

X-ray structures of decamethylplatinocene dication in the crystal of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}(\text{PF}_6^-)_2$ and decamethyliridocenium cation in the crystal of $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+(\text{BPh}_4^-) \cdot \text{CH}_2\text{Cl}_2$

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Abstract

The molecular crystal structures of the $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ cation in the complex of $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+(\text{BPh}_4^-) \cdot \text{CH}_2\text{Cl}_2$ (**1**), (space group $P\bar{1}$, $Z = 2$), and dication $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}$ in the complex of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}(\text{PF}_6^-)_2$ (**2**), (space group $I42d$, $Z = 8$) were proved by an X-ray investigation at 153 K ($R = 0.0661$ and 0.0528 for **1** and **2** respectively). X-ray analysis revealed that in both structures the cations and anions are ordered, cation $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ has the staggered conformation, whereas the dication $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}$ has the ideal eclipsed one. The distances from the metal to the C_5Me_5 ring in **1** (1.817(6) Å and 1.821(6) Å) are close to those in the neutral complex $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2$ (**3**) (1.810(7) Å). The similar distance in the dication $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}$ in **2** (1.84(1) Å) is slightly elongated in comparison with **1** and **3**. © 1997 Elsevier Science S.A.

Keywords: X-ray structure; Iridium; Platinum; Metallocenes

1. Introduction

The synthesis of the first palladocene and platinocene derivatives based on oxidation of η^4 -pentamethylcyclopentadiene complexes $[\text{M}(\eta^4\text{-C}_5\text{Me}_5\text{H})(\eta^5\text{-C}_5\text{Me}_5)]^+$ ($\text{M} = \text{Pd}, \text{Pt}$) was published recently [1,2]. The $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{R}_5)]^{2+}$ ($\text{R} = \text{H}, \text{Me}$) have also been prepared by the interaction of $[\text{Pt}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Br})_3]^{3+}$ with silver fluoroborate in the presence of either cyclopentadiene or pentamethylcyclopentadiene respectively [3]. The cyclic voltammetry data showed [1,2] that 18-electron decamethylpalladocene and decamethylplatinocene dications are more stable than their 19- and 20-electron derivatives contrary to that which was observed for decamethylnickelocene analogues [4].

In order to confirm the molecular structures and to get some information about molecular geometry of the cation $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ and dication $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}$ we have performed X-ray analyses of the

salts $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+(\text{BPh}_4^-) \cdot \text{CH}_2\text{Cl}_2$ (**1**) [5] and $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}(\text{PF}_6^-)_2$ (**2**). Corresponding X-ray structural data for the neutral parent complex $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2$ (**3**) [6,7] will also be given for comparison.

2. Results and discussion

The X-ray structures of **1** and **2** with the atomic numbering schemes are presented in Figs. 1 and 2, important bond lengths and bond angles are given in Table 1. X-ray analysis revealed that in both structures the cations and anions are ordered (note that data collections were performed at 153 K) and no additional orientation of the rings was found in the difference Fourier maps in the ring planes.

An eclipsed conformation close to the ideal is the most common feature for the second- and third-row transition metal complexes of the deca- and pentamethylmetallocenes [7]. The same conformation was also reported in Refs. [6,7] for $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2$. At room temperature this molecule has a crystallographic symmetry plane (space group $P2_1/m$, $Z = 2$), passing

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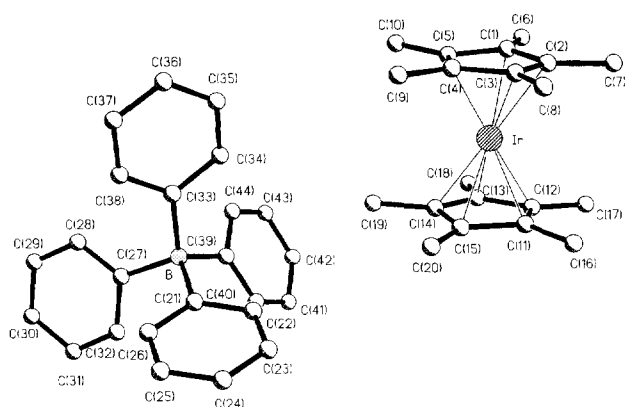


Fig. 1. The general view of the complex (1) and atomic numbering.

through the Os atom and perpendicular to the ring planes. A phase transition takes place on cooling the $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2$ crystal to 183 K [8], and in the low temperature modification (space group $P2_1/n$, $Z = 4$) the molecules have non-ideal and a slightly distorted eclipsed conformation (in-plane ring rotation angle relative to ideal eclipsed conformation is equal to 2.4° at 153 K).

