

**TETRAFLUOROBENZOBARRELENEIRIDIUM COMPLEXES WITH 1,10-PHENANTHROLINE, 2,2'-BIPYRIDINE AND DIKETONATE LIGANDS. CRYSTAL STRUCTURE OF  $[\text{IrI}_2(\text{TFB})(\text{phen})]\text{ClO}_4 \cdot (\text{CH}_3)_2\text{CO}$  (TFB = 5,6,7,8-TETRAFLUORO-1,4-DIHYDRO-1,4-ETHENONAPHTHALENE, phen = 1,10-PHENANTHROLINE)**

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### Summary

The preparations of some new  $\beta$ -diketonate iridium(I) complexes of formula  $[\text{Ir}(\beta\text{-diketonate})(\text{diolefin})]$  and  $[\text{Ir}(\beta\text{-diketonate}-\text{C}^3)(\text{diolefin})(\text{L-L})]$  ( $\beta$ -diketone = acetyl acetone (Hacac), 1-phenyl, butane-1,3-dione (HBzac), 1,3-diphenyl, propane-1,3-dione (HBz<sub>2</sub>ac); diolefin = tetrafluorobenzobarrelene (TFB), trimethyltetrafluorobenzobarrelene (Me<sub>3</sub>TFB); L-L = 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) (not all possible combinations)) are reported. The neutral complexes  $[\text{IrI}(\text{TFB})_2]$  and  $[\text{IrI}(\text{TFB})(\text{phen})]$  were prepared by metathetical reactions from the corresponding chlorides. The oxidative addition of iodine to  $[\text{Ir}(\text{acac}-\text{C}^3)(\text{TFB})(\text{phen})]$  or  $[\text{Ir}(\text{TFB})(\text{phen})][\text{ClO}_4]$  results in formation of the *trans* or *cis* isomers of the iridium(III) cation  $[\text{IrI}_2(\text{TFB})(\text{phen})]^+$ , respectively. The *trans* isomer has been structurally characterized by X-ray diffraction methods; the lattice constants of the monoclinic  $P2_1/n$  cell are  $a$  12.6841(4),  $b$  17.7550(7),  $c$  13.8500(4) Å with  $\beta$  108.874(2)°. The  $R$  factor was 0.058 for 3552 observed reflections. The octahedral coordination of the metal is distorted as to make an I–Ir–I angle of 160.43(4)°.

### Introduction

Recent work in our laboratory has revealed the capacity of the diolefin tetrafluorobenzobarrelene (TFB: 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) to stabilize pentacoordinated iridium(I) complexes [1,2]. For this reason the Ir(TFB) moiety is a candidate for the preparation of iridium carbon-bonded diketonate

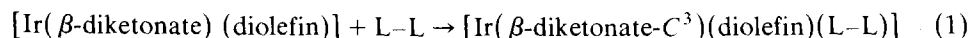
complexes and other related pentacoordinated compounds. On the other hand, although many  $\beta$ -diketonate transition metal complexes showing different coordination modes of the diketonate ligands have been reported [3–6], only very recently has the synthesis and structural characterization of an iridium(I)-carbon-bonded diketonate complex of formula  $[\text{Ir}(\text{acac}-\text{C}^3)(\text{COD})(\text{phen})]$  (acac = acetylacetonate, COD = 1,5-cyclooctadiene, phen = 1,10-phenanthroline) been achieved [7]. We now describe a family of related pentacoordinated iridium(I) complexes, as well as some iridium(III) derivatives, and the X-ray structural determination of *trans*- $[\text{Ir}_2(\text{TFB})(\text{phen})]\text{ClO}_4$ .

