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ARENE-IRIDIUM(I) COMPLEXES. CRYSTAL STRUCTURE OF $[Ir(Me_3TFB)(C_6Me_6)]ClO_4$

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Summary

The crystal structure of $[Ir(Me_3TFB)(C_6Me_6)]ClO_4$ has been determined by X-ray diffraction. Lattice constants are a 16.9092(7), b 17.7120(7), c 16.8635(6) Å and β 97.984(3)° in a $C2/c$ monoclinic lattice. The agreement factors are R, 0.038 and R_w 0.048 for the 3321 reflexions with $I > 3\sigma(I)$. The coordination characteristics are similar to those of the corresponding rhodium analogues.

Introduction

As part of a study of the puckering of the arene rings in η^6-arene-ML_2 complexes and of the position of the arene relative to the ML_2 moiety (L_2 = TFB and Me_3TFB), we previously considered some complexes [1–4], and some of their Ir analogues, namely those in which the arene was 3,6-$Me_2C_6H_4$ (Ia), C_6Me_6 (IIa) with TFB, and 3,6-$Me_2C_6H_4$ with Me_3TFB (Ib) [5,6]. We report here the structure of the related η^6-arene-Ir-diolefin complex with arene = C_6Me_6 and diolefin = Me_3TFB (IIb).

Experimental

Crystals of the complex, prepared as previously reported [5], were supplied by M.A. Esteruelas, D. Carmona and L.A. Oro (University of Zaragoza). Details of the structure determination are given in Table 1. Of interest is the pseudo-isomorphism between the Rh complexes [1,2,4] and the corresponding Ir analogues [5,6] *.

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* The present complex also exists in a triclinic form, with lattice constants: 31.4142(50), 10.5229(7), 9.8959(6) Å, 68.666(5), 90.875(14) and 84.507(14)° with four molecules of the complex in the unit cell. Unfortunately no crystals suitable for a full X-ray study could be obtained.

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TABLE 1

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$C_{27}H_{30}F_4ClO_4Ir$
Crystal habit	Transparent parallepiped
Crystal size (mm)	0.18 × 0.18 × 0.39
Symmetry	Monoclinic, $C2/c$
Unit cell determination: least-squares fit to	59 reflexions, θ(Cu) < 45
Unit cell dimensions (Å)	a, 16.9092(7); b, 17.7120(7); c, 16.8635(6) β 97.984(3)^{0}
Packing: V (Å^3), Z	5001.6(3), 8
D (g cm^{-3}), M, F(000)	1.918, 722.20, 2832
Experimental data	
Radiation & technique	Cu-K_{α}, PW 1100 diffractometer bisecting geometry
Monochromator	Graphite oriented
Collection mode	w/2θ, θ < 65, 1° × 1° det. apertures 1 min/ref., 1.5 scan width
Total independent data	3864
Observed data	3321, $I > 3\sigma(I)$
Stability	Two reflexions every 90 min., no variation
μ(cm^{-1}). Max-min transmission factors	117.17, 0319-0.109
Solution and refinement	
Solution	XRAY76 [7], Vax11/750
Refinement	Least-squares on F's, observed reflexions two blocks
Final shift/error	0.15
Number of variables	454
Degrees of freedom	2867
Ratio of freedom	7.3
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_{22}(04) = 0.15(1)
Final ΔF peaks	3.1 eA^{-3} near the Ir atom
Final R, R_w	0.038, 0.048
Atomic factors	International Tables for X-Ray crystallography [8]

Results

Tables 2 to 4 show the final fractional coordinates and selected geometrical characteristics for the complex, the numbering scheme being the same as that used for the related complexes previously described [1–6]. Figure 1 shows the coordination around the metal as projected on to the best least-squares plane through the arene ring (π). Lists of structure factors, hydrogen coordinates and thermal parameters, can be obtained from the authors.