Dication $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}$ in the structure of (2) has the eclipsed conformation caused by the crystal symmetry requirement (Pt atom occupies two-fold axis parallel to the ring planes). On the contrary, the cation $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ in (1) has the staggered conformation with the C_5Me_5 -rings rotated by 23.8° relative to the ideal eclipsed conformation. The large deviation from the eclipsed conformation of the decamethyliridocenium cation in 1 in comparison with 2 and 3 is probably caused by the presence of bulky BPh_4^- anion.

The methyl groups of the pentamethylcyclopentadienyl rings in both 1 and 2 deviate approximately by 0.08 Å from the mean ring planes and away from the metal atoms. The ring planes are almost parallel (angles between their mean planes are 1.3° and 2.2° respectively). The same deviation of the Me-groups was also found in 3 at 153 and 295 K [6,7].

The distances from the Ir atom to the C_5Me_5 -ring planes in the cation (1.817(6) Å and 1.821(6) Å) are very close, and are a little larger than those for neutral $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2$ (1.810(7) Å at 293 K [6], 1.808(6) Å at

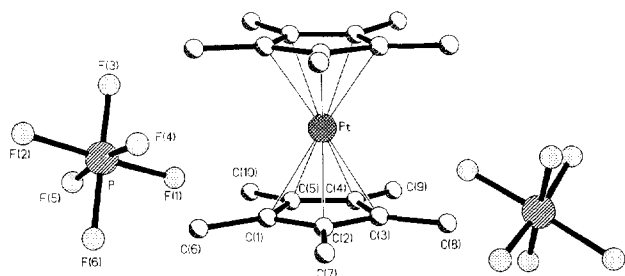


Fig. 2. The general view of the complex (2) and atomic numbering.

Table 1
Important bond lengths (Å) and angles (deg) for structures (1) and (2)