## Results and discussion

### Diketonate complexes

The reaction of  $[\text{IrCl}(\text{TFB})_2]$  [8] or  $[\text{IrCl}(\text{Me}_3\text{TFB})_2]$  ( $\text{Me}_3\text{TFB}$  = trimethyltetrafluorobenzobarrelene: 1,3-dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-[9-methyletheno]-naphthalene) [2] with  $\beta$ -diketones (1-phenyl, butane-1,3-dione (HBzac); 1,3-diphenyl, propane-1,3-dione ( $\text{HBz}_2\text{ac}$ )) in basic medium gives complexes of formula  $[\text{Ir}(\beta\text{-diketonate})(\text{diolefin})]$  (diolefin = TFB;  $\beta$ -diketonate = Bzac (I),  $\text{Bz}_2\text{ac}$  (II). Diolefin =  $\text{Me}_3\text{TFB}$ ;  $\beta$ -diketonate = Bzac (III),  $\text{Bz}_2\text{ac}$  (IV)). These complexes show IR bands characteristic of O-bonded diketonate compounds [9].

These complexes, like the related complexes  $[\text{Ir}(\text{acac})(\text{diolefin})]$  (diolefin = TFB [10],  $\text{Me}_3\text{TFB}$  [2]), react with 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy), to give pentacoordinated iridium carbon-bonded diketonate complexes (eq. 1):



diolefin	$\beta$ -diketonate	L-L	Complex nr.
TFB	acac	phen	V
TFB	acac	bipy	VI
TFB	Bzac	phen	VII
TFB	Bzac	bipy	VIII
TFB	$\text{Bz}_2\text{ac}$	phen	IX
TFB	$\text{Bz}_2\text{ac}$	bipy	X
$\text{Me}_3\text{TFB}$	acac	phen	XI

We used this route previously for the synthesis of the related  $[\text{Ir}(\text{acac}-\text{C}^3)(\text{COD})(\text{phen})]$ . All these iridium- $\text{C}^3$ -bonded diketonate complexes show  $\nu(\text{CO})$  in the range 1645–1550  $\text{cm}^{-1}$  [7]. In dichloromethane solution complexes V–IX have a permanent blue colour, and no significant changes take place in their IR spectra in the 1700–1500 region. However, dichloromethane solutions of complexes X and XI became yellow due to the dissociation of the *N*-donor ligand and regeneration of the original compounds  $[\text{Ir}(\text{Bz}_2\text{ac})(\text{TFB})]$  and  $[\text{Ir}(\text{acac})(\text{Me}_3\text{TFB})]$ .

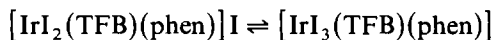
The formation and relative stability of iridium- $\text{C}^3$ -bonded diketonate complexes are dependent on all the involved ligands: thus (i), for given diolefin and bidentate nitrogen donor ligands, the acac groups seems to give stronger Ir– $\text{C}^3$  bonds than the  $\text{Bz}_2\text{ac}$  ligand; e.g., complex VI is stable in dichloromethane solution, but complex X restores the O-bonded complex II; (ii) the phenanthroline ligand stabilizes the Ir- $\text{C}^3$ -bonded diketonate complexes more effectively than the bipyridine ligand; thus, complex IX is prepared at room temperature by treating complex II with the stoichiometric amount of phenanthroline, but the synthesis of the related com-

pound X requires use of a low temperature ( $-15^{\circ}\text{C}$ ) and an excess of the bipyridine ligand. (In this context it is of interest that the cyclooctadiene complex  $[\text{Ir}(\text{acac})(\text{COD})]$  reacts with phenanthroline to give  $[\text{Ir}(\text{acac}-\text{C}^3)(\text{COD})(\text{phen})]$  [7], but no reaction has been observed under similar conditions with bipyridine); (iii) all the observations suggest that the tetrafluorobenzobarrelene ligand is the best diolefin for the formation of iridium- $\text{C}^3$ -bonded diketonate complexes in keeping with the greater ability of TFB than of other diolefins to stabilize pentacoordinated iridium(I) compounds [1,2]. Furthermore, it is noteworthy that while pentacoordinated tetrafluorobenzobarrelene complexes of formula  $[\text{Ir}(\text{OCIO}_3)(\text{TFB})(\text{diolefin})]$  (diolefin = TFB [10] or COD [1]) have been reported, only square planar  $[\text{Ir}(\text{diolefin})_2]\text{ClO}_4$  species are obtained for diolefin = COD [11] or  $\text{Me}_3\text{TFB}$  \*.

