metal-organic papers
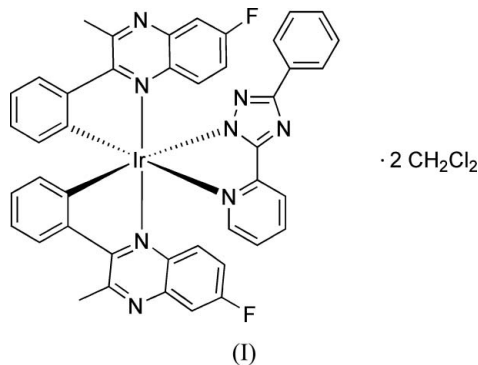
mer-Bis[2-(6-fluoro-3-methylquinoxalin-2-yl-κN^1)-phenyl][3-phenyl-5-(2-pyridyl-κN)-1,2,4-triazol-1-yl]-iridium(III) dichloromethane disolvate

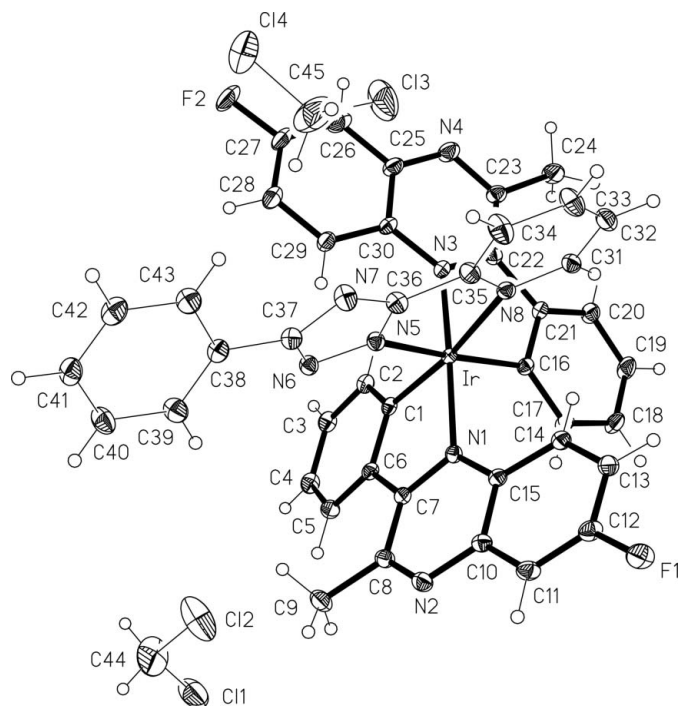Peter G. Jones,[a]* Sven Ammermann,[b] Constantin Daniliuc,[a] Wolf-Walther du Mont,[a] Wolfgang Kowalsky[b] and Hans-Hermann Johannes[b]

[a]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and [b]Institut für Hochfrequenztechnik, Labor für Elektrooptik, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

The title compound, [Ir(C$_{15}$H$_{10}$FN$_2$)$_2$(C$_{13}$H$_9$N$_4$)]·2CH$_2$Cl$_2$ or C$_{43}$H$_{29}$F$_2$IrN$_8$·2CH$_2$Cl$_2$, shows the appreciable *trans* influence of the C donors; the Ir—N bond lengths *trans* to C are 2.129 (2) and 2.210 (2) Å, *cf.* the Ir—N distances *trans* to N, of 2.055 (2) and 2.070 (2) Å. The three chelating ligands are approximately perpendicular to each other.

Comment

Cyclometalated octahedral complexes with $4d^6$ and $5d^6$ metal centres such as ruthenium(II), osmium(II) and iridium(III) have been studied extensively because of their potential applications, *e.g.* as photoreductants (King *et al.*, 1985), oxygen-sensing materials (DeRosa *et al.*, 2004), biological labelling reagents (Lo *et al.*, 2003) and, most importantly, as efficient phosphorescent emitters in organic light-emitting diodes (OLEDs) (Lamansky *et al.*, 2001; Thomas *et al.*, 2005; Tamayo *et al.*, 2003). We report here the structure of the title complex, (I), a heteroleptic metal complex with an octahedral iridium(III) centre, of a type known to be useful in OLEDs. Complex (I) belongs to a group of compounds with appreciable excited state lifetimes. The strong spin-orbit coupling assumed for iridium largely removes the spin-forbidden nature of the phosphorescent transitions and leads to a strong phosphorescence (Lamansky *et al.*, 2001). Compared with singlet emitters such as fluorenes, these triplet emitters can harvest up to 100% internal quantum efficiency by the intersystem crossing of singlet states with triplet states (Tsuboyama *et al.*, 2003). Selecting different chelate ligands for the metal complexes with sufficiently large ligand-centred $\pi\pi^*$ transition energies and/or metal-to-ligand charge transfer (MLCT) energies allows properties such as the colour of the emission to be defined (Yang *et al.*, 2005).

(I)

The molecular structure of (1) is shown in Fig. 1. The coordination geometry is octahedral and the N-donor atoms

Figure 1
The title compound in the crystal structure. Displacement ellipsoids represent 30% probability levels. Bonds of the triazolpyridine ligand are drawn as thin lines. Only the major site is shown for the two solvent molecules.

define a meridional geometry. The bond lengths at iridium (Table 1) clearly show the greater *trans* influence of the C donors: Ir—N *trans* to C, 2.129 (2) and 2.210 (2) Å (the shorter bond is to the formally deprotonated N atom), *cf.* Ir—N *trans* to N, 2.055 (2) and 2.070 (2) Å.