$[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)_2]^+(\text{BPh}_4)^-\cdot\text{CH}_2\text{Cl}_2$			
Bond lengths			
Ir–C(1)	2.244(7)	C(3)–C(4)	1.44(1)
Ir–C(2)	2.182(6)	C(3)–C(8)	1.51(1)
Ir–C(3)	2.181(6)	C(4)–C(5)	1.43(1)
Ir–C(4)	2.176(6)	C(4)–C(9)	1.49(1)
Ir–C(5)	2.177(6)	C(5)–C(10)	1.49(1)
Ir–C(11)	2.173(6)	C(11)–C(12)	1.41(1)
Ir–C(13)	2.200(7)	C(11)–C(16)	1.50(1)
Ir–C(12)	2.182(6)	C(11)–C(15)	1.49(1)
Ir–C(14)	2.178(6)	C(12)–C(13)	1.45(1)
Ir–C(15)	2.233(7)	C(12)–C(17)	1.48(1)
C(1)–C(2)	1.45(1)	C(13)–C(14)	1.43(1)
C(1)–C(5)	1.49(1)	C(13)–C(18)	1.50(1)
C(1)–C(6)	1.49(1)	C(14)–C(15)	1.40(1)
C(2)–C(3)	1.41(1)	C(14)–C(19)	1.50(1)
C(2)–C(7)	1.50(1)	C(15)–C(20)	1.50(1)
Bond angles			
C(2)–C(1)–C(5)	105.7(7)	C(12)–C(11)–C(15)	107.4(6)
C(2)–C(1)–C(6)	126.8(7)	C(12)–C(11)–C(16)	128.5(7)
C(5)–C(1)–C(6)	127.3(7)	C(15)–C(11)–C(16)	123.9(8)
C(3)–C(2)–C(1)	109.4(6)	C(11)–C(12)–C(13)	108.6(6)
C(3)–C(2)–C(7)	126.0(7)	C(11)–C(12)–C(17)	125.4(8)
C(1)–C(2)–C(7)	124.4(7)	C(13)–C(12)–C(17)	125.9(8)
C(2)–C(3)–C(4)	108.7(6)	C(14)–C(13)–C(12)	107.0(7)
C(2)–C(3)–C(8)	126.4(7)	C(14)–C(13)–C(18)	128.1(7)
C(4)–C(3)–C(8)	124.8(7)	C(12)–C(13)–C(18)	124.9(7)
C(5)–C(4)–C(3)	108.2(6)	C(15)–C(14)–C(13)	110.2(6)
C(5)–C(4)–C(9)	124.8(7)	C(15)–C(14)–C(19)	124.9(8)
C(3)–C(4)–C(9)	126.9(7)	C(13)–C(14)–C(19)	124.8(7)
C(4)–C(5)–C(1)	107.7(6)	C(14)–C(15)–C(11)	106.6(7)
C(4)–C(5)–C(10)	127.4(7)	C(14)–C(15)–C(20)	128.9(7)
C(1)–C(5)–C(10)	124.6(7)	C(11)–C(15)–C(20)	124.5(7)
$[\text{Pt}(\eta^5\text{C}_5\text{Me}_5)_2]^{2+}(\text{PF}_6)_2^-$			
Bond lengths			
Pt–C(1)	2.22(1)	C(2)–C(3)	1.43(1)
Pt–C(2)	2.19(1)	C(2)–C(7)	1.50(2)
Pt–C(3)	2.218(9)	C(3)–C(4)	1.46(2)
Pt–C(4)	2.23(1)	C(3)–C(8)	1.48(2)
Pt–C(5)	2.22(1)	C(4)–C(5)	1.42(2)
C(1)–C(2)	1.42(2)	C(4)–C(9)	1.49(2)
C(1)–C(6)	1.48(2)	C(5)–C(10)	1.50(2)
		C(1)–C(5)	1.50(2)
Bond angles			
C(2)–C(1)–C(6)	128.4(12)	C(4)–C(3)–C(8)	126.2(10)
C(2)–C(1)–C(5)	105.0(9)	C(5)–C(4)–C(3)	108.1(10)
C(6)–C(1)–C(5)	126.4(11)	C(5)–C(4)–C(9)	127.1(12)
C(1)–C(2)–C(3)	111.0(10)	C(3)–C(4)–C(9)	124.7(11)
C(1)–C(2)–C(7)	123.9(10)	C(4)–C(5)–C(1)	108.9(10)
C(3)–C(2)–C(7)	124.9(10)	C(4)–C(5)–C(10)	128.6(12)
C(2)–C(3)–C(4)	107.0(9)	C(1)–C(5)–C(10)	122.3(11)
C(2)–C(3)–C(8)	126.8(10)		

153 K [7]). Thus, the positive charge of the cation in 1 does not exert a strong influence on the Ir–C bond lengths. It should be noted that the shortened metal– C_5Me_5 ring distance was observed earlier for positively charged decamethylsoscenium $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ (1.70(4) Å [9]) in comparison with the isoelectronic

neutral decamethylrhene (1.880(8)–1.882(8) Å [10]), but this difference is hardly significant because of the low accuracy of structural data in Ref. [9]. The distance Pt–C₅Me₅ ring in the dication [Pt(η⁵-C₅Me₅)₂]²⁺ of the structure **2** is slightly longer (1.84(1) Å) in comparison with the similar distances in **1** and **3**. It is noteworthy that in the isoelectronic series **3–1–2** of the neutral, mono- and dication 5d-metallocenes with the M = Os, Ir, Pt a small increase of the metal–ring distances is observed.

Analysis of the crystal packing of **1** and **2** shows that there are no shortened intermolecular (inter-ionic) contacts in the structures studied, and only shortened contacts (Cl(1) . . . H(30) (*x*, 1 + *y*, *z*) 2.85(2) Å, Cl(1) . . . H(36) (2 – *x*, – 1 – *y*, *z*) 2.80(2) Å) between the CH₂Cl₂ solvate molecule and hydrogen atoms of the BPh₄[–] in **1** were noted.

