

5. IRIIDIUM

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INTRODUCTION

This review continues the general form of that published for the 1982 literature [1]. This year the chemistry of rhodium and iridium are treated separately. Iridium chemistry is undergoing something of a renaissance at present, and the number of papers published each year in this field is increasing dramatically. Undoubtedly, the widespread use of rhodium complexes as catalysts for a wide variety of processes is a major contribution to this. A number of studies of the mechanisms of oxidation of organic substrates by $[\text{IrCl}_6]^{2-}$, in combination with the numerous studies of the ground state properties of this ion, indicate contemporary interest in the chemistry of these

latter transition metal species. Other areas of interest include homonuclear and mixed metal clusters incorporating iridium, iridaboranes and iridium complexes in hydroformylation and hydrogenation reactions.

A review of the chemistry of the platinum group metals has appeared [2].

The material included in this review corresponds closely with the coverage in volumes 98 and 99 of Chemical Abstracts, although the major journals (J. Am. Chem. Soc., J. Chem. Soc., Chem. Commun., J. Chem. Soc., Dalton Trans., and Inorg. Chem) have been covered through December 1983.

Once again, I must thank Drs. Olga Kennard, Sharon Bellard and Paul Raithby for their assistance in obtaining data from the Cambridge Crystallographic Data Centre.

5.1 Iridium(VI)

There has been remarkably little recent interest in the chemistry of iridium(VI). One of the best known iridium(VI) compounds is the hexafluoride, $[\text{IrF}_6]$. This compound has been shown to react with boron(III) halides (BCl_3 , BBr_3 or BI_3) and tetrachloromethane to produce mixed iridium halides [3]. The complexes $[\text{Ir}_2\text{F}_3\text{Cl}_6]$ and $[\text{Ir}_2\text{Br}_4\text{F}_5]$ were isolated and characterised. No other iridium(VI) complexes have been reported this year.

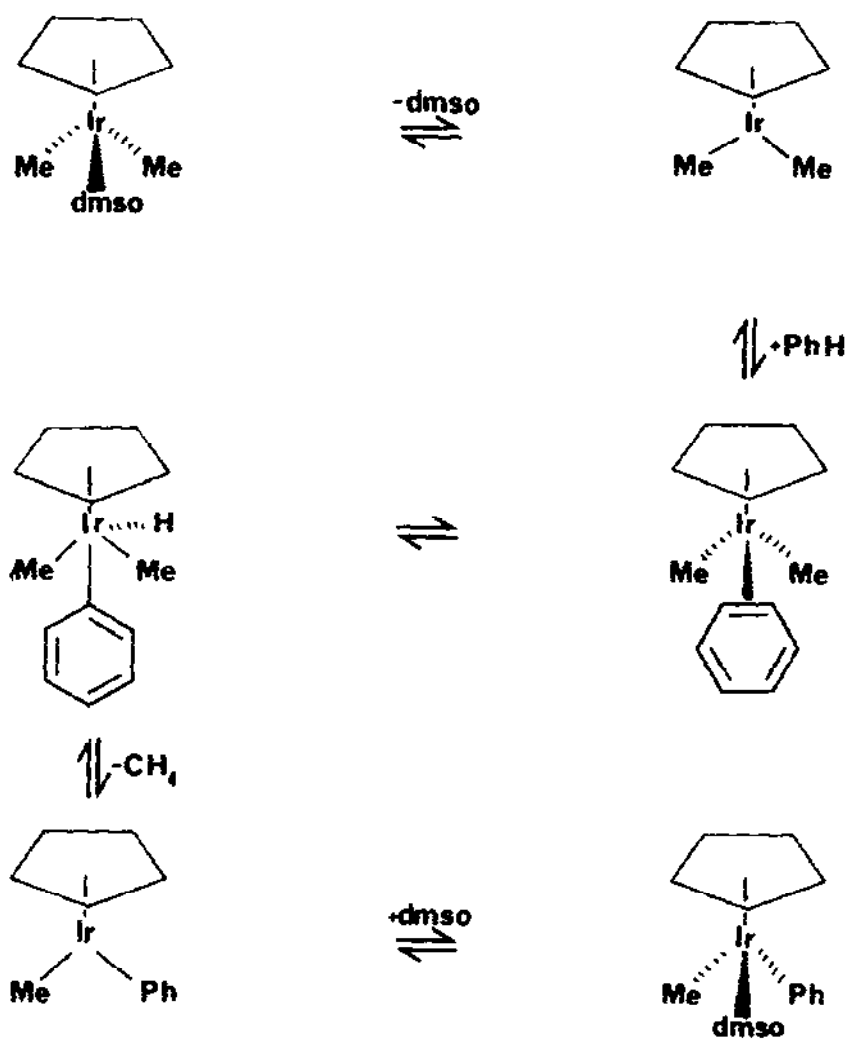
5.2 Iridium(V)

The dearth of reports describing the chemistry of high-oxidation state iridium compounds extends to the +5 state. However, a few isolated studies have been described. Iridium(V) has been shown to be stabilised in the Perovskites $[\text{MLaMgIrO}_6]$ ($\text{M} = \text{Ca}, \text{Sr}$ or Ba) which are readily prepared under high pressures of dioxygen [3]. Magnetic and Mossbauer measurements indicate that the samples contain some (d^5) iridium(IV) impurities. Broad-line ^{19}F NMR studies of the adduct $\text{IrF}_5 \cdot \text{BrF}_3$ have revealed it to be the ionic species $[\text{BrF}_2][\text{IrF}_6]$ [5].

Iridium(V) alkyl hydrides have been proposed as intermediates in alkyl-aryl exchange reactions of iridium(III) compounds. The reaction:



proceeds readily in dmsO; the rate of exchange of coordinated dmsO is high ($k = 5.4 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}$ at 35°C), and the mechanism shown in Scheme 1 is



Scheme 1

was proposed.

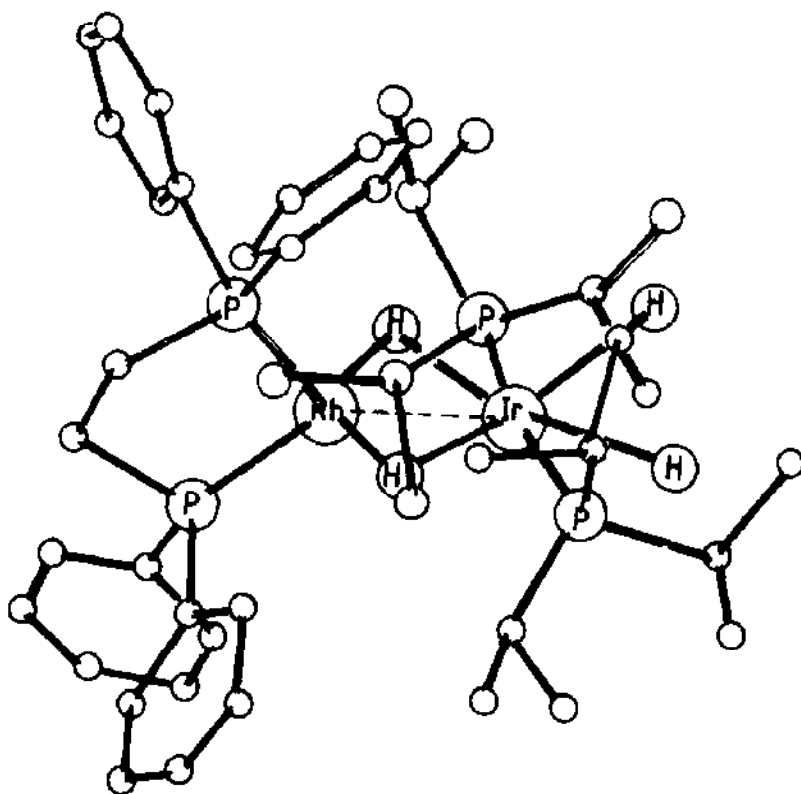
A number of observations are in accord with the proposed mechanism; a) when C_6D_6 is substituted for benzene a kinetic isotope effect $k_H/k_D = 2.24$ is noted, b) a slower second reaction to produce $[(cp)IrAr_2(dmsO)]$ was detected, and c) when iodobenzene was used, a 3:1 mixture of the meta and para isomers of $[(cp)Ir(CH_3)(C_6H_4I)(dmsO)]$ was obtained, but no products from insertion into the C-I bond could be detected. A novel iridium(V) species has been reported by Maitlis and co-workers [25]. When $[(LIrCl(\eta-H))_2]$ ($HL = C_5HMe_5$) is treated with Et_3SiH , the dimer $[(LIrCl(\eta-H))_2]$ is formed. Reaction of this with excess Et_3SiH produces, sequentially, the iridium(V) mononuclear complexes, $[IrLH_2Cl(SiEt_3)]$ and $[IrLH_2(SiEt_3)_2]$. The cation, $[Rh(dppe)(MeOH)_2]^+$, reacts with $[IrH_5(P^iPr_3)_2]$ in methanol to give the bis-hydrido bridged binuclear complex $[(dppe)Rh(\eta-H)_2IrH_2(P^iPr_3)_2]$ in good yield [26]. In the presence of ethyldiisopropylamine, yields in excess of 80% may be obtained. The complex has been characterised spectroscopically by NMR techniques, and in the solid state by X-ray crystallography; the structure is as shown in 1.

5.3 IRIDIUM(IV)

5.3.1 Complexes with halides

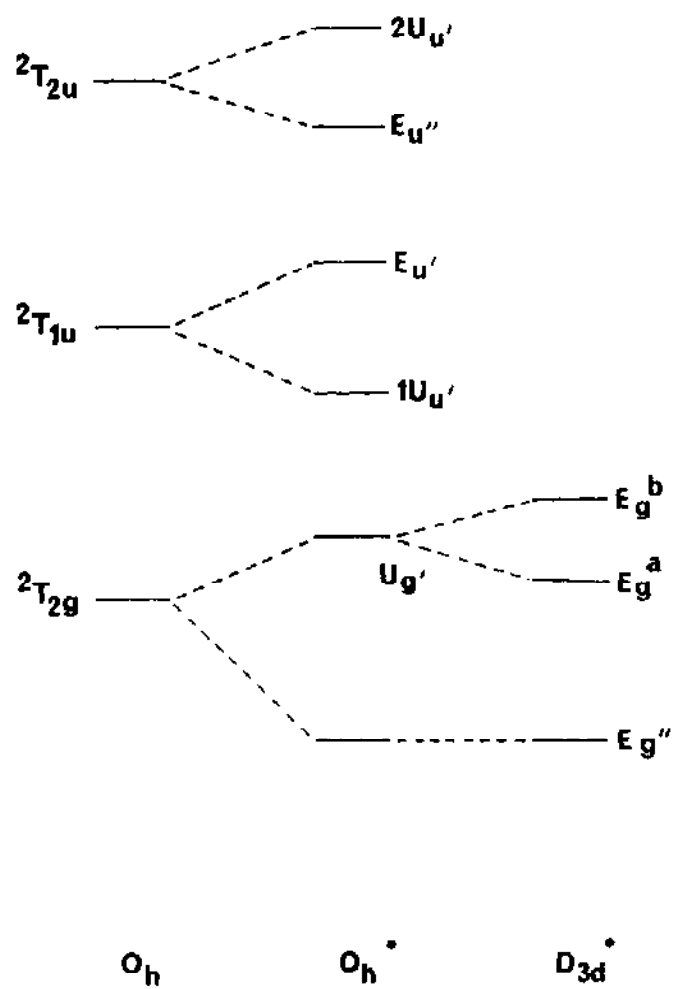
There has been a considerable amount of recent interest in the hexahaloiridate(IV) complexes. The emphasis of this has been on the mechanistic aspects of oxidations by hexahaloiridate(IV) and on the intimate structural and spectroscopic properties of these ions. This year, this emphasis has continued, and a number of interesting mechanistic and structural studies have been reported.

A number of alkali metal NMR studies of the $M_2[IrCl_6]$ salts have been reported; specifically, ^{133}Cs NMR studies of $Cs_2[IrCl_6]$ [7] and ^{87}Rb NMR studies of $Rb_2[IrCl_6]$ [8] have been described. A detailed analysis of the spectroscopic (vibrational, electronic-vibrational, resonance Raman) properties of $[^nBu_4N]_2[IrCl_6]$ at 15 K has been completed. The energy level diagram shown in Scheme 2 was derived [9].



(1)

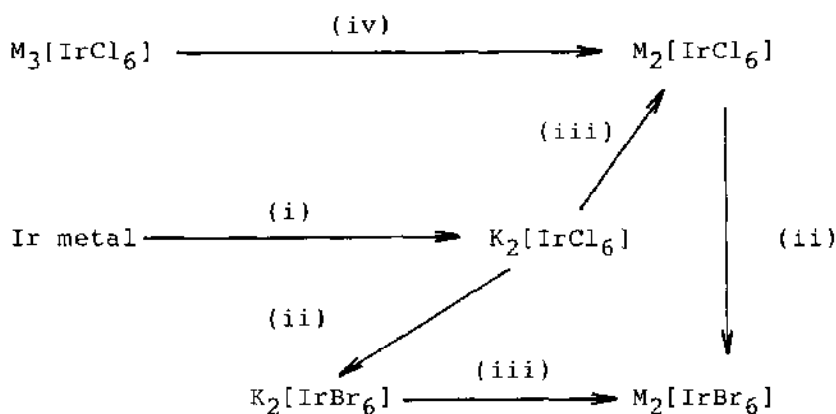
Related resonance Raman [10], absorption and electronic Raman [11] spectroscopic studies of hexachloroiridate(IV) and hexabromoiridate(IV) salts have been reported. The results are generally in agreement, and suggest a significant deviation from O_h octahedral symmetry. There has been a question over the sign of the g value for the hexachloroiridate(IV) ion. It was suggested, on the basis of magnetic Raman optical activity studies, that the ground state g value was negative - a result which called into question the results of some earlier magnetic circular dichroism studies [12]. Schatz has now shown that the calculated value for g from the magnetic circular dichroism data is indeed negative, and that the observed spectra agree well with this value [13]. In the absence of spin-orbit coupling, a 2T_g ground state was assumed. Multiple scattering X_α (MS- X_α) calculations on the hexachloroiridate(IV) anion have been reported;



Scheme 2

significant relativistic corrections were applied [14].

A large number of hexachloroiridate(IV), and hexabromoiridate(IV) salts have been prepared by Fergusson and Dixon [15]. Their work has cleared up a number of ambiguities in the literature regarding the preparation of these compounds. The major synthetic routes which they adopted are detailed in Scheme 3. Of particular note, is the use of ion-exchange techniques in preparing the desired salts.



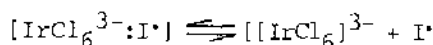
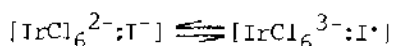
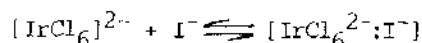
- (i) KCl/Cl_2
- (ii) HBr/H_2O
- (iii) ion exchange
- (iv) O_2/HCl

Scheme 3

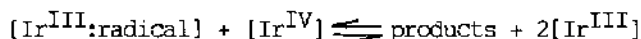
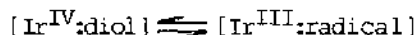
A review of electron transfer redox reactions involving simple free radicals has appeared; included within this article are discussions of the oxidation of thiosulphate, iodide, thiocyanate, azide, nitrite and sulphite by hexachloroiridate(IV) and hexabromoiridate(IV) [16]. The oxidation of the hexaquaumolybdenum(III) ion by hexachloroiridate(IV) has been studied [17]. The products of this reaction are hexachloroiridate(III) and " $\text{Mo}_2\text{O}_4^{2+}$ "; the latter arising from a transient molybdenum(IV) species. The reaction was followed by stopped-flow methods (489 nm observe) with a ten molar excess of the molybdenum(III) complex. A rate equation of the form

$$\text{rate} = (k_1 + k_2[\text{H}^+]^{-1})[\text{Mo}^{3+}][\text{IrCl}_6^{2-}]$$

was determined, at 25° C, $k_1 = 3.4 \pm 1.1 \times 10^4 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = 2.9 \pm 0.2 \times 10^4 \text{ s}^{-1}$. The k_2 term is dominant at $[\text{H}^+] \leq 0.10 \text{ M}$; this is consistent with an outer-sphere electron transfer mechanism, with the k_2 term proceeding through a $[\text{Mo}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ ion. A detailed mechanistic study of the oxidation of iodide or catechol by hexachloroiridate(IV) has been reported [18]. A simple second order rate equation was obtained for the reaction with iodide; at constant ionic strength, no dependence upon chloride or proton concentration was observed. The second order rate constant was of the order $10^2 - 10^3 \text{ mol}^{-1} \text{ s}^{-1}$, depending upon the ionic strength of the medium. Consideration of the activation parameters, and the behaviour in mixed solvents led to the proposal of a mechanism proceeding through an active ion pair. The oxidation of catechol (1,2-dihydroxybenzene) by hexachloroiridate(IV) also obeys a second order rate equation, with k_2 close to $10^4 \text{ mol}^{-1} \text{ s}^{-1}$. The authors of the above paper also addressed themselves to the confusion in the literature regarding the hydration of $\text{K}_2[\text{IrCl}_6]$ - such knowledge is required for the derivation of accurate transfer properties. It was concluded, on the basis of the available evidence, that the salt is anhydrous; the literature reference to the formation of a hexahydrate probably being erroneous. The detailed mechanism for the oxidation of iodide is shown below



A related mechanism has been proposed for the oxidative cleavage of ethylene glycol (1,2-ethanediol), butan-2,3-diol and 2,3-dimethyl-2,3-butandiol by hexachloroiridate(IV) [19]. The organic products are formaldehyde, acetaldehyde and acetone respectively. The mechanism proposed is



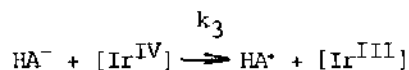
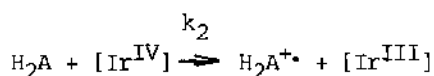
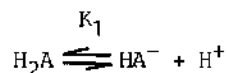
The oxidation of ascorbate by hexachloroiridate(IV) or hexabromoiridate(IV) has also been studied [20]. The rate equation is of the form

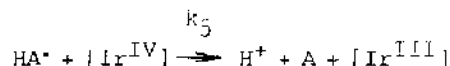
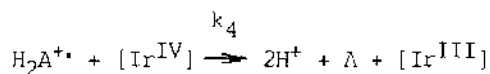
$$-\frac{1}{2} \frac{d[\text{Ir}^{\text{IV}}]}{dt} = (k_a + k_b[\text{H}^+]^{-1})[\text{H}_2\text{A}][\text{Ir}^{\text{IV}}]$$

where H_2A is ascorbic acid. The inverse dependence of k_b upon acid concentration indicates that k_a refers to the reaction of ascorbic acid itself, and k_b to that of the monoanion, HA^- . The reactions exhibited an interesting medium effect associated with the presence of alkali metal anions. The detailed mechanism proposed is shown below.

