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Coordination Chemistry Reviews 152 (1996) 393–409

COORDINATION CHEMISTRY REVIEWS

10. Iridium 1994

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CONTENTS

INTRODUCTION

The chemistry of iridium has continued to attract interest in 1994, an SCI search revealing over 400 references, although much of this work is 'organometallic' in nature. Since organometallic compounds are reviewed elsewhere in this journal , the treatment herein is restricted to those compounds which I feel will be of particular interest to the coordination chemistry community. Such judgements are by their nature subjective, especially in a discipline with such ill-defined boundaries, and I apologise to all those researchers whose research does not feature here. While ignoring most compounds containing metal-carbon bonds I have deliberately included the cyclometallated compounds of ligands containing pyridine units linked to potentially metallating aryl rings. The photophysics and synthesis of such species is inextricably linked to the continuing quest for light-harvesting analogues of ruthenium polypyridyl species and as such is one of the most active areas of modern coordination chemistry. A notable feature of this year's literature has

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been the interest in the iridium complexes of biologically significant ligands, stimulated by potential biological and medicinal applications; while these complexes are reviewed in the appropriate places in the text, readers are also guided to a review of the application of coordination compounds in chemotherapy which includes a review of some iridium-based potential anti-cancer compounds [1].

The introduction of a new reviewer will always bring new slants to an annual report but I trust that this account will continue to provide readers with an broad overview of the year's iridium coordination chemistry. The review follows the format established by previous reviewers, although I have dispensed with the section on dimetallic species, such compounds are now reviewed together with monometallic species, and the section on clusters.

Searches of both the ISI and the Cambridge Crystallographic Data Base (CCDB) have been used in the construction of this article. Crystal structures shown were redrawn using structural coordinate files from the CCDB.

10.1 IRIDIUM(VI) and (IV)

Two reports of the stabilisation of high oxidation states of iridium in perovskite lattices have appeared. Iridium(VI) was isolated in the compounds Ba_2MIrO_6 (M = Ca, Sr) which contain iridium(VI) in an octahedral O_6 site. The expected $t_{2g}{}^3$ configuration of this ion was confirmed [2]. In compounds of formula La_2MIrO_6 (M = Mg, Co, Ni, Cu, Zn) iridium(IV) is stabilised and these compounds show p-type semiconductor behaviour [3].

The iridium(IV) species $[IrCl_6]^{2-}$ has been prepared by *in situ* photoprecipitation [4]. The anion acts as a one-electron acceptor and is unable to acquire further electrons from reductants such as photosystem(I). This is attributed to a high stability of the resulting $[IrCl_6]^{3-}$ anion. An accurate potentiometric titration method for determination of iridium(IV) has also been reported [5]. Titration with hydrazine sulphate gives precision of under 0.5% and the technique may be conducted on the milligramme scale in the presence of a range of other metal ions. A report of the coordination of iridium(IV) to azo dyes has also appeared [6].

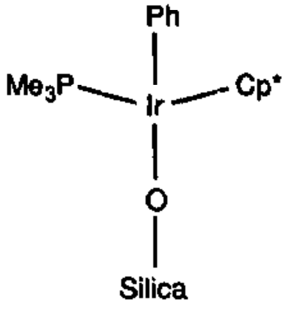
10.2 IRIDIUM(III)

10.2.1 Complexes with halide and pseudo-halide ligands

Halo complexes of iridium(III) are of most interest as stable starting materials for the preparation of complexes in which the halide ligands are replaced. An efficient high-yielding (>90%) route to $[Cp^*IrCl_2]$ starting from $[Ir^ICl(cod)]_2$ has been developed by Jaouen and co-workers [7].

10.2.2 Complexes with oxygen donor ligands

Iridium complexes have been mounted on silica supports (1). In this complex the silica behaves just as a simple monodentate oxygen ligand, the complex giving similar chemistry to analogues containing triflate or hydroxide [8].

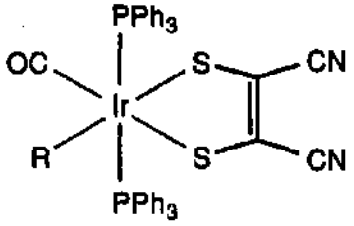


(1)

Thermodynamic measurements have been obtained for iridium tris(acetylacetonate) complexes [9].

10.2.3 Complexes with sulfur donor ligands

The chemistry of maleonitrilethiolate (mnt) with iridium(III) has been investigated and alkyl complexes (2) prepared [10]. These complexes are luminescent in fluid solution with emission wavelengths in the region λ_{em} = 695-780 nm and lifetimes of around 35ns.



