Reactions of Tri(hydrido)(*p*-tolyl isocyanide)bis(triphenylarsine)iridium(III) with Chelating Ligands: Spectroscopic and Magnetic Study

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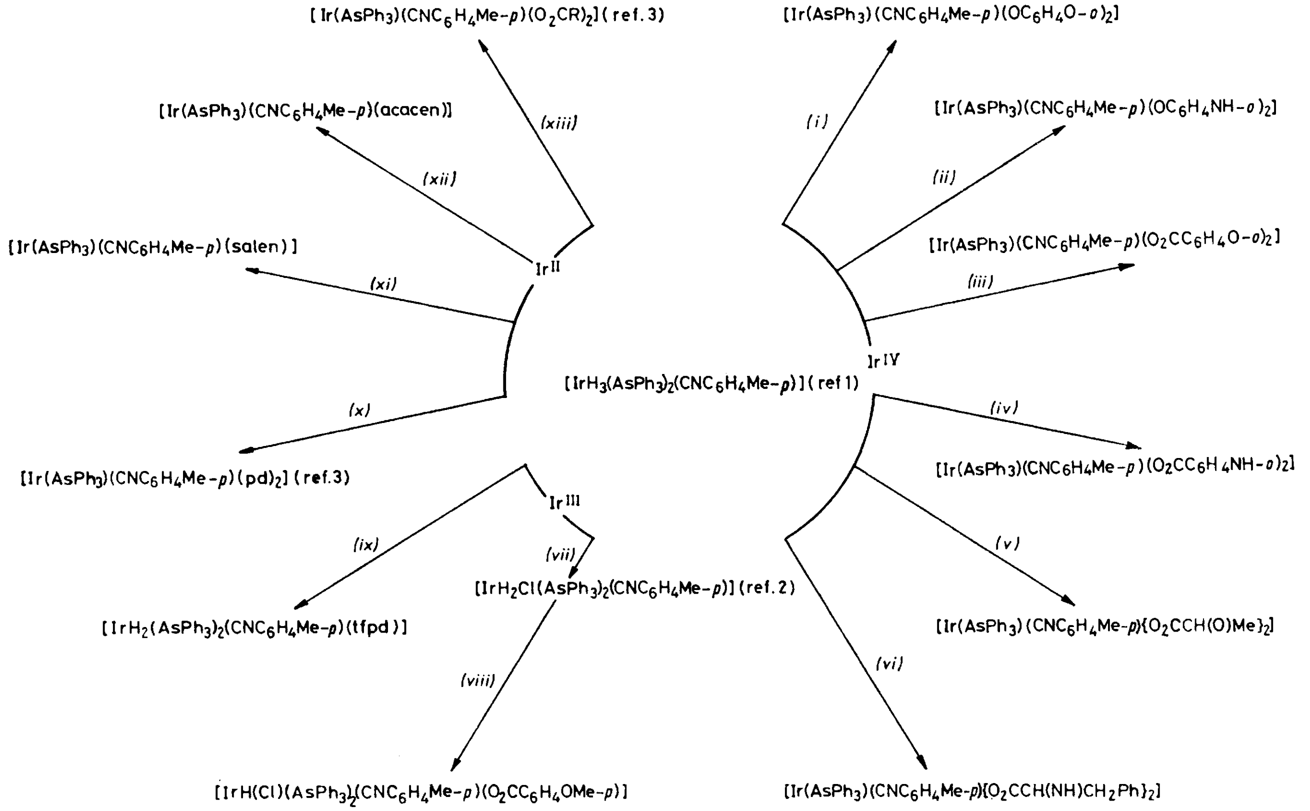
Reactions of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ with chelating ligands yield substitution products having the metal in various oxidation states depending on the nature of the ligand. Carboxylic acids, pentane-2,4-dione, and quadridentate Schiff bases give iridium(II) monomeric paramagnetic complexes; amino- and hydroxy-acids and *o*-amino- and *o*-hydroxy-phenols give paramagnetic iridium(IV) products. The presence of highly electron-attracting groups in the co-ordination sphere keeps Ir in the oxidation state III. All the complexes have been characterised by their vibrational, electronic, and magnetic properties, and in some cases the most probable ground-state electronic configuration of Ir has been suggested. Ligand-field properties favourable to each oxidation state are discussed.

