

3 IRIDIUM

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CONTENTS

Introduction	251
3.1 IRIDIUM(V)	252
3.2 IRIDIUM(IV)	252
3.3 IRIDIUM(III)	253
3.3.1 Complexes with halides	253
3.3.2 Complexes with Gp VI donor ligands	254
3.3.3 Complexes with Gp V donor ligands	260
3.3.4 Complexes with Gp IV donor ligands	266
3.4 IRIDIUM(II)	268
3.5 IRIDIUM(I)	270
3.5.1 Complexes with halides	270
3.5.2 Complexes with Gp VI donor ligands	270
3.5.3 Complexes with Gp V donor ligands	271
References	275

INTRODUCTION

This review continues the general form of that published for the 1983 literature [1]. Once again, the chemistry of rhodium and iridium are treated separately this year. The interest in rhodium and iridium complexes as catalysts shows no sign of abating, and numerous new catalytic reactions and modifications to old catalyst systems continue to be reported. This year the chemistry of cluster compounds will not be reported in great detail, except where it is of direct interest to the coordination chemist. The review in this journal covering the 1985 literature will commence a biennial summary of the application of rhodium and iridium catalysts to organic synthesis.

The material included in this review corresponds to the coverage of Volumes 100 and 101 of Chemical Abstracts, although the major

journals (*Journal of the American Chemical Society, Inorganic Chemistry, Journal of the Chemical Society, Dalton Transactions and Journal of the Chemical Society, Chemical Communications*) have been covered through December 1984.

As usual, I must thank the staff of the Cambridge Crystallographic Data Centre for their invaluable assistance, and, in particular, Dr John Davies for initiating me into Marks 7, 8 and 9.

Wallbridge and Taylor have produced the Annual Report of the chemistry of the Platinum Group Metals for 1982, which is up to their normal high standard [2].

3.1 IRIDIUM(V)

This is not a popular oxidation state for study, and only a few reports have been made this year. The active hydrogenation catalyst precursors, $[\text{Ir}(\text{PPh}_3)_2\text{H}_2\text{L}_2]^+$ (L = MeCN, MeOH or Me₂CO) are readily prepared by the reduction of $[\text{IrH}_5(\text{PPh}_3)_2]$ with HBF₄ in the appropriate solvent [3]. The formation of an iridium(V) complex by oxidative addition to iridium(III) by a silane is discussed in Section 3.3.4 [49].

3.2 IRIDIUM(IV)

The majority of interest in iridium(IV) compounds has centred upon redox reactions involving $[\text{IrCl}_6]^{2-}$ as oxidant. The oxidation of hydrazine by $[\text{IrCl}_6]^{2-}$ has been investigated, and the primary oxidation product shown to be the hydrazine radical cation N_2H_4^+ [4]. The oxidation of chlorite, $[\text{ClO}_2]^-$, to ClO_2 by both hexabromo- and hexachloroiridate(IV) has been studied [5].

The reaction of bromine trifluoride with $[\text{IrCl}_6]^{2-}$ gives mixtures of the ions $[\text{IrF}_n\text{Cl}_{6-n}]^{2-}$ (n = 1-5). A *cis* product is obtained in the cases where n = 2, 3 or 4; however, the *trans* effect of chlorine is larger than that of fluorine, and the reaction of $[\text{IrF}_5\text{Cl}]^{2-}$ or *cis*- $[\text{IrF}_4\text{Cl}_2]^{2-}$ with SO_2Cl_2 results in the formation of *trans* products [6].

Molecular Orbital calculations on the hexachloroiridate(IV) ion at the MS-X_α level gave results in very good agreement with the experimental

photoionisation, optical and e.p.r. spectra [7].

The reduction of 4-cyano-4-arylcyclohexanones by propan-2-ol in the presence of IrCl_4 and trimethyl phosphite has been investigated; high yields (> 95%) of the secondary alcohols may be obtained [9].

The mixed oxidation state sulphato complex ions $[\text{EIr}_3(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$ (E = O or N), which may be formulated as {2Ir(III),Ir(IV)} and {Ir(III),2Ir(IV)} compounds respectively, were included in a study of the thermal stability of iridium sulphato complexes [8].

3.3 IRIDIUM(III)

3.3.1 Complexes with halides

Crystal structure analyses of a number of $[\text{IrX}_6]^{3-}$ complexes have been reported in a study of the iridium-halide systems [10]. The complexes $\text{K}_3[\text{IrCl}_6]$ (Ir-Cl_{av} 2.368 Å), $\text{K}_3[\text{IrCl}_6]\cdot\text{H}_2\text{O}$ (Ir-Cl_{av} 2.368 Å), $[\text{NH}_4]_3[\text{IrCl}_6]\cdot\text{H}_2\text{O}$ (Ir-Cl 2.367 Å) and $\text{Rb}_3[\text{IrBr}_6]\cdot\text{H}_2\text{O}$ (Ir-Br 2.508 Å) have been reported; all the complex anions exhibited distorted octahedral geometries as a result of packing and hydrogen-bonding interactions [10]. The reaction of $\text{K}_3[\text{IrCl}_6]$ with KSCN in the presence of nitric acid results in the formation of the ions $[\text{Ir}(\text{NCS})_n(\text{SCN})_{6-n}]^{3-}$ (n = 0, 1 or 2) and traces of $[\text{Ir}(\text{NCS})_5\text{Cl}]^{3-}$; the complexes may be separated by ion-exchange chromatography. Upon heating the ${}^n\text{Bu}_4\text{N}$ salts, rearrangement occurs to favour the N bonded ligands (n = 2, 3, 4 or 5) [11].

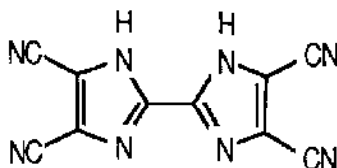
The pseudohalide complex ion $[\text{IrCl}_4(\text{SnCl}_3)_2]^{2-}$ may be affixed to an AV-17-8 anion exchange resin, and the immobilised species is a selective catalyst for double bond isomerisation in 1-hexene [12]. Iridium anions have been similarly immobilised on AN-31 anion exchange resins, from which the iridium may be removed by anodic oxidation [13].

The base catalysed hydration of $\text{cis}-[\text{Ir}(\text{en})_2\text{Cl}_2]^+$ proceeds with retention of configuration to give $\text{cis}-[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$, whereas $\text{trans}-[\text{Ir}(\text{en})_2\text{Cl}_2]^+$ gives a 3:2 mixture of *cis* and *trans* $[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ [14]. The water molecules coordinated to the iridium in both the above complexes are acidic; for $\text{trans}-[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ pK_{a1} 6.29, pK_{a2} 8.1 whilst for $\text{cis}-[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ pK_{a1} 4.8, pK_{a2} 7.86 [14]. The crystal and molecular structure of the low temperature form of $\text{trans}-[\text{Ir}(\text{py})_4\text{Cl}_2]\text{Cl}\cdot 6\text{H}_2\text{O}$, obtained from water at 2°, has been

described (Ir-Cl 2.35 Å, Ir - N 2.06 Å). The lattice water molecules form hydrogen-bonded sheets, which are also hydrogen bonded to chloride [15].

The photophysical properties of *cis*-[IrL₂Cl₂] (L = bipy, phen, 4,7-Me₂phen or 5,6-Me₂phen) in dmf/H₂O mixtures have been investigated, and shown to exhibit very marked solvent effects which were interpreted in terms of different mixed emitting species. In all cases, ¹H n.m.r. studies of the solutions suggested that no appreciable displacement of chloride by solvation or photosolvation pathways had occurred [16]. The complex [Ir(bipy)₂Cl₂]Cl is notoriously resistant to chloride substitution, but reaction with CF₃SO₃H results in the formation of the more labile species [Ir(bipy)₂(O₃SCF₃)₂]⁺ [17].

