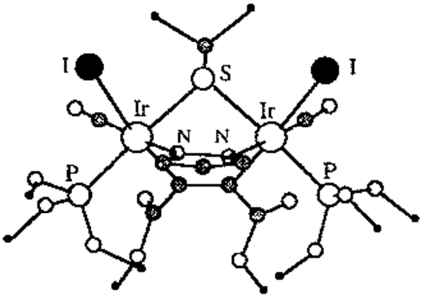


(35)

• = Me
O = O

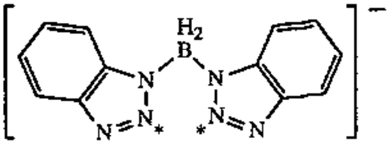
The electrochemistry of the complexes [(cod)Ir(μ-L)]$_2$ (HL = pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole) has been discussed. For each complex, a reversible one electron oxidation and an irreversible one electron reduction are observed and redox potentials are listed in Table 2. On being subjected to a pulsing potential between the cathodic and anodic potentials, the system exhibits an electrogenerated chemiluminescence upon the sequential generation of $[Ir_2]^+$ and $[Ir_2]^-$. [56]

A series of heterobimetallic complexes (M = Rh or Ir and M' = Ru or Os) have been prepared from [M(diolefin)(μ-OMe)]$_2$ and M'H(CO)(HL)(PPh$_3$)$_2$ (diolefin = cod or tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene; H_2L = 2,2'-biimidazole or 2,2'-bibenziimidazole). Products have been characterised by IR and ^1H and ^{31}P NMR spectroscopy and the molecular structure of $(H)(CO)(PPh_3)_2Ru(\mu\text{-}L)_2Rh(cod)$ has been determined for H_2L = 2,2'-biimidazole (see Chapter 5). [57]

Table 2 Redox couples for the complexes $[(cod)Ir(\mu\text{-}L)]_2$

Ligand, HL	$E°(Ir_2^{+/0})$ /mV	$E°(Ir_2^{0/-})$ /mV
pyrazole	+0.342	–2.492
3-methylpyrazole	+0.318	–2.487
3,5-dimethylpyrazole	+0.279	–2.510

The reaction of the iridium(I) complex $IrCl(CO)(PPh_3)_2$ with KL where L^- = (36) leads to *trans*-$(Ph_3P)_2IrL(CO)$; the analogous rhodium(I) complex has also been synthesised along with *trans*-$(Ph_3P)_2RhL(CS)$. Characterisation of the complexes has been by ^1H and ^{31}P NMR and IR spectroscopy and FAB-mass spectrometry. It is proposed that L^- exhibits a chelating mode and lies in the equatorial plane of a trigonal bipyramidal arrangement of donor atoms. [58]



* = coordination site

(36)

4.4.2 *Complexes with phosphorus and arsenic donor ligands*

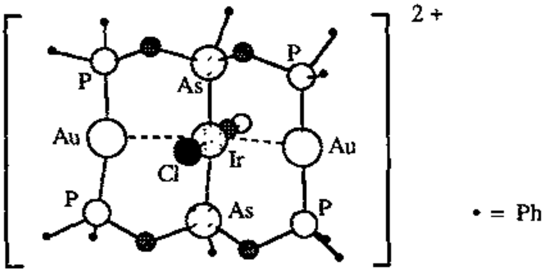
The structure of $[Ir(cod)\{P(4\text{-}MeO\text{-}C_6H_4)_3\}_2][PF_6]$, a complex used for homogeneous hydrogenation, has been determined by X-ray diffraction. By virtue of the presence of the cod ligand, the phosphine ligands are constrained to a *cis*-configuration with ∠PIrP = 95.6 (1)° and Ir-P = 2.359 (3) and 2.341 (3) Å. [59] The reaction of the hydrido complex $HIr(PMe_3)_4$ with thexylborane $(Me_2CHCMe_2BH_2)$ or 9-BBN dimer (9-BBN = borabicyclo[3.3.1]nonane) results in phosphine abstraction from the iridium(I) centre to give $Me_3P.BHRR'$) and the formation of *fac*-$H_2Ir(PMe_3)_3BRR'$ (R = H and R' = CMe_2CHMe_2 or BRR' = 9-BBN). A structural study of the complex for BRR' = 9-BBN illustrates a distorted coordination sphere around the Ir(I) atom; Ir-B =