It is evident that k_b in the experimental expression is simply given by k_3K_1 .

The reaction of methylcobalamin (vitamin B_{12}) with hexachloroiridate(IV) has been studied [27]. The alkylated cobalt(III) complex is demethylated in the reaction. At a 2:1 stoichiometry of $\text{Ir}^{\text{IV}}:\text{Me-B}_{12}$, the products are $\text{H}_2\text{O-B}_{12}^+$, $[\text{IrCl}_6]^{3-}$, $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ and chloromethane; at lower ratios of iridium(IV) to methylcobalamin, the products are $[\text{IrCl}_6]^{3-}$, $\text{H}_2\text{O-B}_{12}^+$ and ethane. The reaction is second order overall, first order in methylcobalamin and hexachloroiridate, and the apparent





second order rate constant is pH dependent. These observations are compatible with the presence of a number of solution species derived from the methylcobalamin. The observed rate constant, k , may be expressed

$$k = (k'K_2 + k''K_1[\text{H}^{+}]) / (K_2 + K_1K_2 + K_1[\text{H}^{+}])$$

where K_1 refers to the on-off coordination of the axial 5,6-dimethylbenzimidazole ligand to cobalt, K_2 to the protonation of the uncoordinated (off-form) 5,6-dimethylbenzimidazole axial ligand, k' to the demethylation of the base-on form, and k'' to the demethylation of the protonated base-off form.

5.3.2 Complexes with other ligands

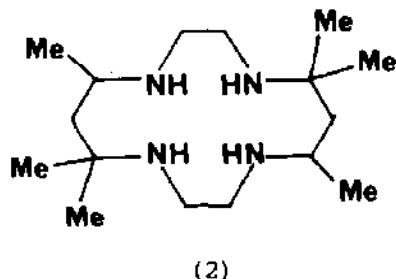
The solution behaviour of $[\text{Ir}(\text{OH})_4(\text{H}_2\text{O})]$ in sulphuric acid has been studied [21]. Dissolution in concentrated sulphuric acid produces $\text{H}_{10}[\text{Ir}_3\text{O}(\text{SO}_4)_9]$; treatment of this complex with water produces another mixed valence $\text{Ir}^{\text{IV}} + 2\text{Ir}^{\text{III}}$ complex ion, $[\text{Ir}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{4-}$. Further hydrolytic decomposition results in the formation of iridium(III) complexes.

The reaction of hexachloroiridate(IV) or hexabromoiridate(IV) with aqueous oxalate has been investigated [22]. The products of these reactions are the iridium(III) oxalato complex ions $[\text{IrX}_4(\text{L})]^{3-}$ ($\text{X} = \text{Cl}$ or Br ; $\text{H}_2\text{L} = \text{HO}_2\text{CCO}_2\text{H}$), which may be extracted into dichloromethane as their pentylammonium salts. Oxidation of these dichloromethane solutions with the appropriate halogen leads to the formation of the corresponding iridium(IV) complex ions, $[\text{IrX}_4(\text{L})]^{2-}$. The complex ions exhibit three charge transfer bands, and give infra-red Raman spectra compatible with a C_{2v} symmetry.

The extraction of iridium(III) and iridium(IV) from aqueous medium by the ligands $\text{PhCOCH}_2\text{CSPh}$, $\text{ROOCH}_2\text{CSNH}_2$ or RCONHCSNH_2 has been investigated; the metal is extracted as the tris chelated $[\text{IrL}_3]^{n+}$ species [23]. A thirty-fold enrichment of iridium was observed with $\text{PhCOCH}_2\text{CSPh}$.

The ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclodecane (2) is

readily prepared by the borohydride reduction of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraza-7,13-cyclotetradecadiene; treatment of the new saturated ligand with chloroiridic(IV) acid led to the isolation of the complex $[\text{Ir}(\text{LCl}_2)]\text{Cl}_2$ ($\text{L} = 2$) [24].

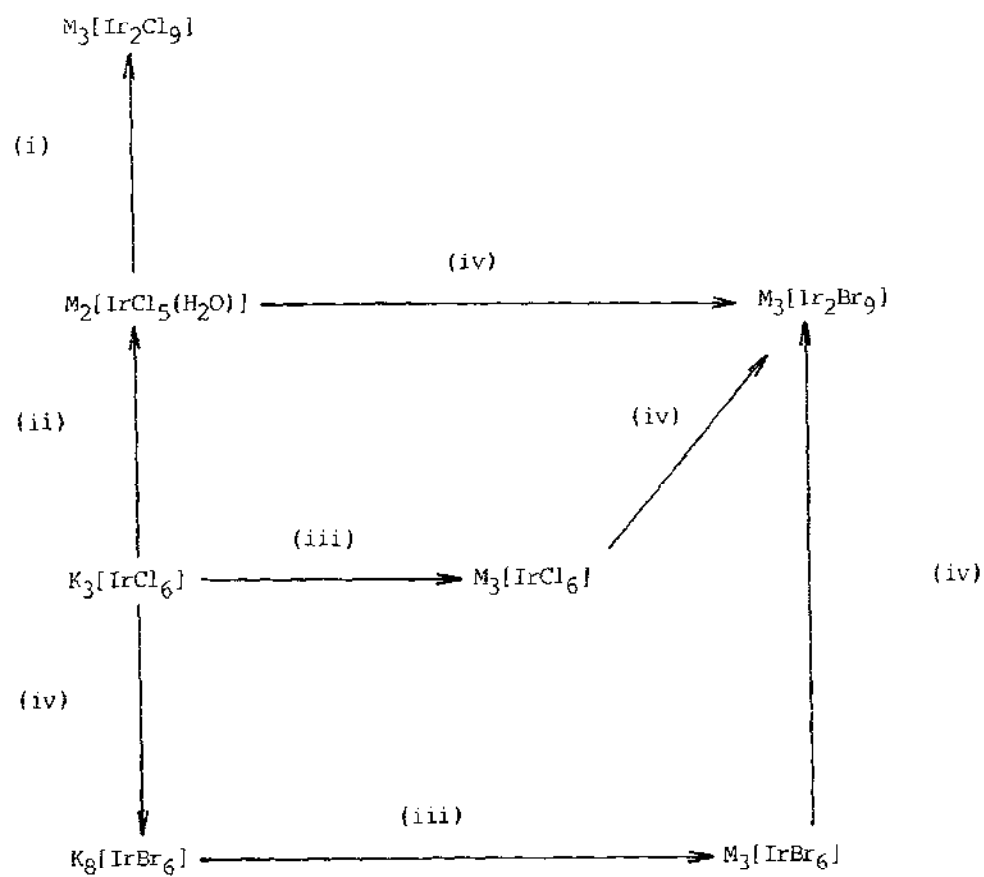


5.4 IRIDIUM(III)

5.4.1 Complexes with halides

There have been a number of isolated reports concerning the $[\text{IrX}_6]^{3-}$ ($\text{X} = \text{halogen}$) ions, although these are normally encountered as the inorganic reduction products from hexahaloiridate(IV) oxidations. High level MS- X_α studies of the hexachloroiridate(III) ion have been described [14]. A recent study of the preparation of the hexahaloiridate(III) ions has removed some of the ambiguities present in the literature. Preparative details for the synthesis of $\text{M}_2[\text{IrX}_6]$ ($\text{X} = \text{Cl}$ or Br ; $\text{M} = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$ or Me_4N) were reported [15]. Also described were the nonahalodiiridate(III) ions, $[\text{Ir}_2\text{X}_9]^{3-}$. The salts $\text{M}_2[\text{IrX}_6]$ ($\text{X} = \text{Cl}$, $\text{M} = \text{K}, \text{NH}_4, \text{Rb}$ or Cs ; $\text{X} = \text{Br}$, $\text{M} = \text{NH}_4, \text{Rb}$ or Cs) were all obtained as monohydrates. No evidence for the formation of a trihydrate of potassium hexachloroiridate(III) was obtained. It was proposed that the previously reported species $\text{K}_3[\text{IrBr}_6] \cdot n\text{H}_2\text{O}$ ($n = 3$ or 4), are better formulated as $[\text{H}_3\text{O}]\text{K}_8[\text{IrBr}_6]_3 \cdot 9\text{H}_2\text{O}$. Some problems were reported in the preparation of $\text{K}_2[\text{IrCl}_5(\text{H}_2\text{O})]$ by the literature methods. These studies are summarised in Scheme 4.

Single crystal X-ray studies of the complexes $\text{K}_3[\text{IrCl}_6]$, $\text{K}_3[\text{IrCl}_6] \cdot \text{H}_2\text{O}$, $[\text{NH}_4]_3[\text{IrCl}_6] \cdot \text{H}_2\text{O}$ and $\text{Rb}_3[\text{IrBr}_6] \cdot \text{H}_2\text{O}$ have been reported [28]. In $\text{K}_3[\text{IrCl}_6]$ the anion is octahedral, with an average Ir-Cl bond length of 2.368 Å. In the monohydrate, the $[\text{IrCl}_6]^{3-}$ ions are arranged in chains, with the potassium ions and water molecules occupying channels between the chains. The octahedra of the anions are somewhat distorted, with Ir-Cl lengths varying from 2.336 to



(i) heat in vacuum

(ii) H_2O/MCl

(iii) ion exchange

(iv) HBr/H_2O

(Scheme 4)

2.387 Å. In an independent study, Burgess and co-workers, have confirmed the existence of the anhydrous and monohydrated forms of $K_3[IrCl_6]$, but they also believe, on the basis of thermogravimetric investigations, that the trihydrate is the solid species present in equilibrium with saturated aqueous solutions [18].

Two reports of the photoluminescent behaviour of iridium(III) complexes doped into single crystals of silver bromide have appeared [29,30].

5.4.2 Complexes with Group VI donor ligands

5.4.2.1 Complexes with oxygen donor ligands

The first structural determination of a compound containing the hexaquaairidium(III) ion has been reported [31]. The compound studied was the alum, $CsIr(SO_4)_2 \cdot 12H_2O$; the iridium-water distance was found to be 2.041 Å. The mixed valence ($2Ir^{III}$, Ir^{IV}) complex ions $[Ir_3O(SO_4)_9]^{10-}$ and $[Ir_3O(SO_4)_6(H_2O)_3]^{4-}$ have already been discussed in Section 5.4.2 [21].

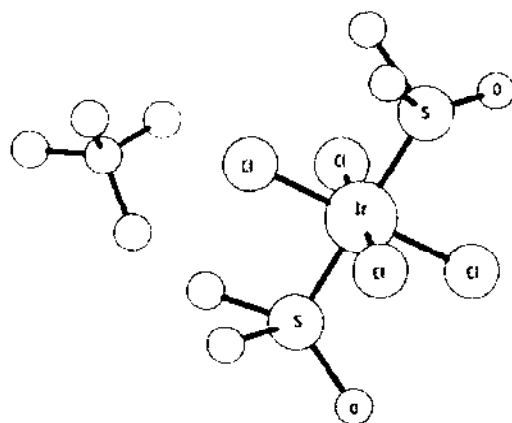
The reaction of hexachloroiridate(IV) with aqueous oxalate results in the formation of the iridium(III) complex ion $[IrCl_4L]^{3-}$ ($H_2L = HOOC-COOH$); the hexabromoiridate(IV) ion behaves in a similar manner [22]. Treatment of potassium hexachloroiridate(IV) with an excess of potassium oxalate, followed by solvent extraction with nitromethane, leads to the formation of $K_3[IrL_3]$ ($H_2L = HOOC-COOH$) in high yield (85%) [32]. The photolytic behaviour of these oxalato complexes has been studied; at 77 K, in a variety of matrices, the predominant process was metal centred reduction [33].

A number of tris chelated $[IrL_3]$ species ($HL = PhCOXHCOR$; $X = CH$, $R = Ph$, $NHPh$ or NBu_2 ; $X = N$, $R = NBu_2$ or 2-pyridyl) have been described [34].

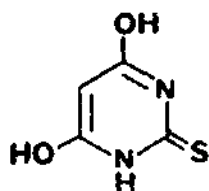
5.4.2.2 Complexes with sulphur donor ligands

A single crystal structural analysis of the salt $[Me_4N][IrCl_4(dmsO)_2]$ has been described; the anion is octahedral, with the two sulfoxide ligands being S-bonded and occupying trans-diaxial positions (3) [35].

A related anion, $cis-[IrCl_4]^-$ ($L = MeSCH_2CH_2SMe$), is present in the salt $[Me_4N][IrLCl_4]$ [36]. 1H NMR spectroscopic studies of the inversion of this complex in $dmsO-d_6/CDCl_3$ have been reported; coalescence occurred at 10° C, with $\Delta G^\ddagger = 63 \text{ kJ mol}^{-1}$. The interaction of iridium(III) with 4,6-dihydroxypyrimidine-2-thione (thiobarbituric acid) (4) has been investigated; the complex $[IrL_2Cl]$ ($HL = 4$) was isolated [37].



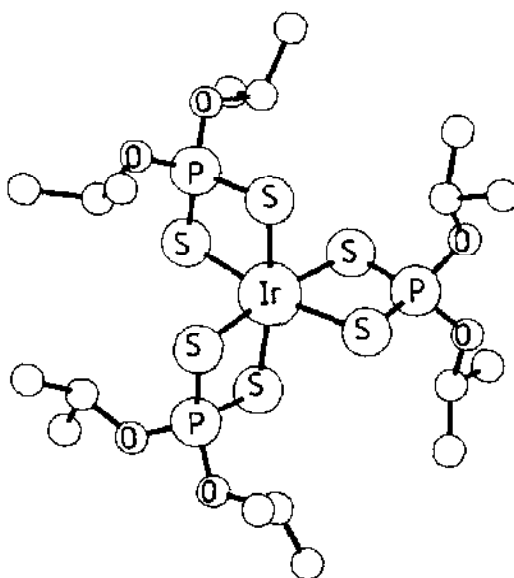
(3)



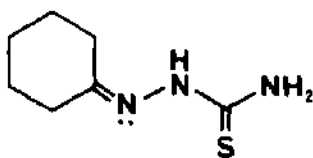
(4)

A crystal structural analysis of the complex $[\text{IrL}_3]$ ($\text{HL} = \text{HS}_2\text{P}(\text{}^i\text{PrO})_2$) (5) has been described; the compound possesses a distorted octahedral geometry [38].

Condensation of cyclohexanone with thiosemicarbazide yields the semicarbazone (6), which forms iridium(III) complexes $[\text{IrL}_3\text{X}_3]$ ($\text{L} = 6$, $\text{X} = \text{Cl}$, Br or I) [39].



(5)



(6)

The thioketone ligands, $\text{PhCOCH}_2\text{CSPh}$, $\text{ROOCH}_2\text{CSNH}_2$ and RCONHCSNH_2 have been investigated as agents for the extraction of iridium from aqueous solution; the metal is extracted as its tris chelate in each case [23].

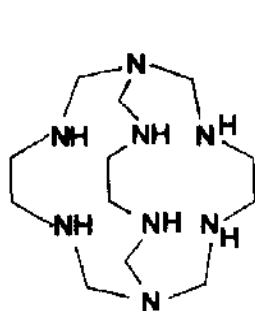
5.4.3 Complexes with nitrogen donor ligands

The electrochemical properties of a series of iridium(III) complexes of the type $[\text{Ir}(\text{NH}_3)_5\text{L}]^{n+}$ ($\text{L} = \text{NH}_3$, H_2O , NCMe , Me_2NCHO , imidazole or dmsO) have been reported. The complexes exhibit an irreversible two electron reduction, remarkably independent of the nature of L (-1.7 V for $\text{L} = \text{NH}_3$, NCMe , Me_2NCHO and dmsO; -1.71 V for $\text{L} = \text{H}_2\text{O}$; -1.8 V for $\text{L} = \text{imidazole}$; all potentials with respect to SCE). No reliable correlations between the value of the reduction

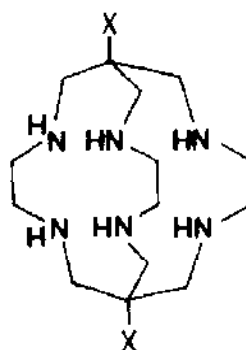
potential and rate of reaction could be drawn [40]. Mechanistic studies of the cation $[\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ have been reported; density measurements in perchlorate media have given a value of $77.4 \pm 1.0 \text{ pm}^3$ for the partial molar volume of the ion [41]. The determined value for the $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ cation is remarkably similar.

The reaction of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with trifluoromethanesulphonic acid results in the formation of the $[\text{Ir}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+}$ cation [42]. This species is proposed as a new, convenient, labile source of the $[\text{Ir}(\text{NH}_3)_5]^{3+}$ unit; the rate of aquation is moderately slow, $k = 1.6 \times 10^{-1} \text{ s}^{-1}$ [42].

