Paramagnetic Bis(carboxylato)(*p*-tolyl isocyanide)triphenylarsine-iridium(II) complexes: Preparation and Characterisation by Spectroscopic and Magnetic Measurements[1]

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The reaction of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$ with carboxylic acids yields the new paramagnetic iridium(II) complexes $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$ [R = Me, p-ClC_6H_4, p-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$; RCO_2 = pentane-2,4-dionate (pd)]. Their characterisation has been carried out by spectroscopic and magnetic measurements. The structure of the complexes and the ground-state electronic configuration of Ir^{II} therein is discussed.

THE complex $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$, (I), reacts[2] with hydrogen halides and pseudohalides HX (X = Cl, Br, I, or N_3) to yield $[IrH_2(AsPh_3)_2(CNC_6H_4Me\text{-}p)X]$.[3] We now find that when an ethanol suspension of (I) is treated with certain carboxylic acids, *e.g.* with *p*-chlorobenzoic acid, an unexpected reaction takes place: the insoluble well known complex[4] $[IrH_3(AsPh_3)_3]$ precipitates and, from the mother liquor, a new complex can be precipitated on addition of benzene and hexane. For the latter, the elemental analysis is consistent with the formula $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$ (II; R = p-ClC_6H_4). This complex is soluble in benzene, chloroform, and ethanol, and was purified by repeated precipitation from benzene and hexane or by chromatography on alumina. The stoicheiometry (1) is tentatively suggested for the reaction. However, a more complicated pattern could be involved, since the yields of the main products varied significantly with the reaction conditions and moreover secondary compounds were often obtained in small and variable quantities.

$$2[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)] + RCO_2H \longrightarrow [Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2] + [IrH_3(AsPh_3)_3] + CNC_6H_4Me\text{-}p + 2H_2 \quad (1)$$

The new complex does not contain hydride ligands. The i.r. spectrum of the precursor (I) (KBr disc) displayed a band at 2 120 cm^{-1} assigned to the CN stretching mode, and two bands (2 080 and 2 060 cm^{-1}) assigned to the Ir–H stretching modes. In the corresponding spectrum of (II) the latter bands were not observed and the ν(CN) was shifted to 2 135 cm^{-1}. The region where the COO stretching vibrations are expected was rather complicated, since other vibrations due to the ligands $AsPh_3$ and p-MeC_6H_4NC were observed; however, on comparison with the spectra of the free carboxylic acid and alkali carboxylate, it is possible to assign the antisymmetric stretching frequency (ν_{asym}) to the band at 1 540 cm^{-1} and the symmetric stretching frequency (ν_{sym}) to the band at 1 400 cm^{-1}. The COO stretching vibrations of (II) lay much closer to the corresponding vibrations of sodium *p*-chlorobenzoate than to those of the free carboxylic acid; this indicates that the vibrational symmetry of the COO group has not changed on co-ordination and the carboxylate anions act as chelate ligands. The separation $\nu_{sym} - \nu_{asym} = 140$ cm^{-1} is also in agreement with that generally reported for chelated carboxylate anions;[5] this chelation explains why, in order to accommodate the carboxylate ligands, one triphenylarsine molecule of the precursor (I) must be displaced. This bis(carboxylate) complex is a derivative of iridium(II) having a d^7 electronic configuration.

Measurements of the magnetic susceptibility confirmed that the new complex is paramagnetic, with $\mu = 1.67$ B.M. (25 °C).† The e.s.r. spectrum of complex (II), recorded on a powdered sample, confirmed this paramagnetism, both at low and room temperature. The resonance lines (Figure 1) were divided into two signals with different intensities: the signal at low field (g 2.039), which was the weaker, has been assigned to the magnetic tensor component out of the carboxylate anion plane; the other, which was stronger, appeared at higher field (g 2.015) and has been assigned to the in-plane components. The poor resolution of the signals in the solid state, and the lack of paramagnetic behaviour in frozen solution, do not allow resolution of the hyperfine coupling. However, the shape of the spectrum indicates an axial symmetry of the magnetic tensors and shows that the most probable structure for the carboxylate complex is distorted octahedral, with the p-MeC_6H_4NC and $AsPh_3$ ligands in a *trans* position as in (A).

