

Comparative Structural Studies of $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(2,2'\text{-bipyridine-4,4'-COOH})]$ and $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{III}}\{2,2'\text{-bipyridine-4,4'-COO}(\text{CH}_2)_3\text{-pyrrole}\}]\text{Cl}|\text{ClO}_4$

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(Received 5 May 1992; accepted 17 November 1992)

Abstract

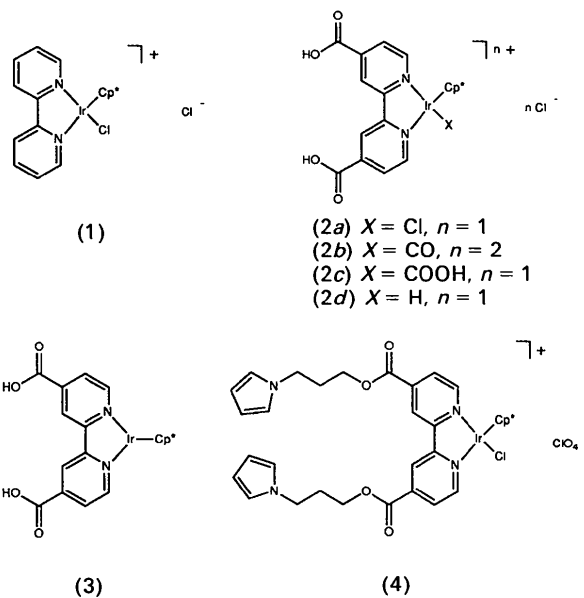
(2,2'-Bipyridine-4,4'-dicarboxylic acid)(η^5 -pentamethylcyclopentadienyl)iridium(I) (3), $[\text{Ir}(\text{C}_{10}\text{H}_{15})(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4)]$, $M_r = 571.64$, monoclinic, $C2/c$ (No. 15), $a = 17.870$ (5), $b = 12.045$ (4), $c = 18.641$ (3) Å, $\beta = 100.66$ (3)°, $V = 3943.1$ Å³, $Z = 8$, $D_x = 1.926$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 67.76$ cm⁻¹, $F(000) = 2224$, room temperature, final $R = 0.043$ for 2733 observed reflections with $I > 5\sigma(I)$. {Bis[3-(1-pyrrolyl)propyl] 2,2'-bipyridine-4,4'-dicarboxylate}chloro(η^5 -pentamethylcyclopentadienyl)iridium(III) perchlorate (4), $[\text{IrCl}(\text{C}_{10}\text{H}_{15})(\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_4)]\text{ClO}_4$, $M_r = 920.86$, monoclinic, $P2_1/c$, $a = 9.870$ (3), $b = 14.908$ (8), $c = 25.931$ (5) Å, $\beta = 96.91$ (2)°, $V = 3788$ (2) Å³, $Z = 4$, $D_x = 1.615$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 37.05$ cm⁻¹, $F(000) = 1840$, room temperature, final $R = 0.069$ for 3173 observed reflections with $I > 3\sigma(I)$. Complex (3) is the first structurally characterized Ir^ICp* species. The Ir atom has a five-coordinate environment with Ir—N(1), Ir—N(2) and Ir—Cp*(centroid) distances of 2.064 (7), 2.068 (6), 1.835 Å, respectively. The bipyridine mean plane makes an angle of ca 75° with the pentamethylcyclopentadienyl (Cp*) mean plane; the deviation from orthogonality may arise from the tendency of the Cp* ring to behave as an η^3 -allyl ene ligand rather

than an η^5 -Me₅C₅ ligand, in accordance with the presence of two long Ir—C(Cp*) distances [2.278 (8) and 2.273 (8) versus 2.149 (9)–2.172 (8) Å for the other Ir—C(Cp*) bond lengths]. Complex (4) has a typical three-legged 'piano stool' structure with Ir—N(1), Ir—N(2), Ir—Cl and Ir—Cp*(centroid) bond distances of 2.12 (1), 2.12 (1), 2.399 (6), 1.801 Å, respectively. In complexes (3) and (4) the Ir—Cp* distances are unusually short due to the strong π -acceptor properties of the bipyridine ligands.