ESR studies of the complex $[\text{Ir}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ have been described; the complex is isomorphous with the cobalt(III) analogue [43]. The chelated cation, $[\text{Ir}(\text{en})_3]^{3+}$, has been shown to form outer-sphere complexes with halide ions (fluoride, chloride and bromide) of moderate stability [44]. A compilation of the thermodynamic data for the formation of these outer-sphere complexes has appeared [45]. The same cation $[\text{Ir}(\text{en})_3]^{3+}$, reacts cleanly with formaldehyde in the presence of ammonia to give the cryptand complex $[\text{IrL}]^{3+}$ ($L = 7$). A similar reaction with formaldehyde and nitromethane results in the formation of $[\text{IrL}_3]^{3+}$ ($L = 8$, $X = \text{NO}_2$); reduction with zinc amalgam in the presence of acid leads to the formation of the new complex $[\text{IrL}_3]^{5+}$ ($L = 8$, $X = \text{NH}_3$). All of these complex are octahedral, and the electronic spectra resemble that of the parent ethylenediamine complex. In aqueous medium, no metal centred reduction could be detected electrochemically [46].

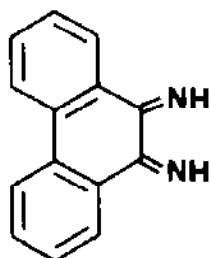


(7)

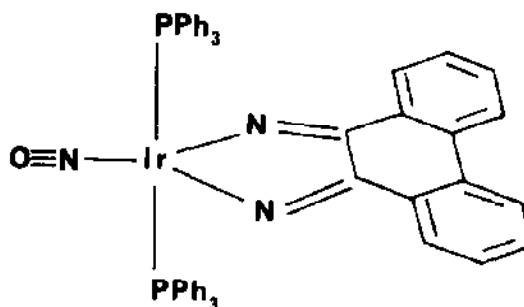


(8)

A series of complexes incorporating nitrosyl and diimine ligands have been reported; the ambiguities in oxidation state and ligand donor properties are of interest. Phenanthrenequinonediimine (LH₂, 9) reacts with [Ir(NO)(MeCN)(PPh₃)₂][PF₆]₂ in benzene/dichloromethane to give the deep red complex [Ir(NO)LH₂(PPh₃)₂][PF₆]₂. This complex was thought, by analogy with the known [Ir(NO)(phen)(PPh₃)₂]²⁺ cation, to possess structure 10. The reaction of this complex



(9)

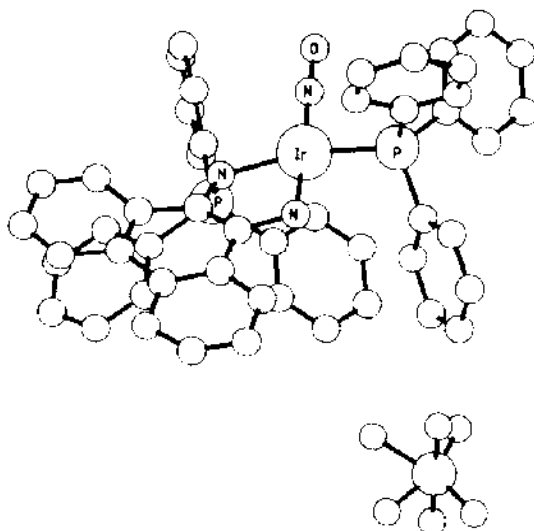


(10)

with sodium hydrogen carbonate resulted in deprotonation of the coordinated diimine, followed by an intramolecular attack of one imine anion upon coordinated triphenylphosphine, to give [Ir(NO)L(PPh₃)][PF₆]. A crystal structure of this (iridium(I)?) complex revealed it to possess a square-planar geometry, with a linear Ir-N-O system (Ir - N, 1.71 Å, N - O, 1.19 Å) (11) [47].

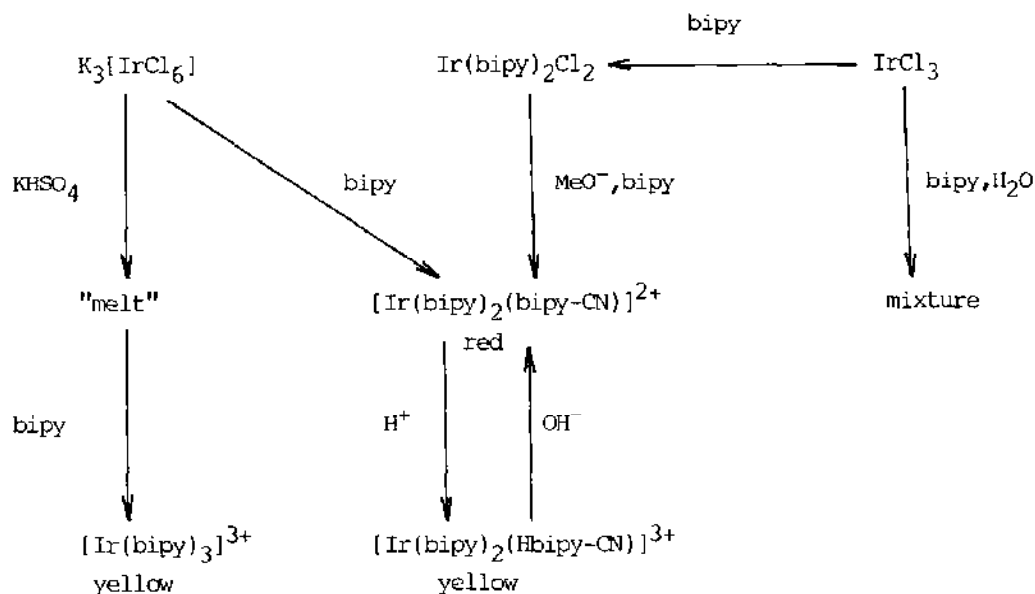
Another nitroso complex, [IrBr₃(NO)(PPh₃)₂] has been investigated by ESR spectroscopy; the spectral properties are best explained in terms of an iridium(III) formulation with a neutral NO ligand ($g_1 = 2.0218$, $g_2 = 1.9515$, $g_3 = 1.8128$, rhombic) [64].

Aryldiazonium salts react with [IrH₃(PPh₃)₂] at -10° C to give the expected coordination compounds [IrH₂(HN=NAr)(PPh₃)₂]⁺ [48]. The complexes react with carbon monoxide sequentially to form the cations [Ir(CO)₂H₂(PPh₃)₂]⁺ and [Ir(CO)₃(PPh₃)₂]⁺. If the reaction with the diazonium salt is performed at 30 -40° C, the product is a cyclometallated complex (see Section 5.4.4).



(11)

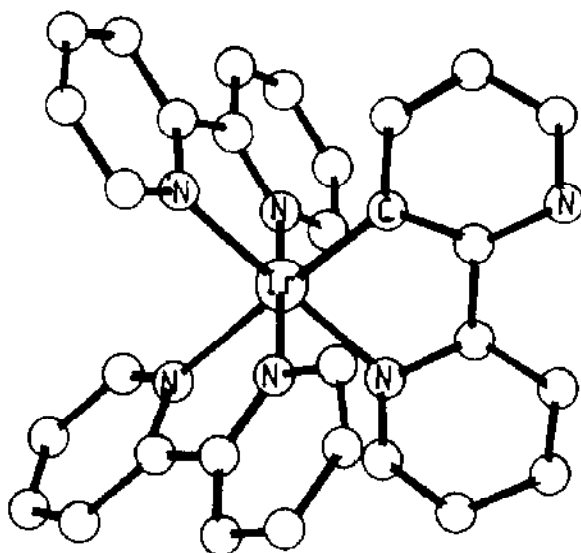
Studies of the anomalous iridium(III) complexes of 2,2'-bipyridine continue, but it is now clear that the various anomalies have a common origin. Various proposals for the structure of these complexes have been made, including monodentate 2,2'-bipyridines and 2,2'-bipyridine pseudo-bases, but it is now clear that they possess cyclometallated 2,2'-bipyridine ligands. A 500 MHz ^1H NMR and 125 MHz ^{13}C NMR study in $\text{dms}\text{-}d_6$ has been shown to be fully in accord with a cyclometallated structure [49]. The complex studied possessed the protonated cyclometallated ligand, $[\text{Ir}(\text{bipy})_2(\text{bipy-C,N})(\text{H}_3\text{O})]^{3+}$. The cyclometallated pyridine ring possesses a metal-carbon bond at C-3, which is in accord with the upfield shift of H-4 (δ 6.70) and H-5 (δ 7.16), and twenty three carbon signals, fourteen of which exhibit a strong proton one-bond coupling. The metallated carbon atom is shifted upfield to δ 139.5. The proton NMR spectrum was assigned on the basis of J-correlated COSY spectra. Nord et al. have made an intensive study of the iridium(III) 2,2'-bipyridine system [50]. They have clarified the confusion in the literature regarding the numerous species of 1:3 stoichiometry (Scheme 5).



Scheme 5

In particular, it is clear that the commonly encountered species are the yellow $[\text{Ir}(\text{bipy})_3]^{3+}$, and the red $[\text{Ir}(\text{bipy})_2(\text{bipy-CN})]^{2+}$ and $[\text{Ir}(\text{bipy})_2(\text{bipy-CN})(\text{H}_3\text{O})]^{3+}$ cations. They have also reported a 270 MHz ^1H NMR study of the complexes, the results of which are broadly in accord with those discussed previously. Final confirmation of the cyclometallated formulation comes from the crystal structural analysis of the complex $[\text{Ir}(\text{bipy})_2(\text{bipy-CN})][\text{ClO}_4]_2 \cdot 1/3\text{H}_2\text{O}$ (**12**). This structure removes any final ambiguities which were present in the previously reported structure of the $[\text{Ir}(\text{bipy})_2(\text{bipy-CN})(\text{H}_3\text{O})]^{3+}$ cation, in which the presence of the water molecule in the vicinity of the pyridine nitrogen atom could be interpreted in terms of a covalently hydrated pseudo-base formulation.

The related diimine complex, $[\text{Ir}(\text{phen})_3][\text{BPh}_4]_3$, has been shown to form fairly stable outer-sphere complexes with nitrate, acetate, bicarbonate and propionate [51]. The stability constants for the formation of the outer-sphere complexes $\{[\text{Ir}(\text{phen})_3]:\text{L}_n\}^{(3-n)+}$ have values of $\lg\beta_n$ in the range 0 - 3. It is possible that outer-sphere complexes of this type may be responsible for some of



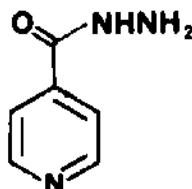
(12)

the anomalous properties of the $[\text{Ir}(\text{phen})_3]^{3+}$ cation, which cannot, of course, form a cyclometallated derivative.

The complex $[\text{Ir}(\text{py})_4\text{Cl}_2][\text{H}(\text{ONO}_2)_2]$ is an example of a salt of the rare acid hydrogen dinitrate anion [52]. Interest in these species has been reawakened, with the suggestion that the anomalous acidic properties of the $[\text{Pt}(\text{py})_4\text{Cl}_2]^{2+}$ cation may be due to the presence of a hydrogen dinitrate anion. The thermal aquation of the $\text{cis}-[\text{IrCl}_4(\text{py})_2]^-$ anion has been studied [53]. The products are the *fac-cis* and *mer-trans* isomers of $[\text{Ir}(\text{H}_2\text{O})(\text{py})_2\text{Cl}_3]$, which cannot be interconverted thermally or photochemically. The configuration of these aqua complexes was determined on the basis of the pK_a values of the coordinated water ligands. The photochemical and thermal hydration and solvolysis of a wide range of other iridium(III) mixed ligand chloro complexes was investigated; remarkable specificity in product formation was observed in a number of cases.

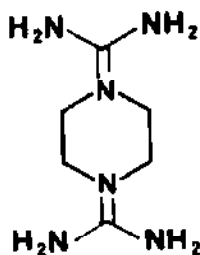
A large number of mixed ligand complexes with pyridine carboxylic acids have been described [54]. Amongst the complexes which have been described are $\text{Na}[\text{IrL}_2]$, $[\text{IrLL}']$, $[\text{IrLL}'']$, $[\text{IrL}(\text{gly})]$ and $[\text{IrLL}''']$ (H_2L = pyridine-2,6-dicarboxylic acid, HL' = pyridine-2-carboxylic acid, HL'' = pyridine-3-carboxylic acid, glyH = glycine, HL''' = 2-nitrophenol); the geometries of these

species is not known with any certainty, but they are thought to be polymeric in nature. The complex $[\text{IrL}_2\text{Cl}_2]\text{Cl}$ (L = pyridine-4-carboxylic acid hydrazide, 13) has been reported [55].

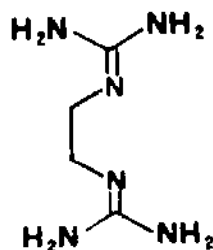


(13)

The reaction of hexachloroiridate(III) with 8-hydroxyquinoline (HL) has been investigated; the various isomers of the tris chelate $[\text{IrL}_3]$ may be separated by chromatography over silica [56]. The tetradentate ligands piperazine biguanide (14) and ethylene biguanide (15) form the octahedral complex ions $[\text{IrLX}_2]^+$ (H_2L = 14 or 15, X = Cl, Br, I, NO_2 or SCN) [57].



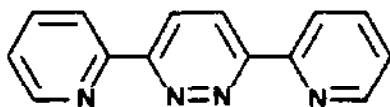
(14)



(15)

The trigonal bipyramidal complex $[\text{Ir}(\text{NO})\text{L}(\text{PPh}_3)_2][\text{PF}_6]_2$ (L = 3,6-bis(2-pyridyl)pyridazine, 16) is formed in the reaction of $[\text{Ir}(\text{NO})(\text{MeCN})_3(\text{PPh}_3)_2][\text{PF}_6]$ with L [69]. The compound reacts with copper(II)

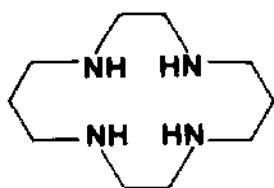
chloride dihydrate to give the heterobinuclear complex $[\text{IrCl}(\text{PPh}_3)_2\text{L}(\text{NO})\text{CuCl}][\text{PF}_6]_2$. This compound was characterised crystallographically (17); the iridium is coordinated to one of the nitrogen atoms of the pyridazine and to one pyridyl group. The copper is coordinated to the other nitrogen atom of the pyridazine and the other pyridyl group. The coordination about the near-tetrahedral copper ion is completed by a bridging nitrosyl ligand and a coordinated chloride.



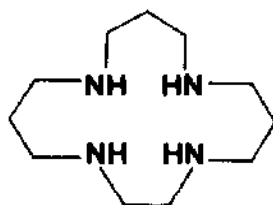
(16)

The reaction of $[\text{Ir}(\text{NO})\text{I}_2(\text{PPh}_3)_2]$ with acetonitrile in the presence of silver(I) hexafluorophosphate leads to the formation of $[\text{Ir}(\text{NO})(\text{MeCN})_3(\text{PPh}_3)_2][\text{PF}_6]_2$ (86).

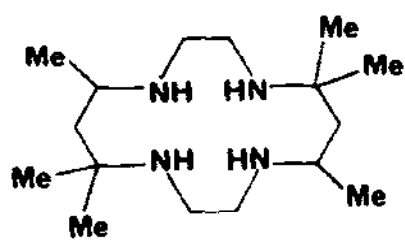
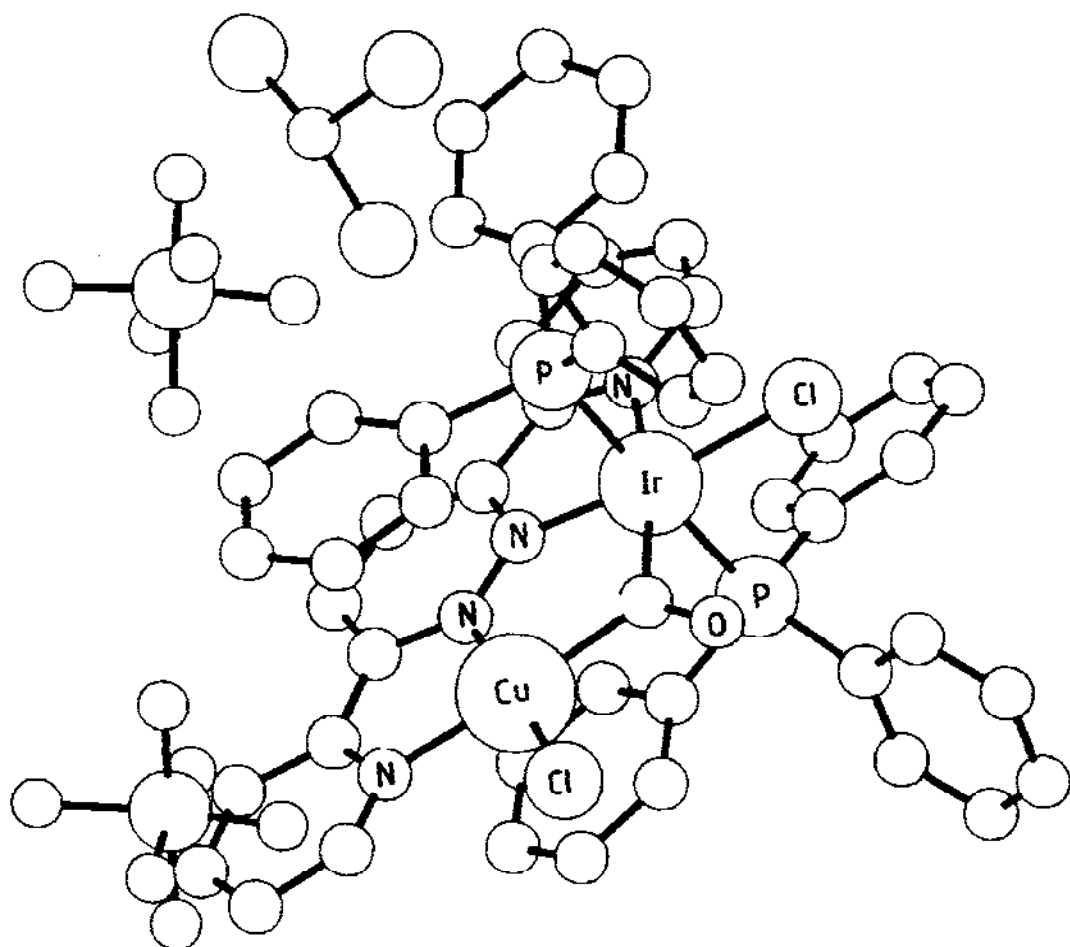
The first complexes of iridium(III) with macrocyclic amines have been reported by Poon and co-workers (58). The ligands in question were 1,5,8,12-tetraazatetradecane (18), 1,5,9,13-tetraazapentadecane (19) and the meso and rac forms of 2,4,4,9,11,11-tetramethyl-1,5,8,12-tetraazatetradecane (20). The complex ions isolated were $\text{cis}-[\text{IrLX}_2]^+$ ($\text{L} = \mathbf{18}$, $\text{X}_2 = \text{Cl}_2$, ClBr , or Br_2), $\text{trans}-[\text{IrLX}_2]^+$ ($\text{L} = \mathbf{18}$, $\text{X} = \text{NO}_2$ or Cl ; $\text{L} = \mathbf{19}$ or $\mathbf{20}$, $\text{X}_2 = \text{Cl}_2$, ClBr or Br_2).