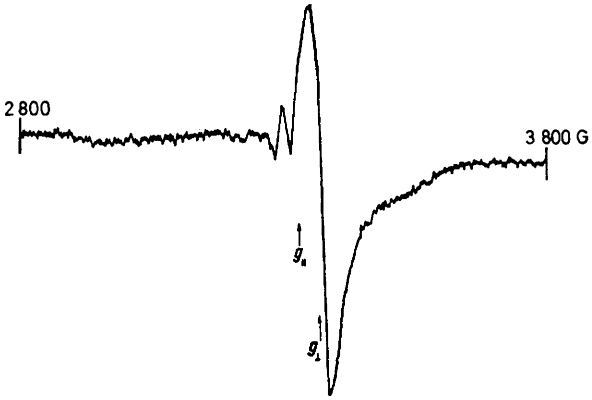

FIGURE 1 E.s.r. spectrum of powdered sample of $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CC_6H_4Cl\text{-}p)_2]$ at −170 °C

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† 1 B.M. ≈ 9.27×10^{-24} A m^2, 1 G = 10^{-4} T, 1M = 1 mol dm^{-3}.

[1] A. Aràneo and T. Napoletano, preliminary communication at 16th Internat. Conf. Co-ordination Chem., Dublin, August 1974.

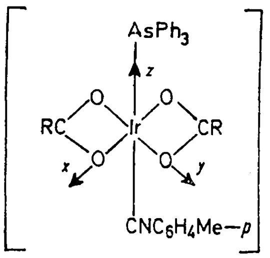
[2] A. Aràneo, F. Bonati, and G. Minghetti, *J. Organometallic Chem.*, 1970, **25**, C25.

[3] A. Aràneo, T. Napoletano, and P. Fantucci, *J. Organometallic Chem.*, 1972, **42**, 471.

[4] F. Canziani, U. Sartorelli, and F. Zingales, *1st Lomb. Sci. Letters*, 1962, **A96**, 513.

[5] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912 and refs. therein.

The values of the magnetic tensor ($g_{\parallel} > g_{\perp} > 2$) suggest that the unpaired electron of the Ir^{II} ion is in the $d_{x^2-y^2}$ orbital, whose energy has been lowered with respect to the d_{z^2} orbital by the tetragonal distortion



(A)

which must be present; however, a considerable contribution to the ground state of the iridium could derive from interaction with the equatorial ligand groups to which a large proportion of the unpaired electron seems to be transferred. The transfer of electronic charge to these ligands also affects the CN bond-stretching vibration. The ν(CN) frequency increases on passing from the precursor (I) to complex (II), although the formal oxidation state II of the iridium causes an increase in the back donation from the metal to the isocyanide. The decrease in iridium–carbon bond order could be attributed to the electron transfer to the carboxylate anions.

Only a few complexes containing iridium(II) are known and all are of a special type, since they are either dimeric and diamagnetic or contain 'suspect' (*i.e.* 'non-innocent') ligands.[6] Examples of the first type are $[IrX_2(CO)_2]$,[7] and $K_2[Ir_2I_6(CO)_4]$ and $[Ph_4As][IrI_3(CO)]$.[8] Dicyclopentadienyliridium(II), the only Ir^{II} complex so far analysed by e.s.r. spectroscopy, is dimeric under ordinary conditions and may be kept as a monomeric complex only under special conditions.[9] The complex $[Ir(NO)(PPh_3)_2Br_3]$ [10] is the only example with a 'suspect' ligand (NO) Complex (II) therefore represents the first well characterised monomeric paramagnetic Ir^{II} species, without any 'suspect' ligand.*

TABLE 1

Analytical, vibrational (cm^{-1}), and magnetic data, for the complexes $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CR)_2]$, (II)

R	M.p. (θ_c/°C)	Analyses [a]/% C	H	N	O	As	Cl	ν_{asym}	ν_{sym}	μ [b]/ B.M.
p-ClC$_6$H$_4$	165	51.3	3.40	1.25	6.40	9.0	6.5	1 540	1 395	1.67
		(51.8)	(3.25)	(1.50)	(6.90)	(8.15)	(7.65)			
Me	140 (decomp.)	49.5	3.70	1.70	7.5			1 550		1.66
		(49.1)	(3.85)	(1.90)	(8.70)					
p-MeOC$_6$H$_4$	155 (decomp.)	53.8	3.90	1.50	9.20			1 535	1 400	1.74
		(54.9)	(3.95)	(1.50)	(10.45)					
2,4,6-Me$_3$C$_6$H$_2$	150 (decomp.)	58.2	4.8	1.10	5.8	7.85		1 535	1 385	1.67
		(58.6)	(4.70)	(1.50)	(6.80)	(7.95)				
pd [c]	110 (decomp.)	52.25	4.30	1.70	7.25					1.65
		(53)	(4.4)	(1.70)	(7.8)					

[a] Calculated values are given in parentheses. [b] At room temperature. [c] RCO_2.