The X-ray structures of two new decamethylmetallocenes [Ir(η⁵-C₅Me₅)₂]⁺ (**1**) and [Pt(η⁵-C₅Me₅)₂]²⁺ (**2**) were studied. It was found that the metal–ring distance for decamethylplatinocene dication is elongated in comparison with those for the other third transition metal row decamethylmetallocenes, namely Re(η⁵-C₅Me₅)₂, Os(η⁵-C₅Me₅)₂, and [Ir(η⁵-C₅Me₅)₂]⁺.

3. Experimental details

Single crystals of [Ir(η⁵-C₅Me₅)₂]⁺(BPh₄)[–]·CH₂Cl₂ (**1**) were grown from a mixture of CH₂Cl₂–dimethoxyethane. Experimental data were obtained at 153 K using a four circle ‘Siemens P3/PC’ diffractometer (monochromatized Mo Kα radiation, θ/2θ-scan, 2θ < 50°). Crystals of **1** are triclinic, at 153 K: *a* = 11.570(4) Å, *b* = 12.611(4) Å, *c* = 14.928(5) Å, α = 82.61(2)°, β = 71.26(2)°, γ = 74.55(2)°, *V* = 1985.9(1.1) Å³, *Z* = 2, space group *P*1, *d*_{calc} = 1.450 g cm^{–3}, μ = 3.526 mm^{–1}, *F*(000) = 876. The total number of measured reflections was 6420. The structure was solved by direct method and refined by a full-matrix least squares in the anisotropic–isotropic (H-atoms) approximation. An empirical (Ψ-curves) absorption correction was applied to the diffraction data. All hydrogen atoms were located by the difference electron density synthesis. The results of the refinement using 4982 independent reflections with *I* > 2σ(*I*) are: *R*1 = 0.0661; *wR*2 = 0.1791, and GOF = 0.973 for all 6420 measured reflections. All calculations were performed with a PC/AT computer using the SHELXTL programs package (version 5). The final atomic parameters and for non-hydrogen atoms are listed in Table 2.

Single crystals of [Pt(η⁵-C₅Me₅)₂]²⁺(PF₆)₂[–] (**2**) were grown from acetone. Experimental data were obtained at 153 K using a four circle ‘Siemens P3/PC’ diffractometer (monochromatized Mo Kα radiation, 0–20-scan, 2θ < 70°). Crystals of **2** are tetragonal, at 153 K:

Table 2
Atomic coordinates (× 10⁴) and their equivalent isotropic displacement parameters (Å² × 10³) for structure [Ir(η⁵-C₅Me₅)₂]⁺(BPh₄)[–]·CH₂Cl₂ (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ir	496(1)	–1889(1)	2914(1)	15(1)
C(1)	–1013(8)	–1440(6)	4285(5)	30(2)
C(2)	–379(7)	–562(5)	3899(5)	20(2)
C(3)	902(7)	–940(5)	3850(5)	21(2)
C(4)	1137(7)	–2085(6)	4159(4)	20(2)
C(5)	–14(7)	–2422(5)	4405(5)	21(2)
C(6)	–2365(8)	–1392(7)	4441(6)	35(2)
C(7)	–1019(9)	585(7)	3654(7)	35(2)
C(8)	1873(9)	–263(7)	3551(7)	33(2)
C(9)	2362(9)	–2814(7)	4223(6)	34(2)
C(10)	–240(9)	3519(7)	4806(6)	35(2)
C(11)	1256(8)	–1443(5)	1424(4)	24(2)
C(12)	16(7)	–1537(6)	1589(5)	24(2)
C(13)	–48(8)	–2662(6)	1921(5)	23(2)
C(14)	1178(8)	–3242(5)	1961(5)	22(2)
C(15)	2017(7)	–2554(6)	1618(5)	24(2)
C(16)	1799(10)	–463(7)	1035(5)	36(2)
C(17)	–1029(10)	–647(8)	1407(7)	47(2)
C(18)	–1194(10)	–3102(9)	2141(8)	44(2)
C(19)	1540(10)	–4443(7)	2251(6)	38(2)
C(20)	3400(7)	–2818(8)	1500(6)	36(2)
B	4694(7)	–7859(6)	2145(5)	18(2)
C(21)	5762(6)	–7244(5)	1431(4)	16(1)
C(22)	5478(8)	–6140(6)	1098(5)	23(2)
C(23)	6410(8)	–5607(6)	568(5)	27(2)
C(24)	7662(8)	–6139(7)	355(5)	31(2)
C(25)	7985(7)	–7237(6)	668(5)	28(2)
C(26)	7063(7)	–7782(6)	1190(5)	25(2)
C(27)	5134(6)	–9207(5)	2008(4)	17(1)
C(28)	5054(6)	–10029(5)	2741(5)	21(1)
C(29)	5396(6)	–11140(5)	2565(5)	24(2)
C(30)	5818(7)	–11483(5)	1636(5)	28(2)
C(31)	5890(7)	–10687(6)	893(5)	26(2)
C(32)	5549(6)	–9580(5)	1084(5)	21(1)
C(33)	4598(6)	–7520(5)	3201(4)	20(1)
C(34)	3739(7)	–6567(5)	3635(4)	21(1)
C(35)	3743(8)	–6230(6)	4492(5)	31(2)
C(36)	4573(8)	–6822(6)	4960(5)	30(2)
C(37)	5435(8)	–7771(7)	4550(5)	32(2)
C(38)	5441(7)	–8092(6)	3690(5)	23(1)
C(39)	3346(6)	–7470(5)	1912(5)	20(1)
C(40)	3238(7)	–7172(6)	999(5)	24(2)
C(41)	2109(8)	–6943(6)	789(6)	37(2)
C(42)	1001(7)	–7002(6)	1516(6)	34(2)
C(43)	1063(8)	–7282(6)	2423(6)	33(2)
C(44)	2200(7)	–7529(5)	2617(5)	26(2)
C(45)	6590(8)	–5644(6)	2871(6)	30(2)
Cl(1)	5895(2)	–4248(2)	2657(1)	42(1)
Cl(2)	7835(2)	–5775(2)	3341(2)	51(1)

