

4. Iridium 1993

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CONTENTS

INTRODUCTION	141
4.1 IRIDIUM(V) AND IRIDIUM(IV)	142
4.2 IRIDIUM(III)	142
4.2.1 Complexes with oxygen donor ligands	142
4.2.2 Complexes with sulfur donor ligands.....	143
4.2.3 Complexes with nitrogen donor ligands including cyclometallated 2-phenylpyridine ligands	144
4.2.4 Complexes with phosphorus donor ligands	146
4.2.5 Complexes with mixed donor ligands	148
4.3 IRIDIUM(I)	148
4.3.1 Complexes with oxygen or tellurium donor ligands	148
4.3.2 Complexes with nitrogen donor ligands	149
4.3.3 Complexes with phosphorus donor ligands	149
4.3.4 Complexes with mixed donor ligands	150
4.4 DI-, TRI- AND TETRANUCLEAR IRIDIUM COMPLEXES	150
REFERENCES	154

INTRODUCTION

This article reviews the coordination chemistry of iridium reported during 1993 and is similar in format to the corresponding review dealing with the 1992 literature [1]. The literature has been searched by using both *Current Contents* and the Cambridge Crystallographic Data Base, and structural figures have been redrawn using coordinates taken from the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2].

Organometallic complexes and iridium carbonyl clusters have generally been excluded, although some complexes containing cyclopentadienyl and carbonyl ligands which are of interest to the coordination chemist are described. The review is not fully comprehensive but rather aims to give an overview of the coordination chemistry of iridium reported in 1993.

A review by Sutton covers the chemistry of diazo compounds, including some of iridium [3].

4.1 IRIDIUM(V) AND IRIDIUM(IV)

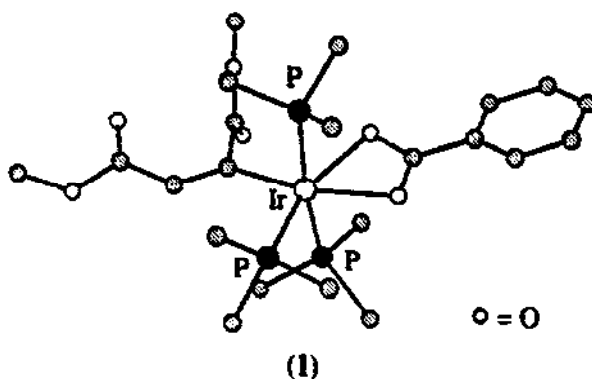
The reaction between Me_3NO and IrMe_3 is quantitative and leads to the green oxo-complex $[\text{Ir}(\text{O})\text{Me}_3]$ which can also be obtained by reacting IrMe_3 or IrMe_4 with O_2 . $[\text{Ir}(\text{O})\text{Me}_3]$ has been characterized by IR and ^1H NMR spectroscopies, and X-ray diffraction methods. In the IR spectrum, a band at 802 cm^{-1} is assigned to the mode $\nu(\text{Ir}=\text{O})$ but overlaps with aryl absorptions. The geometry at the iridium(V) centre is distorted tetrahedral and bond distances are $\text{Ir}-\text{O} = 1.725(9)\text{ \AA}$ and $\text{Ir}-\text{C} = 1.989\text{--}2.034(13)\text{ \AA}$. Attempts to convert the $\text{Ir}=\text{O}$ unit into $\text{Ir}=\text{NR}$ groupings were unsuccessful [4].

The iridium(IV) complexes $[\text{IrCl}_6][\text{ECI}_3]_2$ ($\text{E} = \text{S}, \text{Se}$ or Te) have been studied by ^{35}Cl NQR spectroscopy; related dinuclear complexes including $[\{\text{IrCl}_3(\text{SCl}_2)_2\}_2]$ ($\text{E} = \text{S}$ or Se) have also been investigated [5].

4.2 IRIDIUM(III)

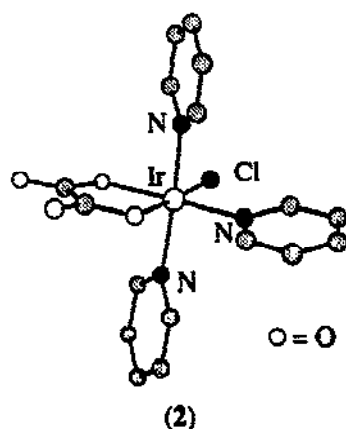
4.2.1 Complexes with oxygen donor ligands

The crystal structure of the aqua complex *trans*- $[\text{IrCl}_2(\text{H}_2\text{O})_4][\text{H}_3\text{L}][\text{SO}_4]_2$ where $\text{L} = 1,4,7\text{-triazacyclononane}$ has been reported [6]. The aqua ligand in the complex cation *trans,mer*- $[\text{IrCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3]^+$ is very labile and the results of a series of substitution reactions have been described. With NH_3 and PH_3 , *trans,mer*- $[\text{IrCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3]^+$ reacts to give the corresponding ammine or phosphine complexes; these are inert with respect to substitution and have been structurally characterized. Deprotonation of *trans,mer*- $[\text{IrCl}_2(\text{PH}_3)(\text{PMe}_2\text{Ph})_3]^+$ leads to *trans,mer*- $[\text{IrCl}_2(\text{PH}_2)(\text{PMe}_2\text{Ph})_3]$, for which structural data are reported. The $\text{Ir}-\text{P}$ bond distance in *trans,mer*- $[\text{IrCl}_2(\text{PH}_3)(\text{PMe}_2\text{Ph})_3]^+$ is $2.25(1)\text{ \AA}$ as compared to $2.440(3)\text{ \AA}$ in *trans,mer*- $[\text{IrCl}_2(\text{PH}_2)(\text{PMe}_2\text{Ph})_3]$. The reaction of *trans,mer*- $[\text{IrCl}_2(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3]^+$ with H_2S leads to ligand displacement with concomitant deprotonation and the structure of the product *trans,mer*- $[\text{IrCl}_2(\text{SH})(\text{PMe}_2\text{Ph})_3]$ has been crystallographically confirmed. Structural comparisons between the new complexes lead to a discussion of the *trans*-influence [7].



