10. Iridium 1992

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of iridium reported during the year 1992 and is similar in format to the corresponding review dealing with the 1991 literature [1]. The literature has been searched by using both *Current Contents* and the Cambridge Crystallographic Data Base. Structural figures have been redrawn using coordinates taken from the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2].

Organometallic complexes and iridium carbonyl clusters have not been included, unless a ligand of particular interest to the coordination chemist is present in the complex.

The review is not fully comprehensive but instead provides the reader with a broad overview of the coordination chemistry of iridium reported during 1992. I apologise to those readers whose work has been omitted.

10.1 IRIDIUM(IV)

Black single crystals of $Cs_4[IrO_4]$ are produced when $CsO_{0.52}$ and IrO_2 (with a Cs : Ir ratio of 4.30 : 1.00) are heated at 740°C for 8 days. X-ray crystallographic studies of the iridate show that it crystallises with a $K_4[IrO_4]$-type structure [3].

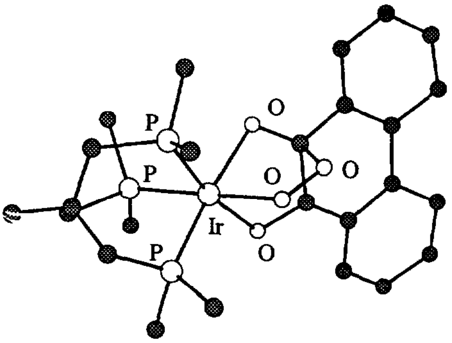
10.2 IRIDIUM(III)

10.2.1 Complexes with oxygen donor ligands

The structures of iridium(III), as well as rhodium(III) and cobalt(III), hexanitrato-complexes, $Na_3[M(NO_3)_6]$ (M = Ir, Rh or Co), have been determined. The iridium(III) centre is in a octahedral environment [4].

Octahedral complexes which include *cis*-$[Ir(NH_3)_4(OH)(H_2O)]^{2+}$, *trans*-$[Ir(NH_3)_4(OH)(H_2O)]^{2+}$ and $[(NH_3)_4Ir(\mu\text{-}OH)_2Ir(NH_3)_4]^{4+}$ have been prepared and characterised. The discussion presented by Galsböl *et al.* includes the results of a spectrophotometric study of the thermodynamics and kinetics of an equilibrium between hydroxy- and dihydroxy-bridged species [5].

The preparation, spectroscopic and electrochemical characterisations of the iridium(III) complexes $[Ir(cat)\{Ph_2PCH_2)_3CMe\}][BPh_4]$ and $[Ir(cat)\{Ph_2PCH_2)_3CMe\}][PF_6]$ where cat^{2-} is one of a range of catecholates have been reported. Cobalt(III) and rhodium(III) analogues have also been studied. All the complexes exhibit electron transfer processes which involve Ir(III), Ir(II) and Ir(I) states and also show catecholate (cat), semiquinone (SQ) and quinine oxidation levels of the ligands. X-Band ESR spectroscopy has been used to characterise the paramagnetic complexes $[Ir^{III}(SQ)\{Ph_2PCH_2)_3CMe\}]^{2+}$ and $[Ir^{II}(cat)\{Ph_2PCH_2)_3CMe\}]$. An interesting part of this work is a study of O_2 uptake by the complexes to give adducts. The crystal structure of $[Ir(O_2)(phenSQ)\{Ph_2PCH_2)_3CMe\}][BPh_4]$, $[(\mathbf{1})][BPh_4]$, has been elucidated (phenSQ = phenanthrene-5,6-semiquinone). The iridium centre is octahedrally sited and the O_2 molecule has inserted between the metal centre and one carbon atom of the *O,O'*-ligand. The influence of adduct formation on the π-bonding in the *O,O'*-ligand is addressed [6].



Only the *ipso*-C atoms of the phenyl groups are shown.

(**1**)

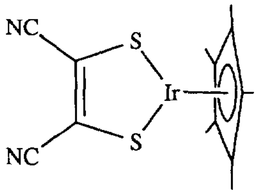
10.2.2 Complexes with sulfur, selenium and tellurium donor ligands

The results of a crystallographic investigation of the complex $[SCl_3][IrCl_4(SCl_2)_2]$ have been reported. The iridium(III) centre is octahedrally coordinated and the SCl_2 ligands are in a *cis*-arrangement. The $[SCl_3]^+$ cation is trigonal pyramidal [7].