2.093 (7) Å. Reaction of $MeIr(PMe_3)_4$ with thexylborane gives *fac*-$HIr(PMe_3)_3(\eta^2\text{-}CH_2BHRR')$ which has also been crystallographically characterised. [60]

A detailed solution NMR spectroscopic study of *trans*-$(^tBu_2PhP)_2M(CO)Cl$ (M = Ir or Rh) has been reported. The $^{31}P\{^1H\}$ DNMR spectra show decoalescence of each complex into four diastereomers. The dominant diastereomers exhibit phenyl groups which are *anti* with respect to each other and are oriented respectively on the same and opposite sides of the plane containing the metal and donor atoms; the coordination plane possesses C_1 symmetry. The remaining two diastereomers, present in minor quantities, exhibit phenyl groups which are *syn* to the carbonyl ligand. These diastereomers possess C_2 and C_s symmetries respectively. [61]

The bis(phosphine) ligand $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (dppf) has received a significant amount of attention of late. The complex cation $[Ir(dppf)_2]^+$ and its rhodium(I) congener have been synthesised and characterised. The iridium(I) complex has been prepared in low yield from the reaction of $[(cod)IrCl]_2$ and dppf in refluxing CH_2Cl_2 and has been the subject of an X-ray diffraction study. An improved synthetic strategy is to use $[Ir(cyclooctene)_2Cl]_2$ in place of the cod derivative. In $[Ir(dppf)_2]^+$, the iridium(I) atom resides in an environment which is intermediate between square planar and tetrahedral: Ir-P = 2.317 (6), 2.389 (5), 2.337 (5) and 2.343 (6) Å, $\angle PIrP_{\text{chelate ring}}$ = 95.0 (2) and 93.6 (2)°. In solution, there is evidence from the ^{31}P NMR spectroscopic data that a dimeric species exists. [62]

The mixed donor ligand $Ph_2PCH_2As(Ph)CH_2Ph_2$, L, iridium(I) via the phosphorus atoms in the complex cation $[L_2Ir(CO)]^+$. The hexafluorophosphate salt has been structurally characterised; the carbonyl ligand occupies one equatorial site of the trigonal bipyramidal complex; Ir-P_{axial} = 2.367 (4) Å and Ir-$P_{\text{equat.}}$ = 2.400 (4) and 2.358 (4) Å. Treatment of $[L_2Ir(CO)][PF_6]$ with two equivalents of Me_2SAuCl leads to a red trinuclear complex dication (**37**) in high yield via a template-like condensation reaction. Complex (**37**) may be described in terms of two $Ph_2PCH_2As(Ph)CH_2Ph_2$ ligands supporting an Au-Ir-Au unit or as an iridium(I) complex of a macrocyclic ligand with a $Au_2As_2P_4$-donor set. Structural characterisation of (**37**) confirms significant Ir--Au interactions: pertinent structural parameters for the two independent molecules in the unit cell are Ir-As = 2.409 (4) and 2.407 (4) Å (molecule *A*) and 2.416 (4) and 2.408 (4) Å (in molecule *B*), Ir-Au = 3.013 (2) and 2.985 (2) Å (molecule *A*) and 3.014 (2) and 3.025 (2) Å (in molecule *B*), and $\angle AuIrAu$ = 157.7 (1)° (molecule *A*) and 152.6 (1)° (molecule *B*). [63] Complex cation (**38**) is closely related to half of (**37**); the two dppm ligands support the dimetal unit with Au--Ir = 2.986 (1) Å and Ir-P = 2.320 (5) and 2.311 (5) Å. [64] In contrast to the structure of $[L_2Ir(CO)]^+$ for L = $Ph_2PCH_2As(Ph)CH_2PPh_2$, that of $[L_2Ir(CO)]^+$, (**39**), for L = $Ph_2PCH_2P(Ph)CH_2PPh_2$ shows two different modes of coordination for the two ligands. The presence of the 4-membered ring distorts the structure quite considerably with $\angle PIrP_{(\text{4-membered ring})}$ = 69.3 (2)° and $\angle PIrP_{(\text{6-membered ring})}$ = 97.8 (2)°. In solution, the ^{31}P NMR spectral data evidence the presence of two isomers, including that characterised in the solid state. The structure of the second solution isomer has not been assigned but the data are not consistent with a symmetrical structure analogous to that observed for $[\{Ph_2PCH_2As(Ph)CH_2Ph_2\}_2Ir(CO)]^+$. [65] For L = $Ph_2PCH_2P(Ph)CH_2Ph_2$), reaction of $[L_2Ir(CO)]^+$ with Me_2SAuCl and KCN results in the formation of $[Ir(CN)_2Au_2(\mu\text{-}L)_2]^+$ which has a framework resembling that of (**37**).



