Crystal and molecular structure of [3-(η^5-tetramethylcyclopentadienyl)-1-(η^6-mesityl)propane]iridium(II) bistetrafluoroborate mononitromethane

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Abstract

The structure of the compound $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$ has been determined by X-ray diffraction. The compound crystallizes in space group *Pbcn* ($Z = 8$) with *a* 26.812(18), *b* 14.275(11), *c* 13.942(5) Å. The structure is a bridged sandwich complex, with an Ir atom bonded to the cyclopentadienyl and benzene rings of the organic ligand. The solvent molecules $MeNO_2$ and the BF_4^- anions are somewhat disordered in the structure, but were located from the difference Fourier maps. The Ir complex cations form discrete units in the structure. The crystal is thermally rather labile, and is held together mainly by Van der Waals forces.

Introduction

Among the bridged cyclopentadienyl and arene complexes of transition metals the cationic complexes have received rather little attention, but a group of bridged cyclopentadienyl-arene cationic complexes were synthesized recently [1]. To confirm the structural conclusions drawn in that connection the crystal structure of the title compound has now been determined. The results are presented below.

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Experimental

Compound

$[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$ was recrystallized from an ethanol/nitromethane mixture by slow evaporation in air at 25°C.

X-Ray crystal structure determination

X-Ray measurements were made on crystals sealed in Lindemann glass capillary tubes together with some of the mother liquor in order to prevent disintegration of the crystals. Intensity data were measured at $22 \pm 1°C$. Cell dimensions were determined from the setting angles of selected reflections on a Nicolet P3F diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator. The pertinent crystallographic data with details concerning data collection for the compound in this study are given in Table 1. Reflections with intensities $I > 3\sigma(I)$ were considered as observed and used in the structure determination. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (through φ-scans) was made for the compound.

Table 1

Crystallographic data for $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$

Formula	$C_{22}H_{32}IrB_2F_8NO_2$
Formula weight	708.31
Crystal system	Orthorhombic
Space group	$Pbcn$ (No. 60)
a (Å)	26.812(18)
b (Å)	14.275(11)
c (Å)	13.942(5)
V (Å^3)	5336(6)
Z	8
D_{measd} (Mg m^{-3})	1.756(10)
D_{calcd} (Mg m^{-3})	1.763
Crystal (mm)	$0.3 \times 0.4 \times 0.2$
Radiation	Mo-K_α
$F(000)$	2768
2θ-limits	4–50
	$(h: 0 \to 17$
	$k: 0 \to 17$
	$l: 0 \to 32)$
Measured unique data	4934
Data, $I > 3\sigma(I)$	2645
μ(Mo-K_α) (cm^{-1})	53.4
R	0.052
R_w	0.057
$w = e/(\sigma^2(F) + gF^2)$	$e = 2.1130$
	$g = 0.00849$
Number of reflexes for cell dimensions	22
2θ range	7–25
Check reflexes	(203), (313)
Scanning type	$\omega - 2\theta$
Scan speed (^{0}/min)	2.5–29.3
Absorption correction factor	0.64–1.00

Table 2

Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$) for $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$