The reaction of *mer*-$[IrCl_3(SEt_2)_3]$ with $[Mg(Mes)_2(thf)_2]$ in ether-thf leads to the formation of the paramagnetic iridium(II) complex *trans*-$[Ir(Mes)_2(SEt_2)_2]$. Treatment with PMe_3 (see section 10.3) followed by NO gives $[Ir(Mes)_2(NO)(PMe_3)_2]$, the crystal structure of which reveals the presence of a nitrosyl ligand coordinated in a bent fashion ($\angle$Ir-N-O = 133.7(10)° for one of two independent molecules) [8].

The reactions of $[(Cp^*MCl_2)_2]$ (M = Rh or Ir) with 1,2-dicyanoethene-1,2-dithiolate, 2,2'-dithiazole and 2,2'-diimidazole (see section 10.2.3) have been studied. The techniques of IR, UV-VIS and ^1H NMR spectroscopies and mass spectrometry were used to characterise the new complexes. The 1,2-dicyanoethene-1,2-dithiolate ligand coordinates in an *S,S'*-manner as shown in structure (**2**); this has been confirmed crystallographically for the rhodium(III) analogue of (**2**). With 2,2'-dithiazole, L, $[(Cp^*IrCl_2)_2]$ reacts to yield $[Cp^*IrCl(N,N'\text{-}L)]$ [9].

The crystal structure of $[IrCl_2(CO)(SOCl)(PPh_3)_2]$ (**3**) has been determined [10].



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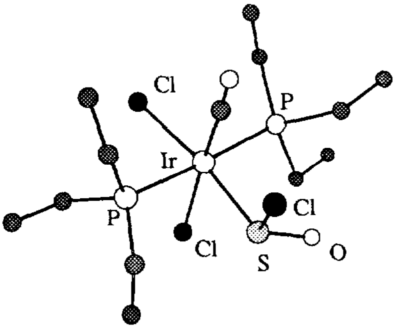


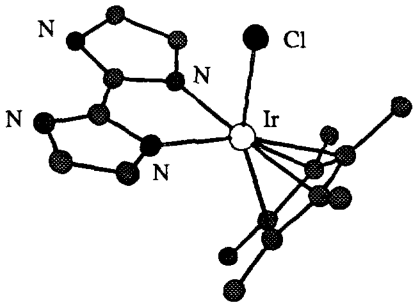
(3)

When $[Fe(\eta^5\text{-}C_5H_4SLi)_2]$ reacts with $[Cp^*IrLCl_2]$ (L = PMe_3, PPh_3 or ^tBuNC), the products are the complexes $[Cp^*IrL\{Fe(\eta^5\text{-}C_5H_4S)_2\}]$; complexes containing the selenium- and tellurium-containing ligand analogues have also been prepared. The new compounds have been characterised by ^1H, ^{13}C and ^{31}P (where appropriate) NMR spectroscopies. The results of a crystal structure determination of the related rhodium(III) complex $[Cp^*Rh(PMe_3)\{Fe(\eta^5\text{-}C_5H_4S)_2\}]$ confirm the didientate nature of the ferrocenyl-based ligand [11].

10.2.3 Complexes with nitrogen donor ligands

Complexes which included *cis*-$[Ir(NH_3)_4(OH)(H_2O)]^{2+}$, *trans*-$[Ir(NH_3)_4(OH)(H_2O)]^{2+}$ and $[(NH_3)_4Ir(\mu\text{-}OH)_2Ir(NH_3)_4]^{4+}$ were mentioned in section 10.2.1 [5], and the iridium(III) complex $[Ir(Mes)_2(NO)(PMe_3)_2]$, which contains a bent Ir-N-O unit, was described in the previous section [8].

Several iridium(III) complexes involving heterocyclic *N*-donor ligands have been reported. Both 2,2'-dithiazole and 2,2'-diimidazole (L) coordinate in a similar fashion when they react with $[(Cp^*IrCl_2)_2]$. The complex $[Cp^*IrCl(N,N'\text{-}L)]Cl$ has been structurally characterised and the cation is shown in figure (4) [9].