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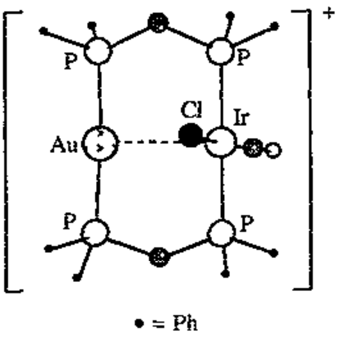

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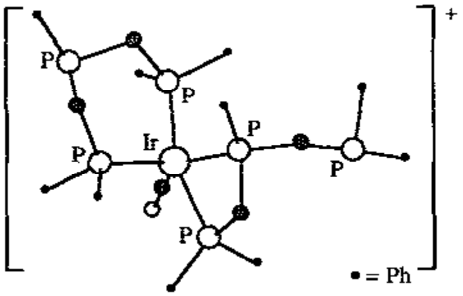

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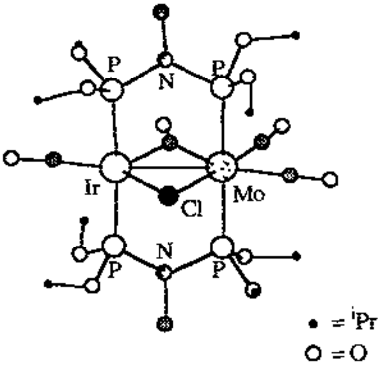


(40)

The ligand, L, $MeN\{P(O^iPr)_2\}_2$ although restricted in its angle of "bite", may be used to support the binuclear complexes $M(CO)M'(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}L)_2$ (M = Rh or Ir, M' = Mo or W). The complexes $Ir(CO)M'(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}L)_2$ are prepared by reacting *mer*-$M'(CO)_3(\eta^2\text{-}L)(\eta^1\text{-}L)$ with $[(cod)IrCl]_2$ and have been characterised by IR, ^{31}P and ^1H NMR spectroscopy. For M' = Mo, an X-ray diffraction study of the dinuclear complex (**40**) has been carried out; Mo-Ir = 2.888 (1) Å, Ir-P = 2.309 (3) and 2.316 (3) Å. [66]

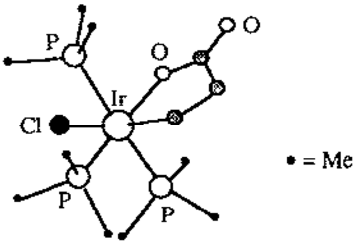
The diiridium complex cation $[Ir_2(CO)_2(C_6H_5)(CN^tBu)(\mu\text{-}MeO_2CCCCO_2Me)(\mu\text{-}dppm)_2]^+$ has been structurally characterised. The two dppm ligands bridge the Ir_2-unit and reside *trans* to one another; Ir-Ir = 2.8987 (4) Å and Ir-P = 2.346 (2), 2.376 (2), 2.341 (2) and 2.373 (2) Å. [67] With an increase in the number of methylene groups in the *bis*(phosphine) ligand, the iridium atoms are moved beyond bonding distance. This is exemplified in $Ir_2(CO)_2Cl_2\{Ph_2P(CH_2)_4PPh_2\}_2$ in which Ir----Ir = 6.683 (1) Å; the molecule is centrosymmetric. $Ir_2(CO)_2Cl_2\{Ph_2P(CH_2)_4PPh_2\}_2$ functions as a macrocyclic ligand and interacts with $SnCl_2$ in thf to give a blue solution. The product has been crystallographically characterised; the $SnCl_2$ unit is bonded between the two iridium atoms with Ir-Sn = 2.751 (1) Å and ∠IrSnIr = 138.8 (1)°. The Ir----Ir separation is thus reduced from that in the free metallamacrocycle. The tin(II) complex is strongly luminescent in solution with λ_{max} = 647 nm. [68]