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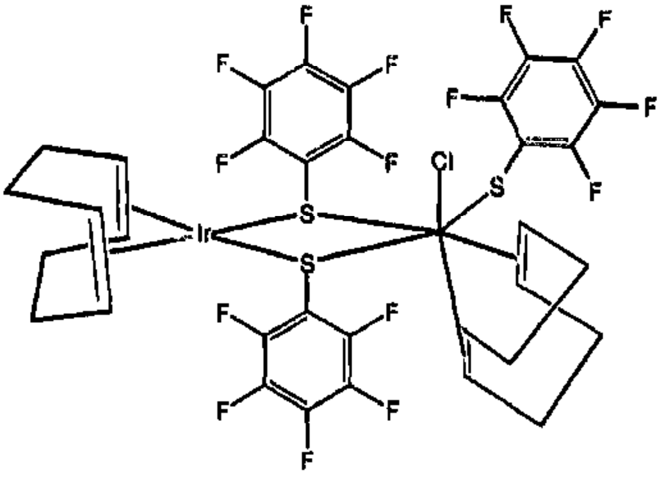
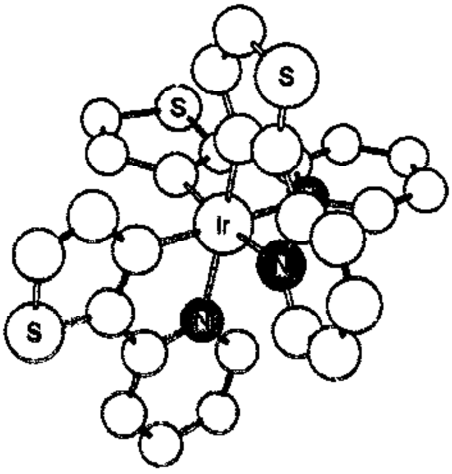


(3)

Heterotrinuclear Ir_2Pt complexes containing bridging perfluorobenzenethiolato ligands have also been prepared, the structures of which have been elucidated by crystallographic studies [11]. ^{19}F NMR spectroscopic studies indicate that several conformers of the species exist in solution. A dinuclear $Ir^{I}Ir^{III}$ complex in which the ligand acts both as a bridging ligand and in a more conventional coordination fashion (3) has been prepared and structurally characterised [12].

10.2.4 Complexes with nitrogen donor ligands

Tris-ligand complexes of the cyclometallating ligands ppyH and thpyH (thpyH = 2-(2-thienyl)pyridine) were prepared by treating the complex $[IrL_2Cl]_2$ with silver(I) triflate in the presence of a thirty fold excess of HL at 110°C (L = ppy, thpy). Heating the mixture under reflux for 24 hours gave the desired complexes, which were purified on Sephadex LH20, in about 50% yield [13]. Mixed ligand complexes were not prepared. The ligands are arranged about the metal ion with the nitrogen donors in a *fac* arrangement as confirmed by solution ^1H NMR spectroscopic studies and a crystal structure of the compound $[Ir(thpy)_3]$ (4). The excited state properties were investigated at 9 K in polymethacrylate. The short luminescent lifetimes observed reflect mixing of CT character into the $^3\pi-\pi*$ lowest excited states. The lowest excited state for the complex $[Ir(thpy)_3]$ is a ligand centred $^3\pi-\pi*$ state, while for the complex $[Ir(ppy)_3]$ it is a ^3MLCT state.

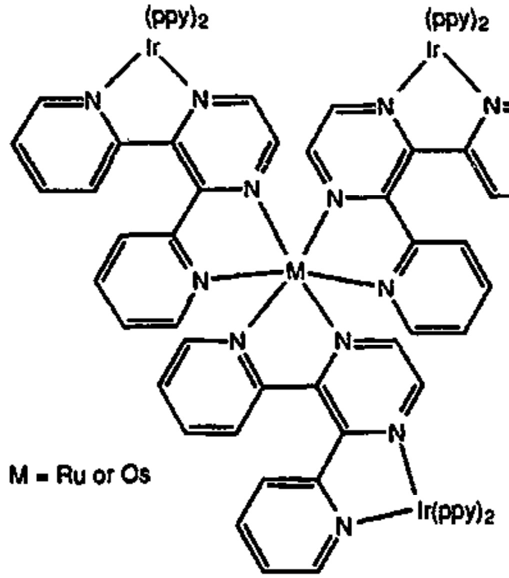


(4)

In a similar fashion, the compounds $[IrL_2S_2]^+$ (S = H_2O, CH_3CN; HL = ppyH, 2-(4-methylphenyl)pyridine) have been prepared by the reaction of $[IrL_2Cl]_2$ with silver(I) triflate in the presence of the required coordinating solvent [14]. The structure of these compounds in solution has been deduced from the ^1H and ^{13}C NMR spectra and NOE experiments. The emission and absorption properties of the complexes have been measured and indicate that the excited states are a combination of ligand localised and MLCT character.

The complex $[Ir(ppy)_3]$ may also be used as an oxygen sensor [15]. $[Ir(ppy)_3]$ embedded in amberlite may be used to detect the presence of O_2 by monitoring the changes in the luminescence of the material. The method may be used for pressures down to 0.4 mbar and at 200 mbar has an accuracy of ±1.5%.

Balzani and co-workers have incorporated the photo-active $[Ir(ppy)_2(bpy)]^+$ unit into their beautiful supramolecular light-harvesting dendrimeric systems [16]. They have prepared tetranuclear systems in which three of these fragments are arranged about a ruthenium(II) or osmium(II) centre and linked together using the bridging ligand 2,3-bis(2-pyridyl)pyrazine. The complexes are shown in structure (5). The compounds contains four chiral octahedral centres and the products are therefore obtained as a mixture of diastereoisomers. In the compound containing three iridium centres and one ruthenium, photoexcitation leads to emission from the iridium centres while in the osmium compound emission is observed from the central osmium. Energy has been channelled to the outside of the complex in the first case and into the centre of the dendrimer in the second. The absorption and electrochemical properties of the complexes are also reported.