(18)

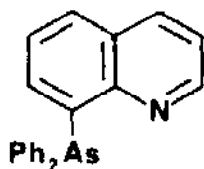


(19)



(20)

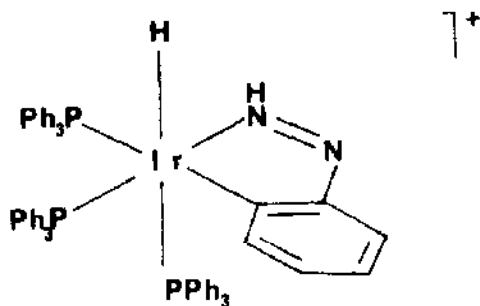
The reaction of the iridium(I) anion $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$ with 8-diphenylarsinoquinoline (21) in $\text{MeOCH}_2\text{CH}_2\text{OH}/\text{EtOH}$ under a carbon monoxide atmosphere results in the formation of pale yellow $[\text{IrHL}(\text{CO})\text{Cl}_2]$ (L = 8-diphenylarsinoquinoline, 21 [59]).



(21)

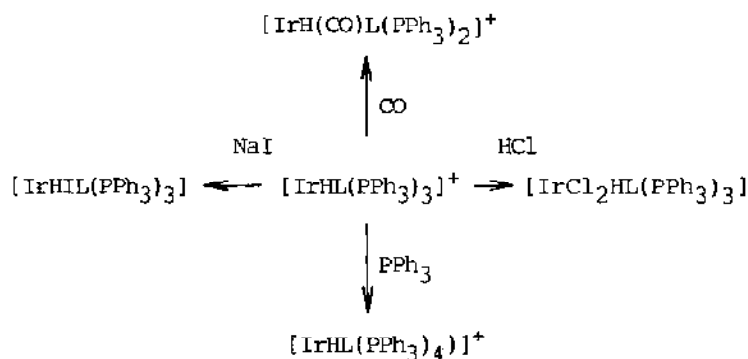
5.4.4 Complexes with Group IV donor ligands

The reaction of $[\text{IrH}_3(\text{PPh}_3)_2]$ with aryl diazonium salts was discussed in the previous section. If the reaction is conducted at $30 - 40^\circ \text{C}$, the cyclometallated product (22) is obtained [48].



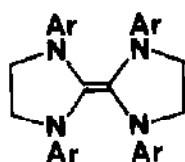
(22)

This bonding mode is commonly observed in ligands of this type. The reactions of the cation produced, $[\text{IrHL}(\text{PPh}_3)_3]^+$ ($\text{L} = \text{RC}_6\text{H}_3\text{N}=\text{NH}$), were investigated (Scheme 6).



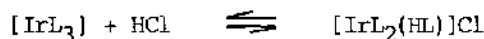
Scheme 6

Lappert and co-workers continue to investigate the chemistry of the carbene precursor hindered olefins (23). The reaction of these species with $[\text{Ir}(\text{cod})\text{Cl}]_2$ has now been described. The

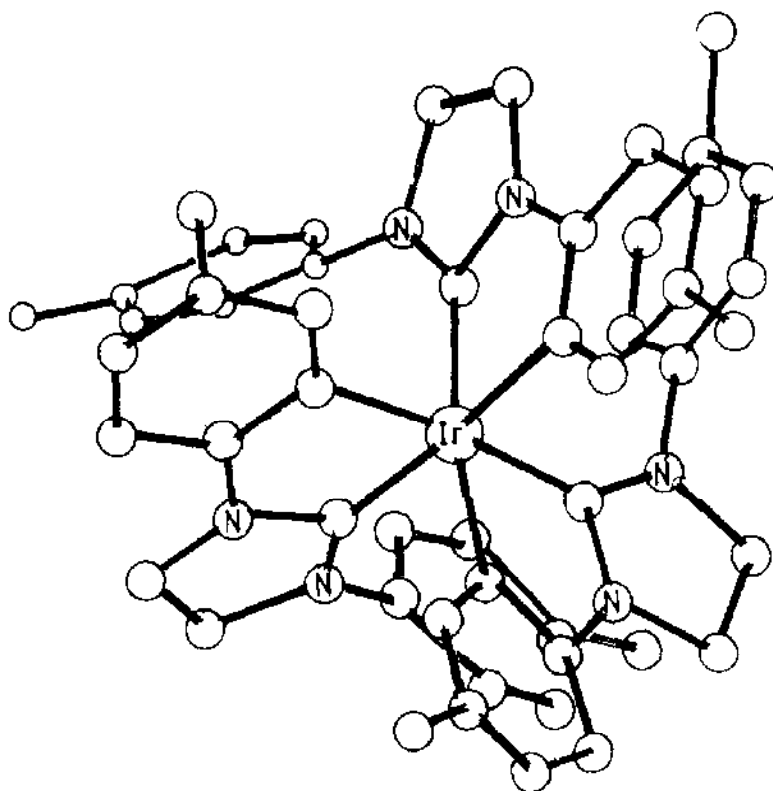


(23)

product of the reaction is a tris chelated cyclometallated species $[\text{IrL}_3]$ ($\text{L}=\text{L} = 23$), which has been characterised crystallographically [62]. Each ligand acts as a bidentate, binding through one cyclometallated aryl ring, and also acting as a carbene (24). The cyclometallated complex $[\text{IrL}_3]$ reacts reversibly with acid



The monoprotonated complex was also characterised crystallographically (25); it seems likely that the complex is protonated upon the aryl ring, although this proton was not located in the crystallographic study. It was noted that one of the aryl Ir-C contacts was considerably longer than the other two. The reactions of complex $[\text{L}(\text{IrMe}_2(\text{dmsO}))]$ ($\text{HL} = \text{C}_5\text{HMe}_5$) have been discussed in Section 5.2 [6].

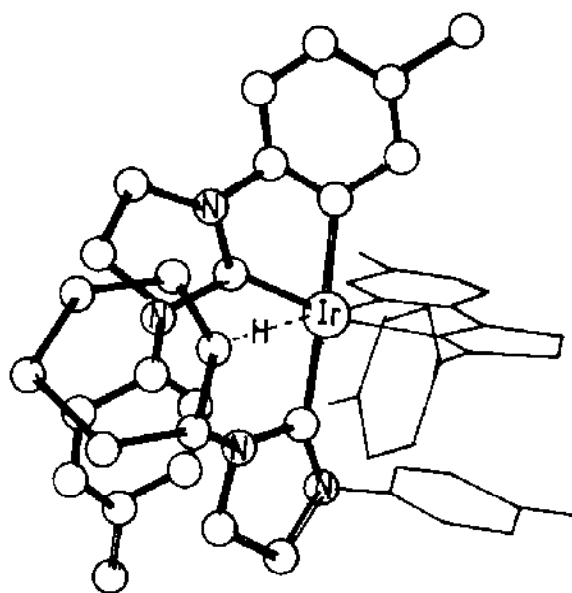


(24)

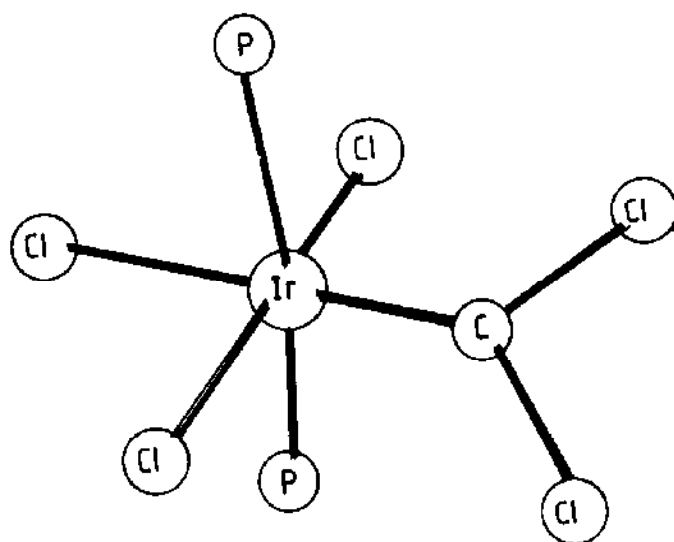
The reaction of bis(trichloromethyl)mercury(II) with $[\text{IrHCl}_2(\text{PPh}_3)_3]$ in toluene leads to the dichlorocarbene complex $[\text{Ir}(\text{CCl}_2)\text{Cl}_3(\text{PPh}_3)_2]$ [63]. This product was characterised crystallographically (26), and shown to be an octahedral iridium(III) complex. A number of reactions of this complex were described (Scheme 7); these are of particular interest as they show the versatility of reactions exhibited by a coordinated carbene [63].

The salt $[\text{IrH}_2(\text{CO})_2(\text{PPh}_3)_2][\text{BPh}_4]$ is remarkably stable; it shows no reaction upon treatment with BCl_3 at -90°C or with AlBr_3 at room temperature [65]. There was no spectroscopic evidence for attack of these Lewis acids upon the coordinated carbonyl. With an excess of aluminium bromide, gross decomposition of the complex cation occurred.

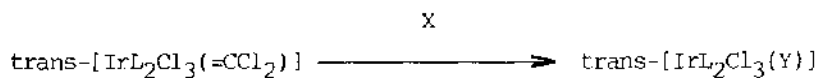
The complex $[(\text{LiIrCl}_2)_2]$ ($\text{HL} = \text{C}_5\text{HMe}_5$) reacts with triphenylphosphine followed by lithium triethylborohydride to give $[\text{LiIr}(\text{PPh}_3)_2\text{H}_2]$ [68]. This



(25)



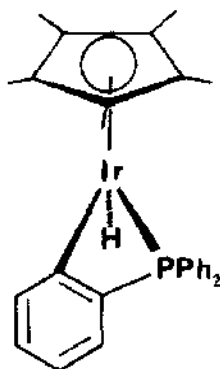
(26)



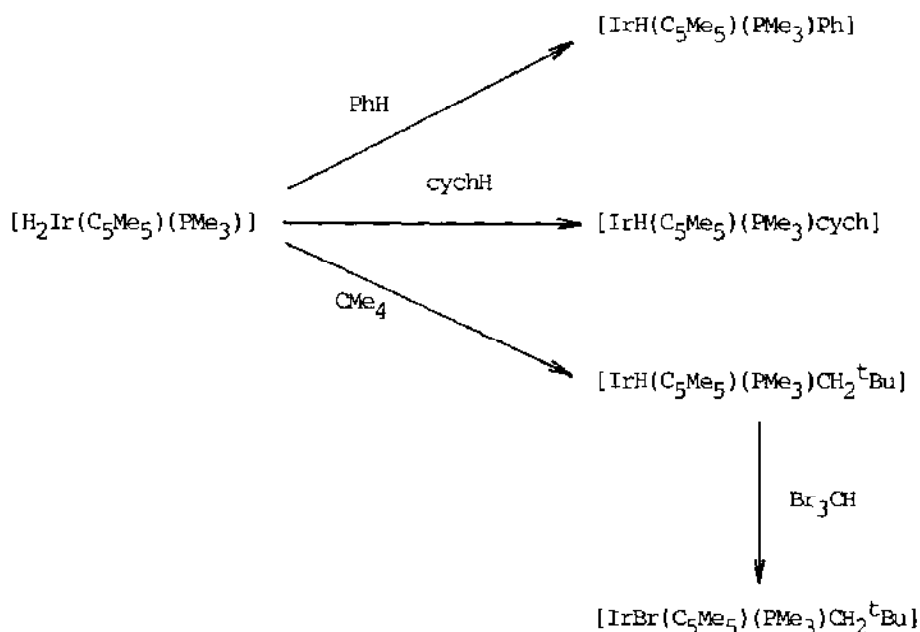
X	Y
H ₂ X	CX
MeNH ₂	CNMe
en	=C(NHCH ₂ CH ₂ NH)
Me ₂ NH	=CClNMe ₂
HSC ₂ H ₄ SH	=C(SCH ₂ CH ₂ S)

Scheme 7

complex undergoes a clean photolytic reaction with benzene to form [LIr(PPh₃)H(Ph)] and the cyclometallated compound (27). The same sequence of reactions occurred with trimethylphosphine, with the exception that the cyclometallated complex was not formed. A number of interesting reactions of [LIr(PMe₃)H₂] (IL = C₅HMe₅) were described (Scheme 8).



(27)



Scheme 8

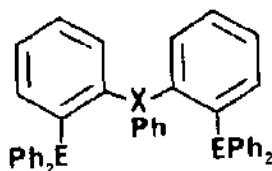
Other iridium(III) complexes with carbon ligands will be found in sections dealing with the oxidative addition of various species to iridium(I) complexes.

The reaction of $\text{H}_3[\text{Ir}(\text{Sn}(\text{OH})_3)_5\text{Cl}]$ with tin(II) chloride in hydrofluoric acid, followed by treatment with potassium ions, led to the isolation of the salt $\text{K}_3[\text{Ir}(\text{SnF}_3)_6]$ [60].

The treatment of Vaska's complex with tin(II) chloride results in the formation of a mixture of the isomers of $[\text{IrCl}(\text{CO})(\text{SnCl}_2)(\text{PPh}_3)_2]$; treatment with hydrogen chloride leads to the formation of the iridium(III) compound $[\text{IrHCl}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2]$. Detailed NMR studies of this complex have been reported. Reaction of Vaska's complex with tin(II) chloride followed by the addition of molecular hydrogen leads to the formation of *cis*- $[\text{IrH}_2(\text{CO})(\text{SnCl}_3)(\text{PPh}_3)_2]$. Similar reactions were shown with derivatives of Vaska's complex containing substituted phosphine ligands [61].

5.4.5 *Complexes with hydride ligands*

Many examples of this class of complexes will be found in the previous sections. The reactions of $[\text{IrHX}_2(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}$ or Br) with the potentially terdentate ligands **28** ($\text{E} = \text{X} = \text{P}$; $\text{E} = \text{X} = \text{As}$; $\text{E} = \text{As}$, $\text{X} = \text{P}$; $\text{E} = \text{P}$, $\text{X} = \text{As}$) have been described [66]. The isolated products included $[\text{IrHCl}_2\text{L}]$ ($\text{L} = \text{28}$, $\text{E} = \text{X} = \text{P}$; $\text{E} = \text{As}$, $\text{X} = \text{P}$; $\text{E} = \text{P}$, $\text{X} = \text{As}$; $\text{E} = \text{X} = \text{As}$), $[\text{IrHBr}_2\text{L}]$ ($\text{L} = \text{28}$, $\text{E} = \text{X} = \text{P}$; $\text{E} = \text{As}$, $\text{X} = \text{P}$; $\text{E} = \text{P}$, $\text{X} = \text{As}$) and $[\text{IrBr}_3\text{L}]$ ($\text{L} = \text{28}$, $\text{X} = \text{E} = \text{As}$). The terdentate nature of the ligand was confirmed by ^1H NMR and ^{31}P NMR spectroscopic studies of the complexes; it was suggested that the preferred conformers of the complexes were the meridional isomers.



(28)

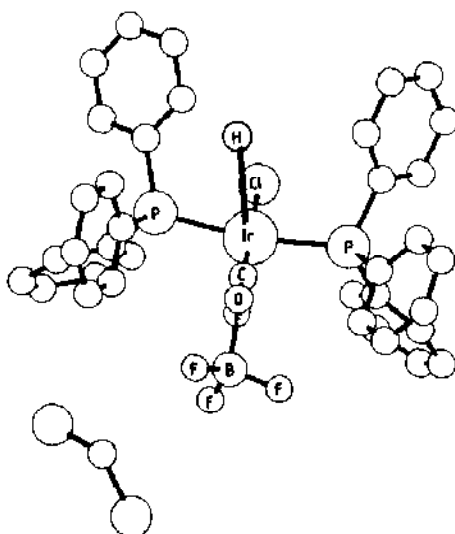
Beck has reported a study of the trans influence of various ligands in a series of neutral and cationic iridium(III) trans- $[\text{IrHL}(\text{CO})\text{Cl}(\text{PPh}_3)_2]^{n+}$ ($n = 0$, $\text{L} = \text{FBF}_3$, $\text{OSO}_2\text{C}_4\text{F}_9$, OSO_2CF_3 , NCSe , Cl , or SeCN ; $n = 1$, $\text{L} = \text{OC}_4\text{H}_8$, OC_3H_6 , OH_2 , NCCH_3 , CNcyc , or PPh_3) [67]. It was shown that the ^1H NMR chemical shift of the hydride ligand depended upon the nature of the trans ligand; if the trans ligand was an oxygen donor, $\delta = -21.6 \pm 0.6$ p.p.m., whereas if it was a nitrogen donor, $\delta = -16.5 \pm 0.5$ p.p.m.. Surprisingly, the chemical shift of the hydride was independent of the charge on the complex. Direct correlations were established between the hydride chemical shift, the Ir-H stretching frequency, and the electronegativity of the trans donor atom. No correlation existed between the hydride chemical shift or the Ir-H stretching frequency, and the C-O stretching frequency of the coordinated carbonyl.