4.4.3 Complexes with oxygen donor ligands

The introduction of $[OR]^-$ ligands by using LiOR (R = Ph_2-2,6-C_6H_4) is exemplified in the reaction of LiOR with $[(cod)IrCl)]_2$. A mixture of products is obtained and the complex $[(cod)Ir(\eta^5\text{-}HOR)][(cod)Ir(OR)_2]$ is formed as a minor constituent. This complex has been structurally characterised; Ir-O = 2.08 (1) and 2.09 (1) Å. [69]

The oxo-bridged complex cations $[Cp_2M\text{-}O\text{-}M'(PPh_3)_2(CO)]^+$ (M = Mo or W; M' = Rh or Ir) have been synthesised by the reaction of $Cp_2M{=}O$ with $[M'(CO)(PPh_3)_2(NCMe)]^+$. ^1H NMR spectroscopic studies of the complexes in CD_3CN solution show that they undergo rapid chemical transformation with the solvent and with excess $Cp_2M{=}O$. An X-ray diffraction study of $[Cp_2Mo\text{-}O\text{-}Rh(PPh_3)_2(CO)]^+$ conforms the oxo-bridge with ∠MoORh = 167.1 (4)°. [70]

Treatment of *mer*-$H_3Ir(PPh_3)_3$ or $HIr(CO)(PPh_3)_3$ with salicylaldehyde leads to $Ir(O\text{-}C_6H_4\text{-}CO)(H)(CO)(PPh_3)_2$; the syntheses are included in a study of related iridium, rhodium and ruthenium complexes. [71] The cyclic ether propiolactone readily undergoes oxidative addition to electron rich, low valent iridium(I) complexes. One example is observed in the reaction of the lactone with (cyclooctene)$Ir(PM_3)_3Cl$ which results in the formation of complex (**41**). Structural characterisation of (**41**) confirms the *mer*-isomeric form for this complex: Ir-O = 2.1242 (49) Å, Ir-$P_{trans\text{-}O}$ = 2.2432 (22) Å, $P_{trans\text{-}P}$ = 2.3364 (19) and 2.3438 (20) Å, $\angle OIrC_{chelate}$ = 83.1 (2)°. The kinetics of the oxidative addition of the lactone have been studied and the process has been found to be first order in both propiolactone and (cyclooctene)$Ir(PMe_3)_3Cl$; a possible mechanism for the addition is discussed. [72]



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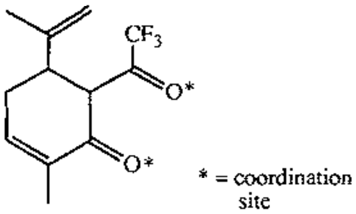
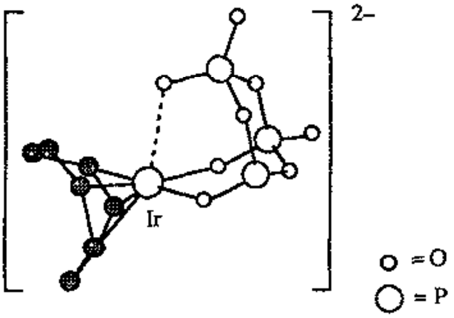


