Coordination Chemistry Reviews, 131 (1994) 177–210

6. Iridium

Catherine E. Housecroft

CONTENTS

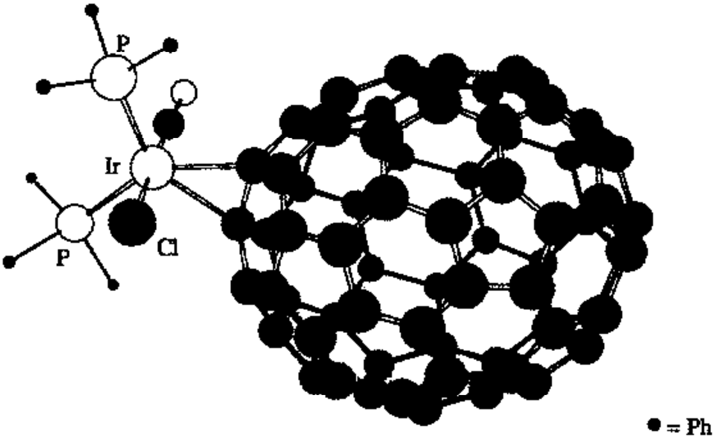
INTRODUCTION

This review surveys the coordination chemistry of iridium published during 1991; work that was published at the end of 1990 and was not included in the previous review [1] in this series is also reported here. The article follows a format similar to that used in the corresponding 1990 review [1] but, this year, a separate section featuring dimetallic complexes has been included. Complexes are arranged in sections according to the oxidation state of the iridium centre. Section 6.6 covers selected cluster species. My thanks go to the Cambridge Crystallographic Data Centre for providing atomic coordinates for selected structures redrawn for this review; hydrogen atoms have generally been omitted from these structural figures.

The organometallic chemistry of iridium has not, in general, been incorporated into this review unless the complexes feature something which will be of interest to the coordination chemist. However, two especially exciting molecules cannot go without a mention. These are the fullerene

0010-8545/94/$26.00
SSDI 0010-8545(93)00999-9

complexes $(\eta^2\text{-}C_{60})Ir(CO)(Cl)(PPh_3)_2$ [2] and $(\eta^2\text{-}C_{70})Ir(CO)(Cl)(PPh_3)_2$, (**1**), [3] both of which have been characterised by X-ray crystallography. In each case, one C-C edge of the fullerene cage interacts with the metal centre in a manner resembling that of an alkene.



(**1**)

Monocyclopentadienyl halide complexes of the *d*- and *f*-block metals have been the subject of a review (697 references); complexes of iridium are included [4].

6.1 IRIDIUM(V) AND IRIDIUM(IV)

A normal coordinate analysis for members of the series of complexes $[IrX_nY_{6-n}]^{z-}$, including geometrical isomers for $n = 2\text{-}4$, has been carried out for $X \neq Y = F$, Cl or Br, $n = 0\text{-}6$, and $z = 1\text{-}3$; for the iridium(V) and iridium(IV) complexes, $z = 1$ and 2, respectively. As a consequence of the differing *trans*-influences ($X < Y$, and $F < Cl < Br$), it is noted that in asymmetrical axes X-M-Y, the M-Y bond is strengthened at the expense of the M-X bond [5]. Reactions of the iridium(IV) salt $Na_2[IrCl_6]$ or the iridium(III) salt $Na_3[IrCl_6]$ with $NaNO_2$ yield products which have been studied by ^{15}N NMR spectroscopy. Species observed were $Ir(NO_2)_3(H_2O)_3$, *trans*-$[Ir(NO_2)_4Cl_2]^{3-}$, $[Ir(NO_2)_6]^{3-}$ and $[Ir(NO_2)_4Cl(H_2O)]^{2-}$; isolated salts (after cation exchange) were $Rb_2Na[Ir(NO_2)_3Cl_3]$ and $Rb_3[Ir(NO_2)_3Cl_3]$ [6]. The syntheses and structural characterisation of a series of hexahalogeno and trichlorostannato complexes of iridium(IV) have been reported; even in the presence of reducing tin(II) halides, iridium(III) is readily oxidised to iridium(IV). The salts $[H_3O]_2[IrBr_6]$, $[NH_4]_2[IrBr_6]$ and $Cs_2[IrCl_6]$ were isolated and their structures determined; distances in each of these complexes are Ir-Br = 2.515 (1) Å, Ir-Br = 2.549

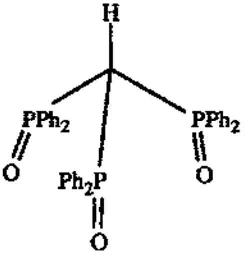
(3) Å, and Ir-Cl = 2.332 (2) Å, respectively [7]. A method has been developed for the selective determination of iridium(IV) ions in 90% dmso solution by using a spectrophotometric titration method [8].

Reactions of the iridium(V) complex $IrH_5(P^iPr_3)_2$ with alkynes have been described; iridium(III) complexes are produced and these are described more fully in Section 6.2.5 [9].

The oxides $Ba_4Ir_2AlO_{10}$ [10] and $Ba_4Ir_3O_{10}$ [11] have both been prepared by flux methods and have been structurally characterised. The lattice of $Ba_4Ir_2AlO_{10}$ exhibits face-connecting IrO_6- or Ir/AlO_6-octahedra; there is a statistical distribution of aluminium and iridium atoms in some of the octahedra. Determination of the coulombic term of the lattice energy for the system indicates that the oxidation state distribution is Ir(V)/Al(III)–Ir(IV)–Ir(V)/Al(III). The crystal lattice of $Ba_4Ir_3O_{10}$ features face-sharing IrO_6-octahedra which are connected *via* their edges into "wave-like" sheets.

A spectroscopic (electronic, infrared, and Raman) study of polycrystalline iridium(IV) sulfide and selenide has been carried out. Complete vibrational assignments have been made in terms of the stretching and bending modes of the IrX_3- and IrX_6-units (X = S or Se) [12].

The *O*-donor ligand L^-, where HL is (**2**), has been used to stabilise the iridium(V) state. The reaction of $LIr(C_2H_4)_2$ with Ph_3SiH gives an iridium(III) complex (see Section 6.2.2). However, when there are smaller steric demands, (for example in reactions with Et_3SiH or Ph_2MeSiH), oxidative addition of two equivalents of the silane occurs to give the iridium(V) complexes $LIr(H)_2(SiEt_3)_2$ or $LIr(H)_2(SiPh_2Me)_2$. The ligand L^- bonds to the iridium centre in an *O*, *O'*,*O''*-mode [13].



(**2**)

The reaction of $K_3[Ir(NO_2)_6]$ and sulfuric acid yields $K_8[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(SO_4)_3]$. In the anion, monodentate sulfate ligands can be replaced by water molecules to give $[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(H_2O)_3]^{2-}$. In 30% H_2SO_4, $[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(SO_4)_3]^{8-}$ hydrolyses to $[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(HSO_4)_2(H_2O)]^{4-}$; this, as the tricesium potassium salt, has been structurally characterised. $K_8[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(SO_4)_3]$ and $Cs_3K[Ir_3(\mu_3\text{-}O)(\mu\text{-}SO_4)_6(HSO_4)_2(H_2O)]$ can be reversibly reduced [14].

6.2 IRIDIUM(III)

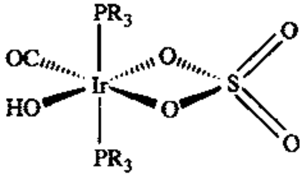
6.2.1 Complexes with halide and pseudo-halide ligands

The ions $[IrX_nY_{6-n}]^{3-}$, for X ≠ Y = F, Cl or Br, n = 0-6, have been the subjects of a normal coordinate analysis (see Section 6.1) [5]. The iridium(III) complexes $K_3[IrCl_5(SnCl_3)]$ and $[NH_4]_3[IrCl_5(SnCl_3)]$ have been prepared from $[IrCl_6]^{3-}$ and $SnCl_2.2H_2O$ in concentrated HCl. The results of a crystallographic study of $K_3[IrCl_5(SnCl_3)]$ confirm the presence of the octahedral iridium centre; pertinent distances are $Ir\text{-}Cl_{trans\text{ to }Sn}$ = 2.438 (3) Å, $Ir\text{-}Cl_{cis\text{ to }Sn}$ = 2.339 (3)–2.376 (2) Å, Ir-Sn = 2.496 (1) Å [7]. The mechanism of the dehydrogenation of propan-2-ol, catalysed by the complex ions *trans*-$[IrCl(H)(SnCl_3)_4]^{3-}$ and *trans*-$[IrCl_2(SnCl_3)_4]^{3-}$, has been discussed; the reaction kinetics support the pre-dissociation of one $[SnCl_3]^-$ ligand. It is proposed that there is a common catalytic cycle for the two iridium(III) complexes [15]. The system is further explored in a related paper [16].

The extraction of iridium(III) and rhodium(III) ions with 4-(non-5-yl)-pyridine, L, has been explored. The rate of extraction of rhodium(III) increases with increasing concentrations of both chloride ion and L. Under conditions for optimum rhodium(III) extraction, iridium(III) is similarly extracted; these conditions are $[Cl^-]$ = 3.7 M, [L] = 0.3 M, $[H^+]$ = 0.8 M. Spectroscopic data suggest that the extracted species are $[MCl_6]^{3-}.3[HL]^+$ (M = Ir or Rh) [17].

6.2.2 Complexes with oxygen donor ligands

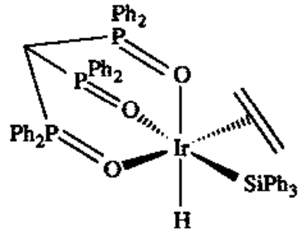
The syntheses of the iridium(III) complexes $Ir(CO)(OH)(SO_4)(PR_3)_2$ (R = Ph or 4-MeC_6H_4) have been reported; the proposed structures of these complexes are shown in (3). Complexes (3) react with carbon monoxide to give CO_2 and $[Ir(CO)_3(PR_3)_2]^+[HSO_4]^-$ [18].



(3)

Evidence has been put forward for there being significant π-donation from an alkoxide ligand to an iridium(III) centre. The crystal structures of $Ir(H)_2(OCH_2CF_3)\{P(c\text{-}C_6H_{11})_3\}_2$ and $Ir(H)_2(OCH_2CF_3)(CO)\{P(c\text{-}C_6H_{11})_3\}_2$ have been determined. In the former, the IrP_2O-core is planar (± 0.01 Å), the distance Ir-O is 2.030 (10) Å, and the angle ∠Ir-O-C is 138.0 (11)°. These data support the presence of O→Ir π-donation. The reactivity of the complex is consistent with such unsaturated character. Structural parameters for $Ir(H)_2(OCH_2CF_3)(CO)\{P(c\text{-}C_6H_{11})_3\}_2$ contrast with those of $Ir(H)_2(OCH_2CF_3)\{P(c\text{-}C_6H_{11})_3\}_2$; in the former, Ir-O = 2.169 (7) Å and ∠Ir-O-C = 118.4 (7)° [19]. Treatment of $Cp^*Ir(PPh_3)Cl_2$ with NaOEt in ethanol yields $Cp^*Ir(PPh_3)(OEt)(H)$. Further reaction with alcohols, ROH, gives $Cp^*Ir(PPh_3)(OR)(H)$, (R = OCD_2CD_3, ^nPr, ^iPr or Ph), and with amines, $R'NH_2$, leads to $Cp^*Ir(PPh_3)(NR'H)(H)$, (R' = Ph or CH_2Ph). The molecular structure of $Cp^*Ir(PPh_3)(O^iPr)(H)$ has been established; the iridium(III) centre is tetrahedrally coordinated with Ir-O = 2.076 (2) Å and Ir-P = 2.236 (1) Å. ^1H and ^{13}C NMR spectroscopic data are reported for the new complexes, and mechanistic studies are described in detail [20].

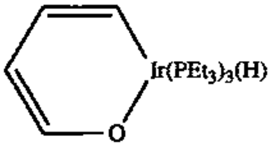
The stabilising influence of the ligand L^-, where HL = (2), with respect to high oxidation states, was described in Section 6.1. The reaction of $LIr(C_2H_4)_2$ with Ph_3SiH leads to complex (4), which is an unusual example of an alkene silyl hydride [13].



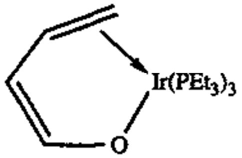
(4)

A model for a metal oxide surface is observed in the complex $(Cp^*Ir)_4V_6O_{19}$; its rhodium analogue has also been reported and structurally characterised. $(Cp^*Ir)_4V_6O_{19}$ is produced in > 90% yield by the reaction of sodium metavanadate with $[Cp^*IrCl_2]_2$. In acidic solutions (pH < 4), $(Cp^*Rh)_4V_6O_{19}$ releases $[Cp^*Rh(H_2O)_3]^{2+}$ into solution and when $(Cp^*Ir)_4V_6O_{19}$ is added to the solution, species of formula $(Cp^*Ir)_n(Cp^*Rh)_{4-n}V_6O_{19}$ ($0 \leq n \leq 4$) are formed. The crystal structure of $(Cp^*Ir)(Cp^*Rh)_3V_6O_{19}$ has been determined by X-ray diffraction. The structure of free $[V_6O_{19}]^{8-}$ has not been elucidated and thus the present work provides indirect information about this vanadate. The structure of $(Cp^*Ir)(Cp^*Rh)_3V_6O_{19}$ (with which $(Cp^*Rh)_4V_6O_{19}$ is isostructural) is described as possessing a "quadruple-cubane framework". The group 9 metals are tetrahedrally disposed with respect to one another; each is bonded to three oxygen atoms of the central V_6O_{19}-core [21].

