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3. IRIDIUM

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CONTENTS

Introduction

INTRODUCTION

Separate reviews for the coordination chemistries of rhodium and iridium have been published this year since it is the author's opinion that the emphasis in the work reported for each of these two elements is sufficiently different to justify their inclusion in different chapters. The coordination chemistry review

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of iridium covering the year 1980, of which this review is a continuation, is published in reference [1].

As with the companion review on rhodium (chapter 2), this manuscript places especial emphasis upon the catalytic reactions of iridium where these are seen to involve aspects of coordination chemistry. Work of an essentially organometallic content has been mentioned if considered to bear any relevance to the coordination chemistry of the element. The annual surveys of the organometallic chemistry of iridium have been published covering the years 1979 [2] and 1980 [3]. The first major international conference devoted to the chemistry of the Platinum Group metals (Ru, Os, Rh, *Ir*, Pd and Pt) took place at Bristol in 1981. The next conference on this theme is scheduled for July, 1984, at the University of Edinburgh.

3.1 IRIDIUM(VI)

The redox reactions of IrF_6 have been studied. IrF_6 is shown to be a stronger oxidising agent than ReF_6 or OsF_6 towards a series of reductants, the products from which are listed in Table 1 [4]. Not surprisingly, IrF_6 is also reduced by carbon monoxide at 200 °C and 200 bar to give IrF_3 and COF_2 [5]. The intercalation of graphite by IrF_6 gives the graphite salt $C_8^+[IrF_6]^-$ [6].

TABLE 1 Products of the Reactions of IrF_6 with Various Reductants

Reductant	Reaction Product(s)
PF_3	Ir, PF_5
PF_3 in HF	IrF_4, PF_5
AsF_3	$IrF_4.AsF_5$
SbF_3	IrF_5, SbF_5
BiF_3	No reaction below 100 °C
CS_2	CF_4, SF_4
H_2	Ir, HF
H_2/HF	IrF_5
metal/KF/HF	$K[IrF_6]$

3.2 IRIDIUM(V)

3.2.1 Fluorides

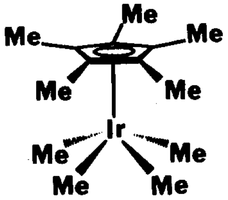
IrF_5 combines with CO at 260-280 °C to give a product that has the stoicheiometry $Ir(CO)_{2.5}F_2$. On further reaction with CO at 200 °C and at high pressure, a brown compound of formula, $Ir(CO_3)F_2$ is produced along with a black compound of formula $Ir(CO)_2F_2$ [5].

3.2.2 Oxides

Perovskites of the type $Ba_2M^{III}Ir^{V}O_6$ are found to be cubic (for M^{III} = La, Nd, Sm, Gd, Dy or Y) or hexagonal (for M^{III} = In). The powder patterns of the new series of compounds of the type $Ba_3M^{III}Ir_2O_9$ (mean oxidation state of iridium = 4.5; M^{III} = Sm, Eu, Gd, Dy, Ho, Yb, Sc, Y or In) reveal a hexagonal crystal structure of the $BaTiO_3$ type [7]. A model for the magnetic behaviour of the pentavalent, perovskite-type iridium oxide, $LaLi_{1/2}Ir_{1/2}O_3$ has been proposed. The electron configuration of iridium in this oxidation state is $(t_2g)^4(eg)^0$ and the magnetic susceptibility has been calculated by assuming cubic symmetry of the crystal field and a Coulomb repulsion that is of the same order as the spin-orbit coupling. Fitting of the experimental data gives a value of the single spin-orbit coupling constant as ca 3470 cm^{-1}, which is close to that of previously examined iridium(V) compounds [8].

3.2.3 Organometallics

Reaction of $[Ir_2(C_5Me_5)_2Cl_4]$ with the methylating agent Al_2Me_6 gives the iridium(V) compound. $[Ir(\eta^5\text{-}C_5Me_5)Me_4]$ (1). The structure has been described as



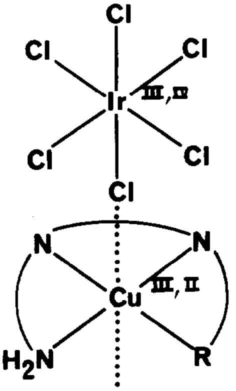
(1)

being similar to that of a four-legged piano stool. It appears to be the first example of an organometallic complex in this oxidation state [9].

3.3 IRIDIUM(IV)

The chlorination of iridium in melts of KCl or KCl-LiCl results in the formation of $K_2[IrCl_6]$ (and $K_3[IrCl_6]$). The products, obtained in the cooled melts, were identified by X-ray diffraction, and IR and UV spectroscopy [10]. The infrared luminescence spectra of $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$ have been recorded in the cubic crystals of $Cs_2[MX_6]$ (M = Sn, Te or Zr; X = Cl or Br) and $Rb_2[SnX_6]$. The $\Gamma_8(^2T_2g) \rightarrow \Gamma_7(^2T_2g)$ transition is observed at ca 5000 cm^{-1} [11].

The kinetics of oxidation of uranium(IV) by $[IrCl_6]^{2-}$ have been studied in aqueous acidic chlorate(VII) solution. The reaction is found to be first order in both $[IrCl_6]^{2-}$ and uranium(IV) [12]. In the oxidation of pyruvate ion by $[IrCl_6]^{2-}$, the reaction is also found to be first order in both the substrate and iridium(IV) [13]. The kinetics of oxidation of ethanedioic acid by $[IrCl_6]^{2-}$ in $H[ClO_4]$ have been determined [14] and the recent development of a pulsed-flow spectrometer has permitted the rates of oxidation of various copper(II)-peptide complexes by $[IrCl_6]^{2-}$ to be measured [15]. The rapid electron transfer is believed to occur *via* the chloride bridged species (2).



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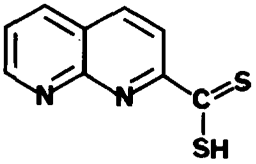
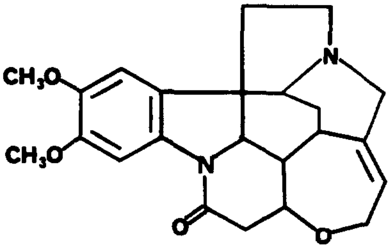
Reaction of $[NH_4]_2[IrCl_6]$ with HL (3) in aqueous solution results in the formation of $[ML_3]$ [16].



(3)

[$IrCl_4(L)$] (L = (4)) contains the brucine ligand coordinated *via* the carbonyl oxygen [17]. Cyclic voltammetry studies of *trans*-[$IrCl_4(PMe_2Ph)_2$] in MeCN have

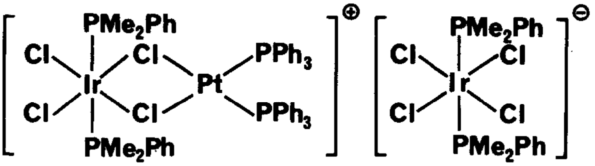


(4)

revealed a well-defined reduction wave consistent with the reduction process:

$$trans\text{-}[IrCl_4(PMe_2Ph)_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} trans\text{-}[IrCl_4(PMe_2Ph)_2]^-$$

[$IrCl_4(PMe_2Ph)_2$] reacts generally with metallocenes to form salts of the type [$M(\eta^5\text{-}C_5H_5)_2$][$IrCl_4(PMe_2Ph)_2$] (*e.g.* M = Fe or Ni). Addition of two equivalents of [$IrCl_4(PMe_2Ph)_2$] to a benzene solution of [$Pt(C_2H_4)(PPh_3)_2$] resulted in the precipitation of the fawn-coloured material (5) [18].



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3.4 IRIDIUM(III)

The ionic radius of Ir^{3+} in solid solutions of rutile is found to be 68 pm [23].

3.4.1 *Halide complexes*

Unlike $Rb_2[IrF_6]$, which is relatively inert to aquation, $Rb_3[IrF_6]$ undergoes aquation to form $[IrF_{6-x}(H_2O)_x]^{(3-x)-}$ [19].

UV irradiation of concentrated hydrochloric acid solutions of $[IrCl_6]^{3-}$ yields $[IrCl_6]^{2-}$ and dihydrogen. The reactive excited states are protonated species such as $[HIrCl_6]^{2-}$ that possess Cl → Ir charge-transfer character and the photoredox mechanism is said to involve the initial release of atomic hydrogen. Irradiation of $[IrCl_6]^{2-}$ in aqueous hydrochloric acid solution results in the formation of $[IrCl_6]^{3-}$ and dichlorine [20]. $[Ir(H_2O)Cl_5]^-$ is more active than $[IrCl_6]^{3-}$ towards the chlorination of ethane [139].

