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Structure of $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2.MeOH$

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Abstract. 3-(η^5-Tetramethylcyclopentadienyl)-1-(η^6-2,4,6-trimethylphenyl)propaneiridium(2+) tetrafluoroborate(1−) methanol solvate, $[Ir(C_{21}H_{29})](BF_4)_2.CH_4O$, $M_r = 679{\cdot}31$, orthorhombic, $Pnma$, $a = 28{\cdot}313\,(6)$, $b = 9{\cdot}137\,(3)$, $c = 9{\cdot}789\,(4)$ Å, $V = 2532\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}79\,(1)$, $D_x = 1{\cdot}782$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 56{\cdot}2$ cm^{-1}, $F(000) = 1328$, $T = 295 \pm 1$ K, $R = 0{\cdot}095$ for 902 observed reflections. In the bridged sandwich structure the Ir atom is bonded to the cyclopentadienyl and benzene rings of the organic ligand. The BF_4^- anions and the solvent molecules MeOH are more or less disordered in the structure, but they could be located from the difference Fourier map. The Ir^{III} complex cations form discrete units in the structure. The crystal structure is thermally rather labile and is held together mainly through van der Waals forces.

Introduction. Recently several bridged cationic complexes with arene and cyclopentadienyl ligands were synthesized by ligand exchange in trifluoroacetic acid (Kaganovich, Kudinov & Rybinskaya, 1987). The title compound was obtained from the corresponding mononitromethane complex through recrystallization. To confirm the structural conclusions made earlier the crystal structure of the title compound has now been determined. The results are presented in this paper.

Experimental. The title compound was obtained from the corresponding mononitromethane complex through slow evaporation from an ethanol–methanol mixture in air at 298 K. The densities of the crystals were determined by flotation in CCl_4–CH_3I mixtures at 298 K. X-ray measurements were made on crystals 0·3 × 0·2 × 0·1 mm 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 295 ± 1 K. Nicolet *P*3*F* diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan; $4 \leq 2\theta \leq 48°$; lattice parameters from 14 reflections (2θ range 6–18°); intensities corrected for Lorentz and polarization effects; absorption correction not applied; h 0→11, k 0→12, l 0→13; scan speed 2·0–29·3° min^{-1}; 2 intensity (200, 231) monitors with no significant intensity variations; 2282 unique reflections, 902 with $I \geq 3\sigma(I)$; structure solved by Patterson and Fourier methods; BF_4^- anions and MeOH were disordered and refined as isotropic rigid groups; the population parameter was set to 0·50 for F(1) to F(8) and for O(1); H atoms not located; full-matrix isotropic refinement, except for Ir (for which $U_{23} = U_{12} = 0$), on F (of non-H atoms) yielded $R = 0{\cdot}095$, $wR = 0{\cdot}085$; $w = 3{\cdot}3292/\sigma^2(F)$; the high R value is related to the disorder, thermal lability and loose packing; max. $\Delta/\sigma = 0{\cdot}038$, min. $\Delta/\sigma = -0{\cdot}023$ in final cycle; final ΔF map showed max. 1·08 e Å^{-3} and min. −2·46 e Å^{-3} near the Ir atom; no correction for secondary extinction; scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography* (1974); calculations performed with *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *XTAL*83 *Crystallographic Programs* (Stewart, Hall, Alden, Olthof-Hazekamp, Doherty, Pagoaga & Norden, 1983) and *MPLN* (Truter & Vickery, 1973); calculations performed on a VAX 8650 computer.

Discussion. The atomic coordinates for $[Ir(\eta^{11}\text{-}C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2.MeOH$ are given in Table 1† and selected bond lengths and angles in Table 2. Fig. 1 illustrates the geometry and the atom labeling of the molecule. The crystal packing is shown in Fig. 2. The bond lengths and angles within the cyclopentadienyl

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† Lists of structure factors and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51514 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) (*Hamilton*, 1959) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}*
Ir	1480 (1)	2500	904 (2)	63 (1)
C(1)	748 (19)	2500	355 (57)	87 (19)
C(2)	965 (14)	1329 (51)	−255 (40)	100 (14)
C(3)	1331 (10)	1635 (39)	−1248 (32)	72 (12)
C(4)	1644 (12)	669 (49)	−2135 (40)	107 (15)
C(5)	837 (12)	−394 (47)	−46 (38)	89 (13)
C(6)	385 (20)	2500	1471 (65)	93 (21)
C(7)	520 (35)	2500	2659 (121)	213 (40)
C(8)	887 (22)	2500	3840 (69)	117 (23)
C(9)	1352 (22)	2500	3163 (62)	104 (23)
C(10)	1602 (10)	1314 (44)	2736 (33)	65 (11)
C(11)	2046 (11)	1234 (43)	2031 (32)	69 (11)
C(12)	2237 (20)	2500	1557 (56)	90 (20)
C(13)	2700 (19)	2500	734 (67)	108 (21)
C(14)	1436 (13)	−256 (48)	3182 (36)	97 (12)
B(1)	2379 (9)	7500	356 (27)	264 (71)
F(1)	2730 (9)	8525	236 (27)	193 (34)
F(2)	2261 (9)	7335	1705 (27)	157 (17)
F(3)	1990 (9)	7948	−364 (27)	218 (27)
F(4)	2535 (9)	6190	−154 (27)	91 (15)
B(2)	−23 (11)	2500	7182 (39)	443 (120)
F(5)	−385 (11)	3480	7371 (39)	570 (109)
F(6)	388 (11)	3244	6929 (39)	123 (18)
F(7)	29 (11)	1666	8336 (39)	144 (19)
F(8)	−125 (11)	1610	6094 (39)	290 (41)
C(15)	4034 (34)	2500	1096 (107)	228 (43)
O(1)	4259 (19)	3835 (75)	1400 (58)	137 (24)