When the iridium(III) complex *mer*-[Ir(PMe₃)₃(H)(O₂CPh)Cl] reacts with thallium(I) hexafluorophosphate, the salt *mer*-[Ir(PMe₃)₃(H)(O₂CPh)][PF₆] is obtained. This reacts with MeO₂CC≡CCO₂Me to give *mer*-[Ir(PMe₃)₃(O₂CPh){MeO₂CC=CH(CO₂Me)}][PF₆] the cation of which is shown in structure (1). Both new compounds have been structurally characterized and both possess chelating carboxylate ligands [8].

The reactions of [Ir(cod)(PMe₃)₃]Cl with alcohols, phenols and carboxylic acids have been shown to give iridium(III) hydrido and carbonylhydrido complexes (from primary and secondary alcohols), a product resulting from the oxidative addition of H₂O to iridium(III) (from ^tBuOH), *mer*-[Ir(PMe₃)₃(OAr)(H)Cl] (from ArOH) and *mer*-[Ir(PMe₃)₃(O₂CR)(H)Cl] (from RCO₂H). Spectroscopic data for the complexes have been reported in addition to the results of X-ray diffraction studies for *mer*-[Ir(PMe₃)₃(OC₆H₃-3,5-Me₂)(H)Cl] and *mer*-[Ir(PMe₃)₃(O₂CR)(H)Cl] in which [RCO₂]⁻ is benzoate or salicylate. The carboxylate ligands coordinate in a monodentate fashion [9]. The oxalato iridium(III) complex *mer*-[Ir(py)₃Cl(ox)] has been prepared from *trans*-[IrCl₂(py)₄]Cl and oxalate in aqueous ethanol. The product is a non-electrolyte and exhibits synergic solubility in water : pyridine mixtures. The oxalate complex reacts with boiling hydrochloric acid to yield *mer*-[Ir(PMe₃)₃Cl₃]. Details of the crystal structure of *mer*-[Ir(py)₃Cl(ox)] (2) have been presented [10].

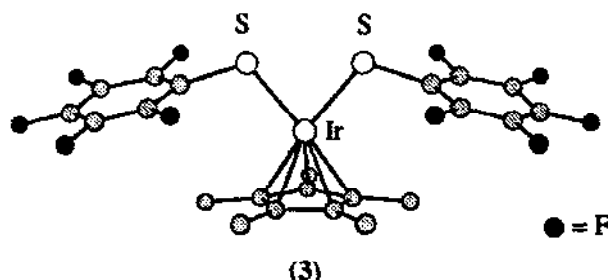


The synthesis of the hydroxo complex [Cp*Ir(PMe₃)(Ph)(OH)] has been achieved by treating the triflate analogue with potassium ^tbutoxide; the mechanism of the formation of [Cp*Ir(PMe₃)(Ph)(OH)] has not yet been confirmed. The product has been studied by using ¹H and ¹⁷O NMR spectroscopies and its reactivity has been investigated [11].

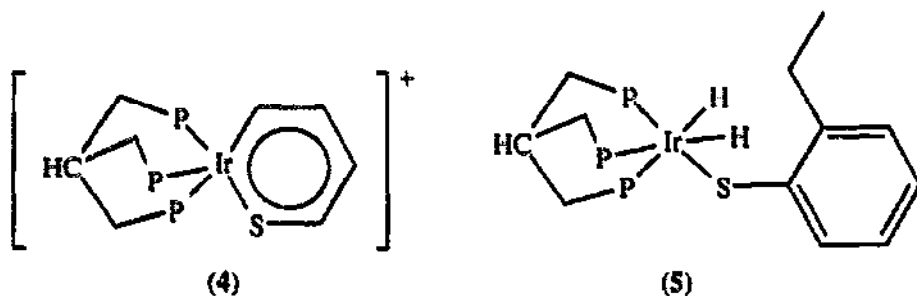
4.2.2 Complexes with sulfur donor ligands

Lead(II) thiolates Pb(SR)₂ (R = C₆F₅, C₆F₄H-4) react with the diiridium complex [Cp*₂Ir₂Cl₂(μ-Cl)₂] to yield the iridium(III) species [Cp*Ir(SR)₂]. In contrast, an analogous reaction involving rhodium yields a complex which is ionic in the solid state (see accompanying review). The single crystal structures of both complexes [Cp*Ir(SR)₂] have been determined and structure (3) shows the spatial arrangement of the ligands in [Cp*Ir(SC₆F₅)₂] [12]. The

macrocyclic complex *fac*-[IrCl₃L] in which L = 1,4,7-trithianonane has been prepared and crystallographically characterized [13].



Reports of the reactions of thiophene and related ligands with iridium(III) complexes include the preparations of [Ir(H)₂L₂(PPh₃)₂][PF₆] where L is thiophene, benzo[*b*]thiophene, dibenzothiophene and tetrahydrothiophene (tht). Structural data for two of the products (L = thiophene and tht) confirm octahedral coordination for the metal centre and for L = thiophene, the hydride ligands have been located. Both complexes possess the same dispositions of phosphine and *S*-donor ligands. The complexes represent models for the initial chemisorption step during the hydrodesulfurization of thiophenes on solid catalysts [14]. Related work from the same group probes the reaction of [Ir{HC(CH₂PPh₂)₃}(C₆H₆)]⁺ with thiophene; reactivity studies of the product (4) have been carried out [15]. Treatment of [Ir{HC(CH₂PPh₂)₃}(C₆H₆)] [BPh₄] with benzo[*b*]thiophene in thf under reflux generates a complex cation related to (4) which, on reaction with H₂, gives complex (5), BPh₃ and benzene. When compound (5) reacts with HCl, 2-EtC₆H₄SH is eliminated and [Ir{HC(CH₂PPh₂)₃}Cl₂(H)] is produced. The relevance of these studies to hydrodesulfurization is discussed [16].