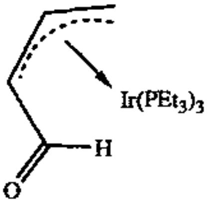
The reaction of $IrCl(PEt_3)_3$ with potassium oxapentadienide leads to the iridium(III) complex (5). The octahedral environment of the iridium centre has been confirmed by the results of an X-ray diffraction study; the three phosphine ligands are in a *fac*-arrangement. Pertinent distances are Ir-O = 2.172 (9) Å and Ir-P = 2.318 (3), 2.368 (3) and 2.330 (3) Å. Oxidative addition of the C–H bond does not occur when the phosphine is PMe_3; instead the product is the iridium(I) complex (6) which rearranges to give derivative (7) [22].



(5)

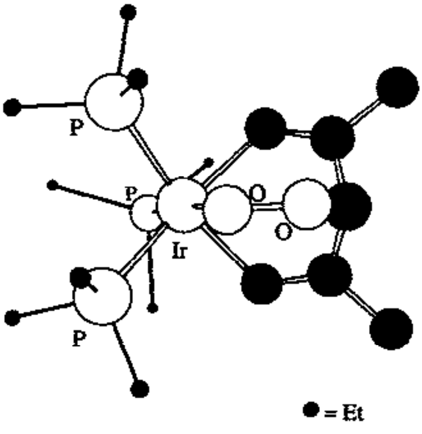


(6)

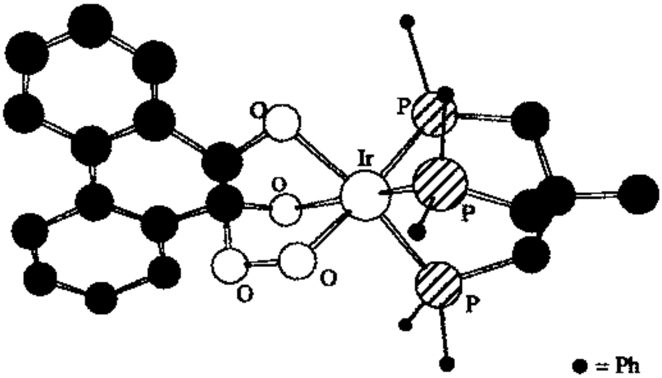


(7)

The reaction of the metallacycle 1,1,1-tris(triethylphosphine)-3,5-dimethyl-1-iridabenzene with dioxygen (i.e. ground state triplet O_2) yields the novel O_2-bridged iridium(III) complex (8). Crystallographic characterisation of (8) has confirmed a boat-configuration; pertinent bond distances are Ir-O = 2.111 (6) Å and O-O = 1.466 (7) Å [23]. An independently researched, but related complex cation, has also been reported; the tetraphenylborate salt of (1,1,1-tris(diphenylphosphinomethyl)ethane-*P*,*P′*,*P″*)-(9-dioxygen-9,10-phenanthrene-catecholato-*O*,*O′*,*O″*-iridium(1+), (9), has been structurally characterised [24].



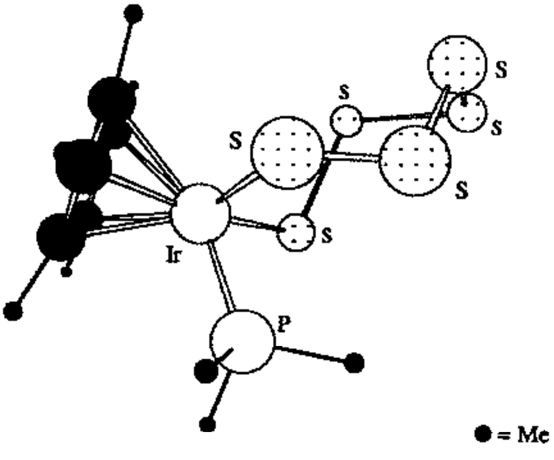
(8)



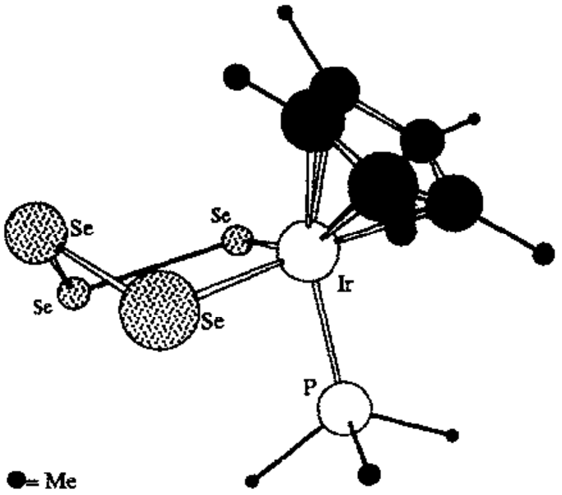
(9)

6.2.3 *Complexes with sulfur and selenium donor ligands*

Sulfido and selenido ligands have been incorporated into several new iridium(III) complexes. Reactions of Cp*Ir(PMe$_3$)Cl$_2$ with [NH$_4$]$_2$[S$_x$] (x = 10), [NEt$_4$]$_2$[Se$_6$], or H$_2$S have been investigated; the "half-sandwich" compounds Cp*Ir(PMe$_3$)(S$_4$) (red), Cp*Ir(PMe$_3$)(S$_6$), **(10)**, (yellow), Cp*Ir(PMe$_3$)(Se$_2$), (red), and Cp*Ir(PMe$_3$)(Se$_4$), **(11)**, (black), have been isolated and characterised. Complexes **(10)** and **(11)** have also been structurally elucidated. The IrS$_6$-ring in **(10)** has a chair-conformation. The IrSe$_4$-ring in **(11)** is puckered at one of the selenium atoms; the remaining four atoms lie in a plane. In compound **(10)**, distances are Ir-S = 2.358 (2) and 2. 345 (3) Å, whilst in **(11)**, Ir-Se = 2.468 (2) and 2.472 (2) Å. Triphenylphosphine can be used to selectively degrade the coordinated sulfur chelate as illustrated in its reaction with **(10)** which leads to Cp*Ir(PMe$_3$)(S$_5$) [25].

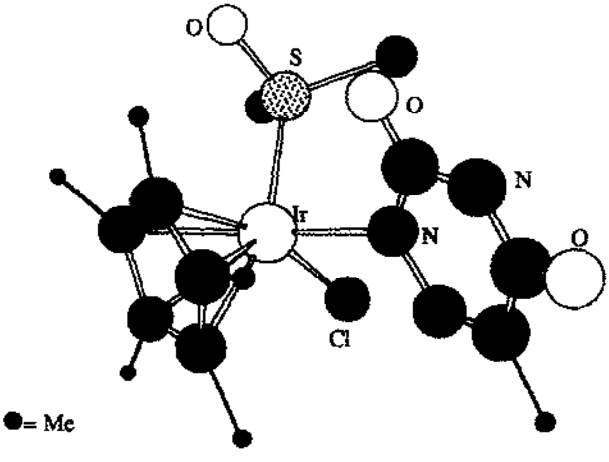


(10)



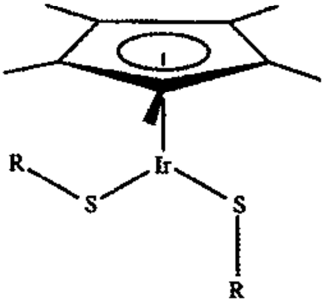
(11)

The solvent dmso is non-innocent in the reaction of $[Cp^*IrCl_2]_2$ with thyminate, L^-. The product is the chiral complex $Cp^*Ir(Cl)(L)(S\text{-dmso})$, **(12)**, the molecular structure of which has been determined (Ir-S = 2.302 (3) Å); see also Section 6.2.4 [26].



(12)

Thiolate ligands feature in a number of new complexes. The reaction of $[Cp^*IrCl_2]_2$ with $Pb(SR)_2$, ($R = C_6F_4H$), leads to the complex $Cp^*Ir(SR)_2$, (13), which has been the subject of a crystallographic investigation. A related reaction with perfluorophenyl thiolates has also been studied. NMR spectroscopic data are consistent with the persistence in solution of the solid state structure of (13). Significant differences are observed between the iridium(III) and analogous rhodium(III) chemistries [27].

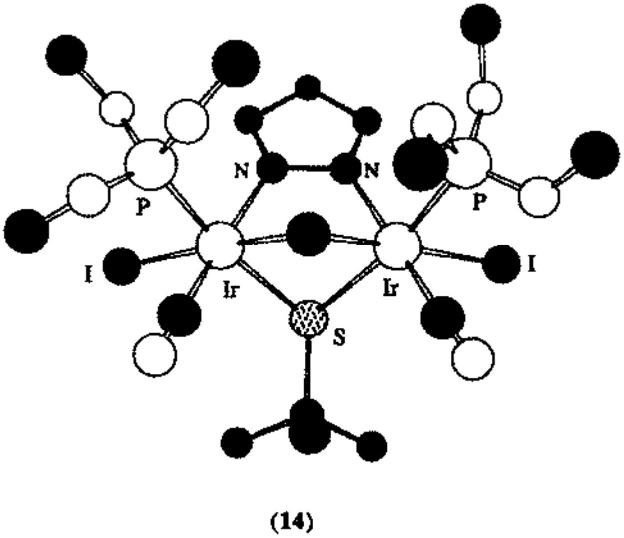


$R = C_6F_4H$

Ir–S = 2.323 (4) and 2.274 (4) Å

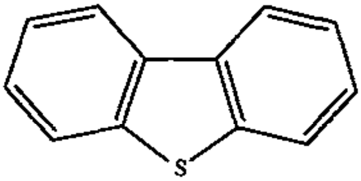
(13)

The reaction of $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)(CO)_2\{P(OMe)_3\}_2$ with methyl iodide gives $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)(Me)(I)(CO)_2\{P(OMe)_3\}_2$ but with CH_2I_2, the iridium(III) complex $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)(\mu\text{-CH}_2)(I)_2(CO)_2\{P(OMe)_3\}_2$, (14), is produced. An analogous result is obtained when $Ir_2(\mu\text{-dmpz})(\mu\text{-S}^tBu)(Me)(I)(CO)_2\{P(OMe)_3\}$ is treated with CH_2I_2 (dmpzH = 3,5-dimethylpyrazole). An X-ray diffraction study of (14) confirms the presence of a bridged diiridium framework; the Ir---Ir separation is 3.2990 (6) Å, and other important distances are Ir-S = 2.431 (2) and 2.425 (2) Å and Ir-N = 2.069 (6) and 2.080 (6) Å [28].



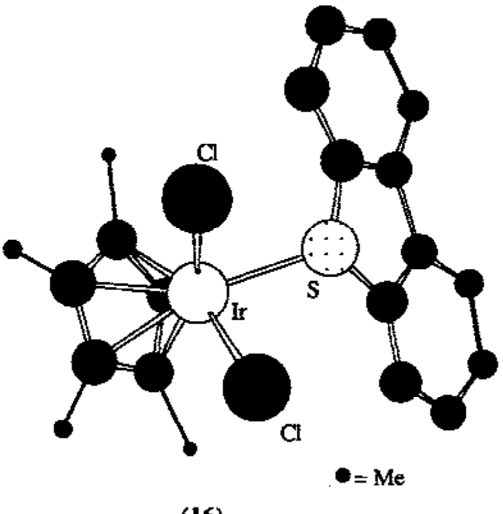
(14)

Dibenzothiophene, **(15)**, L, binds to iridium(III) in both of the modes indicated in the structure. Of interest here is the formation of Cp^*IrCl_2L, **(16)**, as a product in the reaction of $[Cp^*IrCl_2]_2$ with L. Orange crystals of Cp^*IrCl_2L have been analysed crystallographically. The Ir-S distance of 2.375 (2) Å is unexceptional; the sulfur atom is pyramidal (∠Ir-S-X = 128.0° where X is the midpoint of the C-C bond opposite the sulfur atom in the thiophene ring) [29].



