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Crystal and molecular structure of the salt $[\text{C}_5\text{Me}_5\text{RuC}_5\text{Me}_4\text{CH}_2]^+\text{BPh}_4^-\cdot\text{CH}_2\text{Cl}_2$

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Abstract

The $\text{Ru}\cdots\text{CH}_2$ distance of 2.270 Å in the cation of the salt $[\text{C}_5\text{Me}_5\text{RuC}_5\text{Me}_4\text{CH}_2]^+\text{BPh}_4^-\cdot\text{CH}_2\text{Cl}_2$ investigated by means of an X-ray diffraction study, is slightly longer than the $\text{Os}\cdots\text{CH}_2$ distance of 2.244 Å in the osmium analogue. The inclination angle of the exocyclic bond in the ruthenium complex (40.3°) is somewhat smaller than in the osmium compound (41.8°). The results reported, and those obtained previously, support the suggestion that the stabilization of the α -carbocationic centre increases along the series $\text{Fe} \ll \text{Ru} < \text{Os}$.

An X-ray diffraction study of the complexes $[(\text{Me}_5\text{C}_5)\text{Ru}(\text{C}_5\text{Me}_4\text{CH}_2)]^+\text{PF}_6^-$ (I) [1] and $[(\text{Me}_5\text{C}_5)\text{Os}(\text{C}_5\text{Me}_4\text{CH}_2)]^+\text{BPh}_4^-\cdot\text{CH}_2\text{Cl}_2$ (II) [2] has been carried out as a part of systematic study on the stabilization of carbocationic centres bonded to permethylated cyclopentadienyl ligands. But the disorder of the cation in the crystal structure I gave insufficiently accurate values of those geometrical parameters characterizing the interaction of the metal atom with the carbocationic centre. An attempt to synthesize the ruthenium salt III, containing the same anion as the osmium salt II, as single crystals suitable for an X-ray diffraction study, was successful and good quality single crystals were obtained from a methylene chloride-toluene mixture. The crystal structure of III is described herein.

Experimental

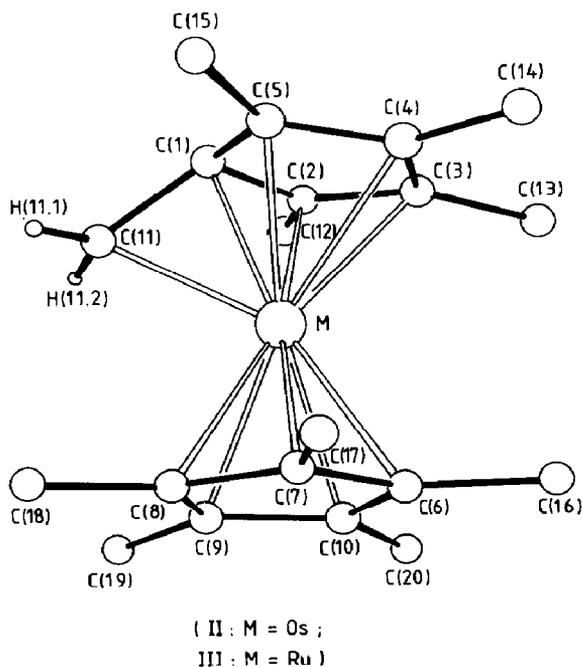
Complex III was obtained by a procedure similar to that for II [2]; thus a solution of $(\text{C}_5\text{Me}_5)\text{Ru}(\text{C}_5\text{Me}_4\text{CH}_2\text{OH})$ [1] in acetic acid was mixed with NaBPh_4 solution in the same solvent. The precipitated crystals were washed with ether and then reprecipitated from its methylene chloride solution by addition of ether. Crystals suitable for the X-ray diffraction study were obtained by slow partial

Table 1

Atomic coordinates ($\times 10^4$, $\times 10^5$ for Ru and Cl, $\times 10^3$ for H) and their equivalent isotropic (isotropic for hydrogens) temperature factors