THE complex $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ [1] reacts with hydrogen halides or pseudohalides to yield the substitution products $[IrH_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)X]$ (X = Cl, Br, I, or N_3); [2] on the other hand, with carboxylic acids and pentane-2,4-dione it forms the chelated complexes $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)L_2]$ (L = carboxylate or pentane-2,4-dionate), in which Ir^{III} has been reduced to Ir^{II}.[3] This change in the metal oxidation state, on co-ordination of chelating ligands, suggested that chelation could result in stabilization of various, perhaps unusual, electronic states of the metal, depending on the nature of the ligands. Thus, we have carried out the reactions shown in the Scheme and identified the products, where possible. The different oxidation states of the metal have been characterized in terms of the vibrational, electronic, and magnetic properties of the products, so that the relations between the ligand field and the metal electronic configuration could be clarified. The reported complexes greatly aid the assignment of electronic properties to the oxidation states, because most of the complexes having different oxidation states only differ in the nature of their chelated ligand.



SCHEME (*i*) $HOC_6H_4OH\text{-}o$; (*ii*) $HOC_6H_4NH_2\text{-}o$; (*iii*) $HO_2CC_6H_4OH\text{-}o$; (*iv*) $HO_2CC_6H_4NH_2\text{-}o$; (*v*) $HO_2CCH(OH)Me$; (*vi*) $HO_2CCH(NH_2)CH_2Ph$; (*vii*) HCl; (*viii*) $HO_2CC_6H_4OMe\text{-}p$; (*ix*) Htfpd; (*x*) Hpd; (*xi*) Hsalen; (*xii*) Hacacen; (*xiii*) RCO_2H

RESULTS

Reactions with Carboxylic Acids.—The products of these reactions were considered in a previous paper [3] and symmetrical co-ordination of two carboxylate groups, in the same molecular plane, was observed. Removal of the three hydrides is followed by the reduction of Ir^{III} to Ir^{II}.

The reaction with *p*-methoxybenzoic acid has been now extended to the chloro-complex $[IrH_2Cl(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$.[2] Reduction does not occur, instead only one hydride is substituted by the carboxylate which acts as a unidentate ligand and the complex $[IrH(Cl)(AsPh_3)_2(CNC_6H_4Me\text{-}p)(O_2CC_6H_4OMe\text{-}p)]$ is obtained. Vibrational analysis shows the bands of the unidentate carboxylate anion (see Table 2); the stretching vibration ν(C–N) occurs almost at the same wavenumber for $[IrHCl_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ and $[IrHCl(AsPh_3)_2(CNC_6H_4Me\text{-}p)(O_2CC_6H_4OMe\text{-}p)]$, while ν(Ir–H) shifts to lower frequencies in the product and is probably overlapped by the more intense ν(C–N) band. The frequency ν(Ir–Cl) is unchanged. The n.m.r. spectra reveal that the strongest perturbation is on the hydride anion, whose chemical shift increases from τ 19.5 (ref. 2) to 27.2. The chemical shifts of the isocyanide CH_3 and of the methoxy-group lie respectively at τ 7.7 and 6.15. The spectroscopic data do not provide any information about the structure of the product, except that, in the presence of halide, the carboxylate anion does not act as a chelating ligand and the reduction of Ir^{III} to Ir^{II} does not occur.

TABLE 1

Analytical data

	Complex	Colour	Analysis (%) [a] C	H	N	Ir	Cl or F	M.p. (θ_c/°C)
(1)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(acacen)]$	Brown	45.6	4.25	4.35	31.75		170 [b]
			(54.5)	(4.75)	(5.00)	(22.95)		
(2)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(salen)]$	Yellow	54.1	5.10	4.70	22.25		110
			(57.2)	(4.10)	(4.75)	(21.8)		
(3)	$[IrH_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)(tfpd)]$	White	52.4	3.65	1.30	19.55	5.15	173
			(54.6)	(4.00)	(1.30)	(17.85)	(5.20)	
(4)	$[IrH(Cl)(AsPh_3)_2(CNC_6H_4Me\text{-}p)(O_2CC_6H_4OMe\text{-}p)]$	Pale yellow	57.05	4.35	1.05	17.4	3.55	117
			(56.3)	(4.05)	(1.25)	(17.3)	(3.20)	
(5)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(OC_6H_4O\text{-}o)_2]$	Brown	52.3	3.95	1.40	25.7		>240
			(54.85)	(3.60)	(1.70)	(23.1)		
(6)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(OC_6H_4NH\text{-}o)_2]$	Black	54.65	4.90	4.95	21.0		140 [b]
			(55.0)	(3.85)	(5.05)	(23.15)		
(7)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CC_6H_4O\text{-}o)_2]$	Pale brown	51.15	3.55	1.50	21.2		160
			(54.1)	(3.40)	(1.60)	(21.65)		
(8)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CC_6H_4NH\text{-}o)_2]$	Pale brown	53.6	3.70	3.75	20.1		151
			(54.25)	(3.65)	(4.75)	(21.7)		
(9)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)\{O_2CCH(O)Me\}_2]$	Pale brown	47.85	3.95	1.50	24.2		155
			(48.55)	(3.80)	(1.75)	(24.25)		
(10)	$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)\{O_2CCH(NH)CH_2Ph\}_2]$	Black	53.2	4.85	3.90	18.95		112 [b]
			(56.1)	(4.25)	(4.45)	(20.4)		

[a] Calculated values are given in parentheses. [b] With decomposition.