A number of iridium(III) halide complexes have been prepared by oxidative addition reactions, and are discussed in more detail in other sections. The reaction of bromine with [Ir(CO)₂L]⁻ (L = 1) results in the formation of [Ir(CO)₂LBr₂]⁻ [18].

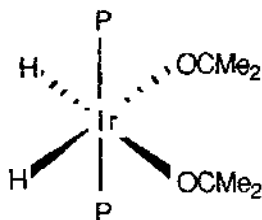


(1)

3.3.2 Complexes with Gp VI donor ligands

3.3.2.1 Complexes with oxygen donor ligands

Swaddle has reported and critically discussed the partial molar volumes for a range of transition metal ions, including [Ir(NH₃)₅(H₂O)]³⁺ [19]. The solvento complexes [IrH₂(PPh₃)₂L₂]⁺ (L = MeCN, MeOH or Me₂CO) have been prepared by the reaction of [IrH₅(PPh₃)₂] with the appropriate solvent in the presence of HBF₄. In the case of the acetone complex, a crystal structural analysis has revealed the complex to possess a distorted octahedral geometry, in which the acetone and hydride ligands occupy *cis* positions in the equatorial plane and the phosphines are *trans*-diaxial (2) [3].



(2)

The thermal decomposition of a range of mono and polynuclear iridium sulphato complexes, including $[\text{OIr}_3(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$, $[\text{NIr}_3(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$, $[\text{Ir}_2(\text{SO}_4)_3(\text{H}_2\text{O})_6]$ and $[\text{Ir}(\text{SO}_4)_2(\text{H}_2\text{O})_4]^-$, has been investigated [8]. The extraction of iridium sulphato complexes by various amines has been investigated [20].

The preparation and acidity of *cis* and *trans* isomers of $[\text{Ir}(\text{en})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ was discussed in Section 3.1 [14].

The hydrolysis of the phosphate in $[\text{Ir}(\text{NH}_3)_5\{(\text{MeO})_3\text{PO}\}]^{3+}$ is 400 times faster than that of the free ligand. The products of the reaction are $(\text{MeO})_2\text{PO}_2$ and methanol, and it is proposed that the hydroxide attacks at the coordinated phosphorus atom with resultant C-O cleavage, rather than M-O cleavage, as is observed in reactions of cobalt(III) phosphate complexes. This modest rate enhancement offers valuable insight into the ways in which ligands may be activated by coordination to a metal ion [21].

Trifluoromethanesulphonate is an extremely good leaving group, and a number of synthetic applications of such complexes have been reported this year. Solvation of $[\text{Ir}(\text{NH}_3)_5(\text{O}_3\text{SCF}_3)]^{2+}$ by dmf or MeCN proceeds rapidly to yield $[\text{Ir}(\text{NH}_3)_5\text{L}]^{3+}$ (L = dmf or MeCN). The solvento complexes are activated with respect to base hydrolysis, and (unusually) single products are obtained from reaction with hydroxide. No ligand loss occurs by conjugate base mechanisms (to give hydroxo complexes), and the products of these reactions are the acetamido or formato complexes $[\text{Ir}(\text{NH}_3)_5\text{L}]^{2+}$ (L = HNCOMe or O_2CH) from MeCN and dmf respectively [22]. The overall rate enhancement over the hydrolysis of the free ligands is about 10^6 and the rate law is of the form

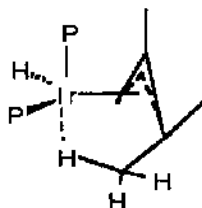
$$\rho = k_{\text{obs}}[\text{Ir}(\text{NH}_3)_5\text{L}]^{3+}$$

where

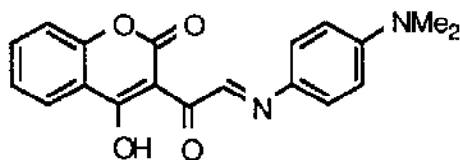
$$k_{\text{obs}} = k_1[\text{OH}^-] + k_2[\text{OH}^-]^2$$

Loss of CF_3SO_3^- from $[\text{Ir}(\text{bipy})_2(\text{O}_3\text{SCF}_3)_2]^+$ is also facile, and reaction with bipy, $\text{Na}[\text{BH}_4]$ or $\text{PPh}_3/\text{HOCH}_2\text{CH}_2\text{OH}$ respectively results in the formation of $[\text{Ir}(\text{bipy})_3]^{3+}$, $[\text{Ir}(\text{bipy})_2\text{H}_2]^+$ or $[\text{Ir}(\text{bipy})_2(\text{PPh}_3)\text{H}]^{2+}$ [17].

The reaction of $[\text{Ir}(\text{PPh}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ with dienes proceeds with loss of acetone to give $[\text{Ir}(\text{PPh}_3)_2\text{H}_2\text{L}]^+$ ($\text{L} = \text{cod}$ or nbd). The reaction was followed by stopped-flow n.m.r. methods, and it was shown that the rate of displacement by nbd was considerably faster than that by cod , and it was proposed that the intermediate monodentate cod ligand dissociates at a faster rate than it chelates. It was also shown that the complex $[\text{Ir}(\text{PPh}_3)_2(\text{nbd})\text{H}_2]^+$ (which is formed as a mixture of isomers) reacted with excess nbd in the dark to yield $[\text{Ir}(\text{PPh}_3)_2(\text{nbd})]^+$ and norbornene. The hydrogen transfer occurred exclusively to C_5 and C_6 of the nbd . Reactions of $[\text{Ir}(\text{PPh}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ with 2,3-dimethylbutadiene, 1,3- or 1,4-cyclohexadiene leads to the formation of η^3 -allyl compounds with agostic interactions between the metal and the CH_2 adjacent to the allyl (3) [23].



(3)

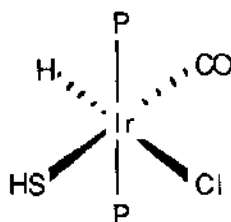


(4)

The complex $[\text{Ir}(\text{HL})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ ($\text{H}_2\text{L} = \mathbf{4}$) has been reported; the deprotonated ligand is terdentate and coordinates to the metal through the imino nitrogen, and the phenolate and carbonyl oxygen atoms [24].

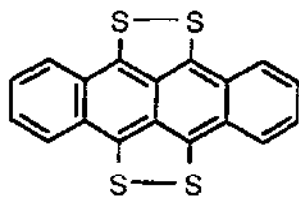
3.3.2.2 Complexes with sulphur, selenium and tellurium donor ligands

The oxidative addition of hydrogen sulphide to iridium(I) complexes results in the formation of iridium(III) hydrosulphide complexes. The reaction of $\text{trans-}[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ with H_2S gives $\text{trans-}[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{SH})\text{H}]$ ($\mathbf{5}$) which has been structurally characterised. The hydride and hydrosulphide are *cis* to each other in the equatorial plane, indicating a side-on approach of the incoming hydrogen sulphide molecule [25].

