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ARENE-IRIDIUM(I) COMPLEXES. CRYSTAL STRUCTURES OF $[Ir(TFB)(arene)]BF_4$ (TFB = tetrafluorobenzobarrelene; arene = $1,4\text{-}Me_2C_6H_4$ or C_6Me_6)

R. USÓN, L.A. ORO, D. CARMONA, M.A. ESTERUELAS,

Departamento de Química Inorgánica, Universidad de Zaragoza,, Zaragoza (Spain)

C. FOCES-FOCES, F.H. CANO and S. GARCIA-BLANCO

Departamento de Rayos X, Instituto Rocasolano, CSIC, Serrano 119, Madrid-6 (Spain)

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Summary

The arene-iridium(I) complexes of formula $[Ir(TFB)(arene)]BF_4$ (TFB = tetrafluorobenzobarrelene; arene = $C_6H_4Me_2$, $C_6H_3Me_3$, $C_6H_2Me_4$, C_6Me_6) have been prepared by treating $[IrCl(TFB)_2]$ with $AgBF_4$ in the presence of the corresponding arene. The iridium(I) complexes formed by addition of several types of ligands to $[Ir(TFB)(1,4\text{-}Me_2C_6H_4)]BF_4$ in the presence of potassium hydroxide catalyze hydrogen transfer from isopropanol to acetophenone. The crystal structures of $[Ir(TFB)(1,4\text{-}Me_2C_6H_4)]BF_4$ and $[Ir(TFB)(C_6Me_6)]BF_4$ have been solved by standard X-ray single methods. Both compounds have similar $R3c$ symmetry and are pseudoisomorphous with the corresponding rhodium analogues. Lattice constants are: 25.6844(3), 15.9664(2) Å and 26.9123(7), 16.9894(5) Å, respectively. Final R factors were 0.037 and 0.033, respectively, for the observed data. Some deviation from the planarity of the coordinated arene ligands is observed. The C_6Me_6 ring roughly eclipses the TFB ligand, whereas for the $C_6H_4Me_2$ derivative the arene and the TFB ligand are staggered.

Introduction

In a recent review of arene-metal complexes [1] it was remarked that the arene ring of most of the η^6-arene-ML_2 complexes which have been examined by X-ray crystallography depart significantly from planarity. Furthermore we recently reported a systematic study of the crystal structures of η^6-arene-diolefin-rhodium complexes of formula $[Rh(arene)(diolefin)]ClO_4$ (diolefin = tetrafluorobenzobarrelene (TFB), arene = $1,4\text{-}Me_2C_6H_4$, $1,3,5\text{-}Me_3C_6H_3$ [2], $1,2,4,5\text{-}Me_4C_6H_2$ [3], C_6Me_6 [2]; diolefin = Me_3TFB, arene = $1,4\text{-}Me_2C_6H_4$ [4], $1,2,4,5\text{-}Me_4C_6H_2$ [3]). In these

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rhodium(I) complexes the tendency of the coordinated arene to depart from planarity is probably electronic in origin [2–4]. These electronic considerations should also operate for the 18-electron iridium(I) congeners. In this line, we report now the synthesis and properties of [Ir(TFB)(arene)]BF_4 complexes and the determination of the crystal structures of [Ir(TFB)(arene)]BF_4 (arene = 1,4-$Me_2C_6H_4$, C_6Me_6). As far as we know these are the first crystallographic determinations of the structure of an arene-iridium complex.

Results and discussion

Chlorobis(tetrafluorobenzobarrelene)iridium(I), [IrCl$(TFB)_2$], is a highly insoluble material, which we prepared in nearly quantitative yield by reaction of $IrCl_3 \cdot xH_2O$ with excess of tetrafluorobenzobarrelene(tetrafluorobenzobicyclo[2.2.2]octatriene) [5] in refluxing ethanol/water. The related [IrCl$(COD)_2$] complex is known [6], but in solution it dissociates and dimerises to form $[IrCl(COD)]_2$. Stable chloro-bridged complexes of the formula $[IrCl(diolefin)]_2$ were obtained when cyclic diolefins were used [7,8].

The [IrCl$(TFB)_2$] complex can be used as starting material for the preparation of cationic arene-iridium(I) complexes. Thus, an acetone suspension of [IrCl$(TFB)_2$] react with $AgBF_4$ and arene ligands under reflux with displacement of one mol of tetrafluorobenzobarrelene and precipitation of silver chloride (eq. 1)

$$[IrCl(TFB)_2] + AgBF_4 + \text{arene} \rightarrow [Ir(TFB)(\text{arene})]BF_4 + AgCl + TFB \qquad (1)$$

(arene = 1,2-$Me_2C_6H_4$, 1,3-$Me_2C_6H_4$, 1,4-$Me_2C_6H_4$, 1,2,4-$Me_3C_6H_3$, 1,3,5-$Me_3C_6H_3$, 1,2,4,5-$Me_4C_6H_2$, C_6Me_6)

