Cationic Complexes of Iridium(I) Containing Phosphites, Phosphines, or Arsines as Ligands

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A series of four- and five-co-ordinate iridium(I) salts of the type $[C_8H_{12}IrL_2]X$, $[C_8H_{12}IrL_3]X$, $[IrL_4]X$, and $[IrL_5]X$ (L = tertiary phosphite, phosphine, or arsine; X = BPh_4, PF_6, or ClO_4) have been prepared from the reactions of $[C_8H_{12}IrCl]_2$ with L. For L = PMe_2Ph the dioxygen adduct $[Ir(O_2)L_4]BPh_4$ has been characterised. The corresponding dioxygen adduct $[Ir(O_2)(AsMe_2Ph)_4]BPh_4$ has also been prepared. The reactions of $[C_8H_{12}IrCl]_2$ with L (L = PEt_2Ph and $PBu^n{}_3$) have given the *cis*-dihydride, *cis*-$[IrH_2L_4]BPh_4$. A new olefin hydride of iridium(III), namely $[(C_8H_{14})_2IrHCl_2]_2$, has been isolated. The reaction of this hydride with $AsMe_2Ph$ gave *trans*-$[IrHCl(AsMe_2Ph)_4]PF_6$. The ^1H n.m.r. spectra of these salts are discussed.

VRIEZE *et al.*[1] have reported detailed n.m.r. kinetic studies on the ligand exchanges in the systems $[IrCl(C_8H_{12})(EPh_3)]$–EPh_3, (E = P or As), and have interpreted their results in terms of the equilibria occurring

$$[IrCl(C_8H_{12})(EPh_3)] + EPh_3 \rightleftharpoons [IrCl(C_8H_{12})(EPh_3)_2] \rightleftharpoons [Ir(C_8H_{12})(EPh_3)_2]^+ + Cl^- \quad (i)$$

in solution. The formation of ionic species in these systems was confirmed by monitoring conductimetrically the addition of the ligands, EPh_3, to solutions of $[IrCl(C_8H_{12})(EPh_3)]$ in nitromethane, though no salts were isolated from these reactions. We have briefly reported[2] that by performing the above reactions in alcohols, or by direct treatment of $[C_8H_{12}IrCl]_2$ with other neutral ligands, L, in alcohols, salts containing the ionic species $[C_8H_{12}IrL_2]^+$ and $[C_8H_{12}IrL_3]^+$, can be isolated at room temperature or $[IrL_4]^+$ and $[IrL_5]^+$ under refluxing conditions. We now report the reactions of $[C_8H_{12}IrCl]_2$ with various ligands, L, in detail, *viz.* the preparations of $[C_8H_{12}IrL_2]X$, $[C_8H_{12}IrL_3]X$, $[IrL_4]X$, and $[IrL_5]X$, together with the formations of the dihydrides $[IrH_2L_4]BPh_4$ and the dioxygen adducts $[Ir(O_2)L_4]BPh_4$. Other workers[3-6] have recently described different routes to some of these salts. However, the preparative methods reported here, yet remain the simplest and most direct routes for the preparations of a large variety of phosphine, phosphite, or arsine salts of iridium(I) in pure form in high yield.

Preparation of Salts of the Type $[C_8H_{12}IrL_2]X$ *and* $[C_8H_{12}IrL_3]X$.—Treatment of a suspension of $[C_8H_{12}IrCl]_2$ in cold methanol or ethanol with an excess of ligand, L [L = $PEtPh_2$, $PMePh_2$, or $P(OMe)Ph_2$] rapidly gave deep red solutions from which the four-co-ordinate salts $[C_8H_{12}IrL_2]X$ (X = BPh_4, PF_6, or ClO_4) were isolated on addition of X^- anions. For $P(OEt)Ph_2$, however, the cation $[C_8H_{12}Ir\{P(OEt)Ph_2\}_2]^+$ was only formed when stoicheiometric amounts of $P(OEt)Ph_2$ were used. With an excess of this ligand only semi-crystalline oils were obtained. In contrast the reactions of $[C_8H_{12}IrCl]_2$ with three molar equivalents per iridium of ligand, L [L = $P(OMe)_3$, $P(OEt)_3$, PMe_2Ph, $AsMe_2Ph$, or $P(OMe)_2Ph$] in cold alcohols gave five-co-ordinate iridium(I) salts of the type $[C_8H_{12}IrL_3]X$ (X = BPh_4 or PF_6) on addition of X^- anions to the reaction solutions. Spectroscopic and conductivity evidence has indicated that the formation of $[C_8H_{12}Ir(PPh_3)_2]^+$ from $[C_8H_{12}IrCl]_2$ and PPh_3 follows reaction scheme (i). We have prepared the five-co-ordinate neutral intermediate in scheme (i), namely $[C_8H_{12}IrCl(PPh_3)_2]$, from $[C_8H_{12}IrCl]_2$ and an excess of PPh_3 in dichloromethane solution. This neutral complex had a small percentage dissociation in chlorinated solvents, acetone, nitromethane, or dimethyl sulphoxide but *ca.* 100% dissociation in methanol or ethanol (based upon conductivity measurements in these solvents, with $[Ir(diphos)_2]Cl$ as the standard used), giving further evidence for mechanism (i) and indicating the strong solvent dependence of the reaction, with alcohols by far the best solvolysing agents.