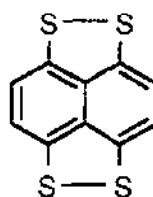


(5)

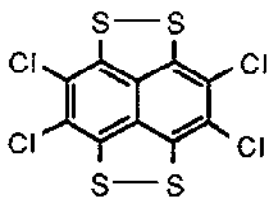
The disulphide complex $[\text{Ir}(\text{dppe})_2\text{S}_2]^+$ may be oxidised by 3-chloroperbenzoic acid to $[\text{Ir}(\text{dppe})_2(\text{S}_2\text{O})]^+$, or to $[\text{Ir}(\text{dppe})_2(\text{S}_2\text{O}_2)]^+$ with an excess of the oxidant. In all of these complexes, the inorganic ligand acts as an $\eta^2\text{-S}_2$ donor, and n.m.r. evidence suggested the formation of a single diastereomer of the complex [27].



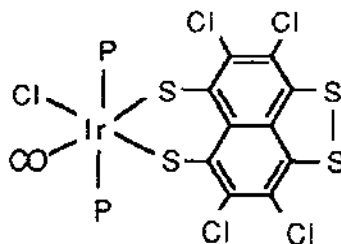
(6)



(7)



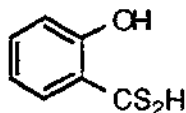
(8)



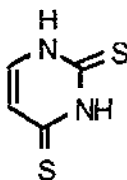
(9)

The aromatic disulphide donors **6**, **7** or **8** may act as 2, 4, 6, 8 or 12 electron donors to one, two, three or four metal centres. Crystal structural analyses of the mononuclear complexes $[\text{Ir}(\text{PPh}_3)_2\text{L}(\text{CO})\text{X}]$ ($\text{L} = \mathbf{7}$; $\text{X} = \text{H}$ or Cl) (**9**) have been reported; the ligand acts as a chelating S_2 donor. The rupture of the first S-S bond results in a shortening (and presumably strengthening) of the remaining disulphide link; this presumably explains the ease of isolation of the mononuclear complexes [26].

The complex $[\text{IrL}_3]$ ($\text{HL} = \mathbf{10}$) is readily prepared by the reaction of $[\text{Et}_4\text{N}]\text{L}$ with $[\text{NH}_4]_3[\text{IrCl}_6]$ [31]. A dithiouracil complex, $[\text{IrL}_3\text{Cl}_3]$ ($\text{L} =$ dithiouracil, **11**) has also been reported [28].

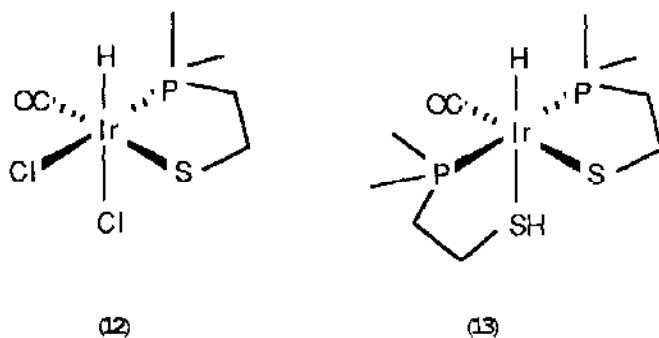


(10)



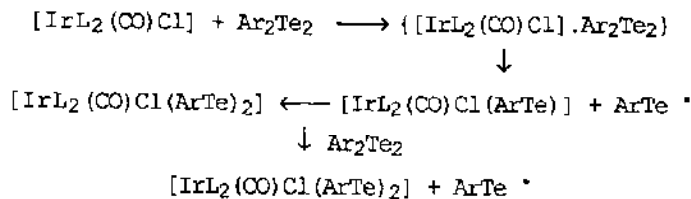
(11)

Trans-[Ir(PPh₃)₂(CO)Cl] reacts with Ph₂PCH₂CH₂SH (HL) to give mixtures of the iridium(I) substitution product [IrPPh₃(CO)L] and [IrPPh₃(CO)H(Cl)L] (**12**). With an excess of HL, the complex cation [Ir(HL)L(CO)H]⁺ (**13**) is formed; the latter has been structurally characterised, and shown to have the two phosphorus atoms *trans* to each other, the thiolato sulphur *trans* to carbonyl and the thiol sulphur *trans* to hydride [29].



The complex [Ir(dppe)₂(Se₂)]⁺ reacts with peracetic acid to give [Ir(dppe)₂(Se₂O)]⁺. In contrast to the analogous sulphur compound, this may not be oxidised further to a {Se₂O₂} derivative, although the compound is an active oxidising agent, and reacts with thiols to give disulphides and the starting diselenide [Ir(dppe)₂(Se₂)]⁺ [27].

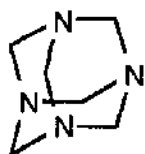
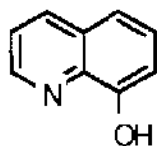
The oxidative addition of diaryl ditellurides to *trans*-[Ir(PPh₃)₂(CO)Cl] results in the formation of isomers of [Ir(PPh₃)₂(ArTe)₂(CO)Cl]. The reaction is found to be first order in the iridium complex and the ditelluride, and e.s.r. evidence suggests that a radical mechanism is followed. The mechanistic scheme overleaf was proposed for the reaction [30].



3.3.3 Complexes with Gp V donor ligands

3.3.3.1 Complexes with amines and related ligands

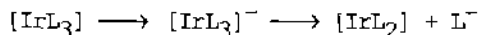
The ^1H n.m.r. spectra of the complexes $[\text{Ir}(\text{NH}_3)_5\text{L}]^{n+}$ ($\text{L} = \text{NO}_2$, $n = 2$; $\text{L} = \text{NH}_3$, $n = 3$) have been recorded in D_2O or dmsO-d_6 solution; separate resonances are observed for the ammine ligands *cis* and *trans* to the NO_2 group [32]. The ^1H n.m.r. spectra of a series of $[\text{Ir}(\text{NH}_3)_5\text{L}]^{3+}$ ($\text{L} = \text{imidazole}$ or methylimidazoles) have also been reported [34]. The use of the trifluoromethanesulphonato ligand as a leaving group in the preparation of $[\text{Ir}(\text{NH}_3)_5\text{L}]^{n+}$ ($\text{L} = \text{dmf}$, MeCN , HNCOMe or O_2CH) complexes has been discussed earlier [22], as has the hydrolysis of $[\text{Ir}(\text{NH}_3)_5\text{L}]^{3+}$ ($\text{L} = (\text{MeO})_3\text{PO}$) [21]. The hydrolysis of *cis* and *trans* $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ was reported in Section 3.1 [14]. A 1:1 adduct of iridium trichloride with hexamethylenetetramine (L , **14**), $\{\text{IrCl}_3 \cdot \text{L} \cdot 6\text{H}_2\text{O}\}$ has been described [33].