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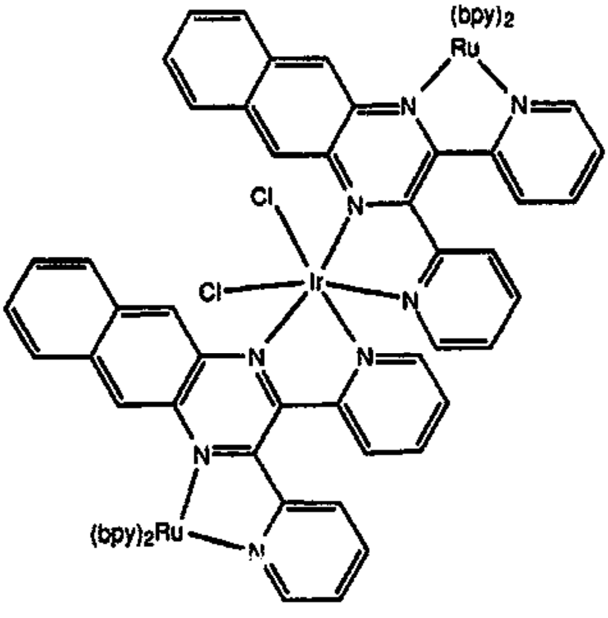
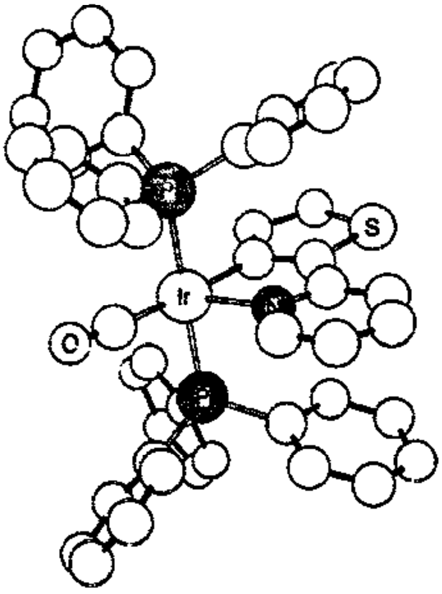


(6)

Related bridging ligands such as 2,3-bis(2-pyridyl)quinoxalinine and 2,3-bis(2-pyridyl)-benzoquinoxalinine have been used by Brewer and co-workers to assemble heterotrimetallic systems about a central iridium centre [17, 18]. Complexes including (6) are prepared in high yield (95%) using a building-block strategy similar to that adopted by Balzani. The terminal ruthenium polypyridyl units act as light harvesting units and the central iridium centre as a reaction centre at which the harvested energy may be used to drive a chemical reaction. On irradiation, one electron is transferred from each ruthenium(II) centre into the bridging ligands. The central iridium fragment is capable of delivering these two electrons, stored on the bridging ligands, to a substrate. For example the centre may be used to reduce carbon dioxide to formate. The properties of these supramolecular devices may be tuned by varying the bridging ligands [18].



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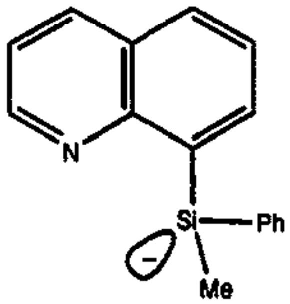


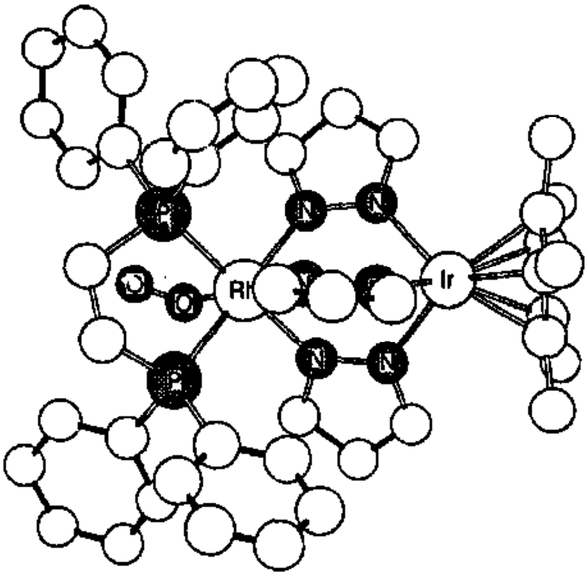
(8)

A complex containing only one cyclometallated thpy$^-$ ligand has also been prepared and the crystal structure of this complex, [Ir(thpy)(H)(CO)(PPh_3)$_2$] (7), determined. The ligand metallates at the 3 position of the thiophene as anticipated [19]. In a related square-planar iridium(I) species (27) the ligand does not metallate and binds as a monodentate *N*-donor ligand.