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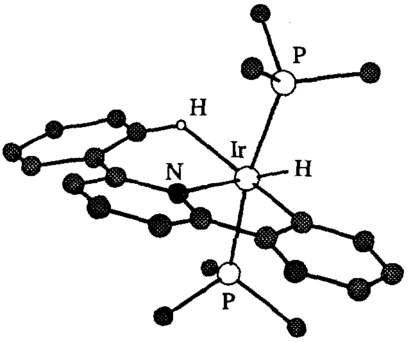
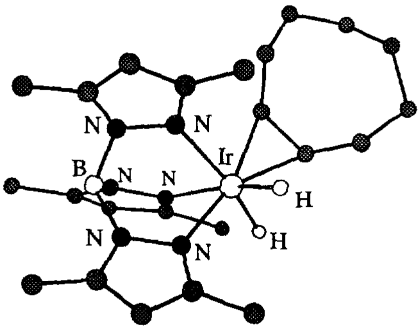


H atoms omitted except for agostic-H and hydrido ligand; only the *ipso*-C atoms of aryl subtituents are shown.

(5)

The reactions of [Ir(cod)(PR_3)]X (PR_3 = PPh_3, P(4-MeC_6H_4)$_3$, P(4-FC_6H_4)$_3$, PPh_2Me or P^nBu_3; X = SbF_6 or BF_4) with 2,6-diarylpyridines (H_2L) under hydrogen lead to the formation of complexes of the general type [Ir(HL)H(PR_3)$_2$]X. An X-ray crystal structure determination of [Ir(HL)H{P(C_6H_4Me-4)$_3$}$_2$][SbF_6] for H_2L = 2,6-diphenylpyridine has been carried out. In the cation, (5), one phenyl ring of the substituted pyridine ligand has undergone orthometallation. One *ortho*-H atom of the second phenyl ring is involved in an agostic Ir-H-C interaction. The results of variable temperature ^1H NMR and ^{31}P NMR spectroscopic studies of the complexes have been explained in terms of rapid oxidative addition of the agostic H atom to the metal centre and reductive elimination of the metal-attached terminal H atom [12].



(6)

The dihydrido complex (6) has been prepared from [Ir{HBpz'$_3$}(coe)] where pz' = 3,5-dimethyl-1-pyrazolyl, and is one of a series of related compounds. Complex (6) is relatively unreactive. It has been investigated both in solution (NMR spectroscopy) and in the solid state (X-ray crystallography). In the latter, the coe ligand lies in an unusual orientation, and the vector defined by the π-bond bisects the H-Ir-H angle. These results have further been investigated by using extended Hückel MO calculations [13].

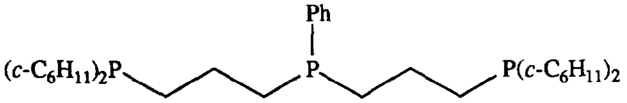
The preparation of the iridium(III) complex [IrL(CO)Cl], where H_2L = 5,10,15,20-tetrakis(3,5-$^tBu_2C_6H_3$)porphyrin, has been described. The product has been characterised by ^1H and UV-VIS spectroscopies, mass spectrometry and X-ray crystallography. The Ir(III) centre is octahedrally coordinated, and the porphyrin ring (Ir-N = 2.04 Å) is essentially planar [14].

10.2.4 Complexes with phosphorus donor ligands

Several phosphine-containing iridium(III) complexes have already been mentioned and the reader is referred back to appropriate references [6,8,10,11,12].

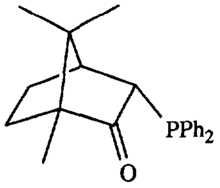
The catalytic activity of $[IrClH_2(P^iPr_3)_2]$ with respect to the hydrogenation of benzylideneacetone has been discussed [15]. Two routes to $[IrClH_2(P^iPr_3)_2(H_2)]$ have been described — the first involves the reaction of the corresponding 16-electron complex with H_2, and the second makes use of $IrCl_3.3H_2O$ as the precursor. A crystallographic study of $[IrClH_2(P^iPr_3)_2(H_2)].C_{10}H_8$ confirms that the phosphine ligands are mutually *trans*. Variable temperature ^1H NMR spectroscopy has been used to investigate the solution dynamics of the system [16].