Atom	x	y	z	U^a	Atom	x	y	z	U^a
Ir	1348.8(2)	2399.0(4)	631.0(4)	38(1)	C(21)	156(7)	1592(14)	782(18)	108(17)
C(1)	1666(6)	1261(12)	1397(13)	63(11)	C(22)	4380(7)	1728(11)	1619(16)	145(11)
C(2)	2072(5)	1809(13)	973(12)	57(11)	B(1)	2454(3)	4171(6)	82252(6)	89(8)
C(3)	2052(5)	2741(11)	1351(13)	55(10)	F(1)	2174(3)	4555(6)	8974(6)	101(4)
C(4)	1675(6)	2744(12)	2048(11)	56(10)	F(2)	2895(3)	4648(6)	8175(6)	200(8)
C(5)	1450(6)	1843(12)	2102(13)	56(11)	F(3)	2548(3)	3249(6)	8455(6)	152(6)
C(6)	2465(7)	1465(15)	282(15)	83(14)	F(4)	2198(3)	4234(6)	7405(6)	271(12)
C(7)	2424(7)	3504(14)	1130(14)	80(14)	B(2) ^{b}	5000(1)	4077(11)	2500(1)	78(10)
C(8)	1568(9)	3579(15)	2675(16)	101(18)	F(5) ^{b}	4825(1)	4946(11)	2748(1)	154(13)
C(9)	1023(7)	1588(16)	2788(13)	83(14)	F(6) ^{b}	4888(1)	3901(11)	1559(1)	169(13)
C(10)	1517(7)	287(12)	1163(15)	73(13)	F(7) ^{b}	4780(1)	3413(11)	3069(1)	139(10)
C(11)	1240(11)	54(16)	284(24)	155(27)	F(8) ^{b}	5506(1)	4049(11)	2624(1)	167(13)
C(12)	901(8)	511(12)	−274(14)	70(13)	B(3) ^{b}	5000(1)	592(10)	7500(1)	161(21)
C(13)	892(6)	1555(10)	−334(10)	43(9)	F(9) ^{b}	4903(1)	1527(10)	7621(1)	145(11)
C(14)	1235(6)	2053(14)	−940(11)	55(11)	F(10) ^{b}	4966(1)	369(10)	6547(1)	141(10)
C(15)	1289(6)	3073(9)	−848(13)	58(11)	F(11) ^{b}	4660(1)	77(10)	8008(1)	307(29)
C(16)	965(7)	3574(11)	−170(15)	63(12)	F(12) ^{b}	5471(1)	396(10)	7824(1)	120(9)
C(17)	611(6)	3052(12)	304(13)	57(11)	N(1)	4098(7)	2097(11)	813(16)	190(12)
C(18)	549(5)	2064(12)	240(11)	48(9)	O(1)	3687(7)	2438(11)	947(16)	296(24)
C(19)	1588(7)	1576(13)	−1637(12)	68(12)	O(2)	4266(7)	2063(11)	0000(16)	309(18)
C(20)	1027(7)	4609(12)	−101(15)	69(12)					

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. $U = U_{iso}$ for the atoms of the tetrafluoroborates and solvent. ^{b} Site occupancy factor 0.5.

The structure was solved by locating the Ir atom from Patterson function, and the positions of the remaining non-H atoms were obtained from Fourier syntheses. In the compound the BF_4^- anions and the solvent molecules were disordered and were refined as isotropic rigid groups. Furthermore, two positions were assigned to the atoms of the other anion. The other heavy atoms were refined as anisotropic as the Ir atoms also. Least squares refinements gave $R = \Sigma|| F_o | - | F_c ||/\Sigma| F_o |$ value 0.052 and $R_w = (\Sigma w(| F_o | - | F_c |)^2/w | F_o |^2)^{1/2}$, where $w = e/(\sigma^2(F_o) + gF_o^2)$ value 0.057. The H atoms of the ligand molecule were included at calculated positions with C–H 1.08 Å and U_i 0.09 Å^2, except for H(30)–H(32), U_i 0.16 Å^2, and were held fixed. After the last refinement cycle the maximum and minimum Δ/σ values were: 0.155 and 0.000. The difference Fourier map showed the maximum and minimum heights: 1.55 and −0.77. The scattering factors, including the anomalous dispersion, were taken from International Tables for X-ray Crystallography, Vol. IV [2]. The programs SHELX-76 [3] and SHELXS-86 [4] were used for the structure determination and refinements. The atomic coordinates with isotropic temperature factors are listed in Table 2. Full lists of bond lengths and angles, thermal parameters, and structure factors are available from the authors.

Results and discussion

The geometry of the $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)]^{2+}$ cation is shown in Fig. 1. The distances from the Ir atom to the carbon atoms of the cyclopentadienyl ring vary from 2.12(2) to 2.22(2) Å. The distances from the Ir atom to the carbon atoms of the benzene ring are longer, and vary from 2.18(1) to 2.28(2) Å (Table 3).

The openness of the sandwich character is reflected in the angle C(1)–Ir–C(13), 96.5(6)°, also in the decrease in the angle C(1)–Ir–C(16), which has a value of 176.6(7)° (Table 4).
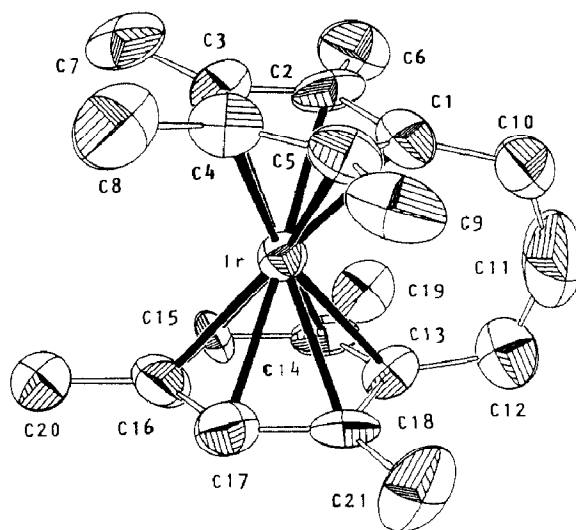