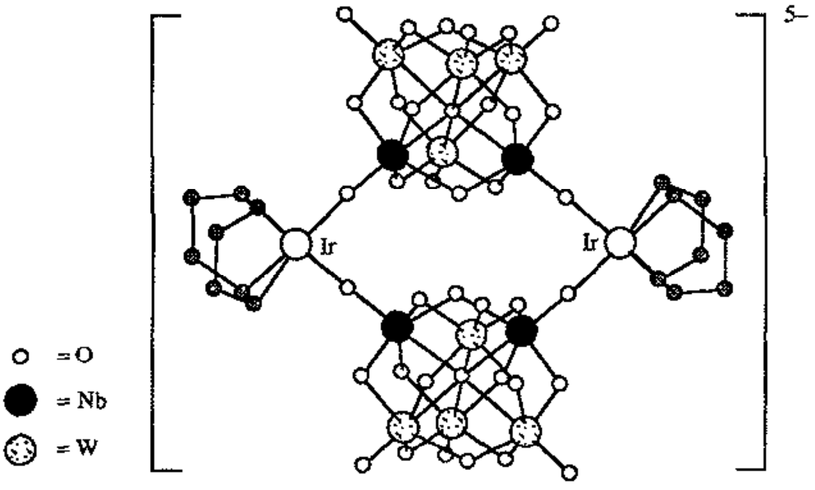
(42)

The β-diketonate complexes (cod)IrL (HL = acac or 1,1,1-trifluoro-2,4-pentanedione) react with MeI in acetone to give iridium(III) alkyls, IrL(cod)(Me)(I). The kinetics of this process have been investigated. The rate of reaction is given by equ. (ix) and 10^3k has been determined at 298K to be 16.9 (2) $M^{-1}s^{-1}$ for HL = Hacac and 1.33 (3) $M^{-1}s^{-1}$ for HL = 1,1,1-trifluoro-2,4-pentanedione. The effect on the reaction rate of bromide ion has been included in this study; addition of $[Br]^-$ to (cod)IrL gives a 5-coordinate intermediate and an enhanced rate of reactivity towards MeI. [73] An X-ray diffraction study of racemic-$Ir(CO)_2L$ where HL = (**42**) has been reported; Ir-O = 1.997 (7) and 1.996 (8) Å. [74]

The complex $LIr(cyclooctene)_2$ (HL = $H[C(Ph_2PO)_3]$) is formed by treating $[(cyclooctene)IrCl]_2$ with NaL in thf; $LIr(cyclooctene)_2$ has been characterised by ^1H and ^{31}P NMR spectroscopy. It reacts with ethylene followed by $HSiPh_2Me$ or Ph_3SiH to give Ir(V) and Ir(III) species respectively; see Section 4.1. [4]



(**43**)



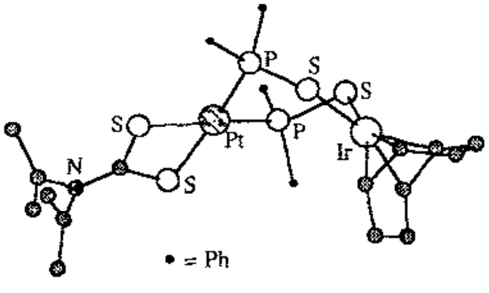
(**44**)