Introduction

The chemistry, physicochemical and structural properties of iridium(III) complexes involving the pentamethylcyclopentadienyl ligand (η^5 -Me₅C₅) and nitrogen-containing ligands such as 2,2'-bipyridine (bpy) have recently been extensively studied (see, for example, Youinou & Ziessel, 1989). Such complexes have been shown to display interesting photochemical properties (Sandrini, Maestri & Ziessel, 1989), and are suitable for photochemical activation of carbon monoxide and water (Ziessel, 1988) or formate (Watson & Ziessel, 1992). In catalysis one of the major challenges is the isolation and structural characterization of the key intermediates involved in the catalytic cycle. In the photochemical water gas

shift reaction (WGS) catalyzed by (2a), one of the possible intermediates is an iridium(III) carboxylate, namely (2c), formed by nucleophilic attack of water on the metal-carbonyl intermediate (2b) (Ziessel, 1991). After decarboxylation, intermediate (2c) gives the photosensitive hydrido complex (2d). Although the formation of an Ir^I intermediate may be postulated in the (2c)→(2d) step such a doubly reduced complex has not been isolated so far in a WGS. We report now the X-ray structure of such an intermediate [complex (3)] which was isolated from an acetonitrile-water mixture (pH 7.0) of (2a) maintained under CO. Complex (3), when dissolved in pure water, is instantly converted to (2d), thus demonstrating that (3) is likely to be an intermediate of the catalytic cycle.



There has also been interest in the development of chemically modified electrodes bearing such catalytically active transition-metal centers linked to a conductive polymer such as polypyrrole. This may notably be achieved with monomeric pyrrole-functionalized bipyridine Ir^{III} units (Cosnier, Deronzier & Moutet, 1988). The X-ray structure of (4), which is such a monomer and hitherto unknown, is reported here and its crystallographic properties compared to the parent complex (3). The influence of the oxidation state of the metal atom on structural data will be discussed.

Experimental

Complex (3)

Orange monocrystals were obtained by slow diffusion at 277 K of carbon monoxide (99.94% purity,

1 atm) into an oxygen-free solution of (2a) (20 mg, 0.03 mmol) in a mixture of CH₃CN (0.5 ml) and 0.1 M aqueous phosphate buffer (pH = 7, 2 ml). This experiment was conducted in a 10 mm sealed glass tube. A single crystal (0.23 × 0.21 × 0.18 mm) was used to collect data at room temperature on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.70926 \text{ \AA}$). Cell parameters were obtained using setting angles from 25 reflections with $14 < 2\theta < 20^\circ$. Data collection details: $\omega/2\theta$ collection mode, scan width = $(1 + 0.35 \tan \theta)^\circ$, variable scan rate with maximum scan time 60 s per reflection, $2\theta = 50^\circ$, collection range, h 0–21, k 0–15, l –22–22; 3671 unique reflections measured, 2733 considered as observed with $I > 5\sigma(I)$. Standards $\bar{1}41$, $\bar{1}3\bar{2}$, 034 measured every hour showed no significant intensity variations. Intensities were corrected for Lorentz-polarization effects. An empirical absorption correction ($T_{\min} = 0.843$, $T_{\max} = 1.316$) (Walker & Stuart, 1983) was applied after isotropic convergence. The crystal structure was solved by direct methods using MULTAN82 (Main *et al.*, 1982) and successive Fourier difference syntheses and refined by full-matrix least squares with anisotropic thermal parameters for all non-H atoms. H-atom positions were calculated with ideal geometry (C–H = 0.95 Å) and included in structure-factor calculation with isotropic thermal parameters of 1.3 times those of the bonded C atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight $w = \{ \frac{1}{4}[\sigma^2(I)/I + (0.08)^2/I] \}^{-1}$ with the resulting $R = 0.043$, $wR = 0.063$ and $S = 1.35$ using 272 refined parameters [$(\Delta/\sigma)_{\max} = 0.08$, residual $|\Delta\rho|_{\max} = 0.74 \text{ e \AA}^{-3}$].

The neutral-atom scattering factors used for all atoms and anomalous-scattering factors for all non-H atoms were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). For all computations the Enraf-Nonius SDP package was used (B. A. Frenz & Associates Inc., 1985).