**(14)****(15)**

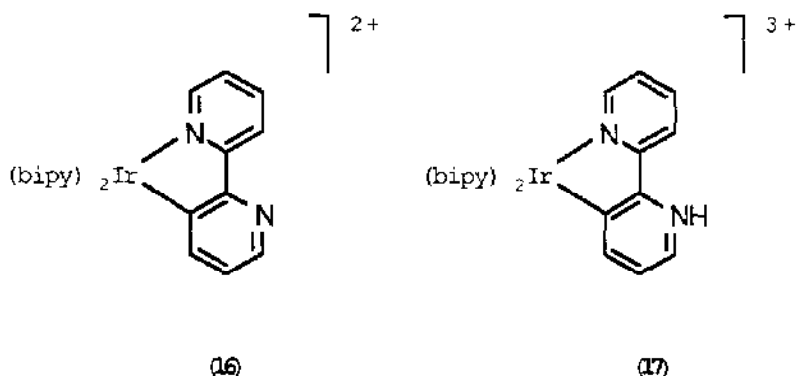
3.3.3.2 Complexes with nitrogen heterocyclic ligands

The properties of coordinated imidazoles in a range of d^6 complexes have been investigated, and a pK_a of 10.05 determined for the imidazole NH in the complex $[\text{Ir}(\text{NH}_3)_5(\text{Him})]^{3+}$ [34]. The crystal structure of the low temperature (recrystallised from water at 2°C) form of *trans*- $[\text{Ir}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ has been determined. The cation exhibits a distorted octahedral geometry about the metal, but interest centres on the hydrogen bonding network exhibited by the lattice water molecules and chloride counter ions [15]. This structure may be of some relevance to the supposedly anomalous properties of the complex $[\text{Pt}(\text{py})_4\text{Cl}_2]^{2+}$. The complex $\{\text{Ir}(\text{HL})_3\text{Cl}_3\}$ ($\text{HL} = \text{dithiouracil}$, **11**) has been reported [28]. The electrochemical properties of the homoleptic complex $[\text{IrL}_3]$ ($\text{HL} = 8\text{-hydroxyquinoline}$, **15**) in dmf solution have been reported. The cyclic

voltammogram exhibits three reversible one-electron reductions at high sweep rates. At lower sweep rates, only one of the reductions is fully reversible. This was interpreted in terms of a dissociative equilibrium involving the electrogenerated $[\text{IrL}_3]^-$ species [35].

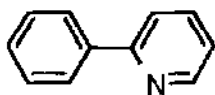


A number of $[\text{Ir}(\text{bipy})_2\text{L}_2]^{n+}$ complexes have been prepared from $[\text{Ir}(\text{bipy})_2(\text{O}_3\text{SCF}_3)_2]^+$ by displacement of trifluoromethanesulphonate with a range of nucleophiles [17]. The complexes $[\text{Ir}(\text{bipy})_3]^{3+}$, $[\text{Ir}(\text{bipy})_2\text{H}_2]^{1+}$ and $[\text{Ir}(\text{bipy})_2(\text{PPh}_3)\text{H}]^{2+}$ were prepared by reaction with bipy, borohydride or triphenylphosphine in ethane-1,2-diol respectively. The photochemical properties of *cis*- $[\text{IrL}_2\text{Cl}_2]\text{Cl}$ (L = bipy, phen, 4,7-Me₂phen or 5,6-Me₂phen) in dmf-water mixtures have been investigated [16].

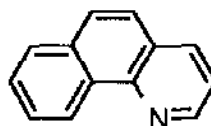


The saga of the $[\text{Ir}(\text{bipy})_3]^{n+}$ complexes continues, but it is now clear that the anomalous compounds contain *cyclo* metallated 2,2'-bipyridine rings. The photochemical, photophysical and spectroelectrochemical properties of authentic (yellow) $[\text{Ir}(\text{bipy})_3]^{3+}$ have been reported; the complex exhibits three reduction processes centered at -1.30, -1.45 and -1.60 V vs Ag/Ag^+ [36]. A similar study has been made of the cyclometallated complex $[\text{Ir}(\text{bipy})_2(\text{bipy-C,N})]^{2+}$ (16). The 200 and 300 MHz ^1H n.m.r. spectra of the complex both exhibit 23 distinct resonances, whilst the 90 MHz ^{13}C n.m.r. spectrum reveals 30 non-equivalent carbon atoms. These observations are fully in accord with the structure that has been established for the complex in the solid state. The electrochemical properties of the complex

are consistent with the electrons residing on only the *N,N'*-bipy rings in the reduced complexes. The electronic spectra of $[\text{Ir}(\text{bipy})_2(\text{bipy-C,N})]^{2+}$, $[\text{Ir}(\text{bipy})_2(\text{bipy-C,N})]^+$ and $[\text{Ir}(\text{bipy})_2(\text{bipy-C,N})]$ were also reported [37]. Solid state structural determinations of the complexes $[\text{Ir}(\text{bipy})_2(\text{Hbipy-C,N})][\text{ClO}_4]_3 \cdot \text{H}_2\text{O}$ (17) and $[\text{Ir}(\text{bipy})_3][\text{ClO}_4]_3 \cdot 2\text{H}_2\text{O}$ have been reported. In the metallated complex, the iridium is in a distorted octahedral environment and two differing Ir-N distances are observed; Ir-N_{trans to C} 2.082(5) Å, Ir-N_{trans to N} 2.042(4) Å. The non-coordinated nitrogen of the metallated ring is protonated. The lattice water oxygen atom is 2.87(2) Å from C₃ of ring 1 and 3.19(2) Å from C₃ of ring 2. There is, thus, a hydrogen bonding interaction with the bipy rings, but there is no direct covalent hydration of the ligand. In both the metallated and the "normal" complex there is a significant interaction between the cation and the perchlorate counter ion, with O-C distances less than 3.2 Å. The cation in $[\text{Ir}(\text{bipy})_3]^{3+}$ is near-octahedral, with Ir-N distances in the range 2.00(2) - 2.02(2) Å [38]. The interest in the photophysical

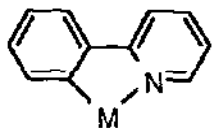


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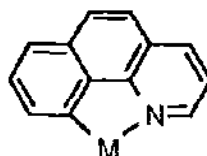


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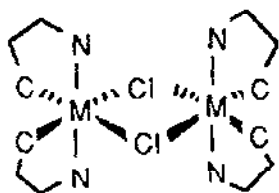
properties of diimine complexes of d^6 metal ions has recently been extended to the metallated derivatives, which have proved to possess rather attractive spectroelectrochemical properties. The reaction of 2-phenylpyridine (18) with $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ in $\text{EtOCH}_2\text{CH}_2\text{OH}$ results in the formation of the chloro-bridged dimer, $[\text{L}_2\text{Ir}(\mu\text{-Cl})_2\text{IrL}_2]$ (HL = 18). Exactly analogous complexes are obtained with benzo[h]quinoline (19). ^1H and ^{13}C n.m.r. spectra of the complexes were consistent with the formation of the metallated complexes (20) and (21); the symmetry of the n.m.r. spectra suggested the formation of the *meso* (22) or *racemic* (23) conformers of the dimers. The photophysical properties of the complexes have



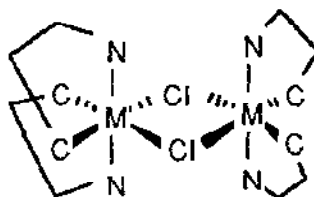
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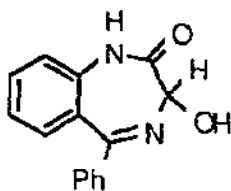
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(23)

been investigated; the metallated ligands act as both strong σ donors and π acceptors [39].

The complex $\{\text{IrL}_3\text{I}_3 \cdot 5\text{H}_2\text{O}\}$ ($\text{L} = \mathbf{24}$) has been prepared; the metal is in a distorted octahedral environment [40].



(24)

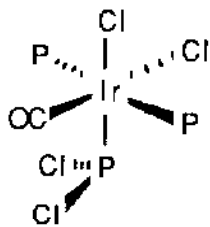
3.3.3.3 Complexes with phosphorus donor ligands

The majority of complexes incorporating phosphines have been dealt with in other sections of this review. The complexes which are considered at this point are those in which the interest is specifically in the phosphorus containing ligand.

