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Crystal and molecular structures of salts of the secondary permethylmetallocenylmethyl cations $(C_5Me_5MC_5Me_4CHR)^+X^-$ (M = Ru, Os; R = Ph, C_6F_5; X = BF_4, PF_6)

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The structures of tetrafluoroborates of the secondary permethylmetallocenylmethyl cations $[Cp^*MC_5Me_4CHR]^+$ ($Cp^* = C_5Me_5$; **1b:** M = Ru, R = Ph; **1c:** M = Os, R = C_6F_5) were established by X-ray diffraction analysis. The angles of inclination (α) of the C(1)—C(11) bond coordinated to the metal atom with respect to the plane of the C_5Me_4 ligand are 31.5° and 35.6°, and the M—C(11) distances are 2.506 and 2.401 Å in **1b,c**, respectively.

Key words: ruthenium, osmium, permethylmetallocenylmethyl cations, X-ray diffraction analysis, NMR spectroscopy.

Previously,[1—3] we have synthesized salts of the primary permethylmetallocenylmethyl cations $(Cp^*MC_5Me_4CH_2)^+X^-$ ($Cp^* = C_5Me_5$; **2a:** M = Fe, X = $B\{C_6H_3(CF_3)_2\}_4^-$;[1] **2b:** M = Ru, X = BPh_4;[2] **2c:** M = Os, X = BPh_4 [3]) as well as salts of the tertiary nonmethylated cations $(CpMC_5H_4CPh_2)^+X^-$ (**3b:** M = Ru, X = PF_6;[4] **3c:** M = Os, X = PF_6 [5]) and established their structures by X-ray diffraction analysis. It was found that Ru- and Os-containing cations **2b,c** and **3b,c** have very unusual geometric characteristics. Thus, the CR_2 group deviates substantially from the plane of the Cp ring toward the M atom; the angles of inclination (α) of the C(1)—C(11) bond coordinated to the metal atom with respect to the planes of the C_5Me_4 ligands as well as the M—C(11) distances (Table 1) are indicative of an efficient interaction between the carbocationic center and the lone electron pair of the M atom giving rise to the donor-acceptor bond and, as a consequence, of the positive-charge transfer from the C atom to the M atom in primary cations **2b,c**. The latter fact was confirmed by the results of MO EHT calculations.[6]

Table 1. Principal X-ray structural parameters of the cations

Cation	$r_{M-C(11)}$	$r_{M-C(1)}$	$r_{C(1)-C(11)}$	α	β	Reference
	Å			deg		
1b	2.506	2.104	1.405	31.5	10.7	*
1c	2.401	2.086	1.428	35.6	12.5	*
2a	2.567	1.968	1.370	23.6	4.7	1
2b	2.270	2.066	1.401	40.3	6.8	2
2c	2.224	2.069	1.426	41.8	6.9	3
3a	2.715	2.009	1.416	20.7	9.3	9
3b	2.482	2.098	1.421	34.0	11.3	4
3c	2.387	2.088	1.459	38.4	14.1	5

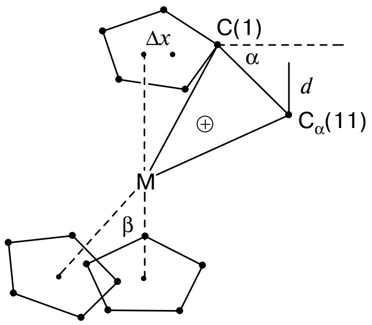
* The present study.

As part of our continuing studies of the effect of the substituents both at the C(11) atom and in the Cp ring on the interaction between the metal atom and the carbocationic center, we carried out X-ray diffraction analysis of two salts of the secondary permethylmetallocenylmethyl cations $(Cp^*MC_5Me_4CHR)^+X^-$ (**1b:** M = Ru, R = Ph, X = BF_4; **1c:** M = Os, R = C_6F_5, X = PF_6) synthesized earlier.[7]

Results and Discussion

Previously, it has been demonstrated (see Table 1) that the replacement of the hydrogen atoms at the carbocationic center by two Ph substituents leads to the elongation of the Os—C_α(11) bond by 0.163 Å (*cf.* compounds **3c** and **2c**) and of the Ru—C_α(11) bond by 0.212 Å (*cf.* **3b** and **2b**) and to the decrease in the angle of inclination α (Scheme 1) by 3.4° and 6.3° for