5.5 IRIDIUM(II)

5.6 IRIDIUM(I)

5.6.1 Complexes with halides

A review dealing with the thermochemistry of oxidative addition reactions has appeared. This is of particular relevance to the oxidative addition reactions of the well-known Vaska's type compounds, $\text{trans-}[\text{IrX}(\text{CO})\text{L}_2]$ and $\text{trans-}[\text{IrXL}'\text{L}_2]$, and numerous data concerning these complexes have been tabulated [70]. The reactions of weakly coordinating acids (tetrafluoroboric, perfluorobutanesulphonic and trifluoromethylsulphonic) with Vaska's compound have been investigated [71]. The products are the octahedral species $[\text{IrHCl}(\text{CO})(\text{PPh}_3)_2\text{X}]$ ($\text{X} = \text{F}_3\text{BF}$, $\text{OSO}_2\text{C}_4\text{F}_9$ or OSO_2CF_3), in which the anion is weakly coordinated, and readily displaced by weak nucleophiles to produce $[\text{IrHCl}(\text{CO})(\text{PPh}_3)_2\text{L}]^+$ ($\text{L} = \text{PPh}_3$, MeCN , H_2O , Me_2CO , thf or $\text{H}_2\text{C}=\text{CH}_2$). The presence of the weakly coordinated anion was confirmed by an X-ray structural analysis of the complex $[\text{IrHCl}(\text{CO})(\text{PPh}_3)_2(\text{F}_3\text{BF})]$ (29). Similar complexes were obtained from the reaction of $[\text{IrHCl}(\text{CO})(\text{PPh}_3)_2]$ with $[\text{Me}_3\text{O}][\text{BF}_4]$ to give $[\text{Ir}(\text{Me})\text{Cl}(\text{CO})(\text{PPh}_3)_2(\text{F}_3\text{BF})]$.



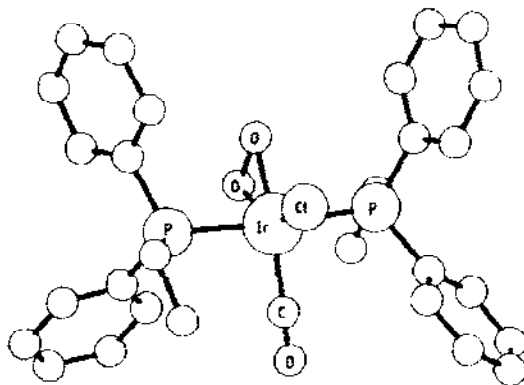
(29)

Other reactions of Vaska's compound and related derivatives will be found in other sections of this review.

5.6.2 Complexes with Group VI donor ligands

5.6.2.1 Complexes with oxygen donor ligands

The Vaska's type complex, $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_2\text{Et})_2]$ is readily prepared by the reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with diphenylethylphosphine in dmf [72]. The compound reacts readily with dioxygen in benzene solution to give $[\text{Ir}(\text{O}_2)(\text{CO})\text{Cl}(\text{PPh}_2\text{Et})_2]$. An X-ray structural analysis of this complex has been reported (30); a pseudo-octahedral geometry is adopted, with a side-on dioxygen ligand [72].

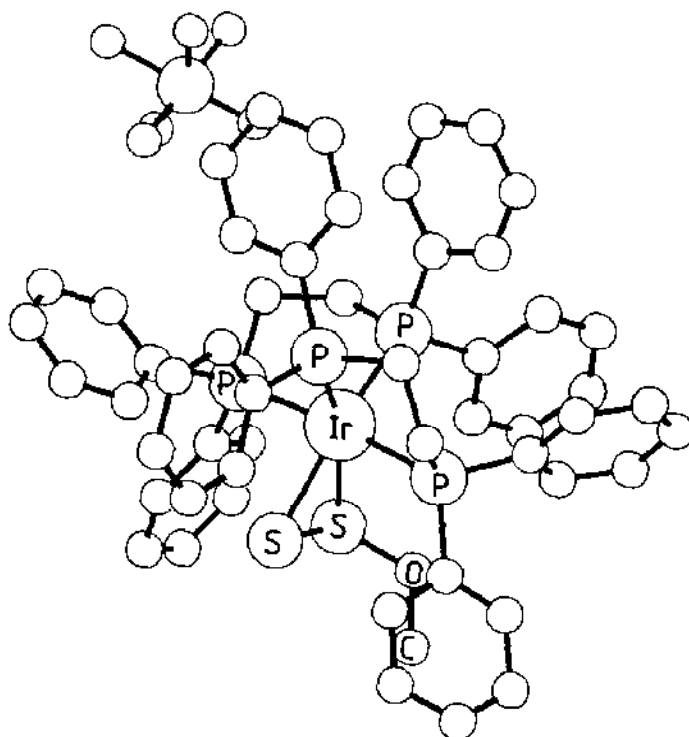


(30)

5.6.2.2 Complexes with sulphur and selenium donor ligands

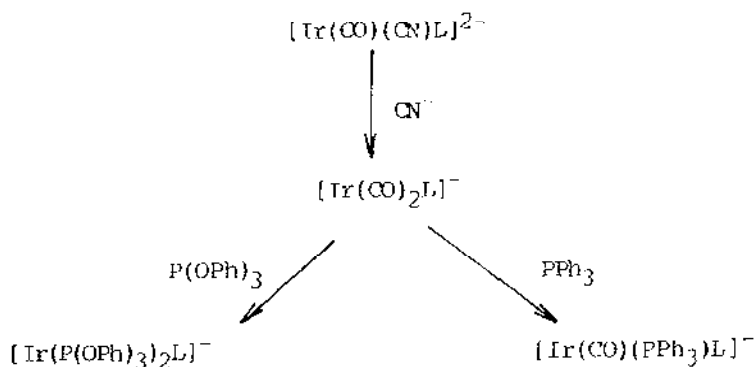
The first examples of transition metal thiosulphinato and thiosulphenate esters have been described. The reaction of $[\text{Ir}(\text{dppe})_2(\text{S}_2)]^+$ with meta-chloroperbenzoic acid results in the formation of the disulphur monoxide complex cation $[\text{Ir}(\text{dppe})_2(\text{S}_2\text{O})]^+$; the latter complex contains a bidentate chelating S_2 donor disulphur monoxide ligand [73]. Treatment of this with methyl fluorosulphonate results in O-alkylation, yielding

$[\text{Ir}(\text{dppe})_2(\text{S}_2\text{OMe})]^{2+}$, which has been structurally characterised (31). This iridium(III) complex possesses a bidentate MeOS_2^- ligand. Reaction with tert-butyl isocyanide gives the neutral complex $[\text{Ir}(\text{dppe})_2(\text{SOMe})(\text{CNMe})]$ and methyl thiocyanate.



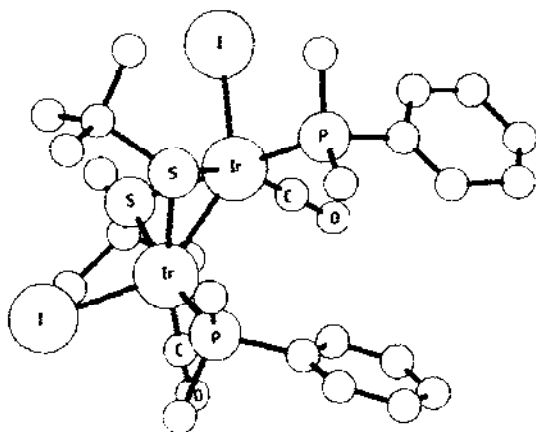
(31)

A number of luminescent dicyanodithiolate complexes of iridium(I) have been described [74]. The reaction of $[\text{Ir}(\text{CO})_2\text{Br}_2]^-$ with L^{2-} ($\text{H}_2\text{L} = \text{HS}(\text{NC})\text{C}=\text{C}(\text{CN})\text{SH}$) results in the formation of $[\text{Ir}(\text{CO})_2\text{L}]^-$. This anion undergoes a number of useful reactions (Scheme 9). The complexes are strongly luminescent in the solid state at room temperature and in frozen glassy solution.



Scheme 9

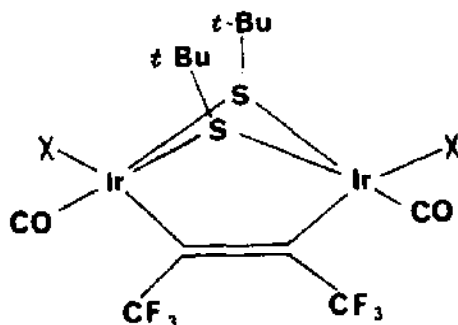
The reactions of the mercapto bridged diiridium complexes $[(\text{CO})\text{LIr}(\mu\text{-S}^t\text{Bu})_2\text{Ir}(\text{CO})\text{L}]$ ($\text{L} = \text{CO}$ or PR_3) have been investigated [75]. The reaction with iodine gives $[(\text{CO})\text{LIr}(\mu\text{-S}^t\text{Bu})_2\text{IrI}(\text{CO})\text{L}]$ ($\text{L} = \text{CO}$, P(OMe)_3 , PMe_2Ph or PMe_3). Similar reactions with other halogens have resulted in the isolation of the complexes $[(\text{CO})\text{LX}_2\text{Ir}(\mu\text{-S}^t\text{Bu})\text{IrX}_2\text{L}(\text{CO})]$ ($\text{L} = \text{CO}$, $\text{X} = \text{Br}$; $\text{L} = \text{P(OMe)}_3$, $\text{X} = \text{I}$, Br or Cl ; $\text{L} = \text{PMe}_3$, $\text{X} = \text{I}$). An X-ray structural analysis of the complex $[(\text{CO})(\text{PPhMe}_2)\text{IIr}(\mu\text{-S}^t\text{Bu})\text{IrI}(\text{PPhMe}_2)(\text{CO})]$ has been reported (32).



(32)

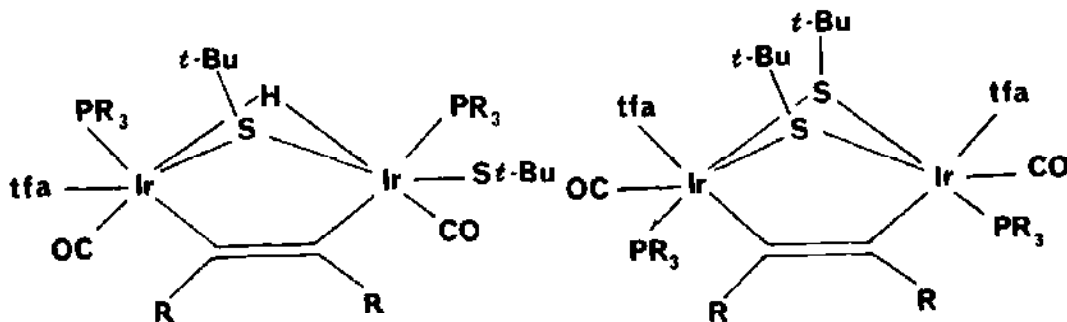
These mercapto-bridged complexes are of interest as they react with electron-deficient alkynes to form tris bridged complexes of the type

$[(\text{CO})(\text{PR}_3)\text{Ir}(\mu\text{-S}^t\text{Bu})_2(\mu\text{-RC=CR})\text{Ir}(\text{CO})(\text{PR}_3)]$ (33); both cis and trans arrangements of the phosphine and carbonyl ligands are observed [76]. These various isomers are in equilibrium via a Berry pseudo rotation process. The protonation reactions of these complexes have been studied.



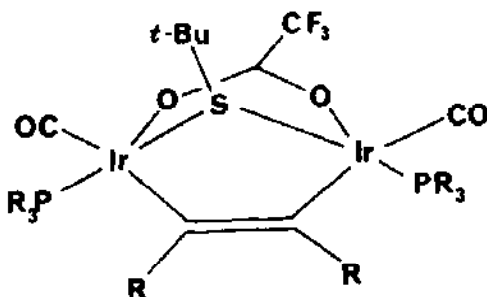
(33)

In no case, was protonation of the coordinated organic ligand noted. Typical products included the trifluoroacetate complexes (34-36).



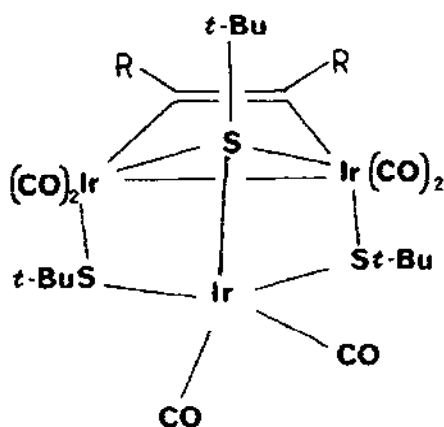
(34)

(35)

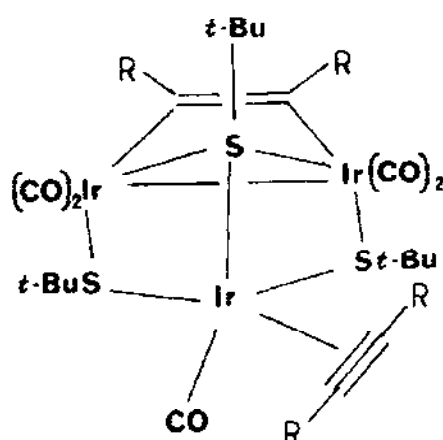


(36)

Related trimetallic complexes are known. The electrochemical behaviour of the complexes (37) ($R = CF_3$ or CO_2Me) and (38) ($R = CF_3$) has been investigated [77]. The complexes undergo irreversible one-electron oxidations and reductions. The corresponding electrochemical behaviour of the bimetallic complexes has also been studied.



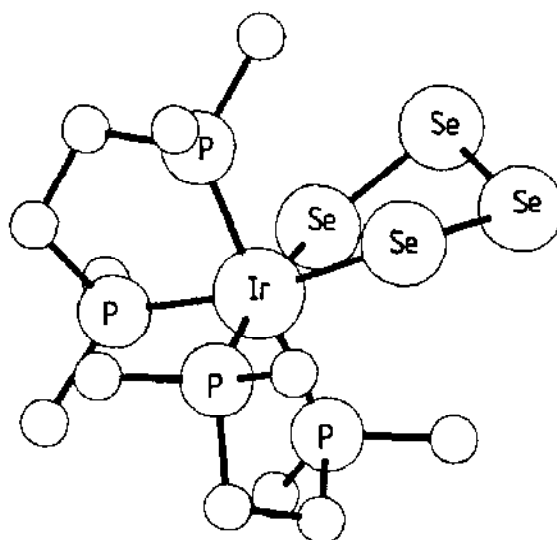
(37)



(38)

Octaselenium reacts readily with $[Ir(dmpe)_2]Cl$ to form the deep purple complexes $[Ir(Se_2)(dmpe)_2]Cl$ and $[Ir(Se_4)(dmpe)_2]Cl$ [78]. The latter complex was converted to $[Ir(Se_2)(dmpe)_2]Cl$ upon reaction with triphenylphosphine. SCF- X_α -SW calculations were carried out on $[Ir(Se_4)(PMe_3)_2]^+$ as a model for the tetraselenium complex. The crystal structure of $[Ir(Se_4)(dmpe)_2]Cl$ was reported (39); the $IrSe_4$ ring forms a half-chair configuration analogous to that of the cyclopentane ring. The diselenium compound contains a side-on bonded diselenium moiety. The calculations upon the tetraselenium complex indicated that the $Ir-Se_4$ bonding occurs mainly by overlap of the metal 5d and 6p orbitals with the ligand 4p orbitals.

The complexes $[Ir(dppe)_2(E_2R)]^{2+}$ ($E = S$ or Se , $R = H$ or Me) have been investigated by Rauchfuss [79]. The complexes were prepared by the protonation or methylation of $[Ir(E_2)(dppe)_2]^+$ ($E = S$ or Se). 1H NMR spectroscopy indicated the presence of the diastereomers of the methylated complexes. $[Ir(S_2Me)(dppe)_2]^{2+}$ reacts with dimethylphenylphosphine to give $[Ir(dppe)_2]^{2+}$, $Me_2PhP=S$ and $Me_2PhPSMe^+$. Similar reactions occurred with triphenylphosphine.



(39)

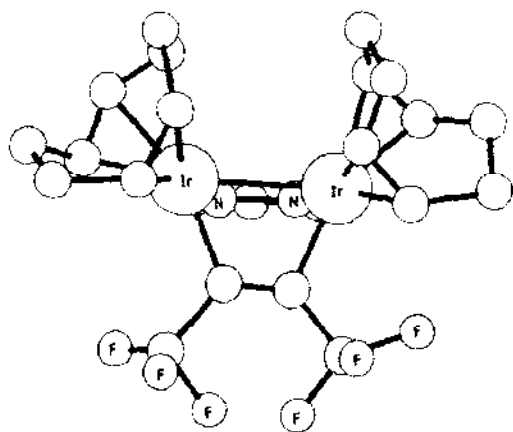
Other reactions with MeNC and CN^- , were reported, the products being $\text{cis-}[\text{Ir}(\text{SMe})(\text{MeNC})(\text{dppe})_2]^{2+}$ and MeNCS or $\text{cis-}[\text{Ir}(\text{SMe})(\text{SCN})(\text{dppe})_2]^+$ respectively. Oxidative addition of MeSH or MeSCl to $[\text{Ir}(\text{dppe})_2]^+$ gave the complexes $[\text{Ir}(\text{SMe})\text{H}(\text{dppe})_2]^+$ or $[\text{Ir}(\text{SMe})\text{Cl}(\text{dppe})_2]^+$ respectively.