Some reactivity studies, with complex V as representative, show that the Ir-acac- $\text{C}^3$  bond can be broken by reaction with a variety of mineral acids and chloro complexes. Thus, V reacts with HCl or  $\text{HBF}_4$  to give  $[\text{IrCl}(\text{TFB})(\text{phen})]$  [10] or  $[\text{Ir}(\text{TFB})(\text{phen})]\text{BF}_4$ , and with the tetrafluorobenzobarrelene complexes  $[\text{RhCl}(\text{TFB})_2]$  [12] or  $[\text{IrCl}(\text{TFB})_2]$  to yield  $[\text{IrCl}(\text{TFB})(\text{phen})]$  and  $[\text{M}(\text{acac})(\text{TFB})]$  ( $\text{M} = \text{Rh}$  [12], Ir).

#### Other complexes

Complex V reacts with iodine to give a red material analyzing as  $[\text{IrI}_2(\text{TFB})(\text{phen})]\text{I}$  (XII). This iridium(III) complex can also be obtained by adding iodine to  $[\text{IrI}(\text{TFB})(\text{phen})]$  (XIII). The latter complex was prepared in high yield by metathetical reaction of  $[\text{IrCl}(\text{TFB})(\text{phen})]$  with KI, or by addition of phenanthroline to  $[\text{IrI}(\text{TFB})_2]$  (XIV) (prepared by metathesis of  $[\text{IrCl}(\text{TFB})_2]$  with KI). Molar conductivity measurements for complex XII suggest the existence in solution of the following equilibrium:



This implies that there is probably a monodentate coordination of one of the bidentate ligands in the neutral species.

Acetone solutions of complex XII react with stoichiometric amounts of  $\text{AgClO}_4$  to give the red ionic complex  $[\text{IrI}_2(\text{TFB})(\text{phen})][\text{ClO}_4]$  (XV). In order to determine the detailed geometry of the latter complex an X-ray structural determination was undertaken (see below). This revealed a *trans* disposition of the iodine ligands. Interestingly, an orange complex with the same formulation  $[\text{IrI}_2(\text{TFB})(\text{phen})][\text{ClO}_4]$  (XVI), can be prepared by oxidative addition of molecular iodine to  $[\text{Ir}(\text{TFB})(\text{phen})][\text{ClO}_4]$  [10] in dichloromethane; its solid IR spectrum shows some significant differences compared with that of the *trans* isomer, and we think it likely that it is the *cis*-isomer, it isomerizes in acetone solution to give the *trans* isomer XV.

Table 1 lists the analytical and physical data for the new iridium complexes.

#### Crystal structure

The structure of the cation is shown in Fig. 1, together with the atom numbering

\* This previously unreported complex was prepared by reaction of  $[\text{IrCl}(\text{Me}_3\text{TFB})_2]$  [2] with  $\text{AgClO}_4$  and  $\text{Me}_3\text{TFB}$ .