The reaction between $HBF_4.OEt_2$ and $[IrH_2(MeCN)(PMe_2Ph)_3]^+$ in the presence of acetonitrile leads to the evolution of dihydrogen and the formation of the dication *cis,mer*-$[IrH(MeCN)_2(PMe_2Ph)_3]^{2+}$. A corresponding reaction using *cis,mer*-$[IrMe_2(MeCN)(PMe_2Ph)_3]^+$ proceeds much more slowly. In the absence of acetonitrile, $[IrH_2(MeCN)(PMe_2Ph)_3]^+$ is converted to equal amounts of *cis,mer*-$[IrH(MeCN)_2(PMe_2Ph)_3]^{2+}$ and $[IrH_4(PMe_2Ph)_3]^+$. In the presence of water, $[IrMe_2(MeCN)(PMe_2Ph)_3]^+$ is converted to *mer*-$[IrMe(H_2O)(MeCN)(PMe_2Ph)_3]^{2+}$. The structure of the tetrafluoroborate salt of this cation has been determined [17]. The ligand (8-quinolyl)dimethylsilane (HL) reacts with $[Ir(PPh_3)_3(CO)H]$ in toluene under reflux to generate *fac*-$[IrL_3]$ (see section 10.2.5) [18].



(7)

Ligand (7) has been incorporated into the complexes $[IrH_2Cl(7)]$, $[IrH_2(CO)(7)]^+$ and $[IrH_2(MeCN)(7)]^+$. The tris(phosphine) ligand adopts a *mer*-configuration, and the presence of the phenyl substituent leads to diastereomers which have been characterised by an NOE difference NMR spectroscopic technique. The reaction of $[\{Ir(cod)Cl\}_2]$ with (7) in EtOH provides a route to a single diastereomer — *cis,anti,mer*-$[IrH_2Cl(7)]$; the same (and only) diastereomer is formed when [Ir(cod)Cl(7)] is treated with H_2 in benzene. The ligand substitution reactions of *cis,anti,mer*-$[IrH_2Cl(7)]$ have been studied, and their stereochemical course has been followed by using the phenyl group as a stereochemical label [19].

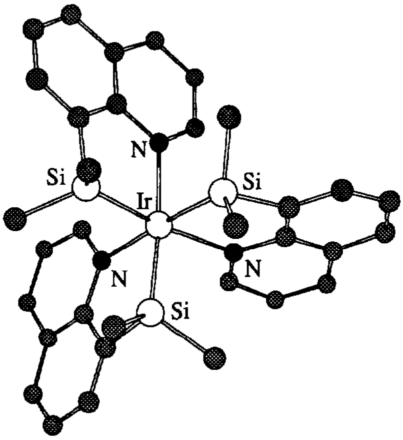


(8)

The complex *trans,mer*-[$IrCl_3(8)_2$] has been prepared by reacting ligand (8) with $IrCl_3.3H_2O$. One ligand is in monodentate, coordinating through the phosphorus donor atom, and the other is *P,O*-bonded. When *trans,mer*-[$IrCl_3(8)_2$] is treated with an excess of silver(I) tetrafluoroborate, *cis,trans*-[$IrCl_2(8)_2$][BF_4] results. These complexes have been spectroscopically characterised and structural data are available for the related rhodium(III) complex *cis,mer*-[$RhCl_3(8)_2$] [20].

10.2.5 Complexes with mixed donor ligands

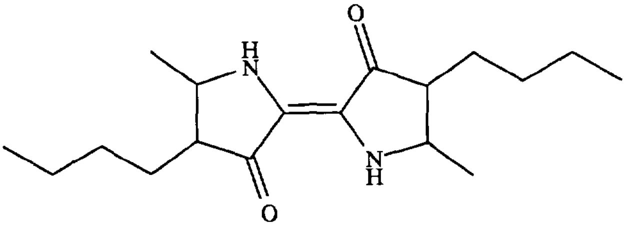
The ligand (8-quinolyl)dimethylsilane (HL) reacts with [$Ir(PPh_3)_3(CO)H$] in toluene under reflux to generate *fac*-[IrL_3] (9); analogous chemistry is observed for rhodium(III). The product (9) is stable to air and moisture, and may be heated to 150°C without decomposition. The complex has been characterised by ^1H and ^{29}Si NMR and UV-VIS spectroscopies, and by X-ray crystallography [18].