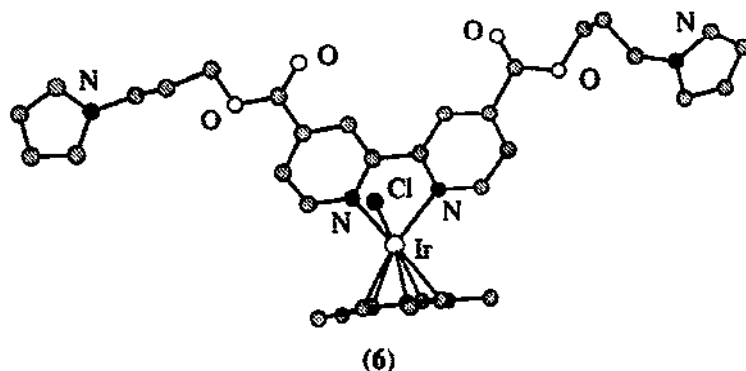
4.2.3 Complexes with nitrogen donor ligands including cyclon: related 2-phenylpyridine ligands

The crystal structure of the salt [Ir(NH₃)₅Cl]₂[PtCl₆] has been determined. The iridium(III) centre is, as expected, octahedrally coordinated [17]. The preparation of the iridium(III) dien complex [Ir(dien)₂][ClO₄]₃ and the separation of the *mer*-, *sym*-, *fac*- and *unsym*, *mer*-isomers by chromatography have been reported. Only trace amounts of the *fac*-isomers were found and the *mer*-isomer has been structurally characterized. Attempts to prepare [IrL₃]³⁺ in which L is

$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2$ were unsuccessful; contrast this with the results for rhodium(III) described in the accompanying review [18]. The ligand cyclam, L, reacts with $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ or $[\text{IrCl}_3(\text{tht})_3]$ to give *cis*- and *trans*- $[\text{IrCl}_3\text{L}]$. The electronic and ^{13}C NMR spectroscopic properties of the products have been reported as well as the results of powder diffraction studies. The data suggest *R,R,R,R/S,S,S,S-cis* and *R,R,S,S-trans*-configurations. Complexes involving oxidized cyclam ligands (with a C=N bond) have also been described [19].

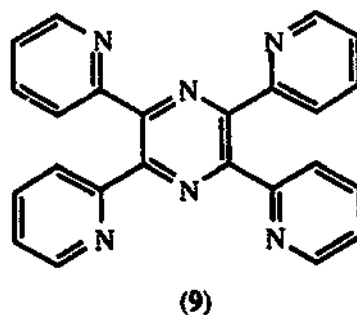
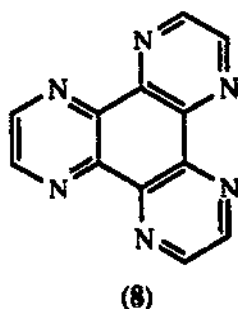
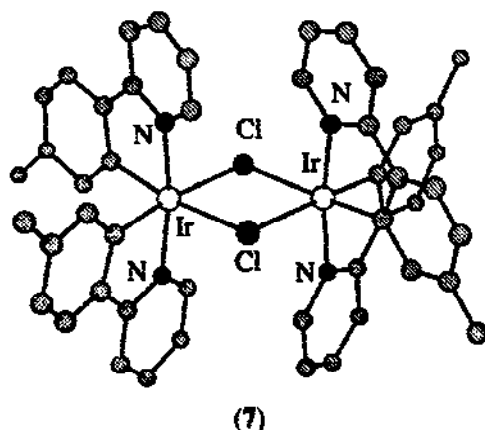
When the iridium(III) complexes *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$, $[\text{IrCl}_2(\text{H})(\text{PPh}_3)_3] \cdot \text{NEt}_3$ and $[\text{IrCl}_2(\text{H})(\text{PPh}_3)_3]$ are treated with HL (HL = $\text{PhN}=\text{C}(\text{R})\text{NHPh}$, R = H, Me, Et or Ph) in boiling benzene or toluene, the products are $[\text{IrH}_2\text{L}(\text{PPh}_3)_2]$, $[\text{IrCl}(\text{H})\text{L}(\text{PPh}_3)_2]$ and $[\text{IrCl}_2\text{L}(\text{PPh}_3)_2]$ respectively. These compounds have been characterized by elemental analysis and IR and ^1H , ^{13}C and ^{31}P NMR spectroscopies [20].

The chemistry of iridium(III) complexes involving 2,2'-bipyridine or related pyridine-based ligands continues to flourish. Ziessel *et al.* have compared the structural features of the iridium(III) complex $[\text{Cp}^*\text{IrLCl}][\text{ClO}_4]$ where L = 2,2'-bipyridine-4,4'- $\text{CO}_2(\text{CH}_2)_3\text{NC}_4\text{H}_9$ with a related iridium(I) analogue (see section 4.3.2). The structure of the iridium(III) cation is shown in (6) [21].



The synthesis and high resolution absorption and luminescence spectra of $[\text{IrL}_2(\text{bpy})]^+$ (HL = 2-(2-thienyl)pyridine) have been reported. When the cation is present in the host lattices $[\text{Ru}(\eta\text{py})_2(\text{bpy})][\text{PF}_6]$ and $[\text{Ir}(\eta\text{py})_2(\text{bpy})][\text{PF}_6]$, the lowest excited states ($\approx 18\,900\text{ cm}^{-1}$) correspond to the spin-forbidden $^3\pi \rightarrow \pi^*$ transition on ligand L^- . The next excited state ($21\,700\text{ cm}^{-1}$) has been assigned to Ir $\rightarrow$ bpy charge transfer [22]. In an accompanying paper, the absorption, excitation and luminescence spectra of $[\text{Ir}(\eta\text{py})_2(\text{bpy})]^+$ in various environments are presented. The lowest excited state in glasses or solutions has been assigned to Ir $\rightarrow$ bpy charge transfer but in a crystalline lattice of $[\text{Rh}(\eta\text{py})_2(\text{bpy})][\text{PF}_6]$ the lowest state ($21\,450\text{ cm}^{-1}$) appears to be due to a ligand $^3\pi \rightarrow \pi^*$ transition [23]. The luminescence properties of the complex cations $[\text{Ir}(\text{bpy})_x(\text{phen})_{3-x}]^{3+}$ ($x = 1, 2$) have been probed using 337 nm pulsed dinitrogen laser excitation, 360 nm Kr^+ continuous wave excitation, and pulsed dye laser excitation ($\approx 446\text{ nm}$) in methanol/ethanol glasses. The results have been rationalized in terms of a simple model with a phen-based $^3\pi \rightarrow \pi^*$ state which is in thermal equilibrium with bpy-based $^3\pi \rightarrow \pi^*$ state. The apparent dual emission has been discussed [24]. The iridium(III) complex $[\text{Ir}(\eta\text{py})_3]$ has been used in the formation of monolayer and multilayer Langmuir-Blodgett films; the electronic spectroscopic

and electrochemical properties of the films have been described [25]. The crystal structures of the cyclometallated complexes $[\text{Ir}\{2-(4\text{-MeC}_6\text{H}_4)\text{py}\}_3]$ and the related dimer $[[\text{Ir}\{2-(4\text{-MeC}_6\text{H}_4)\text{py}\}_2]_2(\mu\text{-Cl})_2]$ (7) have been determined [26].