TABLE 2

Vibrational data (cm^{-1})

Compound	ν(C–N)	ν(Ir–H)	ν(C–O)	ν(C–O)	ν(Ir–Cl)
(1)	2 120vs				
(2)	2 120vs				
$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(pd)_2]$	2 145vs		1 590m	1 400m	
$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CC_6H_4OMe\text{-}p)_2]$	2 130s		1 535mw	1 400mw	
$[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$	2 130vs	2 100 2 078ms			
(3)	2 140vs	2 220ms	1 702—1 680vs		
$[IrH_2Cl(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$	2 150vs	2 200ms			333vs
(4)	2 160vs	not visible	1 690vs	1 390m	333vs
(5)	2 130vs				
(6)	2 145s				
(7)	2 120vs		1 580s	1 370ms	
(8)	2 130s		1 615s	1 350m	
(9)	2 140vs		1 620	1 350w	
(10)	2 150s		1 640vs	1 380m	
$p\text{-}MeC_6H_4NC$	2 130s				

Comparison of the Reactions with Pentane-2,4-*dione and* 1,1,1-*Trifluoropentane*-2,4-*dione*.—A comparison between these reactions is very important because the two chelating ligands, differing only in the presence of the three fluorine atoms, give iridium complexes having different oxidation states. Details of the reaction with pentane-2,4-dione have been discussed previously.[3] 1,1,1-Trifluoropentane-2,4-dione (Htfpd) gives the product $[IrH_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)(tfpd)]$ with tfpd acting as a unidentate ligand through the carbon (see later). The ν(Ir–H) stretching vibrations and the isocyanide ν(C–N) band of the latter product lie between 2 220 and 2 000 cm^{-1}; the ligand tfpd shows the bands of *C*-bonded pentanedionate[4] (Table 2). This kind of co-ordination is unusual for the pentanedionate anion; however, it has been already found in platinum complexes,[4] confirming the tendency of the 5*d* elements to co-ordinate pd in the keto-form. The n.m.r. spectrum is diagnostic of two very different hydride anions, with resonances at τ 35.2 and 19. The splitting of the signals indicates an AB system, with a small coupling constant (6 Hz). It is suggested that two hydrides are mutually *cis* and *trans* to two very different groups; tfpd and $AsPh_3$ or tfpd and $CNC_6H_4Me\text{-}p$. Both structures are equally probable. The vibrational spectra surprisingly show only one ν(Ir–H) absorption band. It is probable that the second band is obscured by the more intense and broader ν(C–N) absorption band, as in the case of the complex (4). The resonances of the CH_3 groups of tfpd and of the isocyanide lie respectively at τ 7.75 and 7.83, while that of the CH group of tfpd is obscured by the benzene ring resonances; no resonances of the enol form of tfpd are observed.

Reactions with Quadridentate Schiff Bases.—The reactions with *NN'*-ethylenebis(salicylideneimine) (Hsalen) and *NN'*-ethylenebis(acetylacetoneimine) (Hacacen) demonstrate the readiness of hydride and arsine groups to undergo substitution by polydentate and rigid systems. The complexes obtained, $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(salen)]$ and $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(acacen)]$, may exhibit a structure in which the quadridentate ligand is in the equatorial plane, and $AsPh_3$ and CNC_6H_4Me-*p* in *trans* axial positions.

All the ligand bands are clearly visible in the vibrational spectra. The bands of acacen and salen are very similar to those reported for these ligands when co-ordinated to other transition-metal ions.[5,6] The ν(C–N) stretching band in the complexes is not sensitive to the reduction from Ir^{III} to Ir^{II}, analogous to the other iridium(II) complexes reported (Table 2). Magnetic moments are given in Table 3.

TABLE 3

Magnetic parameters

Complex	μ/B.M.*	g_1	g_2
(1)	1.76	3.19	1.9
(2)	1.97		
(5)		1.997	1.906
(6)	1.74	1.986	1.940
(7)	2.30	1.996	1.912
(8)	1.96	1.988	1.930
(9)	2.04	2.008	1.940
(10)	1.82	1.991	1.894

* At room temperature; 1 B.M. ≈ 9.27×10^{-24} A cm^2.