Mode (I): η^6-benzene
Mode(II): *S*-donation

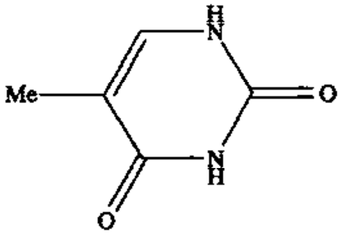
(15)



(16)

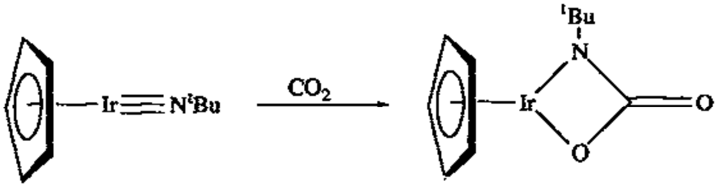
6.2.4 *Complexes with nitrogen donor ligands*

The chiral complex Cp*Ir(Cl)(L)(*S*-dmso), where HL = thymine, **(17)**, was mentioned in Section 6.2.3 in respect of the involvement of dmso as a ligand. An X-ray diffraction study of Cp*Ir(Cl)(L)(*S*-dmso), **(12)**, confirms that the thyminate ligand is *N*-bound (Ir-N = 2.120 (5) Å) [26].



(17)

Members of a series of terminal imido complexes, Cp*IrNR, (R = ^{t}Bu, SiMe$_2{}^t$Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$, or 2,6-Me$_2$C$_6$H$_3$) have been prepared from [Cp*IrCl$_2$]$_2$ and LiNHR in thf. The dimer [Cp*IrCl$_2$]$_2$ reacts with amines R'NH$_2$ (R' = ^{t}Bu or 2,6-^{i}Pr$_2$C$_6$H$_3$) to give the complexes Cp*Ir(R'NH$_2$)Cl$_2$ which are converted to the imido complexes Cp*IrNR' upon treatment with KN(SiMe$_2$)$_2$. The reactivity of the imido complexes has been studied; included are the reactions of Cp*IrN^{t}Bu with ^{t}BuNC, CO, CO$_2$ (Scheme 1) and MeO$_2$CC≡CCO$_2$Me. The molecular structures of Cp*IrN^{t}Bu, Cp*IrNSiMe$_2{}^t$Bu, Cp*IrN(2,6-^{i}Pr$_2$C$_6$H$_3$), or Cp*IrN(2,6-Me$_2$C$_6$H$_3$), as well as the product shown in Scheme 1, have been determined by X-ray diffraction. Parameters that describe the coordination of the imido groups to the iridium(III) centre are listed in Table 1 [30].



Scheme 1

Table 1 Selected structural data for Cp*IrNR, R = ^{t}Bu, SiMe$_2{}^t$Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$ or 2,6-Me$_2$C$_6$H$_3$.

R	^{t}Bu	SiMe$_2{}^t$Bu	2,6-^{i}Pr$_2$C$_6$H$_3$	2,6-Me$_2$C$_6$H$_3$
Distance Ir-N / Å	1.712 (7)	1.750 (3)	1.749 (7)	1.729 (7)
Angle Ir-N-C(or Si) / deg	177.2 (5)	170.8 (2)	174.0 (6)	174.9 (7)

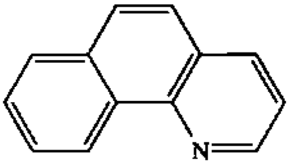
Interest in 2,2'-bipyridine and 2-phenylpyridine complexes of iridium(III) continues, particularly with respect to electron transfer and luminescence properties. A new method for the high-yield synthesis of *fac*-tris(metallated) iridium(III) complexes involving $[ppy]^-$ (Hppy = 2-phenylpyridine) and derivative ligands has been reported. The complex *fac*-$Ir(ppy)_3$ is prepared from $Ir(acac)_3$ and Hppy in glycerol under reflux conditions followed by treatment with HCl; the complexes *fac*-$Ir(R\text{-}ppy)_3$, where R = 4-Me, 4-Pr, 4-^{t}Bu, 4-F, 4-Cl, 4-MeO or 5-MeO, have been similarly synthesised. Reasons for the success of the method have been discussed and a mechanism which emphasises the *trans*-effect of the Ir-C bonds has been proposed. Emission spectroscopic and cyclic voltammetric data for *fac*-$Ir(R\text{-}ppy)_3$ are given in Table 2 [31].

Table 2 Emission spectroscopic and cyclic voltammetric data for *fac*-$Ir(R\text{-}ppy)_3$.

R	Emission lifetime (room temp.) / μs	$\lambda_{emission}$ / nm	$E_{1/2}(+1/0)$ / V^a
H	1.90	494	+0.77
4-Me	1.94	493	+0.70
4-Pr	1.93	496	+0.67
4-^{t}Bu	1.97	497	+0.66
4-F	2.04	498	+0.97
4-Cl	2.16	494	+1.08
4-MeO	2.24	481	+0.75
5-MeO	2.86	539	+0.55

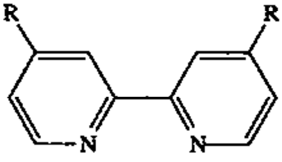
$^a E_{1/2}(+1/0)$ is for the process $[Ir(R\text{-}ppy)_3]^+$ / $Ir(R\text{-}ppy)_3$; measured vs. SCE

Shifts in the absorption and emission maxima in the electronic spectra of several metallated complexes of iridium(III) in a range of solvents have been measured. Some complexes involved in the study are $[Ir(bzq)_2(bpy)]Cl$, $[Ir(bzq)_2(phen)]Cl$, $[Ir(ppy)_2(phen)]Cl$ and $[Ir(ppy)_2(bpy)]Cl$, (Hbzq = benzo[*h*]quinoline, (**18**)). The solvent-induced spectral shifts are interpreted in terms of the theories of McRae and Marcus [32]. In an accompanying paper, the emission spectra of $[Ir(bzq)_2(bpy)]^+$ and $[Ir(bzq)_2(phen)]^+$ have been resolved into their component emissions by using time-resolved emission spectroscopy. For each spectrum, the lower and higher energy components are assigned to MLCT excited states associated with the bpy or phen ligand, and the metallated ligand, respectively [33]. Photoinduced electron transfer by a diffusible electron carrier from an immobilised photosensitiser (the acceptor) to an immobilised donor has also been illustrated. The trapped excited complex ion $[Ir(bpy)_3]^{3+*}$ accepts an electron from a donor such as 1,4-dimethoxybenzene, D; a charge-separated pair is produced, i.e. $\{Ir(II) \equiv A^-, D^+\}$, and this is the trapped photosensitiser. Detailed studies have been made in fluid solution and in sol-gel matrices in the presence and absence of ternary components ($[Ru(bpy)_3]^{2+}$). The data suggest the possibility of very long lifetime photoinduced electron transfer systems [34]. The luminescence spectral properties of *cis*-$[Ir(bpy)_2Cl_2]Cl$ have been reinvestigated with particular reference to the red luminescence at 680 nm. It is now suggested that the simple three state system initially proposed (MLCT, *d-d*, and ground) needs to be modified. Specifically, a new thermally accessibe state lying above the first MLCT is involed [35].



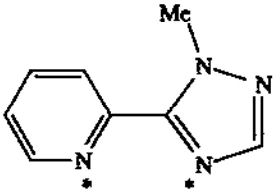
(18)

With respect to the water-gas shift reaction, it is of importance to probe systems which might exhibit catalytic properties at *low* temperatures. With this in mind, the complexes [Cp*IrLCl]Cl, where L = (**19**), have been prepared, as have [Cp*IrL'(X)]Y (L' = L with R = H; X = Y = Cl; X = Y = CF_3SO_3; X = H, Y = BPh_4; X = OH, Y = CF_3SO_3). These iridium(III) complexes have been characterised by ^1H and ^{13}C NMR spectroscopy, FAB mass spectrometry, and elemental analysis, and have been tested for activity in the water-gas shift reaction (1 atm. CO and H_2O at 25°C) [36].



(19)

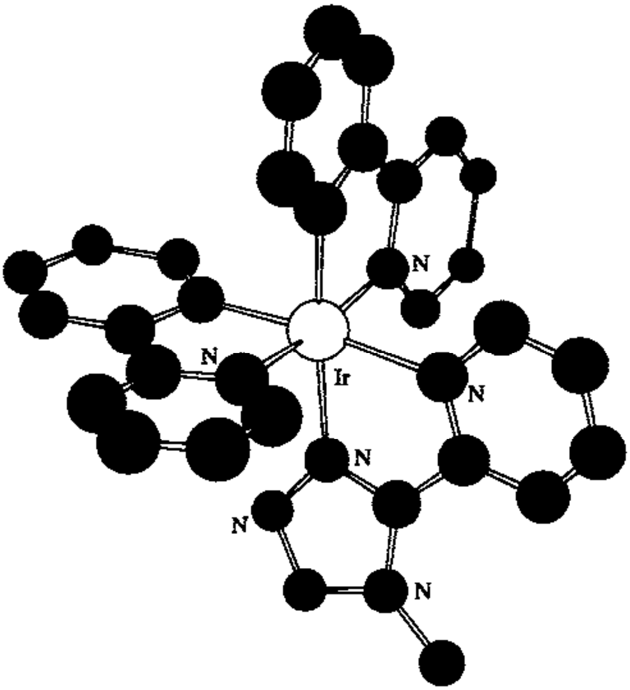
R
CO_2H
$CO_2{}^iPr$
Br
NO_2
NMe_2



* = coordination site

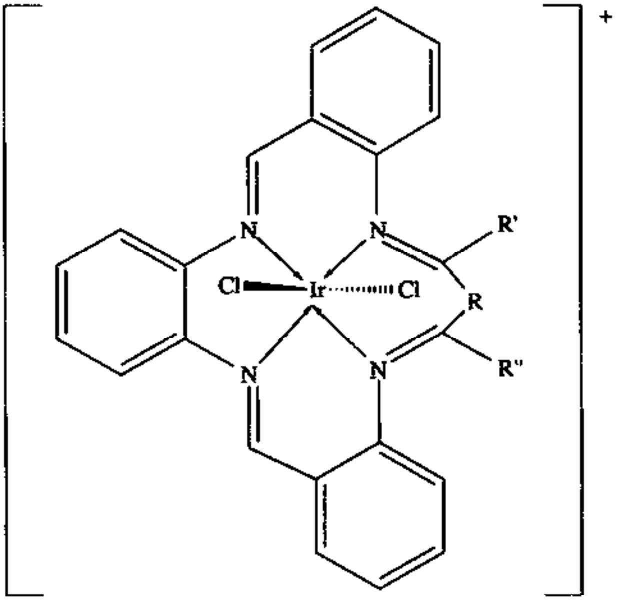
(20)

The synthesis of the metallated complex $[Ir(ppy)_2L][PF_6]$ (L = (**20**)) has been reported. This iridium(III) complex has been characterised by NMR, UV-visible, and emission spectroscopies; the lowest energy absorption in the UV-visible spectrum occurs at 380 nm (ε = 5400) and this feature is assigned to a $d \rightarrow \pi^*(ppy^-)$ MLCT. The electrochemistry of $[Ir(ppy)_2L][PF_6]$ has been investigated; reversible reduction occurs in acetonitrile solution at –1.57 V (vs. SCE) and an irreversible oxidation process is observed at +1.20 V (vs. SCE). The crystal structure of the complex has been determined; the cation $[Ir(ppy)_2L]^+$ is shown in structure (**21**). The iridium centre is, as expected, octahedrally sited and important distances within the coordination sphere are $Ir\text{-}N_L$ = 2.175 (11) and 2.139 (10) Å and $Ir\text{-}N_{ppy}$ = 2.046 (11) and 2.051 (9) Å [37].



(21)

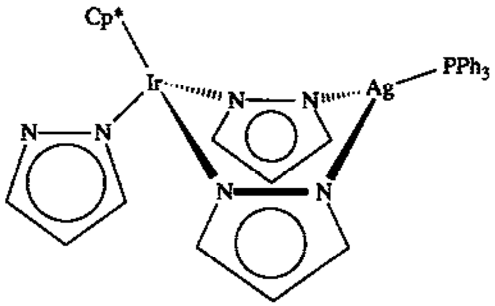
Complex formation between Schiff's bases, L, and iridium(III) ions has been investigated and complexes of the type $[IrLCl_2]Cl$, [(**22**)][Cl], in which ligand cyclisation has occurred, have been isolated. The products have been characterised by elemental analysis, electrical conductivity and magnetic susceptibility measurements, and infrared and ^1H NMR spectroscopies [38].