Complex (4)

Yellow monocrystals (4) were obtained by slow diffusion, at room temperature, of diethyl ether into an acetonitrile solution of (4). A single crystal (0.45 × 0.32 × 0.22 mm) was used to collect data at room temperature in the same conditions as described above. The cell parameters were obtained using 25 reflections ($7 < \theta < 10^\circ$). The data collection ($2\theta_{\max} = 50^\circ$, $\omega/2\theta$ scans, $t_{\max} = 60$ s, range hkl : h 0–11, k 0–14, l –30–30, intensity controls without appreciable decay (0.4%), gave 6923 measured reflections of which 3173 were unique (3750 unobserved reflections), $R_{\text{int}} = 0.029$ with $I > 3\sigma(I)$.

After Lorentz and polarization corrections, the structure was solved with a Patterson map which

revealed the Ir atom. The remaining non-H atoms of the structure were found after successive scale-factor refinements and Fourier differences. After isotropic ($R = 0.11$) refinement, the ClO_4 anion appeared disordered and an absorption correction was made with *DIFABS* (Walker & Stuart, 1983; $T_{\text{min}} = 0.811$, $T_{\text{max}} = 1.364$). The whole structure was refined on F by full-matrix least-squares techniques $\{x, y, z, \beta_{ij}$ for Ir, Cl, N, O and C atoms for the cation and x, y, z and B_{iso} for O atoms of the anion (x, y, z fixed for H atoms); 457 variables and 3173 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with the resulting $R = 0.071$, $wR = 0.069$ and $S = 2.30$ using 457 refined parameters [$(\Delta/\sigma)_{\text{max}} = 0.3$, residual $|\Delta\rho|_{\text{max}} = 0.80 \text{ e } \text{\AA}^{-3}$]. H atoms were introduced with computed coordinates (distances C—H = 0.95 \AA) in structure-factor calculations and were assigned isotropic thermal parameters of $B = 5.0 \text{ \AA}^2$. The somewhat high R value is due to the observed disorder of the ClO_4^- anion. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a Digital MicroVAX 3100 computer with the *MOLEN* package (Enraf-Nonius, 1990).

Discussion

Atomic coordinates and equivalent isotropic temperature factors are given in Tables 1 and 2. Tables 3 and 4† give selected bond lengths and bond angles. Figs. 1 and 2 show the atomic numbering of a single molecular unit of complexes (3) and (4) respectively. The X-ray structure determination of (3) confirms the +1 oxidation state of the metal. Crystals of (3) contain eight equivalent molecules of $[(\eta^5\text{-Me}_5\text{C}_5\text{-Ir}(\text{bpy-4,4'-COOH}))]$ in the unit cell. Each molecule may be described as a basket with a flat bottom (Cp^* ring), the handle being the C(6)—C(5) bond of the 2,2'-bipyridine chelate. The iridium(I) center possesses an unusual five-coordinate geometry. To the best of our knowledge this study constitutes the first X-ray structural determination of a $\text{Cp}^*\text{Ir}^{\text{I}}L_2$ complex. The only other $\text{Cp}^*\text{Ir}^{\text{I}}LL'$ complex known ($L = 2e^-$ donor ligand) is $[\text{Cp}^*\text{Ir}(\text{CO})_2]$ (Kang, Moseley & Maitlis, 1969); however its X-ray structure has not been published so far. In complex (3), the bipyridine unit is bonded in a quasi-symmetric fashion to the metal [Ir—N(1) $2.064(7)$ and Ir—N(2) $2.068(6) \text{ \AA}$]. In contrast with the structure of (3), the Ir^{III} atom of (4) has a six-coordinate environment and displays a

† Lists of structure factors, anisotropic thermal parameters, intraligand bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55747 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0305]

Table 1. Positional parameters and their e.s.d.'s for complex (3)