The complexes $[C_8H_{12}IrL_2]X$ and $[C_8H_{12}IrL_3]X$ were stable in air over extended periods and soluble in a variety of polar solvents. Their colours ranged from red or orange for $[C_8H_{12}IrL_2]X$ to white or pale yellow for $[C_8H_{12}IrL_3]X$. The ^1H n.m.r. spectra of these salts are summarised in Table 1. No useful information was derived from their i.r. spectra.

The complex $[C_8H_{12}Ir\{P(OEt)Ph_2\}_2]PF_6$ contained a single triplet resonance in its ^1H n.m.r. spectrum for the magnetically equivalent methyls on the ethyl groups, with $J(P-H) = 0$ for the long range coupling through four bonds. The ^1H n.m.r. spectrum of $[C_8H_{12}Ir(PEtPh_2)_2]PF_6$ however, contains two broad methyl triplets of equal intensity with $J(P-H) = 17$ Hz. A similar spectrum has been observed for the methyl spectrum of the ethyl groups bonded to the phosphine ligand in *trans* position to the chlorine in the complex *mer*-$[IrCl_3(PEt_2Ph)_3]$.[7] The ^1H n.m.r. spectra of the methyl groups on the ligands in the complexes $[C_8H_{12}IrL_2]X$ [L = $PMePh_2$, X = ClO_4 and L = $P(OMe)Ph_2$, X = PF_6] show a resonance pattern characteristic of

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'virtually coupled' $AX_3A'X_3'$ systems with intermediate ^2J(P–P) couplings.[8] The methyl resonances of the ions $[C_8H_{12}IrL_3]^+$ [L = $P(OMe)_3$ and $P(OMe)_2Ph$] occur as single triplets comprising of a broad central component and two sharp outer peaks. No change was observed in these spectra between 35 and −80° or on the addition of free ligand to the n.m.r. solution (apart from the appearance of free ligand resonances). Thus the observed spectra of $[C_8H_{12}IrL_3]^+$ are indicative of virtually coupled systems in which the ions in solution are undergoing rapid Berry-type rotations.[9] It is apparent that the intramolecular rate of ligand exchange in these ions must be such that although the three ligands, L, are equivalent on the n.m.r. time scale the effects of phosphorus to hydrogen and phosphorus to phosphorus couplings are still observed. The ^1H n.m.r. of the ions $[C_8H_{12}IrL_3]^+$ (L = PMe_2Ph and $AsMe_2Ph$) are more complex, however, and show temperature, free ligand, as well as solvent dependence and the full mechanistic study of these ions in solution will be the subject of a forthcoming publication.

^1H N.m.r. data for the ionic derivatives recorded at 34° and 60 MHz [a]

Compound	Diene protons		$-CH_2-$ or $-O-CH_2-$ protons	Ligand methyl groups	Hydride resonances
$[C_8H_{12}Ir(PEtPh_2)_2]PF_6$	5·40bs	7·83m	Obscured	8·7t J(H–H) 8·5 Hz [e] 9·0t J(H–H) 8·5 Hz J(P–H) 17·5 Hz	
$[C_8H_{12}Ir(PMePh_2)_2]ClO_4$	5·64bs	7·81bs		8·22pt J 7·5 Hz [d]	
$[C_8H_{12}Ir\{P(OMe)Ph_2\}_2]PF_6$	5·15bs	7·7bs		6·8pt J 11·5 Hz [d]	
$[C_8H_{12}Ir\{P(OEt)Ph_2\}_2]PF_6$	5·2bs	7·73bs	6·5m	9·2t J(H–H) 7·5 Hz [d]	
$[C_8H_{12}Ir\{P(OMe)_3\}_3]BPh_4$	6·13bs	7·63m		6·45 [f] J 11·4 Hz [b]	
$[C_8H_{12}Ir\{P(OEt)_3\}_3]BPh_4$	Obscured	7·6m	6·05m	8·77t J(H–H) 7·2 Hz [b]	
$[C_8H_{12}Ir\{P(OMe)_2Ph\}_3]BPh_4$	6·38bs	7·90m		6·62pt J 11·4 Hz [b]	
$[C_8H_{12}Ir(AsMe_2Ph)_3]BPh_4$	6·8bs	8·00m		8·69s [b]	
$[C_8H_{12}Ir(PMe_2Ph)_3]ClO_4$	6·8bs	7·84m		8·23m [b]	
$[Ir(PMePh_2)_4]PF_6$				9·65bt J 6·4 Hz [c]	
$[Ir\{P(OMe)Ph_2\}_4]PF_6$				7·38m J 11·3 Hz [b]	
$[Ir\{P(OMe)_2Ph\}_4]PF_6$				6·82m J 12·1 Hz [b]	
$[Ir\{P(OEt)Ph_2\}_4]PF_6$			7·05q J 6·9 Hz	9·86t J 8·4 Hz [b]	
$[Ir\{P(OMe)_3\}_5]BPh_4$				6·46m [b]	
$[Ir\{P(OEt)_3\}_5]BPh_4$			6·1m	8·69t J 7·0 [b]	
$[Ir(O_2)(PMe_2Ph)_4]BPh_4$				8·28d J(P–H) 9 Hz [c] 8·59t J 8 Hz *	
$[Ir(O_2)(AsMe_2Ph)_4]BPh_4$				8·41s 8·60s [b]	
$[IrH_2(PBu^n{}_3)_4]BPh_4$			Broad multiplet centred at	8·65	23·3d J(P–H) 96 Hz [b]
$[IrH_2(PEt_2Ph)_4]BPh_4$			8·25m	9·21m	23·8d J(P–H) 100 Hz [b]
$[IrHCl(AsMe_2Ph)_4]PF_6$				8·4s	31·2s [b]