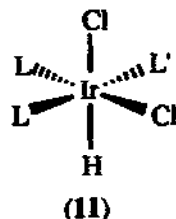
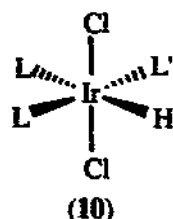
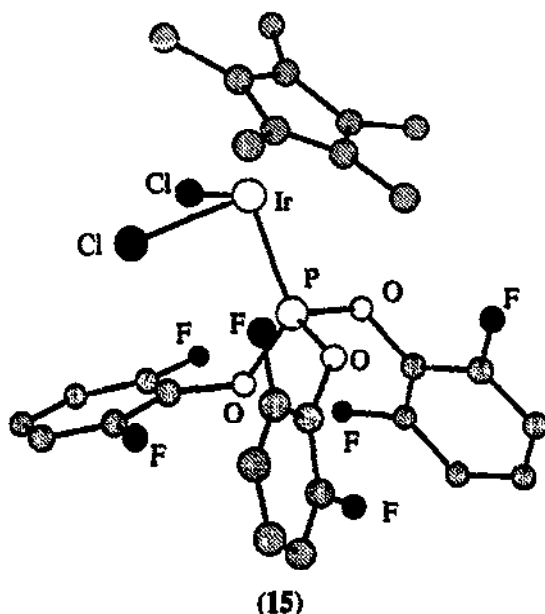
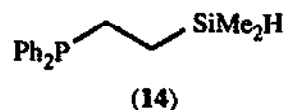
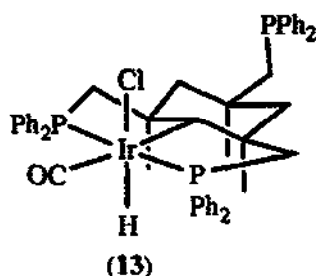
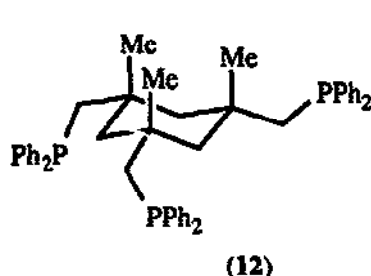


Ligand (8) has been incorporated into the complexes $[\text{IrL}(\text{ppy})_2]\text{X}$ ($\text{X} = \text{Cl}$ or PF_6) and related rhodium(III) complexes have also been prepared. The electrochemical properties of the complexes have been investigated; there are two reversible reduction processes centred on ligand (8) and an irreversible oxidation wave. Detailed discussion of the electrochemistry, and absorption and emission spectroscopic characteristics of the complexes have been presented [27]. The complex $[\text{Ir}(\text{9})\text{Cl}_3]$ has been prepared and characterized by spectroscopy, electrochemistry, spectroelectrochemistry and X-ray diffraction studies. The compound emits in fluid solution at room temperature and the luminescence lifetimes and energies have been determined [28]. A related dinuclear complex is described in section 4.4.

4.2.4 Complexes with phosphorus donor ligands

The results of a neutron diffraction study (at 55 K) of the phosphine complex *fac*- $[\text{IrH}_3(\text{PMePh}_2)_3]\cdot\text{MeOH}$ have been reported. The iridium(III) centre is in a distorted octahedral environment with the H atoms pushed towards one another; the Ir atom lies on a 3-fold axis. Pertinent bond distances are $\text{Ir-H} = 1.627(4)\text{\AA}$, $\text{Ir-P} = 2.314(2)\text{\AA}$, $\angle\text{H-Ir-H} = 83.4(2)^\circ$ and $\angle\text{P-Ir-P} = 948.6(1)^\circ$ [29]. The stereoisomers (10) and (11) have been prepared and structurally

characterized [30]. Variable temperature ^1H and ^{31}P NMR spectroscopies have been used to study the complexes $[\text{IrX}(\text{H})_2(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I), with an emphasis on the influence of the halide ligands on the reversible loss of H_2 [31].


 $\text{L} = \text{PMe}_2\text{Ph}$
 $\text{L}' = \text{P}^i\text{Pr}_3$


The preparation and characterization of ligand (12) have been described. The tris(phosphine) ligand reacts with $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ to yield the iridium(III) complex (13) — the result of C–H oxidative addition and coordination of only two of the three *P*-donor atoms. The structure has been crystallographically confirmed [32]. The iridium dimer $[\text{Cp}^*\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2]$ reacts with ligand (14) to give the complex $[\text{Cp}^*\text{IrCl}_2(14)]$ in which coordination is through the phosphorus atom. The complex has been characterized by ^1H , ^{13}C and ^{31}P NMR and IR spectroscopies; related rhodium chemistry is described in the accompanying review [33]. The condensation reaction between PCl_3

and 2,6-F₂C₆H₃OH in the presence of Et₃N in thf leads to the corresponding phosphite ligand. The reaction of [Cp*₂Ir₂Cl₂(μ-Cl)₂] with this ligand, L, produces the iridium(III) complex [Cp*IrCl₂L] (15) which has been characterized by ¹H, ³¹P, ¹⁹F NMR and IR spectroscopies and by a single crystal X-ray diffraction study. The environment about the iridium atom is distorted tetrahedral with an Ir–P bond distance of 2.211(2) Å [34].

The anionic complex [Cp*Ir{P(O)(OMe)₂}][–] has been prepared as the sodium salt and functions as a ligand towards metal centres, coordinating through O-donor atoms. Reactions between [Cp*Ir{P(O)(OMe)₂}][–] (L[–]) and Mg²⁺ or Zn²⁺ ions leads to complexes of the type [ML₂] (M = Mg or Zn), and with [Pt₂Me₆][SO₄].4H₂O, the product is the 6-coordinate platinum(IV) complex [PtMe₃L]. When treated with [Rh₂(cod)Cl₂], [Cp*Ir{P(O)(OMe)₂}][–] forms the compound [LRh(cod)]. The products have been characterized by spectroscopic methods [35].