The lower purity of the acacen complex, with respect to the other paramagnetic complexes, and the difficulty in packing of the powder, results in the approximate value for this complex.

The e.s.r. spectrum, at low temperature, of the acacen complex shows broad resonances which can be resolved into two principal components, $g_1 = 3.19$ and $g_2 = 1.9$ [Figure 1(*a*)]. These values are very similar to those for the isoelectronic [Co(acacen)],[6] although the unresolved spectrum of the iridium(II) complex prevents one from observing any rhombic anisotropy. By considering the ligand-field strengths, an octahedrally elongated geometry can be suggested for the iridium complex, with the elongation axis being along the axis of the arsine and isocyanide ligands. Thus, a metal ground-state configuration different to that of iridium(II) carboxylato-complexes[3] can be expected. The assignment of the *g* values to the principal components of the magnetic parameters is difficult from the powder spectra; however, the similarity of the *g* values obtained to those of [Co(acacen)] suggests a metal ground-state configuration similar to that of the cobalt complex. The unpaired electron of the iridium(II) ion should be in the mixed d_{z^2} and $d_{xz,yz}$ orbitals,[6] though the d_{z^2} contribution is probably higher in this six-co-ordinate iridium(II) complex than in the planar cobalt complex. The difference in the iridium ground state between the carboxylato-complexes[3] and the acacen complex is also evident from the electronic spectra (Figure 2). More extended ligand-field calculations require better resolved e.s.r. spectra. The e.s.r. spectrum of the corresponding salen complex is similar, but too broad for the components to be separated.

Iridium complexes of Schiff bases were previously unknown. Any attempt to prepare them from Schiff bases and $[IrBr_6]^{2-}$, $[IrBr_3(AsPh_3)_2]$, or $[IrH_3(AsPh_3)_2]$, which are precursors of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$, failed. Only the simultaneous presence of hydride and isocyanide groups seems to stabilize such complexes.

Reactions with Carboxylic Acids and Phenols.—These reactions are reported together because they all yield iridium(IV) products by oxidation of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ and by double deprotonation of the chelating ligand. This behaviour is unusual for these types of chelating ligands and indicates the high reducing activity of the hydride in the iridium(III) complex.

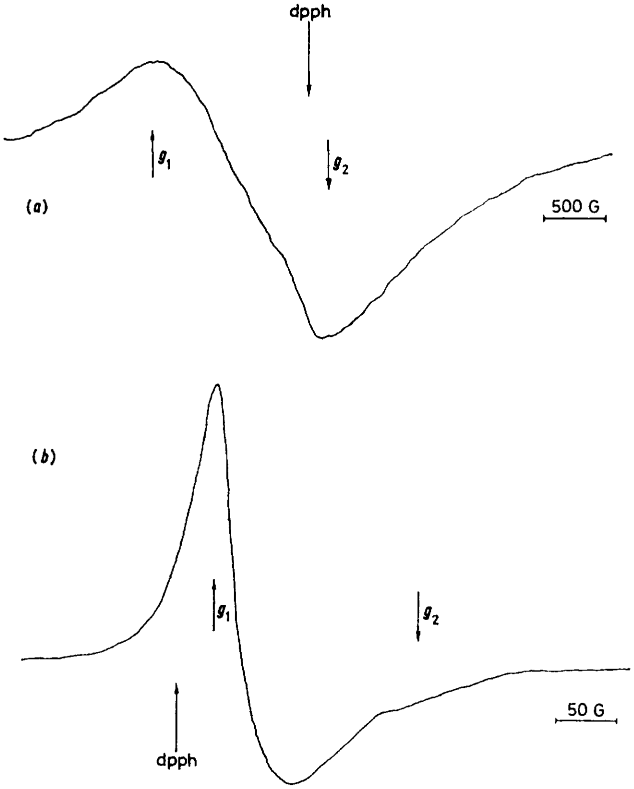


FIGURE 1 E.s.r. spectra of polycrystalline powders, recorded at liquid nitrogen temperature: (*a*) $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(acacen)]$; (*b*) $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(OC_6H_4O\text{-}o)_2]$. dpph = Diphenylpicrylhydrazyl; 1 G = 10^{-4} T

The vibrational spectra of iridium(IV) complexes have been compared with the spectra of the alkali-metal salts of the related chelating ligands. The vibrational frequencies $\nu(NH_2)$ of amino-acids or aminophenols and ν(OH) of hydroxyacids or hydroxyphenols disappear on complex-formation with iridium. In amino-acids or aminophenols ν(NH) appears as a broad low-intensity band. The frequency differences ($\nu_{asym} - \nu_{sym}$) of the carboxylate groups have values intermediate between those of the free acid and of the salts of the ligands, so that a unidentate behaviour of the carboxylate group can be suggested (Table 2). The magnetic moments of the complexes are in the expected range (Table 3), although for the *o*-hydroxyphenolato-complex difficulties in packing gave poor data.