[a] τ Scale; [b] $CDCl_3$; [c] CH_2Cl_2; [d] CD_2Cl_2; [e] $[^2H_6]$Acetone; s = singlet; d = 1 : 1 doublet; t = 1 : 2 : 1 triplet; pt = pseudo-triplet; m = multiplet; b = broad; q = quartet. [f] See Figure 1.

* Complexes may be analysed as a limiting case of an $AX_3A'X_3'$ system [8] with 'J' the separation of the outer peaks of the observed resonance.

The reactions of $[C_8H_{12}IrCl]_2$ with the ligands, L (L = phosphine, phosphite, or arsine) in cold alcohols to give the cations $[C_8H_{12}IrL_2]^+$ and $[C_8H_{12}IrL_3]^+$ are in complete contrast to corresponding reactions of $[C_8H_{12}RhCl]_2$.[10] With the rhodium–diene dimer, diene replacement was readily effected in cold alcohols to give the $[RhL_4]^+$ and $[RhL_5]^+$ species, indicating weaker rhodium–diolefin bonds. This is presumably due to the higher energies of the rhodium *d* orbitals facilitating poorer overlap between the ligand and substrate orbitals.

Formation of the Complexes $[IrL_4]X$ *and* $[IrL_5]X$.—Treatment of $[C_8H_{12}IrCl]_2$ with eight molar equivalents of the ligand, L [L = $PMePh_2$, $P(OMe)Ph_2$, $P(OMe)_2Ph$, and $P(OEt)Ph_2$] in refluxing ethanol for up to 30 min gave solutions containing the cationic species $[IrL_4]^+$, from which the salts $[IrL_4]X$ (X = BPh_4, PF_6, or ClO_4) could be readily isolated. For the salt $[Ir(PMe_2Ph)_4]BPh_4$, the reaction was performed under strict anaerobic conditions to prevent the formation of the dioxygen adduct. In the reaction involving $PMePh_2$, a second product was isolated, depending upon the refluxing time used. With refluxing times longer than 15 min, increasing yields (up to 45%) of the highly insoluble $[IrHCl_2(PMePh_2)_3]$ precipitated from the boiling reaction solution. The reaction of $[C_8H_{12}IrCl]_2$ with an excess of $AsMe_2Ph$ in boiling ethanol gave only the cation $[C_8H_{12}Ir(AsMe_2Ph)_3]^+$. No salt containing the cation $[Ir(AsMe_2Ph)_4]^+$ could be isolated from $[C_8H_{12}IrCl]_2$ and $AsMe_2Ph$. The ability of phosphines to co-ordinate more strongly than arsines with iridium [11,12] and platinum [13] complexes has previously been observed, and could account for the inability of $AsMe_2Ph$ to replace the strongly chelating C_8H_{12} group. With the ligands $P(OR)_3$ (R = Me or Et), treatment of $[C_8H_{12}IrCl]_2$ with fourteen molar equivalents of $P(OR)_3$ in refluxing ethanol gave the five-co-ordinate complexes $[IrL_5]BPh_4$ [L = $P(OR)_3$] on adding $NaBPh_4$ to the reaction solution.

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The salts $[IrL_4]X$ and $[IrL_5]X$ with the exception of $[Ir(PMe_2Ph)_4]X$ are reasonably stable in air, but some show decomposition in light over extended periods. Once again their colours ranged from red to orange for $[IrL_4]X$ to white for $[IrL_5]BPh_4$. It is pertinent to note, however, that with the limited number of ligands used in these preparations, the red cations all seemed to be formed with ligands having high steric requirements. Complexes of rhodium(I) and iridium(I) containing ligands of low steric size, *e.g.* $[C_8H_{12}MClL]$ (M = Rh and Ir; L = phosphine) are orange whereas known non-planar compounds, *e.g.* $[Ir(PMePh_2)_4]BF_4$ [5] and $[RhCl(PPh_3)_3]$ [14] are red, indicating some degree of distortion from planarity in the red cations $[C_8H_{12}IrL_2]^+$ and $[IrL_4]^+$. The isolation of salts containing the cations $[C_8H_{12}IrL_3]^+$ for both strong π-, and strong σ-donor ligands indicate that the formations of these five-co-ordinate iridium(I) species are dependent only upon the steric size of the ligand L.