Fig. 1. An ORTEP [5] drawing of the $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)]^{2+}$ cation (with 295 K parameters) of the compound showing the ion geometry and the atom numbering scheme. Thermal ellipsoids are drawn at 50% probability level for the non-H atoms.

Table 3

Selected bond lengths (Å) for $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$

Ir–C(1)	2.12(2)	C(1)–C(10)	1.48(2)	C(14)–C(15)	1.47(2)
Ir–C(2)	2.17(2)	C(2)–C(3)	1.43(2)	C(14)–C(19)	1.52(2)
Ir–C(3)	2.19(1)	C(2)–C(6)	1.51(2)	C(15)–C(16)	1.47(2)
Ir–C(4)	2.28(2)	C(3)–C(4)	1.40(2)	C(16)–C(17)	1.38(2)
Ir–C(5)	2.22(2)	C(3)–C(7)	1.51(2)	C(16)–C(20)	1.49(2)
Ir–C(13)	2.18(1)	C(4)–C(5)	1.42(2)	C(17)–C(18)	1.42(2)
Ir–C(14)	2.27(2)	C(4)–C(8)	1.51(2)	C(18)–C(21)	1.46(2)
Ir–C(15)	2.28(2)	C(5)–C(9)	1.54(2)	C(22)–N(1)	1.453
Ir–C(16)	2.26(2)	C(10)–C(11)	1.47(3)	N(1)–O(1)	1.220
Ir–C(17)	2.23(2)	C(11)–C(12)	1.36(3)	N(1)–O(2)	1.221
Ir–C(18)	2.26(2)	C(12)–C(13)	1.49(2)	C–H	1.080
C(1)–C(2)	1.47(2)	C(13)–C(14)	1.44(2)	B–F	1.370
C(1)–C(5)	1.41(2)	C(13)–C(18)	1.42(2)		

The strength of the sandwich character is also reflected in the distances of the Ir atom from the mean planes of the cyclopentadienyl and benzene rings, although the differences are within experimental errors. The values are 1.81(1) (Plane I) and 1.73(1) Å (Plane II) (Table 5), respectively. The results in Table 5 show that the methyl groups of the cyclopentadienyl and benzene rings lie outside from their calculated mean planes. The Ir atom is at distance 0.11(3) Å from the mean plane calculated through the atoms C(1), C(10), C(11), C(12) and C(13) (Plane III). The angles between the Planes I and II, I and III, and II and III are 11(2), 87.4(5) and 88.5(3)°, respectively. These values imply that the cyclopentadienyl and benzene

Table 4

Selected bond angles (°) for $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$