Scheme 1



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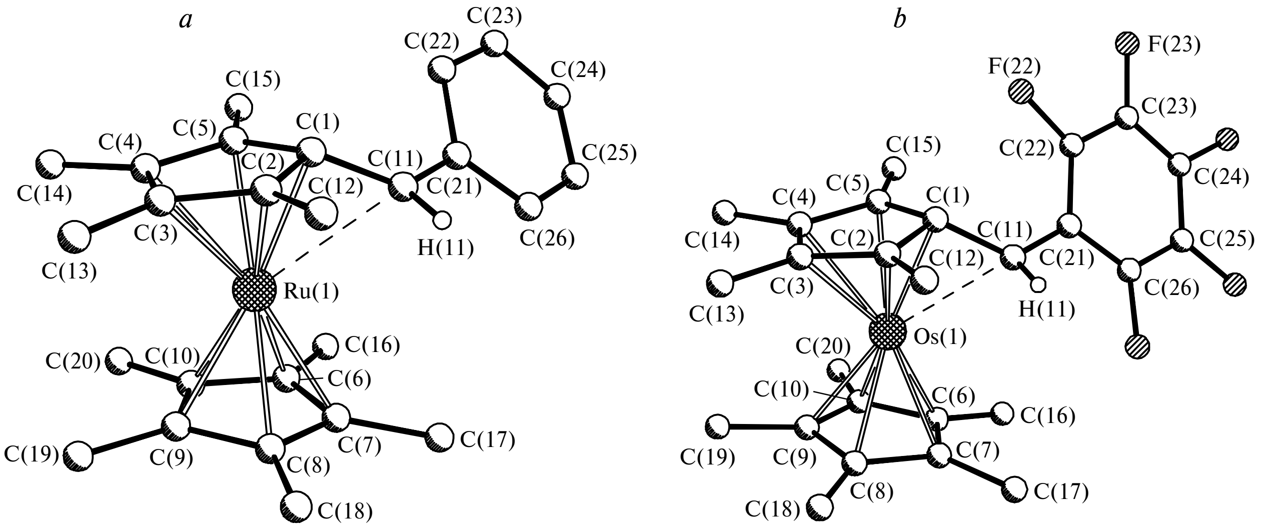

Fig. 1. Structures of cations **1b** (*a*) and **1c** (*b*). The H atoms are omitted except for the H(11) atom at the C(11) atom.

the Os- and Ru-containing cations, respectively. The M—C(1) bonds are also elongated (by 0.019 and 0.032 Å for the Os- and Ru-containing cations, respectively) compared to those found in primary cations **2b,c**. The angles between the planes of the Cp ligands (β) in the Os- and Ru-containing cations are increased by 7.2° and 4.5°, respectively. In addition, the results of X-ray diffraction analysis showed that both Ph substituents in **3b,c** are in the propeller conformation with respect to the C_5H_4 ring.[4,5]

The structures of secondary methylated cations **1b** and **1c** are shown in Fig. 1. The principal geometric characteristics are given in Table 2.

Cations **1b** and **1c** are structurally similar to the compounds of this series, which have been studied by X-ray diffraction analysis previously[1—5] (see Scheme 1).

The displacement of the M atom toward the carbocationic center leads to the redistribution of the M—C bond lengths ($r_{M-C(1)} < r_{M-C(2)} \approx r_{M-C(5)} < r_{M-C(3)} \approx r_{M-C(4)}$). The C(1)—C(2) and C(1)—C(5) bonds are elongated by ~0.05 Å compared to the remaining bonds in the ring due, apparently, to the effect of the carbocationic substituent (see Table 2). In the Ru- and Os-containing cations, the aryl groups are rotated with respect to the C_5Me_4 ligand by 57.9° and

Table 2. Selected bond lengths, bond angles, and torsion angles in cations **1b** and **1c**