On the basis of previous work [5,11] it is known that carboxylic acids react with trihydride complexes to give only monocarboxylate derivatives by replacing one hydride ligand. In our case, the particular trend of reaction is probably due to the presence of the isocyanide ligand. Therefore the reaction of complex (I) with carboxylic acids can be considered a useful method for obtaining other Ir^{II} species. Accordingly we prepared similar complexes to (II), containing acetate, p-methoxybenzoate, trimethylbenzoate, and pentane-2,4-dionate (pd) anions (Table 1).

The vibrational properties of these complexes show that the carboxylate ligand is always bidentate. For (II; RCO_2 = pd) the observed absorption frequencies at 1 580 and 1 400 [$\nu(C\overset{\cdots}{-}O)$] and 1 520 and 1 310 cm^{-1} [$\nu(C\overset{\cdots}{-}C)$] show that the pd acts as a chelate ligand and co-ordinates to the metal through its oxygen atoms.[12] The magnetic moments do not differ strongly from that of (II; R = p-ClC$_6$H$_4$), while e.s.r. measurements on powdered samples of the complexes revealed significant differences between them. Complex (II; RCO_2 = pd)

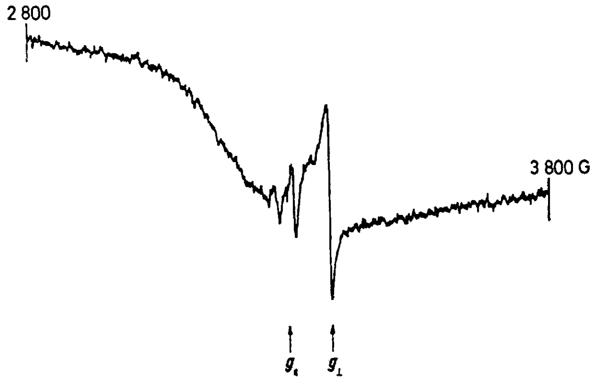


FIGURE 2 E.s.r. spectrum of powdered sample of $[Ir(AsPh_3)(NC_6H_4Me\text{-}p)(pd)_2]$ at −170 °C

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* A paper on paramagnetic Ir^{II} complexes (R. Mason, *J.C.S. Chem. Comm.*, 1974, 612) appeared between our communication[1] and the submission of this paper.

[6] C. K. Joergensen, 'Modern Aspects of Ligand Field Theory,' North-Holland Publishing Company, Amsterdam, 1971, p. 40.

[7] L. Malatesta and F. Canziani, *J. Inorg. Nuclear Chem.*, 1961, **19**, 81.

[8] L. Malatesta, L. Naldini, and F. Cariati, *J. Chem. Soc.*, 1964, 961.

[9] E. O. Fisher and H. Wawersik, *J. Organometallic Chem.*, 1966, **5**, 559; H. J. Keller and H. Wawersik, *ibid.*, 1967, **8**, 185.

[10] M. Angoletta and G. Caglio, *Gazzetta*, 1963, **93**, 1584.

[11] M. Angoletta and A. Arâneo, *Gazzetta*, 1963, **93**, 1343.

[12] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' J. Wiley, 1970, p. 248.

showed well resolved resonances (Figure 2), divided into two signals with different intensities. The signal at lower field was split into four lines due to hyperfine interaction; the signal at higher field was sharp and unresolved. The resonance lines at lower field have been assigned to the out of plane component of the g magnetic tensor and the hyperfine splitting (*ca.* **33** G) arises from coupling with the As nucleus of the $AsPh_3$ ligand. This confirms that $AsPh_3$ lies in an axial position with respect to the pd ligands. In the light of these results a better explanation of the e.s.r. spectrum of (II; $R = p\text{-}ClC_6H_4$) can be given by assigning the lines at lower field to two of the four components of the hyperfine coupling due to the $AsPh_3$ axial ligand. The spectra of complexes (II; $R = p\text{-}MeOC_6H_4$ and 2,4,6-$Me_3C_6H_2$) were quite similar to that with $R = p\text{-}ClC_6H_4$. Complex (II; R = Me) showed an isotropic e.s.r. spectrum (Figure 3), clearly divided into four hyperfine coupling lines due to the interaction with $AsPh_3$. The values of the magnetic parameters of all the Ir^{II} complexes are in Table 2.

TABLE 2

E.s.r. parameters for complexes (II)

				$A_{\parallel}(As)$	$A_{\perp}(As)$	$A_{iso}(As)$
R	$g_{\parallel}$	$g_{\perp}$	g_{iso}		$10^4\ cm^{-1}$	
$p\text{-}ClC_6H_4$, $p\text{-}MeOC_6H_4$, and 2,4,6-$Me_3C_6H_2$	2.039	2.015	2.023 [a]	31.38	12.52 [b]	18.80 [a]
pd [c]	2.06	2.011	2.027 [a]	31.70	4.12 [b]	13.31 [a]
Me			2.038			31.36

[a] Calculated. [b] Estimated. [c] RCO_2.