The methyl resonance pattern in the ^1H n.m.r. spectra of the compounds $[IrL_4]PF_6$ [L = $P(OMe)_2Ph$ and $P(OMe)Ph_2$] is identical with that observed for the corresponding rhodium salts $[RhL_4]PF_6$.[10] The ^1H n.m.r. spectrum of $[Ir(PMePh_2)_4]ClO_4$ contains a broad ill-defined triplet centred at τ 9·65 with J = 6·4 Hz. No change in the observed spectrum occurred on addition of free ligand and hence the observed spectrum is not due to exchange of the methyldiphenylphosphine ligands. Similar spectra have been observed for other complexes in which four phosphine ligands are coplanar *e.g.* $[ReCl(CO)(PMe_2Ph)_4]$ and $[RuCl(CO)(PMe_2Ph)_4]BPh_4$.[15] The methyl resonances observed in the spectra of the compounds $[Ir\{P(OEt)Ph_2\}_4]PF_6$, $[Ir(PMePh_2)_4]ClO_4$, and $[C_8H_{12}Ir\{P(OEt)Ph_2\}_2]BPh_4$ occur at τ 1·17, 1·28, and 0·58 respectively to high field of the corresponding resonances in the spectra of the free ligands $P(OEt)Ph_2$ and $PMePh_2$. This could possibly be due to the 'neighbour-anisotropy effect' [16] of the phenyl rings or the proximity of these methyl groups to the metal atom which would cause them to experience considerable magnetic anisotropic shielding.

The complex $[Ir(PMe_2Ph)_4]BPh_4$ reacts with air to give the dioxygen adduct too rapidly in solution for satisfactory n.m.r. data to be obtained. The ^1H n.m.r. resonance for $[Ir\{P(OMe)_3\}_5]BPh_4$ is given in Figure 1, and is consistent with a limiting case of a 'virtually-coupled' system in which the ligands in the cation $[Ir\{P(OMe)_3\}_5]^+$ are undergoing a Berry or pseudorotation at such a rate as to preserve J(P–H). A similar mechanism also explains the doublet of quartets ($P–O–CH_2–$) and the single triplet ($–CH_3$) observed in the ^1H n.m.r. spectrum of the salt $[Ir\{P(OEt)_3\}_5]BPh_4$.

Cations of the Type $[Ir(O_2)L_4]^+$.—The salt $[Ir(PMe_2Ph)_4]BPh_4$ slowly absorbs oxygen in the solid state but rapidly in solution to give the dioxygen product $[Ir(O_2)(PMe_2Ph)_4]BPh_4$. Treatment of $[C_8H_{12}IrCl]_2$ with an excess of PMe_2Ph and $NaBPh_4$ in methanol in air, similarly gave the product $[Ir(O_2)(PMe_2Ph)_4]BPh_4$. The corresponding $AsMe_2Ph$ dioxygen adduct $[Ir(O_2)(AsMe_2Ph)_4]BPh_4$ could be formed only *via* the cyclooctene complex [17] $[(C_8H_{14})_2IrCl]_2$. Thus treatment of $[(C_8H_{14})_2IrCl]_2$ with $AsMe_2Ph$ in methanol at room temperature in air gave the cation $[Ir(O_2)(AsMe_2Ph)_4]^+$, characterised as the BPh_4 salt. Both these dioxygen complexes have recently been prepared by the decomposition in air of the carbonyl complexes $[Ir(CO)L_4]BPh_4$ (L = PMe_2Ph and $AsMe_2Ph$) in acetone–methanol mixtures.[18]

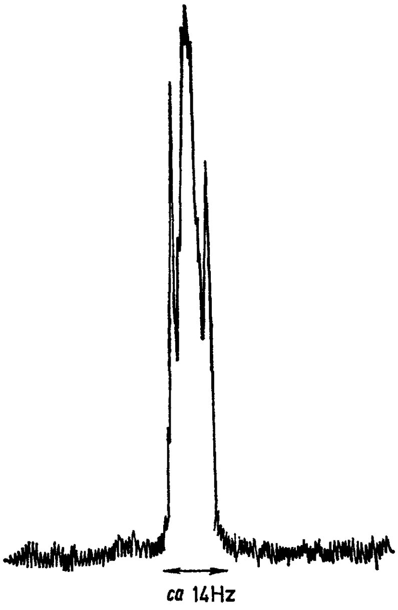

FIGURE 1 Methyl resonance pattern observed in the ^1H n.m.r. spectrum of $[Ir\{P(OMe)_3\}_5]BPh_4$

The solid-state i.r. spectrum of $[Ir(O_2)(AsMe_2Ph)_4]BPh_4$ contained a band at 838 cm^{-1} characteristic of an oxygen–oxygen vibration.[19] For $[Ir(O_2)(PMe_2Ph)_4]BPh_4$, no ν(O–O) could be unambiguously assigned because of overlapping anion resonances. The ^1H n.m.r. spectrum of $[Ir(O_2)(PMe_2Ph)_4]BPh_4$ in CH_2Cl_2 consists of a doublet and triplet of equal intensity which is in accord [20] with the structure (L = PMe_2Ph) shown in Figure 2. Similarly the two methyl singlets of equal intensity in the ^1H n.m.r. spectrum of $[Ir(O_2)(AsMe_2Ph)_4]BPh_4$ are also consistent [20] with the proposed structure (L = $AsMe_2Ph$) in Figure 2.