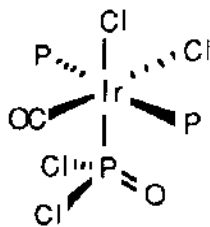
The interaction of phosphorus(III) halides with iridium(I) complexes has been investigated by Ebsworth and co-workers. The reaction

of PCl_3 with $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}]$ results in oxidative addition and the formation of $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2)]$ (25). A crystal structural analysis confirmed the structure of the product and established the two phosphines were *trans*, the two chlorides were *cis*, and that the PCl_2 was *trans* to chloride. The complex does not react with BF_3 , but does react with BCl_3 to yield *trans*- $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2\text{BCl}_3)]$. In the presence of HCl the reaction proceeds further to yield $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2\text{H})][\text{BCl}_4]$.

Related reactions of $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2)]$ with B_2H_6 and HCl result in the formation of $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2\text{BH}_3)]$ or *trans*- $[\text{Ir}(\text{PET}_3)_2\text{H}(\text{CO})\text{Cl}_2]$ respectively. The dichlorophosphide complex $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2)]$ is oxidised slowly by O_2 (or more rapidly by N_2O_4) to the corresponding dichlorooxophosphide complex $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{OPCl}_2)]$ (26), the structure of which was

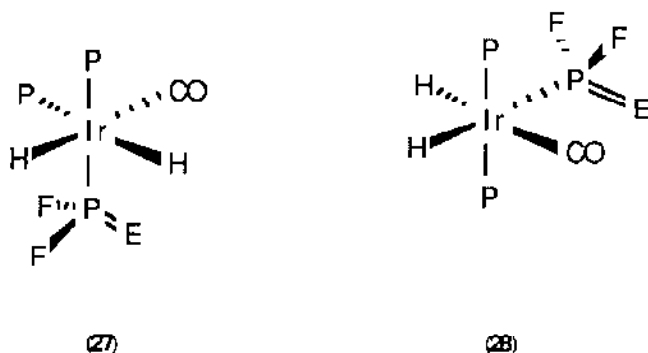


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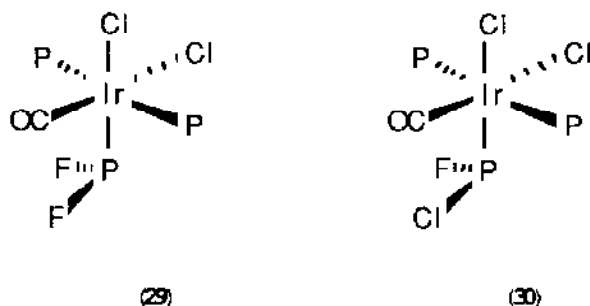


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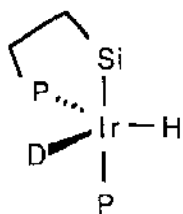
established by a crystal structural analysis. The related selenium complex $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{SePClH})]$ is obtained by the reaction of H_2Se with $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PCl}_2)]$, but further reactions occur to yield $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{SePH}(\text{SeH}))]$ and $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{SePH}_2)]$. Similar reactions occur with H_2S or H_2O to yield $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{SPClH})]$ or $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{OPH}(\text{OH}))]$ respectively [41]. The direct reaction of PF_2HE ($\text{E} = \text{O}, \text{S}$ or Se) with $[\text{Ir}(\text{PPh}_3)_3(\text{CO})\text{H}]$ results in the initial formation of the salts $[\text{Ir}(\text{PPh}_3)_3(\text{CO})\text{H}_2][\text{PF}_2\text{E}]$, which decompose on warming to give PPh_3 and mixtures of *cis* (27) and *trans*- $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{H}_2(\text{PF}_2\text{E})]$ (28), and traces of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{H}(\text{PF}_3)]$. The *cis* product slowly isomerises to the *trans* form [42]. The reaction of



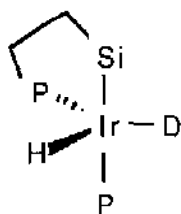
$[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}]$ with PF_2Cl is analogous to that with PCl_3 , and the initial product is $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PF}_2)]$ (29), which undergoes halogen exchange to yield $[\text{Ir}(\text{PET}_3)_2(\text{CO})\text{Cl}_2(\text{PClF})]$ (30) [43].



The reactions of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SH}$ were discussed in Section 3.3.2.2 [29]. A related reaction is observed in the interaction with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2\text{H}$ ($\text{R} = \text{various}$), which results in the formation of various enantiomers or diastereomers of *cis* $[\text{Ir}(\text{PPh}_3)\text{H}_2(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}_2)]$ [44]. The reaction of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiMe}_2\text{D}$ with $[\text{Ir}(\text{PPh}_3)_3(\text{CO})\text{H}]$ is regiospecific and consistent with coplanar entry of the P, Si and D atoms to yield **31** which is in equilibrium with the isomer **32** [45].



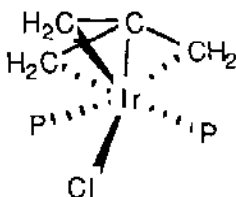
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3.3.4 Complexes with Gp IV donor ligands

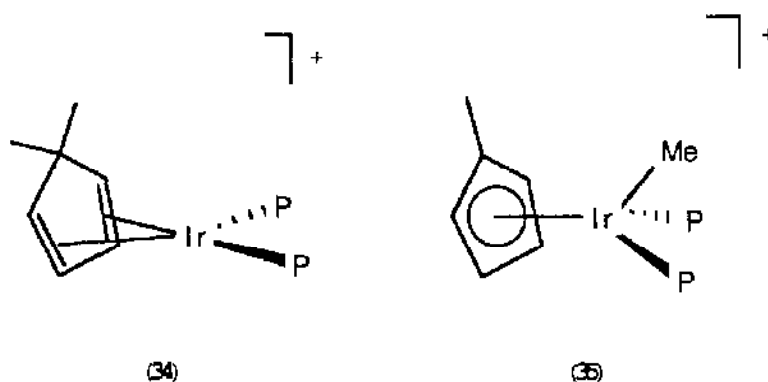
The reaction of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ with $\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{Cl}$ in benzene proceeds with loss of a trimethylsilyl group to yield the novel complex $[\text{Ir}(\eta^4\text{-C}(\text{CH}_2)_3)(\text{PPh}_3)(\text{CO})\text{Cl}]$ (**33**) which has been structurally characterised. The $\text{C}(\text{CH}_2)_3$ ligand may be regarded as



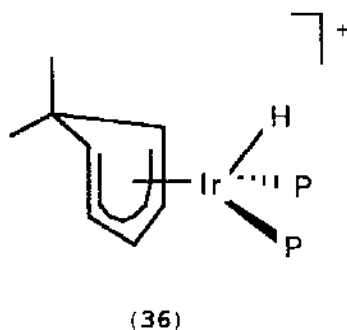
(33)

a 4-electron donor, with each carbon atom acting as the site of a single negative charge. The three $\text{Ir}-\text{CH}_2$ distances are in the range 2.173(15) - 2.288(15) Å, and are significantly longer than the capping $\text{Ir}-\text{C}$ distance of 2.053(12) Å and the $\text{Ir}-\text{CO}$ distance of 1.898(15) Å. If the reaction is performed in acetonitrile in the presence of KPF_6 instead of benzene, the salt $[\text{Ir}(\eta^4\text{-C}(\text{CH}_2)_3)(\text{PPh}_3)_2(\text{CO})][\text{PF}_6]$ may be isolated [46].