The crystal structures of the *fac*- and *mer*- isomers of $[IrCl_3(PMe_2Ph)_3]$ have been resolved. Both compounds have monoclinic crystal forms and an approximately octahedral geometry around the metal [21]. $[IrCl_3(CO)L_2]$, $[IrCl_3L_3]$ and $[IrHCl_2(CO)L_2]$ $\{L = As(PhCH_2)_3\}$ have been examined by infrared spectroscopy in the metal-chlorine region. When $[IrHCl_2(CO)L_2]$ is treated with NaOMe, HCl is eliminated to form $[IrCl(CO)L_2]$ indicating that Cl is *trans* to the hydride ligand in the original iridium(III) complex [22].

3.4.2 Complexes with Group VI donor ligands

3.4.2.1 Complexes with oxygen donor ligands

Thermogravimetry has been used to establish the stoicheiometry of the reaction of $IrCl_3$ with mixtures of molten alkali metal nitrites to form the *O*-bonded nitrito species $[Ir(NO_2)_6]^{3-}$. IrO_2 was formed at higher temperatures accompanied by the evolution of nitrogen oxides [24].

Na[IrCl(edtaH)].$2H_2O$ and Na[IrCl(pdtaH)].$3H_2O$ ($pdtaH_4$ = propylenediaminetetraacetic acid) have been prepared from $IrCl_4$ and the sodium salts of the corresponding ligands. The hemihydrate of $[Ir(edtaH)(H_2O)]$ was prepared from Na[IrCl(edtaH)].$2H_2O$ [25].

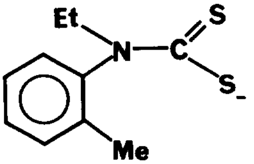
Treatment of $[IrCl(CO)(PPh_3)_2]$ with fluorosulphuric acid, HSO_3F, gives the hydride $[IrCl(CO)(PPh_3)(H)(SO_3F)]$. The $[SO_3F]^-$ group is displaced by chloride ion from $[Bu_4N]$ Cl, by bromide ion from $[Ph_3MeP]Br$ and by $[SCN]^-$ from $[NH_4][SCN]$ [69].

3.4.2.2 Complexes with sulphur donor ligands

The IR and Raman spectra of the sulphito complexes $[Ir(SO_3)_2Cl_4]^{5-}$, $[Ir(SO_3)_2(NH_3)_2Cl_2]^{3-}$, $[Ir(SO_3)_3(NH_3)_3]^{3-}$ and $[Ir(SO_3)_4Cl_2]^{7-}$ indicate that they contain iridium-sulphur bonds, unlike the iron complex, $[Fe(SO_3)_6]^{9-}$, which is known to contain metal-oxygen bonds [26].

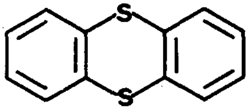
The sulphinato complex, $[Ir(PPh_3)_2(CO)Cl_2(SO_2CH_2R)]$ (R = H, 4-MeC_6H_4 or 4-$O_2NC_6H_4$) was prepared by reaction of RCH_2SO_2Cl with *trans*-$[IrCl(CO)(PPh_3)_2]$. An attempt to prepare the coordinated sulphine by dehydrochlorination was not successful [65].

$[IrL_3]$ {L = (6)}, prepared from aqueous solution, is octahedral, diamagnetic



(6)

and non-conducting, and forms a monomeric species in which the dithiocarbamate acts as a bidentate ligand [27]. $IrCl_3.3H_2O$ reacts with thianthrene (7) to give $[IrCl_3(thianthrene)_3]$ and with phenoxathiin (8) to give $[IrCl_3(phenoxathiin)_3]$



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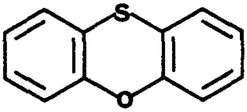

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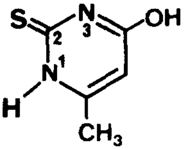
[28]. $[Ir(HL)_3Cl_3]$ {HL = (9)} contains the 6-methyl-2-thiouracil ligand bidentately bonded through the C(2)=S and N(3) positions [29].



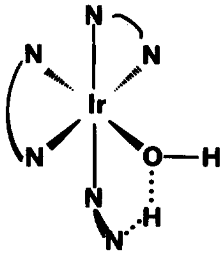
(9)

Oxidative addition of C_6F_5SSCl to *trans*-$[IrCl(CO)(PPh_3)_2]$ produces the octahedral compound, $[IrCl_2(SSC_6F_5)(CO)(PPh_3)_2]$. This material is considered to be the first example of a transition metal complex containing a monodentate organoperthio group [58].

3.4.3 *Complexes with nitrogen donor ligands*

The sulphato and selenato outer-sphere complexes of *cis*- $[Ir(en)_2Cl_2]^+$ have been studied and their stability constants and associated thermodynamic parameters determined [30].

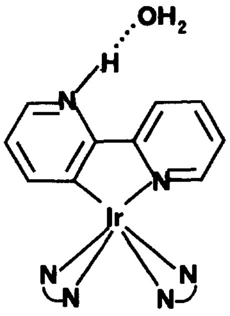
The highly-debated complex which has frequently been formulated both as $[Ir(bipy)_2(H_2O)(\eta'\text{-}bipy)]Cl_3$ and as a "covalent hydrate" $[Ir(bipy)_2\{bipy(H_2O)\}]Cl_3$ has been re-examined using ^{13}C NMR spectroscopy; the results were interpreted to suggest that it exists as the monodentate bipyridine species (10) [31]. However, from the crystal structure of the chlorate(VII) salt



(10)

of "$[Ir(bipy)_2(H_2O)(bipy)]^{3+}$", all of the three bipy ligands were shown to be chelated to the iridium(III) but one of the ligands is attached to the metal through the nitrogen atom of one ring and the C(3) carbon of the other ring [32]. There is no evidence of a monodentate bipy ligand in the structure, and also no evidence of a covalently hydrated bipy ligand. The structure of the complex is considered by these authors to be consistent with that illustrated in (11) (compare with (10)).

The cyclometallated structure (11) contains six non-equivalent pyridine rings, and would thus account for the complex nature of the ^{13}C NMR spectrum reported by the authors of [31] without the need of postulating the monodentate bipy of structure (10). Moreover, the observation of cyclometallation is consistent with the recent observation by Constable and Seddon [32a] that the 3,3' protons of $[Ru(bipy)_3]^{2+}$ are acidic.



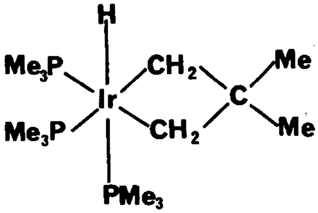
(11)

The luminescence, lifetimes and polarisation spectra have been measured for $[Ir(bipyam)_2Cl_2]^+$ (bipyam = di(2-pyridylamine) in acidic, basic and neutral solution. The results are similar to those described for the analogous rhodium system described in section 2.2.4.2 [33]. The photoluminescence of *cis*-$[Ir(phen)_2Cl_2]Cl$ and *cis*-$[Ir(4,4'-Me_2-2,2'-bipy)_2Cl_2]Cl$ have been investigated between 2 and 77 K. The shift of origin with change in solvent polarity, the emission decay time, and the spectral band shape indicate that the luminescing excited state of each species can be classified as metal-ligand charge transfer [34]. The luminescence, lifetimes, quantum yields and spectra of $[Ir(phen)_2Cl_2]^+$, $[Ir(bipy)_2Cl_2]^+$, $[Ir(bipy\text{-}d_8)_2Cl_2]^+$, $[Ir(5,6\text{-}Me_2phen)_2Cl_2]$, $[Ir(bipy)(5,6\text{-}Me_2phen)Cl_2]^+$, $[Ir(4,7\text{-}Ph_2phen)_2Cl_2]^+$ and $[Ir(4,4'Ph_2bipy)_2Cl_2]^+$ in a variety of solvents at 295 K have been reported. Two emission bands, originating from dd* and dπ* or mixed dd*-ππ*, are observed with bipy, phen or 5,6-Me_2phen as the coordinating ligands whereas a single emission band, of dπ* or mixed dπ*-ππ* origin, is observed when 4,7-Ph_2phen or 4,4'-Ph_2bipy are coordinated [35].