In Section 4.2.4, the iridium(III) complex anion (**25**) was described. Its precursor, $[(cod)IrP_3O_9]^{2-}$, (**43**), has been prepared from $[(cod)Ir(NCMe)_2]^+$ and $[P_3O_9]^{3-}$ and has been crystallographically characterised. The coordination geometry of the iridium(I) atom is square pyramidal with the cod ligand occupying two sites of the square plane; Ir-O distances are 2.15 (2), 2.21 (2) and 2.70 (2) Å. [41,75] In related work, the synthesis of $[\{(cod)Ir\}_5\{Nb_2W_4O_{19}\}_2]^{3-}$ has been reported. Infrared and ^{13}C NMR spectroscopic data indicate that the trianion is isostructural with $[\{(C_7H_8)Rh\}_5\{Nb_2W_4O_{19}\}_2]^{3-}$ and contains two octahedral $[Nb_2W_4O_{19}]^{4-}$ ions linked via five 4-coordinate iridium(I) centres. The reaction of $[\{(cod)Ir\}_5\{Nb_2W_4O_{19}\}_2]^{3-}$ with $[Nb_2W_4O_{19}]^{4-}$ and $MeCO_2H$ in MeCN leads to $[\{(cod)Ir\}_2(H)\{Nb_2W_4O_{19}\}_2]^{5-}$; the structure of the tetrabutyl ammonium salt, (**44**), has been determined. [75] The synthesis and spectroscopic characterisation of $[Bu_4N]_5Na_3[\{(cod)Ir\}\{P_2W_{15}Nb_3O_{62}\}]$ has been described. The data suggest that the iridium atom is coordinated to the cod ligand and to three oxygen atoms of the surface of the $[P_2W_{15}Nb_3O_{62}]^{9-}$ polyoxoanion. The complex is an effective catalyst precursor. [76] Other polyoxoanion supported metal carbonyl complexes which were reported during 1990 are $[(OC)_2Ir(P_3O_9)]^{2-}$, $[\{(CO)_2Rh\}_5\{Nb_2W_4O_{19}\}_2]^{3-}$, $[\{(CO)_2Rh\}_3\{Nb_2W_4O_{19}\}_2]^{5-}$ and $[\{(CO)_2Ir\}_2(H)\{Nb_2W_4O_{19}\}_2]^{5-}$. [78]

4.4.4 Complexes with sulphur donor ligands

The preparations of complexes $[(cod)Ir(tht)(PR_3)][ClO_4]$ (R = Me, Ph, C_6H_4-4-Me, C_6H_4-4-Cl, OMe, OPh) have been reported; the complexes are catalyst precursors and the influence of the substituent R on the catalytic activity with respect to hydrogenation of alkenes has been assessed. The trend in activity cannot be correlated simply to either the steric (measured by the Tolman cone angle of PR_3) or the electronic (σ-donor/π-acceptor) properties of the phosphines. [79]

The iridium(I) complex $(cod)Ir(\mu\text{-}SPPh_2)_2PtS_2CNEt_2$, (**45**), and its rhodium analogue have been prepared and structurally characterised; the $\{IrS_2P_2Pt\}$-ring is in a boat conformation and important distances at the iridium atom are Ir-S = 2.315 (4) and 2.378 (4) Å. [80]



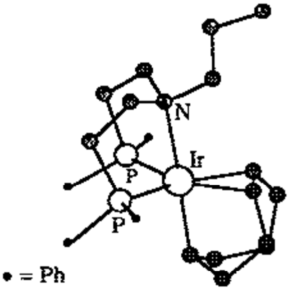
(45)

Complexes of iridium(I) with SO_2 have been described. *Trans*-$Ir(CO)(PPh_3)_2Cl$ reacts with SO_2 to give the 5-coordinate complex $Ir(CO)(PPh_3)_2Cl(SO_2)$. This can also be obtained via the reaction of *trans*-$Ir(CO)(PPh_3)_2Cl$ with RNSO (R = C_6H_4-2-Me, C_6H_4-4-Me or SO_2-C_6H_4-4-Me) followed by hydrolysis. For R = SO_2-C_6H_4-4-Me, the intermediate product reacts with H_2S to give $Ir(CO)(PPh_3)_2Cl(\eta^2\text{-}S_2O)$. [81]

4.4.5 Complexes with mixed donor atom ligands

The complexation of the conjugate bases of 2,3- and 2,5-pyrazinedicarboxylic acid (H_2L and H_2L' respectively) with iridium(I) and rhodium(I) has been studied. The complexes include $Ir_2L'(cod)_2$, $[IrL(cod)]^-$, $IrL(cod)_2$ and $Ir_2L'(CO)_2(PPh_3)_2$ and these have been characterised spectroscopically and by elemental analysis. In the dinuclear species, it is proposed that the pyrazinedicarboxylate ligands coordinate via one *N,O*-donor set to each metal ion.