* For the Ir atom: $U_{11} = 0{\cdot}0410$ (10), $U_{22} = 0{\cdot}0812$ (21), $U_{33} = 0{\cdot}0672$ (13), $U_{23} = U_{12} = 0$, $U_{13} = 0{\cdot}0020$ (16) Å^2. $U_{eq} = U_{iso}$ for the other atoms.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ir—C(1)	2·14 (5)	C(3)—C(4)	1·52 (5)
Ir—C(2)	2·14 (4)	C(6)—C(7)	1·22 (11)
Ir—C(3)	2·29 (3)	C(7)—C(8)	1·55 (11)
Ir—C(9)	2·24 (6)	C(8)—C(9)	1·47 (7)
Ir—C(10)	2·12 (3)	C(9)—C(10)	1·36 (4)
Ir—C(11)	2·26 (3)	C(10)—C(11)	1·44 (4)
Ir—C(12)	2·24 (6)	C(10)—C(14)	1·57 (5)
C(1)—C(2)	1·37 (5)	C(11)—C(12)	1·36 (4)
C(1)—C(6)	1·50 (7)	C(12)—C(13)	1·54 (7)
C(2)—C(3)	1·45 (4)	C(15)—O(1)	1·41 (7)
C(2)—C(5)	1·63 (5)	B—F	1·370
Ir—C(1)—C(2)	71 (3)	C(11)—Ir—C(12)	35 (1)
Ir—C(1)—C(6)	119 (4)	C(1)—C(2)—C(3)	118 (4)
Ir—C(2)—C(3)	77 (2)	C(1)—C(2)—C(5)	127 (3)
Ir—C(2)—C(5)	125 (3)	C(1)—C(6)—C(7)	119 (7)
Ir—C(3)—C(4)	128 (2)	C(2)—C(3)—C(4)	133 (4)
Ir—C(9)—C(8)	126 (4)	C(3)—C(2)—C(5)	116 (4)
Ir—C(9)—C(10)	67 (3)	C(6)—C(7)—C(8)	156 (9)
Ir—C(10)—C(11)	76 (2)	C(7)—C(8)—C(9)	105 (6)
Ir—C(10)—C(14)	131 (2)	C(8)—C(9)—C(10)	127 (3)
Ir—C(11)—C(12)	71 (3)	C(9)—C(10)—C(11)	130 (5)
Ir—C(12)—C(13)	132 (4)	C(9)—C(10)—C(14)	119 (3)
C(1)—Ir—C(2)	37 (1)	C(10)—C(11)—C(12)	118 (4)
C(2)—Ir—C(3)	38 (1)	C(11)—C(10)—C(14)	110 (4)
C(9)—Ir—C(10)	36 (1)	C(11)—C(12)—C(13)	121 (3)
C(10)—Ir—C(11)	38 (1)	F—B—F	109·5

and benzene rings are normal. The ligand forms a sandwich structure around the Ir atom. The distances from the Ir atom to the C atoms of the cyclopentadienyl and benzene rings are very similar and vary from 2·12 (3) to 2·29 (3) Å (Table 2). These values are comparable with those obtained for [Ir(η^{11}-C_5Me_4-$C_3H_6C_6H_2Me_3$)]$(BF_4)_2$.$MeNO_2$ (Lumme, Turpeinen, Kaganovich, Kudinov & Rybinskaya, 1988).*

The commensurate open sandwich character and lability of the present complex is reflected in the angle C(1)—Ir—C(9), which is 95 (2)° compared with 96·5 (6)° for the nitromethane complex. Similarly, the angle C(1)—Ir—C(12), which is 178 (2)°, compares with the value 176·6 (7)° for the nitromethane complex.