3.4.4 Complexes with Group IV donor ligands

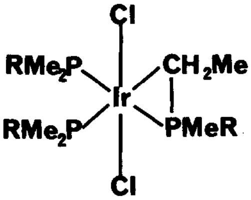
3.4.4.1 Complexes with carbon donor ligands

$[Ir(PMe_3)_4]Cl$, upon reaction with $LiCH_2CMe_3$ at room temperature, produces (12). A similar reaction occurs with iridium(I) chloro complexes containing



(12)

arsine ligands to produce analogous products such as *fac*-$[IrH(CH_2CMe_2CH_2)(AsR_3)_3]$ [36]. The three-membered ring metallocycle (13) is formed from the treatment of *mer*-$[IrCl_3(PMe_2R)_3]$ (R = Me or Ph) with strong bases ($LiNCHMe_2$, LiBu or $Li(CH_2)_5Li$). Treatment with hydrogen chloride reverses the reaction. Reaction of (13) with X_2 (X = Cl, Br or I) gives



(13)

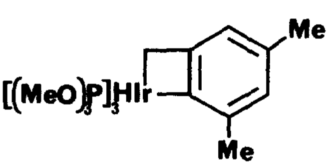
$[IrCl_2X(PMe_2Ph)_2(PMePhCH_2X)]$. On irradiation of the *mer*- isomer of this complex with visible light the *fac*- isomer is formed [37]. The tridentate ligand (E)-2-$Ph_2PC_6H_4CH = CHCH_2C_6H_4PPh_2$-2 can be dehydrogenated by $[Ir(cod)Cl]_2$ to give $[IrCl_2(2\text{-}Ph_2PC_6H_4CH = CHCHC_6H_4PPh_2\text{-}2)]$ [77].

Treatment of *trans*-$[IrH(FBF_3)(CO)Cl(PPh_3)_2]$ with ethene at -40 °C is reported to replace the weakly-coordinated $[BF_4]^-$ ion to give *trans*-$[IrH(C_2H_4)(CO)Cl(PPh_3)_2][BF_4]$. This material reacts with $[Re(CO)_5]^-$ to give $[Ir(CO)Cl(PPh_3)_2]$ and $[C_2H_5Re(CO)_5]$ [38].

Reaction of RCOCl (R = CH_2Cl, CH_2OPh, CO_2Et, $CH_2CH_2CO_2Me$ or CH_3CO) with *trans*-$[IrCl(N_2)(PPh_3)_2]$ gave the coordinatively-unsaturated complexes, $[IrCl_2(OCR)(PPh_3)_2]$ [39]. Reaction of $[IrCl_2(COR)(PMe_2Ph)_3]$ (R = Me or Et) with

$[NH_4][PF_6]$ in air gives $[Ir_2Cl_3(COR)_2(PMe_2Ph)_4]$ $[PF_6]$. The methyl derivative consists of a bioctahedral geometry with each metal atom octahedrally-coordinated by an ethanoyl group, two phosphine ligands and three bridging chlorine atoms. An unusual feature from the X-ray structure determination is the finding of 1,2-dichloroethane in the unit cell. The source of this material is reported to be unknown [40].

The compound previously described as having the formulation (14) has been shown to be (15) by X-ray analysis. The geometry of (15) consists of a distorted octahedron and contains $P(OMe)_3$ ligands in the *fac*- positions [41].



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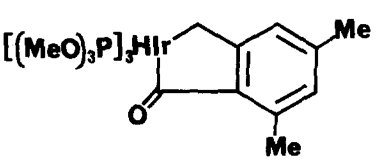
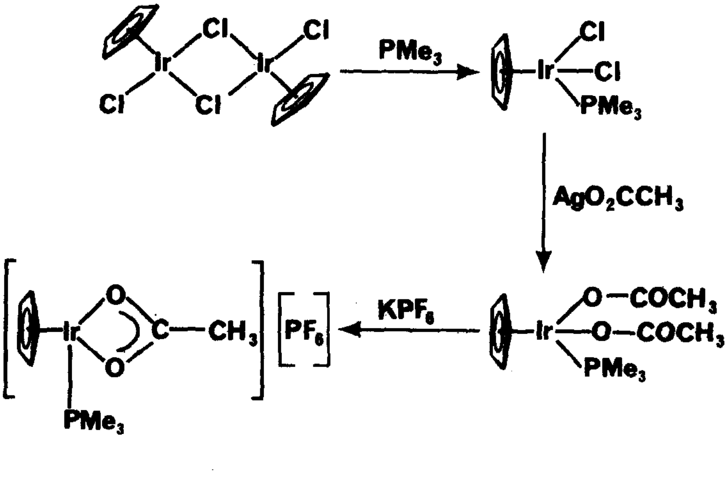


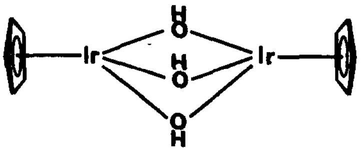
(15)

The η^5-C_5Me_5 iridium complex $[\{Ir(C_5Me_5)\}_2Cl_4]$ undergoes the reactions illustrated in Scheme I [42]. The cation in $[\{Ir(C_5Me_5)\}_2(OH)_3][O_2CMe].14H_2O$ has



Scheme I: Some transformations of $[\{Ir(C_5Me_5)\}_2Cl_4]$[42].

the structure illustrated in (16) [43] and the related material



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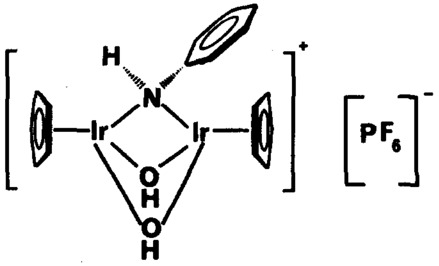
$[\{Ir(C_5Me_5)\}_2(OH)_3]OH$ reacts with $PhNH_2$ in the presence of $[PF_6]^-$ to give $[\{Ir(C_5Me_5)\}_2(\mu\text{-}NHPh)(\mu\text{-}OH)_2][PF_6]$ (17) [44].



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3.4.4.2 Carborane complexes

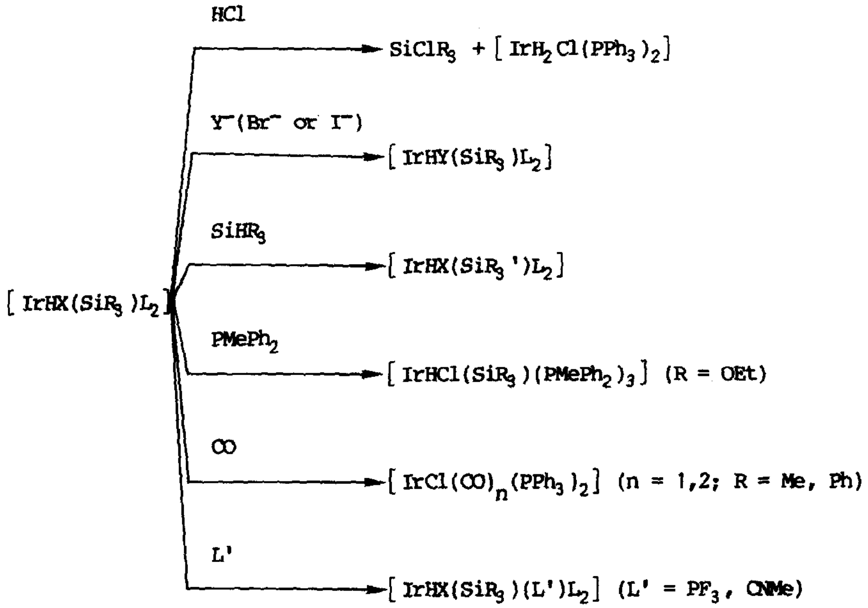
$[IrCl(PPh_3)_3]$ reacts with $Na[1,3\text{-}C_2B_7H_{12}]$ to give $[$*closo*$\text{-}6,6\text{-}(PPh_3)_2\text{-}6\text{-}H\text{-}6,2,3\text{-}IrC_2B_7H_9]$ and with $Na[1,3\text{-}(CH_3)_2\text{-}1,3\text{-}C_2B_7H_{10}]$ to give $[$*closo*$\text{-}2,3\text{-}(CH_3)_2\text{-}6,6\text{-}(PPh_3)_2\text{-}6\text{-}H\text{-}6,2,3\text{-}IrC_2B_7H_7]$. Both complexes are inactive as catalysts for alkene hydrogenation or isomerisation [45].

Complexes of the type $[Ir(H)(\sigma\text{-}CR = CHR)(\sigma\text{-}carb)(CO)(PPh_3)L]$ (L = MeCN or PhCN; carb = $\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}$) are formed in the reaction of $[IrH_2(\sigma\text{-}carb)(CO)(PPh_3)L]$ with alkynes. The complexes are considered to be reaction intermediates in the hydrogenation of substituted ethynes when catalysed by $[Ir(\sigma\text{-}carb)(CO)(PPh_3)L]$ [46]. Dynamic ^1H and ^{31}P $\{^1H\}$ NMR spectra have been recorded for the 12-vertex *closo*-phosphinometallacarboranes; $[IrL_2H(carb)]$ (L = PPh_3, PEt_3 or PMe_2Ph; carb = 1,2-, 1,7-, or 1,12- $C_2B_9H_{10}R$;

R = H, Me, Ph or Bu) [47].