4.2.5 Complexes with mixed donor ligands

A report of chiral iridium(III) complexes incorporating L-proline, L[–], has included the S_{Ir},S_N,S_C– and R_{Ir},S_N,S_C–diastereomers of [Cp*IrL(C≡C^tBu)], prepared from the corresponding chloride complexes and alkyne in the presence of NEt₃. Spectroscopic (including CD spectra) and crystallographic data (for the R_{Ir},S_N,S_C–diastereomer) confirm the nature of the products [36].

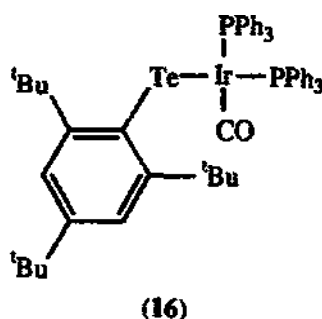
4.3 IRIDIUM(I)

4.3.1 Complexes with oxygen or tellurium donor ligands

A polyoxoanion incorporating an iridium(I) unit has been studied by ¹⁷O NMR spectroscopy. Enrichment with ¹⁷O of [P₂W₁₅Nb₃O₆₂]^{9–} and of the compound [nBu₄N][₅Na₃{(cod)IrP₂W₁₅Nb₃O₆₂}] has allowed direct observation of the site to which the iridium unit binds — that is, to the niobium-attached oxygen atoms. Possible fluxional processes involving the [Ir(cod)]⁺ unit and which generate the observed (average) C_{3v} symmetry of the Nb₃O₆-site have been discussed [37].

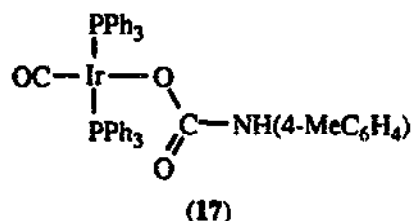
The carbamate complex *trans*-[Ir(PPh₃)₂(CO){OC(O)NH(4-MeC₆H₄)}] is described in the next section.

A series of alkali metal complexes containing [ArTe][–] ligands (Ar = aryl) and of the type [2,4,6-R₃C₆H₂]TeM(solvate)_n (R = various, M = group 1 metal, solvate = thf, dme, tmeda, 18-crown-6) have been prepared. The reaction of [2,4,6-^tBu₃C₆H₂][–]Li(thf)₃ with *trans*-[Ir(PPh₃)₂(CO)Cl] leads to the formation of the red complex (16); the *cis* arrangement of the PPh₃ ligands has been confirmed by a single crystal X-ray diffraction study. Whilst the geometry is 4-coordinate and is described as 'square', it is not planar but suffers a slight tetragonal distortion; the Ir–Te bond distance is 2.615(1) Å. Compound (16) has also been characterized by elemental analysis, and IR and ³¹P NMR spectroscopies [38].



4.3.2 Complexes with nitrogen donor ligands

Treatment of Vaska's compound with LiNHAr ($\text{Ar} = \text{Ph}$, 4-MeC₆H₄, 2,6-Me₂C₆H₃) leads to the formation of the iridium(I) complexes $\text{trans}[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{NHAr})]$. For $\text{Ar} = 4\text{-MeC}_6\text{H}_4$, crystallographic data have confirmed the square planar geometry and arrangement of the ligands ($\text{Ir-N} = 2.041(3)\text{\AA}$). Nuclear magnetic resonance spectroscopic data are consistent with the retention of the *trans*-geometry in solution. The reaction of $\text{trans}[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{NH}(4\text{-MeC}_6\text{H}_4))]$ with CO_2 results in an insertion product and from IR and NMR spectroscopic data this is proposed to be the carbamate complex (17). Further reactivity studies include the reactions of $\text{trans}[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{NHAr})]$ ($\text{Ar} = \text{Ph}$, 4-MeC₆H₄) with CO, and spectroscopic data suggest the formation of octahedral iridium(III) complexes [39].



The synthesis of the iridium(I) complex $[\text{IrH}(\text{CS})\text{L}_3]$ in which L = isonicotinic acid hydrazide has been reported. The diamagnetic product has been characterized by elemental analysis and IR spectroscopy (with the assignments of some absorptions) and the ligand is proposed to be N-bonded through the imino group [40].

Structure (6) showed the iridium(III) cation $[\text{Cp}^*\text{IrLCl}]^+$ where L = 2,2'-bipyridine-4,4'-CO₂(CH₂)₃NC₄H₄ and the related iridium(I) complex $[\text{Cp}^*\text{IrL}]$ has also been crystallographically characterized [21].

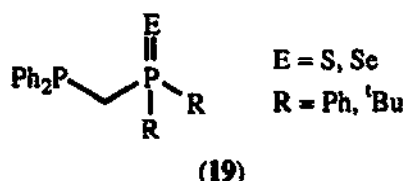
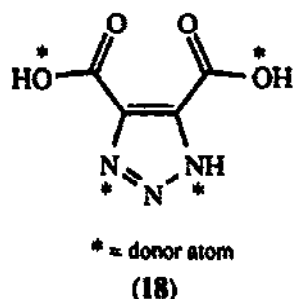
4.3.3 Complexes with phosphorus donor ligands

Two structural papers describe details of the phosphine complexes $[\text{Ir}(\text{cod})(\text{py})\{\text{P}(2,6\text{-(OMe)}_2\text{C}_6\text{H}_3)_3\}][\text{PF}_6]$ [41] and $[\text{Ir}(\text{cod})(\text{dppf})][\text{PF}_6]$ [42]. In the latter, the iridium(I) centre is, as expected, in a square planar environment, with the dppf ligand adopting a chelating mode and the cyclopentadienyl rings staggered.

Two related papers report chemistry of the ligand $(\text{C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2$, **L**. It reacts with the dimer $[\text{Ir}_2(\text{cod})_2\text{Cl}_2]$ to give the dinuclear complex $[\text{Ir}_2\text{L}_2(\mu\text{-Cl})_2]$ which exhibits a high thermal stability and does not undergo oxidative addition with H_2 , O_2 or halogenoalkanes. Treatment of the phosphine complex with Et_2NH leads to the mononuclear complex $[\text{IrL}(\text{NEt}_2\text{H})\text{Cl}]$, the square planar structure of which has been crystallographically confirmed. When heated in *thf* at reflux with $[\text{CpTi}]$, $[\text{Ir}_2\text{L}_2(\mu\text{-Cl})_2]$ cleaves to produce the complex $[\text{CpIrL}]$ [43, 44].