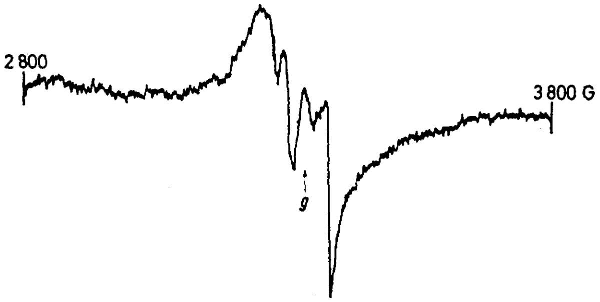

FIGURE 3 E.s.r. spectrum of powdered sample of $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CMe)_2]$ at −170 °C

It is possible that all the Ir^{II} complexes have tetragonally distorted octahedral geometry; the magnitude of the distortion decreases from the pd complex to (II; R = Me), where an isotropic resonance was observed. The tetragonal distortion increases with the ability of the planar ligands to delocalise the electronic charge of the iridium and is at a minimum in (II; R = Me), whose undistorted geometry confirms the monomeric structure of all these complexes in the solid state.

The hyperfine coupling with the ^{75}As nucleus has relatively small values in all these complexes, showing that the unpaired electron is poorly transferred to the axial ligand. The increase in isotropic A value, on decreasing the tetragonal distortion, would be in accordance with the greater spin density on As when the contribution of the electronic configuration of Ir^{II}, $(xz)^2(yz)^2(xy)^2(z^2)$, increases with respect to the ground state $(xz)^2(yz)^2(xy)^2(x^2 - y^2)$. A superhyperfine coupling could arise from the interaction with the iridium nucleus; however, its value is too small to be detectable.

In benzene solution the resonance lines markedly decreased in intensity after a short time, probably due to molecular association. In fact osmometric measurements in benzene solution (1%) showed molecular weights higher than those calculated: 1.5 times the molecular weight (II; R = 2,4,6-$Me_3C_6H_2$); 1.9 for (II; $R = p\text{-}ClC_6H_4$, $p\text{-}MeOC_6H_4$, and RCO_2 = pd); and 2.5 for (II; R = Me). From these data it appears that, on dissolution, the molecular association increases as the steric hindrance of the equatorial ligand decreases. Reprecipitation with hexane again gave the paramagnetic products, whose e.s.r. spectra showed greater resolution.

EXPERIMENTAL

M.p.s were determined in air on a Leitz apparatus. I.r. spectra (KBr discs) were recorded on a Perkin-Elmer 621 spectrophotometer. The magnetic measurements were made by the Gouy method at room temperature. E.s.r. spectra were recorded on a Varian 4502 spectrometer at liquid-nitrogen and room temperature.

Bis(p-*chlorobenzoato*)(p-*tolyl isocyanide*)*triphenylarsineiridium*(II), $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(O_2CC_6H_4Cl\text{-}p)_2]$, (II; $R = p\text{-}ClC_6H_4$).—An ethanol suspension (50 cm^3) of $[IrH_3(AsPh_3)_2(CNC_6H_4Me\text{-}p)]$, (I) (300 mg, 0.32mM), was treated with $p\text{-}ClC_6H_4CO_2H$ (125 mg, 0.8mM) under reflux for 4—5 h. A white precipitate $[IrH_3(AsPh_3)_3]$ sometimes formed and was filtered off (30—60 mg). The resulting brown solution was then evaporated to dryness and the residue extracted with benzene (20 cm^3). Chromatography on alumina (grade II, elution with EtOH) yielded the *product* (60 mg), which was isolated by adding benzene and hexane to the residue from the mixed benzene and ethanol eluates.

The complexes (II; R = Me, $p\text{-}MeOC_6H_4$, and 2,4,6-$Me_3C_6H_2$) were similarly obtained on treating (I) (300 mg) with a 1.5M-ethanol solution of acetic (1 cm^3), p-methoxybenzoic (120 mg, 0.8mM), or 2,4,6-trimethylbenzoic acid (135 mg, 0.8mM), respectively. *Bis*(*pentane*-2,4-*dionato*)(p-*tolyl isocyanide*)*triphenylarsineiridium*(II), $[Ir(AsPh_3)(CNC_6H_4Me\text{-}p)(pd)_2]$, was similarly obtained on heating (I) (300 mg) under reflux in Hpd (25 cm^3) for 25 min.

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