Parameter	**1b** (M = Ru)	**1c** (M = Os)	Parameter	**1b** (M = Ru)	**1c** (M = Os)	Parameter	**1b** (M = Ru)	**1c** (M = Os)
Bond	*d*/Å		Bond	*d*/Å		Bond angle	ω/deg	
M—C(1)	2.104(3)	2.086(5)	C(2)—C(12)	1.481(5)	1.489(8)	C(2)—C(1)—C(11)	116.8(3)	116.3(5)
M—C(2)	2.183(3)	2.190(6)	C(3)—C(13)	1.494(5)	1.477(8)	C(5)—C(1)—C(11)	123.5(3)	120.3(5)
M—C(3)	2.257(3)	2.281(5)	C(4)—C(14)	1.495(5)	1.490(8)	C(1)—C(11)—C(21)	127.1(3)	124.8(5)
M—C(4)	2.252(3)	2.261(5)	C(5)—C(15)	1.501(5)	1.486(8)	C(1)—C(11)—H(11)	115(2)	114(4)
M—C(5)	2.173(3)	2.190(5)	C(6)—C(7)	1.438(5)	1.457(8)	C(21)—C(11)—H(11)	115(2)	113(4)
M—C(6)	2.191(3)	2.236(5)	C(7)—C(8)	1.404(5)	1.439(8)			
M—C(7)	2.226(3)	2.201(5)	C(8)—C(9)	1.433(5)	1.452(8)	Torsion angle	φ/deg	
M—C(8)	2.225(3)	2.216(6)	C(9)—C(10)	1.437(5)	1.427(9)	C(3)—C(2)—C(1)—C(11)	−144.0(3)	−139.6(5)
M—C(9)	2.193(3)	2.212(6)	C(6)—C(10)	1.430(5)	1.430(8)	C(2)—C(1)—C(11)—C(21)	−174.3(3)	−169.8(5)
M—C(10)	2.187(3)	2.229(6)	C(6)—C(16)	1.499(5)	1.495(8)	C(1)—C(11)—C(21)—C(22)	23.0(5)	25.9(9)
M—C(11)	2.506(3)	2.401(6)	C(7)—C(17)	1.492(5)	1.486(8)	C(1)—Cp(1)...Cp(2)—C(7)*	18.5	41.1
C(1)—C(2)	1.469(5)	1.465(8)	C(8)—C(18)	1.498(6)	1.479(8)			
C(2)—C(3)	1.410(5)	1.420(8)	C(9)—C(19)	1.490(6)	1.483(8)			
C(3)—C(4)	1.433(5)	1.437(8)	C(10)—C(20)	1.489(6)	1.479(8)			
C(4)—C(5)	1.415(5)	1.416(9)	C(11)—C(21)	1.474(5)	1.471(8)			
C(1)—C(5)	1.470(5)	1.479(8)	C(11)—H(11)	0.98(4)	0.88(7)			
C(1)—C(11)	1.405(5)	1.428(8)						

* Cp(1) and Cp(2) are the geometric centers of the Cp rings C(1)—C(2)—C(3)—C(4)—C(5) and C(6)—C(7)—C(8)—C(9)—C(10), respectively.

65.8°, respectively. It can be seen from the data in Table 1 that the introduction of the aryl substituent leads to the elongation of the Ru—C(11) bond by 0.226 Å (*cf.* **1b** and **2b**) and of the Os—C(11) bond by 0.177 Å (*cf.* **1c** and **2c**) and to the decrease in the angle of inclination by 8.8° and 6.2° in the Ru- and Os-containing secondary cations, respectively, compared to the corresponding primary cations.

In secondary **1b,c** and tertiary **3b,c** cations, the spatial effect of the aryl substituent is complex in character. On the one hand, the bulkier substituents can hinder the approach of the cationic center to the M atom for the purely geometric reasons (the "negative" effect).* On the other hand, the nonparallel arrangement of the C_5Me_4 ligand and the aryl substituent in **1b,c** as well as the propeller arrangement of two phenyl groups and the C_5Me_4 ligand in **3b,c** results in virtually complete disruption of the conjugation between this ligand and the carbocationic center, which leads to the enhancement of the electrophilicity. This, in turn, causes strengthening of donor-acceptor interaction between the lone electron pair of the M atom and the cationic center (the "positive" stereoelectronic effect). Since the M—C(11) bond in cations **1b,c** and **3b,c** is elongated and the α angle is reduced, the "negative" effect, evidently, prevails. Compounds **1b** and **1c** are also characterized by an increase in the β angle (see Scheme 1) by 3.9° and 5.6° for the Ru- and Os-containing cations, respectively.