4.3.4 Complexes with mixed donor ligands

New iridium(I) complexes of ligand (**18**), H_3L , have been prepared and characterized. The deprotonated ligand binds two iridium centres, each associated with one *O,N*-donor set. The anions $[\text{Ir}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-L})]^-$ and $[\text{Ir}_2(\text{CO})_4(\mu\text{-L})]^-$ undergo electrochemical oxidation to give partially oxidized conducting materials; similar observations are reported for the corresponding rhodium(I) complexes and the conductivities of the oxidized products lie in the range 10^{-4} to $10^{-5} \Omega^{-1} \text{cm}^{-1}$ [45].



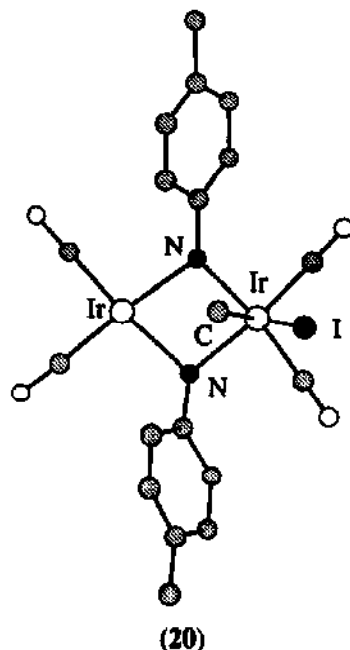
Treatment of the dimer $[\text{Ir}_2(\text{cod})_2\text{Cl}_2]$ with ligand (**19**) (HL) leads to the formation of the complex cations $[\text{Ir}(\text{cod})(\text{HL-}P,S)]^+$. Deprotonation with sodium hydride gives $[\text{Ir}(\text{cod})(\text{L-}P,S)]$. For $\text{E} = \text{S}$, an alternative method of synthesis has also been successful. The reactions of $[\text{Ir}(\text{cod})(\text{HL-}P,S)]^+$ with two equivalents of CO or CN^tBu , or with one equivalent of dppm result in displacement of the *cod* ligand. The compound $[[\text{Ir}(\text{cod})(\text{HL-}P,S)][\text{BF}_4] \cdot \text{CHCl}_3$ has been crystallographically characterized [46].

4.4 DI-, TRI- AND TETRANUCLEAR IRIDIUM COMPLEXES

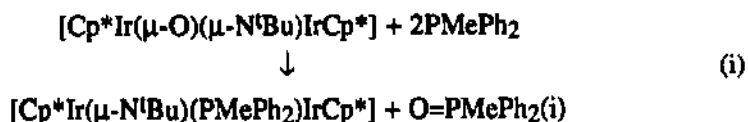
Several diiridium complexes have already been mentioned [26, 43, 44, 45] and in this section we consider dimetallic species with bridging ligands both with and without metal-metal bonds.

The polyhydrides $[\text{ReH}_7(\text{PPh}_3)_2]$ and $[\text{ReH}_7(\text{dppf})]$ react with the cation $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]^+$ with the quantitative formation of $[\text{L}_2\text{H}_3\text{Re}(\mu\text{-H})_3\text{IrH}(\text{PPh}_3)_2]^+$ ($\text{L}_2 = (\text{PPh}_3)_2$ or dppf). The dinuclear species have been characterized by IR and variable temperature ^1H and ^{31}P NMR spectroscopies and the geometries of the complexes have been discussed [47].

Oxidative addition of Cl_2 , Br_2 , HCl or MeI to $[\text{Ir}_2(\mu\text{-NH}(4\text{-MeC}_6\text{H}_4))_2(\text{CO})_4]$ yields iridium(I)-iridium(III) dinuclear products that have been characterized by IR and ^1H and ^{13}C NMR spectroscopies. The addition product with methyl iodide is complex (20) and structural data for confirm the presence of a square planar iridium(I) centre and an octahedral iridium(III) atom — the Ir—Ir separation is $3.209(1)\text{\AA}$. When I_2 adds to $[\text{Ir}_2(\mu\text{-NH}(4\text{-MeC}_6\text{H}_4))_2(\text{CO})_4]$ however, an iridium(II)-iridium(II) dimer is formed, and the structure of this product is proposed to be symmetrical [48].



The syntheses of bridging bis(imido) and imido-oxo complexes of the type $[\text{Cp}^*\text{Ir}(\mu\text{-X})(\mu\text{-NR})\text{IrCp}^*]$ ($\text{X} = \text{O}$, $\text{R} = \text{tBu}$; $\text{X} = \text{O}$, $\text{R} = \text{Ph}$; $\text{X} = \text{NR}$, $\text{R} = \text{Ph}$) have been described by Bergman and coworkers. For example, $[\text{Cp}^*\text{Ir}(\mu\text{-O})(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$ is prepared by treating $[\text{Cp}^*\text{Ir}=\text{N}^t\text{Bu}]$ with water. Imide and oxygen transfer from these compounds is achieved by reaction with phosphine [equation (i)]. Reduction of the bis(imido) complex occurs on reaction with H_2 . Crystallographic data for $[\text{Cp}^*\text{Ir}(\mu\text{-NPh})_2\text{IrCp}^*]$ and $[\text{Cp}^*\text{Ir}(\mu\text{-N}^t\text{Bu})(\text{PMePh}_2)\text{IrCp}^*]$ are reported [49]. In related work, Bergman *et al* have studied the reaction of $[\text{Cp}^*\text{Ir}=\text{N}^t\text{Bu}]$ with $[\text{Cp}_2\text{ZrCl}_2]$ and $n\text{BuLi}$; the heterometallic product $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$ has been crystallographically characterized and important bond parameters are $\text{Ir-Zr} = 2.08(1)$, $\text{Ir-N} = 1.887(3)\text{\AA}$ and $\angle\text{Zr-N-Ir} = 81.6(5)^\circ$. The reactivity of $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$ with respect to H_2NAr , ROH , ArSH and RR'PH has been investigated [50].