The syntheses of iridium(I) complexes (σ,η^2-cyclooctenyl)IrL involving the ligands $\{Ph_2P(CH_2)_2\}_2NR$ (R = ${}^nPr$ or $(CH_2)_2NEt_2$) have been reported. The structure of (σ,η^2-cyclooctenyl)Ir$\{Ph_2P(CH_2)_2\}_2N^nPr$, **(46)**, confirms an *N,P,P'*-coordination mode with pendant propyl group; Ir-P = 2.282 (1) and 2.284 (1) Å, Ir-N = 2.369 (4) Å and Ir-C_{axial} = 2.109 (5) Å. An analogous structure is also observed for the second complex with the $(CH_2)_2NEt_2$ substituent as the pendant group. In solution, each complex exhibits an equilibrium with the η^4-cod isomer. Interest in the complexes arises from their potential use as catalysts in the hydrogen atom transfer reduction of α,β-unsaturated ketones. [83]



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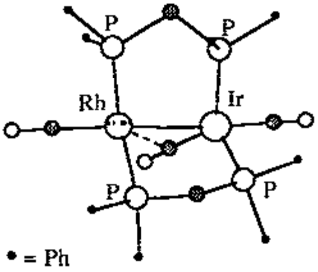


(47)

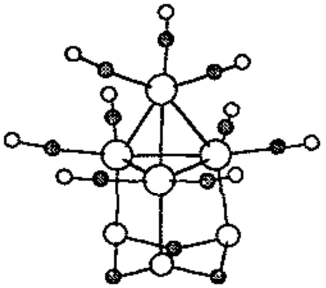
4.5 IRIDIUM(-I)

The reaction of $RhIrCl_2(CO)_2(\mu\text{-dppm})_2$ with sodium borohydride under hydrogen gives $RhIrH(CO)_2(\mu\text{-H})(\mu\text{-dppm})_2$ and under carbon monoxide gives $RhIr(CO)_3(\mu\text{-dppm})_2$. The two dinuclear complexes are interconvertible upon treatment of H_2 or CO. Crystallographic characterisation of $RhIr(CO)_3(\mu\text{-dppm})_2$, **(47)**, shows that the complex does not have the typical A-frame structure. The $MM'P_4$-unit is severely distorted; Ir-P = 2.309 (2) and 2.321 (2) Å, Rh-P = 2.312 (2) and 2.295 (2) Å, Rh-Ir = 2.7722 (7) Å and $\angle PIrP$ = 104.95 (7)°. The two metal atoms are formulated to be in oxidation states Ir(–I) and Rh(I) and a dative Ir→Rh bond is proposed. The complex protonates twice with the sequential addition of two bridging hydrogen atoms. [84]

4.6 CLUSTERS CONTAINING IRIDIUM

4.6.1 Homometallic clusters

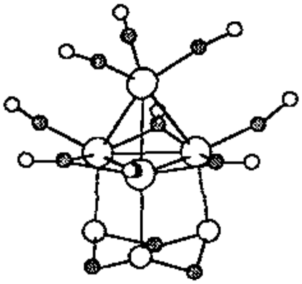
Several clusters based upon $Ir_4(CO)_{12}$ have been described, the first being $Ir_4(CO)_9L_3$ in which L = PPh_xR_{3-x}, R = pyridyl substituent. [85] Nonacarbonyl-μ_3-(1,3,5-trithiane)-tetrairidium is formed by the reaction of $[Ir_4(CO)_{11}I]^-$ with 1,3,5-trithiane in thf in the presence of $AgBF_4$. The complex crystallises in the two isomeric forms **(48)** and **(49)** which differ in that **(48)** possesses only terminal carbonyl ligands while **(49)** exhibits three bridging carbonyl groups. Isomer **(49)** converts into **(48)** in solution; **(48)** provides the first experimental evidence for the proposed intermediate in the "merry-go-round" process which is exhibited by many tetrahedral transition metal carbonyl clusters. [86]



(48)

○ = Ir

○ = S



(49)