All the arene complexes are white and behave as 1/1 electrolytes in acetone. Their IR spectra show the absorptions due to the BF_4^- anion with T_d symmetry,

TABLE 1

ANALYSES, MOLAR CONDUCTIVITIES, AND YIELDS FOR THE COMPLEXES PREPARED

Complex	Analyses (Found(Calc.) (%))		Λ_M (ohm^{-1}cm^{2}mol^{-1})	Yield (%)
	C	H		
[IrCl$(TFB)_2$]	42.7 (42.4)	2.0 (1.8)	–	94
[Ir(TFB)(1,2-$Me_2C_6H_4$)]BF_4	40.0 (39.3)	2.7 (2.6)	143	42
[Ir(TFB)(1,3-$Me_2C_6H_4$)]BF_4	39.1 (39.3)	3.0 (2.6)	142	72
[Ir(TFB)(1,4-$Me_2C_6H_4$)]BF_4	40.0 (39.3)	3.3 (2.6)	127	70
[Ir(TFB)(1,2,4-$Me_3C_6H_3$)]BF_4	41.1 (40.3)	3.4 (2.9)	139	68
[Ir(TFB)(1,3,5-$Me_3C_6H_3$)]BF_4	39.8 (40.3)	2.9 (2.9)	135	82
[Ir(TFB)(1,2,4,5-$Me_4C_6H_2$)]BF_4	42.0 (41.3)	3.6 (3.2)	144	80
[Ir(TFB)(C_6Me_6)]BF_4	42.3 (43.2)	3.5 (3.6)	142	72

TABLE 2

REDUCTION OF ACETOPHENONE WITH CATALYTIC SYSTEMS OF THE TYPE [Ir(TFB)(1,4-$C_6H_4Me_2$)]BF_4 + 2 L (or L-L)

L (or L-L)	Reduction (%) after 1 h	L (or L-L)	Reduction (%) after 1 h
4-MeObzn[a]	31	8-NH_2quin[b]	21
2-Clbzn[a]	17	1-Meen[i]	63
2,4-Me_2quin[b]	27	en[i]	52
4-Me_2Npy[c]	15	stien[j]	40
4-NH_2py[c]	10	dpen[k]	21
NPh_3[d]	30	tmeda[l]	8
P(4-$MeOC_6H_4$)$_3$	63	dpm[m]	29
PPh_3	38	dpet[n]	51
$AsPh_3$	27	dpe[o]	23
$SbPh_3$	2	dpp[p]	78
phtaln[e]	84	dpb[q]	91
sucn[f]	42	dae[r]	33
phen[g]	84	Ophen[s]	53.5
bipy[h]	66	O_2dpe[t]	18

[a] bzn = benzonitrile. [b] quin = quinoline. [c] py = pyridine. [d] Formation of iridium metal was observed. [e] phtaln = phtalonitrile. [f] sucn = succinonitrile. [g] phen = 1,10-phenanthroline. [h] bipy = 2,2′-bipyridine. [i] en = ethylenediamine. [j] stien = 1,2-diphenylethylenediamine. [k] dpen = *N,N′*-diphenylethylenediamine. [l] tmeda = *N,N,N′,N′*-tetramethylethylenediamine. [m] dpm = bis(diphenylphosphino)methane. [n] dpet = *cis*-bis(1,2-diphenylphosphino)ethylene. [o] dpe = bis(1,2-diphenylphosphino)ethane. [p] dpp = bis(1,3-diphenylphosphino)propane. [q] dpb = bis(1,4-diphenylphosphino)butane. [r] dae = bis(1,2-diphenylarsino)ethane. [s] Ophen = 1,10-phenantroline mono-*N*-oxide. [t] O_2dpe = bis(1,2-(diphenylphosphino)ethane dioxide.

along with strong bands characteristic of coordinated TFB (1490, 1100, 890 and 845 cm^{-1}) and weak bands from the coordinated arene. Analytical data, conductivities and yields are listed in Table 1.