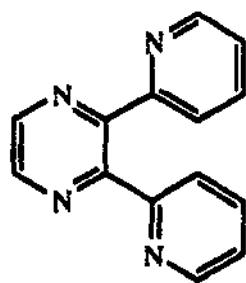


The diiridium complex $[\text{Ir}_2(\mu\text{-L})_2(\text{CO})_4]$ [$\text{L}^- = (21)$] is oxidized by AgBF_4 or AgOAc ; for example, treatment with AgOAc gives $[\text{Ir}_2(\mu\text{-L})_2(\text{CO})_4(\text{OAc})_2]$ in which the acetate ligands are coordinated axially in a monodentate manner. Related oxidations are also reported, and both head-to-head and head-to-tail (with respect to the different *N*-donor atoms in ligand (21)) isomers have been studied. Product characterization has been by elemental analysis and IR and ^1H NMR spectroscopies [51]. In a related paper, the same group has reported a large-scale preparation of $[\text{Ir}_2(\mu\text{-L})_2(\text{cod})_2]$ [$\text{L}^- = (21)$] and the reactions of this compound with I_2 and CO to give $[\text{IrL}_2(\text{cod})]$ and $[\text{Ir}_2(\mu\text{-L})_2(\text{CO})_4]$ respectively. The solution properties of $[\text{Ir}_2(\mu\text{-L})_2(\text{cod})_2]$ have been studied by NMR spectroscopy [52].

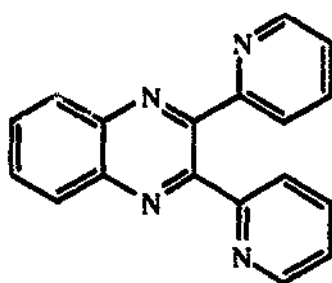


(21)

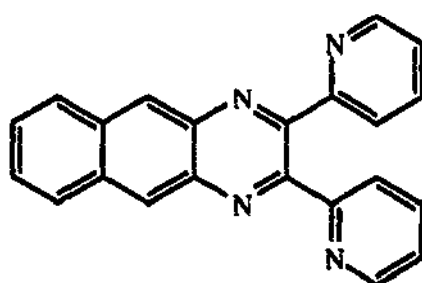
The reaction of $\text{K}[\text{tcne}]$ ($\text{tcne} = 1,1,2,2\text{-tetracyanoethene}$) with *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ leads to the formation of the complexes $[\text{Ir}(\text{CO})(\text{PPh}_3)_2]_2[\text{tcne}]\cdot\text{MeCN}$ and $[\text{Ir}(\text{CO})(\text{PPh}_3)_2]_2[\text{C}_4(\text{CN})_6]$ — the anion in the second complex arises from the dimerization of tcne and the rhodium analogue of this complex has been reported previously. An X-ray diffraction study of $[\text{Ir}(\text{CO})(\text{PPh}_3)_2]_2[\text{tcne}]\cdot\text{MeCN}$ shows that square planar iridium(I) centres are bridged by $[\text{tcne}]^{2-}$ ligands, each being coordinated (σ -bound) through two nitrogen atoms to two metal centres. The 2- charge on the tetracyanoethene ligand is manifested in a long central C–C bond (1.478(8) Å) [53].



(22)



(23)

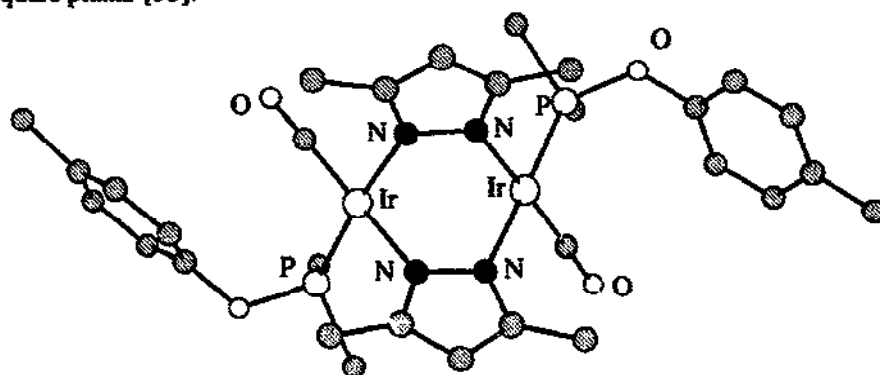


(24)

The preparations, characterizations and spectroelectrochemical properties of the heterometallic complexes $\{[(\text{bpy})_2\text{RuL}]_2[\text{IrCl}_2]_2\}^{5+}$ have been reported [$\text{L} = (22)\text{--}(24)$]. The interest in these cations lies in the presence of two centres that absorb in the visible region which are coupled by a catalytically active metal site. The products show absorbances throughout the visible region and exhibit a range of electrochemical processes including a ruthenium-centred oxidation, bridging ligand *L*-based reductions, and iridium and *bpy*-centred reductions. The authors have also discussed the effects of changing *L* on the orbital energies and on the $\text{Ru}(d\pi) \rightarrow \text{L}(\pi^*)$ metal-to-ligand charge transfer transition [54]. Ligand (9) is related to (22) to (24), and the same group has

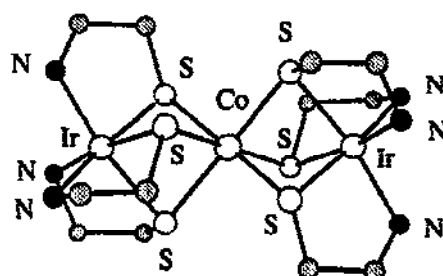
prepared the complex $[(\text{tpy})\text{Ru}\{\mu-(\mathbf{9})\}\text{IrCl}_3]$; spectroscopic, electrochemical and spectroelectrochemical properties have been studied and the compound emits in fluid solution at room temperature [28]; see also section 4.2.3.

The crystal structure of the diiridium complex $[\text{Ir}_2(\mu\text{-Me}_2\text{pz})_2(\text{CO})_2\{\text{PPh}_2(\text{O}-4\text{-MeC}_6\text{H}_4)\}_2]$ (**25**) has been determined. Each iridium centre is formally in a +1 oxidation state and is square planar [55].



Only the ipso-C atoms of Ph rings are shown.