TABLE 1  
COLOUR, ANALYTICAL RESULTS, YIELDS AND IR DATA FOR THE NEW COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))			Yield (%)	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
		C	H	N		
[Ir(Bzac)(TFB)] (I)	yellow	45.2 (45.6)	3.1 (2.6)	–	34	1500–1550br,vs
[Ir(Bz <sub>2</sub> ac)(TFB)] (II)	yellow	50.3 (50.5)	2.8 (2.7)	–	85	1500–1560br,vs
[Ir(Bzac)(Me <sub>3</sub> TFB)] (III)	yellow	48.1 (48.3)	3.5 (3.4)	–	72	1500–1560br,vs
[Ir(Bz <sub>2</sub> ac)(Me <sub>3</sub> TFB)] (IV)	orange	52.5 (52.7)	3.8 (3.4)	–	69	1500–1560br,vs
[Ir(acac-C <sup>3</sup> )(TFB)(phen)] (V)	dark-blue	49.2 (49.9)	3.4 (3.0)	3.9 (4.0)	72	1590vs, 1612s
[Ir(acac-C <sup>3</sup> )(TFB)(bipy)] (VI)	dark-blue	47.9 (48.1)	3.5 (3.2)	4.1 (4.2)	30	1590vs, 1618s
[Ir(Bzac-C <sup>3</sup> )(TFB)(phen)] (VII)	dark-blue	53.4 (53.7)	2.9 (3.0)	3.8 (3.7)	31	1595s, 1620s
[Ir(Bzac-C <sup>3</sup> )(TFB)(bipy)] (VIII)	dark-blue	52.4 (52.2)	3.3 (3.2)	3.8 (3.8)	51	1582s, 1605vs
[Ir(Bz <sub>2</sub> ac-C <sup>3</sup> )(TFB)(phen)] (IX)	red	55.8 (57.0)	3.0 (3.1)	3.5 (3.4)	57	1635vs
[Ir(Bz <sub>2</sub> ac-C <sup>3</sup> )(TFB)(bipy)] (X)	red	55.7 (55.7)	3.7 (3.2)	3.2 (3.5)	71	1632vs
[Ir(acac-C <sup>3</sup> )(Me <sub>3</sub> TFB)(phen)] (XI)	orange	52.9 (52.0)	3.7 (3.7)	4.0 (3.8)	35	1620s, 1647s
[IrI <sub>2</sub> (TFB)(phen)]I <sup>a</sup> (XII)	red	29.2 (29.4)	1.6 (1.4)	2.6 (2.9)	78	–
[IrI(TFB)(phen)] (XIII)	dark-blue	40.2 (39.7)	2.2 (1.9)	3.7 (3.9)	92	–
[IrI(TFB) <sub>2</sub> ] (XIV)	white	38.1 (37.4)	1.6 (1.6)	–	50	–
<i>trans</i> -[IrI <sub>2</sub> (TFB)(phen)][ClO <sub>4</sub> ] ·(CH <sub>3</sub> ) <sub>2</sub> CO (XV)	red	32.2 (32.1)	2.2 (2.0)	2.7 (2.8)	60	–
<i>cis</i> -[IrI <sub>2</sub> (TFB)(phen)][ClO <sub>4</sub> ] (XVI)	orange	30.1 (30.3)	1.4 (1.5)	2.9 (2.9)	58	–

<sup>a</sup> Molar conductivities: 16 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>), 88 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> ((CH<sub>3</sub>)<sub>2</sub>CO).

scheme. Selected parameters are given in Table 2. There is a rather distorted octahedral coordination around the Ir metal. The N(1),N(2) and Ir atoms and the midpoints of the olefinic bonds are coplanar within the error limits. The phen ring system makes an angle of 87.3(5)° with the plane through the olefinic bonds. The iodine atoms occupy *trans* positions at 2.757(1) and 2.741(1) Å from the metal. These distances are slightly longer than those observed in a related carbomethoxy Ir<sup>III</sup> complex [IrI<sub>2</sub>(COOCH<sub>3</sub>)(CO)(bipy)] [13], (2.672(2), 2.684(2) Å), which also have a *trans* disposition for the the iodine ligands. The I(1)–Ir–I(2) angle, 160.43(4)°, is distorted from the ideal value of 180°, probably due to the steric restrictions imposed by the hydrogen atoms of the TFB moiety, which even after the observed distortions show contacts with the iodine atoms in the range 2.86(21) to 3.14(22) Å, close to the sum of the Van der Waals radii [14]. Probably, the same effect is responsible for the elongation of the Ir–C(olefin) distances with respect to those