The factors affecting the uptake of oxygen in these systems have been shown to be related to the residual electron density on the metal atom centre and hence

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[20] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

to the properties of all the ligands in the co-ordination sphere.[21] The more basic the ligands, the stronger is the metal–oxygen π overlap, and the longer the O–O bond distance. It will be of interest to compare the O–O distance in the cation $[Ir(O_2)(PMe_2Ph)_4]^+$ containing the strongly basic PMe_2Ph ligand with that value reported [21] for the cation $[Ir(O_2)(dpe)_2]^+$.

Formations of $[IrH_2L_4]^+$.—When refluxing times of longer than 15 min are used for the reactions of $[C_8H_{12}IrCl]_2$ with L (L = PEt_2Ph and PBu^n_3) in ethanol, the deep red solutions containing the cations $[IrL_4]^+$ gradually turn white and addition of $NaBPh_4$ gave the dihydrides $[IrH_2L_4]BPh_4$. The metal hydride resonances in the ^1H n.m.r. spectra of $[IrH_2L_4]BPh_4$ appear as broad featureless doublets with separations *ca.* 100 Hz. The splitting, however is characteristic of coupling between hydride groups and mutually *trans* phosphorus nuclei and is thus consistent with a *cis*-configuration for the cations $[IrH_2L_4]^+$. We have prepared a series of salts containing the cation $[IrH_2L_4]^+$ by other routes however, and their ^1H n.m.r. together with those of $[IrH_2L_4]^+$ (L = PEt_2Ph and PBu^n_3) show temperature and solvent dependence and will form the basis of a forthcoming publication. The formations of the dihydrides for the ligands L = PEt_2Ph and PBu^n_3 in the above reactions is in keeping [22] with their strongly basic [23] natures.

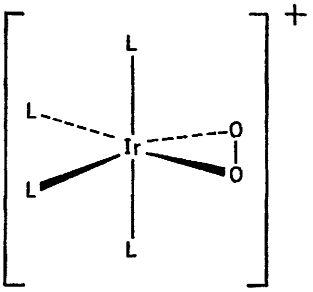

FIGURE 2 Proposed structure for the $[Ir(O_2)L_4]^+$ cations

It has previously been reported [17] that chloroiridic acid reacts with an excess of cyclo-octene in refluxing isopropyl alcohol to give the complex $[(C_8H_{14})_2IrCl]_2$. It has now been found that a second product can also be isolated in low yield from this reaction.

The i.r. spectrum of this second product contains a sharp peak at 2262 cm^{-1}, indicative of a hydride group bonded to the metal atom. The complex could not be obtained pure and was not fully characterised, but its nature was inferred from its reactions with $AsMe_2Ph$. When a suspension of the hydride in methanol was treated with an excess of $AsMe_2Ph$ and NH_4PF_6, a white crystalline salt $[IrHCl(AsMe_2Ph)_4]PF_6$ was formed. On the basis of this observation it is suggested that the secondary product isolated from the reaction of chloroiridic acid with C_8H_{14} is the iridium(III) dimer, $[(C_8H_{14})_2IrHCl_2]_2$ by analogy with $[C_8H_{12}IrHCl_2]_2$.[24] Furthermore, the mode of isolation of $[(C_8H_{14})_2IrCl]_2$ from the chloroiridic acid–cyclo-octene reaction mixture requires water addition to the solution formed to precipitate the product. It has been shown that a suspension of $[C_8H_{12}IrHCl_2]_2$ in ethanol rapidly gives a suspension of $[C_8H_{12}IrCl]_2$ when water is added to the mixture,[25] so we suggest that in the original cyclo-octene reaction solution, the hydride $[(C_8H_{14})_2IrHCl_2]_2$ is formed initially and is then converted by the weak base, water to the iridium(I) complex $[(C_8H_{14})_2IrCl]_2$.

The i.r. spectrum of $[IrHCl(AsMe_2Ph)_4]PF_6$ contains a sharp band at 2171 cm^{-1} corresponding to ν(Ir–H). The ^1H n.m.r. spectrum in $CDCl_3$ contains a single ligand methyl resonance consistent with a *trans*-configuration for the cation $[IrHCl(AsMe_2Ph)_4]^+$. The hydride resonance was observed as a singlet at τ 31·2.