(25)

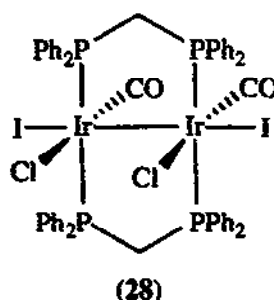
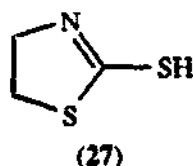


(26)

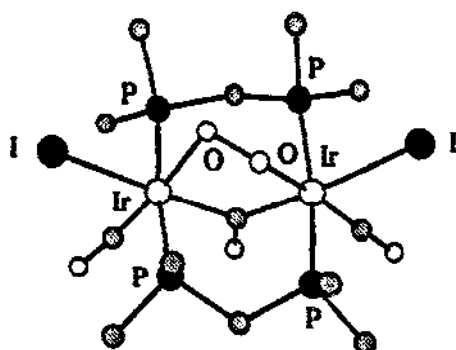
The syntheses and properties of the trinuclear complex cations $[\text{Co}\{\text{IrL}_3\}_2]^{3+}$ in which $\text{HL} = \text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$ or L-cysteine have been described. The methods of preparation involves the reaction of *fac*(S)- $[\text{IrL}_3]$ ($\text{HL} = \text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$ or L-cysteine) with cobalt(II) ions followed by oxidation in air or with H_2O_2 . The mixtures of products have been optically resolved to give $\Delta\Delta$, $\Delta\Lambda$ and $\Lambda\Lambda$ -isomers. For $\text{HL} = \text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$, the compound $\Delta\Lambda\text{-}[\text{Co}\{\text{IrL}_3\}_2][\text{NO}_3]_3$ has been crystallographically characterized; the cation is shown in structure (26), and features sulfur donor atoms in bridging positions, linking the three metals to give a linear $\text{Ir}^{\text{III}}\text{-Co}^{\text{III}}\text{-Ir}^{\text{III}}$ array. Additional data include electronic, CD and ^{13}C NMR spectra [56].

A number of diiridium 'A-frame' and related compounds were reported in 1993. The conjugate base of ligand HL (**27**) functions as an *N,S*-donor and bridges the two metal centres in the compound $[\text{Ir}_2\text{L}_2(\text{CO})_4]$. Treatment of this complex with dppm produces $[\text{Ir}_2(\mu\text{-L})_2(\mu\text{-dppm})(\text{CO})_4]$, or, in the presence of two equivalents of dppm, $[\text{Ir}_2(\mu\text{-L})(\eta^1\text{-L})(\mu\text{-dppm})_2(\text{CO})_2]$. Solution and reactivity studies have been carried out, and related rhodium complexes have also been prepared [57]. Treating the complex $[\text{Ir}_2(\text{CO})_2\text{I}_2(\text{dppm})_2]$ with PhICl_2 results in the

formation of $[\text{Ir}_2(\text{CO})_2\text{I}_2\text{Cl}_2(\text{dppm})_2]$ (28), the crystal structure of which has been determined. This confirms the *syn*-arrangements of the CO and the chloride ligands; the Ir–Ir distance is 2.859(2) Å. The new 'A-frame' complex has also been characterized by IR and ^1H and ^{31}P NMR spectroscopies [58].



Hydrogen sulfide reacts with $[\text{Ir}_2(\text{CO})_3(\text{dppm})_2]$ to yield $[\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\text{dppm})_2]$, CO and H_2 . A hydride intermediate has been observed allowing mechanistic details to be proposed. An analogous reaction with H_2Se proceeds by a similar type of intermediate compound, and reactions of $[\text{RhIr}(\text{CO})_3(\text{dppm})_2]$ with H_2S and H_2Se give $[\text{RhIr}(\text{H})(\text{CO})_2(\mu\text{-EH})(\text{dppm})_2]$ ($\text{E} = \text{S}$ or Se) followed by rearrangement or loss of H_2 . Several related reactions are also included in this paper including the formation of the complex $[\text{Ir}_2(\text{CO})_2(\mu\text{-CO})(\text{SPh})_2(\text{dppm})_2]$, the crystal structure of which has been determined. Detailed spectroscopic data are given [59]. The reaction of $[\text{Ir}_2(\text{CO})_2(\mu\text{-CO})\text{I}_2(\text{dppm})_2]$ with dioxygen leads to the formation of the peroxo-complex (29), the structure of which has been crystallographically confirmed (Ir–Ir = 2.705(1) Å). Complex (29) reacts with SO_2 to give a sulfate-bridged compound, and with NO_2 or NO to yield $[\text{Ir}_2(\text{CO})_2(\mu\text{-X})\text{I}_2(\text{dppm})_2][\text{NO}_3]$ ($\text{X} = \text{NO}$ or NO_3). The reactivity of compound (29) with CO, isocyanides, HCl and HBF_4 have also been investigated and the products have been characterized by IR and ^{31}P and ^1H spectroscopies, elemental analysis, and (where appropriate) conductivity measurements [60].



Only the ipso-carbon atoms of the Ph rings are shown.

(29)

The results of spectroelectrochemical investigations (in $[\text{nBu}_4\text{N}][\text{PF}_6]$ in MeCN) of the diiridium complex cation $[\text{Ir}_2\text{L}_4]^{2+}$ in which L = 1,8-diisocyano-*p*-menthane have been reported. Oxidation and reduction products — $[\text{Ir}_2\text{L}_4]^{4+}$ and $[\text{Ir}_2\text{L}_4]^0$ — have been characterized from UV-VIS and IR spectroscopic data [61].

The reactions of IrCl_3 with carboxylic acids have yielded complexes containing oxygen-centred triangular Ir_3 -cores — $[\text{Ir}_3\text{O}(\mu\text{-O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{n+}$. Although these complexes were previously known, the present work reports the use of ion-exchange chromatography to isolate and crystallize several species. Crystallographic data for salts containing $[\text{Ir}_3\text{O}(\mu\text{-O}_2\text{CR})_6(\text{H}_2\text{O})_3]^+$ and $[\text{Ir}_3\text{O}(\mu\text{-O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{2+}$ are reported and it is concluded that the structural parameters for cores which are formally $\{\text{Ir}^{\text{III}}\}_3$ or $\{\text{Ir}^{\text{III}}_2\text{Ir}^{\text{IV}}\}$ are essentially the same [62].

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