The photochemistry of complexes containing the chiral ligand (8-quinolyl)phenylmethyl silane (8) has also been investigated [20]. The ligand acts as an *N,Si*-didentate ligand forming tris-iridium(III) complexes of *fac*-geometry. The lifetimes of the various diastereoisomers of the complex have been determined and differ by a factor of two. The quenching of the excited state by the formation of exciplexes has also been studied. σ-Donor solvents form exciplexes by binding at the metal, while in π-donor solvents, the solvent binds at the quinolyl radical anion site.

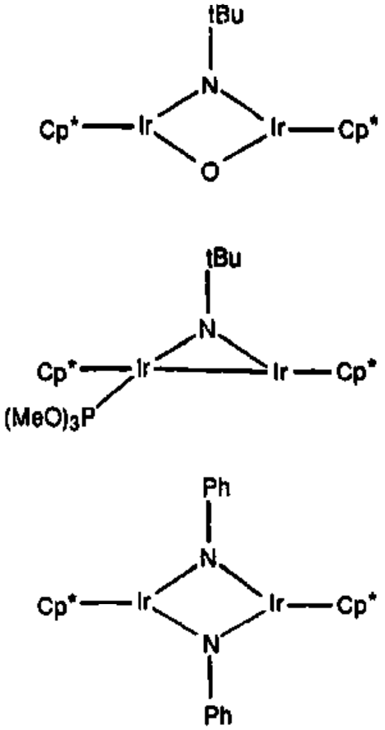
The interaction of pyrazole ligands with iridium(III) has been investigated and both mono and dinuclear compounds prepared [21]. The ligand may either act as a terminal ligand as in the complex cations $[IrH_2(pzH)(L)(PPh_3)_2]^+$ (pzH = pyrazole; L = Me_2CO, CO, MeCN, pzH, $P(OMe)_3$) or may be deprotonated to reveal a coordination site to which other metals might be bound. In this manner homo and hetero-bimetallic $Ir^{III}Ir^{III}$, $Ir^{III}Ir^{I}$ and $Ir^{III}Rh^{I}$ systems containing pz$^-$ bridging ligand(s) have been systematically synthesised. Such heterodinuclear systems are proposed as potential catalysts.

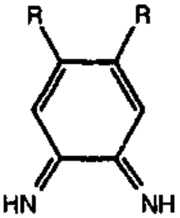
A mixed metal dinuclear Ir^{III} Rh^{III} species supported by three bridging pyrazolato ligands $[Cp^*Ir(\mu\text{-}pz)_3Rh(OOH)(dppe)]^+$ has been prepared and structurally characterised (**9**). The rhodium bears a hydroperoxy ligand and the species has been prepared to investigate its potential as a catalyst for olefin oxygenation [22].



(9)

Interactions of a range of 1,4-diimine ligands (**10**) with $\{Cp^*Ir^{III}\}$ fragments have been studied; the complexes have ben characterised by X-ray techniques and their electrochemical and absorption properties reported [23].





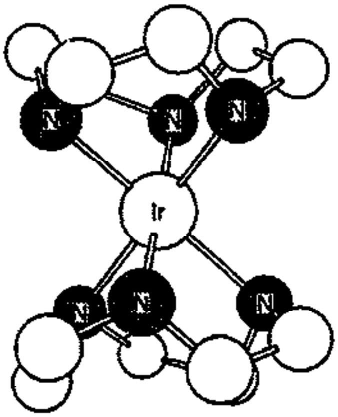
R = H, Me, Cl

(10)

(11)

A variety of complexes containing bridging imido ligands have been prepared and are shown in (**11**). Iridium imido compounds appear to be more stable when the imido group acts as a bridging ligand and these dimeric compounds may be prepared by the water catalysed dimerisation of appropriate monomers or by thermal dimerisation. The effect on the rate of dimerisation of placing substituents on the phenyl groups of the ligand have been studied [24].

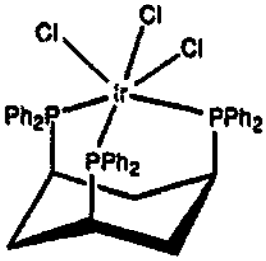
Reports of iridium(III) with amine ligands include the crystal structures of a bis(ligand) iridium(III) complex of the macrocycle 1,4,7-triazacyclononane (**12**) and of the two optical isomers of the tris(*trans*-1,2-cyclohexanediamine)iridium(III) cation [25, 26].



(**12**)

10.2.5 Complexes with phosphorus donor ligands

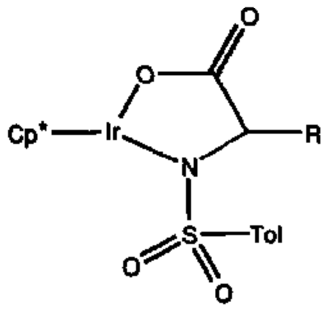
A new tripodal phosphine complex has been reported, together with a crystal structure of an iridium(III) complex (**13**). The ligand acts as a facially capping tridentate ligand and the remaining sites on the octahedral iridium ion are filled with chloride ligands [27].