R = CH_2, R' = R" = Me; R = CH_2, R' = Ph R" = Me; R = nothing, R' = R" = Me or Ph

(22)

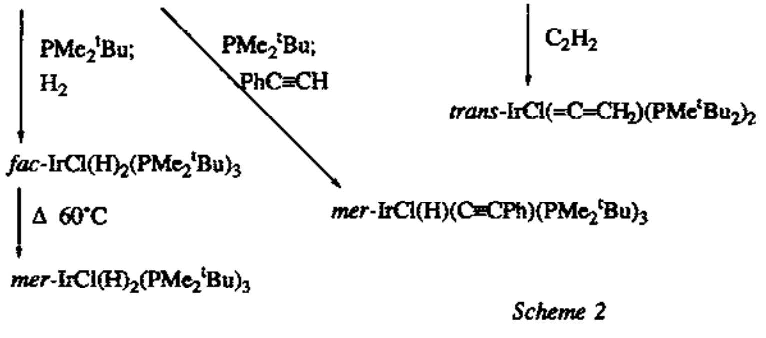
The formation and characterisation of the iridium(III) complexes $Ir_2(\mu\text{-}pz)(\mu\text{-}S^tBu)(\mu\text{-}CH_2)(I)_2(CO)_2\{P(OMe)_3\}_2$, **(14)**, and $Ir_2(\mu\text{-}dmpz)(\mu\text{-}S^tBu)(\mu\text{-}CH_2)(I)_2(CO)_2\{P(OMe)_3\}_2$ (dmpzH = 3,5-dimethylpyrazole) were described in Section 6.2.3 [27]. Pyrazole-based ligands are exhibited in the complexes *trans,cis*-$Ir(PPh_3)_2(H)_2(CO)L$ where HL = 3,5-Me_2-pyrazole, 3,5-Me_2-4-NO_2-pyrazole or 3,5-$(CF_3)_2$-pyrazole. The ^{193}Ir Mössbauer spectra of these complexes have been recorded and the results discussed along with the spectral data for the iridium(I) complexes *trans*-$Ir(PPh_3)_2(CO)L$ and *trans*-$Ir(PPh_3)_2(CO)(\mu\text{-}L'\text{-}N,N')AuX$ (HL' = 3,5-Me_2-pyrazole; X = Cl or Br). The results indicate to what extent the heterocyclic ligands affect the electron density associated with the iridium centres [39]. A bridging mode for the pyrazolate ligand is also observed in the heterometallic complexes $Cp^*Ir(pz)_3M(PPh_3)$, (M = Cu, Ag, Au). These species are prepared by reacting $Cp^*Ir(Hpz)(pz)_2$ with $\{M(PPh_3)Cl\}_n$ (M = Cu or Ag, $n = 4$; M = Au, $n = 1$) and potassium hydroxide. The complex $Cp^*Ir(pz)_3Ag(PPh_3)$, **(23)**, has been crystallographically characterised; two of the three pyrazolate ligands bridge between the two metal centres but in solution, **(23)** and its copper and gold analogues are fluxional with the $M(PPh_3)$ unit exchanging rapidly between all three $[pz]^-$ ligands. The reaction of $Ag[BF_4]$ and PPh_3 with complex **(23)** leads to $[Cp^*Ir(pz)_3\{Ag(PPh_3)\}_2][BF_4]$ [40]. In related work, a wide range of complexes including $Cp^*(Cl)Ir(pz)_2Rh(cod)$, $Cp^*(Cl)Ir(pz)_2Ir(cod)$ and $Cp^*(Cl)Ir(pz)_2Rh(CO)_2$ has also been reported; see also Section 6.4.3 [41].



(23)

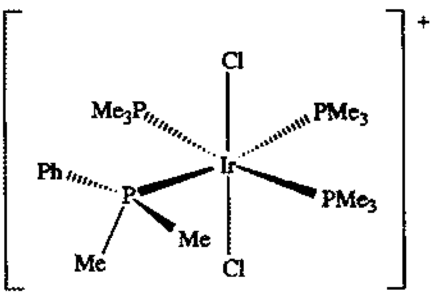
6.2.5 *Complexes with phosphorus donor ligands*

The iridium(V) complex $IrH_5(P^iPr_3)_2$ reacts with diphenylacetylene to yield the iridium(III) complex $Ir(C_2Ph)_3(P^iPr_3)_2$. In contrast, with the alkynes HC≡CH and MeC≡CMe, the products are $Ir(C_2R)_2(CR{=}CH_2)(P^iPr_3)_2$ (R = H or Me). The chemistry of these and related systems has been investigated [9]. The electrochemical and chemical oxidation of *fac*-$IrH_3(PPhMe_2)_3$ produces $[IrH_2(PPhMe_2)_3(S)]^+$ where S = solvent, (MeCN or $(CH_3)_2CO$); a product noted when the solvent is dichloromethane is $[IrH_4(PPhMe_2)_3]^+$. There is evidence for the presence of the transient radical $[IrH_3(PPhMe_2)_3]^{+\bullet}$ and the characteristics of this species have been probed *via* the introduction of various radical scavengers. Reaction schemes are proposed and discussed in detail [42]. The iridium(III) complexes *trans*-$IrCl({=}C{=}CH_2)(PR_3)_2$ (PR_3 = PMe^tBu_2 or PPh_3) and $Ir(H)Cl(C{\equiv}CPh)(PMe^tBu_2)_3$ have been prepared; Scheme 2 summarises some of the reactions studied [43].



Scheme 2

The preparation of the complex Cp*Ir(PPh$_3$)(Me)Cl and its reactions with MeCO$_2$Ag, PhNHLi, PhCH$_2$MgCl, PhONa and EtONa have been reported; related reactions are also described. Kinetic data have been presented for the substitution of PPh$_2$Me for PPh$_3$ in the iridium(III) complex Cp*Ir(PPh$_3$)(Me)(NHPh) and a mechanism for the process has been proposed. The rate of reaction does not depend on the concentration of PPh$_2$Me and it is proposed that there is a slipped-Cp* intermediate which is stabilised by the donation of a lone pair of electrons from the nitrogen atom to iridium centre [44]. The syntheses of the cationic iridium(III) complexes [IrCl$_2$L(PMe$_3$)$_3$]$^+$ where L = PMe$_3$, PMe$_2$Ph or PMePh$_2$ have been detailed and one salt, *trans*-[IrCl$_2$(PMe$_2$Ph)(PMe$_3$)$_3$][ClO$_4$], has been crystallographically characterised. The cation [IrCl$_2$(PMe$_2$Ph)(PMe$_3$)$_3$]$^+$, (24), is chiral. The low temperature ^{31}P{^{1}H} NMR spectrum (–75°C in acetone-d$_6$) is consistent with the same chiral conformer observed in the solid state, but a minor component, attributed to an achiral isomer, is also present. Above +45°C, the isomers interconvert in solution [45].



Ir-Cl = 2.375 (4), 2.366 (4) Å

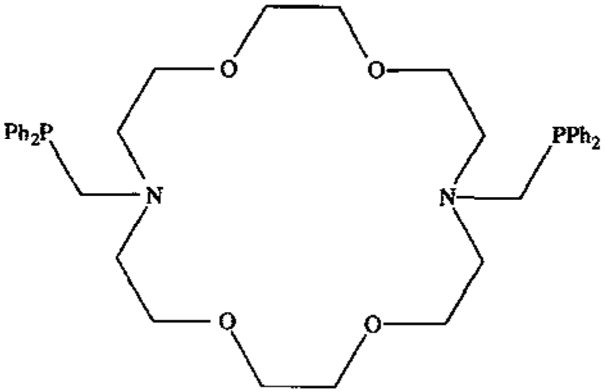
Ir-P(PMe$_3$) = 2.375 (4), 2.375 (4), 2.357 (5) Å

Ir-P(PMe$_2$Ph) = 2.381 (4) Å

(24)

Reactions between IrH$_3$(CO)(dppe) and silanes including Ph$_3$SiH, Et$_3$SiH, Me$_3$SiH, Me$_2$ClSiH, Me$_2$SiH$_2$, Ph$_2$SiH$_2$ and PhSiH$_3$ lead to iridium(III) complexes of the type IrH$_2$(SiRR'$_2$)(CO)(dppe) and IrH(SiRR'$_2$)$_2$(CO)(dppe). Complexes have been characterised spectroscopically and, in addition, the molecular structures of IrH(SiMe$_2$Cl)$_2$(CO)(dppe) and IrH(SiMe$_2$H)(SiMe$_2$Cl)(CO)(dppe) have been determined. In both of these complexes, the silane groups are mutually *cis* and each silane is *trans* to a phosphine donor [46]. Iridium(III) complexes of formulae Cp*IrCl$_2$(PHRR'), [Cp*IrCl(PHR$_2$)$_2$][BF$_4$] and [Cp*Ir(acac)(HPR$_2$)][BF$_4$] (R = Ph or H; R' = H) have been synthesised from {Cp*IrCl$_2$}$_2$ or Cp*IrCl(acac) and PHRR' or PHR$_2$ [47].

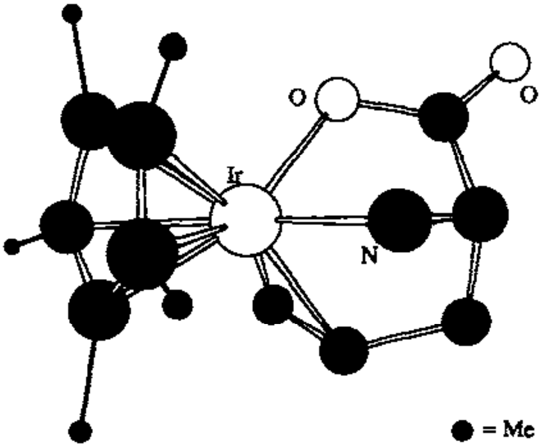
The macrocyclic ligand, L, (25), reacts with Ir(CO)$_2$Cl(4-MeC$_6$H$_4$NH$_2$) to give a square planar iridium(I) complex, LIr(CO)Cl, in which the two phosphorus donor atoms of L are mutually *trans*. This complex reacts with thallium(I) nitrate and the thallium ion is incorporated into the macrocycle to yield [Tl(L)Ir(CO)Cl]$^+$ (see Section 6.4.4 and structure (39)); oxidative addition of either chlorine or iodine, (X$_2$), to this cation produces the iridium(III) complex [X(Cl)(CO)Ir(L)TlX]$^+$. Ligand L, thus, acts as a bis(phosphine) donor towards the iridium(III) centre, but at the same time encapsulates the thallium ion bringing it to within bonding distance of the iridium atom [48].



(25)

6.2.6 *Complexes with mixed donor-atom ligands*

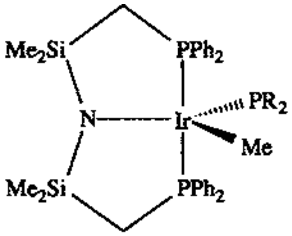
A series of metal complexes involving *C*-allylglycine and C-vinylglycine ligands has been prepared. Amongst these is the cationic complex **(26)** which has been crystallographically characterised [49].



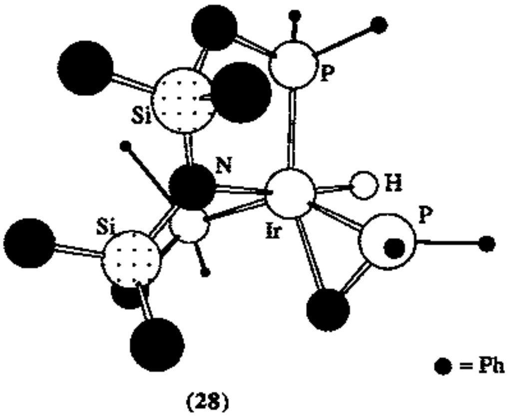
(26)

The nitrate salt of the linear *S*-bridged complex cation $[Co(III)\{IrL_3\}_2]^{3+}$ (HL = $HSCH_2CH_2NH_2$) reacts with zinc powder in water followed by zinc(II) bromide to give the cationic cage-like complexes $[Zn_{4-x}Co(II)_x(O)\{IrL_3\}_4]^{6+}$. As the nitrate salt, the complex has been isolated as dark green crystals, and analysis shows that the ratio Ir : Zn : Co = 4 : 2.8 : 1.2. The results of a crystallographic study of $[Zn_{4-x}Co(II)_x(O)\{IrL_3\}_4]Br_6.9.5H_2O$ confirm the presence, in the cation, of an *O*-centred $\{M'_4O\}$-core (M' = Zn/Co) surrounded by four $\{IrL_3\}$-units. Each iridium(III) centre is octahedrally coordinated by three *N,S*-chelates in a *fac*-configuration. Each *S*-donor also bridges between iridium and zinc/cobalt atoms, thereby supporting the cage-structure. The spontaneous resolution of the complex cation has been discussed [50].

The thermal and photolytic transformations of members of a group of iridium(III) phosphide complexes have been studied. For example, $Ir(Me)(PR_2)L$, **(27)**, (R = Ph or Me; HL = $HN\{SiMe_2CH_2PPh_2\}$) rearranges thermally to give the cyclometallated products, *fac*-$Ir(\eta^2\text{-}CH_2PR_2)(H)L$. The complexes **(27)** for R = Ph, and *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)(H)L$, **(28)**, have been structurally characterised. Further heating of *fac*-$Ir(\eta^2\text{-}CH_2PR_2)(H)L$ yields the iridium(I) complexes $Ir(PMeR_2)L$; these complexes can be obtained directly upon the photolysis of **(27)** [51]. The conjugate base of the ligand HL has also been incorporated into the complex *fac*-$Ir\{\eta^4\text{-}C(CH_2)_3\}L$. This compound is synthesised from the reaction of $Ir{=}CH_2(L)$ with allene and has been structurally characterised; important distances are Ir-P = 2.296 (1) and 2.295 (1) Å and Ir-N = 2.198 (4) Å. The iridium centre is considered to be in an pseudo-octahedral environment with the organic ligand and the *N,P,P'*-donor set being mutually staggered [52].