(9)

The products of the reaction between iridium(III) chloride or rhodium(III) chloride and *S*-methyl-L-cysteine (HL) illustrate that there is competition between the donor atoms of the ligand. The product-type is dependent upon the conditions of the reaction, and upon the metal involved. For iridium, the complex [Ir(HL-*S*,*N*)(L-*S*,*O*)Cl_2] has been isolated and characterised by IR spectroscopy and TGA [21].

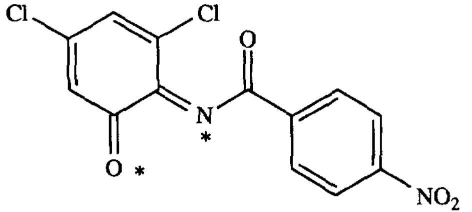
Ligand (**10**), H_2L, reacts with [{Cp*$IrCl_2$}$_2$] to give the dimetallic complex [{Cp*IrCl}$_2$(μ-L)]. The conjugate base of (**10**), L^{2-}, functions as an *N*,*O*-donor to each iridium(III) centre. This and related complexes have been characterised by UV-VIS and IR spectroscopies; a large bathochromic shift of absorptions in the visible region (as compared to the free ligand) is observed [22].



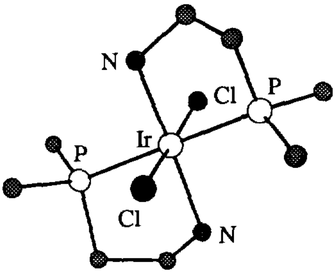
(**10**)

The oxidative addition of ligand (**11**) to [IrCl(CO)$(PPh_3)_2$] leads to isomers of the iridium(III) complex [Ir(L)Cl(CO)$(PPh_3)_2$] which are separable by chromatography. The results of spectroscopic studies (^1H, ^{13}C and ^{31}P NMR and IR) indicate that two out of twelve possible isomers of the complex have been formed. Their structures have been confirmed crystallographically. Ligand (**11**) coordinates in an *N*,*O*-mode and the isomers differ in the relative orientations of the two PPh_3 ligands (orange *cis*-isomer, and yellow *trans*-isomer) [23].

The crystal structure of the complex [$IrCl_2(Me_2PCH_2CH_2NH_2)_2$][$PF_6$] has been determined. The complex cation (**12**) possesses an octahedral iridium(III) centre with *trans*-chloride ligands. The two chelating ligands are arranged to give *trans*-*P* and *trans*-*N* donor atoms [24].



(**11**)

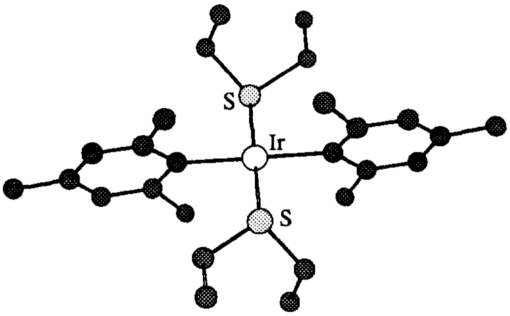


(**12**)

10.3 IRIDIUM(II)

Pandey has written a review (242 references) covering the coordination chemistry of mononuclear d^7 metals; the survey looks at preparations, structures, magnetic and spectroscopic (IR, UV-VIS, PES) properties of complexes which include those of iridium(II) [25].

The reaction of the iridium(III) complex *mer*-[$IrCl_3(SEt_2)_3$] with [$Mg(Mes)_2(thf)_2$] in ether-thf yields the paramagnetic iridium(II) complex *trans*-[$Ir(Mes)_2(SEt_2)_2$] **(13)**. This has been characterised by X-ray diffraction methods; the Ir-S distance is 2.298(4)Å. The thioether ligands may be replaced by PMe_3 to yield *trans*-[$Ir(Mes)_2(SEt_2)_2$]. With carbon monoxide, compound (13) reacts to give the square-planar iridium(I) complex [$Ir(Mes)(CO)_2(SEt_2)$] [8].