(**13**)

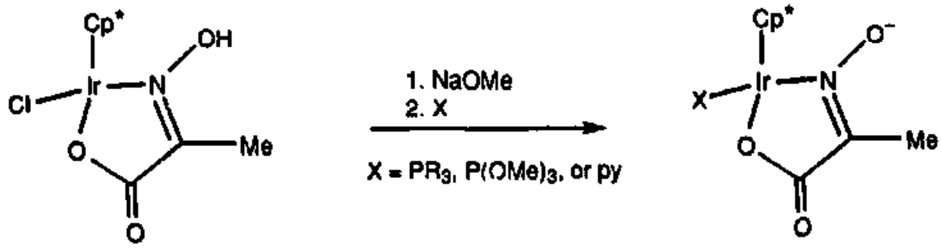
10.2.6 Complexes with ligands with mixed donor atoms

A variety of complexes of iridium(II) with amino acids have been prepared. The 16e⁻ complexes (**14**) (R = H or Ph) have been structurally characterised [28]. The presence of an electron withdrawing group covalently attached to the amine group stabilises the coordinatively unsaturated species and the complex is stable in air.



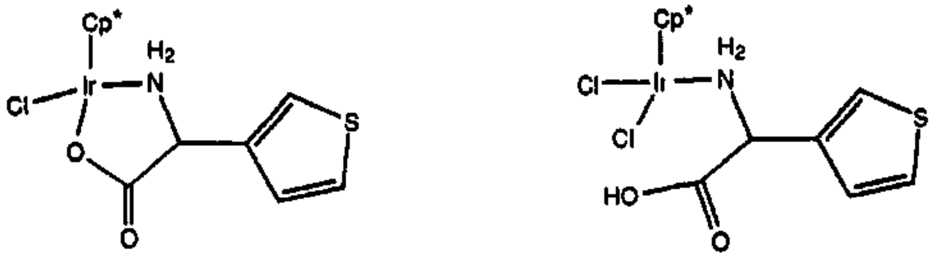
(14)

Iridium(III) complexes of the mixed phosphine/amine ligands $NH_2CH_2CH_2PMe_2$ (edmp) and $NH_2CH_2CH_2PPh_2$ (edpp) have been prepared. The structure of a tris complex $[Ir(edmp)_3]^{3+}$ confirmed a *fac* ligand arrangement and the structure of a bis complex $[Ir(edpp)_2Cl_2]^+$ revealed a *trans*-Cl,Cl and *cis*-P,P-arrangement. The absorption spectra of these species were recorded and compared with those of related species [26].



(15)

The complexes of a related ligand in which the toluene sulfonyl group is replaced by a hydroxy to give an oxyiminocarboxylate have also been investigated. Deprotonation at the hydroxy group (**15**) permits facile ligand exchange at the iridium centre. A structural determination for the complex with X = PMe_3 has been conducted [29, 30]. The same workers, Besk *et al.*, have also investigated the reaction of 2-(3-thienyl)glycine with iridium(III) and have characterised complexes (**16**) containing the ligand in both an *N,O*-didentate and *N*-monodentate bonding mode [31]. In the course of their studies these workers have also investigated complexation of the ligand (**17**). This ligand may acts as a tridentate *N,O,S*-bonding ligand and this bonding mode has been structurally characterised in the cation $[Cp^*Ir(\mathbf{17})]^+$ [32].



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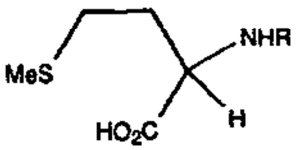

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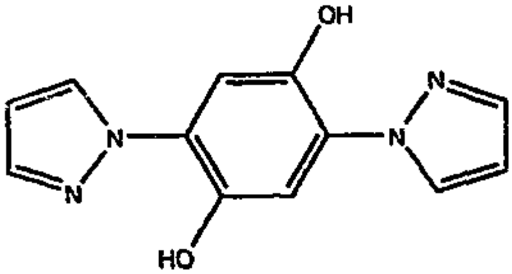


(18)

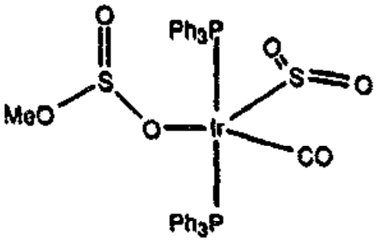
The behaviour of the ligand (**18**) (H_2L) towards iridium(I) and iridium(III) species has been reported. The ligand can potentially act either as a neutral (H_2L), monoanionic (HL^-) or dianionic (L^-) ligand. 'Complexes' of all three types have been reported and characterised crystallographically, although in the case of the neutral ligand (H_2L) there are no metal-ligand bonds and instead clathrates are formed. Similarly, in the complexes containing the monoanionic ligand (HL^-) only one metal ion binds to the ligand and the other binding site, bearing the proton, is left uncoordinated [33].

10.3 IRIDIUM(I)

10.3.1 Complexes with oxygen donor ligands

A systematic study of alkoxy and aryloxy iridium(I) complexes has been undertaken to determine whether π–donation can be established in these complexes. A series of 16 electron square-planar complexes of formula *trans*-$[Ir(CO)(OR)(PR'_3)_2]$ were synthesised and the crystal structures of three of them reported. In these complexes, which are important because of the wide range of reactions that they may undergo, no evidence for π–donation could be found [34].