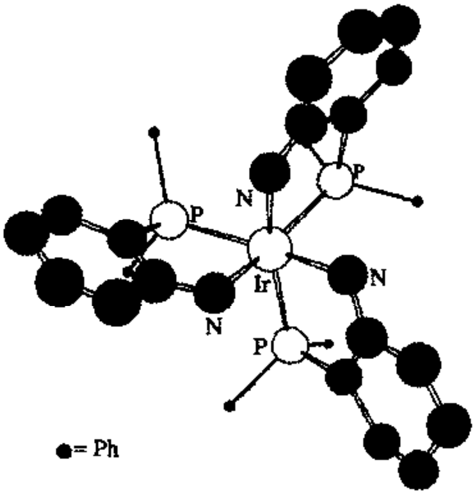


(27)



(28)

In a study of the roles of the ligands 2-(R_2N)$C_6H_4PPh_2$ (R = H or Me) in iridium hydrogenation catalysts, the complex *fac*-IrL_3, (**29**), (HL = 2-(H_2N)$C_6H_4PPh_2$) has been isolated and structurally characterised. The iridium(III) centre is octahedrally sited and important distances are Ir-P = 2.35 (1), 2.32 (2) and 2.32 (1) Å and Ir-N = 2.10 (6), 2.09 (4) and 2.10 (5) Å [53].



(**29**)

6.3 IRIDIUM(II)

The oxidative addition of iodine to $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)(\mu\text{-dppm})(CO)_2$ leads to the dinuclear iridium(II) complex $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)(\mu\text{-dppm})(CO)_2(I)_2$. An analogous complex incorporating a bridging 3,5-dimethylpyrazolate (dmpz$^-$) ligand has also been prepared. Reaction of either iridium(II) complex with silver nitrate results in the exchange of nitrate for iodide ligand. Related reactions have also been reported. The new complexes have been characterised by elemental analysis, and by infrared and ^{31}P NMR spectroscopies [54]. In related studies carried out by by the same researchers, the iridium(II) complexes $Ir_2(\mu\text{-pz})(\mu\text{-S}^tBu)\{P(OMe)_3\}_2(CO)_2(I)(CH_3)$ and $Ir_2(\mu\text{-dmpz})(\mu\text{-S}^tBu)\{P(OMe)_3\}_2(CO)_2(I)(CH_2I)$ have been prepared (see also Section 6.2.3) [28].

6.4 IRIDIUM(I)

6.4.1 Complexes with oxygen donor ligands

When *trans*-$Ir(PPh_3)_2(CO)(OSO_2CF_3)$ is treated with water in benzene, ligand displacement occurs and the cationic iridium(I) complex *trans*-$[Ir(PPh_3)_2(CO)(H_2O)]^+$ results. This, and the rhodium analogue, have been characterised by infrared, and ^1H, ^{31}P and ^{19}F (for the $[CF_3SO_3]^-$

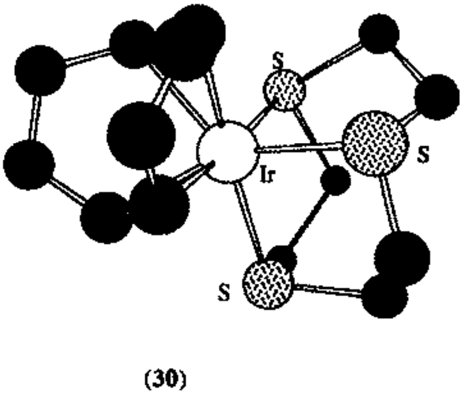
counter-ion) NMR spectroscopies. The square planar coordination sphere has been confirmed by X-ray diffraction for the rhodium complex *trans*-$[Rh(PPh_3)_2(CO)(H_2O)]^+$ [55].

The polyoxoanion-supported iridium(I) complex $[^nBu_4N]_5Na_3[(1,5\text{-cod})Ir\bullet P_2W_{15}Nb_3O_{62}]$ catalyses the oxygenation of cyclohexene by dioxygen. This iridium species has the highest activity of three related complexes studied and exhibits a turnover frequency of 2.9 h^{-1} in CH_2Cl_2 (T = 38°C). The kinetics of the process have been investigated and the rate law follows equation (i) where X^{8-} is the anion $[(1,5\text{-cod})Ir\bullet P_2W_{15}Nb_3O_{62}]^{8-}$; the concentration ranges for the components are $[X^{8-}] = 1.3 \times 10^{-3}$ to 4.0×10^{-3} M, [cyclohexene] = 0 to 2 M, and the partial pressure of O_2 = 0 to 760 mm Hg. In the proposed structure of $[(1,5\text{-cod})Ir\bullet P_2W_{15}Nb_3O_{62}]^{8-}$, the {Ir(cod)}-unit is supported on the surface of the polyoxoanion, and ^{17}O NMR spectroscopic studies indicate that the iridium(I) centre interacts with two Nb-O-Nb bridging oxygen atoms and one Nb-O terminal oxygen atom [56].

$$\frac{-d[\text{cyclohexane}]}{dt} = k_{2,obs}\,[(X^{8-})]^1[\text{cyclohexene}]^1 p(O_2)^{1\rightarrow 0} \qquad \text{Equ (i)}$$

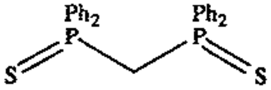
6.4.2 *Complexes with sulfur donor ligands*

The synthesis and full characterisation of $[IrL(cod)]^+$, (**30**), where L = 1,4,7-trithiacyclononane, have been reported. The complex cation is isolated as the tetrafluoroborate salt in the reaction of $\{(cod)IrCl\}_2$ with L in dichloromethane solution in the presence of $NaBF_4$. The related cation $[IrL(C_2H_4)_2]^+$ has also been synthesised. An X-ray diffraction study of $[(\mathbf{30})][BF_4]$ reveals that for the cation, the iridium(I) centre is 5-coordinate; distances involving the macrocyclic thioether ligand are Ir-S = 2.319 (5), 2.343 (4) and 2.419 (4) Å [57].

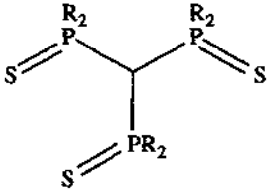


(30)

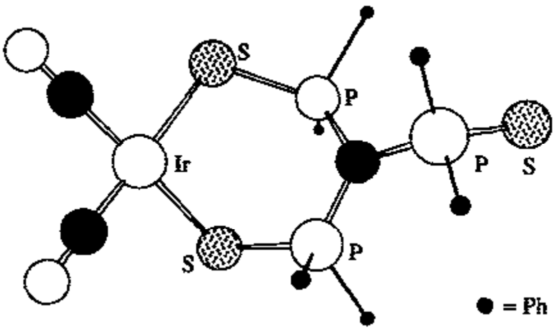
Iridium(I) complexes incorporating ligand (31) have been prepared and characterised by infrared and ^{31}P NMR spectroscopies [58]. For HL = (32), the complex (cod)IrL has been synthesised and structurally characterised. Ligand L^- functions in a bidentate manner, and thus the iridium(I) centre is in a square-planar environment (Ir-S = 2.382 (2) and 2.326 (3) Å). Variable temperature $^{31}P\{^1H\}$ NMR spectroscopic studies illustrate that the complex (cod)IrL exhibits fluxional behaviour down to –80°C [59]. The reaction of HL, (33), with $\{(cod)IrCl\}_2$ leads to $[(cod)Ir(HL)]^+$, which has been isolated as the tetraphenylborate and perchlorate salts. These, and their rhodium(I) analogues, are the first examples of complexes in which the methine proton of HL is retained upon coordination to a metal ion. The methine proton of the coordinated ligand in $[(cod)Ir(HL)]^+$ is very acidic, however, and deprotonation occurs readily to yield (cod)IrL. A detailed analysis of the ^{31}P NMR spectroscopic data for this neutral complex has been presented. The iridium(I) complex $Ir(CO)_2L$, (34), has also been prepared, and, here, full structural data are available. The sulfur-donor ligand acts in a bidentate manner and, thus, the iridium atom is in a square planar coordination site, with Ir-S distances of 2.348 (8) and 2.370 (7) Å and ∠S-Ir-S = 93.4 (3)°. The 6-membered chelate ring in (34) is in a boat-conformation [60].



(31)



R = Me (32)
R = Ph (33)

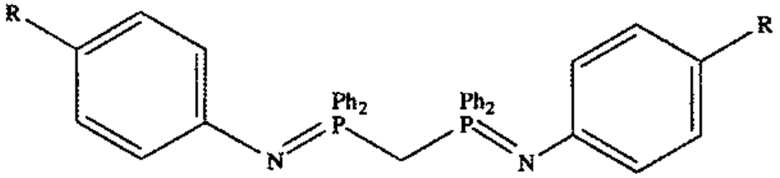


(34)

6.4.3 Complexes with nitrogen donor ligands

New iridium(I) complexes of the type $[Ir(cod)L(PPh_3)][ClO_4]$ have been prepared from $IrCl(cod)(PPh_3)$ and L in the presence of $AgClO_4$, for L = PhCN, PhCH=CHCN, CH_2=CHCN, CH_2=C(Me)CN, MeCH=CHCN, and CH_2=$CHCH_2CN$. In each case the ligand L is coordinated to the iridium atom through the nitrogen donor atom. The reactivity of $[Ir(cod)L(PPh_3)]^+$ has been studied; reactions include the oxidative addition of H_2, and the displacement of the nitrile ligand by triphenylphosphine or carbon monoxide. The catalytic activity of the new cationic complees with respect to the isomerisation of unsaturated alcohols has been investigated [61].

Treatment of $[L'_2IrCl]_2$, (L'_2 = cod, nbd, or $(CO)_2$), with ligands, L, (35), generally gives mixtures of products containing either an *N,N'*- or *N,C*-coordinated ligand. The *N,C*-coordination mode arises when one methine proton has been transferred to a nitrogen atom, i.e. a tautomeric 1,3-hydrogen shift. Solution equilibria (dependent upon the iridium : ligand ratio) have been investigated. Related rhodium(I) complexes have been similarly prepared and the two modes of coordination of L have been confirmed in the crystal structures of $[Rh\{(4\text{-}MeC_6H_4N{=}PPh_2)_2CH_2\}(cod)][PF_6]$ and $[Rh(4\text{-}MeC_6H_4N{=}PPh_2CHPPh_2\text{-}HNC_6H_4\text{-}4\text{-}Me)(cod)][PF_6]$ [62].



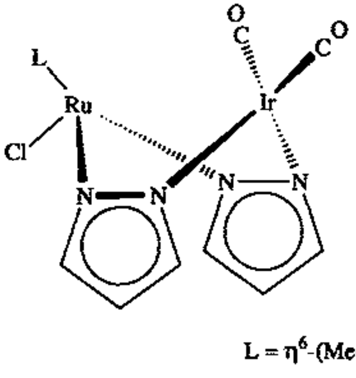
R = Me, OMe, NO_2

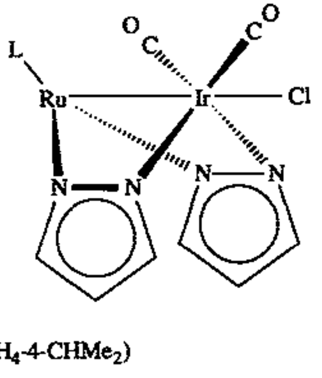
(35)

Reactions of the complex *trans*-$[Ir(CO)(MeCN)(PPh_3)_2][PF_6]$ with 2-phenylpyridine (ppyH) or 8-methylquinoline (mqH) result in the displacement of acetonitrile by the heterocyclic *N*-donor ligand. Cyclometallated complexes are also observed, albeit in low yields. The new iridium(I) complexes have been characterised by ^{31}P, ^1H and ^{13}C NMR spectroscopies, and the crystal structure of a salt of *trans*-$[Ir(CO)(mqH)(PPh_3)_2]^+$ has been determined. The iridium(I) centre is in a square-planar environment and the plane of the mqH ligand is approximately perpendicular to that containing the iridium and two phosphorus atoms. Pertinent bond parameters are Ir-N = 2.313 (9) Å, Ir-P = 2.335 (3) and 2.323 (2) Å, and ∠P-Ir-P = 168.3 (1)° [63].

The benzimidazoles 2-R-bzH react with $\{(cod)IrCl\}_2$ in acetone to give complexes of the type IrCl(cod)(2-R-bzH) where R = H, Me, Et, Pr, Me_2CH, Bu, or 2-quinoyl. If triethylamine is present in the reaction mixture, a trimeric species, $\{(cod)Ir(\mu\text{-}2\text{-}R\text{-}Bz)\}_3$ is formed (R = H, Me, Et, Pr, or Bu). The chloride ligand in IrCl(cod)(2-R-bzH) can be replaced by PPh_3, and in the presence of $NaClO_4$, complexes of formula $[Ir(PPh_3)(cod)(2\text{-}R\text{-}bzH)][ClO_4]$ are isolated. The rather unusual behaviour of the CHMe$_2$ substituent in [Ir(PPh$_3$)(cod)(2-Me$_2$CH-bzH)]$^+$ has been revealed through ^{1}H and ^{13}C NMR spectroscopic solution studies; in one particular conformer, anomalous shielding of the methyl protons is observed (δ −0.28) [64].