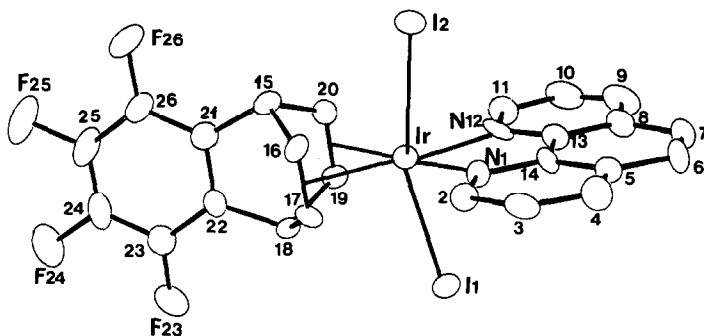


Fig. 1. A view of the structure of the cation showing the atom numbering.

found in some Ir(TFB)-containing compounds previously studied [2,8,15], where the observed range was 2.082(14) to 2.199(21) Å. The pattern observed for these distances in the present complex is similar to that in the  $[\text{Ir}(\text{TFB})(\eta^2\text{-PhNPh}_2)]^+$  cation [2], with the metal atom nearer to one olefin bond than to the other.

The remaining coordination positions are occupied by two nitrogen atoms of the phen ligand and by the midpoints of the olefin bonds. The Ir–N distances (2.072(13) and 2.099(19) Å) are shorter than those in other Ir<sup>III</sup>–phen (2.25(3),

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) <sup>a</sup>

Ir–I(1)	2.757(1)	Ir–I(2)	2.741(1)
Ir–N(1)	2.072(13)	Ir–N(12)	2.099(12)
Ir–C(16)	2.246(13)	Ir–C(17)	2.216(18)
Ir–C(19)	2.194(18)	Ir–C(20)	2.195(14)
N(1)–C(2)	1.304(18)	N(12)–C(11)	1.357(20)
N(1)–C(14)	1.371(18)	N(12)–C(13)	1.326(25)
C(16)–C(17)	1.380(18)	C(19)–C(20)	1.366(19)
N(2)–Ir–N(12)	79.1(5)	C(67)–Ir–C(910)	67.3(6)
I(1)–Ir–N(1)	82.7(3)	I(2)–Ir–N(1)	80.8(3)
I(1)–Ir–N(12)	82.1(4)	I(2)–Ir–N(12)	84.4(3)
I(1)–Ir–C(67)	98.6(4)	I(2)–Ir–C(67)	96.4(4)
I(1)–Ir–C(910)	98.0(5)	I(2)–Ir–C(910)	99.4(4)
I(1)–Ir–I(2)	160.43(4)		
N(1)–Ir–C(910)	174.5(5)	N(12)–Ir–C(67)	173.8(5)
Ir–N(1)–C(2)	126.6(10)	Ir–N(1)–C(14)	112.0(9)
Ir–N(12)–C(11)	126.6(12)	Ir–N(12)–C(13)	113.6(9)
C(14)–N(1)–C(2)	121.3(13)	C(11)–N(12)–C(13)	119.7(13)
N(1)–C(2)–C(3)	121.3(15)	N(12)–C(13)–C(8)	121.5(14)
C(5)–C(14)–N(1)	120.1(13)	C(10)–C(11)–N(12)	120.4(18)
N(1)–C(14)–C(13)	118.4(13)	N(12)–C(13)–C(14)	116.8(14)
C(20)–C(15)–C(16)	98.8(12)	C(17)–C(18)–C(19)	99.4(11)
C(15)–C(16)–C(17)	113.8(13)	C(18)–C(17)–C(16)	113.4(12)
C(15)–C(20)–C(19)	115.3(13)	C(18)–C(19)–C(20)	112.3(12)
C(21)–C(15)–C(16)	107.3(12)	C(21)–C(15)–C(20)	108.3(13)
C(22)–C(18)–C(17)	106.6(13)	C(22)–C(18)–C(19)	107.9(11)

<sup>a</sup> C(67) and C(910) are the midpoints of the olefinic bonds.