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	B (\AA^2)
Ir	0.62837 (2)	0.15324 (2)	0.09936 (2)	1.714 (7)
O(1)	0.8486 (4)	-0.0715 (6)	-0.1354 (4)	3.9 (2)
O(2)	0.8747 (6)	-0.2008 (9)	-0.0522 (6)	11.6 (2)
O(3)	0.6232 (5)	0.3194 (6)	-0.2604 (4)	3.7 (2)
O(4)	0.5962 (7)	0.4777 (8)	-0.2156 (5)	9.7 (3)
N(1)	0.6143 (4)	0.2272 (6)	-0.0021 (4)	1.8 (1)
N(2)	0.6952 (4)	0.0565 (6)	0.0446 (4)	1.8 (1)
C(1)	0.7355 (5)	-0.0363 (8)	0.0719 (5)	2.9 (2)
C(2)	0.7802 (6)	-0.0909 (9)	0.0342 (5)	3.1 (2)
C(3)	0.7924 (5)	-0.0539 (8)	-0.0318 (5)	2.5 (2)
C(4)	0.7545 (4)	0.0418 (7)	-0.0595 (4)	1.7 (2)
C(5)	0.7042 (4)	0.0920 (7)	-0.0217 (4)	1.5 (1)
C(6)	0.6570 (5)	0.1882 (7)	-0.0493 (5)	1.7 (2)
C(7)	0.6541 (5)	0.2333 (6)	-0.1174 (5)	1.8 (2)
C(8)	0.6076 (5)	0.3230 (7)	-0.1393 (5)	2.1 (2)
C(9)	0.5637 (6)	0.3635 (7)	-0.0902 (6)	2.8 (2)
C(10)	0.5685 (5)	0.3131 (8)	-0.0232 (5)	2.8 (2)
C(11)	0.8438 (6)	-0.1160 (9)	-0.0767 (6)	3.1 (2)
C(12)	0.6076 (5)	0.3816 (8)	-0.2100 (6)	2.7 (2)
C(13)	0.5551 (5)	0.0325 (8)	0.1496 (5)	2.5 (2)
C(14)	0.6190 (5)	0.0763 (8)	0.2016 (5)	2.4 (2)
C(15)	0.6107 (5)	0.1927 (8)	0.2071 (5)	2.6 (2)
C(16)	0.5456 (5)	0.2259 (7)	0.1575 (5)	1.8 (2)
C(17)	0.5088 (5)	0.1251 (8)	0.1219 (5)	2.3 (2)
C(18)	0.5379 (7)	-0.0861 (9)	0.1327 (8)	4.6 (3)
C(19)	0.6769 (6)	0.004 (1)	0.2506 (6)	3.7 (2)
C(20)	0.6646 (7)	0.265 (1)	0.2608 (6)	4.3 (3)
C(21)	0.5126 (6)	0.3394 (8)	0.1476 (6)	3.3 (2)
C(22)	0.4349 (6)	0.123 (1)	0.0709 (7)	3.7 (2)

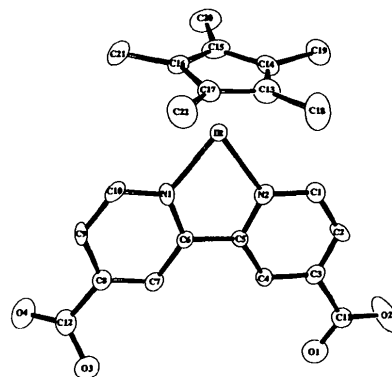


Fig. 1. Molecular configuration and labeling scheme for $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(2,2'\text{-bipyridine-4,4'-COOH})]$ (3). The ellipsoids are scaled to represent the 50% probability surface. H atoms are omitted for clarity.

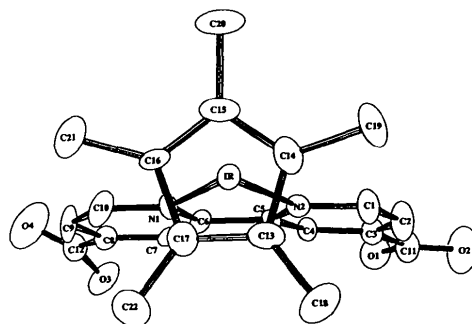


Fig. 2. Molecular configuration and labeling scheme for $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir}^{\text{I}}(2,2'\text{-bipyridine-4,4'-COOH})]$ (3) viewed through the Cp^* (centroid) and the Ir-atom axis.