A study has been made of the kinetics of photoinduced electron transfer in some covalently linked donor-acceptor complexes containing pyrazolate bridged iridium(I) dimers with pyridinium groups bound to terminal phosphinite ligands [65]. A pyrazolate ligand also features in the dinuclear complex Ir$_2$(μ-pz)(μ-S^{t}Bu)(μ-dppm)(CO)$_2$. This complex is formed in the reaction of Ir$_2$(μ-pz)(μ-S^{t}Bu)(cod)$_2$ with CO and dppm; see also Section 6.3 [54]. The reaction of η^6-(Me-C$_6$H$_4$-4-CHMe$_2$)RuCl(μ-pz)$_2$Ir(cod) with carbon monoxide (1 atm.) in thf or CH$_2$Cl$_2$ results in the displacement of the cod ligand by two molecules of CO. The two isomeric complexes, (36) and (37), have both been crystallographically characterised. In (36), the Ir-N distances are equivalent (2.062 (4) Å), whilst in (37), Ir-N = 2.069 (5) and 2.059 (5) Å and Ir-Ru = 2.6962 (6) Å. In solution, ^{1}H NMR spectral data are consistent with the establishment of an equilibrium between the two isomers ($K = 2.4 \pm 0.1$ in CDCl$_3$). The results of a study of the isomerism of (37) to (36) illustrate that the process obeys a second order rate law with $k = 3 \times 10^{-3}$ mol^{-1}dm^{3}min^{-1}; a mechanism has been proposed [66]. A series of complexes related to (36) and (37), and including these species, has been reported. The replacement of two carbonyl ligands in an individual complex by a bis(phosphine) ligand leads to a series of related derivatives. The molecular structure of [Cp*Ir(μ-pz)$_2$(μ-CO)Ir(CO)(L-L)][BF$_4$] where L-L = Ph$_2$PCH=CHPPh$_2$ has been determined [41].



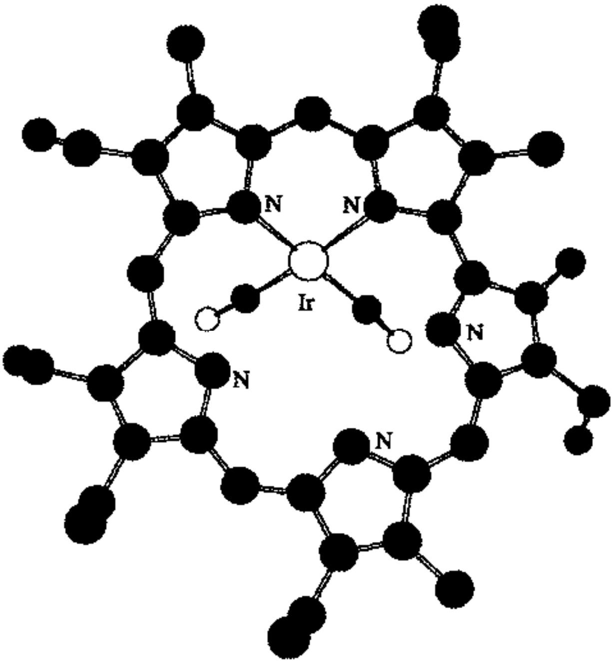


L = η^6-(Me-C$_6$H$_4$-4-CHMe$_2$)

(36) (37)

The complexes *trans*-Ir(PPh$_3$)$_2$(CO)X where X$^-$ is chloride or pyrazolate ligands derived from 3,5-Me$_2$-pzH, 3,5-Me$_2$-4-NO$_2$-pzH or 3,5-(CF$_3$)$_2$-pzH have been the subject of an ^{193}Ir Mössbauer study. The investigation has been extended to include the heterometallic complex *trans*-(PPh$_3$)$_2$(CO)Ir{μ-3,5-Me$_2$-pz}AuY (Y = Cl or Br) and the results indicate that the bridging pyrazolate ligand transmits electronic effects between the two metal centres [39]. The reaction of {(cod)IrCl}$_2$ with Tl{H$_n$B(pz)$_{4-n}$} gives a route to the complexes Ir(cod){H$_n$B(pz)$_{4-n}$} (n = 0 or 2). These can be converted to the species Ir(CO)$_2${H$_n$B(pz)$_{4-n}$} on treatment with carbon monoxide.

The related iridium(I) complexes [Ir(cod){N(CH$_2$pz)$_3$}][BF$_4$] and [IrL$_2${N(CH$_2$pz)$_3$}][BF$_4$] (L = cyclooctene) have similarly been prepared. The new complexes have been characterised by elemental analysis, and by infrared and ^{1}H NMR spectroscopies [67].



(38)

The macrocyclic ligand sapphyrin, H$_3$L, has been described [68] as an "expanded porphyrin"; the radius of the *N*-donor cavity is ≈ 2.7 Å. The reaction of H$_3$L with IrCl(CO)$_2$(py) in the presence of triethylamine yields the complex Ir(CO)$_2$(H$_2$L). This complex readily protonates (a transformation that occurs during work-up of the neutral complex) and [Ir(CO)$_2$(H$_3$L)]Cl has been isolated and spectroscopically and crystallographically characterised. In the cation [Ir(CO)$_2$(H$_3$L)]$^+$, (38), the iridium(I) centre is bound to two nitrogen donors and lies to one side of the *N*$_5$-cavity (Ir-N = 2.064 (5) and 2.091 (6) Å). The square planar coordination sphere is completed by the two carbonyl ligands. The structure of the sapphyrin ligand is perturbed and it shows significant deviation from planarity [68].

6.4.4 *Complexes with phosphorus donor ligands*

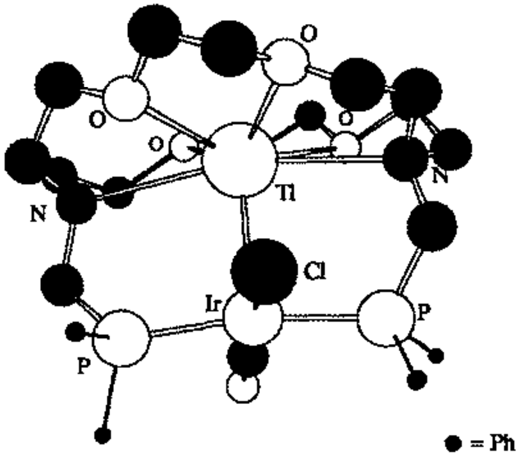
A wide range of iridium(I) complexes incorporate phosphine ligands, but many such molecules are primarily organometallic in nature and are therefore not generally included in this section.

The reaction of C_6F_6 with $MeIr(PEt_3)_3$ at 60°C yields the square planar complex $Ir(PEt_3)_2(C_6F_5)(PEt_2F)$, the generation of which involves C-F and P-C bond cleavage and P-F bond formation. The evolution of methane and ethene accompanies the reaction. The product $Ir(PEt_3)_2(C_6F_5)(PEt_2F)$ has been characterised by ^{19}F and ^{31}P NMR spectroscopy and by single crystal X-ray diffraction. The two PEt_3 ligands are mutally *trans* with Ir-P = 2.305 (6) and 2.310 (6) Å; for the PEt_2F ligand, Ir-P = 2.199 (6) Å [69]. Use of ^{31}P NMR spectroscopy has been made to investigate intermolecular exchange between the square planar iridium(I) complexes *trans*-$Ir(CO)L_2X$ (L = $P(4\text{-}MeC_6H_4)_3$ or $PMePh_2$; X = Cl or Me). For example, a CD_2Cl_2 solution containing *trans*-$Ir(CO)\{P(4\text{-}MeC_6H_4)_3\}_2(Me)$ and *trans*-$Ir(CO)(PMePh_2)_2(Me)$ was monitored over the temperature range of –70°C to ambient. The spectral data indicate that the two starting complexes are in equilibrium with *trans*-$Ir(CO)\{P(4\text{-}MeC_6H_4)_3\}(PMePh_2)(Me)$. Mechanistic proposals have been discussed [70].

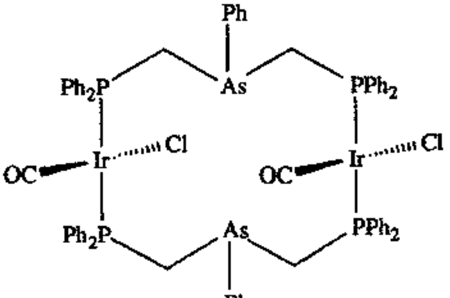
The complex $[Ir(cod)(PhCN)(PPh_3)][ClO_4]$ catalyses the double bond migration of $CH_2{=}C(Et)CH_2OH$ and CH_2CHCH_2OH to give $Et(Me)C{=}CHOH$ and $MeHC{=}CHOH$, respectively. The two products slowly undergo ketonisation to yield $Et(Me)CHCHO$ and $EtCHO$, respectively. Detailed ^1H and ^{13}C NMR spectral results have been reported [71].

An investigation of the reactions of $IrL_2L'Cl$ (L = L' = PEt_3 or PMe_3; L = PPh_3 or PEt_3 and L' = CO) with pentadienides has been carried out. The molecular structures of the complexes (1,4,5-η-pentadienyl)$Ir(PEt_3)_3$, (1,4,5-η-2,4-dimethylpentadienyl)$Ir(PMe_3)_3$, (1,4,5-η-2,4-dimethylpentadienyl)$Ir(PPh_3)_2(CO)$, and (*syn*-1–3-η-pentadienyl)$Ir(PPh_3)_2(CO)$ have been determined [72]. (2-Methoxyphenyl)methylphenylphosphine, L, displaces both pyridine ligands from $[Ir(cod)(py)_2]^+$. The product, *cis*-$[Ir(cod)L_2]^+$ has been structurally characterised (hexafluorophosphate salt); the iridium(I) centre is in a square planar environment and important structural parameters are Ir-P = 2.320 (5) and 2.323 (5) Å and ∠P-Ir-P = 92.3 (2)° [73]. The complexes $[Ir(cod)(L\text{-}L)][BPh_4]$ and $[Ir(L\text{-}L)_2][BPh_4]$ (L-L = $(c\text{-}C_6H_{11})_2PCH_2CH_2P(c\text{-}C_6H_{11})_2$) have been synthesised and characterised by elemental analysis, and infrared and ^1H and ^{31}P NMR spectroscopies. The reactions of these iridium(I) complexes with carbon monoxide have been studied [74].

The complex LIr(CO)Cl, where L is the macrocyclic ligand (**25**), was descibed in Section 6.2.5. LIr(CO)Cl reacts with thallium(I) nitrate to give the iridium(I) complex $[Tl(L)Ir(CO)Cl]^+$, (**39**), which has been characterised as the nitrate salt by X-ray crystallography. The iridium centre is coordinated by the two *trans*-phosphorus donor atoms of ligand (**25**) and by a carbonyl and a chloride ligand. The Ir-P distances are 2.327 (3) and 2.321 (3) Å, but the P-Ir-P unit is non-linear (∠P-Ir-P = 169.5 (12)°). The thallium ion is coordinated within the macrocyclic cavity of ligand (**25**) and is sited in an axial site with respect to the $IrP_2(CO)Cl$-unit. The Ir-Tl distance is 2.875 (1) Å and this distance is consistent with a bonding interaction [48]. The iridium(I) complex (**40**) can function as a macrocyclic ligand and a range of reactions with main group ions has lead to a series of new complexes. For example, (**40**), $Ir_2(\mu\text{-}L)_2(CO)_2Cl_2$, reacts with PbI_2, NaI and $NH_4[PF_6]$ to yield $[Ir_2(\mu\text{-}L)_2(PbI)(CO)_2Cl_2][PF_6]$, the molecular structure of which has been determined. The {PbI}-unit bridges between the two iridum centres. Similarly, $Ir_2(\mu\text{-}L)_2(CO)_2Cl_2$, SbF_3 and $NaBF_4$ react together to generate the complex $[Ir_2(\mu\text{-}L)_2(SbF_2)(CO)_2Cl_2][BF_4]$. Infrared, UV-vis, emission, and $^{31}P\{^{1}H\}$ NMR spectroscopic details of these and related complexes have been reported [75].



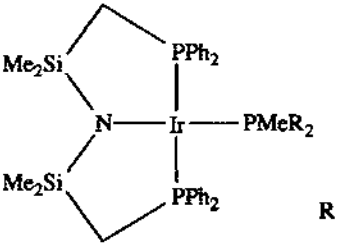
(39)



(40)

6.4.5 Complexes with mixed donor-atom ligands

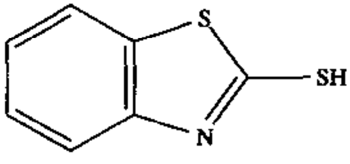
The prolonged thermolysis of Ir(Me)(PR$_2$){N(SiMe$_2$CH$_2$PPh$_2$)$_2$} (R = Ph or Me) leads to the iridium(I) complex **(41)** via an iridium(III) intermediate (see Section 6.2.6). Under coniditions of photolysis, Ir(Me)(PR$_2$){N(SiMe$_2$CH$_2$PPh$_2$)$_2$} is converted directly to **(41)** [51].