The chelate rings are planar and orthogonal to a reasonable approximation; the r.m.s. deviations are 0.09, 0.06 and 0.01 Å for the rings involving Ir/N1/C1, Ir/N3/C16 and Ir/N5/N8, respectively, and the angles between rings 1/3 and 2/3 in the same order are 73.3 (1) and 80.2 (1)°. Within the quinoxaline ligands, the phenyl rings subtend interplanar angles of 16.4 (1) and 19.8 (1)° with the quinoxaline ring systems based on N1 and N3, respectively. Within the triazolpyridine ligand, the phenyl ring subtends an angle of 22.5 (1)° with the triazolpyridine plane.

Experimental

2-(5-Phenyl-4*H*-1,2,4-triazol-3-yl)pyridine was prepared as described by Case (1965, 1970); 6-fluoro-3-methyl-2-phenylquinoxaline was obtained from commercially available 4-fluorobenzene-1,2-diamine and 1-phenylpropane-1,2-dione according to More *et al.* (2005). The preparation of the bridged dinuclear complex tetrakis[2-(6-fluoro-3-methylquinoxalin-2-yl-κN^1)phenyl]bis(μ-chloro)diiridium(III) was based on a procedure by Nonoyama (1974).

The bridged dinuclear starting complex (250 mg, 178 µmol) and 2-(5-phenyl-4*H*-1,2,4-triazol-3-yl)pyridine (99 mg, 445 µmol) were added to 6.6 ml of dry dichloromethane and 2 ml of dry ethanol in a nitrogen-flushed Schlenk flask. The dark-red solution was stirred for

10 min at room temperature, and then potassium-*t*-butylate (50 mg, 445 µmol) was added in one portion. The solution was stirred for another 50 h at room temperature and then quenched with 60 ml of *n*-hexane. A red solid precipitated and was filtered off. The product was washed with water and *n*-hexane, dried under vacuum and then purified by flash chromatography [SiO$_2$, *n*-hexane/ethyl acetate 1:1 → dichloromethane/acetone 8:1, R_f (dichloromethane/acetone 8:1) = 0.52], yielding the red title material in 74% yield. Crystals were grown from dichloromethane/*n*-hexane (1:1).

Crystal data

[Ir(C$_{15}$H$_{10}$FN$_2$)$_2$(C$_{13}$H$_9$N$_4$)]·2CH$_2$Cl$_2$	$V = 4105.7$ (5) Å^3
$M_r = 1057.79$	$Z = 4$
Monoclinic, $P2_1/c$	$D_x = 1.711$ Mg m^{-3}
$a = 19.1184$ (14) Å	Mo $K\alpha$ radiation
$b = 12.5390$ (8) Å	$\mu = 3.57$ mm^{-1}
$c = 18.2869$ (12) Å	$T = 133$ (2) K
$\beta = 110.521$ (4)°	Prism, red
	$0.24 \times 0.18 \times 0.17$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	85935 measured reflections
φ and ω scans	12496 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	10326 reflections with $I > 2\sigma(I)$
$T_{min} = 0.523$, $T_{max} = 0.582$ (expected range = 0.489–0.545)	$R_{int} = 0.035$
	$\theta_{max} = 30.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 7.1619P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.07$	$\Delta\rho_{max} = 1.29$ e Å^{-3}
12496 reflections	$\Delta\rho_{min} = -1.18$ e Å^{-3}
566 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ir—C1	1.988 (3)	Ir—N1	2.070 (2)
Ir—C16	1.993 (3)	Ir—N5	2.129 (2)
Ir—N3	2.055 (2)	Ir—N8	2.210 (2)
C1—Ir—C16	91.61 (10)	N3—Ir—N5	103.42 (9)
C1—Ir—N3	93.98 (10)	N1—Ir—N5	80.73 (9)
C16—Ir—N3	79.20 (10)	C1—Ir—N8	171.73 (9)
C1—Ir—N1	79.30 (10)	C16—Ir—N8	96.12 (9)
C16—Ir—N1	97.71 (10)	N3—Ir—N8	84.62 (9)
N3—Ir—N1	172.59 (8)	N1—Ir—N8	102.48 (9)
C1—Ir—N5	97.31 (9)	N5—Ir—N8	75.16 (9)
C16—Ir—N5	170.46 (9)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···F2^i	0.95	2.53	3.225 (4)	130
C44—H44B···N7^{ii}	0.99	2.61	3.510 (5)	151
C45—H45B···N7	0.99	2.70	3.437 (10)	131

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Methyl H atoms were identified in difference syntheses, idealized and then refined using a rigid methyl group (C—H = 0.98 Å, H—C—H = 109.5°) allowed to rotate but not tip. Other H atoms were included using a riding model with C—H = 0.95 (aromatic) or 0.99 Å (sp^3 CH$_2$). All U_{iso}(H) values were fixed at $1.2U_{eq}$(C) of the parent C atom. The dichloromethane molecules are both disordered over two sites. The minor occupied atoms were refined isotropically. Similarity restraints were used to improve stability of refinement, but the dimensions and U values of the less-occupied sites are less than satisfactory. The site occupancy factors for the two solvent molecules refined to 0.686 (5):0.314 (5) and 0.647 (6):0.353 (6). It is probable that the disorder is more complex (*e.g.* overlap of partially occupied dichloromethane and hexane sites), but no suitable model could be refined successfully. The highest residual density peakis 0.26 Å from Cl3′ and the depest hole is 0.51 Å from Cl4′.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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