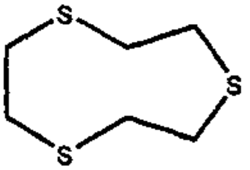
In the quest to develop new reagents for the removal of sulfur dioxide, the interaction of this gas with iridium(I) methoxy compounds *trans* $[Ir(CO)(OMe)(PR_3)_2]$ was examined. The sulfur dioxide inserts into the iridium-oxygen bond to give a coordinated sulfito ligand. Equilibrium constants for sulfur dioxide binding have been evaluated for these complexes and it is found that increasing the size of the coordinated phosphine ligand decreases the sulfur dioxide binding. The structure of a complex (**19**) in which one SO_2 has both inserted into the metal-methoxy bond while another acts as an *S*-coordinated monodentate ligand has been determined [35].



(19)

10.3.2 Complexes with sulfur donor ligands

The coordination chemistry of iridium(I) with sulfur ligands has been dominated by the work of two groups of macrocyclic chemists. In the first reports, Schröder and Halcrow studied the reaction of a variety of iridium(I) starting materials with the potentially tridentate macrocycle 1,4,7-trithiacyclononane (9S3) (**20**). The ligand binds in a facial capping manner presenting six electrons to the metal ion and might therefore be thought of as a neutral analogue of the cyclopentadienyl class of ligands. Three complexes containing the metal in a five-coordinate environment were reported and two of these are shown below (**21**). In each case the macrocycle acts as an S_3 chelating ligand and the two remaining coordination sites are filled by alkene ligands [36].



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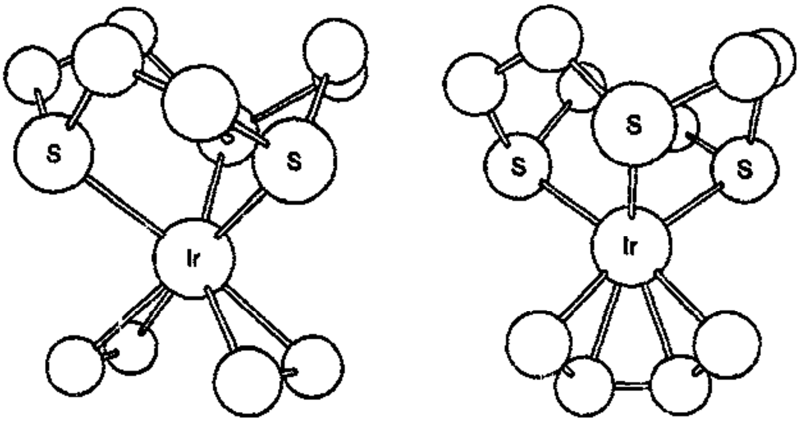

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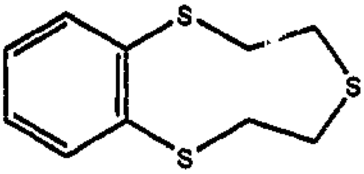
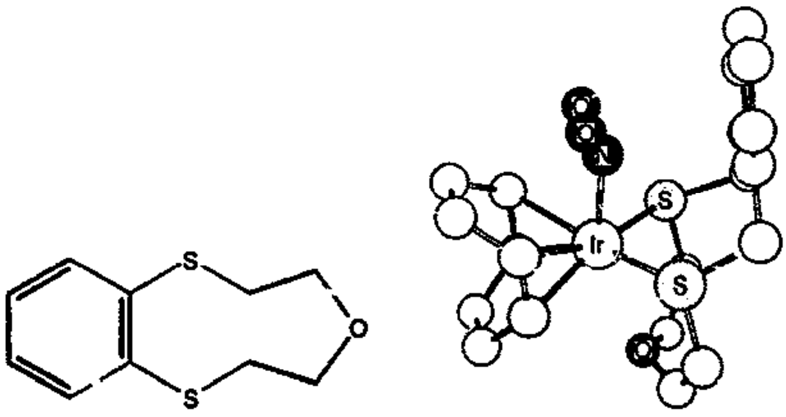


(22)

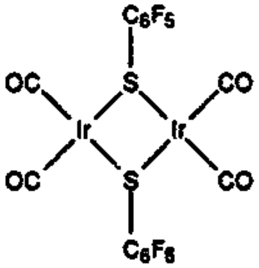
Jenkins and Loeb have investigated the chemistry of the related ligand (Ph9S3) (**22**). The chemistry appears to be structurally analogous to that of 9S3 (**20**) and they have isolated and crystallographically identified a similar five coordinate species [37]. The phenyl ring restricts the movement of this macrocycle and this is reflected in the chemistry of the complexes [Ir(L)(cod)]$^+$ (L = 9S3 or Ph9S3). In the Ph9S3 complex the olefin ligands may slowly be replaced by carbon monoxide to give [Ir(L)(CO)$_2$]$^+$. This reaction does not occur for the 9S3 complex. This ligand exchange reaction is thought to occur via a didentate macrocyclic intermediate and to gain further support for this mechanism, the complex of the related macrocycle Ph9S2O (**23**) was prepared.