a = 18.075(5) Å, *c* = 18.861(10) Å, *V* = 6162(4) Å³, *Z* = 8, space group *I*42*d*, *d*_{calc} = 1.629 g cm^{–3}, μ = 4.737 mm^{–1}, *F*(000) = 2928. The total number of measured reflections was 3635. The structure was solved by direct method and refined by a full-matrix least squares in the anisotropic–isotropic (H-atoms) approximation. An empirical absorption correction (Ψ-curves) was applied. Positions of H atoms were calculated geometri-

Table 3

Atomic coordinates ($\times 10^4$) and equivalent displacement parameters ($\text{\AA}^2 \times 10^3$) for structure $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)_2]^{2+}(\text{PF}_6^-)_2$ (2)

Atom	x	y	z	U
Pt	3241(1)	2500	1250	20(1)
C(1)	2994(7)	1637(7)	445(6)	26(2)
C(2)	2564(7)	1510(6)	1067(5)	23(2)
C(3)	3030(5)	1373(5)	1668(6)	19(2)
C(4)	3792(6)	1409(6)	1418(6)	26(2)
C(5)	3780(7)	1572(7)	683(6)	28(2)
C(6)	2734(9)	1738(7)	-294(7)	39(3)
C(7)	1737(7)	1461(8)	1071(8)	38(3)
C(8)	2789(8)	1202(8)	2397(6)	39(3)
C(9)	4453(8)	1259(8)	1863(9)	46(4)
C(10)	4418(8)	1615(8)	174(8)	42(3)
P	642(2)	3218(3)	-747(2)	38(1)
F(1)	1078(7)	2770(8)	-172(7)	104(5)
F(2)	211(7)	3710(10)	-1318(9)	131(6)
F(3)	1095(10)	3862(7)	-591(16)	224(15)
F(4)	0(11)	3422(16)	-266(7)	170(10)
F(5)	1280(9)	2900(10)	-1221(10)	151(8)

cally and were refined using a 'riding' model. The results of the refinement using 2680 independent reflections with $I > 2\sigma(I)$ are: $R1 = 0.0528$; $wR2 = 0.1431$ and $GOF = 1.089$ for all 3635 measured reflections. All calculations were performed with a PC/AT computer using the SHELXTL programs package (version 5). The final atomic parameters for non-hydrogen atoms are listed in Table 3.

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