Ir–C(1)–C(2)	71.7(9)	C(2)–Ir–C(3)	38.3(6)	C(3)–C(4)–C(5)	110(2)
Ir–C(2)–C(3)	71.7(8)	C(3)–Ir–C(4)	37.1(6)	C(3)–C(4)–C(8)	123(2)
Ir–C(2)–C(6)	128(1)	C(4)–Ir–C(13)	153.4(6)	C(4)–C(5)–C(1)	109(1)
Ir–C(3)–C(4)	72.4(9)	C(4)–Ir–C(5)	37.5(6)	C(4)–C(5)–C(9)	124(2)
Ir–C(3)–C(7)	130(1)	C(5)–Ir–C(1)	37.9(6)	C(10)–C(11)–C(12)	135(2)
Ir–C(4)–C(5)	71(1)	C(13)–Ir–C(14)	37.6(5)	C(11)–C(12)–C(13)	121(2)
Ir–C(4)–C(8)	128(1)	C(14)–Ir–C(15)	37.7(6)	C(12)–C(13)–C(14)	121(2)
Ir–C(5)–C(9)	125(1)	C(15)–Ir–C(16)	37.7(6)	C(13)–C(14)–C(15)	120(1)
Ir–C(13)–C(12)	121(1)	C(16)–Ir–C(17)	35.6(6)	C(13)–C(14)–C(19)	124(2)
Ir–C(13)–C(14)	74.4(9)	C(17)–Ir–C(18)	36.9(6)	C(13)–C(18)–C(17)	118(1)
Ir–C(14)–C(15)	71.7(9)	C(18)–Ir–C(13)	37.2(5)	C(13)–C(18)–C(21)	122(2)
Ir–C(14)–C(19)	129(1)	C(1)–C(2)–C(3)	109(1)	C(14)–C(15)–C(16)	119(2)
Ir–C(15)–C(16)	70(1)	C(1)–C(2)–C(6)	127(2)	C(14)–C(13)–C(18)	120(1)
Ir–C(16)–C(17)	71(1)	C(1)–C(5)–C(4)	109(1)	C(15)–C(16)–C(17)	117(2)
Ir–C(16)–C(20)	131(1)	C(1)–C(5)–C(9)	127(2)	C(15)–C(16)–C(20)	117(2)
Ir–C(17)–C(18)	72.7(8)	C(1)–C(10)–C(11)	122(2)	C(16)–C(17)–C(18)	126(2)
Ir–C(18)–C(13)	68.2(8)	C(2)–C(1)–C(5)	106(2)	F–B–F	109.5
Ir–C(18)–C(21)	131(1)	C(2)–C(1)–C(10)	128(2)	O(1)–N(1)–O(2)	119.4
C(1)–Ir–C(2)	39.9(6)	C(2)–C(3)–C(4)	107(1)	O(1)–N(1)–C(22)	119.8
C(1)–Ir–C(13)	96.5(6)	C(2)–C(3)–C(7)	125(2)	O(2)–N(1)–C(22)	120.8
C(1)–Ir–C(16)	176.6(7)				

Table 5

Selected mean planes and atom deviations (Å) for $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$

Plane I	$17.5578(1)x - 4.1519(1)y + 9.7523(1)z = -3.7981(1)$
	^{a} C(1) $-0.04(2)$, ^{a} C(2) $0.04(1)$, ^{a} C(3) $-0.02(2)$, ^{a} C(4) $-0.00(2)$,
	^{a} C(5) $0.03(2)$, Ir $-1.81(1)$, C(6) $0.20(3)$, C(7) $0.10(3)$, C(8) $-0.07(3)$,
	C(9) $-0.05(3)$, C(10) $-0.12(3)$, C(11) $-1.37(4)$
Plane II	$17.7185(1)x - 1.5993(1)y + 10.3466(1)z = -0.9252(1)$
	^{a} C(13) $0.06(2)$, ^{a} C(14) $-0.04(2)$, ^{a} C(15) $-0.01(2)$, ^{a} C(16) $0.04(2)$
	^{a} C(17) $-0.02(2)$, ^{a} C(18) $-0.03(1)$, Ir $1.73(1)$, C(11) $1.56(4)$,
	C(12) $0.31(3)$, C(19) $-0.06(2)$, C(20) $0.05(3)$, C(21) $-0.09(3)$
Plane III	$20.5306(1)x + 0.3352(1)y - 8.9611(1)z = -2.1762(1)$
	^{a} C(1) $0.03(2)$, ^{a} C(10) $-0.09(2)$, * C(11) $0.12(3)$, ^{a} C(12) $-0.06(2)$,
	^{a} C(13) $0.01(2)$, Ir $0.11(3)$

^{a} Atom defining the plane.

rings are tilted towards each other, and are not fully perpendicular to the mean plane of the connecting side chain.

The molecular packing of the compound in the unit cell was also studied. In the structure the molecules are present as discrete units. The cations, anions and solvent molecules form separate columns in the b direction. The H atoms could not be located, but were placed in calculated positions. The disorder of the anions and solvent molecules must also be taken into account, and so the only hydrogen bond found in the structure, C(19)–H(21)...F(2), may be doubtful. The basic data and results of the calculations on this H bond are: C(19)–H(21) 1.08, C(19)...F(2) 3.093, H(21)...F(2) 2.331 Å and C(19)–H(21)–F(2) 126°.

Because of the general lack of H bonds in the structure, it can be regarded as held together by Van der Waals forces, and this may be the reason for the lability of the complex. The present results confirm the conclusions drawn about the structure of the Ir cation and the products of the syntheses described earlier [1].

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