This macrocycle acts only as a didentate S_2 ligand and indeed the iridium(I) complexes of this ligand react very rapidly with carbon monoxide [37].



(23)

Elsewhere in the field, a dinuclear iridium(I) complex (24) supported by bridging thiolato ligands has been reported [12] as has a complex in which an iridium(I) centre is linked to a dithiacarborane structure [38].

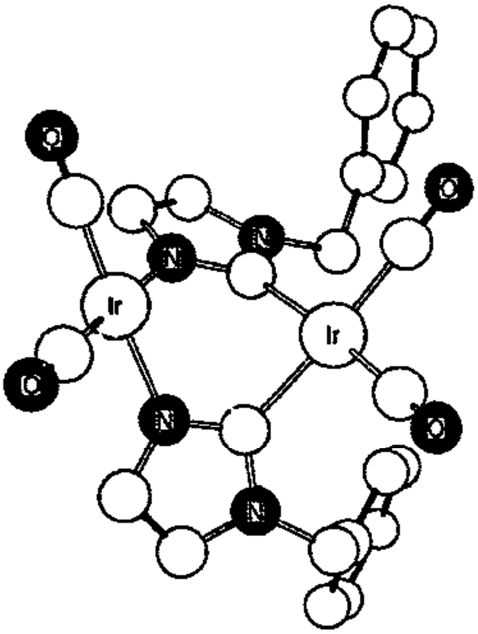


(24)

10.3.3 Complexes with nitrogen donor ligands

While the work on complexes with sulfur donors has centred around the theme of macrocycles, the chemistry with nitrogen donors has proved to be more varied.

The interaction of benzylimidazole with iridium(I) gives a dinuclear cyclometallated complex, $[Ir_2(L)_2(CO)_4]$, the crystal structure of which is shown in (25) [39]. Dinuclear complexes containing bridging pyrazole ligands (26) have been synthesised by Gray and co-workers. The R groups on the phosphine may be functional groups and the complexes synthesised have pyridinium moieties appended to the phosphines. The rates of electron transfer between the metal and the pyridinium are reported [40]. The same workers have also prepared related complexes in which the phosphine and carbonyl ligands are replaced by a diolefin. The rate of intermolecular electron transfer to pyridium species is reported [41]. Mixed ruthenium(II)-iridium(I) compounds containing bridging 3-aryl pyrazolato ligands have also been prepared. In solution, an equilibrium is reached between two isomers; a metal-metal bond formation accompanied by halide migration is proposed to explain this [42].



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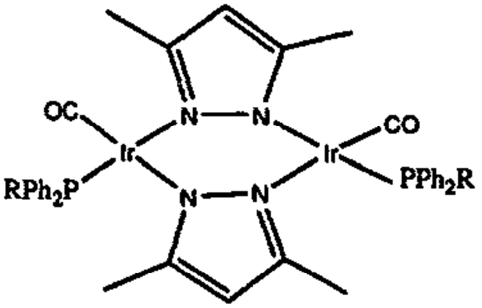
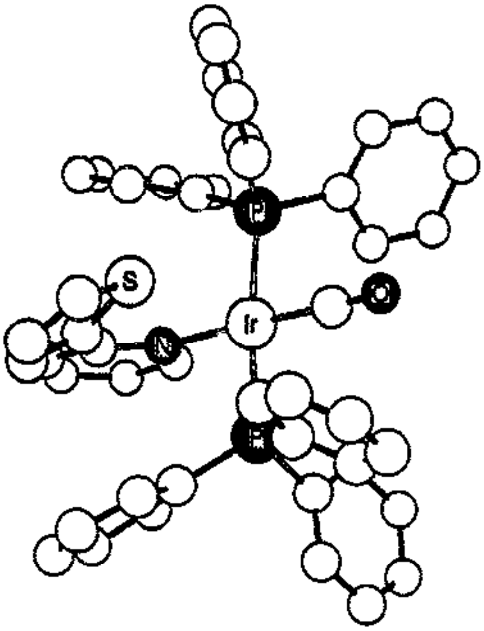


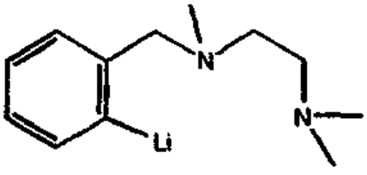
(26)

As noted earlier the reaction of the ligand thpyH with iridium(I) gives a complex in which the ligand does not cyclometallate but acts as a monodentate *N*-donor [19]. The thiophene ring is slightly twisted with respect to the pyridyl ring and an Ir-S distance of 3.045(4) Å is observed, possibly indicating some interaction. The structure of this complex is shown in (27).