The distances of the Ir atom from the mean planes of the cyclopentadienyl (Plane I) and benzene (Plane II) rings are 1·82 (2) and 1·73 (1) Å, respectively, and

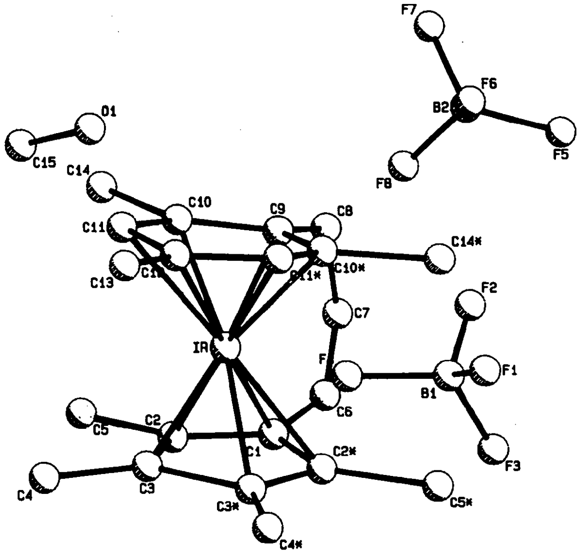

Fig. 1. *PLUTO* (Motherwell, 1970) drawing with the numbering scheme of the [Ir(η^{11}-$C_5Me_4C_3H_6C_6H_2Me_3$)]$(BF_4)_2$.MeOH complex.

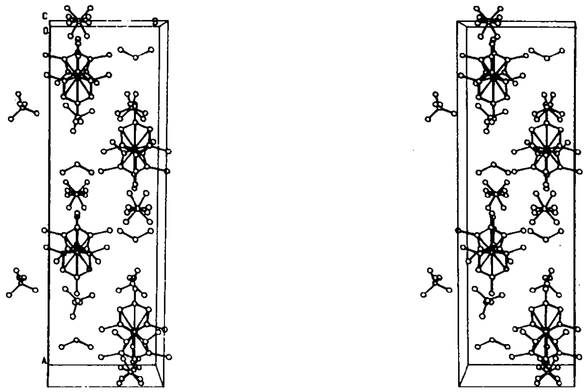

Fig. 2. Stereoview of the molecular packing as viewed down **c**.

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* The oxidation state of iridium in [Ir(η^{11}-$C_5Me_4C_3H_6C_6H_2$-Me_3)]$(BF_4)_2$.$MeNO_2$ is III and not II as stated (Lumme *et al.*, 1988).

comparable with 1·81 (1) and 1·73 (1) Å for the nitromethane complex. The Ir atom lies in the mirror plane (Plane III). The results of the calculations show that the methyl groups of the cyclopentadienyl and benzene rings are bent away from their calculated mean planes. The cyclopentadienyl and benzene rings are tilted to each other, the dihedral angle being 14·4 (2)°. They are perpendicular to the plane of the connecting side chain by symmetry.

The molecular packing of the compound in the unit cell was also studied (Fig. 2). In the structure the components may be considered to form distinct units. The cations, anions and solvent molecules form separate columns in the **c** direction. The disorder of the anions and solvent molecules should also be considered. There seems, however, to be one intramolecular H bond C(4)—H···F(3) [C(4)···F(3) = 3·18 (5) Å] and five intermolecular H bonds O(1)—H···F($6^{\rm i}$), O(1)—H···F($8^{\rm ii}$), C($5^{\rm iii}$)—H···F(5), C($5^{\rm iv}$)—H···F(7) and C($11^{\rm v}$)—H···F(4), because the heavy-atom distances are 2·90 (7), 3·03 (7), 3·09 (5), 3·18 (5) and 3·00 (4) Å, respectively. The symmetry codes are: (i) $0·5-x$, $-y$, $0·5+z$; (ii) $0·5+x$, $0·5-y$, $0·5-z$; (iii) $-x$, $0·5+y$, $-z$; (iv) $-x$, $-y$, $-z$; (v) $-0·5-x, y-0·5, z-0·5$.

Because of the lack of a general H-bond net in the structure, it is held together mainly through van der Waals forces. These circumstances may account for the lability of the complex. The exchange of the solvent molecule $MeNO_2$ for MeOH affects the molecular packing in the crystal structure and increases the H-bond formation to some extent as is to be expected. The present results confirm the conclusions drawn concerning the structure of the Ir cation and the products of the syntheses described earlier (Kaganovich *et al.*, 1987).

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Cobaloximes Containing Planar Neutral Ligands. Structures of *trans*-(Cyanoethyl)bis(dimethylglyoximato)(1-methylimidazole)cobalt(III) and *trans*-(Alkyl)bis(dimethylglyoximato)(1,2-dimethylimidazole)cobalt(III) with Alkyl = Nitromethyl and Cyanopropyl

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Abstract. (I) *trans*-(Cyanoethyl)bis(dimethylglyoximato)(1-methylimidazole)cobalt(III), $[Co(C_4H_7N_2O_2)_2(C_3H_4N)(C_4H_6N_2)]$, $M_r = 425·3$, monoclinic, $P2_1/c$, $a = 10·904\ (2)$, $b = 11·676\ (2)$, $c = 15·738\ (2)$ Å, $\beta = 102·31\ (1)°$, $V = 1957·5\ (3)$ Å^3, $Z = 4$, $D_x = 1·44$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 9·1$ cm^{-1}, $F(000) = 888$, $T = 295\ (1)$ K, $R = 0·042$ for 2619 unique observed reflections. (II) *trans*-Bis(dimethylglyoximato)(1,2-dimethylimidazole)(nitromethyl)cobalt(III), $[Co(C_4H_7N_2O_2)_2(CH_2NO_2)(C_5H_8N_2)]$,

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