Atom	x	y	z	$E_{eq}/B_{iso} (\text{\AA}^2)$	Atom	x	y	z	$B_{iso} (\text{\AA}^2)$
Ru	2489(2)	32909(2)	28001(2)	1.394(5)	H(112)	-200(3)	403(2)	232(2)	3.5(7)
C(1)	-245(3)	3442(2)	1521(2)	2.14(8)	H(121)	-89(3)	104(3)	263(2)	5.9(9)
C(2)	-66(3)	2268(2)	1851(2)	2.14(8)	H(122)	-180(3)	210(3)	229(2)	5.0(8)
C(3)	1208(3)	1850(2)	1856(2)	1.87(8)	H(123)	-102(3)	129(3)	153(2)	5.2(9)
C(4)	1848(3)	2710(2)	1502(2)	1.86(8)	H(131)	254(3)	61(2)	237(2)	2.4(6)
C(5)	969(3)	3695(2)	1281(2)	2.13(8)	H(132)	211(3)	24(2)	163(2)	3.4(7)
C(6)	1135(3)	2932(2)	4006(2)	1.94(8)	H(133)	133(3)	38(2)	269(2)	4.2(8)
C(7)	907(3)	4095(2)	3737(2)	2.01(8)	H(141)	352(3)	200(2)	174(2)	3.5(7)
C(8)	-408(3)	4537(2)	3859(2)	1.88(8)	H(142)	341(3)	326(2)	137(2)	3.5(7)
C(9)	-1005(3)	3646(2)	4220(2)	1.90(8)	H(143)	362(3)	231(3)	69(2)	4.6(8)
C(10)	-43(3)	2662(2)	4321(2)	2.06(8)	H(151)	185(3)	491(2)	107(2)	2.8(6)
C(11)	-1282(3)	4199(2)	2047(2)	2.93(9)	H(152)	154(3)	475(2)	18(2)	3.9(7)
C(12)	-1039(3)	1630(3)	2106(3)	3.7(1)	H(153)	42(3)	545(2)	103(2)	4.2(8)
C(13)	1826(3)	677(2)	2143(2)	2.80(9)	H(161)	253(3)	213(2)	463(2)	3.2(7)
C(14)	3223(3)	2569(3)	1338(2)	2.80(9)	H(162)	303(3)	238(2)	357(2)	3.5(7)
C(15)	1235(3)	4781(3)	848(2)	3.4(1)	H(163)	243(3)	140(2)	390(2)	3.2(7)
C(16)	2395(3)	2158(2)	4015(2)	2.79(9)	H(171)	198(3)	501(2)	397(2)	4.3(8)
C(17)	1870(3)	4748(3)	3409(2)	3.0(1)	H(172)	253(3)	432(3)	316(2)	5.0(8)
C(18)	-1050(3)	5742(2)	3708(2)	2.65(9)	H(173)	163(3)	536(3)	297(2)	4.8(8)
C(19)	-2396(3)	3749(2)	4515(2)	2.71(9)	H(181)	-183(3)	585(2)	361(2)	4.2(8)
C(20)	-235(3)	1542(2)	4723(2)	3.10(9)	H(182)	-114(3)	611(2)	427(2)	4.4(8)
C(21)	4244(2)	2279(2)	8549(2)	1.38(7)	H(183)	-64(3)	610(2)	316(2)	4.0(7)
C(22)	2952(3)	2815(2)	8731(2)	1.88(8)	H(191)	-274(3)	384(2)	517(2)	3.6(7)
C(23)	2027(3)	2294(2)	9209(2)	2.21(8)	H(192)	-258(3)	315(2)	436(2)	3.6(7)