(*Continued on p. 367*)

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°)

Ir–C(1)	2.335(8)	C(1′)–F(1)	1.344(11)
Ir–C(2)	2.255(7)	C(2′)–C(3′)	1.357(14)
Ir–C(3)	2.306(7)	C(2′)–F(2)	1.357(10)
Ir–C(4)	2.303(7)	C(3′)–C(4′)	1.369(12)
Ir–C(5)	2.258(7)	C(3′)–F(3)	1.349(10)
Ir–C(6)	2.338(7)	C(4′)–C(12′)	1.366(10)
Ir–C(6′)	2.152(7)	C(4′)–F(4)	1.368(10)
Ir–C(7′)	2.124(7)	C(5′)–C(6′)	1.532(10)
Ir–C(9′)	2.156(7)	C(5′)–C(10′)	1.513(9)
Ir–C(10′)	2.170(7)	C(5′)–C(12′)	1.512(10)
C(1)–C(2)	1.428(10)	C(6′)–C(7′)	1.433(10)
C(1)–C(6)	1.411(10)	C(6′)–C(14′)	1.508(11)
C(1)–C(7)	1.521(13)	C(7′)–C(8′)	1.549(9)
C(2)–C(3)	1.428(11)	C(8′)–C(9′)	1.508(11)
C(2)–C(8)	1.510(11)	C(8′)–C(11′)	1.525(10)
C(3)–C(4)	1.435(11)	C(8′)–C(13′)	1.532(11)
C(3)–C(9)	1.506(11)	C(9′)–C(10′)	1.453(11)
C(4)–C(5)	1.453(10)	C(10′)–C(15′)	1.471(11)
C(4)–C(10)	1.504(13)	C(11′)–C(12′)	1.409(10)
C(5)–C(6)	1.414(11)	Cl–O(1)	1.440(8)
C(5)–C(11)	1.490(12)	Cl–O(2)	1.425(9)
C(6)–C(12)	1.500(11)	Cl–O(3)	1.408(10)
C(1′)–C(2′)	1.391(11)	Cl–O(4)	1.403(13)
C(1′)–C(11′)	1.376(11)		
C(6)–C(1)–C(7)	118.7(7)	C(3′)–C(2′)–F(2)	120.0(8)
C(2)–C(1)–C(7)	121.2(7)	C(2′)–C(3′)–F(3)	120.1(8)
C(2)–C(1)–C(6)	120.1(7)	C(2′)–C(3′)–C(4′)	119.7(8)
C(1)–C(2)–C(8)	120.4(7)	C(4′)–C(3′)–F(3)	120.3(8)
C(1)–C(2)–C(3)	120.9(7)	C(3′)–C(4′)–F(4)	118.1(7)
C(3)–C(2)–C(8)	118.5(7)	C(3′)–C(4′)–C(12′)	121.1(8)
C(2)–C(3)–C(9)	121.2(7)	C(12′)–C(4′)–F(4)	120.8(7)
C(2)–C(3)–C(4)	119.2(6)	C(10′)–C(5′)–C(12′)	112.2(6)
C(4)–C(3)–C(9)	119.5(7)	C(6′)–C(5′)–C(12′)	109.4(6)
C(3)–C(4)–C(10)	120.4(7)	C(6′)–C(5′)–C(10′)	99.1(6)
C(3)–C(4)–C(5)	118.4(7)	C(5′)–C(6′)–C(14′)	119.7(6)
C(5)–C(4)–C(10)	121.1(7)	C(5′)–C(6′)–C(7′)	111.3(6)
C(4)–C(5)–C(11)	117.7(7)	C(7′)–C(6′)–C(14′)	123.9(6)
C(4)–C(5)–C(6)	121.3(7)	C(11′)–C(8′)–C(13′)	117.2(6)
C(6)–C(5)–C(11)	120.9(7)	C(9′)–C(8′)–C(13′)	111.3(6)
C(5)–C(6)–C(12)	119.9(7)	C(9′)–C(8′)–C(11′)	110.0(6)
C(1)–C(6)–C(12)	120.7(7)	C(5′)–C(10′)–C(15′)	121.3(6)
C(1)–C(6)–C(5)	119.5(7)	C(1′)–C(11′)–C(12′)	118.3(7)
C(11′)–C(1′)–F(1)	123.1(7)	C(1′)–C(11′)–C(8′)	129.1(7)
C(2′)–C(1′)–F(1)	116.4(7)	C(8′)–C(11′)–C(12′)	112.6(6)
C(2′)–C(1′)–C(11′)	120.4(8)	C(5′)–C(12′)–C(11′)	113.8(6)
C(1′)–C(2′)–F(2)	119.4(8)	C(5′)–C(12′)–C(4′)	126.2(7)
C(1′)–C(2′)–C(3′)	120.6(8)	C(4′)–C(12′)–C(11′)	119.9(7)
O(2)–Cl–O(4)	112.6(7)	C(7′)–C(8′)–C(9′)	97.1(6)
O(1)–Cl–O(2)	108.1(5)	C(7′)–C(8′)–C(11′)	107.8(5)
O(3)–Cl–O(4)	110.7(7)	C(7′)–C(8′)–C(13′)	111.6(6)
O(3)–Cl–O(2)	109.5(6)		
O(1)–Cl–O(3)	105.6(6)		
O(1)–Cl–O(4)	110.2(7)		