The reactions of dienes with $[\text{Ir}(\text{PPh}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ was discussed earlier [23]. The related complex $[\text{Ir}(\text{PAr}_3)_2(\text{OCMe}_2)_2\text{H}_2]^+$ ($\text{Ar} = 4\text{-fluorophenyl}$) reacts with 1,1-dimethylcyclopentane in the presence of 3,3-dimethylbutene to yield initially $[\text{Ir}(\text{PAr}_3)_2\text{L}]^+$ ($\text{L} = \eta^4\text{-5,5-dimethylcyclopentadienyl}$) (**34**), which rearranges by a methyl migration to the iridium(III) complex $[\text{Ir}(\eta^5\text{-Mecp})(\text{PAr}_3)_2\text{Me}]^+$ (**35**). In contrast, 1,1-dimethylcyclohexane



reacts under similar conditions to yield the η^5 -dienyl complex **36** [47]. An interesting example of a reversible equilibrium between alkanes is observed in the reaction of $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{H}(\text{cych})]$ with pentane, when an equilibrium is set up with $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{H}(\text{pentyl})]$ and cyclohexane. A similar reaction occurs on treating $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{H}(\text{cych})]$ with methane, when

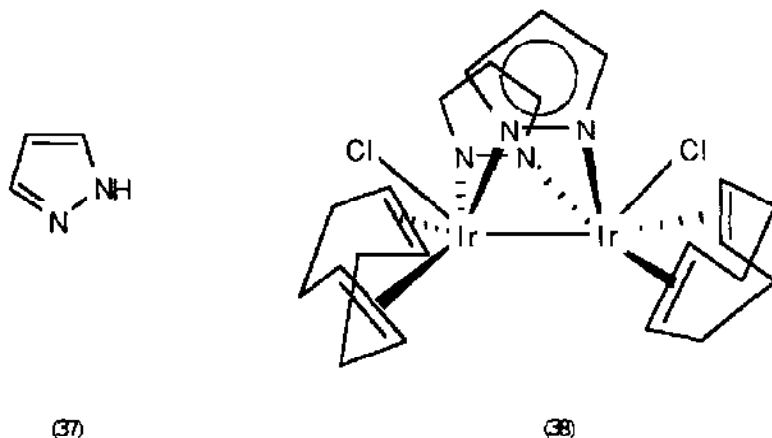


$[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{H}(\text{Me})]$ is formed; this latter compound reacts with CHCl_3 (in a reaction reversed by LiBH_4) to yield $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{Cl}(\text{Me})]$, which may also be prepared by the reaction of $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{Cl}_2]$ with LiMe or $[\text{Ir}(\text{PMe}_3)(\text{cp}^*)\text{Me}_2]$ [48].

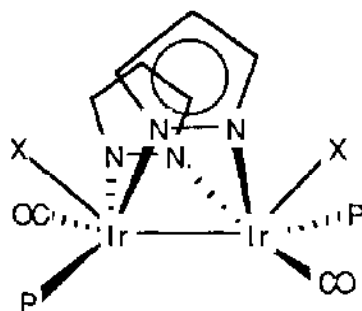
The complex $[(\text{cp}^*)\text{IrCl}(\mu\text{-Cl})_2\text{IrCl}(\text{cp}^*)]$ reacts with R_3SiH ($\text{R} = \text{Et}$ or Ph) in an unusual reaction to yield $[\text{Ir}(\text{cp}^*)(\text{SiR}_3)\text{ClH}_2]$. This complex is also obtained from the reaction of SiEt_3H with $[(\text{cp}^*)\text{IrCl}(\mu\text{-H})_2\text{IrCl}(\text{cp}^*)]$; an excess of the silane converts the $[\text{Ir}(\text{cp}^*)(\text{SiR}_3)\text{ClH}_2]$ to $[\text{Ir}(\text{cp}^*)(\text{SiR}_3)_2\text{H}_2]$ [49]. These are examples of an extremely unusual oxidative addition to a d^6 centre to give a formally iridium(V) d^4 complex.

3.4 IRIDIUM(II)

This formal oxidation state is only commonly encountered in binuclear complexes, and a number of such species have been investigated this year. The photochemical reaction of $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ (HL = pyrazole, **37**) with $\text{ClCH}_2\text{CH}_2\text{Cl}$ results in the formation of $[(\text{cod})\text{Ir}(\mu\text{-CH}_2\text{CH}_2)_2\text{Ir}(\text{cod})]$ (**38**) [50]. A complex related to the previous starting material is $[(\text{CO})(\text{PPh}_3)\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})(\text{PPh}_3)]$ which is formed in the reaction of

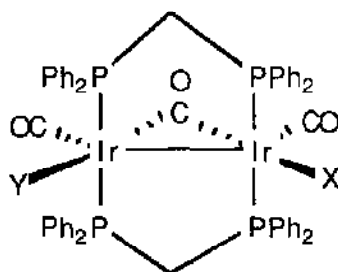


$[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ with NaL ; $[(\text{CO})(\text{PPh}_3)\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})(\text{PPh}_3)]$ is an iridium(I) complex, and a crystal structural analysis has revealed the non-bonded Ir...Ir distance to be 3.163(2) Å (which increases to 3.290(1) Å in the hexane solvate). However, $[(\text{CO})(\text{PPh}_3)\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})(\text{PPh}_3)]$ undergoes an oxidative addition reaction with X_2 (X = I or Br) to give the iridium(II) complexes $[(\text{CO})(\text{PPh}_3)\text{XIr}(\mu\text{-L})_2\text{IrX}(\text{CO})(\text{PPh}_3)]$ (**39**). A crystal structural analysis of this complex established an Ir-Ir distance of 2.737 Å, consistent with an Ir-Ir single bond. The reaction of $[(\text{CO})(\text{PPh}_3)\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})(\text{PPh}_3)]$ with chlorine resulted in electrophilic attack at the ligand rather than at the metal, with the formation of 4-chloropyrazole [51].



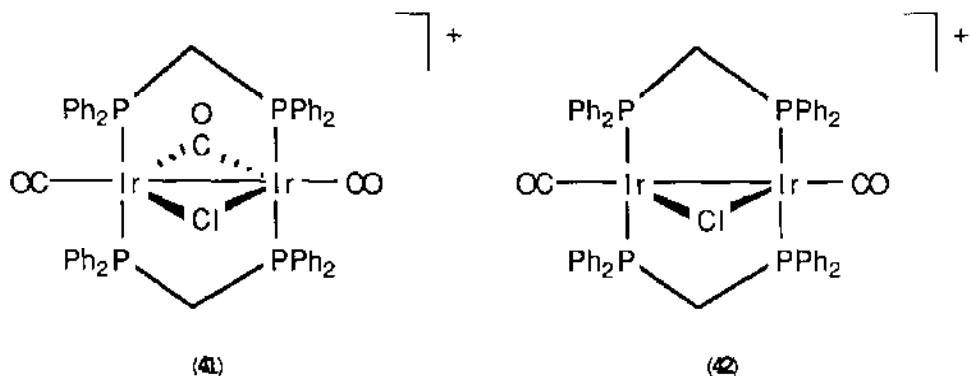
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The reaction of $[(\text{cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cod})]$ with dppm in the presence of CO results in the formation of $[(\text{CO})_2\text{Ir}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Ir}(\text{CO})\text{Cl}]^+$ (**40**, $X = \text{Cl}$, $Y = \text{CO}$). The latter compound reacts with chloride to produce a mixture of the *cis* and *trans* isomers of $[(\text{CO})\text{ClIr}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Ir}(\text{CO})\text{Cl}]$ (**40**), $X = Y = \text{Cl}$). A preliminary crystal structural analysis of this product was hindered by disorder associated with the presence of both *cis* and *trans* isomers in the crystal. The reaction of $[(\text{CO})_2\text{Ir}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Ir}(\text{CO})\text{Cl}]$ with $[\text{BF}_4]^-$, or of



(40)

$[(\text{CO})\text{ClIr}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Ir}(\text{CO})\text{Cl}]$ with Ag^+ gives the chloro bridged dimer $[(\text{CO})\text{Ir}(\mu\text{-dppm})_2(\mu\text{-CO})(\mu\text{-Cl})\text{Ir}(\text{CO})]^+$ (**41**). Upon warming $[(\text{CO})\text{ClIr}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Ir}(\text{CO})\text{Cl}]$ under nitrogen, the iridium(I) complex $[(\text{CO})\text{ClIr}(\mu\text{-dppm})_2\text{Ir}(\text{CO})\text{Cl}]$ is formed, which reacts with Ag^+ to give $[(\text{CO})\text{Ir}(\mu\text{-dppm})_2(\mu\text{-Cl})\text{Ir}(\text{CO})]^+$ (**42**) [52].