C(24)	2350(3)	1190(2)	9545(2)	2.20(9)	H(193)	-279(3)	432(3)	415(2)	4.5(8)
C(25)	3608(3)	632(2)	9392(2)	1.96(8)	H(201)	-90(3)	143(2)	463(2)	3.0(7)
C(26)	4522(2)	1164(2)	8902(2)	1.56(7)	H(202)	-30(3)	143(2)	543(2)	3.7(7)
C(27)	6655(2)	2449(2)	8181(2)	1.63(7)	H(203)	47(3)	94(2)	444(2)	4.0(7)
C(28)	7806(3)	2461(2)	7518(2)	2.50(9)	H(22)	269(2)	354(2)	853(2)	1.9(6)
C(29)	8937(3)	2152(2)	7771(3)	3.3(1)	H(23)	119(3)	266(2)	930(2)	2.5(6)
C(30)	8975(3)	1808(2)	8704(3)	3.6(1)	H(24)	176(3)	84(2)	988(2)	2.8(6)
C(31)	7875(3)	1802(2)	9381(2)	2.94(9)	H(25)	389(2)	-10(2)	961(2)	1.6(5)
C(32)	6740(3)	2120(2)	9119(2)	2.09(8)	H(26)	526(2)	81(2)	884(2)	0.7(5)
C(33)	5440(2)	2570(2)	6791(2)	1.52(7)	H(28)	787(3)	266(2)	690(2)	2.8(6)
C(34)	6285(3)	1611(2)	6393(2)	2.02(8)	H(29)	963(3)	222(2)	732(2)	3.2(7)
C(35)	6301(3)	1278(2)	5521(2)	2.50(9)	H(30)	964(3)	165(2)	886(2)	4.2(8)
C(36)	5470(3)	1901(2)	5004(2)	2.59(9)	H(31)	790(3)	163(2)	997(2)	3.0(7)
C(37)	4618(3)	2860(2)	5369(2)	2.29(9)	H(32)	607(2)	213(2)	956(2)	2.0(6)
C(38)	4605(2)	3169(2)	6243(2)	1.85(8)	H(34)	684(2)	120(2)	670(2)	2.0(6)
C(39)	4857(2)	4230(2)	8009(2)	1.46(7)	H(35)	690(3)	64(2)	526(2)	2.8(6)
C(40)	4987(2)	5066(2)	7269(2)	1.66(7)	H(36)	550(3)	169(2)	446(2)	2.9(6)
C(41)	4634(3)	6186(2)	7440(2)	1.96(8)	H(37)	406(2)	329(2)	501(2)	1.8(6)
C(42)	4151(3)	6515(2)	8356(2)	2.01(8)	H(38)	404(2)	375(2)	646(2)	1.3(5)
C(43)	4020(3)	5721(2)	9107(2)	2.17(8)	H(40)	534(2)	491(2)	663(2)	1.4(5)
C(44)	4368(3)	4610(2)	8929(2)	2.05(8)	H(41)	472(2)	671(2)	692(2)	2.3(6)
B	5309(3)	2885(2)	7878(2)	1.47(8)	H(42)	392(2)	720(2)	849(2)	1.6(5)
Cl(1S)	42182(9)	92994(6)	73062(6)	3.97(3)	H(43)	371(3)	594(2)	971(2)	2.3(6)
Cl(2S)	22462(9)	108157(8)	65134(7)	4.46(3)	H944	430(2)	409(2)	946(2)	2.1(6)
CS	3487(3)	10694(2)	7034(2)	2.80(9)	H(1S)	307(3)	1102(3)	759(2)	4.7(8)
H(III)	-130(3)	501(2)	197(2)	3.6(7)	H(2S)	405(3)	1100(3)	661(2)	5.8(9)



evaporation of the solution of the salt in a solvent mixture of methylene chloride-toluene at -5° .

Crystals of III are triclinic, and at -120°C a 11.466(3), b 12.606(3) c 14.595(4) Å, α 81.61(2), β 73.75(2), γ 73.26(2) $^\circ$, V 1934.6 Å³, d_{calc} 1.33 g/cm³, $Z = 2$, space group $P\bar{1}$. The unit cell parameters and intensities of 5620 reflections with $F^2 \geq 2\sigma$ were measured with a four-circle automated Syntex P2₁ diffractometer (-120°C , $\lambda\text{Mo-K}\alpha$, graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 25^\circ$).

The structure was solved by the standard heavy-atom technique. Coordinates of the Os atom in structure II were taken as the initial approximate position of the Ru atom. The remaining non-hydrogen atoms, including those of the solvating CH₂Cl₂ molecule, were located by subsequent electron density syntheses. The structure was refined, first isotropically, then anisotropically, by full-matrix least squares. All H atoms of the cation, anion and the solvating molecule were located directly in the difference Fourier synthesis and included in the anisotropic refinement. The final discrepancy factors are $R = 0.029$ and $R_w = 0.028$. All calculations were carried out by use of the INEXTL program package [3] with an Eclipse S/200 computer. Atomic coordinates and the equivalent temperature factors for III are listed in Table 1.

Results and discussion

The X-ray diffraction study reveals that the crystals of the ruthenium complex III are isomorphous with those of the osmium analogue II, their unit cell parameters are equal within experimental error, and differences in the cell edges (at -120°C) do not exceed 0.2%. The structures of cations II and III which have very similar