The e.s.r. spectra directly confirm the oxidation state and the symmetry of the new iridium(IV) complexes (Figure 1).

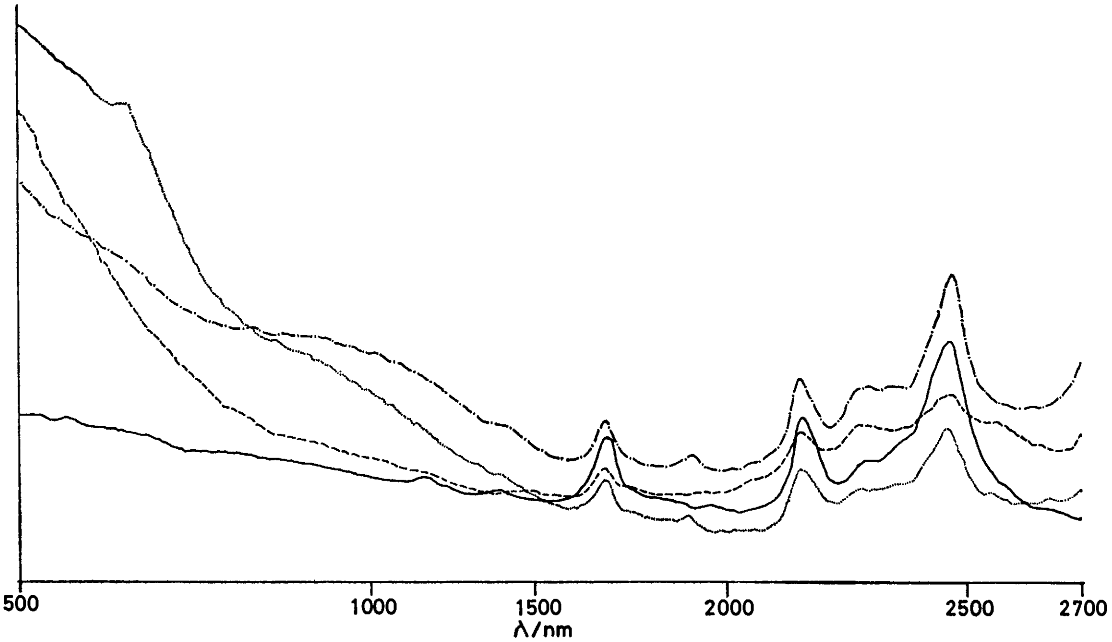


FIGURE 2 Electronic diffuse-reflectance spectra of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ (——), $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$ (· · ·), and $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(salen)]$ (— — —), and $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)\{O_2CCH(O)Me\}_2]$ (— · —)

Resonance lines of the polycrystalline samples are characteristic of low-spin d^5 complexes, with two principal g values attributable to parallel and perpendicular components of the magnetic tensor. This means that all these complexes are axially symmetric, and that the only possible structure has the two chelating ligands in the equatorial plane. Small rhombic distortions would also be expected due to the geometrical properties of the equatorial ligands, but the spectra did not show any resolved axial anisotropy. The spectra can be interpreted in terms of molecular C_{4v} point-group symmetry, and calculations were performed to determine the ground-state electronic configuration and to propose the most probable order of the iridium d orbitals. Perturbations due to spin–orbit coupling and tetragonal distortion have been considered in terms of the hole formalism which regards the t_{2g}^5 configuration as a one-hole configuration.[7]

TABLE 4

Calculated e.s.r. parameters

Complex	$g_\perp$	$g_\parallel$	A	B	k [a]	ΔE_1 [b]	ΔE_2 [b]	η [c]
(5)	1.997	−1.906	0.586 1	0.810 2	0.975 2	1.488 8	1.511 5	−0.034 2
(6)	1.986	−1.940	0.581 8	0.813 3	0.978 2	1.494 3	1.505 8	−0.017 3
(7)	1.996	−1.912	0.585 5	0.810 7	0.976 2	1.489 7	1.510 7	−0.031 7
(8)	1.988	−1.930	0.582 9	0.812 4	0.976 8	1.492 8	1.507 3	−0.021 8
(9)	2.008	−1.940	0.583 9	0.811 8	0.989 1	1.491 7	1.503 8	−0.025 5
(10)	1.991	−1.894	0.586 7	0.809 8	0.969 1	1.488 1	1.512 2	−0.036 3

[a] Stevens constant. [b] ΔE_1 and ΔE_2 are the calculated differences among three energy levels of the electronic system, in units of the spin--orbit coupling constant. [c] The tetragonal-distortion parameter, in units of the spin-orbit coupling constant.