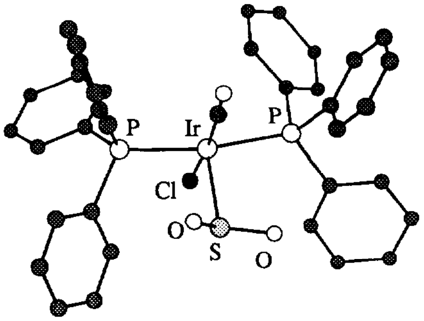


(13)

10.4 IRIDIUM(I)

Ab initio methods have been used to study the oxidative addition of dihydrogen to *trans*-[$IrX(CO)(PR_3)_2$] (X and R = various). Results indicate that when X^- is a weak electron donor (*e.g.* chloride), the H_2 molecule adds in the plane of the Cl-Ir-CO unit. In contrast, when $X^- = H^-$ or Ph^-, H_2 adds in the plane containing the P-Ir-P vector [26].

The crystal structure of the complex [$IrCl(CO)(SO_2)(PPh_3)_2$] **(14)** has been determined. The sulfur dioxide molecule is *S*-bonded to the iridium(I) centre; this ligand occupies an axial site in a square-based pyramidal array [27]. When [$\{Ir(cod)Cl\}_2$] reacts with $RCH\{P(=S)Ph_2\}_2$ (R = H or Me), the cationic complexes [$Ir(cod)(RCH\{P(=S)Ph_2\}_2)$]$^+$ are formed in which the $RCH\{P(=S)Ph_2\}_2$ ligand is *S,S'*-bonded. These species undergo facile loss of H^+ on treatment with NaH to give [$Ir(cod)(RC\{P(=S)Ph_2\}_2)$]. Analogous rhodium complexes have also been prepared and characterised. The crystal structure of [$Ir(cod)(HC\{P(=S)Ph_2\}_2)$] shows that the chelate ring is puckered [28].



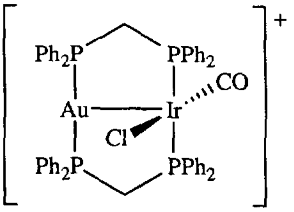
(14)

The chemical and electrochemical two-electron reduction of [Cp*IrCl(bpy)]Cl leads to the formation of the very reactive species [Cp*Ir(bpy)], the conjugate acid of which has been proposed as an intermediate in homogeneous photo-catalysis of the water-gas shift reaction. [Cp*Ir(bpy)] has been characterised by UV-VIS, and ^1H and ^{13}C NMR spectroscopies. A large negative reduction potential indicates a large degree of π-back donation from the metal to bpy ligand; this result is supported by NMR and IR spectroscopic data [29].

The reactions of $[Ir(CO)(PPh_3)_2(OSO_2CF_3)]$ with 1,4-dicyanobenzene or ,4-dicyanobut-2-ene yield the bridged complexes $[(Ph_3P)_2(CO)Ir(\mu\text{-}L)Ir(CO)(PPh_3)_2](OSO_2CF_3)_2$ where L is either of the cyano ligands. The products have been characterised by ^1H and ^{31}P NMR and IR spectroscopies. The oxidative addition reactions of H_2 or I_2 to the complex $[(Ph_3P)_2(CO)Ir(\mu\text{-}L)Ir(CO)(PPh_3)_2](OSO_2CF_3)_2$ for L = 1,4-dicyanobenzene have been investigated [30].

10.5 DI-, TRI- AND TETRANUCLEAR IRIDIUM COMPLEXES

Several 'A-frame' complexes containing iridium have been reported. Cation (**15**) forms weak adducts with BF_3. It reacts with $HgCl_2$ giving, first, an unstable intermediate at low temperature which converts, on warming, to complex (**16**). The structural features of (**16**) have been confirmed by crystallographic studies. The iridium centre is octahedrally sited, whilst the two mercury centres are trigonal planar and tetrahedral respectively. Spectroscopic data are also reported [31].