R = Ph or Me

(41)

The reaction of LiL, (where HL = **(42)**, with $\{(cod)IrCl\}_2$ provides a route to the red complex $\{(cod)Ir(\mu\text{-}L)\}_2$. Spectroscopic data for $\{(cod)Ir(\mu\text{-}L)\}_2$ have been detailed and it is proposed that the two iridium atoms are bridged by the two *N,S*-donor ligands such that each iridium(I) centre is in a square planar (cod)Ir(*N,S'*)-environment. When $\{(cod)Ir(\mu\text{-}L)\}_2$ is treated with $[(cod)Ir(Me_2CO)_x][ClO_4]$ in acetone, the triiridium complex $[(cod)_3Ir_3(\mu_3\text{-}L)_2][ClO_4]$. The proposed structure of $[(cod)_3Ir_3(\mu_3\text{-}L)_2]^+$ features an open Ir_3-core in which pairs of iridium(I) centres are bridged in an *N,S*-mode; the thiolate sulfur atom is involved in coordination. The heterometallic complexes $(cod)_2Ir_2(\mu_3\text{-}L)_2Ag(O_2ClO_2)$, $(cod)_2Ir_2(\mu_3\text{-}L)_2AgCl$, $(cod)_2Ir_2(\mu_3\text{-}L)_2CuCl$ and $(cod)_2Ir_2(\mu_3\text{-}L)_2AuCl$ have also been prepared and characterised by spectroscopic methods [76].

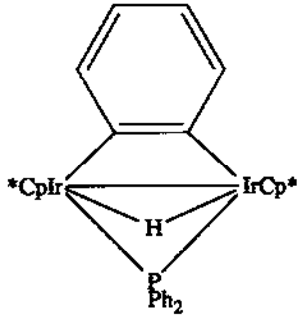


(42)

6.5 DIMETALLIC COMPLEXES INCLUDING A-FRAME COMPLEXES

Some di- and trinuclear complexes have already been covered in previous sections. In this section, the emphasis is on metal-metal bonded compounds, including some A-frame complexes.

When $\{Cp^*IrCl(\mu\text{-}H)\}_2$ reacts with triphenylphosphine in benzene, aqueous potassium hydroxide and $[PhCH_2NEt_3]Cl$, two equivalents of HCl are eliminated and complex **(43)** is formed. That the oxidative addition of C-P and C-H bonds to the iridium(III) centres has occurred has been confirmed by a crystallographic study of **(43)** [77].

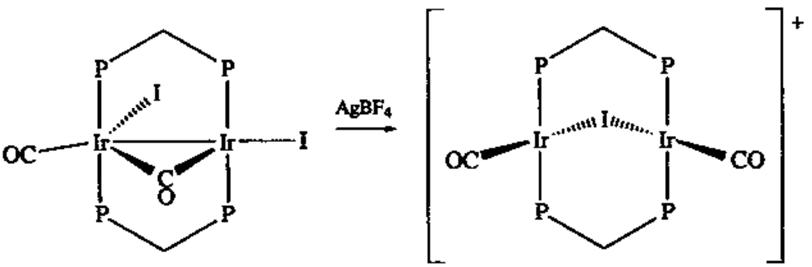


Ir-P = 2.263 (2) Å

Ir-Ir = 2.8901 (4) Å

(43)

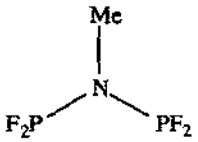
The complex $Ir_2I_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2$ has been synthesised by treating $Ir_2Cl_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2$ with potassium iodide. The molecular structure of $Ir_2I_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2$ has been determined; the ligand arrangement is quite unexpected. The two iridium centres are within bonding distance (2.8159 (5) Å) and the Ir-Ir bond is bridged by one carbonyl ligand. The second carbonyl and one iodide ligand (Ir-I = 2.8032 (8) Å) are termally bonded to one of the iridium centres, whilst the second iridium atom carries a single terminal iodide ligand (Ir-I = 2.6811 (7) Å). Reasons for the unusual geometry have been discussed. In solution, spectroscopic data are consistent with the complex undergoing a fluxional process. The abstraction of one iodide ion by $AgBF_4$ from $Ir_2I_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2$ causes rupture of the Ir-Ir bond (Scheme 3) and ligand rearrangement. The heterometallic complex $IrRhI_2(CO)(\mu\text{-}CO)(\mu\text{-}dppm)_2$ has also been prepared and spectrosocpic data are consistent with a structure similar to that confirmed for the diiridium analogue. Reactions of the dimetallic complexes with dimethyl acetylenedicarboxylate and with ethene have been studied [78].



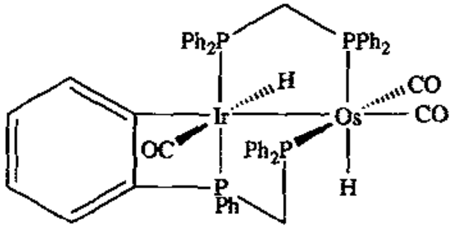
Scheme 3

The iridium(I) complex $IrCl(CO)(PPhMe_2)_2$ reacts with CpFeClL, in which L = (44), to yield $CpFe(\mu\text{-}L)_2IrCl_2(PPhMe_2)$ for which ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data have been detailed. The crystal structure of $CpFe(\mu\text{-}L)_2IrCl_2(PPhMe_2)$ has been elucidated; the Fe-Ir unit is supported by two bridging phosphorus-donor ligands. The iridium centre is octahedrally sited; the

$PPhMe_2$ ligand lies *trans* to the Fe-Ir bond, the two chloride ligands are mutally *cis*, each lying *trans* to a phosphorus atom of one bridging ligand [79].



(44)



(45)

The heterometallic complex $IrRe(CO)_5(\mu\text{-dppm})_2$ reacts with dioxygen to give $IrRe(CO)_3(\mu\text{-}CO_3)(\mu\text{-dppm})_2$. Infrared and NMR spectroscopic data have been recorded, although monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy did not reveal intermediate species. The molecular structure of a related complex, $RhMn(CO)_3(\mu\text{-}CO_3)(\mu\text{-dppm})_2$, has been determined [80]. When the iridium(I) complex $IrCl(\eta^2\text{-dppm})_2$ reacts with $[HOs(CO)_4]^-$, the product is the metal-metal bonded compound $IrOs(H)_2(CO)_3\{\mu_2\text{-}\eta^3\text{-}(2\text{-}C_6H_4)PhPCH_2PPh_2\}(dppm)$, **(45)**. The structure of **(45)** has been proposed from ^1H NMR and infrared spectroscopic data; one phenyl ring of one dppm ligand has been orthometalled. The dppm ligand reforms when complex **(45)** reacts with electrophiles. After reaction with H^+, the product is $[IrOs(\mu\text{-}H)_2(CO)_3(dppm)_2]^+$, and with $AuPPh_3^+$, the cationic complex $[IrOs(\mu\text{-}H)(\mu\text{-}AuPPh_3)(CO)_3(dppm)_2]^+$ is formed. Related reactions have been reported [81].

The syntheses of a series of chalcogen-bridged complexes have been reported. These include $Ir_2(CO)_2(\mu\text{-dppm})_2(\mu\text{-}S)(\mu\text{-}SO_2)$ and $M(CO)_3(\mu\text{-dppm})_2IrCl(\mu\text{-}SO_2)$ (M = Mo or W). Related rhodium-containing species have also been prepared and the molecular structure of $Mo(CO)_3(\mu\text{-dppm})_2RhCl(\mu\text{-}SO_2)$ has been determined [82].

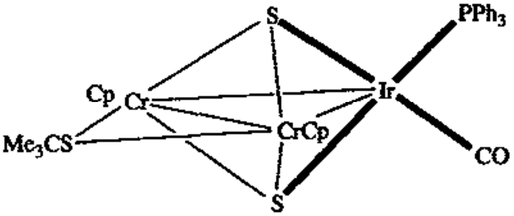
The reactivity of $[Ir(CO)ClAu(\mu\text{-dppm})_2]^+$ with methyl isocyanide has been investigated. The products depend upon the stoichiometry of the reaction, and either $[Ir(CNMe)_2Au(\mu\text{-dppm})_2]^{2+}$ or $[Ir(CNMe)_3Au(\mu\text{-dppm})_2]^{2+}$ can been isolated. Both complexes have been structurally characterised (as the hexafluorophosphate salts). The addition of the third CNMe ligand to the iridium atom causes significant distortion of the $\{IrAuP_4\}$-framework [83].

6.6 CLUSTERS

In this section, selected iridium clusters are described. The aim of the survey is to highlight a few especially interesting examples.

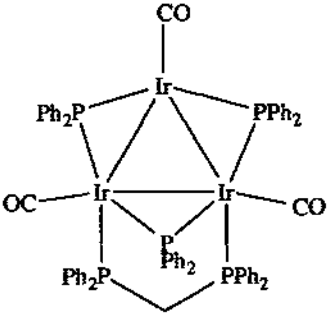
The iridium(I) complex $Ir(CO)Cl(PPh_3)_2$ reacts with $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)$ to yield $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Ir(CO)(PPh_3)$, **(46)**. This cluster has been structurally characterised;

ignoring the Ir-Cr interactions (3.229 (2) and 3.034 (1) Å), the iridium environment is a square planar one with distances Ir-S = 2.408 (2) and 2.385 (2) Å [84].

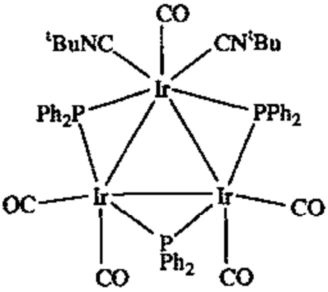


(46)

The syntheses of the clusters $Ir_3(\mu\text{-}PPh_2)_3(CO)_nL_2$ (n = 3, L = CO or PPh_3, L_2 = dppm; n = 5, L = ^tBuNC). The molecular structures of $Ir_3(\mu\text{-}PPh_2)_3(CO)_3(dppm)$, **(47)**, and $Ir_3(\mu\text{-}PPh_2)_3(CO)_5(^tBuNC)_2$, **(48)**, have been determined; the former molecule contains a crystallographic mirror plane. In **(48)**, the two ^tBuNC ligands lie above and below the plane of the Ir_3-triangle. A detailed discussion of the results of ^{31}P NMR spectral studies have been presented [85].



(47)



(48)

The preparations and crystal structures of $[PPh_4][Ir_4(CO)_{10}(CH_2CO_2Me)_2]$ and $[PPh_4][Ir_4(CO)_{11}(CH_2CO_2Me)]$ have been described. The two cluster anions are formed in a stepwise manner in the reaction of $[Ir(CO)_4]^-$ with CH_2BrCO_2Me. Each cluster anion exhibits a tetrahedral metal core and the important feature of each is the observation of the terminally bound CH_2CO_2Me substituent(s) [86]. A tetranuclear cluster is also formed in the reaction of $[HFe(CO)_4]^-$ with $Ir(CO)_3Br$ (3 : 1); the product is $[HFe_3Ir(CO)_{12}]^{2-}$. Protonation leads to $[H_2Fe_3Ir(CO)_{12}]^-$. This study has been extended to include some higher nuclearity clusters. The dianion $[Ir(CO)_4]^{2-}$ reacts with $[FeIr_4(CO)_{15}]^{2-}$ in MeCN under reflux to yield $[FeIr_5(CO)_{15}]^{3-}$. This trianion protonates to the corresponding dianion, or, in the presence of an excess of H^+, to $[H_2FeIr_5(CO)_{15}]^-$. This anion is unstable at room temperature and transforms to $[FeIr_5(CO)_{16}]^-$. Structural and electrochemical studies have been reported [87].

The iridium(I) complex $Ir(CO)_2(acac)$ is the precursor to zeolite encapsulated tetrairidium clusters. Infrared spectral data are consistent with the formation of $Ir_4(CO)_{12}$ within the zeolite cage. This cluster can be decarbonylated (H_2, 300°C, 1 atm.) and recarbonylated (CO, 40°C, 1 atm.) [88]. In related work, the formation of two isomers of $Ir_6(CO)_{16}$ within Na zeolite-Y has been observed. Under conditions of carbon monoxide (10^5 Pa), $Ir(CO)_2(acac)$ is converted to an isomer of $Ir_6(CO)_{16}$ exhibiting μ-CO ligands. On the other hand, with H_2 and CO at pressures of 2×10^6 Pa, the presence of μ_3-carbonyl ligands in the product is evidenced. Both isomers of $Ir_6(CO)_{16}$ may be reversibly decarbonylated in the zeolite environment [89].

The reactions of $[Ir_6(CO)_{15}]^{2-}$ with mercury(II) chloride or triphenylphosphine gold(I) chloride have been described. In each case, a heavy metal fragment ($HgCl^+$ or $AuPPh_3^+$) adds to the dianion. The products have been characterised by infrared and NMR spectroscopic and X-ray diffraction methods [90]. The anion $[Ir_6(CO)_{15}]^{2-}$ is synthesised from $Ir_4(CO)_{12}$ and $[Ir(CO)_4]^-$, but if a slight excess of the tetranuclear cluster is present, the cofacial bioctahedral cluster anion $[Ir_9(CO)_{20}]^{3-}$ may be isolated. Interestingly, this trianion has the same metal core geometry as $[Rh_9(CO)_{19}]^{3-}$, despite the different electron count [91].