TABLE 3

SELECTED TORSION ANGLES (°) (C ATOMS DENOTED BY NUMBERS)

1-2-3-4	6.7(10)	5'-6'-7'-8'	-0.3(7)
2-3-4-5	-0.8(10)	6'-7'-8'-11'	-53.9(8)
3-4-5-6	-5.2(11)	7'-8'-11'-12'	55.0(8)
4-5-6-1	5.3(10)	8'-11'-12'-5'	-1.8(8)
5-6-1-2	0.7(10)	11'-12'-5'-6'	-54.0(7)
6-1-2-3	-6.7(10)	12'-5'-6'-7'	54.2(7)
5'-6'-7'-8'	-0.3(7)	6'-5'-8'-9'	-110.2(5)
6'-7'-8'-9'	59.8(8)	6'-5'-8'-11'	122.9(5)
7'-8'-9'-10'	-59.4(7)	6'-5'-8'-7'	-0.2(4)
8'-9'-10'-5'	-1.7(8)	10'-5'-8'-9'	-1.0(5)
9'-10'-5'-6'	63.9(7)	10'-5'-8'-11'	89.0(4)
10'-5'-6'-7'	-63.4(7)	10'-5'-8'-7'	109.0(5)
		12'-5'-8'-9'	126.0(5)
5'-10'-9'-8'	-1.7(8)	12'-5'-8'-11'	-1.0(5)
10'-9'-8'-11'	52.5(8)	12'-5'-8'-7'	-124.0(5)
9'-8'-11'-12'	-49.7(8)		
8'-11'-12'-5'	-1.8(9)		
11'-12'-5-'10'	55.0(8)		
12'-5'-10'-9'	-51.5(8)		