EXPERIMENTAL

The ^1H n.m.r. spectra were recorded with a Varian A-60A instrument. Conductivities were determined on *ca.* 10^{-3}M solutions in acetone using a Van Waters and Rogers model 31 conductivity bridge. M.p.s were determined on a Kofler hot-stage and are corrected. All ligands were obtained commercially. The preparative methods used for the isolation of cations with BPh_4^-, PF_6^-, or ClO_4^- as the anion were identical and only one analysis is given for the relevant compound. Most of the salts $[C_8H_{12}IrL_2]X$, $[C_8H_{12}IrL_3]X$, and $[IrL_4]X$ could be isolated from the reaction mixture analytically pure when stoicheiometric amounts of ligand were used. For reactions requiring an excess of ligand, the method of recrystallisation is given with the experimental details. It was not found necessary to perform these reactions under nitrogen, with the exception of the preparation of $[Ir(PMe_2Ph)]BPh_4$. Yields varied between 60 and 95%.

Bis(methyldiphenylphosphine)cyclo-octadieneiridium(I) *Hexafluorophosphate*, $[C_8H_{12}Ir(PMePh_2)_2)PF_6$.—Methyldiphenylphosphine (0·2 g) was added to a suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·2 g) in ethanol (10 ml) and the mixture was stirred until all the original suspension had dissolved (*ca.* 10 min). To the deep red filtered solution was added a filtered solution of excess of NH_4PF_6 in ethanol. After cooling to 0°, the precipitate was filtered off and washed with ethanol, then ether, to give the required product as *red prisms* (0·36 g), m.p. 236° decomp. (Found: C, 48·2; H, 4·7; P, 10·6. $C_{34}H_{38}F_6P_3Ir$ requires C, 48·3; H, 4·55; P, 10·95%); conductivity = 135 Ω^{-1} cm^2 mol^{-1}. The following salts were similarly prepared from di-μ-chlorobis(cyclo-octadiene)-di-iridium(I) and the appropriate ligand.

Bis(methyldiphenylphosphinite)cyclo-octadieneiridium(I) *Hexafluorophosphate*, $[C_8H_{12}Ir\{P(OMe)Ph_2)_2\}PF_6$, from ethanol as *red prisms*, m.p. 195—196° (Found: C, 46·45; H, 4·2. $C_{34}H_{38}F_6O_2P_3Ir$ requires C, 46·50; H, 4·35%); conductivity 129 Ω^{-1} cm^2 mol^{-1}.

Bis(ethyldiphenylphosphine)cyclo-octadieneiridium(I) *Hexafluorophosphate*, $[C_8H_{12}Ir(PEtPh_2)_2]PF_6$, from ethanol as *red prisms*, m.p. 172—178° decomp. (Found: C, 49·25;

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H, 4·7. $C_{36}H_{42}F_6P_3Ir$ requires C, 49·5; H, 4·85%); conductivity 131 Ω^{-1} cm^2 mol^{-1}.

Bis(ethyldiphenylphosphinite)cyclo-octadieneiridium(I) *Hexafluorophosphate*, $[C_8H_{12}Ir\{P(OEt)Ph_2\}_2]PF_6$, from ethanol as *red prisms*, m.p. 197—198° decomp. (Found: C, 53·15; H, 4·8. $C_{36}H_{42}F_6O_2P_3Ir$ requires C, 53·45; H, 4·8%); conductivity 119 Ω^{-1} cm^2 mol^{-1}.

Tris(triethylphosphite)cyclo-octadieneiridium(I) *Tetraphenylborate*, $[C_8H_{12}Ir\{P(OEt)_3\}_3]BPh_4$.—To a suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·05 g) in methanol (8 ml) was added triethylphosphite (0·1 g) and the mixture stirred until all the initial suspension had dissolved. Addition of sodium tetraphenylboron (0·1 g) to the solution gave a white precipitate which on recrystallisation from dichloromethane–methanol gave the required product as *white prisms* (0·06 g), m.p. 145° decomp. (Found: C, 53·7; H, 7·0; P, 8·5. $C_{50}H_{77}BO_9P_3Ir$ requires C, 53·5; H, 7·0; P, 8·3%); conductivity = 85 Ω^{-1} cm^2 mol^{-1}. The following salts were similarly prepared from di-μ-chlorobis(cyclo-octadiene)di-iridium(I) and the appropriate ligand in ethanol, and recrystallised from dichloromethane–methanol.

Tris(trimethylphosphite)cyclo-octadieneiridium(I) *Tetraphenylborate*, $[C_8H_{12}Ir\{P(OMe)_3\}_3]BPh_4$, as *white prisms*, m.p. 168° decomp. (Found: C, 50·0; H, 6·05; P, 9·2. $C_{41}H_{59}BO_9P_3Ir$ requires C, 49·65; H, 6·0; P, 9·4%); conductivity 104 Ω^{-1} cm^2 mol^{-1}.

Tris(dimethylphenylphosphonite)cyclo-octadieneiridium(I) *Tetraphenylborate*, $[C_8H_{12}Ir\{P(OMe)_2Ph\}_3]BPh_4$, as *white prisms*, m.p. 138° decomp. (Found: C, 59·4; H, 5·85; P, 8·4. $C_{56}H_{65}BO_6P_3Ir$ requires C, 59·5; H, 5·8; P, 8·2%); conductivity 80 Ω^{-1} cm^2 mol^{-1}.