2.17(1) Å [16] and Ir<sup>III</sup>-bipy (2.13(2), 2.15(2) Å) [13] complexes, but comparable to those in the Ir<sup>III</sup>-pyrazolate complex [ $\{(C_5Me_5)Ir\}_2(\mu-H)_2(\mu-pz)[BF_4]$ ], (2.089(10), 2.065(11) Å) [17], and in [Ir(acac-C<sup>3</sup>)(COD)(phen)], (2.111(15), 2.097(19) Å) [7], in spite of the lower oxidation state of the metal in the last complex. It is noteworthy that longer Rh-N bonds have been associated with the metals in higher oxidation states [18–20].

## Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer in the range 4000–200 cm<sup>-1</sup>, using Nujol mulls between polyethylene sheets or dichloromethane solutions between sodium chloride windows, and calibration with polyethylene. All reactions were carried out under dry nitrogen, and solvents were dried by standard methods and distilled before use.

### *Preparation of the complexes [Ir(β-diketonate)(TFB)] (I,II)*

A suspension of the complex [IrCl(TFB)<sub>2</sub>] (206.1 mg, 0.30 mmol) in 25 ml of acetone was treated with 0.30 mmol of the corresponding β-diketone and 3.2 ml of a methanolic solution of potassium hydroxide (0.0937 M, 0.30 mmol). After 2 h stirring the mixture was evaporated to dryness. The residue was treated with dichloromethane (50 ml) and the resulting suspension was filtered. The yellow filtrate was concentrated under vacuum to ca. 0.5 ml, and 10 ml of methanol were added. The precipitate was filtered off, washed with methanol, and vacuum-dried.

### *Preparation of the complexes [Ir(β-diketonate)(Me<sub>3</sub>TFB)] (III,IV)*

The procedure described for I and II was used, but starting from 104.5 mg (0.10 mmol) of [IrCl(Me<sub>3</sub>TFB)<sub>2</sub>].

### *Preparation of complexes of the type [Ir(β-diketonate-C<sup>3</sup>)(diolefin)(L-L)] (V–XI)*

These were prepared by two methods:

(i) (V–IX). Addition of the corresponding L–L (0.10 mmol) to solutions of [Ir(β-diketonate)(TFB)] (0.10 mmol) in 10 ml of ether led to immediate precipitation of a dark solid. After 1 h stirring the solid was filtered off, washed with ether, and vacuum-dried.

(ii) (X, XI). At –15°C, a solution (0.10 mmol) of the corresponding [Ir(β-diketonate)(diolefin)] in 5 ml of ether was treated with a large excess of L–L during several hours. The solid formed was filtered off and vacuum-dried.

### *Preparation of [IrI(TFB)<sub>2</sub>] (XIV)*

A suspension of [IrCl(TFB)<sub>2</sub>] (200.0 mg, 0.29 mmol) in methanol/water (36 ml, 2/1, v/v) was treated with a large excess of KI (500 mg) and the mixture was stirred for 24 h. The solid formed was filtered off, washed with water then with pentane, and dried in vacuo.

### *Preparation of [IrI(TFB)(phen)] (XIII)*

This was prepared by two routes:

(i) A suspension of [IrCl(TFB)(phen)] (460.2 mg, 0.72 mmol) in 25 ml of acetone

was treated with KI (123.1 mg, 0.72 mmol) and the mixture was stirred for 24 h. Addition of 25 ml of water caused precipitation of a dark-blue solid, which was filtered off, washed with water then with pentane, and dried in vacuo.

(ii) A suspension of  $[\text{IrI}(\text{TFB})_2]$  (155.1 mg, 0.20 mmol) in 20 ml of acetone was treated with 36.2 mg (0.20 mmol) of phen and the mixture was stirred for 16 h. After concentration under vacuum to ca. 0.5 ml, addition of pentane caused precipitation of a solid, which was filtered off, washed with pentane, and vacuum-dried.