The phosphido cluster $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ reacts with $Ph_2PC{\equiv}CPh$ to give initially a simple carbonyl substitution product. After 24 hr at room temperature in solution, the alkyne adds to one Ir_3-face of the cluster with concomitant P-C bond cleavage. However, the anion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ reacts with $Ph_2PC{\equiv}CPh$ and, after protonation, $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}PPh_2CCPh)(\mu\text{-}PPh_2)$ in which the integrity of the ligand is retained. [87] Treatment of $Ir_4(CO)_{11}(PPhH_2)$ or $Ir_4(CO)_{10}(PPhH_2)L$ (L = PPh_3 or PPh_2Me) with $[Cp^*M(NCMe)_3]^{2+}$ (M = Ir or Rh) in MeCN in the presence of the base DBU results in the formation of $Cp^*MIr_4(CO)_9L(\mu_4\text{-}PPh)$. Complexes have been characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and X-ray diffraction studies of $Ir_5(CO)_8(\mu\text{-}CO)_2Cp^*(\mu_4\text{-}PPh)$ and $Ir_5(CO)_7(\mu\text{-}CO)_2Cp^*(PPh_3)(\mu_4\text{-}PPh)$ confirm a square based pyramidal Ir_5-core for the family of clusters. [88]

The octahedral cluster $Ir_6(CO)_{16}$ reacts with LiCl to give both $[Ir_6(CO)_{15}Cl]^-$ and $[Ir_6(CO)_{14}(\mu\text{-}Cl)]^-$ but the reaction time is very long. Treatment of $Ir_6(CO)_{16}$ with $FeCl_3$ gives specifically $[Ir_6(CO)_{15}Cl]^-$, the structure of which has been crystallographically determined. In solution, $[Ir_6(CO)_{15}Cl]^-$ converts to $[Ir_6(CO)_{14}(\mu\text{-}Cl)]^-$, the structure of which has also been determined. The pentadecacarbonyl cluster has an octahedral core with an average Ir-Ir distance of 2.774 Å and the chloro-ligand is terminally bonded with Ir-Cl = 2.395 (5) Å. The transformation from $[Ir_6(CO)_{15}Cl]^-$ to $[Ir_6(CO)_{14}(\mu\text{-}Cl)]^-$ is accompanied by a change in bonding mode of the chloro-ligand from terminal to bridging (Ir-Cl(average) = 2.484 Å). The Ir_6-core of the tetradecacarbonyl cluster anion is therefore distorted (Ir-Ir(average) = 2.767 Å). [89]

4.6.2 Heterometallic clusters

The degradation of $[FeIr_4(CO)_{15}]^{2-}$ under an atmosphere of CO leads to $[FeIr_3(CO)_{12}]^-$. The structure of the $[PPN]^+$ salt has been determined; pertinent distances for the tetrahedral core are are Ir-Ir(average) = 2.696 Å and Ir-Fe(average) = 2.682 Å. The dianion $[Fe_2Ir_2(CO)_{12}]^{2-}$ and its gold(I) phosphine derivative $[Fe_2Ir_2(CO)_{12}(\mu_3\text{-}AuPPh_3)]^-$ have also been reported and structurally characterised. [90] The paramagnetic 46 electron trimetallic clusters $(Cp^*Ir)(CpCo)_2(CO)_2$ and $(Cp^*Ir)_2(CpCo)(CO)_2$ have been prepared and characterised both spectroscopically and crystallographically. Analogous rhodium clusters have also been prepared. The structural parameters imply that the clusters should be described in terms of an M_2-unit interacting with the heterometal atom. The paramagnetically shifted ^1H NMR spectra have been presented. [91]

The capping of an Re_7-carbido cluster by $\{Ir(C_8H_{14})(CO)\}$ occurs during the reaction of $[Re_7(CO)_{21}C]^{3-}$ with $[(C_8H_{14})_2Ir(CO)Cl]_2$ and $AgBF_4$ in THF. (In the absence of $AgBF_4$, the reaction path is slow and complex). The product, $[Re_7(CO)_{21}CIr(CO)(C_8H_{14})]^{2-}$ undergoes alkene substitution upon treatment with C_2H_4 and an X-ray diffraction study of $[PPN]_2[Re_7(CO)_{21}CIr(CO)(C_8H_{14})]$ shows that the cluster has a bicapped octahedral core. [92]

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