Attempts to use the [Ir(TFB)(1,4-$Me_2C_6H_4$)]BF_4 complex as a homogeneous catalyst for the hydrogenation of benzene were unsuccesful because of formation of iridium metal on exposure to hydrogen. Iridium metal is also formed when this complex is used for the catalytic hydrogen transfer from isopropanol to acetophenone. However, the iridium(I) complexes formed by addition of various types of ligands to [Ir(TFB)(1,4-$Me_2C_6H_4$)]BF_4 in the presence of potassium hydroxide catalyze hydrogen transfer from isopropanol to acetophenone (Table 2). $[Ir(TFB)L_2]^+$ or $[Ir(TFB)(L{-}L)]^+$ species are probably formed in the polar solvent used [2,9], and on addition of potassium hydroxide these interact with the isopropoxide group. After one hour of reaction the extent of reduction of acetophenone is 10–30% for monodentate nitrogen ligands ($Ir/L = 2/1$), and for other monodentate ligands it decreases in the sequence: P(4-$MeOC_6H_4$)$_3$ > PPh_3 > $AsPh_3$ > $SbPh_3$. (Decomposition to iridium metal is observed for $BiPh_3$ and NPh_3). Bidentate ligands give more active systems, specially phtaln and phen (N-ligands) or dpp and dpb (P-ligands). Oxygen donor ligands as Ophen or O_2dpe produce less active systems than those derived from phen or dpe. For the diamine derivatives, primary amines lead to higher activity than tertiary amines, as previously observed for related rhodium [10] or iridium [11] complexes. No clear general relation between the electronic or steric properties of ligands and catalytic activity can be discerned.

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TABLE 3

BOND LENGTHS (Å) AND ANGLES (°)

Bond	Ir2Me	Ir6Me	Bond	Ir2Me	Ir6Me
Ir–C(1)	2.295(10)	2.267(10)	C(1′)–C(2′)	1.427(36)	1.429(41)
Ir–C(2)	2.252(16)	2.232(12)	C(1′)–F(1′)	1.349(30)	1.336(36)
Ir–C(3)	2.326(14)	2.273(15)	C(1′)–C(11′)	1.367(19)	1.366(24)
Ir–C(4)	2.296(17)	2.254(18)	C(2′)–C(3′)	1.378(45)	1.316(58)
Ir–C(5)	2.253(20)	2.317(17)	C(2′)–F(2′)	1.355(19)	1.371(26)
Ir–C(6)	2.305(16)	2.348(14)	C(3′)–C(4′)	1.310(21)	1.390(30)
Ir–C(6′)	2.109(17)	2.162(15)	C(3′)–F(3′)	1.329(27)	1.335(34)
Ir–C(7′)	2.159(14)	2.082(14)	C(4′)–C(12′)	1.367(23)	1.359(30)
Ir–C(9′)	2.149(14)	2.122(18)	C(4′)–F(4′)	1.367(24)	1.313(30)
Ir–C(10′)	2.159(15)	2.199(21)	C(5′)–C(6′)	1.502(26)	1.534(31)
C(1)–C(2)	1.438(30)	1.456(20)	C(5′)–C(10′)	1.504(23)	1.511(26)
C(2)–C(3)	1.399(26)	1.399(26)	C(5′)–C(12′)	1.523(16)	1.533(23)
C(3)–C(4)	1.391(30)	1.466(27)	C(6′)–C(7′)	1.399(25)	1.377(24)
C(4)–C(5)	1.480(27)	1.396(26)	C(7′)–C(8′)	1.526(25)	1.443(29)
C(5)–C(6)	1.406(37)	1.406(29)	C(8′)–C(9′)	1.523(24)	1.569(25)
C(6)–C(1)	1.379(43)	1.457(25)	C(8′)–C(11′)	1.522(21)	1.503(23)
C(3)–C(7)/C(1)–C(7)	1.455(30)	1.469(31)	C(9′)–C(10′)	1.449(20)	1.389(29)
C(6)–C(8)/C(2)–C(8)	1.583(39)	1.496(30)	C(11′)–C(12′)	1.390(25)	1.390(34)
– C(3)–C(9)	–	1.537(24)	B–F(1)	1.323(39)	1.259(38)
– C(4)–C(10)	–	1.489(39)	B–F(2)	1.294(50)	1.401(39)
– C(5)–C(11)	–	1.521(53)	B–F(3)	1.285(28)	1.289(36)
– C(6)–C(12)	–	1.504(24)	B–F(4)	1.350(24)	1.312(30)