3.4.4.3 Complexes with silicon or germanium donor ligands

Oxidative addition of $SiHR_3$ {R_3 = F_3, Cl_3, F_2Me, Cl_2Me, FMe_2, $ClMe_2$, Me_3, Et_3, Ph_3 or $(OEt)_3$} to [$IrX(N_2)L_2$] (X = Cl or Br; L = PPh_3 or $AsPh_3$) or [$IrXL_2$] {X = Cl or Br; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(cych)_3$, $P(C_6H_4Me\text{-}4)_3$ or $PMePh_2$} gives the five-coordinate complex, [$IrHX(SiR_3)L_2$]. These complexes have been found to undergo the reactions illustrated in Scheme II. Introduction of an additional neutral ligand (L' = CO, PF_3 or CNMe) gives six-coordinate compounds of the type [$IrHX(SiR_3)(L')L_2$] in which L' occupies, predominantly, the position *trans* to the silyl group [48].



Scheme II: Some reactions of [$IrHX(SiR_3)L_2$] [48].

$E(SiH_3)_2$ {E = O, S or Se} react with *trans*-[$Ir(CO)I(PEt_3)_2$] in benzene to give [$Ir(CO)HI(PEt_3)_2(SiH_2XSiH_3)$] or [{$Ir(CO)HI(PEt_3)_2(SiH_2)$}$_2$X]. Reaction between *trans*-[$Ir(CO)I(PEt_3)_2$] and $N(SiH_3)_3$ gives [$Ir(CO)HI(PEt_3)_2${$SiH_2N(SiH_3)_2$}] and [{$Ir(CO)HI(PEt_3)_2(SiH_2)$}$_2NSiH_3$] [59]. [$IrH(CO)(PPh_3)_3$] reacts with EH_3X (E = Si or Ge and X = H, F, Cl, Br or I; E = Si and X = SiH_3 or Me) to give [$IrH_2(CO)(PPh_3)_2(EH_2X)$]. The germanium complexes have predominantly *trans*- geometry relative to the phosphine ligands whereas the silane complexes possess predominantly *cis*- geometry [60].

3.4.4.4 Complexes with tin donor ligands

Iridium was extracted in the presence of $\mathrm{SnCl_2}$ by 2-octylaminopyridine (L) according to Scheme III [49].

$$[\mathrm{IrCl_6}]^{3-} + m[\mathrm{SnCl_3}]^- \rightleftharpoons [\mathrm{Ir(SnCl_3)_mCl_{6-m}}]^{3-} + \mathrm{mCl^-}$$

$$[\mathrm{Ir(SnCl_3)_mCl_{6-m}}]^{3-} + \mathrm{x[LH]Cl} \rightleftharpoons [\mathrm{IrL_x(SnCl_3)_{m-x}Cl_{6-m-x}}]^{3-} + \mathrm{xH^+} + \mathrm{xCl^-} + \mathrm{x[SnCl_3]^-}$$

$$[\mathrm{IrL_x(SnCl_3)_{m-x}Cl_{6-m-x}}]^{3-}\mathrm{(aq)}. + \mathrm{(3-x)[LH]Cl(org)}.$$

$$\rightleftharpoons [\mathrm{LH}]_{3-x}[\mathrm{IrL_x(SnCl_3)_{m-x}Cl_{6-m-x}}]^{x-3}\mathrm{(org)}. + \mathrm{(3-x)Cl^-(aq)}.$$

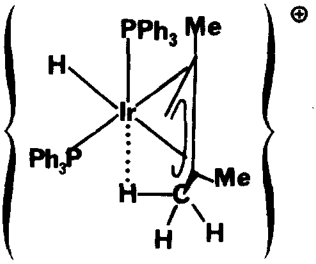
Scheme III: Extraction of iridium [49].

3.4.5 Hydride complexes

The *fac*- and *mer*- isomers of $[\mathrm{IrH_3(CO)(PPh_3)_2}]$ have been prepared and the kinetics of their interconversion has been examined. The interconversion occurs by a reversible reductive elimination/oxidation sequence involving the species $[\mathrm{IrH(CO)(PPh_3)_2}]$ as an intermediate [50]. *Fac*-$[\mathrm{IrH_3(AsPh_3)_3}]$ is obtained by reduction of $\mathrm{Na_2[IrCl_6].6H_2O}$ with $\mathrm{AsPh_3}$ and $\mathrm{Na[BH_4]}$ in ethanol. By adjustment of pH and chloride ion concentration, the reaction of $\mathrm{Na_2[IrCl_6].H_2O}$ with $\mathrm{AsPh_3}$ in boiling $\mathrm{MeOCH_2CH_2OH}$ gave $[\mathrm{IrH_2Cl(AsPh_3)_3}]$, $[\mathrm{IrHCl_2(AsPh_3)_3}]$, or $[\mathrm{IrCl_3(AsPh_3)_3}]$ [51].

Solvent exchange in $[\mathrm{Ir(PPh_3)_2(MeCN)_2H_2}]^+$, $[\mathrm{Ir(PPh_3)_2(Me_2CO)_2H_2}]^+$ and $[\mathrm{Ir\{P(cych)_3\}(MeCN)_2H_2}]^+$ (all complexes containing MeCN or $\mathrm{Me_2CO}$ *trans*- to hydrides) have been examined. The propanone solvates are found to be more labile than the ethanenitrile complexes owing to their lower $\Delta H^\ddagger$ values [52]. Dihydrogen reacts with $[\mathrm{Ir\{(Ph_2P)_2N\text{-}4\text{-}MeC_6H_4\}_2]Cl.3C_6H_6}$ in dichloromethane to give *cis*-$\{\mathrm{IrH_2\{(Ph_2P)_2N\text{-}4\text{-}MeC_6H_4\}_2]Cl.CH_2Cl_2}$. Oxidative addition of HCl to the $\mathrm{C_6H_6}$ solvate and reaction with $\mathrm{Na[BPh_4]}$ gave *trans*-$\{\mathrm{Ir(H)(Cl)\{(Ph_2P)_2N\text{-}4\text{-}MeC_6H_4\}_2][BPh_4]}$ [53].

$[\mathrm{Ir(H)(PPh_3)_2}(\eta^3\text{-2,3-dimethylbutenyl})]^+$, derived from the reaction of $[\mathrm{Ir(H)_2(PPh_3)_2(OCMe_2)_2}]$ with 2,3-dimethylbutadiene, has been identified in $\mathrm{CD_2Cl_2}$ solution from its proton and $^{31}\mathrm{P}$ NMR spectra. A novel C-H....Ir(III) interaction has been revealed which undergoes facile hydrogen transfer between the metal and the hydrocarbon. The cation (18) is known to activate C-H bonds [54].



(18)

Oxidative addition of HX (H[BF$_4$], CF$_3$SO$_3$H or C$_4$F$_9$SO$_3$H) to *trans*-[(Ph$_3$P)$_2$Ir(L)Cl] (L = CO or N$_2$) gives the highly reactive [(Ph$_3$P)$_2$Ir(L)(Cl)(H)(X)]. The anion, X, can be readily substituted for σ- and π-donor ligands. In the dinitrogen complex, [(Ph$_3$P)$_2$Ir(N$_2$)(Cl)(H)(FBF$_3$)], both N$_2$ and [BF$_4$] are readily replaced by valinate, diethyldithiocarbamate or tertiary phosphines [55]. H[BF$_4$] adds oxidatively to [Ir(CO)Cl(PPh$_3$)$_2$] to give *trans*-[IrH(FBF$_3$)(CO)Cl(PPh$_3$)$_2$], containing a weakly-bound [BF$_4$]$^-$ ion [38]. [Ir(PPh$_3$)$_2$(CO)(Cl)(H)(X)] (X = SCN or SeCN) were prepared from [Ir(PPh$_3$)$_2$(CO)(Cl)(H)(CH$_3$SO$_3$)] and [Ir(PPh$_3$)$_2$(CO)(Cl)(H)(BF$_4$)], respectively. The thiocyanate ligand is S-bonded and the selenocyanate ligand is obtained as a mixture of linkage isomers. [Ir(PPh$_3$)$_2$(CO)(Cl)(H)(SCN)] reacts with [Ir(PPh$_3$)$_2$(CO)(Cl)(H)(BF$_4$)] to give a mixture of stereoisomers of [(PPh$_3$)$_2$(CO)(Cl)(H)Ir(SeCN)Ir(H)(Cl)(CO)(PPh$_3$)$_2$][BF$_4$] [56].