5.6.3 Complexes with Group V donor ligands

5.6.3.1 Complexes with nitrogen donor ligands

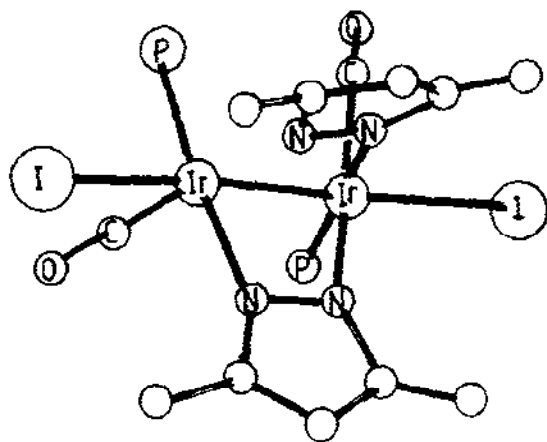
The complex $[(\text{cod})\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{cod})]$ (HL = 3,5-bis(trifluoromethyl)pyrazole) does not react with electrophiles such as iodine, $\text{MeO}_2\text{CCCCO}_2\text{Me}$ or iodomethane, but reacts with hexafluorobut-2-yne to yield $[(\text{cod})\text{Ir}(\mu\text{-L})(\mu\text{-F}_3\text{CC}\equiv\text{CCF}_3)(\text{cod})]$; the latter complex has been characterised by a single crystal X-ray analysis (40) [80]. One of the cyclooctadiene ligands adopts the expected η^2, η^2 mode, whereas the other is in the η^2, η^3 mode.

The carbonyl analogues of these materials, $[(\text{CO})_2\text{Ir}(\mu\text{-L})_2\text{Ir}(\text{CO})_2]$ (HL = 3,5-dimethylpyrazole) react with tertiary phosphines, arsines or phosphites to give the complexes $\text{trans-}[(\text{CO})\text{IrL}'(\mu\text{-L})_2\text{IrL}'(\text{CO})]$ (L = 3,5-dimethylpyrazole,



(40)

$L' = \text{PhMe}_2\text{P}, \text{Ph}_2\text{MeP}, (\text{PhO})_3\text{P}$ or PhMe_2As . These complexes react with iodine or with 1,2-diiodoethane to yield $[(\text{CO})\text{IL}'\text{Ir}(\mu\text{-L})_2\text{IrL}'\text{I}(\text{CO})]$. A crystal structural analysis of the complex $[(\text{CO})\text{IL}'\text{Ir}(\mu\text{-L})_2\text{IrL}'\text{I}(\text{CO})]$ ($L' = (\text{PhO})_3\text{P}$) has been described; the linear I-Ir-Ir-I arrangement is of note (41) [81].

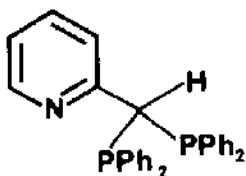


(41)

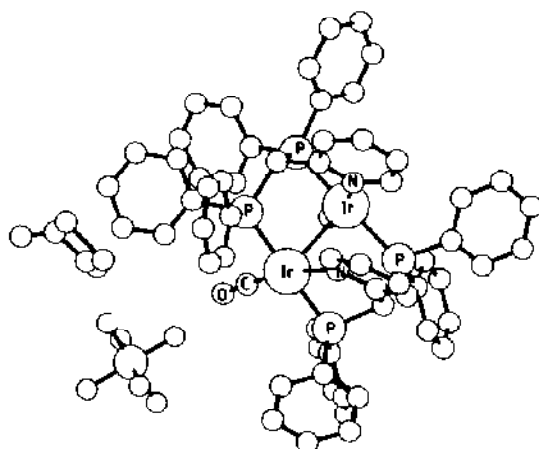
The reaction of $[(\text{Ir}(\text{coe})_2\text{Cl})_2]$ with $(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)_2\text{NLi}$ in toluene results in the formation of $[\text{Ir}(\text{coe})\text{L}]$ ($\text{HL} = \text{HN}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$, $\text{coe} = \text{cyclooctene}$), in which the ligand acts a terdentate N,P,P donor in the square-planar complex. Further reaction with other monodentate ligands results in the formation of $[\text{IrLL}']$ ($\text{HL} = \text{HN}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$ [82]. A related reaction of $[(\text{Ir}(\text{cod})\text{Cl})_2]$

with $\text{LiN}(\text{CH}_2\text{Ph})(\text{SiMe}_2\text{CH}_2\text{PPh}_2)$ leads to the formation of $[\text{Ir}(\text{cod})\text{L}]$ ($\text{HL} = \text{HN}(\text{CH}_2\text{Ph})(\text{SiMe}_2\text{CH}_2\text{PPh}_2)$).

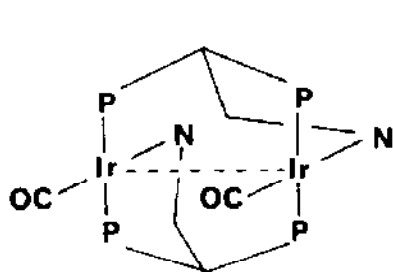
The chemistry of the mixed hard-soft donor ligand 2-(bis(diphenylphosphinomethyl))pyridine (**L**) (**42**) has been investigated [83]. The reaction of $[\text{Ir}(\text{cod})\text{Cl}]_2$ with **L** in the presence of silver(I) tetrafluoroborate leads to the formation of the complex $[\text{Ir}(\text{cod})(\text{L})][\text{BF}_4]$; the latter compound reacting with carbon monoxide to form the cation $[\text{Ir}_2(\text{CO})_2(\mu\text{-CO})\text{L}_2]^{2+}$, which has been characterised crystallographically (**43**). This complex readily loses the bridging carbonyl group to form $[\text{Ir}_2(\text{CO})_2\text{L}_2]^{2+}$ (**44**), which reacts with iodide to form $[\text{Ir}_2(\text{CO})_2\text{L}_2\text{I}]^+$ (**45**) possessing a dangling pyridyl ligand.



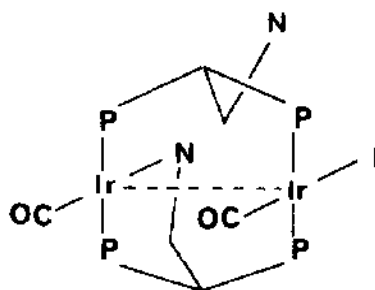
(42)



(43)



(44)



(45)

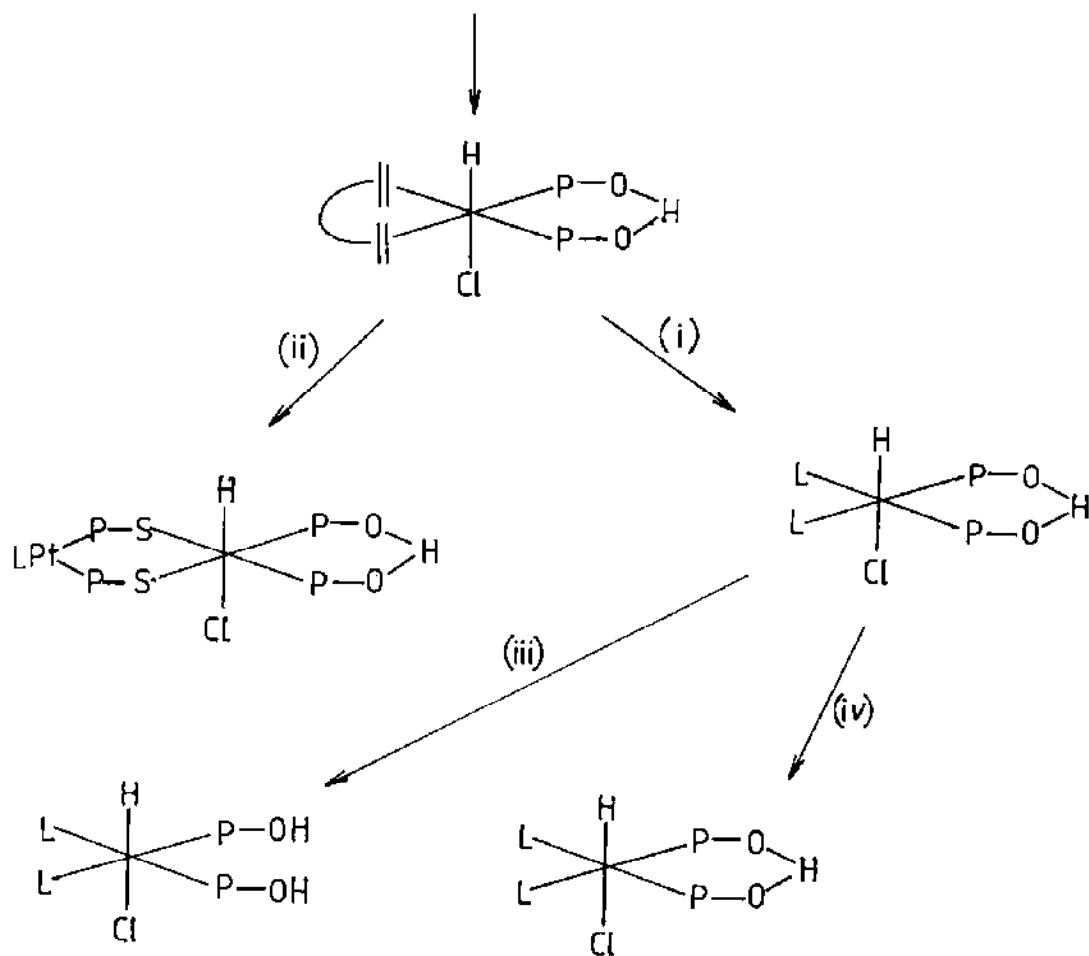
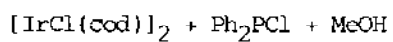
5.6.3.2 Complexes with phosphorus and arsenic donor ligands

A number of analogues of Vaska's compound have been described in the recent literature. The reaction of iridium(III) chloride trihydrate with tri-*tert*-butylphosphine in dmf leads to the formation of *trans*-[Ir(CO)Cl(*t*Bu₂PH)₂] and isobutene in near quantitative yield [84]. The related complex [Ir(CO)Cl(PhMe₂P)₂] is readily prepared by a transligation reaction of Vaska's compound with phenyldimethylphosphine [85].

The reaction of [Ir(CO)Cl(PET₃)₂] with phosphorus trichloride results in the formation of [Ir(CO)Cl₂(PET₃)₂(PCl₂)], which may be oxidised by chlorine gas to give [Ir(CO)Cl₂(PET₃)₂(PCl₄)] [87]. These complexes were investigated by ³¹P NMR spectroscopy. The unusual five-coordinate phosphorus complex reacts with triethylphosphine to reform the starting complex.

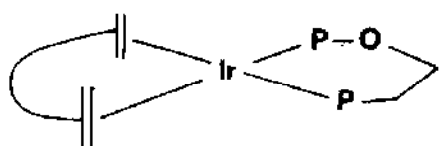
A solution of diphenylchlorophosphine in methanol reacts with [(Ir(cod)Cl)₂] to give a complex with a six-membered hydrogen bonded IrP₂O₂H ring (46) [88]. The reactions of this novel complex have been investigated (Scheme 10); the cyclooctadiene is readily displaced by other bidentate ligands such as dppe, Ph₂AsCH₂CH₂AsPh₂ or PhSCH₂CH₂SPh. After reaction with boron trifluoride etherate or with fluoroboric acid, a novel boracycle was obtained. Treatment of 46 with [Et₂NH₂][Pt(S₂CNEt₂)(Ph₂PS)] leads to the interesting binuclear polycyclic complex 47 [88]. Similar reactions were observed with [Ir(MeCN)(CO)(PPh₃)₂][ClO₄].

The square-planar complex cation [Ir(cod)L]⁺ (L = Ph₂PCH₂CH₂OPPh₂) (48) reacts with hydrogen in a stereospecific reaction to produce only isomer 49 [89]. The starting material is prepared by the reaction of [(Ir(cod)Cl)₂] with L in the presence of silver(I) tetrafluoroborate; comments upon the stereospecificity of the reaction were made.

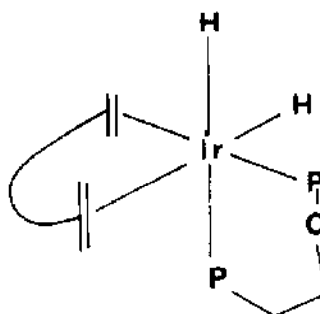


- (i) L_2 (dppe, dpae or $\text{PhSC}_2\text{H}_4\text{SPh}$)
 (ii) $[\text{Et}_2\text{NH}_2][\text{PtL}(\text{Ph}_2\text{PS})_2]$, HL = $\text{Et}_2\text{NCS}_2\text{H}$
 (iii) HBF_4
 (iv) $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Scheme 10



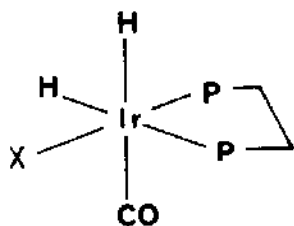
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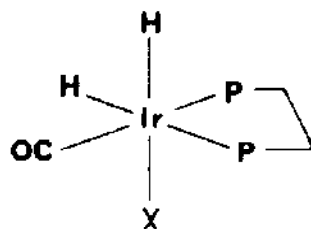
(49)

$[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ reacts with lithium diphenylphosphide to form $\{[\text{Ir}(\eta\text{-PPh}_2)(\text{CO})(\text{PPh}_3)_2]_2\}$; an analogous reaction occurs with $[\text{Ir}(\text{cod})\text{Cl}]_2$ to give $\{[\text{Ir}(\eta\text{-PPh}_2)(\text{cod})]_2\}$, the latter being demonstrated not to react with carbon monoxide or diphenylphosphinopropane [90].

The addition of dihydrogen to iridium(I) complexes is of obvious relevance to the homogeneous hydrogenation of alkenes and alkynes using iridium catalysts. Harrod has reported some interesting observations upon the stereochemistry of hydrogen addition [91]. The reaction of $[\text{Ir}(\text{CO})\text{H}_3(\text{PPh}_3)_2]$ with styrene results in the formation of $[\text{IrH}(\pi\text{-H}_2\text{C=CHPh})(\text{CO})(\text{PPh}_3)_2]$; close to 0°C the complex was shown to be in equilibrium with a square-planar species $[\text{IrH}(\text{CO})(\text{PPh}_3)_2]$ and free styrene. Detailed NMR studies of the products resulting from the addition of dihydrogen and dideuterium to the complex provided support for the author's contention that a square-planar intermediate is important in the reaction. Eisenberg has studied the addition of dihydrogen to the Vaska's compound analogues, $[\text{Ir}(\text{CO})\text{X}(\text{dppe})]$, to yield $[\text{IrH}_2(\text{CO})\text{X}(\text{dppe})]$ [92]. Two isomeric products (50 and 51) were obtained from the reaction; 51 is the initial kinetic product which rearranges to the thermodynamic product 50.

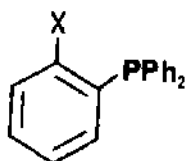


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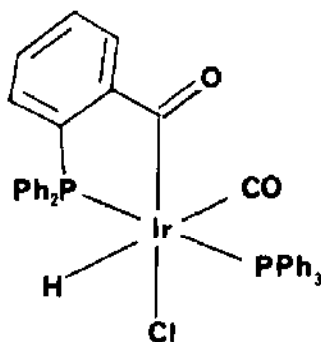


(51)

A detailed study of the oxidative addition of PhX (X = CHO or COOH) and the substituted phosphine 52 (X = CHO or COOH) to $\text{trans-}[\text{Ir}(\text{CO})\text{Cl}(\text{EPh}_3)_2]$ (E = P or As) has been reported [93]. The potentially chelating ligands give stable acyl hydrides (53).



(52)

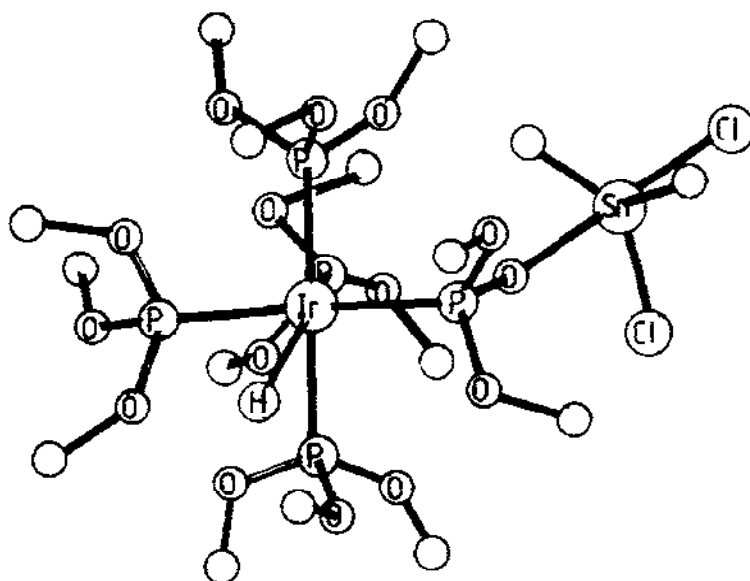


(53)

The addition of dihydrogen to $[\text{IrL}_2]^+$ (L = $\text{ArPhPCH}_2\text{CH}_2\text{PPhAr}$; Ar = 2-methoxyphenyl) has been investigated; both cis and trans dihydrides are formed [94].

The novel complex $[\text{IrP}(\text{O})(\text{OMe})_2\{\text{P}(\text{OMe})_3\}_4]$ is formed either by the reaction of $[\text{IrL}(\text{H}_2\text{C}=\text{CH}_2)_2]$ (HL = indene) or by the reaction of $[\text{IrCl}\{\text{P}(\text{OMe})_3\}_5]$ with sodium in ether, or with acetone. The complex is fluxional at room temperature, and slowly adds dihydrogen to form cis- $[\text{IrH}_2\text{P}(\text{O})(\text{OMe})_2\{\text{P}(\text{OMe})_3\}_3]$ [95]. Reactions with iodomethane or HX to give $[\text{Ir}\{\text{P}(\text{OMe})_3\}_5]\text{I}$ or $[\text{IrHP}(\text{O})(\text{OMe})_2\{\text{P}(\text{OMe})_3\}_4]\text{X}$ respectively. The reaction with $[\text{Me}_2\text{SnCl}_2]$ in thf with the complex results in the formation of the unusual five-coordinate tin O-metallated derivative $[\text{Ir}\{\text{P}(\text{OMe})_3\}_4\text{HP}(\text{OMe})_2\text{OSnCl}_2\text{Me}_2][\text{SnCl}_3\text{Me}_2]$ (54) which was characterised crystallographically.