Angle	Ir2Me	Ir6Me	Angle	Ir2Me	Ir6Me
C(6)–C(1)–C(2)	118.(2)	117.(1)	C(3′)–C(4′)–C(12′)	123.(2)	120.(2)
C(1)–C(2)–C(3)	122.(2)	121.(1)	C(12′)–C(4′)–F(4′)	120.(2)	124.(2)
C(2)–C(3)–C(4)	119.(2)	120.(1)	C(10′)–C(5′)–C(12′)	108.(1)	106.(2)
C(3)–C(4)–C(5)	120.(2)	119.(2)	C(6′)–C(5′)–C(12′)	111.(1)	110.(2)
C(4)–C(5)–C(6)	118.(2)	122.(2)	C(6′)–C(5′)–C(10′)	98.(1)	98.(1)
C(5)–C(6)–C(1)	122.(2)	121.(2)	C(5′)–C(6′)–C(7′)	115.(2)	112.(2)
C(2)–C(3)–C(7)/C(6)–C(1)–C(7)	120.(2)	120.(1)	C(6′)–C(7′)–C(8′)	111.(1)	115.(2)
C(4)–C(3)–C(7)/C(2)–C(1)–C(7)	121.(2)	123.(1)	C(7′)–C(8′)–C(11′)	109.(1)	114.(2)
– C(1)–C(2)–C(8)	–	118.(1)	C(7′)–C(8′)–C(9′)	100.(1)	95.(1)
– C(3)–C(2)–C(8)	–	122.(1)	C(9′)–C(8′)–C(11′)	110.(1)	109.(2)
– C(2)–C(3)–C(9)	–	122.(2)	C(8′)–C(9′)–C(10′)	110.(1)	111.(2)
– C(4)–C(3)–C(9)	–	118.(2)	C(5′)–C(10′)–C(9′)	114.(1)	115.(2)
– C(3)–C(4)–C(10)	–	120.(2)	C(1′)–C(11′)–C(8′)	126.(2)	127.(2)
– C(5)–C(4)–C(10)	–	121.(2)	C(8′)–C(11′)–C(12′)	114.(1)	112.(2)
– C(4)–C(5)–C(11)	–	119.(2)	C(1′)–C(11′)–C(12′)	120.(2)	121.(2)
– C(6)–C(5)–C(11)	–	119.(2)	C(5′)–C(12′)–C(11′)	112.(1)	114.(2)
– C(5)–C(6)–C(12)	–	121.(2)	C(4′)–C(12′)–C(11′)	120.(2)	120.(2)
– C(1)–C(6)–C(12)	–	119.(2)	C(4′)–C(12′)–C(5′)	128.(2)	125.(2)
C(11′)–C(1′)–F(1′)	122.(2)	122.(2)	F(1)–B–F(2)	101.(3)	112.(2)
C(2′)–C(1′)–F(1′)	120.(2)	122.(2)	F(1)–B–F(3)	105.(2)	106.(3)
C(2′)–C(1′)–C(11′)	118.(2)	115.(2)	F(1)–B–F(4)	101.(2)	116.(3)
C(1′)–C(2′)–F(2′)	116.(2)	117.(3)	F(2)–B–F(3)	117.(2)	107.(3)
C(1′)–C(2′)–C(3′)	121.(2)	124.(3)	F(2)–B–F(4)	118.(2)	112.(2)
C(3′)–C(2′)–F(2′)	124.(2)	119.(3)	F(3)–B–F(4)	112.(2)	103.(3)
C(2′)–C(3′)–F(3′)	117.(2)	120.(3)	C(2′)–C(3′)–C(4′)	119.(2)	118.(3)
C(4′)–C(3′)–F(3′)	124.(2)	121.(3)	C(3′)–C(4′)–F(4′)	117.(2)	115.(2)

TABLE 4

SELECTED TORSION ANGLES (°)

Angle	Ir2Me	Ir6Me	Angle	Ir2Me	Ir6Me
6-1-2-3	4(3)	−1(2)	7′-8′-9′-10′	62(2)	64(2)
1-2-3-4	−5(3)	−5(2)	8′-9′-10′-5′	−1(2)	−2(2)
2-3-4-5	1(3)	8(2)	9′-10′-5′-6′	−60(2)	−58(2)
3-4-5-6	5(3)	−4(3)	10′-5′-6′-7′	63(2)	57(2)
4-5-6-1	−7(3)	−2(3)	5′-6′-7′-8′	−3(2)	6(2)
5-6-1-2	3(3)	5(2)	6′-7′-8′-11′	55(2)	47(2)
11′-8′-5′-12′	1(1)	2(1)	7′-8′-11′-12′	−54(2)	−52(2)
11′-8′-5′-10′	124(1)	122(2)	8′-11′-12′-5′	1(2)	3(2)
11′-8′-5′-6′	−127(1)	−127(1)	11′-12′-5′-6′	51(2)	47(2)
7′-8′-5′-12′	125(1)	132(2)	12′-5′-6′-7′	−50(2)	−52(2)
7′-8′-5′-10′	−112(1)	−107(1)	5′-10′-9′-8′	−1(2)	−2(2)
7′-8′-5′-6′	−2(1)	3(1)	10′-9′-8′-11′	−53(2)	−54(2)
9′-8′-5′-12′	−124(1)	−122(1)	9′-8′-11′-12′	54(2)	53(2)
9′-8′-5′-10′	−1(1)	−2(1)	8′-11′-12′-5′	1(2)	3(2)
9′-8′-5′-6′	109(1)	109(1)	11′-12′-5′-10′	−55(2)	−58(2)
5′-6′-7′-8′	−3(2)	6(2)	12′-5′-10′-9′	56(2)	56(2)
6′-7′-8′-9′	−60(2)	−66(2)			