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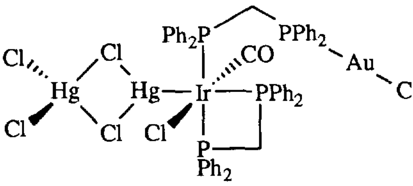

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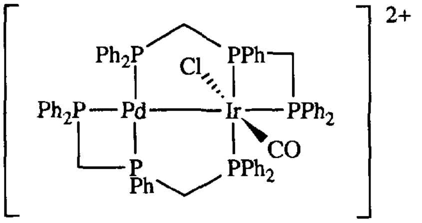
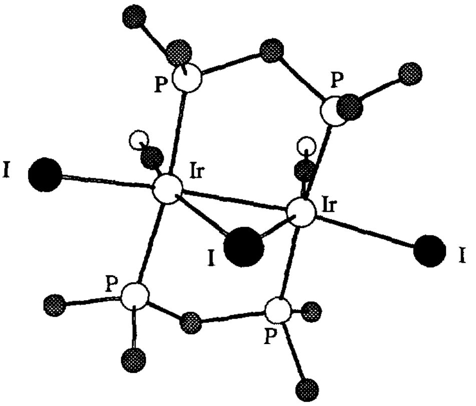


(17)

The reaction of $[IrCl(CO)(AsPh_3)_2]$ with $[PdL_2][PF_6]_2$ (where L = $Ph_2CH_2PPhCH_2PPh_2$) leads to the dimetallic complex dication (**17**) which has been fully characterised. The Pd-Ir distance is 2.694(2)Å. In CH_2Cl_2 solution, the complex exhibits a strong absorption at 458 nm (ε = 11,000 $dm^3\ mol^{-1}\ cm^{-1}$) which is assigned to a $\sigma_{MM'} \rightarrow \sigma^*_{MM'}$ transition. Excitation into this band generates a fluorescence emission at 520 nm (at 25°C), whilst at a temperature of −196°C, phosphorescence is observed (665 nm). The platinum analogue of complex (**17**) has also been studied [32].

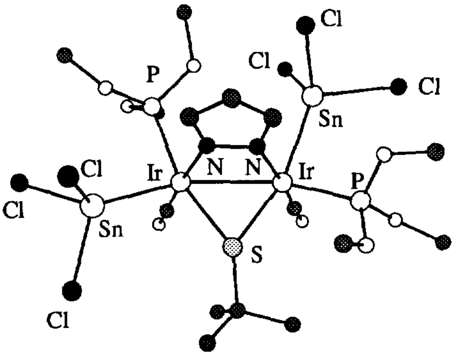
When chlorine reacts with *trans*-$[\{IrCl(CO)(dppm)\}_2]$, the diiridium complex $[\{IrCl_2(CO)(dppm)\}_2]$ forms. This has been characterised spectroscopically. Iodine reacts with *trans*-$[\{IrCl(CO)(dppm)\}_2]$ to give $[\{IrCl(I)(CO)(dppm)\}_2]$, in which it is proposed that the iodide ligands are coordinated *trans* to the Ir-Ir bond. With a 5-fold excess of lithium iodide, *trans*-$[\{IrCl(CO)(dppm)\}_2]$ is converted to its iodo analogue, and further treatment with I_2 leads to the formation of $[\{IrI(CO)(dppm)\}_2(\mu\text{-}I)]I$, [(**18**)]I [33].



(**18**)

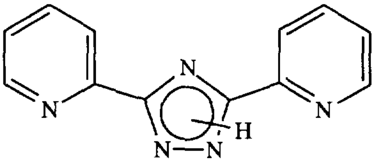
The diiridium complex $[Ir_2(CO)_4\{\mu\text{-}NH(C_6H_4Me\text{-}4)\}_2]$ been prepared as part of a study of similar iridium and rhodium compounds. The synthetic method utilises the reaction of NaOR' (R' = Me, Et or Ph) with *cis*-$[IrCl(CO)_2\{NH_2(C_6H_4Me\text{-}4)\}]$; $[Ir_2(CO)_4\{\mu\text{-}NH(C_6H_4Me\text{-}4)\}_2]$ has been characterised by IR and ^1H NMR spectroscopies and by X-ray crystallography. Two polymorphs exist in the solid state: a yellow triclinic form and a purple orthorhombic form. However, there are no significant differences in structure at the molecular level; the Ir-Ir distance in one form is 2.933(1)Å [34].