(27)

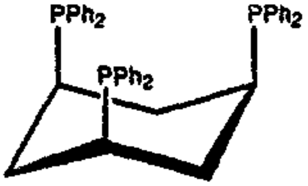
Transmetallation between an iridium(I) compound and the lithio complex of a potentially terdentate *N*$_2$*C* donor ligand (28), L, yield a square planar *N,C*-coordinated species [IrL(cod)] in solution. In the solid-state the compound has the same molecular formula but contains the ligand bound in a terdentate manner, the geometry at the metal being approximately square-pyramidal. Substitution of the olefin ligand with carbon monoxide or phosphines gives species which are fluxional in solution, switching between the didentate and terdentate modes being observed [43]. The first examples of iridium(I) bridging azavinylidenes have also been described [44].



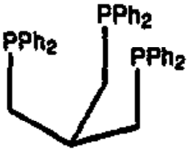
(28)

10.3.4 Complexes with phosphorus donor ligands

The reaction of the tripodal phosphine ligand (29) with the complex [Ir(PPh$_3$)(CO)Cl] gives a trigonal bipyramidal complex [Ir(29)(CO)Cl] which is highly fluxional and has been studied by ^{31}P NMR spectroscopy. Reaction with borohydride replaces the chloride with a hydride ligand, whilst the reaction with chlorine leads to oxidation to an iridium(III) species [27].



(29)



(30)

The related tridentate facially capping ligand triphos, (30), reacts with iridium olefin complexes to give five-coordinate species containing a tridentate capping ligand and two olefin molecules. These complexes have been shown to be active catalysts for acetylene cyclotrimerisation [45].

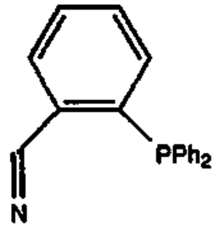
A series of derivatives of the ligand (cyclopentadienylethyl)diphenylphosphine have been prepared. These ligands may behave either as chelating *Cp,P*-ligands or as bridging ligands and complexes containing both bonding modes have been synthesised and characterised [46].

A new high yielding synthetic approach to derivatives of Vaska's complex [Ir(PPh$_3$)$_2$(CO)Cl] has been developed [47]. *Ab initio* calculations performed on the iodo analogue have been shown to compare well with the experimental structural and spectroscopic data [48].

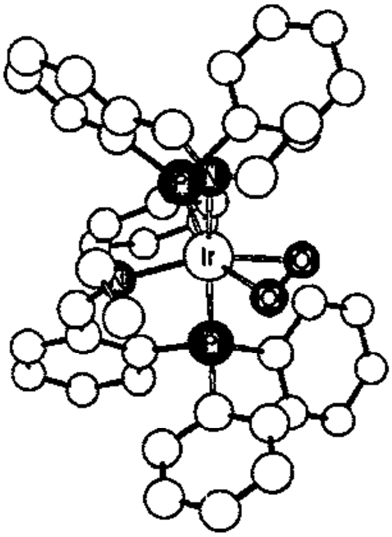
Phosphine exchange between square planar complexes (Ir^{I} and Ir^{I} or Ir^{I} and Pt^{II}) has been investigated. The rate of exchange reflects the size of the phosphine substituents (larger substituent — faster exchange) and the mechanism is thought to proceed via phosphine dissociation at one complex followed by association at the other [48].

10.3.5 Complexes with ligands with mixed donor atoms

Three mixed phosphorus-nitrogen donor ligands have been prepared and their coordination chemistry with iridium(I) investigated. The ligand (**31**) gives a bis complex with iridium(I) in which a *cis* square planar structure is observed [50]. The complex binds dioxygen irreversibly and a crystal structure of the adduct (**32**) has been obtained. In contrast reversible-binding occurs with carbon monoxide to give a square-based pyramidal complex.

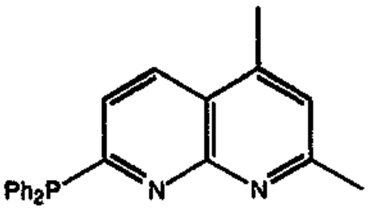


(**31**)

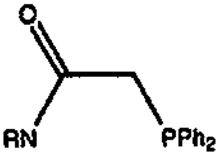


(**32**)

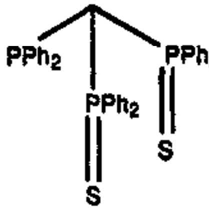
The ligand (**33**) does not act as a chelating ligand but rather as a bridging ligand and a bis iridium(I) complex [{Ir(cod)Cl}$_2$L] has been isolated in which the ligand coordinates to one metal ion via the phosphorus atom and to the other via the pyridine nitrogen at the other end of the molecule. No iridium-iridium interactions are observed [51].



(**33**)



(**34**)



(**35**)

The phospinamido ligand (**34**) reacts with [Ir(PPh$_3$)$_3$Cl] to form a species [Ir(PPh$_3$)$_2$Cl(L)] which has been characterised by a range of spectroscopic techniques [52]. The ligand (**35**) has been shown to behave as a terdentate *S$_2$,P*-ligand and the five-coordinate complex cation [Ir(cod)L]$^+$ has been structurally characterised [53].

The diiridium complex [Ir$_2$(CO)$_4$L] of the doubly deprotonated ligand (**36**) has been shown to behave as a calamitic mesomorphic material. The compound exhibits smetic A behaviour and has a larger mesophage range than the analogous rhodium compound [54].

(36)

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