3.5 IRIDIUM(II)

Iridium(II) fluoride complexes, derived from the reduction of IrF$_5$ with carbon monoxide, have been described in Section 3.2.1 [5].

The absorption spectrum of *cis*-[IrCl$_2$(phen)$_2$] was obtained from excitation by a 306 nm sub-picosecond pulse and showed the presence of a precursor (p) of the lowest triplet (T$_1$) state: The isosbestic wavelength of P and T$_1$ is located at 590-570 nm [57].

3.6 IRIDIUM(I)

3.6.1 Halide complexes

The reaction enthalpies for the oxidative addition of RI (R = I, H, Me, Et, Pr, Me_2CH, MeCO, PhCO or $PhCH_2$) to the Vaska-type complex, *trans*-$[IrCl(CO)(PMe_3)_2]$ have been determined in 1,2-dichloroethane [61]. Oxidative addition of RCOCl (R = Me, Pr or Me_2CH) to $[IrCl(PMe_2Ph)_3]$ gives $[IrCl_2(COR)(PMe_2Ph)_3]$ [62].

$[RhCl_3(CO)(PMe_2Ph)_2]$ reacts with *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ to produce $[RhCl(CO)(PMe_2Ph)_2]$ and $[IrCl_3(CO)(PMe_2Ph)_2]$. The analogous PEt_2Ph species react similarly but more slowly [63].

The He(I) photoelectron spectrum of $[Ir_2Cl_2(PF_3)_4]$ has been recorded [64].

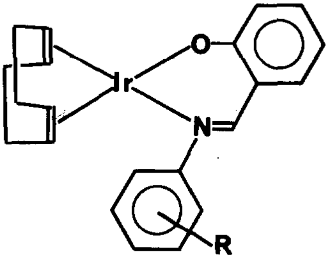
3.6.2 Complexes with oxygen donor ligands

The first-order rate constant for the reaction of $[Ir(OH)(CO)(PPh_3)_2]$ with CO_2 in CH_2Cl_2 to give the bicarbonate species, $[Ir(OCO_2H)(CO)(PPh_3)_2]$, is estimated to be 2×10^{-3} s^{-1} [66].

[Ir(acac)(cod)] has a monoclinic crystal structure with a square planar configuration about the metal [67]. $[\{IrL_2(tfa)\}_2]$ (L = cyclooctene) when treated with benzene and tfaH gives $[IrL_2(\eta\text{-}C_6H_6)][H(tfa)_2]$. Disproportionation of the cyclooctene ligand occurs when $[\{IrL_2(tfa)\}_2]$ is dissolved in CH_2Cl_2. Cyclooctane and [Ir(cod)(tfa)] are formed [68].

The 16-electron complex [Ir(cod)(O-8-quin)] adds phosphines, phosphites or alkenes irreversibly to give the pentacoordinate [Ir(cod)(O-8-quin)L] $\{L = PPh_3, P(OPh)_3$, tcne or maleic anhydride$\}$. Reaction of [Ir(cod)(O-8-quin)] with dppe gives [Ir(O-8-quin)(dppe)]. CO displaces cod to give $[Ir(O\text{-}8\text{-}quin)(CO)_2]$ or [Ir(O-8-quin)(CO)L], the latter undergoing oxidative addition with $SnCl_4$, Me_3SiCl, Me_3SnCl, MeI, allyl bromide, PhCOCl, MeCOCl, Cl_2, Br_2, $TlCl_3$ or HCl [70].

Reaction of $[\{Ir(OCH_3)(cod)\}_2]$ with bidentate Schiff bases derived from salicylaldehyde gives complexes of type (19) [71].

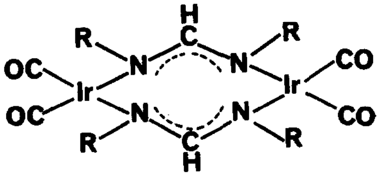


(19)

3.6.3 *Complexes with Group V donor ligands*

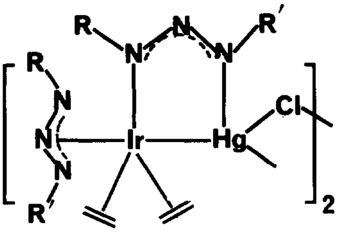
3.6.3.1 *Complexes with nitrogen donor ligands*

[{Ir(μ-Cl)(cod)}$_2$] reacts with (Ph$_2$P)$_2$NR (R = Me, Ph, 4-MeC$_6$H$_4$) to give the ionic, square planar complexes [Ir{(Ph$_2$P)$_2$NR}$_2$]Cl.nC$_6$H$_6$ (in benzene) and [Ir{(Ph$_2$P)$_2$NR}$_2$]Cl.thf (in thf). Reaction of these complexes with Na[BPh$_4$] gives [Ir{(Ph$_2$P)$_2$NR}$_2$] [BPh$_4$] [72]. [Ir(CO)$_3$Cl] reacts with LiCH(NC$_6$H$_4$R-4)$_2$ (R = H, Me, MeO, Cl or F) to give (20) [73]. The triazenido complex (21) has been



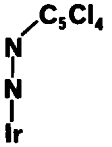
(20)

synthesised from {Ag(RN$_3$R')}$_n$ (R = Me, Et or 4-tolyl), HgCl$_2$ and [{IrCl(cod)}$_2$] [74].



(21)

$[IrCl(N_2C_5Cl_4)(PPh_3)_2]$, prepared from the reaction of $[IrCl(CO)(PPh_3)_2]$ with tetrachlorodiazocyclopentadiene, contains the $N_2C_5Cl_4$ molecule bound to iridium *via* the singly-bent linkage (22). The reaction of diazofluorene with



(22)

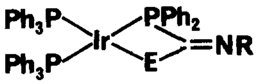
$[IrCl(N_2)(PPh_3)_2]$ gives fluorenone ketazine but no complex containing diazofluorene. The instability of the hypothetical $[IrCl(diazofluorene)(PPh_3)_2]$ is believed to be electronic in origin [75].

The oxidation of $[Ir(phen)_2]^+$ has been examined by chemiluminescence: *cis*-$[Ir(phen)_2Cl_2]^+$ was the emission product [76].

3.6.3.2 Complexes with phosphorus donor ligands

$[IrCl(L\text{-}L\text{-}L)]$ ($L\text{-}L\text{-}L = PhP\{(CH_2)_3PPh_2\}_2$) was derived from the reaction of $[\{Ir(C_8H_{14})_2\}_2]$ and L-L-L. Reaction with CO gives the five-coordinate $[IrCl(CO)(L\text{-}L\text{-}L)]$ and $[Ir(CO)_2(L\text{-}L\text{-}L)]Cl$ containing a trigonal bipyramidal geometry with equatorial CO ligands. Reaction of $[IrCl(L\text{-}L\text{-}L)]$ with HCl gives $[IrHCl_2(L\text{-}L\text{-}L)]$ and, similarly, reaction of the iridium(I) complex with dihydrogen gives the dihydride, $[IrH_2Cl(L\text{-}L)]$ [78]. PHF_2 and *trans*-[$Ir(CO)I(PEt_3)_2$] react in toluene at low temperature to give the pentacoordinate [$Ir(CO)I(PEt_3)_2(PF_2H)$] which, on warming, rearranges to the hexacoordinate [$Ir(CO)I(PEt_3)_2(PF_2)H$]. Similarly, PF_2X reacts with *trans*-[$Ir(CO)X(PEt_3)_2$] to give the five-coordinate [$Ir(CO)X(PEt_3)_2(PF_2X)$] when X = Cl. When X = Br, the concentration of the pentacoordinate species is small and none of the pentacoordinate species is detected when X = I. However, NMR signals were observed for all three hexacoordinate complexes, [$Ir(CO)X_2(PEt_3)_2(PF_2)$] (X = Cl, Br, I) [79].

The phosphine complexes of iridium(I) with [$Ph_2PC(E)NR$]$^-$ and with [$Ph_2P(Q)C(S)NR$]$^-$ (E = S, O, NR; Q = S, O) have the structures illustrated in (23) and (24) and react with carbon monoxide by displacing the triphenylphosphine ligand that is under the lowest *trans*- influence [80].



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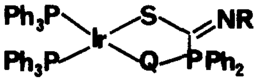
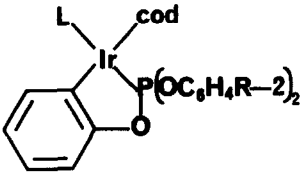


(24)

Compounds of the type illustrated in (25) {L = $P(OC_6H_4R\text{-}2)_3$; R = H or Me} react with tertiary phosphine ligands {L' = PMe_2Ph, $PMePh_2$ or $P(OMe)Ph_2$} to produce [Ir(P-C)(cod)(L')]. The cod ligand is displaced by CO to give *cis*-[$Ir(P\text{-}C)(CO)_2L$] which isomerises to the *trans*- geometry in hot alcoholic solution [81].