Tris(dimethylphenylphosphine)cyclo-octadieneiridium(I) *Perchlorate*, $[C_8H_{12}Ir(PMe_2Ph)_3]ClO_4$, as *white prisms*, m.p. 122—125° decomp. (Found: C, 47·0; H, 5·6; Cl, 4·15. $C_{32}H_{45}ClO_4P_3Ir$ requires C, 47·2; H, 5·55; Cl, 4·35%); conductivity 122 Ω^{-1} cm^2 mol^{-1}.

Tris(dimethylphenylarsine)cyclo-octadieneiridium(I) *Hexafluorophosphate*, $[C_8H_{12}Ir(AsMe_2Ph)_3]PF_6$, as *pale yellow prisms*, m.p. 130—134° decomp. (Found: C, 38·75; H, 4·55. $C_{32}H_{45}As_3F_6PIr$ requires C, 38·75; H, 4·45%); conductivity 109 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(methyldiphenylphosphine)iridium(I) *Hexafluorophosphate*, $[Ir(PMePh_2)_4]PF_6$.—Methyldiphenylphosphine (0·52 g) was added to a suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·21 g) in methanol (8 ml) and the mixture was refluxed for 15 min. The deep red solution formed was filtered and a filtered solution of excess of ammonium hexafluorophosphate in methanol was added. The precipitate which formed was washed with methanol, then ether, to give the required product as *deep red plates* (0·4 g), m.p. 218—220° decomp. (Found: C, 55·2; H, 4·6; P, 13·8. $C_{52}H_{52}F_6P_5Ir$ requires C, 54·9; H, 4·6; P, 13·6%); conductivity 85 Ω^{-1} cm^2 mol^{-1}. The following compounds were similarly prepared.

Tetrakis(methyldiphenylphosphinite)iridium(I) *Tetraphenylborate*, $[Ir\{P(OMe)Ph_2\}_4]BPh_4$, as *red prisms*, m.p. 225—226° decomp. (Found: C, 66·25; H, 5·4; P, 9·05. $C_{76}H_{72}BO_4P_4Ir$ requires C, 66·35; H, 5·4; P, 9·0%); conductivity 78 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(dimethylphenylphosphonite)iridium(I) *Hexafluorophosphate*, $[Ir\{P(OMe)_2Ph\}_4]PF_6$, as *orange prisms*, m.p. 192—193° decomp. (Found: C, 38·1; H, 4·3. $C_{32}H_{44}F_6O_8P_5Ir$ requires C, 37·8; H, 4·4%); conductivity 130 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(ethyldiphenylphosphinite)iridium(I) *Hexafluorophosphate*, $[Ir\{P(OEt)Ph_2\}_4]PF_6$, as *orange prisms*, m.p. 197—198° decomp. (Found: C, 53·2; H, 4·75. $C_{56}H_{60}F_6O_4P_5Ir$ requires C, 53·45; H, 4·8%); conductivity 124 Ω^{-1} cm^2 mol^{-1}.

Tetrakis(dimethylphenylphosphine)iridium(I) *Tetraphenylborate*, $[Ir(PMe_2Ph)_4]BPh_4$, from ethanol under an atmosphere of nitrogen, as *beige microcrystals*, m.p. 85—95° decomp. (Found: C, 63·40; H, 6·05. $C_{56}H_{64}BP_4Ir$ requires C, 63·25; H, 6·05%). The complex decomposed too rapidly in solution for a reliable conductivity to be measured.

Pentakis(triethyl phosphite)iridium(I) *Tetraphenylborate*, $[Ir\{P(OEt)_3\}_5]BPh_4$.—To a suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·3 g) in ethanol (10 ml) was added triethyl phosphite (1·5 g) and the mixture was refluxed for 4 h. To the very pale yellow solution formed was added sodium tetraphenylborate (0·6 g), and recrystallisation of the precipitate formed from dichloromethane–methanol gave the required product as *white prisms* (0·4 g), m.p. 212—214° decomp. (Found: C, 48·15; H, 7·3; P, 11·3. $C_{54}H_{95}BO_{15}P_5Ir$ requires C, 48·3; H, 7·15; P, 11·5%); conductivity 88 Ω^{-1} cm^2 mol^{-1}. Similarly prepared was *pentakis(trimethyl phosphite)iridium*(I) *tetraphenylborate*, $[Ir\{P(OMe)_3\}_5]BPh_4$, as *white needles*, m.p. 158—160° decomp. (Found: C, 41·6; H, 5·75. $C_{39}H_{65}BO_{15}P_5Ir$ requires C, 41·35; H, 5·8%); conductivity 100 Ω^{-1} cm^2 mol^{-1}.