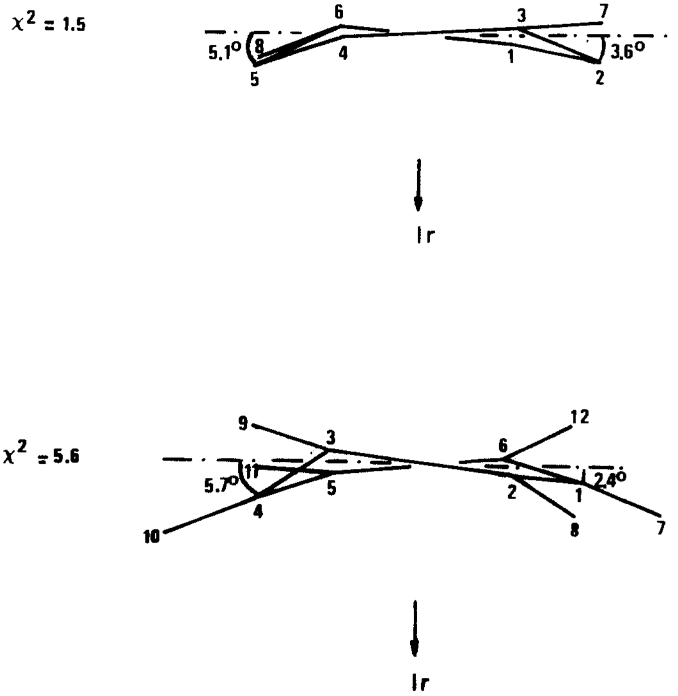

Fig. 1. The puckering of the arene rings in the Ir2Me (above) and Ir6Me (below) showing the angular deviations.

TABLE 5

PUCKERING OF THE ARENE RING (q_2, q_3 AND Q VALUES ARE IN Å; ϕ_2 AND θ IN °)

Compound	Cremer and Pople found parameters [14] (n being any integer)				
	q_3	q_2	ϕ_2	θ	Q
Theoretical boat	0	Q	$0+60\times n$	90	Q
Theoretical skew	0	Q	$30+60\times n$	90	Q
Ir2Me	0.012(20)	0.067(20)	261(17)	80(16)	0.068(20)
Ir6Me	−0.015(16)	0.070(16)	326(13)	102(13)	0.072(16)

Crystal structure

The Ir–C(arene) distances observed for [Ir(TFB)(1,4-$Me_2C_6H_4$)]BF_4 and [Ir(TFB)(C_6Me_6)]BF_4 [Ir2Me and Ir6Me thereafter] (Table 3) show similar features and generally similar parameters to those for the corresponding [Rh(TFB)-(arene)]ClO_4 complexes [2]. The Ir6Me complex shows four shorter distances [to C(1), C(2), C(3) and C(4)], while the Ir2Me complex displays only two [to C(2) and C(5)]. The Ir–C(olefin) distances show some differences from those for the rhodium analogues: while in Rh2Me and in Rh6Me there were three short values, of about 2.12 Å, and one longer of 2.15 Å, in the Ir2Me complex the reverse is the case, with three longer values around 2.15 Å, and a short one of 2.11 Å. In the Ir6Me complex the distribution is more irregular, with values between 2.08 and 2.20 Å. The olefinic bonds are more alike in the Ir6Me complex than in the Rh counterpart, and more different in the Ir2Me complex.

Deviations from planarity in the coordinated arene rings are observed for these complexes (see Fig. 1), as well as for the rhodium analogues [2], supporting an electronic origin. The arene of the Ir6Me complex has the same "skew" conforma-

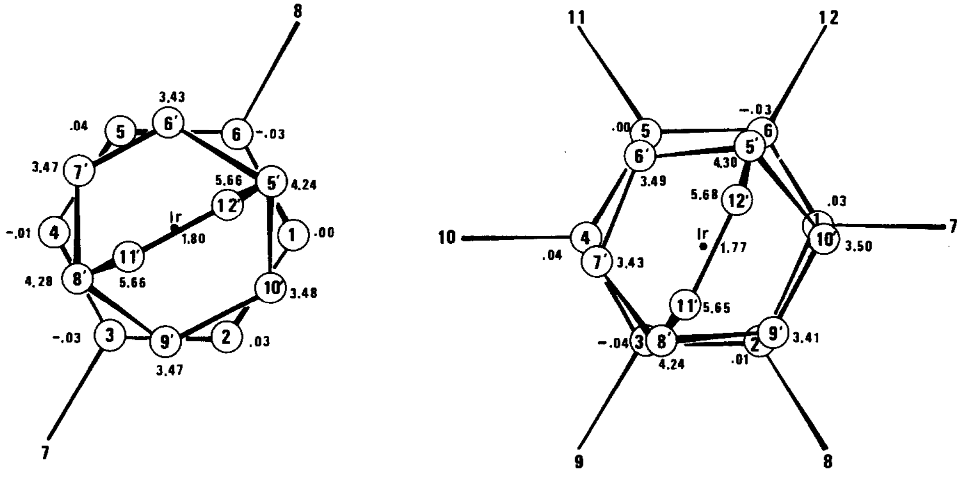

Fig. 2. Iridium coordination projected onto the best least squares plane through the arene ring, with atomic deviations in Å.