(25)

The emission spectrum and lifetimes of $[IrL_2][ClO_4]$ {L = *cis*-1,2-bis(diphenylphosphino)ethene} have been determined and the following parameters recorded: ΔE = 143 cm^{-1}; τ(lower) = 999 μs; τ(higher) = 1.54 μs [89].

3.6.3.3 Complexes with arsenic donor ligands

The pentacoordinated cationic complexes, $[Ir(CO)_xL_{5-x}]X$ (x = 2,3; L = tribenzylarsine; X = $[ClO_4]^-$, $[BPh_4]^-$) have been prepared by firstly passing CO through a stream of $[IrCl(CO)L_2]$ to give $[Ir(CO)_2L_3]^+$. Passage of further carbon monoxide then gives $[Ir(CO)_3L_2]^+$ and the complexes isolated as the perchlorate or tetraphenylborate salts [82]. $[IrHX_2(CO)L_2]$ (L = tribenzylarsine; X = Cl, Br), upon treatment with Na[OMe] in methanol gave *trans*-$[IrX(CO)L_2]$. Reaction of $[IrHBr_2(CO)L_2]$ with NaI gave $[IrI(CO)L_2]$ [83].

3.6.4 Complexes with Group IV donor ligands

3.6.4.1 Complexes with carbon donor ligands

Reaction enthalpies have been determined for the oxidative addition of ethanoyl chloride to *trans*-$[IrCl(CO)L_2]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_2(4-tolyl), PEt_3, $P(CH_2Ph)_3$, $P(CMe_3)Ph_2$ or $P(oph)_3$) and the results correlated as a function of the electronic and steric parameters of the phosphine ligand. In addition the enthalpies of oxidative addition of RCOCl (R = Me, Et, Pr, CMe_2H, CMe_3, CH_2Cl, $CHCl_2$ or Ph) to *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ were determined. The bond dissociation energy of Ir–$COCH_3$ was calculated to be 205 ± 46 kJ mol^{-1} [84].

$[Ir(cod)L_2][BF_4]$ adds dihydrogen when L is an electron-accepting ligand such as PPh_3 or alkenes but not when it is an electron-donating ligand such as pyridine. The ^{13}C NMR spectra of the complexes containing various addition compounds (H_2, HCl, HBr, HI or Cl_2) leads to the conclusion that the reaction with dihydrogen should be properly called a reductive addition [85]. $[\{Ir(cod)Cl\}_2]$ reacts with *meso*-1,3-diisocyanocyclohexane (L) to produce $[Ir_2L_4]Cl_2$ [86].

The molecular structures of *cis*- and *trans*-$[(2,4,6\text{-}Me_3C_6H_2)Ir(CO)(PH_3)_2]$ have been determined by X-ray diffraction. The *cis*- isomer shows a degree of tetrahedral distortion because of steric crowding. The carbonyl ligand is reported, on the basis of the intermolecular distances, to exert a stronger *trans*- effect on Ir–P than the aryl group [87].

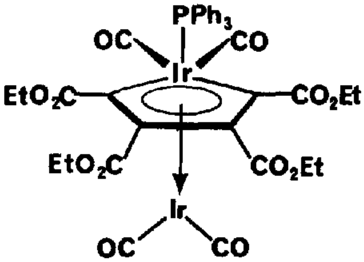
3.6.4.2 Carborane complexes

The ten-vertex *iso- nido-* iridacarbadecaborane $[\{IrC(OH)B_8H_6(OMe)\}(C_6H_4PPh_2)(PPh_3)]$, has been isolated from the combination of *trans*-$[IrCl(CO)(PPh_3)_2]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in methanol solution [88].

3.7 IRIDIUM(0)

$[(triphos)Co(\mu\text{-}P_3)Ir(triphos)][BF_4]_2.CH_2Cl_2$ has been prepared from $[(triphos)Ir(\mu\text{-}P_3)]$ and $[Co(H_2O)_6][BF_4]_2$ in the presence of triphos [90].

$[\{Ir(CO)_3(PPh_3)\}_2]$ reacts with $EtO_2CC{\equiv}CCO_2Et$ to produce (26) [91] and with PhC≡CH, in boiling dichloromethane, the dinuclear iridium complex $[\{Ir(CO)_2(PPh_3)\}_2\text{-}\mu\text{-}(HC_2Ph)]$ is formed. This latter species is reported to have approximately C_s symmetry containing a *quasi*-tetrahedral $\{Ir_2C_2\}$ grouping [92].



(26)

3.8 IRIDIUM CARBONYL CLUSTERS

3.8.1 Trimeric clusters

$Na[Ir(CO)_4]$ reacts with CH_3CCl_3, $PhCCl_3$, Cl_3SiMe or Cl_3GeMe to form the new cluster compounds; $[Ir_3(CMe)(CO)_9]$, $[Ir_3(CPh)(CO)_9]$, $[Ir_3(SiMe)(CO)_9]$ and $[Ir_3(GeMe)(CO)_9$, respectively. These materials are believed, on the basis of the infrared spectra, to be isostructural with $[Co_3(\mu_3\text{-}CMe)(CO)_9][93]$.

The reaction of $[Ir(CO)_2(3\text{-toluidine})Cl]$ with *trans*-$Ph_2PCH = CHPPh_2$ in the presence of zinc and carbon monoxide gave the triangular cluster, $[Ir_3(CO)_7\{\mu\text{-}(cis\text{-}PPhCH = CHPPh_2)\}]$. The *cis*-$PPhCH = CHPPh_2$ portion acts as a tridentate ligand [94].

Complexation of $[(\mu\text{-}Me_3CS)_3Ir(\mu\text{-}C_4F_6)(CO)_6]$ with $CF_3C{\equiv}CCF_3$ gave the trimeric carbonyl cluster species $[(Me_3CS)_3Ir_3(CO)_5(C_4F_6)_2]$ [95].

3.8.2 Tetrameric clusters

$[Ir_4(\mu_3\text{-}PPh)(\mu_2\text{-}CO)_3(CO)_3(PPh_3)_4]$ is formed from the reaction of $[Ir_4(CO)_{12}]$ with PPh_3 in toluene [96]. In order to stabilise the cluster against fragmentation, $[Ir_4(CO)_{12}]$ was treated with the "tripod" ligand $HC(PPh_2)_3$ to give $[Ir_4(CO)_6(\mu\text{-}CO)_3\{HC(PPh_2)_3\}]$ [97]. Treatment of $[Ir_4(CO)_{12}]$ with alcoholic solutions of alkali metal alkoxides under CO gives the anions $[Ir_4(CO)_{11}(CO_2R)]^-$ (R = Me, Et). Alcoholysis occurs with EtOH or Me_2CHOH, whereas treatment with thf in acids gives a quantitative conversion to $[Ir_4(CO)_{12}]$. The anions are formulated more precisely as $[Ir_4(\mu\text{-}CO)_3(CO)_8(COOR)]^-$ [98]. The substituted isonitrile clusters, $[Ir_4(CO)_{12-x}(RNC)_x]$ (x = 1-4; R = Me_3C or Me), have been prepared from the reaction of $[Ir_4(CO)_{12}]$ with Me_3CNC or MeCN. The complexes have structures related to $[Ir_4(CO)_{12}]$ containing only terminal carbonyl groups [99].

The decomposition of $[Ir_4(CO)_{12}]$ to metallic iridium has been examined by thermogravimetry and IR spectroscopy. The KBr discs used in the study were noted to give a matrix effect which increased the decomposition temperature of the cluster [100]. The temperature programmed decomposition of $[Ir_4(CO)_{12}]$ supported upon $\gamma\text{-}Al_2O_3$ under a flow of dihydrogen has shown the highest methane: metal complex ratio of sixteen assorted mononuclear, dinuclear and cluster complexes [101].

Substitution of L = $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$ or $As(C_6H_5)_3$ for carbon monoxide in $[Ir_4(CO)_{12}]$ between 30 and 125 °C has been shown to follow the rate law:

$$\text{Rate} = \{k_1 + k_2[L]\}[Ir_4(CO)_{12}]$$

In the phosphorus compounds the second-order term contributes over 95% of the total rate. The k_2 term represents nucleophilic attack at iridium whereas the k_1 term involves CO dissociation. The reaction products and degree of substitution are a function of the nature of the ligand and the reaction conditions [102].