Dioxygentetrakis(dimethylphenylphosphine)iridium(I) *Tetraphenylborate*, $[Ir(O_2)(PMe_2Ph)_4]BPh_4$.—A suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·33 g) and dimethylphenylphosphine (0·59 g) were refluxed for ½ h. The deep red solution which formed gradually turned very pale yellow on cooling in air. Addition of sodium tetraphenylborate (0·3 g) to this pale yellow solution gave a precipitate which on recrystallisation from acetone–methanol gave the required product as *pale yellow needles*, (0·3 g), m.p. 171—172° decomp. (Found: C, 61·5; H, 6·2; P, 11·35. $C_{56}H_{64}BO_2P_4Ir$ requires C, 61·35; H, 5·9; P, 11·3%); conductivity 91 Ω^{-1} cm^2 mol^{-1}.

Dioxygentetrakis(dimethylphenylarsine)iridium(I) *Tetraphenylborate*, $[Ir(O_2)(AsMe_2Ph)_4]BPh_4$.—Dimethylphenylarsine (0·204 g) and di-μ-chlorotetrakis(cyclo-octene)di-iridium(I) (0·1 g) were stirred in methanol (10 ml) until all the initial suspension had dissolved. To this colourless solution was added sodium tetraphenylborate (0·2 g) and recrystallisation of the white precipitate formed from dichloromethane–methanol gave the required product as *white needles* (0·1 g), m.p. 168—170° decomp. (Found: C, 52·8; H, 5·0. $C_{56}H_{64}As_4BO_2Ir$ requires C, 52·9; H, 5·1%); conductivity 83 Ω^{-1} cm^2 mol^{-1}.

cis-*Dihydrotetrakis(tri*-n-*butylphosphine)iridium*(III) *Tetraphenylborate*, *cis*-$[IrH_2(PBu^n_3)_4]BPh_4$.—A suspension of di-μ-chlorobis(cyclo-octadiene)di-iridium(I) (0·1 g) ethanol (10 ml) and tri-*n*-butylphosphine (0·4 g) were refluxed for 2 h. Addition of sodium tetraphenylborate (0·2 g) to the resultant solution gave a white precipitate which on recrystallisation from dichloromethane–methanol in the cold gave the product as *white prisms* m.p. 160° (Found: C, 65·4; H, 9·7; P, 9·7. $C_{72}H_{130}BP_4Ir$ requires C, 65·4; H, 9·9; P, 9·4%); conductivity 92 Ω^{-1} cm^2 mol^{-1}. Similarly prepared was cis-*dihydrotetrakis(diethylphenylphosphine)iridium*(III) *tetraphenylborate*, *cis*-$[IrH_2(PEt_2Ph)_4]BPh_4$, as *white prisms*, m.p. 160—162° (Found: C, 65·15; H, 7·0. $C_{64}H_{82}BP_4Ir$ requires C, 65·25; H, 7·05%); conductivity 88 Ω^{-1} cm^2 mol^{-1}.

trans-*Hydrochlorotetrakis(dimethylphenylarsine)iridium*(III) *Hexafluorophosphate*, *trans*-[IrHCl(AsMe$_2$Ph)$_4$]PF$_6$.—Treatment of a suspension of di-μ-chlorodichlorodihydridotetrakis(cyclo-octene)di-iridium(III) (0·1 g) in methanol (10 ml) with dimethylphenylarsine (0·22 g) rapidly gave a colourless solution from which a white solid was deposited on addition of ammonium hexafluorophosphate (0·2 g). Recrystallisation from dichloromethane–methanol gave the required product as *white prisms* (0·2 g) containing methanol of crystallisation. Heating the prisms under high vacuum at 80° for 16 h gave crystals of analytical purity, m.p. 209—211° (Found: C, 34·45; H, 4·15; Cl, 3·4. $C_{32}H_{45}As_4ClF_6PIr$ requires C, 34·85; H, 4·1; Cl, 3·2%); conductivity 131 Ω^{-1} cm^2 mol^{-1}.

Di-μ-chlorodichlorodihydridotetrakis(cyclo-octene)di-iridium(III), [IrHCl$_2$(C$_8$H$_{14}$)$_2$]$_2$.—Chloroiridic acid (5 g) and cyclo-octene (5 ml) were refluxed in propan-2-ol (20 ml) for 2½ h. Water (5—10 ml) was added slowly with stirring to the deep brown solution formed and the brick red precipitate of di-μ-chlorotetrakis(cyclo-octene)di-iridium(I) which formed was filtered off. Excess of water (*ca.* 20 ml) was then added rapidly to the solution, depositing *pale brown microcrystals* (0·8 g), m.p. decomp. above 190° without melting. No sample of analytical purity could be obtained from this reaction.

Chloro(cyclo-octadiene)bis(triphenylphosphine)iridium(I), [C$_8$H$_{12}$IrCl(PPh$_3$)$_2$].—To a solution of di-μ-chlorobis(cyclo-octadiene) di-iridium(I) (0·34 g) in dichloromethane (5 ml) was added triphenylphosphine (1·154 g). The dichloromethane was removed under reduced pressure and the resultant oil formed crystallised from ether. This gave the required product as *orange prisms* (0·6 g), m.p. 105—109° (Found: C, 60·9; H, 4·9. $C_{44}H_{42}ClIrP_2$ requires C, 61·4; H, 4·9%).

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