The complexes $[\text{IrL}(\text{CO})\text{Cl}]$ (L = 8-diphenylphosphinoquinoline or 8-aminoquinoline) are readily prepared by the reaction of L with $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$ [59].



(54)

5.6.4 Complexes with Group IV ligands

5.6.4.1 Complexes with carbon donor ligands

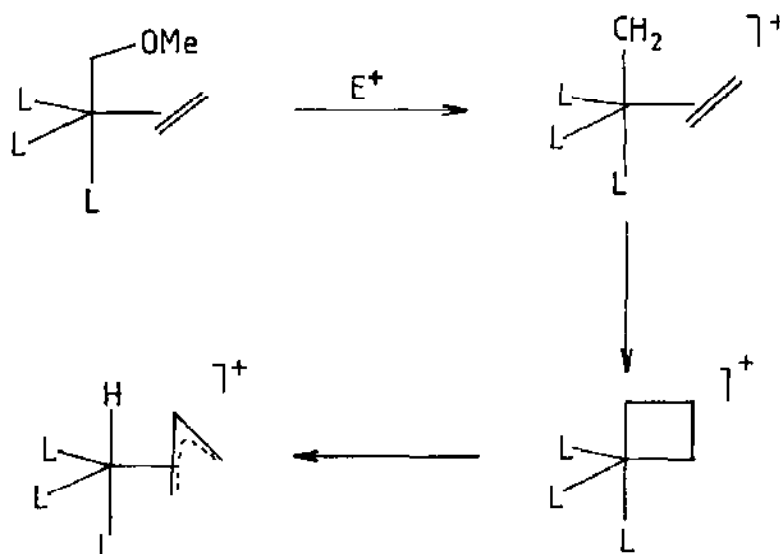
Reliable synthetic routes to some iridium carbon dioxide complexes have been published. The reaction of $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ (coe = cyclooctene) with dmpe in toluene results in the formation of $[\text{Ir}(\text{dmpe})_2\text{Cl}]$ (75%), which cleanly adds carbon dioxide to give $[\text{Ir}(\text{dmpe})_2(\text{CO}_2)]\text{Cl}$ [96]. The complex $[\text{Ir}(\text{PMe}_3)_3\text{Cl}(\text{C}(\text{=O})\text{OC}(\text{=O})\text{O})]$ is prepared by the reaction of carbon dioxide with either $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ or $[\text{IrCl}(\text{coe})(\text{PMe}_3)_3]$ (coe = cyclooctene) [97].

A large number of organometallic analogues of Vaska's compound $[\text{Ir}(\text{CO})\text{R}(\text{PR}_3)_2]$ (R = various) have been reported; particular interest has centred upon those complexes in which the alkyl group is further functionalised. Simple alkyl derivatives, $[\text{Ir}(\text{CO})\text{R}(\text{PPh}_3)_2]$ (R = CH_3 , PhCH_2 , Me_3SiCH_2 or Me_3CCH_2) are prepared by the reaction of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ with the appropriate alkyl lithium; mixtures of the cis and trans isomers of these complexes are formed [98].

Electrochemical reduction of $[\text{IrClI}(\text{CH}_2\text{CN})\text{CO}(\text{PPh}_3)_2]$ in acetonitrile results in the formation of the cyanomethyl analogue of Vaska's compound, $[\text{Ir}(\text{CO})(\text{CH}_2\text{CN})(\text{PPh}_3)_2]$ [99]. The product was shown to possess the trans

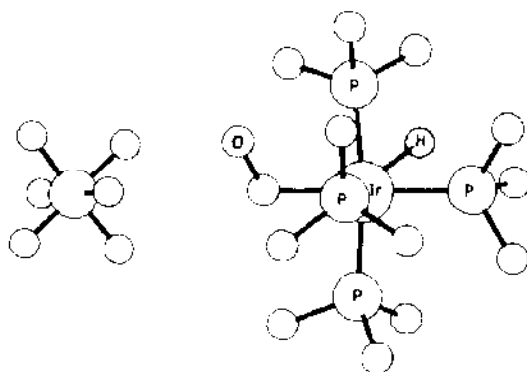
configuration by a range of spectroscopic techniques. Reaction with carbon monoxide led, not to insertion into the Ir-C bond, but to the formation of the five-coordinated cocomplex $[\text{Ir}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}_2\text{CN})]$, in which the two phosphine ligands occupy the axial sites. The compound undergoes all the reactions expected from an analogue of Vaska's complex. Oxidative additions of dioxygen, acids in acetonitrile, iodomethane or dihydrogen occurred to yield $[\text{Ir}(\text{O}_2)(\text{CO})(\text{CH}_2\text{CN})(\text{PPh}_3)_2]$, $[\text{Ir}(\text{MeCN})\text{H}(\text{CO})(\text{CH}_2\text{CN})(\text{PPh}_3)_2]^+$, $[\text{IrIme}(\text{CO})(\text{CH}_2\text{CN})(\text{PPh}_3)_2]$ or $[\text{IrH}_2(\text{CO})(\text{CH}_2\text{CN})(\text{PPh}_3)_2]$ respectively. Two isomers of the dihydrido complex were isolated, which were shown to interconvert thermally.

Dihydrogen reacts with $[\text{Ir}(\text{PMe}_3)_4]\text{Cl}$ to form the octahedral iridium(III) complex $[\text{IrH}_2(\text{PMe}_3)_4]\text{Cl}$, which is deprotonated to the neutral complex $[\text{IrH}(\text{PMe}_3)_4]$ by potassium tert-butoxide [100]. Treatment of this complex with BrCH_2OMe leads to the formation of $[\text{IrH}(\text{CH}_2\text{OMe})(\text{PMe}_3)_4]\text{Br}$, which is deprotonated (again by potassium tert-butoxide) to yield $[\text{Ir}(\text{CH}_2\text{OMe})(\text{PMe}_3)_4]$. The reactivity of this compound with alkenes has been investigated. Displacement of one phosphine by ethylene is facile, to give $[\text{Ir}(\text{H}_2\text{C}=\text{CH}_2)(\text{PMe}_3)_3]$. This ethylene complex reacts with electrophiles to give isomers of $[\text{Ir}(\text{PMe}_3)_3\text{H}(\eta^3-\text{C}_3\text{H}_6)]^+$ (Scheme 11).



Scheme 11

The related complex $[\text{Ir}(\text{PMe}_3)_4\text{H}(\text{CH}_2\text{OSiMe}_3)]\text{I}$ is prepared by analogous routes [101]. Treatment with ammonium hydrogen fluoride resulted in the formation of the hydroxymethyl complex cation $[\text{Ir}(\text{PMe}_3)_4\text{H}(\text{CH}_2\text{OH})]^+$ (55), which is also prepared by the reaction of $[\text{Ir}(\text{PMe}_3)_4]^+$ with formaldehyde, followed by borohydride reduction. An X-ray crystal structural analysis of the hydroxymethyl complex was reported.

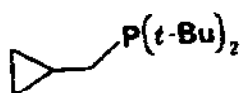


(55)

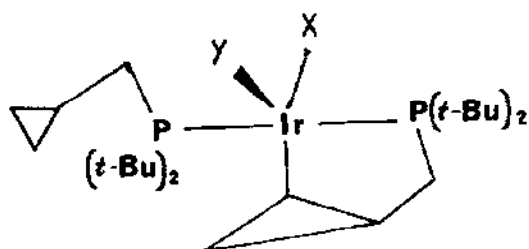
A number of methane activation reactions catalysed by iridium complexes have been described. Methane reacts with $[\text{IrL}(\text{CO})_2]$ ($\text{HL} = \text{C}_5\text{HMe}_5$) in dodecafluorocyclohexane under photochemical activation to give 20-25% of $[\text{IrL}(\text{CO})\text{HMe}]$, which reacts with tetrachloromethane to give $[\text{IrL}(\text{CO})\text{ClMe}]$ [102]. A comparable reaction with $[\text{Ir}(\text{cp})(\text{CO})_2]$ leads to the formation of $[\text{Ir}(\text{cp})(\text{CO})\text{HMe}]$, which is brominated with N-bromosuccinimide to form $[\text{Ir}(\text{cp})(\text{CO})\text{BrMe}]$ [102].

Cyclopropanes normally react with iridium(I) complexes to give iridium(III) alkyl hydrides, however, bis(tert-butylphosphinomethyl)cyclopropane (HL , 56) reacts with $[(\text{Ir}(\text{coe})_2\text{Cl})_2]$ ($\text{coe} = \text{cyclooctene}$) to form two diastereoisomers of the complex $[\text{IrHCl}(\text{HL})\text{L}]$ (57) [103]. This complex reacts with carbonyl sulphide or carbon disulphide leading to reductive elimination of the cyclopropane; carbon monoxide adds to form the six-coordinate complex $[\text{IrHCl}(\text{HL})\text{L}(\text{CO})]$. Reaction with dihydrogen gives the five coordinate complex $[\text{Ir}(\text{HL})_2\text{H}_2\text{Cl}]$, in which the phosphine ligands occupy the axial sites.

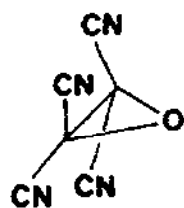
Tetracyanooxirane (58) reacts with Vaska's complex to form two isomers of the iridacyclobutane (59) ($\text{X} = \text{Cl}$, $\text{Y} = \text{CO}$; $\text{X} = \text{CO}$; $\text{Y} = \text{Cl}$) [104]. In contrast, the reaction of $[(\text{Ir}(\text{coe})_2\text{Cl})_2]$ with an excess of phenyloxirane in the presence of triphenylphosphine merely led to the formation of Vaska's compound.



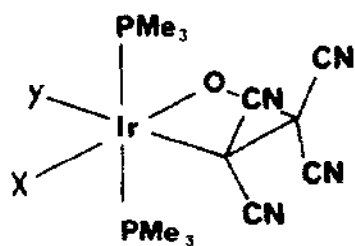
(56)



(57)

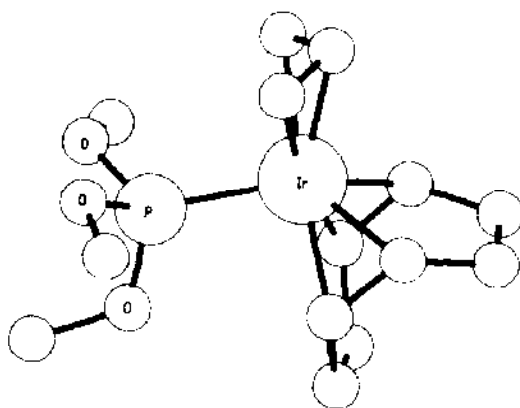


(58)



(59)

Allyllithium reacts with $[\text{Ir}(\text{cod})\text{Cl}]_2$ in the presence of $\text{P}(\text{OMe})_3$ to form in the formation of $[\text{L}(\text{Ir}\{\text{P}(\text{OMe})_3\}_3(\text{cod})] (\text{L} = \eta^3\text{-C}_3\text{H}_5)$ [105]. On heating in hexane with an excess of trimethylphosphite, an interconversion to an η^1 -allyl complex occurs $[\text{Ir}(\eta^1\text{-C}_3\text{H}_5)(\text{cod})\{\text{P}(\text{OMe})_3\}_2]$. In toluene, loss of the cod occurs, and the complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Ir}\{\text{P}(\text{OMe})_3\}_3]$ is formed, which reacts with dihydrogen to give $[\text{H}(\text{Ir}\{\text{P}(\text{OMe})_3\}_4)]$. None of these complexes were of any application as hydrogenation catalysts. A crystal structural analysis of $[(\eta^3\text{-C}_3\text{H}_5)\text{Ir}(\text{cod})\{\text{P}(\text{OMe})_3\}_3]$ (60) was reported.



(60)

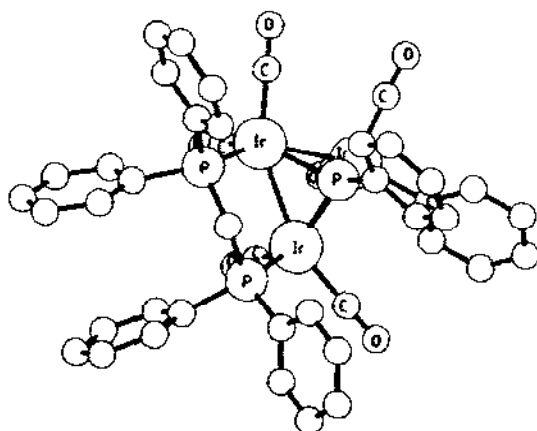
The reaction of pentadiene with $[\text{IrCl}(\text{coe})_2]_2$ in the presence of EPh_3 ($\text{E} = \text{As}, \text{Sb}$ or P) to give $\text{trans-}[\text{IrCl}(\text{C}_5\text{H}_8)\text{L}_2]$ ($\text{L} = \text{EPh}_3$) has been described [106]. Two isomers of this complex were isolated, and the unsaturated species $[\text{IrCl}(\text{coe})_2(\text{thf})]$ was proposed as an intermediate. A similar reaction occurred with cyclobutene to give a complex in which the cyclobutene ring was retained intact.

The reaction of $[\text{IrL}_2\text{Cl}]$ ($\text{L} = 2,3\text{-dimethylbutadiene}$) with silver(I) tetrafluoroborate results in the formation of $[\text{L}_2\text{Ir}][\text{BF}_4]$; this unsaturated species reacts with dmsO to form $[\text{Ir}(\text{dmsO})\text{L}_2]^+$ [107].

5.7 CLUSTER COMPOUNDS

5.7.1 Trinuclear clusters

The reaction of $(\text{Ph}_2\text{P})_3\text{CH}$ with $[\text{IrCl}(\text{CO})_2(\text{ArNH}_2)]$ (Ar = 4-methylphenyl) in the presence of carbon monoxide and zinc gives $[\text{Ir}_3(\text{CO})_6\text{Ph}(\mu_3\text{-PPh})(\mu\text{-dppm})]$ in an interesting example of an aryl group transfer reaction. The new trinuclear cluster was characterised crystallographically (61) [108]. The tetranuclear cluster, $[\text{Ir}_4(\text{CO})_9\{(\text{Ph}_2\text{P})_3\text{CH}\}]$ is also formed as a side-product in this reaction.

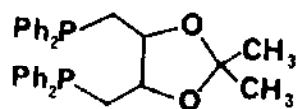


(61)

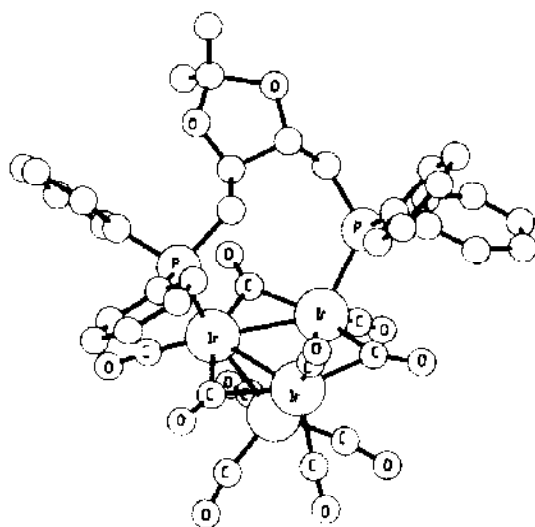
5.7.1 Tetranuclear clusters

The crystal structural analysis of the tetranuclear cluster $[\text{Ir}_4(\text{CO})_{10}\text{L}]$ (L = +-diop, 62) (63) has been reported [109].

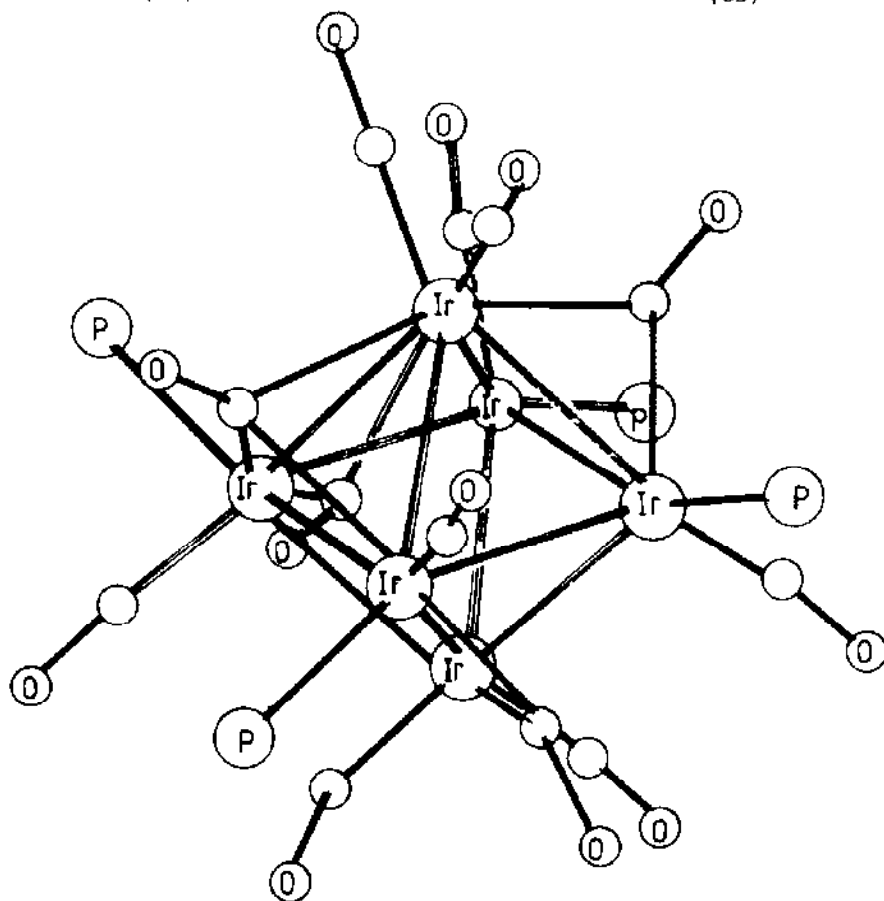
The mononuclear anion $[\text{Ir}(\text{CO})_4]^-$ results from the reaction of $[\text{Ir}_4(\text{CO})_{12}]$ with KOH in dmsO or dmf, potassium tert-butoxide, KOH/ 18-crown-6, or sodium/benzophenone [110]. Mann has investigated the fluxional processes by which the isomers of $[\text{Ir}_4(\text{CO})_{11}(\text{PET}_3)]$ interconvert. At -90°C , a 1:7 mixture of isomers may be observed in the ^{31}P NMR spectrum; the major species is about 0.8 kJ mol^{-1} more stable at -90° [111]. The major component was shown to possess an axial phosphine ligand, and the minor to possess an equatorial phosphine; a Cotton 'merry-go-round' mechanism was proposed for their interconversion. Kinetic studies of the addition of an excess of L to the clusters $[\text{Ir}_4(\text{CO})_{10}\text{L}_2]$ (L = PPh_3 , P(OPh)_3 , PBu_3 or AsPh_3) [112]. Pseudo-first



(62)



(63)



(64)

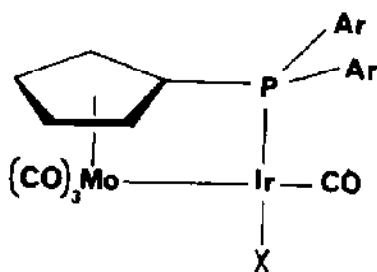
order kinetics were observed, consistent with dissociation of carbon monoxide as the rate determining step.