$[Ir_4(CO)_8(PMe_3)_4]$ consists of a distorted tetrahedral array of metal atoms possessing three symmetrical edge-bridging carbon monoxide groups on one triangular face with each iridium atom attached to a PMe_3 ligand. The complex reacts with CO to give $[Ir_4(CO)_9(PMe_3)_3]$ through the dissociative process:

$$[Ir_4(CO)_8(PMe_3)_4] + CO \rightarrow [Ir4(CO)_9(PMe_3)_3] + PMe_3$$

This reaction is considerably slower than the analogous reaction involving the sterically more demanding PEt_3 [103]:

$$[Ir_4(CO)_8(PEt_3)_4] + CO \rightarrow [Ir_4(CO)_9(PEt_3)_3] + PEt_3$$

The X-ray crystal structure of the tetrahedral cluster species $[PPh_4][Ir_4Br(\mu\text{-}CO)_3(CO)_8]$ has been recorded [104].

3.8.3 Hexameric clusters

The dianion $[Ir_6(CO)_{15}]^{2-}$ may be protonated to give $[HIr_6(CO)_{15}]^-$ and may be reacted with allyl chloride, $CH_2 = CHCH_2Cl$, to give $[Ir_6(CO)_{14}(C_3H_5)]^-$. Reaction of iodine with $[Ir_6(CO)_{15}]^{2-}$ gives $[Ir_6(CO)_{15}I]^-$. The acyl derivative, $[Ir_6(CO)_{15}(COC_2H_5)]^-$, was produced from $[Ir_6(CO)_{16}]$ and this species is found to react with X^- (X = Cl, Br or I) to give $[Ir_6(CO)_{15}X]^-$ [105].

3.8.4 Octameric clusters

Reaction of $[Ir_4(CO)_{12}]$ with KOH in 1,2-dimethoxyethane under an inert atmosphere affords the species $[Ir_8(CO)_{22}]^{2-}$ consisting of a double cluster of two tetrahedral $Ir_4(CO)_{11}$ groups joined by a metal-metal bond. This single Ir-Ir bond cleaves readily with, for example, PPh_3, $FeCl_3$, H_2 or I_2 to give $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (x = 1, 2 or 3), $[Ir_4(CO)_{12}]$, $[Ir_4(CO)_{11}H]^-$ and $[Ir_4(CO)_{11}I]^-$, respectively [106].

3.8.5 Mixed-metal clusters

The pseudo-tetrahedral, mixed-metal clusters, $[(cp)WIr_3(CO)_{11}]$ [107,108] and $[(cp)_2W_2Ir_2(CO)_{10}]$ [107] have been synthesised and their molecular structures reported. The structures are analogous to that of $[Ir_4(CO)_{12}]$ with one and two $\{Ir(CO)_3\}$ units, respectively, replaced by the isoelectronic $\{(cp)W(CO)_2\}$ groups. When impregnated onto γ-alumina from cyclohexane solutions and decomposed by heating in flowing dihydrogen, most of the coordinated CO is hydrogenated to methane rather than being released intact [107].

The dianion, $[RuIr_4(CO)_{15}]^{2-}$ has been prepared by the reductive carbonylation of $[Ir_4(CO)_{12}]$ and "$RuCl_3.xH_2O$" mixtures. The $[(Ph_3P)_2N]^+$ salt was characterised by X-ray diffraction and found to contain an elongated trigonal bipyramidal array of metal atoms in which the ruthenium atom occupies an apical position [109].

3.9 IRIDIUM NITROSYLS

The reactions of N_2O_3 with $[IrCl(CO)(PPh_3)_2]$, $[IrH(CO)(PPh_3)_3]$, $[IrCl(CO)(SO_2)(PPh_3)_2]$ or $[IrCl(CO)(H_2S)(PPh_3)_2]$ gave $[IrCl(CO)(NO)(NO_2)(PPh_3)_2]$, $[IrH(CO)(NO)(NO_2)(PPh_3)]$, $[IrCl(CO)(NO)(NO_3)(PPh_3)_2]$ or $[IrCl(CO)(NO)(NO_2)(PPh_3)_2]$, respectively. $[IrCl(CO)(NO)(NO_2)(PPh_3)_2]$ reacts with dioxygen to produce $[IrCl(CO)(NO_2)(NO_3)(PPh_3)_2]$ [110].

3.10 IRIDIUM CATALYSTS

The chemistry of iridium-catalysed carbonylation and their applications to commercial processes has been reviewed by Forster [111] as has the mechanistic pathways in the catalysis of alkene hydrocarboxylation by iridium complexes [112]. The heterolytic activation of dihydrogen by iridium complexes has been discussed [140].

3.10.1 Hydrogenation

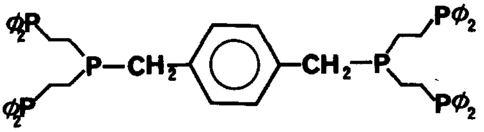
3.10.1.1 Alkenes

The silica-bound tetrairidium clusters, $[Ir_4(CO)_{11}(PPh_2)]$-$\{SiO_2\}$ and $[Ir_4(CO)_{10}(PPh_2)]$-$\{SiO_2\}$, have been identified using FT IR spectroscopy [113]. These catalysts were examined for their activity in the hydrogenation of ethene and the kinetic results fitted to the empirical equation:

$$\text{rate} = k\, P_{C_2H_4}^{x}\, P_{H_2}^{y}$$

The polymer-bound tetrairidium carbonyl cluster, $[Ir_4(CO)_{12-x}(PPh_3)_x]$, has also been found to catalyse the hydrogenation of ethene. The Ir_4 framework is reported to provide the catalytic sites for hydrogenation by reversible Ir-Ir bond breaking to form coordinatively-unsaturated metal centres [114].

In the catalytic hydrogenation of 1-heptene in dichloromethane using $[IrCl(cod)(PR_3)]$ ($R = 4\text{-}R'C_6H_4$; R' = MeO, Me, H, F or Cl), the maximum activity was obtained for $PR_3 : Ir = 1$; the hydrogenation rate was correlated with phosphine basicity [115]. Hydrogenation of 1-heptene is also catalysed by $[Ir_2Cl_2(tddx)]$ (tddx = (27)) which is said to form species of the type



(27)

$[Ir_2Cl_2H_4(tddx)]$ from which transfer of hydrogen to the alkene can occur. The reaction is reported to be first order in catalyst concentration and fractional order in substrate concentration [116]. By a similar process $[Ir_2Cl_2(tddx)]$ also catalyses the hydrogenation of cyclohexene [116] as does the dinitrogen complex, $[(PPh_3)_2Ir(N_2)Cl(H)(FBF_3)]$ [55] and the polymer-bound species, $[Ir_4(CO)_{12-x}(PPh_3)_x]$ [114].

$[IrHCl_2(PPh_3)_3]$ catalyses the hydrogenation of geraniol (a mixture of *cis*- and *trans*- $Me_2C{=}CH(CH_2)_2C(Me){=}CHCHO$) to give $Me_2CH(CH_2)_3CHMe(CH_2)_2OH$ and $Me_2C{=}CH(CH_2)_2CH(Me)(CH_2)_2OH$, both of which are formed through a common intermediate. The catalysis is reported to be accelerated by addition of H_2O_2 and retarded by addition of Et_3N [117].

$[Ir(cyclooctadienyl)(py)(PR_3)][PF_6]$ (R = cyclohexyl) is an efficient catalyst for the hydrogenation of unsaturated steroids and alicyclic compounds from the α-face without accompanying reduction of the ketone groups, carbon-halogen bonds or cyclopropane rings [118].

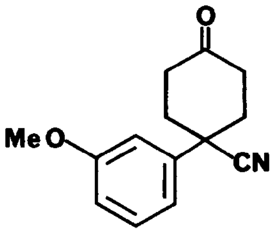
3.10.1.2 Carbon monoxide

A quantitative investigation of the $[Ir_4(CO)_{12}]$-catalysed hydrogenation of carbon monoxide to methane has been reported. The rate of methane formation is enhanced by the addition of trimethyl phosphite, and isotopic labelling has shown that the methane is derived largely from the phosphite methyl groups. The mechanism is therefore considered to involve methyl group transfer from the phosphite to iridium and hydrogenolysis of the Ir-C bond to give methane. The hydrogenation rates in this reaction, carried out in a sealed tube at 160-180 °C, are very low [119]. Catalytic hydrogenation of carbon monoxide by $[Ir_4(CO)_{12}]$ in a $NaCl$-$AlCl_3$ melt takes place under flow conditions at atmospheric pressure and, preferably, 170-180 °C. Under the optimum conditions the following yields were obtained: isobutane, 54%, propane, 17%; neo- and isopentane, 17%; methylcyclopentane, 6%; butane, 2%; methane, 1.5% and ethane, 1.5%. The infrared spectrum of the quenched catalyst was examined following its exposure to the reaction conditions. This revealed the presence of new iridium carbonyl species - probably containing Ir-C-O-Al bonds [120].