3.5 IRIDIUM(I)

3.5.1 Complexes with halides

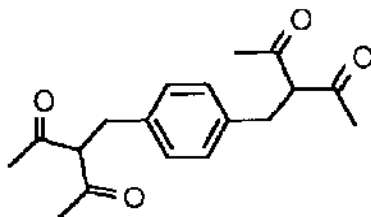
The commonest starting materials for the preparation of iridium(I) complexes are $[\text{Ir}(\text{PR}_3)_2(\text{CO})\text{Cl}]$ and $[\text{L}_2\text{Ir}(\mu\text{-Cl})_2\text{IrL}_2]$ ($\text{L}_2 = (\text{CO})_2$ or diene). In general, the chemistry of these materials will be found at the appropriate points in the text. The most common reaction of iridium(I) complexes is oxidative addition to yield iridium(III) compounds; these are dealt with under the appropriate iridium(III) section, however, notable examples of compounds undergoing oxidative addition reported this year include Ar_2Te_2 [30], H_2S [25], disulphides [26], and allyl halides [46].

The complex $[\text{Ir}(\text{CO})_3\text{Cl}]$ is polymeric, with staggered $[\text{Ir}(\text{CO})_3\text{Cl}]$ units running along a principal crystal axis. The Ir-Ir contact is 2.844 Å. Partial oxidation of the compound with iodine results in the formation of a polymeric material with significantly shorter Ir-Ir contacts of 2.644 Å. The band structure of these one-dimensional materials has been investigated [53,54].

3.5.2 Complexes with Gp VI donor ligands

The novel bridging diketonate ligand **43** reacts with $[(\text{cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cod})]$ to give the binuclear complex $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ ($\text{H}_2\text{L} = \mathbf{43}$), which reacts with monodentate ligands to yield $[\text{X}_2\text{Ir}(\mu\text{-L})_2\text{IrX}_2]$ ($\text{H}_2\text{L} = \mathbf{43}$, $\text{X} = \text{PPh}_3$ or CO). The compounds are catalyst precursors for hydrogenation systems. [55]

The reactions of $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SH}$ have been described in Section 3.3.2. Although reaction with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SH}$ results in oxidative addition, a simple displacement reaction occurs with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}^-$ to give $[\text{Ir}(\text{PPh}_3)(\text{CO})\text{L}]$ ($\text{HL} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{SH}$) in which the two phosphorus atoms are *trans* to each other [29]

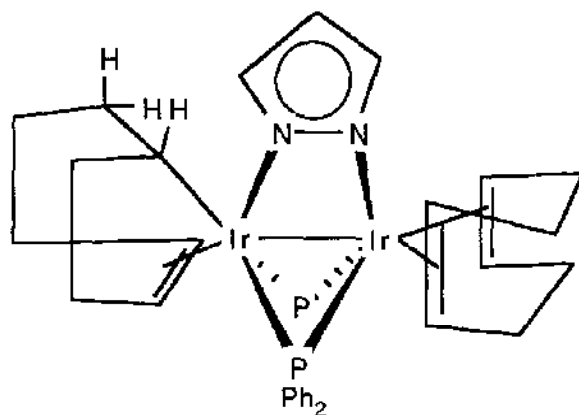


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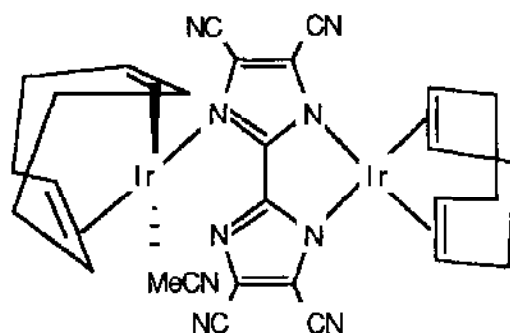
3.5.3 Complexes with Gp V donor ligands

Complexes of iridium(I) incorporating bridging pyrazolate ligands have attracted a considerable amount of recent interest. The complex $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ ($\text{HL} = \text{pyrazole}$, **37**) is prepared by the reaction of $[(\text{cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cod})]$ with NaL ($\text{HL} = \text{pyrazole}$) [51], and undergoes oxidative addition upon reaction with $\text{ClCH}_2\text{CH}_2\text{Cl}$ [50]. The spectrochemical and electrochemical properties of $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ ($\text{HL} = \text{pyrazole}$, **37**) have been investigated. The complex is luminescent, with emission occurring from the $^1\text{B}_2$ and $^3\text{B}_2$ states [56]. The related complex $[(\text{CO})(\text{PPh}_3)\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})(\text{PPh}_3)]$ ($\text{HL} = \text{pyrazole}$, **37**) is prepared by the reaction of $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ with PPh_3 in the presence of CO [51]. Reaction of $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ ($\text{HL} = \text{pyrazole}$, **37**) with PPh_2H results in the formation of $[(\sigma\eta^2\text{-cyclooctenyl})\text{Ir}(\mu\text{-L})(\mu\text{-PPh}_2)_2\text{Ir}(\eta^4\text{-cod})]$ (**44**) which has been structurally characterised. One of the cyclooctadiene ligands has been partially reduced, and adopts the $1\text{-}\sigma\text{-4,5-}\eta^2\text{-}$ bonding mode. The Ir-Ir distance in the complex is $2.780(1)$ Å [57].

The versatile ligand 4,4',5,5'-tetracyanobiimidazole (H_2L , **1**) reacts with $[\text{Ir}(\text{cod})(\text{acac})]$ in acetonitrile to give $[(\text{cod})\text{Ir}(\mu\text{-L})\text{Ir}(\text{cod})]$ or $[(\text{cod})\text{Ir}(\mu\text{-L})\text{Ir}(\text{MeCN})(\text{cod})]$ (**45**). The



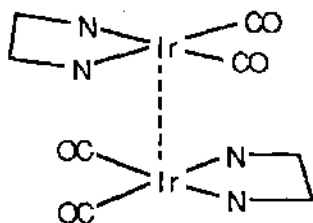
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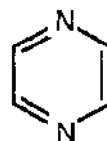
(45)

first of these complexes incorporates a bridging tetradentate ligand, whereas the latter contains a bridging terdentate ligand, with the remaining coordination site on one of the iridium atoms occupied by an acetonitrile ligand. This has been confirmed by a structural analysis of the complex $[(\text{cod})\text{Ir}(\mu\text{-L})\text{Ir}(\text{MeCN})(\text{cod})]$. The reaction of $[(\text{cod})\text{Ir}(\mu\text{-L})\text{Ir}(\text{cod})]$ with carbon monoxide results in the formation of $[\text{Ir}_4(\text{CO})_8\text{L}_2]$, from which $[\text{Ir}_4(\text{CO})_4(\text{PPh}_3)_4\text{L}_2]$ may be prepared by reaction with PPh_3 . Reaction of $[(\text{cod})\text{Ir}(\mu\text{-L})\text{Ir}(\text{MeCN})(\text{cod})]$ with bromine gives $[(\text{cod})\text{IrBr}_2(\mu\text{-L})\text{IrBr}_2(\text{cod})]$ [58]. A similar addition of bromine to $[\text{Ir}(\text{CO})_2\text{L}]^-$ has been reported to yield $[\text{Ir}(\text{CO})_2\text{Br}_2\text{L}]^-$. The starting