5.7.3 Pentanuclear and higher clusters

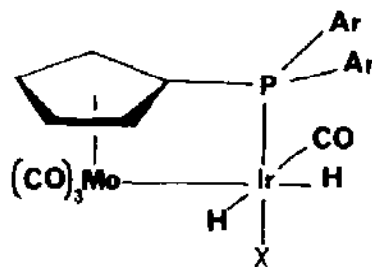
The reaction of triphenyl phosphite with $[\text{Ir}_6(\text{CO})_{16}]$ results in the formation of $[\text{Ir}_6(\text{CO})_{12}\{\text{P}(\text{OPh})_3\}_4]$ (**64**) which has been characterised crystallographically [113].

5.7.4 Mixed metal systems

The reaction of $[\text{Ir}(\text{CO})_2\text{Cl}(\text{ToINH}_2)]$ with $[\text{MoL}(\text{CO})_3]^-$ ($\text{HL} = \text{C}_5\text{H}_5\text{PAr}_2$) results in the formation of the metal-metal bridged binuclear complexes (**65**, $\text{X} = \text{CO}$). Substitution reactions with PMe_3 or PPh_3 led to (**65**) ($\text{X} = \text{PMe}_3$ or PPh_3). Hydrogenation of any of these complexes leads to the iridium(III) compounds (**66**) [114].



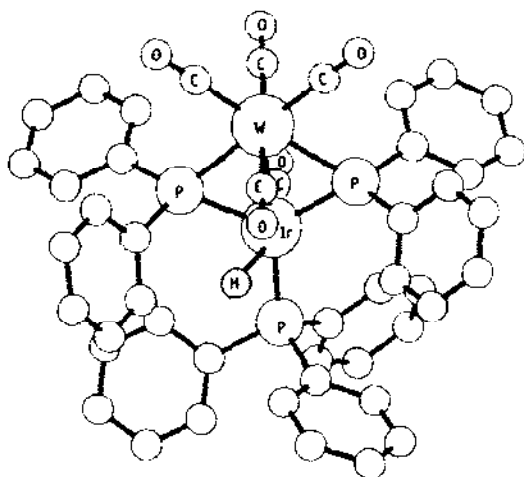
(65)



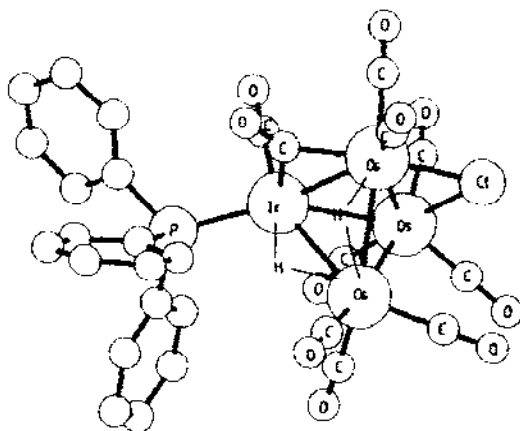
(66)

The anion $\text{cis-}[\text{W}(\text{CO})_4(\text{PPh}_2)(\text{PPh}_2\text{H})]^-$ reacts with Vaska's compound to give $[(\text{CO})_4\text{W}(\text{PPh}_2)\text{Ir}(\text{CO})(\text{PPh}_3)\text{H}]$ in 80% yield. This product was characterised by NMR techniques, and by a single crystal X-ray structure, and was shown to possess structure (**67**) [115]. A number of reactions of this novel complex were reported; the formation of the carbene complexes is of particular interest.

The cluster $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ reacts with $[\text{Ir}(\text{N}_2)(\text{PPh}_3)_2\text{Cl}]$ in benzene to give $[\text{H}_2\text{IrOs}_3\text{Cl}(\mu\text{-CO})(\text{CO})_9(\text{PPh}_3)]$ which was shown crystallographically to possess the structure (**68**) [116].



(67)



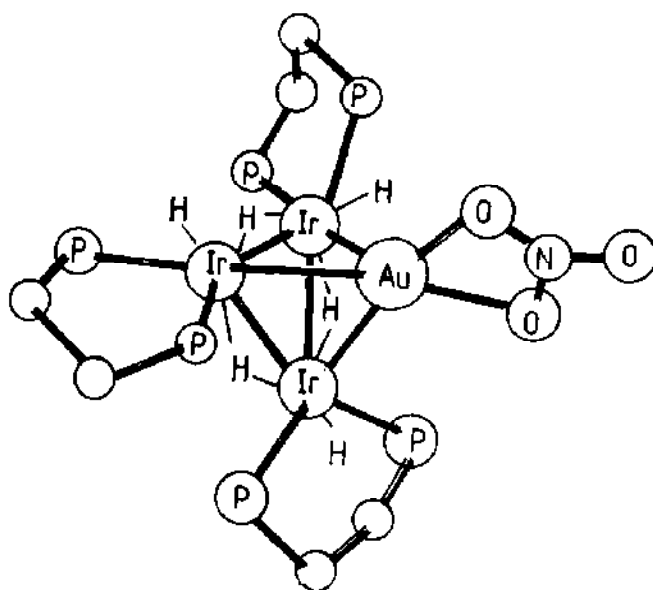
(68)

A crystal structural analysis of the product of the reaction of $[\text{Au}(\text{NO}_3)(\text{PPh}_3)]$ with $[\text{Ir}_3\text{H}_6(\text{dppe})_3]^+$ has shown it to possess structure (69) [117]. The product has a gold atom bridging the triiridium triangle, three terminal hydrides, three hydrides bridging Ir-Ir edges, three chelating dppe ligands and a nitrate ion coordinated to the gold. The reaction of the same gold(I) mononuclear unit with $[\text{Ir}_2\text{H}_5(\text{PPh}_3)_4]^+$ led to the formation of the very unusual complex $\{(\text{ONO}_2)\text{Ir}(\text{PPh}_3)_2(\text{AuPPh}_3)_3\}$, which was also characterised

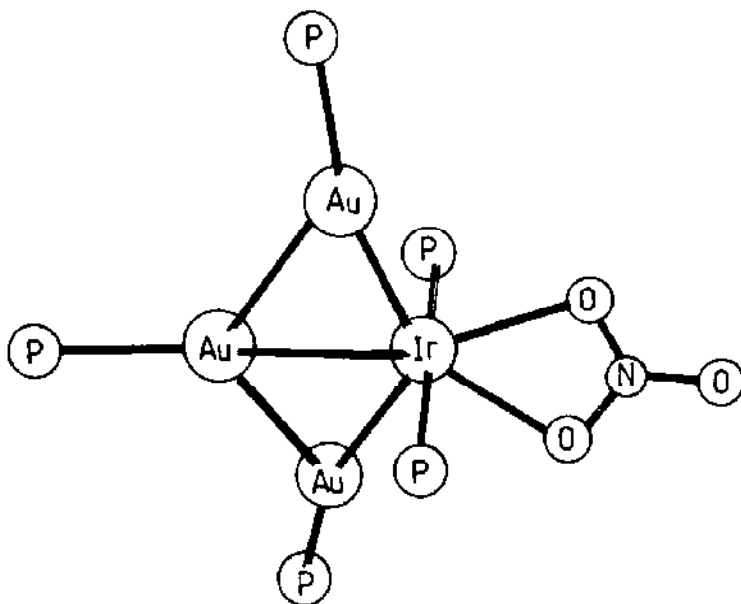
crystallographically (70) [117].

5.8 IRIDABORANES

A review of the reactions of rhodium and iridium complexes with the arachno- $B_4H_9^-$ anion has appeared [118]. A rearrangement of the arachno nine

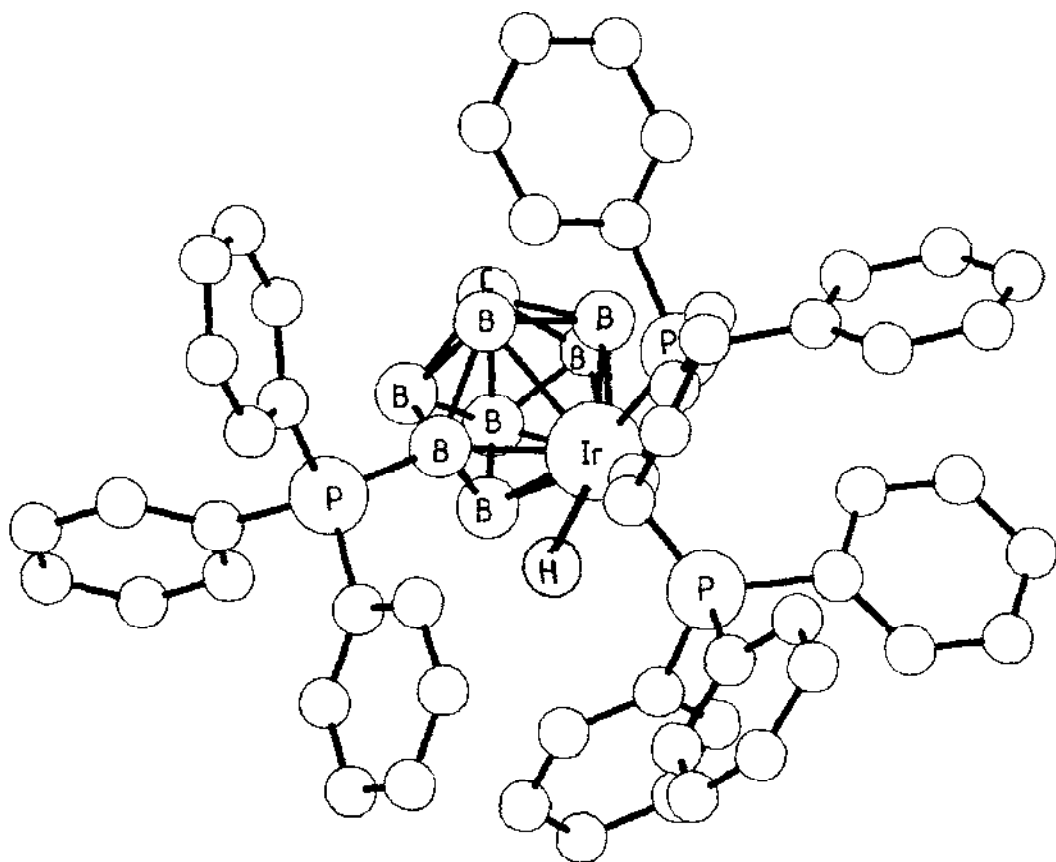


(69)



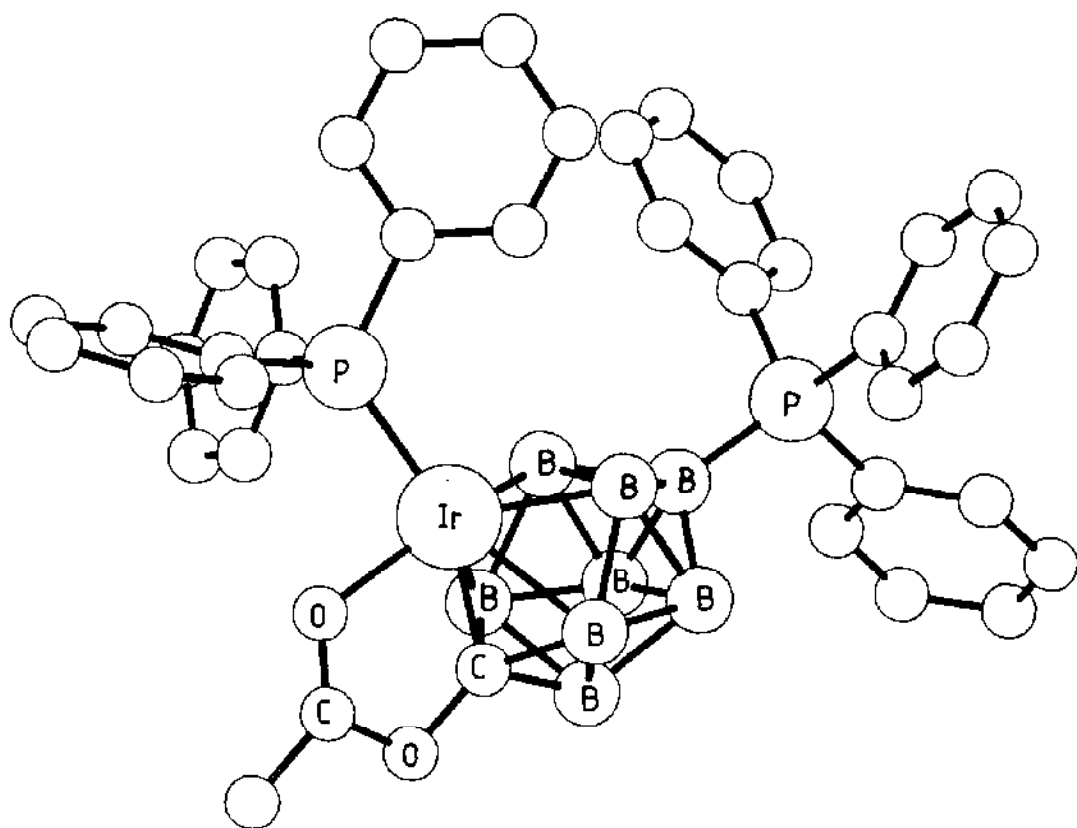
(70)

vertex CB_8 cluster anion $[\text{CB}_8\text{H}_{13}]^-$ to a closo ten-vertex CB_8Ir cluster upon treatment with $[\text{IrCl}(\text{PPh}_3)_3]$; the product, $[\text{IrCB}_8\text{H}_8(\text{PPh}_3)_2\text{HPPH}_3]$, was shown by an X-ray structural analysis to possess the bicapped Archimedean square antiprismatic structure (71) [119].



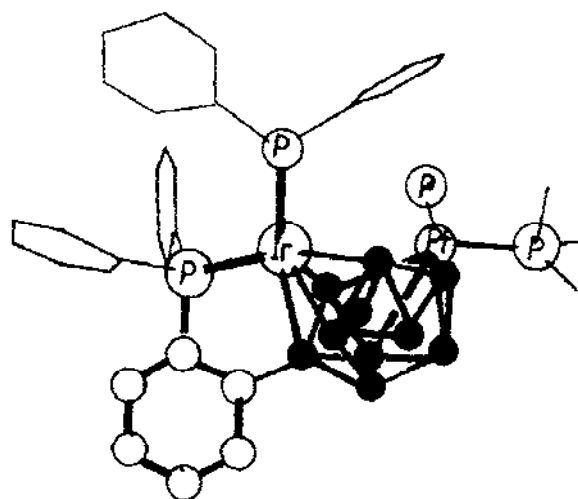
(71)

The novel complex $[(\text{MeCOO})(\text{PPh}_3)\text{H}]\text{IrCB}_8\text{H}_7(\text{PPh}_3)]$ (72) is obtained (in less than 1% yield) from the reaction of $\text{trans-}[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ with $\text{closo-B}_{10}\text{H}_{10}^{2-}$ in methanol [120]. The coordinated acetate anion is assumed to be derived by the attack of methanol upon the coordinated carbonyl ligand. The structure is seen to be a bicapped Archimedean square antiprism.

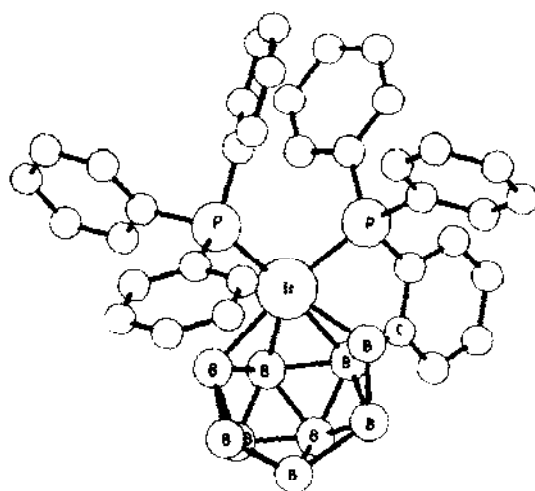


(72)

The crystal structural analyses of two other iridaboranes (73) and (74) have been reported [121].



(73)



(74)

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