Table 2. Positional parameters and their e.s.d.'s for complex (4)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\alpha)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	B (Å ²)
Ir	0.35041 (7)	0.28286 (6)	0.76889 (3)	3.09 (1)
Cl(1)	0.4199 (6)	0.4370 (4)	0.7683 (2)	6.0 (2)
O(1)	-0.261 (1)	0.428 (1)	0.6263 (5)	5.6 (4)
O(2)	-0.150 (1)	0.399 (1)	0.5584 (4)	4.7 (3)
O(3)	-0.093 (1)	0.4457 (9)	0.9423 (4)	3.7 (3)
O(4)	-0.210 (1)	0.483 (1)	0.8663 (4)	4.5 (3)
N(1)	0.198 (1)	0.330 (1)	0.8132 (5)	3.2 (3)
N(2)	0.190 (1)	0.3212 (9)	0.7114 (5)	2.5 (3)
N(3)	-0.131 (2)	0.423 (1)	0.3950 (6)	5.5 (5)
N(4)	-0.227 (2)	0.368 (1)	1.0581 (7)	7.1 (6)
C(1)	0.191 (2)	0.316 (1)	0.6600 (6)	3.4 (5)
C(2)	0.082 (2)	0.343 (1)	0.6258 (6)	3.2 (4)
C(3)	-0.030 (2)	0.376 (1)	0.6435 (6)	2.8 (4)
C(4)	-0.035 (1)	0.385 (1)	0.6961 (6)	2.0 (4)
C(5)	0.075 (2)	0.355 (1)	0.7296 (6)	2.9 (4)
C(6)	0.080 (2)	0.360 (1)	0.7857 (5)	2.2 (4)
C(7)	-0.020 (1)	0.401 (1)	0.8114 (6)	2.8 (4)
C(8)	-0.001 (2)	0.403 (1)	0.8654 (6)	3.0 (4)
C(9)	0.116 (2)	0.370 (1)	0.8924 (6)	3.6 (5)
C(10)	0.214 (2)	0.335 (1)	0.8651 (6)	4.0 (5)
C(11)	-0.159 (2)	0.405 (1)	0.6087 (7)	4.4 (5)
C(12)	-0.272 (2)	0.424 (2)	0.5240 (7)	6.5 (7)
C(13)	-0.248 (2)	0.402 (2)	0.4706 (9)	8.6 (8)
C(14)	-0.144 (2)	0.448 (2)	0.4478 (9)	7.6 (7)
C(15)	-0.214 (2)	0.447 (2)	0.3511 (7)	5.1 (6)
C(16)	-0.166 (2)	0.412 (2)	0.3089 (7)	5.3 (6)
C(17)	-0.048 (2)	0.367 (2)	0.3264 (9)	6.9 (7)
C(18)	-0.031 (2)	0.371 (2)	0.3799 (8)	6.1 (6)
C(19)	-0.115 (2)	0.450 (1)	0.8915 (7)	3.7 (5)
C(20)	-0.187 (2)	0.496 (1)	0.9693 (6)	4.2 (5)
C(21)	-0.313 (2)	0.444 (2)	0.9756 (8)	6.4 (6)
C(22)	-0.286 (2)	0.356 (2)	1.005 (1)	9.2 (7)
C(23)	-0.083 (3)	0.371 (2)	1.127 (1)	8.8 (8)
C(24)	-0.208 (3)	0.399 (2)	1.1410 (9)	9.8 (8)
C(25)	-0.294 (2)	0.399 (2)	1.0971 (8)	9.4 (8)
C(26)	-0.096 (2)	0.346 (2)	1.076 (1)	8.9 (8)
C(27)	0.548 (2)	0.235 (1)	0.7538 (7)	5.1 (5)
C(28)	0.538 (2)	0.234 (1)	0.8103 (6)	3.6 (5)
C(29)	0.433 (2)	0.172 (1)	0.8177 (6)	3.4 (4)
C(30)	0.373 (1)	0.138 (1)	0.7694 (7)	3.8 (4)
C(31)	0.448 (1)	0.177 (1)	0.7286 (6)	2.7 (4)
C(32)	0.661 (2)	0.285 (2)	0.7332 (8)	6.1 (5)
C(33)	0.628 (2)	0.279 (2)	0.8531 (9)	7.1 (6)
C(34)	0.389 (2)	0.141 (2)	0.8690 (7)	5.4 (6)
C(35)	0.260 (2)	0.064 (2)	0.7561 (8)	5.7 (6)
C(36)	0.433 (2)	0.153 (1)	0.6734 (7)	5.0 (5)
Cl(2)	0.3103 (6)	0.2656 (5)	0.5118 (2)	6.5 (2)
O(1A)	0.349 (3)	0.177 (2)	0.483 (1)	7.7 (8)*
O(2A)	0.264 (4)	0.215 (3)	0.552 (1)	10 (1)*
O(3A)	0.353 (3)	0.250 (2)	0.563 (1)	9 (1)*
O(4A)	0.382 (4)	0.331 (3)	0.493 (2)	12 (1)*
O(5A)	0.208 (4)	0.314 (3)	0.483 (1)	10 (1)*
O(6A)	0.372 (3)	0.227 (2)	0.476 (1)	8.0 (9)*
O(7A)	0.367 (5)	0.345 (4)	0.546 (2)	17 (2)*
O(8A)	0.166 (3)	0.255 (2)	0.504 (1)	9 (1)*

* Anisotropic parameters.