*Preparation of  $[\text{IrI}_2(\text{TFB})(\text{phen})]\text{I}$  (XII)*

This was prepared by two routes:

TABLE 3  
DETAILS OF THE STRUCTURE DETERMINATION

<i>Crystal data</i>	
Formula	$\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}_5\text{F}_4\text{ClI}_2\text{Ir}$
Crystal habit	Transparent red
Crystal size (mm)	$0.06 \times 0.06 \times 0.12$
Symmetry	Monoclinic, $P2_1/n$
Unit cell determination:	
least-squares fit to	79 reflexions, $\theta(\text{Cu}) < 45^\circ$
Unit cell dimensions ( $\text{\AA}$ )	$a$ 12.6841(4), $b$ 17.7550(7), $c$ 13.8500(4) $\beta$ 108.874(2) $^\circ$
Packing: $V$ ( $\text{\AA}^3$ ), $Z$	2951.4(2), 4
$D$ ( $\text{g cm}^{-3}$ ), $M$ , $F(000)$	2.272, 1009.92, 1888
<i>Experimental data</i>	
Radiation and technique	$\text{Cu-K}_\alpha$ , PW1100 diffractometer bisecting geometry
Monochromator	Graphite-oriented
Collection mode	$\omega/2\theta$ , $\theta < 65^\circ$ , $1 \times 1$ det. apertures 1 min/ref., 1.5 scan width
Total independent data	4164
Observed data	3552, $I > 3\sigma(I)$
Stability	Two reflexions every 90 min, no variation
$\mu$ ( $\text{cm}^{-1}$ ), Max-min transmission factors	266.74, 0.242–0.416
<i>Solution and refinement</i>	
Solution	XRAY76 [21], Vax11/750
Refinement	Least-squares on $F$ 's, observed reflexions one block
Final shift/error	0.17
Number of variables	434
Degrees of freedom	2867
Ratio of freedom	7.3
Weighing scheme	Empirical as to give no trends in $\langle \omega\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin \theta / \lambda \rangle$
Max. thermal values ( $\text{\AA}^2$ )	$U_{11}(\text{C}(27)) = 0.23(5)$
Final $\Delta$ peaks	$1.6 \text{ e}\text{\AA}^{-3}$ near the Ir atom
Final $R$ , $R_w$	0.058, 0.059
Atomic factors	International Tables for X-Ray Crystallography [22]

(i) Solid I<sub>2</sub> (40.6 mg, 0.16 mmol) was added to a solution of [Ir(acac-C<sup>3</sup>)(TFB)(phen)] (99.4 mg, 0.14 mmol) in 25 ml of dichloromethane. After 24 h stirring the suspension was concentrated under vacuum to ca. 10 ml and the precipitation completed by addition of 20 ml of ether. The red solid was filtered off, washed with methanol and vacuum-dried.

(ii) Solid I<sub>2</sub> (25.4 mg, 0.10 mmol) was added to a solution of [IrI(TFB)(phen)]