tion as in the corresponding Rh complex, but in the Ir2Me compound this ring is distorted towards a "skew" shape from the "boat" form present in the Rh2Me derivative (see Tables 4 and 5). It is noteworthy that while the 18-electron complex $Ni(C_6F_5)_2(C_6H_5Me)$ presents a "boat" distortion, the toluene ligand in the analogous 17-electron cobalt complex is planar [12], in agreement with recent theoretical interpretations [1]. Furthermore, in the above mentioned toluene or *p*-xylene 18-electron complexes of nickel [12], rhodium [2,3,13] or iridium, the auxiliary ligands are not situated opposite to the methyl-substituted carbon atoms, which have a relatively lower π-electron density.

It is of interest that although the distances of the olefinic carbons to the best least squares plane through the arene ring are similar in the cationic iridium and rhodium complexes (see Fig. 2), the iridium atom is slightly closer, (distances 1.798(6) and 1.772(6) Å) to the arene ring than is the rhodium atom in the corresponding complexes (1.815(4) and 1.807(4) Å, respectively).

On the other hand, the relative twist between the arene ring and the TFB moiety, as measured by the coincidence of C(5′)... C(8′)/C(3)... C(6) in projection (see Fig. 2), averages −31.8° for Ir2Me and +6.8° for Ir6Me. The reasons for this are not clear, but the same situation is observed for the Rh analogues [2].

The geometry of the BF_4 groups, bond lengths and angles in the arene ring and the geometry of the TFB moiety are within the standard range of reported values (Tables 3 and 4).

Experimental

The C, H and N analyses were carried with a Perkin–Elmer 240 microanalyzer. Conductivities were measured in approx. 5×10^{-4} *M* acetone solution with a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. The analysis of the products from the catalysed reactions were carried out on Perkin–Elmer 3920B chromatograph connected to a Perkin–Elmer M-2 integrator.

Preparation of [IrCl(TFB)₂]

To a mixture of water (12 ml), ethanol (24 ml) and tetrafluorobenzobarrelene (4.5 g, 19.8 mmol) was added $IrCl_3 \cdot 3H_2O$ (1.4 g, 4 mmol). The suspension was refluxed for 24 h under nitrogen and the pale-yellow precipitate was filtered off, washed with diethyl ether, and air dried (Yield: 94%).

Preparation of complexes of the type [Ir(TFB)(arene)]BF₄

At room temperature, in the absence of light and under nitrogen, a suspension of $[IrCl(TFB)_2]$ (213 mg, 0.313 mmol) in 20 ml of acetone was treated with $AgBF_4$ (61 mg, 0.313 mmol) and a large excess of the corresponding arene (C_6Me_6 (0.5 g, 3.13 mmol); 1,2,4,5-$Me_4C_6H_2$ (0.42 g, 3.13 mmol); 1,3,5-$Me_3C_6H_3$ (1 ml); 1,2,4-$Me_3C_6H_3$ (3 ml); 1,4-$Me_2C_6H_4$ (1 ml); 1,3-$Me_2C_6H_4$ (3 ml); 1,2-$Me_2C_6H_4$ (1 ml)). After 30 min the mixture was refluxed with stirring during several hours (C_6Me_6 (3 h); 1,2,4,5-$Me_4C_6H_2$ (5 h); 1,3,5-$Me_3C_6H_3$ (5 h); 1,2,4-$Me_3C_6H_3$ (24 h); 1,4-$Me_2C_6H_4$ (6 h); 1,3-$Me_2C_6H_4$ (48 h); 1,2-$Me_2C_6H_4$ (6 h)) and the AgCl formed was filtered off. The colourless filtrate was concentrated under reduced pressure and the complex was precipitated with diethyl ether and recrystallized from dichloromethane/diethyl ether.