Table 2
Comparison of bond lengths (Å) in cations II and III

	II	III		II	III
M-C(1)	2.069(4)	2.066(3)	C(3)-C(13)	1.502(6)	1.499(4)
M-C(2)	2.187(5)	2.186(3)	C(4)-C(5)	1.413(6)	1.417(4)
M-C(3)	2.264(4)	2.266(3)	C(4)-C(14)	1.509(7)	1.488(5)
M-C(4)	2.269(4)	2.274(3)	C(5)-C(15)	1.486(7)	1.498(4)
M-C(5)	2.181(4)	2.178(3)	C(6)-C(7)	1.449(6)	1.428(4)
M-C(6)	2.222(4)	2.200(3)	C(6)-C(10)	1.435(7)	1.423(4)
M-C(7)	2.225(4)	2.211(3)	C(6)-C(16)	1.491(7)	1.495(4)
M-C(8)	2.193(4)	2.191(3)	C(7)-C(8)	1.414(7)	1.418(4)
M-C(9)	2.194(4)	2.190(3)	C(7)-C(17)	1.499(7)	1.496(5)
M-C(10)	2.221(4)	2.211(3)	C(8)-C(9)	1.451(6)	1.442(4)
M-C(11)	2.244(5)	2.270(3)	C(8)-C(18)	1.497(6)	1.499(4)
C(1)-C(2)	1.470(6)	1.461(4)	C(9)-C(10)	1.432(6)	1.423(4)
C(1)-C(5)	1.461(7)	1.453(5)	C(9)-C(19)	1.504(7)	1.502(4)
C(1)-C(11)	1.426(7)	1.401(4)	C(10)-C(20)	1.490(7)	1.500(4)
C(2)-C(3)	1.403(7)	1.404(4)	C(11)-H(11.1)	0.99(5)	1.01(3)
C(2)-C(12)	1.492(8)	1.493(5)	C(11)-H(11.2)	0.91(5)	0.88(3)
C(3)-C(4)	1.439(6)	1.436(4)			

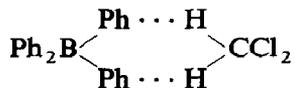
geometrical parameters are shown in the Figure; their bond lengths are compared in Table 2.

Owing to lanthanide contraction, the atomic radii of the transition metals of the fifth and sixth long periods of the Periodic Table are almost equal; the atomic radii of Ru and Os are 1.49 and 1.50 Å, respectively [4]. It then follows that the geometrical parameters of both cations should also be almost equal. From Table 2 it can be seen that the differences between the bond lengths in cations II and III in most cases do not exceed $< 3\sigma$. It is noteworthy that the differences become significant ($5-8\sigma$) for those geometrical parameters which are directly related to the degree of metal atom participation in the stabilization of the exocyclic carbocationic centre in the cation. Thus the metal-carbocationic centre separation, M-C(11), of 2.270(3) Å in the ruthenium complex is somewhat longer than the analogous separation of 2.244(5) Å in the osmium derivative, and the inclination angle of the C(1)-C(11) bond to the plane of the Cp ligand C(1)-C(5) 40.3° in III is somewhat smaller than the corresponding inclination angle 41.8° in II. These minor differences may indicate that the stabilization of the carbocationic centre by interaction with the metal atom in the case of Ru complex is less effective than in the Os derivative. These results are consistent with the increase in α -carbocationic centre stabilization along the series $\text{Fe} \ll \text{Ru} < \text{Os}$ as suggested in Ref. 5, in which we discuss both the differences in the geometrical parameters of the ruthenium and osmium salts, and the data on the shielding of the ^1H and ^{13}C nuclei in the NMR spectra of the salts.

All the geometrical features of cation II that have been described [2] are also observed in the isomorphous complex, III. Thus the C(1)-C(11) bond is significantly shortened (to 1.401(4) Å) and the C(1)-C(5) Cp ring bonded to the α -carbocationic centre exhibits some fulvene-type bond length redistribution (see Table 2). In contrast to decamethylruthenocene [6], having the eclipsed conformation of the Cp-rings, both III and II have Cp rings in the staggered conformation: the

C(1)Cp(1)Cp(2)C(6) torsion angle is $-177.8(4)^\circ$ (Cp(1) and Cp(2) are the centroids of corresponding Cp rings).

Finally, both III and II have H bonds of the C–H $\cdots\pi$ type involving the CH₂Cl₂ molecules and Ph rings of the BPh₄[−] anions, in the crystalline state. These H bonds (in III H(1s) \cdots C(21–26) 2.76–3.04, H(2s) \cdots C(33–38) 2.71–2.96 Å) give rise to the associates



made up of one molecule of methylene chloride and one BPh₄[−] anion.

References

- 1 A.Z. Kreindlin, P.V. Petrovskii, M.I. Rybinskaya, A.I. Yanovsky, Yu.T. Struchkov, *J. Organomet. Chem.*, 319 (1987) 229.
- 2 M.I. Rybinskaya, A.Z. Kreindlin, Yu.T. Struchkov, A.I. Yanovsky, *J. Organomet. Chem.*, 359 (1989) 233.
- 3 R.G. Gerr, A.I. Yanovsky, Yu.T. Struchkov, *Kristallografia* 28 (1983) 1029.
- 4 V.G. Andrianov, B.P. Biryukov, *Zh. Strukt. Khim.*, 6 (1969) 1129.
- 5 M.I. Rybinskaya, A.Z. Kreindlin, S.S. Fadeeva, *J. Organomet. Chem.*, 358 (1989) 363.
- 6 M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiece, *Organometallics*, 5 (1986) 2321.