TABLE 4  
FINAL ATOMIC COORDINATES

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ir	0.02587(4)	0.30615(3)	0.39675(5)
I(1)	0.19510(7)	0.39608(5)	0.51635(8)
I(2)	-0.08965(9)	0.20965(5)	0.24493(9)
N(1)	0.0874(8)	0.3410(6)	0.2825(9)
C(2)	0.0491(13)	0.3958(8)	0.2180(12)
C(3)	0.0959(15)	0.4127(9)	0.1447(16)
C(4)	0.1887(17)	0.3743(11)	0.1409(16)
C(5)	0.2320(12)	0.3160(9)	0.2110(12)
C(6)	0.3286(12)	0.2725(12)	0.2168(15)
C(7)	0.3649(13)	0.2167(11)	0.2841(17)
C(8)	0.3087(12)	0.1973(10)	0.3576(14)
C(9)	0.3356(20)	0.1389(11)	0.4261(19)
C(10)	0.2799(21)	0.1280(10)	0.4926(25)
C(11)	0.1894(14)	0.1748(9)	0.4880(14)
N(12)	0.1576(11)	0.2299(6)	0.4164(11)
C(13)	0.2153(12)	0.2414(8)	0.3532(13)
C(14)	0.1789(10)	0.3001(8)	0.2820(11)
C(15)	-0.1945(11)	0.2921(8)	0.4081(12)
C(16)	-0.1475(11)	0.3530(8)	0.3564(12)
C(17)	-0.0729(11)	0.4005(7)	0.4238(11)
C(18)	-0.0573(11)	0.3830(7)	0.5364(12)
C(19)	-0.0123(10)	0.3024(7)	0.5419(12)
C(20)	-0.0841(12)	0.2557(9)	0.4730(13)
C(21)	-0.2442(12)	0.3300(9)	0.4768(13)
C(22)	-0.1723(12)	0.3790(8)	0.5457(13)
C(23)	-0.2086(14)	0.4195(9)	0.6158(13)
F(23)	-0.1388(9)	0.4641(6)	0.6868(8)
C(24)	-0.3152(16)	0.4102(11)	0.6131(17)
F(24)	-0.3536(12)	0.4496(9)	0.6791(12)
C(25)	-0.3875(14)	0.3627(13)	0.5478(17)
F(25)	-0.4948(10)	0.3569(11)	0.5439(12)
C(26)	-0.3527(13)	0.3219(11)	0.4764(15)
F(26)	-0.4243(9)	0.2729(8)	0.4133(11)
C(1)	0.6551(3)	0.0726(2)	0.3484(3)
O(1)	0.7593(10)	0.0977(9)	0.4177(11)
O(2)	0.6043(12)	0.1310(8)	0.2783(11)
O(3)	0.5815(11)	0.0524(8)	0.4027(11)
O(4)	0.6675(14)	0.0095(8)	0.2912(13)
C(27)	-0.0400(56)	0.0083(26)	0.6085(41)
C(28)	0.0457(22)	0.0590(16)	0.6895(28)
C(29)	0.0977(26)	0.0249(15)	0.7888(28)
O(30)	0.0714(20)	0.1209(11)	0.6696(20)



(72.5 mg, 0.10 mmol) in 25 ml of dichloromethane. After 30 min stirring the suspension was concentrated under vacuum to ca. 5 ml and the precipitation completed by addition of 20 ml of ether. The red solid was filtered off, washed with methanol, and vacuum-dried.

*Preparation of trans-[IrI<sub>2</sub>(TFB)(phen)][ClO<sub>4</sub>] (XV)*

A suspension of [IrI<sub>2</sub>(TFB)(phen)]I (68.5 mg, 0.07 mmol) in 50 ml of acetone was treated with AgClO<sub>4</sub> (15.1 mg, 0.07 mmol), and the mixture was stirred for 30 min. The AgCl was removed by filtration through anhydrous MgSO<sub>4</sub>, which was washed with 250 ml of acetone. The yellow filtrate was concentrated under vacuum until a red precipitate separated, and 20 ml of ether were added to complete the precipitation. The red solid was filtered off, washed with ether, and vacuum-dried.

*Preparation of cis-[IrI<sub>2</sub>(TFB)(phen)][ClO<sub>4</sub>] (XVI)*

Solid I<sub>2</sub> (25.4 mg, 0.10 mmol) was added to a suspension of [Ir(TFB)(phen)][ClO<sub>4</sub>] (70.0 mg, 0.10 mmol) in 10 ml of dichloromethane. The solid dissolved and, a slow precipitation of an orange solid began at once. The suspension was stirred for 6 h and the precipitation was completed by addition of 25 ml of ether. The orange complex was filtered off, washed with ether, and vacuum-dried.

*X-ray analysis*

Details are given in Table 3. An acetone molecule of crystallization is present in the crystal. Some hydrogen parameters, namely six thermal factors and the coordinates of five atoms had to be kept fixed in the final cycle of refinement. Table 4 lists the final atomic coordinates. Lists of thermal factors, hydrogen coordinates, and structure factors are available from the authors on request.

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