REFERENCES

1. C.E. Housecroft, *Coord. Chem. Rev.*, 115 (1992) 163.
2. A.L. Balch, V.J. Catalano and J.W. Lee, *Inorg. Chem.*, 30 (1991) 3980.
3. A.L. Balch, V.J. Catalano, J.W. Lee, M.M. Olmstead and S.R. Larkin, *J. Am. Chem. Soc.*, 113 (1991) 8724.
4. R. Poli, *Chem. Rev.*, 91 (1991) 509.
5. K. Irmer and W. Preetz, *Z. Naturforsch., Sect. B*, 46B (1991) 1200.
6. A.B. Venediktov, S.V. Korenev, M.A. Fedotov and A.V. Belyaev, *Koord. Khim.*, 16 (1990) 1400.
7. R.K. Coll, J.E. Fergusson, B.R. Penfold, D.A. Rankin and W.T. Robinson, *Inorg. Chim. Acta*, 177 (1990) 107.
8. V.V. Kuznetsov, V.N. Reshetnikova and A.I. Donskikh, *Zh. Anal. Khim.*, 45 (1990) 1832.
9. H. Werner, A. Hohn and M. Schulz, *J. Chem. Soc., Dalton Trans.*, (1991) 777.
10. M. Neubacher and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 594 (1991) 133.
11. J. Wilkens and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 592 (1991) 79.
12. C. Sourisseau, R. Cavagnat, M. Fouassier, S. Jobic, P. Deniard, R. Brec and J. Rouxel, *J. Solid State Chem.*, 91 (1991) 153.
13. R.S. Tanke and R.H. Crabtree, *Organometallics*, 10 (1991) 415.
14. A.N. Zhilyaev, T.A. Fomina, P.A. Koz'min, T.B. Larina, M.D. Surazhskaya and I.B. Baranovskii, *Zh. Neorg. Khim.*, 36 (1991) 400.
15. T. Matsubara, Y. Saito, T. Yamakawa and S. Shinoda, *J. Mol. Catal.*, 66 (1991) 171.
16. T. Matsubara, Y. Saito, T. Yamakawa and S. Shinoda, *J. Mol. Catal.*, 67 (1991) 175.
17. M.T. Kostanski and H. Freiser, *Anal. Chim. Acta*, 242 (1991) 191.
18. S.L. Randall, J.S. Thompson, L.A. Buttrey, J.W. Ziller, M.R. Churchill and J.D. Atwood, *Organometallics*, 10 (1991) 683.
19. D.M. Lunder, E.B. Lobkovsky, W.E. Streib and K.G. Caulton, *J. Am. Chem. Soc.*, 113 (1991) 1837.

20. D.S. Glueck, L.J.N. Winslow and R.G. Bergman, *Organometallics*, 10 (1991) 1462.
21. Y. Hayashi, Y. Ozawa and K. Isobe, *Inorg. Chem.*, 30 (1991) 1025.
22. J.R. Bleeke, T. Haile and M.Y. Chiang, *Organometallics*, 10 (1991) 9.
23. J.R. Bleeke, Y.-F. Xie, L. Bass and M.Y. Chiang, *J. Am. Chem. Soc.*, 113 (1991) 4703.
24. P.Barbaro, C. Bianchini, C. Mealli and A. Meli, *J. Am. Chem. Soc.*, 113 (1991) 3181.
25. M. Herberhold, G.X. Jin and A.L. Rheingold, *Chem. Ber.*, 124 (1991) 2245.
26. R. Krämer, K. Polborn and W. Beck, *J. Organomet. Chem.*, 410 (1991) 111.
27. J.J. Garcia, H. Torrens, H. Adams, N.A. Bailey and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1991) 74.
28. M.T. Pinillos, A. Elduque, J.A. López, F.J. Lahoz and L.A. Oro, *J. Chem. Soc., Dalton Trans.*, (1991) 1391.
29. K.M. Rao, C.L. Day, R.A. Jacobson and R.J. Angelici, *Inorg. Chem.*, 30 (1991) 5046.
30. D.S. Glueck, J.X. Wu, F.J. Hollander and R.G. Bergman, *J. Am. Chem. Soc.*, 113 (1991) 2041.
31. K. Dedeian, P.I. Djurovich, F.O. Garces, G. Carlson and R.J. Watts, *Inorg. Chem.*, 30 (1991) 1685.
32. A.P. Wilde and R.J. Watts, *J. Phys. Chem.*, 95 (1991) 622.
33. A.P. Wilde, K.A. King and R.J. Watts, *J. Phys. Chem.*, 95 (1991) 629.
34. A. Slama-Schwok, D. Avnir and M. Ottolenghi, *J. Am. Chem. Soc.*, 113 (1991) 3984.
35. L. Wallace, G.A. Heath, E. Krausz and G. Morgan, *Inorg. Chem.* 30 (1991) 347.
36. R. Ziessel, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 844.
37. J.H. Vandiemen, J.G. Haasnoot, R. Hage, E. Müller and J. Reedijk, *Inorg. Chim. Acta*, 181 (1991) 245.
38. V.K. Sharma, O.P. Pandey and S.K. Sengupta, *Bull. Soc. Chim. Fr.*, (1991) 469.
39. A.L. Bandani, G. Banditelli, F. Bonati, S. Calogero and F.E. Wagner, *J. Organomet. Chem.*, 410 (1991) 241.
40. D. Carmona, F.J. Lahoz, L.A. Oro, M.P. Lamata and S. Buzarra, *Organometallics*, 10 (1991) 3123.
41. D. Carmona, J. Ferrer, F.J. Lahoz, L.A. Oro, J. Reyes and M. Esteban, *J. Chem. Soc., Dalton Trans.*, (1991) 2811.
42. D.E. Westerberg, L.F. Rhodes, J. Edwin, W.E. Geiger and K.G. Caulton, *Inorg. Chem.*, 30 (1991) 1107.
43. H. Werner, T. Dirnberger and A. Hohn, *Chem. Ber.*, 124 (1991) 1957.
44. D.S. Glueck and R.G. Bergman, *Organometallics*, 10 (1991) 1479.
45. A.J. Deeming, S. Doherty and J.E. Marshall, *Polyhedron*, 10 (1991) 1857.
46. M.K. Hays and R. Eisenberg, *Inorg. Chem.*, 30 (1991) 2623.
47. M. Esteban, A. Pequerul, D. Carmona, F.J. Lahoz, A. Martin and L.A. Oro, *J. Organomet. Chem.*, 402 (1991) 421.
48. A.L. Balch, F. Neve and M.M. Olmstead, *J. Am. Chem. Soc.*, 113 (1991) 2995.
49. I. Zahn, K. Polborn, B. Wagner and W. Beck, *Chem. Ber.*, 124 (1991) 1065.
50. T. Konno, K. Okamoto and J. Hidaka, *Inorg. Chem.*, 30 (1991) 2253.
51. M.D. Fryzuk, K. Joshi, R.K. Chadha and S.J. Rettig, *J. Am. Chem. Soc.*, 113 (1991) 8724.
52. M.D. Fryzuk, K. Joshi and S.J. Rettig, *Organometallics*, 10 (1991) 1642.
53. E. Farnetti, G. Nardin and M. Graziani, *J. Organomet. Chem.*, 417 (1991) 163.
54. M.T. Pinillos, A. Elduque and L.A. Oro, *Inorg. Chim. Acta*, 178 (1990) 179.
55. P.J. Stang, L.S. Song, Y.H. Huang and A.M. Arif, *J. Organomet. Chem.*, 405 (1991) 403.
56. N. Mizuno, D.K. Lyon and R.G. Finke, *J. Catal.*, 128 (1991) 84.
57. A.J. Blake, M.A. Halcrow and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1991) 253.
58. M.S. Abbassioun, P.A. Chaloner, C. Claver, P.B. Hitchcock, A.M. Masdeu, A. Ruiz and T. Saballs, *J. Organomet. Chem.*, 403 (1991) 229.
59. S.O. Grim, P.B. Kettler and J.S. Merola, *Inorg. Chim. Acta*, 185 (1991) 57.
60. J. Browning, K.R. Dixon, R.W. Hilts, N.J. Meanwell and F. Wang, *J. Organomet. Chem.*, 410 (1991) 389.
61. C.S. Chin and B. Lee, *J. Chem. Soc., Dalton Trans.*, (1991) 1323.
62. P. Imhoff, R. Vanasselt, C.J. Elsevier, M.C. Zoutberg and C.H. Stam, *Inorg. Chim. Acta*, 184 (1991) 73.
63. F. Neve, M. Ghedini, G. Demunno and A. Crispini, *Organometallics*, 10 (1991) 1143.
64. Y.S. Ramaswany, R. Halesha, N.M.N. Gowda and G.K.N. Reddy, *Indian J. Chem., Sect. A*, 30 (1991) 393.
65. R.S. Farid, L.S. Fox, H.B. Gray, M. Kozok, I.J. Chang and J.R. Winkler, *Mol. Cryst. Liq. Cryst.*, 194 (1991) 259.

66. D. Carmona, J. Ferrer, A. Mendoza, F.J. Lahoz, J. Reyes and L.A. Oro, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 1171.
67. M.J. Fernandez, M.J. Rodriguez and L.A. Oro, *Polyhedron*, 10 (1991) 1595.
68. A.K. Burrell, J.L. Sessler, M.J. Cyr, E. McGhee and J.A. Ibers, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 91.
69. O. Blum, F. Frolow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, (1991) 258.
70. J.S. Thompson and J.D. Atwood, *J. Am. Chem. Soc.*, 113 (1991) 7429.
71. C.S. Chin, B.G. Lee, S.T. Kim and J.P. Chun, *J. Chem. Soc., Dalton Trans.*, (1991) 443.
72. J.R. Bleeke, D. Boorsma, M.Y. Chiang, T.W. Clayton, T. Haile, A.M. Beatty and Y.F. Xie, *Organometallics*, 10 (1991) 2391.
73. M.S. Abbassioun, P.A. Chaloner, P.B. Hitchcock and J.M. Koziorowski, *Acta Crystallogr., Sect. C*, 47 (1991) 437.
74. A. Delzotto, L. Costella, A. Mezzetti and P. Rigo, *J. Organomet. Chem.*, 414 (1991) 109.
75. A.L. Balch, V.J. Catalano, M.A. Chatfield, J.K. Nagle, M.M. Olmstead and P.E. Reedy, *J. Am. Chem. Soc.*, 113 (1991) 1252.
76. M.A. Ciriano, J.J. Pérez-Torrente, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, (1991) 255.
77. V.V. Grushin, A.B. Vymenits, A.I. Yanovsky, Y.T. Struchkov and M.E. Vol'pin, *Organometallics*, 10 (1991) 48.
78. B.A. Vaartstra, J.L. Xiao, J.A. Jenkins, R. Verhagen and M. Cowie, *Organometallics*, 10 (1991) 2708.
79. J.T. Mague, *Organometallics*, 10 (1991) 513.
80. D.M. Antonelli and M. Cowie, *Organometallics*, 10 (1991) 2173.
81. R.W. Hilts, R.A. Franchuk and M. Cowie, *Organometallics*, 10 (1991) 1297.
82. O. Heyke, W. Hiller and I.P. Lorenz, *Chem. Ber.*, 124 (1991) 2217.
83. A.L. Balch and V.J. Catalano, *Inorg. Chem.*, 30 (1991) 1302.
84. A.A. Pasynskii, I.L. Eremenko, V.R. Zalmanovitch, V.V. Kaverin, B. Orazsakhatov, S.E. Nefedov, O.G. Ellert and V.M. Novotortsev, *J. Organomet. Chem.*, 414 (1991) 55.
85. D.E. Berry, J. Browning, K. Dehghan, K.R. Dixon, N.J. Meanwell and A.J. Phillips, *Inorg. Chem.*, 30 (1991) 396.
86. F. Ragaini, F. Porta and F. Demartin, *Organometallics*, 10 (1991) 185.
87. A. Ceriotti, R.D. Pergola, L. Garlaschelli, F. Laschi, M. Manassero, N. Masciocchi, M. Sansoni and P. Zanello, *Inorg. Chem.*, 30 (1991) 3349.
88. S. Kawi and B.C. Gates, *Catal. Lett.*, 10 (1991) 263.
89. S. Kawi and B.C. Gates, *J. Chem. Soc., Chem. Commun.*, (1991) 994.
90. R.D. Pergola, F. Demartin, L. Garlaschelli, M. Manassero, S. Martinengo, N. Masciocchi and M. Sansoni, *Organometallics*, 10 (1991) 2239.
91. R.D. Pergola, F. Demartin, L. Garlaschelli, M. Manassero, S. Martinengo, N. Masciocchi and D. Strumolo, *Inorg. Chem.*, 30 (1991) 846.