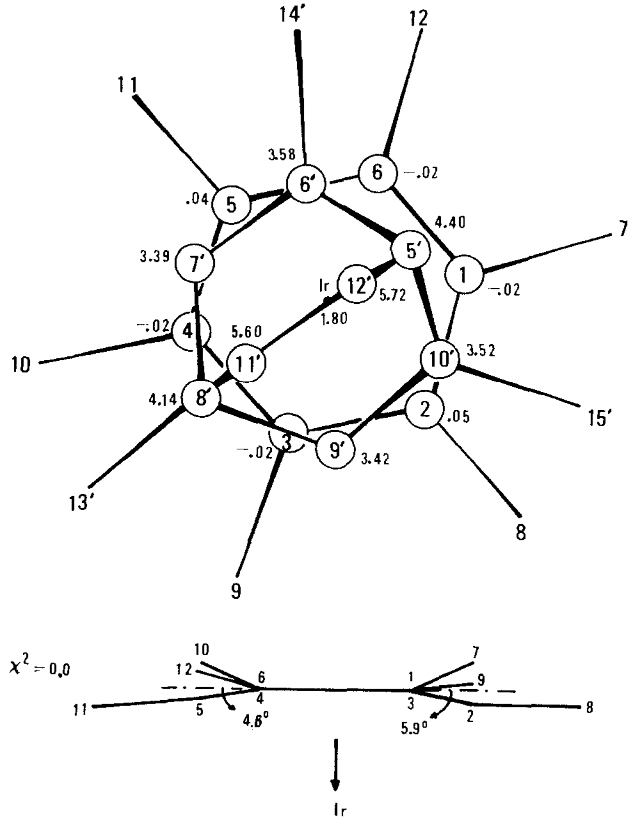

Fig. 1. Projection of the coordination system around the metal atom on to the best least-squares plane through the arene ring, showing the atomic deviations (Å).

TABLE 4

FINAL ATOMIC COORDINATES

Atom	*x*	*y*	*z*
Ir	0.27085(1)	0.10116(1)	0.22675(2)
C(1)	0.2898(4)	0.0287(4)	0.1153(4)
C(2)	0.2141(4)	0.0657(4)	0.1035(4)
C(3)	0.1562(4)	0.0517(4)	0.1558(5)
C(4)	0.1777(4)	0.0062(4)	0.2258(5)
C(5)	0.2579(4)	−0.0249(4)	0.2403(5)
C(6)	0.3118(4)	−0.0163(4)	0.1839(4)
C(7)	0.3473(6)	0.0350(6)	0.0537(6)
C(8)	0.1907(7)	0.1147(5)	0.0307(6)
C(9)	0.0743(5)	0.0867(6)	0.1407(7)
C(10)	0.1174(5)	−0.0109(6)	0.2810(7)
C(11)	0.2799(6)	−0.0706(5)	0.3143(6)
C(12)	0.3911(5)	−0.0557(5)	0.1968(6)
C(1′)	0.2844(5)	0.3329(4)	0.4238(5)
C(2′)	0.3449(6)	0.3828(4)	0.4533(5)
C(3′)	0.4164(5)	0.3811(4)	0.4253(5)
C(4′)	0.4291(5)	0.3294(4)	0.3680(5)
C(5′)	0.3807(4)	0.2145(4)	0.2820(4)
C(6′)	0.3616(4)	0.1395(4)	0.3204(4)
C(7′)	0.2845(4)	0.1414(4)	0.3465(4)
C(8′)	0.2409(4)	0.2179(4)	0.3300(5)
C(9′)	0.2383(4)	0.2177(4)	0.2403(5)
C(10′)	0.3152(4)	0.2144(4)	0.2111(5)
C(11′)	0.2967(4)	0.2800(4)	0.3670(4)
C(12′)	0.3716(4)	0.2784(4)	0.3395(4)
C(13′)	0.1566(5)	0.2157(5)	0.3536(5)
C(14′)	0.4287(5)	0.0887(5)	0.3563(6)
C(15′)	0.3293(5)	0.2431(5)	0.1324(5)
F(1)	0.2157(3)	0.3386(3)	0.4550(3)
F(2)	0.3322(4)	0.4331(3)	0.5108(3)
F(3)	0.4746(4)	0.4299(3)	0.4540(4)
F(4)	0.5020(3)	0.3290(3)	0.3417(4)
Cl	0.4532(1)	0.1902(1)	−0.0738(1)
O(1)	0.3717(4)	0.2006(5)	−0.0603(6)
O(2)	0.4714(6)	0.1118(5)	−0.0660(7)
O(3)	0.4554(6)	0.2130(6)	−0.1535(5)
O(4)	0.5043(8)	0.2349(8)	−0.0205(8)

Discussion

As can be seen in Fig. 1, the relative position of the arene and diolefin moieties fits the usual pattern, the olefin bonds being situated over C(2) and C(5) when projected on the π-plane [4]. In this projection, the angle between the two moieties averages −35.8(14)°, with respect to the position in which the double bonds overlap the C(1)–C(2) and C(4)–C(5) arene bonds.