The expression for the Hamiltonian operator is as in (1)

$$H = -\zeta ls + V_T \qquad (1)$$

where ζ is the spin–orbit coupling constant which has a positive value; and V_T is the tetragonal-distortion operator. If the basic set of d orbitals is (2)—(4) and we assume (5), the eigenfunctions of the perturbation matrix are three Kramer's doublets with expressions (6) and (7) where A and B are mixing coefficients between the associated orbitals. For a first-order interaction of the ground Kramer's doublets ϕ' with the magnetic operator we obtain the expressions (8) and (9) for the principal g components. The assignment of the ground-state configuration is related to an unequivocal determination of the mixing coefficients and to an unambiguous assignment of the g components; the value of the Stevens constant k may be obtained from a normalization of the coefficients A and B.

$$it_2(0) = 2^{-\frac{1}{2}}(d_2 - d_{-2}) = t_2'(0) \qquad (2)$$

$$t_2(+1) = d_{+1} \qquad (3)$$

$$t_2(-1) = d_{-1} \qquad (4)$$

$$<t_2(\pm 1)|V_T|t_2(\pm 1)> = -\delta \qquad (5)$$

$$\phi' = At_2'^{\pm}(0) \mp Bt_2^{\mp}(\mp 1) \qquad (6)$$

$$\phi'' = t_2^{\pm}(\mp 1) \qquad (7)$$

$$g_\parallel = 2(A^2 - B^2 - kB^2) \qquad (8)$$

$$g_\perp = 2\,(A^2 + 2^{\frac{1}{2}}kAB) \qquad (9)$$

In the absence of single-crystal analysis, the assignment of the principal g components was carried out on the basis of intensity differences (see Tables 3 and 4). Several combinations are possible depending on the signs of the experimental g values. The choice has been carried out as follows. (*a*) Four different sign combinations of $g_{\parallel}$ and $g_{\perp}$ were considered and four different combinations of the coefficients A and B were obtained, together with an equal number of k values. (*b*) The combinations which poorly reproduced the experimental g values or which gave k values differing greatly from unity were ruled out. In this way only one assignment for each complex can be considered (Table 4). (*c*) Knowledge of the coefficients A and B, which are known functions of the spin–orbit coupling constant (ζ) and of the tetragonal-distortion parameter (δ), allows calculation of δ as a function of ζ ($\eta = \delta/\zeta$ in Table 4); as a consequence, this enables the diagonalization of the spin–orbit coupling and tetragonal perturbation matrix and the determination of the energy levels of our system as a function of ζ (ΔE_1 and ΔE_2 in Table 4). The ground-state single-hole configuration thus obtained is (10) and first and second excited states are (11) and (12) lying at energy

$$\phi_1 = A\ t_2'^{-}(0) + Bt_2^{+}(+1) \qquad (10)$$

$$\phi_2 = At_2^{+}(+1) - Bt_2'^{-}(0) \qquad (11)$$

$$\phi_3 = t_2^{+}(-1) \qquad (12)$$

values ΔE_1 and ΔE_2 from the ground doublet state (see Table 4). The relative magnitude of A and B indicates that the unpaired electron is mainly in the e type d_π orbitals of the metal ion in all the iridium(IV) complexes.

The electronic spectra of the iridium(IV) complexes show broad bands in the 4 000—4 700 and 8 000—12 000 cm^{-1} regions (Figure 2). From their intensities, these bands can be attributed to electronic *d–d* transitions, although for the bands at higher frequencies a mixing with the charge-transfer bands is possible. The other sharp bands belong to vibrationally coupled transitions. The calculated values of ΔE_1 and ΔE_2 suggest that the *d–d* transitions between the combinations of d_π orbitals ($\phi_1 \rightarrow \phi_2$ and $\phi_1 \rightarrow \phi_3$) can be assigned to the bands in the 4 000—4 700 cm^{-1} region, with a ζ value of *ca.* 2 900 cm^{-1}. The bands in the 8 000—12 000 cm^{-1} region can be assigned to transitions from the combinations of d_π orbitals to combinations of d_σ orbitals. The value of the spin–orbit coupling constant which fits the experimental $\phi_1 \rightarrow \phi_2$ and $\phi_1 \rightarrow \phi_3$ transitions suggests that these iridium(IV) complexes have a high percentage of covalent character in their metal–ligand bonds,[7a] which also follows from the values of the Stevens constant (see Table 4). The position and intensity of the *d–d* bands do not vary throughout the series of iridium(IV) complexes.