TABLE 6

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data		
Formulae	$[Ir(C_6H_4Me_2)(TFB)]BF_4$	$[Ir(C_6Me_6)(TFB)]BF_4$
Crystal habit	Triangular: Transparent, colourless prisms: Hexagonal	
Crystal size (mm)	Heights: 0.07, 0.07, 0.16, 0.26	Basis diameter: 0.11; height: 0.27
Symmetry	$3/m$, Rhombohedral, $R3c$ Acentric: Statistical tests on E's and $N(z)$	
Unit cell determination: Least squares fit to $\theta(Cu) < 45°$	47 reflections	57 reflections
Unit cell dimensions (Å)	25.6844(3), 15.9664(2)	26.9123(7), 16.9894(5)
Packing: $V(Å^3)$, Z	9121.8(2), 18	10656.4(5), 18
$D(g\ cm^{-3})$, M, $F(000)$	2.00, 611.34, 5220	1.87, 667.45, 5796
Experimental data		
Radiation and technique	Cu-$K_{\bar{\alpha}}$, PW1100 Philips Diffractometer. Bisecting geometry.	
Monochromator	Graphite oriented	
Sample orientation	$00l$: $\chi \sim 84°$, $\phi \sim 171°$ $hh0$: $\chi \sim 0°$, $\phi \sim 77°$	$00l$: $\chi \sim 86°$, $\phi \sim 2°$ $hh0$: $\chi \sim -4°$, $\phi \sim 356°$
Collection mode	$\omega/2\theta$, $1° \times 1°$det.apertures, $\theta < 65°$, 1 min/reflx., scan width of 1.4°	
Total independent data	1730	1964
Observed data: $I < 3\sigma_c(I)$	1638	1849
Stability	Two reflections every 90 min. No variation	
Absorption:		
faces	$1\bar{2}0$, 100, $\bar{1}10$, ± 101	$\pm(100, 010, \bar{1}10, 001)$
$\mu(cm^{-1})$, Min-Max. transmissions	132.42, 0.190–0.510	113.93, 0.238–0.392
Solution and refinement		
Solution mode	Patterson. X-ray 70 System [15]. Univac 1108	
Refinement mode	Least squares on F's, observed reflections only 3 and 4 blocks in the final cycle, respectively	
Final shift/error	0.22	0.32
Parameters:		
n° of variables	308	370
degrees of freedom	1330	1479
ratio of freedom	5.3	5.0
Weighting scheme	Empirical as to give no trends in $\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$	
Max. thermal values ($Å^2$)	$U_{33}(F1) = 0.52(5)$	$U_{33}(F2') = U_{11}(F2) = 0.32(4)$
Final ΔF-peaks	0.5 $eÅ^{-3}$	0.5 $eÅ^{-3}$
Final R, R_w	0.037, 0.042	0.033, 0.037
Atomic factors	International Tables for X-Ray Crystallography [16] neutral atoms. Real part of anomalous dispersion applied for Ir species.	

Crystals of $[Ir(TFB)(1,4\text{-}Me_2C_6H_4)]BF_4$ and $[Ir(TFB)(C_6Me_6)]BF_4$ were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex.

Catalytic activity

The transfer hydrogenation reactions were carried out under argon in refluxing isopropanol with magnetic stirring. The equipment consisted of a 50 ml round bottom flask, fitted with a condenser and provided with a serum cap. The catalysts were prepared in situ by adding 0.04 mmol of L (0.02 mmol of L–L) to an

TABLE 7

NORMAL PROBABILITY RESULTS

Compounds	Type	Points	Excluded	Total-R	Slope	Intercept	Correlation	Dp max.
Ir2Me	$\|F_0\|$ vs. $\|F_c\|$: (Full normal)	1730	5	0.043	0.795(2)	0.037(2)	0.996	±3.0
Ir6Me	$\|F_0\|$ vs. $\|F_c\|$: (Full normal)	1946	67	0.036	0.9204(4)	−0.0013(4)	0.999	±2.0
Rh2Me vs. Ir2Me	Atomic coordinates: (Half normal)	89	8	0.120	4.23(5)	0.35(4)	0.994	+7.0
	Thermal factors: (Full normal)	180	12	0.206	1.312(8)	0.650(7)	0.997	±3.0
Rh6Me vs. Ir6Me	Atomic coordinates: (Half normal)	101	1	0.009	2.69(4)	0.10(4)	0.991	+8.0
	Thermal factors: (Full normal)	204	6	0.187	1.312(5)	0.22(5)	0.999	±5.0