The arene plane π and the least-squares plane through the olefin bonds are parallel, and about 3.464(3) Å apart from each other, a value comparable with that found in the Rh analogue. However, the Ir atom is closer to the π arene plane than in the Rh analogue (1.802(3) compared with 1.854(1) Å), following the trend for the

TABLE 5

CONFORMATIONAL PARAMETERS FOR THE ARENE RINGS OF THE Ir COMPLEXES

Compound	q_3 ($\times 10^3$)	q_2 ($\times 10^3$)	ϕ_2	θ	Q ($\times 10^3$) [a]	T_m	q	Σ	δ [b]	Conformation
Ia	−12(20)	67(20)	−99(17)	100(16)	68(20)	0.8(17)	6.3(17)	266(17)	165(16)	Monoplanar-skew (222 through C(1), C(4))
IIa	15(16)	70(16)	−34(13)	78(13)	72(16)	1.5(14)	6.4(14)	130(12)	153(13)	Skew' (222 through C(2), C(5))
Ib	−84(9)	11(9)	−89(7)	98(6)	85(9)	1.4(7)	7.9(7)	244(5)	160(6)	Skew (222 through C(1), C(4))
IIb (This work)	6(6)	74(7)	−120(5)	85(9)	74(7)	−0.7(6)	6.9(6)	300(5)	192(4)	Boat (*mm*2 through C(2), C(5))

[a] q_3, q_2, Q (Å) and ϕ_2, θ (°) are the parameters of the criterion on atomic displacements [9], starting at C(1) then C(2) and so on. Theoretical values for a boat and a skew conformation are: Q, 0, $n \times 60°$, 90°, Q and Q, 0, $30° + n \times 60°$, 90°, Q (n being any integer). [b] T_m, q, Σ, δ (°) are the parameters of the criterion [10] on torsion angles starting at C(1)–C(2), then C(2)–C(3) and so on. Phases ϕ_2 and Σ are related by the expression $\Sigma + 2\phi_2 = 60°$ (mod. 360°).

Ir complexes [5,6], so that the Ir complexes have the metal atom a little further away from the TFB moiety. Correspondingly, the Ir–C(arene) distances range from 2.255(7) to 2.338(9) Å, less than in the Rh analogue [2.274(3)–2.368(3) Å], but they follow the same pattern: there are two shorter ones (to C(5) and C(2)), two intermediate ones (to C(3) and C(4)) and two larger ones (to C(1) and to (C(6)). The Ir–C(olefin) bond, although a little longer, have a similar distribution of values to that in the Rh complex: one short to C(7′), one long to C(10′), and intermediate ones to C(6′) and C(9′).

The C–C arene bonds range from 1.411(10) to 1.453(10) Å, within the range of values observed in the Rh complexes. The endocyclic C–C–C angles have higher values at C(2) and C(5). The C–C olefin bonds, 1.433(10) and 1.453(11) Å, are higher than the corresponding values found in the Rh complexes, but similar to those in the other reported Ir complexes (1.449(20), 1.426(11), 1.443(10) Å) [5,6].

The pattern of Ir–C(arene) distances suggests a distorted inverted boat conformation for the arene ring, consistent with the electronic effect of the puckering. The distortion is best considered in terms of the atomic deviations from the best least-squares plane through the arene ring [9] or of the torsion angles [10]. Table 5 shows the parameters corresponding to these models, representing the conformations, which are similar to those for the arene rings in the Rh analogues, the major differences being found for the arene 3,6-$Me_2C_6H_4$ in the complex involving TFB (Ia). The phase values, Σ, show that the differences between the puckering in complexes with, methyl groups in the TFB moiety compared with those without is about 20° (10° in ϕ_2 phase values); in the Rh analogues the difference was about twice as large [4].

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