Conclusions.—The study of reactions of [IrH$_3$(AsPh$_3$)$_2$-(CNC$_6$H$_4$Me-*p*)] enables some conclusions to be made about the stabilization of different oxidation states of iridium. We suggest that the first condition for the stabilization of monomeric iridium(II) complexes is the possibility that the unpaired electron of the metal can be delocalized on the ligands and that electron exchange between the metal and ligands can freely occur. This prevents the localization of the unpaired electron on either the metal or the ligand and the consequent dimerization of the product through the metal or the ligand. In fact such cases of dimerization [8] are frequently found in iridium(II) complexes.

The electronic properties of the equatorial ligands suggest that the electron delocalization on them occurs *via* the π-orbital system; thus by substituting the hydride ligands with chelating π-delocalizing molecules, Ir^{III} can be reduced to Ir^{II}. The most important evidence for the role of the chelating ligand is surely the reactivity of the [IrH$_3$(AsPh$_3$)$_2$-(CNC$_6$H$_4$Me-*p*)] complex with the Schiff bases which are well known π-delocalizing ligands, and should provide the required overlap between the d_π orbitals of the metal and the π system of the ligand. The ground-state electronic configuration of these complexes, as derived from the e.s.r. data, confirms the distribution of the unpaired electron over the $(xz,yz)^3(xy)^2(z^2)^2$ configuration. The destabilization of Ir^{II} in the case of [IrH(Cl)(AsPh$_3$)$_2$(CNC$_6$H$_4$Me-*p*)-(O$_2$CC$_6$H$_4$OMe-*p*)] and [IrH$_2$(AsPh$_3$)$_2$(CNC$_6$H$_4$Me-*p*)(tfpd)] suggests that the possibility of dynamic exchange between metal and ligands is removed by the presence of an electron-attracting group (Cl or F). The presence of a co-ordinated isocyanide molecule seems to be essential for iridium(II) stabilization; any attempt to reduce iridium(III) complexes without an isocyanide group failed, and was also the case when π-delocalizing and chelating systems were used. The considerable back donation to isocyanide (see vibrational data) may be evidence for electron exchange between the metal and this ligand. In general the ν(C–N) frequency of a co-ordinated isocyanide is much higher than that of the free ligand; for all our complexes this stretching vibration is very similar to that of the free ligand and in some cases lies at a lower frequency. Delocalization may take place along the axial direction of the d_π metal orbitals and the π isocyanide system, and be increased by the presence of AsPh$_3$ in a position *trans* to isocyanide.

The general structure proposed for the complexes of Ir^{II} and Ir^{IV}, with the chelating ligands in the equatorial plane, is strongly supported by the reaction of [IrH$_3$-(AsPh$_3$)$_2$(CNC$_6$H$_4$Me-*p*)] with Schiff bases. The singular stability of these complexes confirms that both the geometrical and electronic properties are particularly favourable. The reasons for the electronic stability have been discussed; the geometrical properties of the Schiff bases result in only one possible co-ordination type.

The oxidation state (IV) is rare,[7a] but more common than II in iridium complexes. For Ir^{IV}, the ground-state configuration of the metal, with the unpaired electron in the d_π orbitals, suggests that the possibility of exchanging the unpaired electron in both the equatorial plane and the axial direction stabilizes the electronic distribution in the complexes. The oxidation state IV is so stable here with respect to II that the double deprotonation of phenol compounds or amino-acids occurs. The choice between double and single deprotonation, and thus between Ir^{IV} and Ir^{II}, is generally favourable to Ir^{II} only in the case of *o*-aminobenzoic acid. With this ligand an impure and not readily indentifiable product was obtained, whose e.s.r. spectrum revealed the presence of an iridium(II) complex; the i.r. spectrum shows the co-ordination of the NH$_2$ group (3 300 and 3 140 cm^{-1}, *cf.* 3 450 and 3 340 cm^{-1} for the alkali-metal salt) and of a unidentate carboxylate group (1 550 and 1 400 cm^{-1}, *cf.* 1 530 and 1 390 cm^{-1} for the alkali-metal salt). It is probable that the electronic system of the equatorial *o*-aminobenzoate facilititates sufficient electron exchange to stabilize the Ir^{II} oxidation state. For the other equatorial ligands such exchange is very limited, due to the limited possibilities of delocalization over molecules such as aliphatic amino-acids or hydroxy-acids.