$[\text{Ir}(\text{CO})_2\text{L}]^-$ anion is prepared by the reaction of $[(\text{cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cod})]$ with L^{2-} , followed by carbonylation of the intermediate $[\text{Ir}(\text{cod})\text{L}]^-$. The crystal structure of the complex $[\text{Me}_4\text{N}][\text{Ir}(\text{cod})\text{L}]$ has been reported. The anions form dimers with Ir...Ir contacts of $3.183(1)\text{\AA}$, which form a slipped stack, with non-bonded inter-dimer Ir-Ir distances of $4.738(2)\text{\AA}$ (**46**). Addition of PPh_3 to $[\text{Ir}(\text{cod})\text{L}]^-$ gives the trigonal bipyramidal complex $[\text{Ir}(\text{cod})(\text{PPh}_3)\text{L}]^-$ [18].



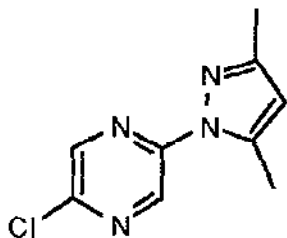
(46)



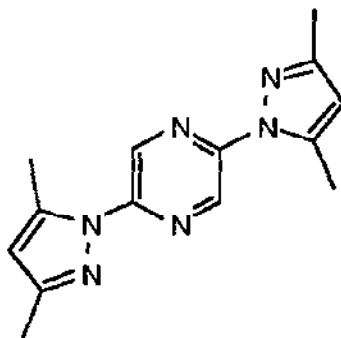
(47)

Pyrazine (**47**) reacts with $[(\text{cod})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cod})]$ to give $[\text{Ir}(\text{cod})\text{ClL}]$ ($\text{L} = \text{47}$), whereas the pyrazolylpyrimidines **48** and **49** react with $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ to give $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{L}]^+$ ($\text{L} = \text{48}$ or **49**) [59]. Iridium(I) complexes in the presence of bipy or 4,4'- Me_2 bipy have been investigated as catalysts for the transfer of hydrogen from alcohols to enones [66].

The condensation of 2-diphenylphosphinobenzaldehyde with 2,2'-dimethyl-6,6'-diaminobiphenyl results in the formation of the chiral P_2N_2 ligand (**50**); the use of the resolved *d* or *l* forms of the 2,2'-dimethyl-6,6'-diaminobiphenyl allows the preparation of the enantiomers. Reaction of **50** with $[\text{Ir}(\text{PPh}_3)_2(\text{N}_2)]$ gives the structurally characterised square-planar complex $[\text{IrL}]^+$, which

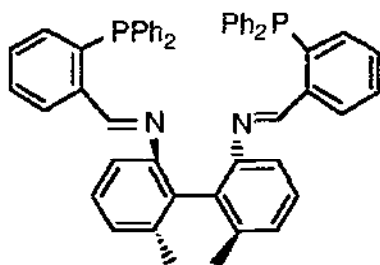


(48)

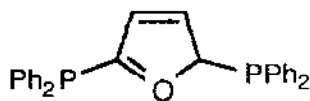


(49)

reacts with CO to give $[\text{IrL}^+(\text{CO})]$. The addition of H_2 to $[\text{IrL}]^+$ proceeds in a *cis* manner to give *cis*- $[\text{IrLH}_2]^+$. The complexes are not significantly active as hydrogenation catalysts [60].



(50)



(51)

The reactions of $[\text{Ir}(\text{dppe})_2(\text{CO})]^+$ have been investigated by Ibers; reaction with halogens results in the formation of the iridium(III) complexes $[\text{Ir}(\text{dppe})_2(\text{CO})\text{X}]^{2+}$, whilst HBF_4 gives $[\text{Ir}(\text{dppe})_2(\text{CO})\text{H}]^{2+}$. Treatment of $[\text{Ir}(\text{dppe})_2]^+$ with NOCl or $[\text{Fe}(\text{cp})_2]^+$ in the presence of CO gives *trans*- $[\text{Ir}(\text{dppe})_2(\text{CO})\text{Cl}]^{2+}$ [61]. The sulphur dioxide adduct $[\text{Ir}(\text{dppe})_2(\text{SO}_2)]^+$ has been reported [27]. The cofacial dimeric complexes $\{(\text{CO})\text{XIr}(\mu\text{-dppp})_2\text{Ir}(\text{CO})\text{X}\}$ ($\text{X} = \text{Br}$ or I) are formed from the reaction of dppp with $[(\text{CO})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CO})_2]$, and react with H_2 to yield $[\text{H}_2(\text{CO})\text{XIr}(\mu\text{-dppp})_2\text{IrH}_2(\text{CO})\text{X}]$. In contrast, the reaction of $[\text{Ir}(\text{CO})\text{I}_2]^-$ with dppp or dppe results in the mononuclear complexes $[\text{Ir}(\text{CO})_2\text{I}(\text{dppp})]$ or

$[\text{Ir}(\text{CO})_2\text{I}(\text{dppe})]$ in which the diphosphine adopts a chelating mode. The reaction of $[\text{Ir}(\text{CO})_2\text{I}(\text{dppp})]$ with H_2 gives $[\text{Ir}(\text{CO})\text{I}(\text{dppp})\text{H}_2]$ [62]. A related complex $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ ($\text{L} = 2,5\text{-bis}(\text{diphenylphosphino})\text{furan}$, **51**) has been investigated as a hydrogenation catalyst, but is generally inferior to mononuclear catalysts [63]. The complex $[\text{IrClL}]$ ($\text{L} = (\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$) has been prepared and evaluated as a hydrogenation catalyst in the conversion of cyclohexene to cyclohexane. Treatment of $[\text{IrClL}]$ with H_2 results in the formation of $[\text{IrClLH}_2]$ [67].

A crystal structural analysis of the complex $[(\text{PF}_3)_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{PF}_3)_2]$ has been reported. The basic molecular structure consists of folded dimers, in which the Ir_2Cl_2 rings are non-planar, and the PF_3 ligands are folded back to minimise intermolecular chlorine-fluorine interactions. The Ir-Ir contact within the dimeric unit is 2.941(1) Å, but interdimer contacts of 3.271(1) Å are also present. The interdimer contacts result in the formation of infinite zig-zag chains. The interdimer contacts are longer than the Ir...Ir contacts in $[\text{Ir}(\text{CO})_3\text{Cl}]$ (2.844(1) Å), in $[\text{Ir}(\text{CO})_2(\text{acac})]$ (3.20 Å) [64]. In contrast to the above observations, PF_2NMe_2 reacts with the complex $[(\text{cyclooctene})\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{cyclooctene})]$ to give the square planar complex $[\text{Ir}(\text{PF}_2\text{NMe}_2)_3\text{Cl}]$ which exhibits no extended Ir...Ir interactions.

A detailed analysis of the ^{31}P n.m.r. properties of the complexes $[(\text{R}^t\text{Bu}_2\text{P})_2\text{Ir}(\text{CO})\text{Cl}]$ ($\text{R} = \text{H}, \text{Me}, \text{Et}, \text{tBu}$ or Ph) has been reported [65].

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