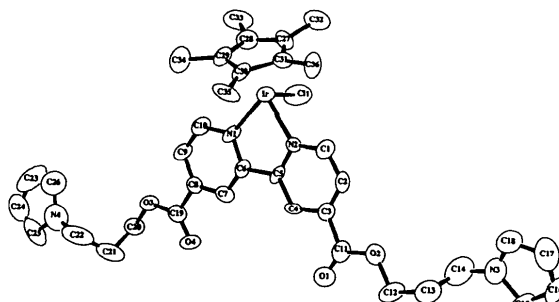
Table 4. Selected bond lengths (Å) and angles (°) for complex (4)

Ir—Cl(1)	2.399 (6)	C(6)—C(5)	1.45 (2)
Ir—N(1)	2.12 (1)	C(8)—C(19)	1.54 (2)
Ir—N(2)	2.12 (1)	C(3)—C(11)	1.53 (2)
Ir—C(27)	2.15 (2)	C(19)—O(4)	1.19 (2)
Ir—C(28)	2.16 (2)	C(11)—O(1)	1.20 (2)
Ir—C(29)	2.18 (2)	C(19)—O(3)	1.31 (2)
Ir—C(30)	2.18 (2)	C(11)—O(2)	1.32 (2)
Ir—C(31)	2.18 (2)	C(20)—O(3)	1.43 (2)
N(1)—C(6)	1.37 (2)	C(22)—N(4)	1.45 (3)
N(1)—C(10)	1.34 (2)	C(12)—O(2)	1.46 (2)
N(2)—C(1)	1.34 (2)	C(14)—N(3)	1.44 (3)
N(2)—C(5)	1.38 (2)	C(27)—C(28)	1.48 (2)
		C(28)—C(29)	1.42 (3)
		C(29)—C(30)	1.42 (2)
		C(30)—C(31)	1.48 (2)
		C(31)—C(27)	1.42 (2)
Cl(1)—Ir—N(1)	84.8 (4)	C(19)—O(3)—C(20)	115 (1)
Cl(1)—Ir—N(2)	85.8 (4)	C(11)—O(2)—C(12)	116 (1)
N(1)—Ir—N(2)	77.0 (5)	C(22)—N(4)—C(26)	124 (2)
Ir—N(1)—C(10)	124 (1)	C(22)—N(4)—C(25)	125 (2)
Ir—N(2)—C(1)	126 (1)	C(14)—N(3)—C(18)	126 (2)
Ir—N(1)—C(6)	116 (1)	C(14)—N(3)—C(15)	127 (2)
Ir—N(2)—C(5)	115.8 (9)	O(1)—C(11)—O(2)	124 (2)
C(8)—C(19)—O(4)	121 (1)	O(4)—C(19)—O(3)	127 (2)
C(3)—C(11)—O(1)	122 (2)		

typical three-legged 'piano-stool' arrangement (Isobe, Bailey & Maitlis, 1981), with opening angles of Cl(1)—Ir—N(1) = 85.4 (2), Cl(1)—Ir—N(2) = 85.8 (4) and N(1)—Ir—N(2) = 77.0 (5)°; these values are not unusual when compared to the values previously found in the related unsubstituted 2,2'-bipyridine complex (1) (Youinou & Ziesel, 1989). The ClO₄⁻ counter anion is remote from the cation and is disordered over two positions. The Ir—N distances in complex (4) are of comparable length [Ir—N(1) = 2.12 (1) and Ir—N(2) = 2.12 (1) Å]. It is noteworthy that these distances are significantly longer than those found in complex (1) [2.076 (8) and 2.090 (9) Å], owing to the electron-withdrawing effect of the two ester substituents. Interestingly, the Ir—N bond distances of this latter Ir^{III} complex are close to the values found in (3). This may indicate that the higher electron density of the Ir^I center in (3) is somewhat discharged towards the functional substituents of the bipyridine chelate. In both com-

Table 3. Selected bond lengths (Å) and angles (°) for complex (3)