EXPERIMENTAL

Iridium elemental analyses were made with a Varian Techtron atomic-absorption spectrophotometer. Infrared spectra (KBr discs) were recorded on a Perkin-Elmer 621 spectrophotometer, electronic-reflectance spectra on a Beckman DK2A spectrophotometer, and e.s.r. spectra on a Varian 4502 spectrometer. The magnetic measurements were made by the Gouy method at room temperature.

Preparations of Complexes.—[NN′-*Ethylenebis*(*acetylacetoneiminato*)](p-*tolyl isocyanide*)(*triphenylarsine*)*iridium*(II), $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(acacen)]$ (1), *and* NN′-*Ethylenebis*(*salicylideneiminato*)](p-*tolyl isocyanide*)(*triphenylarsine*)-*iridium*(II), $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(salen)]$, (2). A propanol suspension (50 cm^3) of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ [1] (300 mg, 0.32 mmol) was treated with *NN′*-ethylenebis(acetylacetoneimine) (H_2acacen) (100 mg, 0.45 mmol) or *NN′*-ethylenebis(salicylideneimine) (H_2salen) (120 mg, 0.45 mmol) and heated under reflux under nitrogen for 24 h. The resulting solution was then evaporated to dryness and the residue extracted with benzene (10 cm^3). Addition of n-hexane caused the precipitation of the product. The purification of the complexes was attempted by recrystallization from benzene–n-hexane (1 : 10) and by chromatography on alumina, but only complex (2) was obtained as the pure product.

Dihydrido(p-*tolyl isocyanide*)(1,1,1-*trifluoropentane*-2,4-*dionato*)*bis*(*triphenylarsine*)*iridium*(III), $[IrH_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)(tfpd)]$ (3). The complex $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ (300 mg, 0.32 mmol) was dissolved in 1,1,1-trifluoropentane-2,4-dione (Htfpd) (15 cm^3) at room temperature with stirring. A white crystalline complex precipitated from the solution after a few minutes and was filtered off.

Chlorohydrido(p-*methoxybenzoato*) (p-*tolyl isocyanide*)*bis*-(*triphenylarsine*)*iridium*(III), $[IrH(Cl)(AsPh_3)_2(CNC_6H_4Me\text{-}p)(O_2CC_6H_4OMe\text{-}p)]$ (4). A suspension of $[IrH_2Cl(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$[2] (300 mg, 0.30 mmol) in benzene–ethanol (1 : 1) was treated with *p*-methoxybenzoic acid (100 mg, 0.66 mmol) under reflux for 1 h. The resulting solution was then evaporated to dryness and the residue extracted with ethanol (10 cm^3); unchanged parent complex, insoluble in ethanol, was filtered off. The ethanol solution was evaporated to dryness and extracted with benzene; the insoluble unchanged *p*-methoxybenzoic acid was filtered off. Finally, by addition of n-hexane to the benzene solution, the product precipitated. Pale yellow microcrystals of the product were obtained by recrystallization from benzene–n-hexane (1 : 10).

$[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)L_2]$[L = OC_6H_4O-*o* (5), OC_6H_4NH-*o* (6), $O_2CC_6H_4O$-*o* (7), $O_2CC_6H_4NH$-*o* (8), $O_2CCH(O)Me$ (9), *or* $O_2CCH(NH)CH_2Ph$ (10)]. These complexes were obtained in the same way. Typically an ethanol suspension (50 cm^3) of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ (300 mg, 0.32 mmol) was treated with *o*-hydroxyphenol (80 mg, 0.73 mmol), and heated under reflux under nitrogen for 24 h. The resulting solution was evaporated to dryness and the residue extracted with benzene (10 cm^3). The products precipitated by addition of n-hexane. Pure microcrystals of the complexes were obtained by repeated recrystallization from benzene–hexane (1 : 10). During the preparation of complex (8) a small amount of a pale brown paramagnetic compound precipitated from the ethanol solution; it was impossible to purify it, because of the low yield, and only spectroscopic analyses could be carried out.

Analytical data for all the reported complexes are in Table 1. The precision of the analytical method for Ir is $\pm 2\%$ and in some cases the poor agreement with the calculated values is due to the small quantity of the pure complex available. Indeed, it is very important that the elemental analysis could be carried out on the same samples used for spectroscopic and spectromagnetic analysis, owing to the possibility of obtaining other reaction products beside the main product.

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