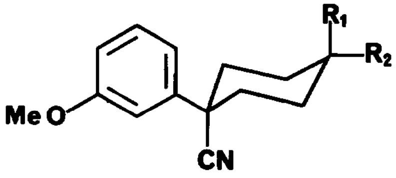
3.10.1.3 Alcohols and ketones

$[IrH_3(PPh_3)_3]$, $[IrH_5(PPh_3)_2]$, $[IrCl_3(PhPEt_2)_3]$ or $[IrHCl(PhPMe_2)_3]$ catalyse the hydrogenation of Ph_3COH. In trifluoroethanoic acid the reaction is considered to proceed *via* the transfer of H^- from the catalyst [121].

In the presence of soluble iridium catalysts, prepared by complexation of $IrCl_4$ with $P(OMe)_3$ or dmso, (28) is reduced in aqueous solutions of isopropanol to (29) (R_1 = H or OH; R_2 = OH or H) [122].



(28)



(29)

$[IrH_3(PPh_3)_3]$ and $[IrH_5(PPh_3)]$ are also reported to catalyse the hydrogenation of ketones in a tfaH medium. The mechanism is understood to involve hydride transfer from the complex to the protonated ketone [123].

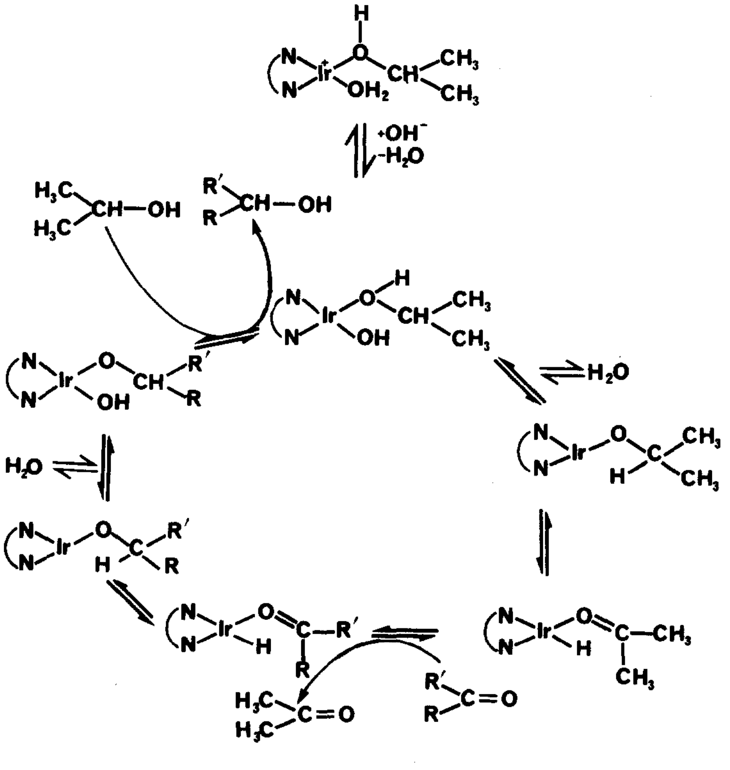
3.10.1.4 Nitro and imino derivatives

$[NH_4]_2[IrCl_6]$, when associated with chloranilic acid, is reported to behave as an efficient homogeneous catalyst in the hydrogenation of RNO_2 to RNH_2 (R = 2, 3 or $4\text{-}ClC_6H_4$; 2, 5- or $3,4\text{-}Cl_2C_6H_3$). Yields of 99.7-99.9% are claimed for this process [124].

$[(PPh_3)_3IrH_2Cl]$ catalyses the hydrogenation of PhCH=NPh with equal effectiveness in ethanoic acid or trifluoroethanoic acid solutions. Hydride is said to be transferred from dihydrogen to protonated azomethines [125].

3.10.1.5 Hydride transfer

Iridium complexes containing nitrogen donor ligands are known to be active catalysts for the hydrogen transfer from alcohols to ketones. [Ir(chel)cod]X (chel = 2-pyridinalmethylimine, 2-pyridinalisopropylimine, S-2-pyridinalphenylethylimine or R-2-pyridinalphenylethylimine; X = $[PF_6]$ or $[ClO_4]$) has been reported to catalyse hydrogen transfer from 2-propanol to cyclohexanones [126] and the kinetics of the $[Ir(3,4,7,8\text{-}Me_4phen)(cod)]Cl$ - catalysed hydrogen transfer between 2-propanol and $4\text{-}CMe_3$cyclohexanone have been studied [127]. Catalysts of the type [Ir(cod)(L-L)]Cl (L-L = 4,4'-bipy; phen; $4,4'\text{-}Me_2bipy$; $4,7\text{-}Me_2phen$; $3,4,7,8\text{-}Me_4phen$ or $4,7\text{-}Ph_2phen$) have also been used to reduce ketones by means of hydride transfer from 2-propanol. The catalytic scheme is illustrated in Scheme IV [128].



Scheme IV: $[Ir(cod)(L\text{-}L)]^+$-catalysed reduction of ketones [128].

$[Ir(SbPh_3)_3Cl]$ catalyses the homogeneous hydrogen transfer from 2-propanol to cyclohexanone but is not as effective as many of the ruthenium complexes tested. For example, using equivalent catalyst and reactant concentrations, at 100 °C and a reaction time of 13.5 h, the yield of cyclohexanol was 0.8% with the

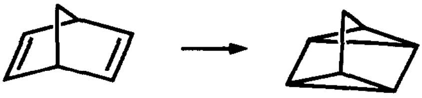
$[Ir(SbPh_3)_3Cl]$ but 86% with the five-coordinate $[RuCl_2(dpptp)_3]$ (dpptp = diphenyl-*p*-tolylphosphine) [129].

3.10.2 *Isomerisation*

Aqueous solutions of $K_3[IrCl_6]$ have been employed for the isomerisation of water-soluble allylic compounds, e.g. $CH_2 = CHCH_2Ph$ and $CH_2 = CHCH_2OPh$. With the aid of quaternary or phosphonium salts, the catalyst is extracted into the organic phase and returned to the aqueous layer by lipophilic anions after completion of the catalytic process [130].

The dinitrogen complex, $[Ir(PPh_3)_2(N_2)(Cl)(H)(FBF_3)]$ catalyses the isomerisation of cod [55].

$[IrCl(CO)(PPh_3)_2]$ is found not to catalyse the photo-assisted conversion of nbd (30) to quadricyclene (31) [131].



(30) (31)

3.10.3 *Carbonylation*

$[IrCl(CO)(PPh_3)_2]$, $[IrClH_2(PPh_3)_3]$ or $[IrH(CO)(PPh_3)_3]$ catalyse the carbonylation of nitrobenzene in methanol to give $PhNHCO_2Me$ in a yield of about 10% [132].

3.10.4 *Water gas-shift reaction*

The water gas-shift reaction ($H_2O + CO \rightarrow CO_2 + H_2$) has been reported to be catalysed by complexes of the type $[Ir(cod)L_2]^+$ ($L_2 = (PPh_3)_2$, $(PMePh_2)_2$, dppe, phen or substituted phen). These catalysts are reported to be more active than $[Rh(CO)_2I_2]^-$ but not as active as $[Ru_3(CO)_{12}]$ [133, 134].

3.10.5 *Oxidation*

$[Ir(H_2O)Cl_5]^-$ has been found to be a much more active catalyst than $[IrCl_6]^{2-}$ in the oxidation of propane and isobutane by aqueous solutions of $H_2Cr_2O_7$ [135].

However, unlike their ruthenium(IV) analogues, these iridium(IV) chloride complexes were discovered not to be active for the oxidation of saturated hydrocarbon using a P/Mo/V heteropoly acid [136].

3.10.6 Hydrosilylation

$[IrX(CO)L_2]$, $[IrCl(N_2)(PPh_3)_2]$, $[\{IrCl(C_8H_{14})_2\}_2]$ or $[IrClL_2]$ (X = halide, L = tertiary phosphine or arsine) catalyse the reactions of $HSiR_3$ (R = Ph, Et or OEt) with methanol or ethanol. The mechanism of the reaction with $[IrX(CO)L_2]$ is believed to involve the intermediate formation of $XSiR_3$ by elimination from the silyl complex $[IrHX(SiR_3)(CO)L_2]$ [137].

3.10.7 Polymerisation

Radical polymerisation of styrene occurs in the presence of $[Ir(CO)Cl(PPh_3)_2]$ and Me_3COOH. The overall activation energy was found to be 68.6 kJ mol^{-1} compared to the value of 150.2 kJ mol^{-1} obtained in the absence of the iridium complex [138].

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