Some reactions of the diiridium complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(CO)_2\{P(OMe)_3\}_2]$ (Hpz = pyrazole) have been investigated. The complex forms an adduct with tin(II) chloride, with the group 14 unit entering into a bridging site. With mercury(II) chloride or mercury(II) iodide, the complexes $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)X_2(CO)_2\{P(OMe)_3\}_2]$ (X = Cl or I) are formed. These react with $SnCl_2$ to give $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(SnCl_2X)_2(CO)_2\{P(OMe)_3\}_2]$ and for X = Cl, product (**19**) has been structurally characterised. The Ir-Ir distance of 2.7221(6)Å suggests bonding character. All compounds in the study have been characterised by IR and ^{31}P NMR spectroscopies and by ^{119}Sn NMR spectroscopy where appropriate [35]. The electronic spectra of a series of pyrazolyl-bridged dinuclear iridium complexes have been recorded and discussed [36].

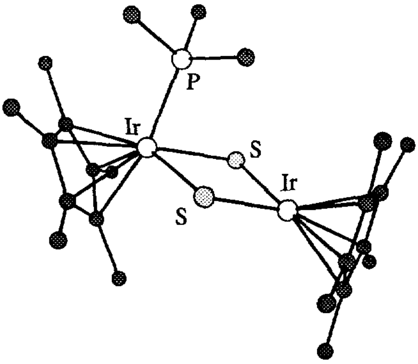


(19)

A series of new triazole bridged complexes, including iridium-containing species, has been reported. The conjugate base of ligand (**20**), HL, is incorporated in the complexes $[(bpy)_2Ru^{II}(\mu\text{-}L)Ir^{III}(ppy)_2]^{2+}$ and $[\{Ir^{III}(ppy)\}_2(\mu\text{-}L)]^+$. Electrochemical studies of the complexes show that the first oxidation of the heterometallic species is ruthenium-centred. Reduction of the diiridium complex occurs at the triazole ligand. The absorption spectrum of $[(bpy)_2Ru^{II}(\mu\text{-}L)Ir^{III}(ppy)_2]^{2+}$ shows bands that can be assigned to Ru→bpy and Ir→[ppy]⁻ transitions. Efficient energy transfer occurs from the higher energy excited states centred on the $Ir(ppy)_2$-unit to the lowest energy excited state which is a MLCT level centred on the $Ru(bpy)_2$-unit [37].



(20)



(21)

Lithium hexamethyldisilazane reacts with [Cp*Ir(PMe$_3$)SHCl] at –78°C to yield the sulfur-bridged diiridium complex (**21**). The structure of this compound has been confirmed by X-ray crystallography. When heated at 150°C in toluene, compound (**21**) loses PMe$_3$ and a cubane assembles. The product [Cp*IrS]$_4$ has been crystallographically characterised. Related systems which have also been studied include the mixed iridium-rhodium species [{Cp*IrS}$_2${Cp*RhS}$_2$]. This heterometallic cluster has been characterised by ^{1}H and ^{13}C NMR spectroscopies and mass spectrometry; an X-ray diffraction study revealed a disordered (with respect to the Rh/Ir sites) structure. A possible mechanism for the formation of the cubanes has been proposed [38].

When *fac(S)*-[Ir(aet)$_3$] (Haet = 2-aminoethanethiol) is treated with copper(II) nitrate in water, the complex that results contains a hexacation with a $Cu^I_4Ir^{III}_4$-core supported by sulfur-containing bridges. These units consist of μ_2- and μ_3-thiolato and disulfide bridges. The crystal structure of the rhodium analogue of the product has confirmed the structure of the cluster [39]. The preparations of the di- and triiridium species [Ir$_2$(μ-SPh)$_2$(alkene)$_2$] and [Ir$_3$(μ_3-SPh)$_2$(alkene)$_3$]$^+$ (for various alkenes) have been reported. Mixed rhodium-iridium complexes have also been synthesised. The products have been characterised spectroscopically, and an X-ray crystallographic study of the rhodium complex [Rh$_3$(μ_3-SPh)$_2$(cod)$_3$][ClO$_4$] confirms the details of the solid state structure of the trimetallic species. In the latter, each rhodium centre is in a square planar environment and the Rh·····Rh separations are classed as being non-bonding [40].

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