Ir—N(1)	2.064 (7)	C(6)—C(5)	1.47 (1)
Ir—N(2)	2.068 (6)	C(8)—C(12)	1.49 (1)
Ir—C(13)	2.273 (8)	C(3)—C(11)	1.55 (1)
Ir—C(14)	2.154 (9)	C(12)—O(4)	1.18 (1)
Ir—C(15)	2.142 (9)	C(12)—O(3)	1.27 (1)
Ir—C(16)	2.172 (8)	C(11)—O(1)	1.24 (1)
Ir—C(17)	2.278 (8)	C(11)—O(2)	1.21 (1)
N(1)—C(10)	1.33 (1)	C(13)—C(14)	1.45 (1)
N(1)—C(6)	1.35 (1)	C(14)—C(15)	1.42 (1)
N(2)—C(1)	1.38 (1)	C(15)—C(16)	1.40 (1)
N(2)—C(5)	1.34 (1)	C(16)—C(17)	1.48 (1)
		C(17)—C(13)	1.43 (1)
N(1)—Ir—N(2)	76.9 (3)	C(3)—C(11)—O(2)	118.6 (9)
Ir—N(1)—C(6)	117.3 (5)	C(8)—C(12)—O(4)	121 (1)
Ir—N(1)—C(10)	124.7 (6)	O(4)—C(12)—O(3)	125 (1)
Ir—N(2)—C(5)	117.0 (5)	O(1)—C(11)—O(2)	126.8 (9)
Ir—N(2)—C(1)	125.9 (6)		

Fig. 3. Molecular configuration and labeling scheme for [(η⁵-Me₅C₅)Ir^{III}{2,2'-bipyridine-4,4'-COO(CH₂)₃-pyrrole}Cl]ClO₄ (4). The ellipsoids are scaled to represent the 50% probability surface. H atoms are omitted for clarity.

plexes, (3) and (4), an angle of $4(1)^\circ$ between the planes defined by the two pyridine rings illustrates the slight distortion within the bipyridine ligand, a situation already observed for complex (1) where the corresponding angle is $9(1)^\circ$. The Ir—C(Cp*) bond lengths in both complexes [(3) mean = 1.835 and (4) mean = 1.801 Å], are relatively short compared to those found in Ir—Cp*—phosphine complexes in which this distance is usually close to 2.2 Å (Buchanan, Stryker & Bergman, 1986). This shortening seems to be a general trend in complexes containing aromatic polyimine chelates (see, for example, Youinou & Ziesel, 1989; Ziesel, Youinou, Balegrone & Grandjean, 1992) and may be ascribed to the strong π -acceptor character of such ligands. In complex (3), two Ir—C(Cp*) bond lengths appear to be significantly longer than the other three. This may be indicative of a η^3 -allyl-ene bonding mode of the Cp* ligand, a situation which has previously been found in [Cp*Rh(CO)₂] (Lichtenberger, Blewins & Ortega, 1984). This lack of symmetry is also consistent with the observation that the bipyridine plane slightly deviates [$14.5(3)^\circ$] from orthogonality with respect to the Cp* mean plane (see Fig. 3), leading to a flattened basket-shaped molecule. However, this effect could arise from packing forces. For complex (3), the O(4)—C(12)—C(8)—C(9) and the O(2)—C(11)—C(3)—C(2) dihedral angles of $1.9(3)$ and $29.9(3)^\circ$, respectively, indicate a high degree of conjugation of each carbonyl function with the aromatic ring to which it is connected. A similar observation is made for the ester groups in complex (4) [O(1)—C(11)—C(3)—C(4) = $4.4(5)$ and O(4)—C(19)—C(8)—C(7) = $4.1(5)^\circ$].

In conclusion, this study constitutes the first structural characterization of an Ir^I—Cp* complex. It furthermore confirms the nature of a possible intermediate in the photochemical water gas shift reaction. The structural data obtained for (3) and (4) unambiguously demonstrate, by comparison with known Ir—Cp* phosphine complexes, that strong

π -acceptor bipyridine ligands induce a shortening of the Ir—Cp* distances. Complex (4) is the first example of a monomeric species containing pyrrole subunits. Further studies will be centered on its use as a synthon for the preparation of conductive polymeric films.

D. Biltz is warmly thanked for help with the preparation of the manuscript. Financial support from the Centre National de la Recherche Scientifique is gratefully acknowledged.

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