TABLE 8

FINAL ATOMIC COORDINATES FOR $[Ir(TFB)(1,4\text{-}Me_2C_6H_4)]BF_4$

Atom	x	y	z
C(1′)	0.68241(87)	0.22759(69)	0.25522(153)
C(2′)	0.71158(63)	0.27026(67)	0.32076(242)
C(3′)	0.69049(87)	0.25719(71)	0.40180(169)
C(4′)	0.64586(82)	0.20332(76)	0.41867(127)
C(5′)	0.56224(63)	0.09754(59)	0.36970(109)
C(6′)	0.57306(69)	0.05104(59)	0.32915(122)
C(7′)	0.59408(65)	0.06367(59)	0.24662(106)
C(8′)	0.59736(69)	0.12147(61)	0.21570(112)
C(9′)	0.53157(65)	0.10389(56)	0.22494(93)
C(10′)	0.51330(54)	0.09151(59)	0.31192(84)
C(11′)	0.63541(63)	0.17234(57)	0.27612(115)
C(12′)	0.61650(59)	0.16023(56)	0.35896(106)
F(1′)	0.70222(74)	0.24211(56)	0.17570(118)
F(2′)	0.75975(57)	0.32316(46)	0.29738(142)
F(3′)	0.72095(65)	0.29921(50)	0.45902(127)
F(4′)	0.62782(67)	0.19104(47)	0.50034(80)
C(1)	0.40245(86)	−0.06249(95)	0.28978(140)
C(2)	0.40019(71)	−0.03793(76)	0.20980(109)
C(3)	0.43182(67)	−0.04035(67)	0.14001(95)
C(4)	0.47035(71)	−0.06329(69)	0.15009(105)
C(5)	0.47668(105)	−0.08545(71)	0.23288(135)
C(6)	0.43920(123)	−0.08699(71)	0.29813(135)
C(7)	0.42627(109)	−0.01671(122)	0.05977(132)
C(8)	0.45082(152)	−0.11057(117)	0.38374(169)
Ir	0.49724(1)	0.01007(1)	0.25000(0)
B	0.30552(109)	0.04357(78)	0.17575(117)
F(1)	0.36375(166)	0.08267(112)	0.17016(177)
F(2)	0.28443(144)	0.07966(121)	0.18451(129)
F(3)	0.30030(105)	0.00982(89)	0.23829(91)
F(4)	0.29599(97)	0.01434(69)	0.10209(91)

TABLE 9

FINAL ATOMIC COORDINATES FOR [Ir(TFB)(C_6Me_6)]BF_4

Atom	*x*	*y*	*z*
C(1′)	0.61859(89)	0.18365(80)	0.22722(165)
C(2′)	0.65031(87)	0.22583(82)	0.28588(270)
C(3′)	0.63959(99)	0.21770(101)	0.36182(221)
C(4′)	0.59689(84)	0.16408(97)	0.38728(145)
C(5′)	0.52272(63)	0.05940(80)	0.35599(117)
C(6′)	0.53667(63)	0.01680(65)	0.31551(105)
C(7′)	0.54484(65)	0.02654(69)	0.23574(95)
C(8′)	0.54463(69)	0.07703(65)	0.20766(105)
C(9′)	0.47975(65)	0.05397(65)	0.22740(123)
C(10′)	0.47030(63)	0.04631(76)	0.30798(119)
C(11′)	0.58093(59)	0.13019(63)	0.25529(152)
C(12′)	0.56789(61)	0.12121(76)	0.33504(136)
F(1′)	0.63163(84)	0.19321(65)	0.15082(135)
F(2′)	0.69076(71)	0.27922(52)	0.25990(174)
F(3′)	0.66893(61)	0.26033(61)	0.41276(143)
F(4′)	0.59045(71)	0.15782(71)	0.46389(105)
C(1)	0.36157(46)	−0.09082(56)	0.25836(82)
C(2)	0.37970(50)	−0.08274(56)	0.17636(80)
C(3)	0.42037(61)	−0.09694(65)	0.15031(87)
C(4)	0.44883(61)	−0.11554(61)	0.20704(109)
C(5)	0.42970(65)	−0.12583(63)	0.28490(110)
C(6)	0.38653(61)	−0.11499(72)	0.31142(84)
C(7)	0.32001(67)	−0.07540(109)	0.28897(138)
C(8)	0.35460(80)	−0.05729(86)	0.12206(126)
C(9)	0.43927(122)	−0.09026(110)	0.06375(101)
C(10)	0.49479(99)	−0.12707(112)	0.18017(242)
C(11)	0.45617(178)	−0.14947(131)	0.34218(262)
Ir	0.45790(1)	−0.03216(1)	0.25000(0)
B	0.30337(99)	0.04982(91)	0.20277(129)
F(1)	0.35174(89)	0.06152(91)	0.22923(247)
F(2)	0.29701(87)	0.09836(78)	0.19908(102)
F(3)	0.26624(149)	0.01544(134)	0.25314(185)
F(4)	0.28772(113)	0.02042(101)	0.13696(114)

isopropanol solution (8 ml) of [Ir(TFB)(1,4-$Me_2C_6H_4$)]BF_4 (0.02 mmol) under argon, and a solution of 0.1 mmol of KOH in 1 ml of isopropanol was then added. The resulting solution was refluxed for 1 h (preactivation time) and 2 mmol of the substrate in 1 ml of isopropanol was injected. Samples of the mixture were withdrawn every 30 min and analyzed by GLC.

X-Ray analysis

Crystal analysis parameters for both compounds are given in Table 6. Table 7 lists the parameters of the δR plots [17] testing the refinements and the results of the normal probability plots of comparison with the corresponding Rh-complexes. Deviations from linearity are due to the parameters of the metal atom, thus giving rise to the pseudoisomorphism present in these structures. Tables 8 and 9 present the atomic coordinates, the numbering used being that adopted for the corresponding rhodium analogues [2]. Lists of structure factors, thermal parameters and hydrogen atom coordinates can be obtained from the authors on request.

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