It is noteworthy that the elongation of the M—C(11) and M—C(1) bonds and the reduction of the α angles in the secondary methylated cations (containing one aryl substituent) compared to the primary derivatives are more noticeable than those observed in the tertiary cations (containing two phenyl substituents). The difference in the changes of the bond lengths and the bond angles in the secondary and tertiary cations compared to the primary derivatives are $\Delta r = 0.024$ Å and $\Delta\alpha = 2.5°$ for the Ru-containing cations (*cf.* **1b** and **3b**) and $\Delta r = 0.014$ Å and $\Delta\alpha = 2.8°$ for the Os-containing cations (*cf.* **1c** and **3c**). It might be suggested that the Me groups at positions 2 and 5 (α and α′) of the Cp ring produce greater steric hindrances than the second Ph substituent at the C(11) atom. However, in the correct comparison, the fact that the C_5Me_5 rings in compounds **1b,c** are stronger electron donors than the Cp rings in **3b,c** (which should lead to weakening of the M—C(11) interaction) must be taken into account. The negative inductive effect of one and two Ph groups (one C_6F_5 group and two Ph groups) must also be considered. Therefore, it is difficult to unambiguously reveal the reasons for the change in the geometric parameters of the cations under study. However, the steric effects, probably, dominate over the electronic factors.

One of the principal conclusions, which can be drawn from Table 1, is that the Fe—C(11) bonds are longer than the Ru—C(11) bonds and the latter are longer than the Os—C(11) bonds in all seven cations under study, *viz.*, in primary **2a,b,c**, secondary **1b,c**, and tertiary **3b,c** cations (and in cation **3a**).[8] This difference is minimum for the primary derivatives: 0.23 Å ($\Delta\alpha = 14.7°$) (**2a,b:** Fe—Ru) and 0.046 Å ($\Delta\alpha = 1.5°$) (**2b,c:** Ru—Os). For the secondary cations, this difference is 0.105 Å ($\Delta\alpha = 4.1°$) (**1b,c:** Ru—Os); for the tertiary cations, the differences are 0.233 Å ($\Delta\alpha = 13.3°$) (**3a,b:** Fe—Ru) and 0.096 Å ($\Delta\alpha = 4.4°$) (**3b,c:** Ru—Os). This fact is attributable to the enhancement of the diffusion character of AO of the metal atom (the covalent radii $r_{Fe} = 1.34$, $r_{Ru} = 1.49$, and $r_{Os} = 1.50$ Å [9]) and, according to the EHT calculations,[6] to the increase in the M—C(11) bond order (0.01 < 0.16 < 0.22) on going from Fe to Ru and then to Os (**1a**→**1b**→**1c**). From the aforesaid, it can be concluded that the interaction is strengthened in the series Fe << Ru < Os.

The C(1)—C(11) bond lengths in the cations under study, are in the range of 1.40—1.46 Å, and this length is slightly increased in the series Fe < Ru < Os. The X-ray diffraction data agree with the results of the EHT calculations[6] according to which the bond order decreases monotonically in the series Fe > Ru > Os (1.16 > 1.03 > 0.98); it is well known that the bond is elongated as its order decreases.

Strengthening of the M—C(11) interaction in the series Fe < Ru < Os can also be confirmed by the ^{13}C chemical shifts for the C(11) atom[7,10] (Table 3). For the methylated primary (**2a—c**), secondary phenyl- (**1b**) and C_6F_5-substituted (**1c**), and tertiary (**3a—c**) cations under consideration, the shielding of the ^{13}C nucleus in the C(11)R′R″ group increases (the chemical shifts $\delta_{^{13}C}$ are decreased) in the series Fe < Ru < Os.

The observed increase in shielding (a decrease in the chemical shift for the C(11) atom) is explicable based on the fact that the shielding constant σ (or its paramagnetic component σ_{para}, which makes the major contribution to this constant) is a function of the charge density and the bond order (in the case under consideration, the M—C(11) bond order increases in the series Fe < Ru < Os). Therefore, the data from X-ray diffraction analysis and ^{13}C NMR spectroscopy correlate with each other and with the results of the EHT calculations.

Table 3. Chemical shifts (δ) of the C(11) atom in the ^{13}C NMR spectra[7,10]

Compound	δ	Compound	δ
1b	104.4	**3b**	139.6
1c	55.7	**3c**	95.7
2a	90.7	$Cp^*FeC_5Me_4CHPh^+$	132.1
2b	74.6	$Cp^*RuC_5Me_4CHC_6F_5^+$	83.9
2c	55.4	$Cp^*OsC_5Me_4CHPh^+$	79.0
3a	171.6		

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* The effect of the steric factors on the structures of the compounds will be discussed elsewhere.

Table 4. Crystallographic data and details of the refinement for compounds **1b** and **1c**

Parameter	**1b**	**1c**
Molecular formula	$C_{26}H_{33}BF_4Ru$	$C_{26}H_{28}F_{11}OsP$
Molecular weight	533.40	770.66
Crystal dimensions/mm	0.2×0.1×0.05	0.2×0.1×0.05
T/K	110(2)	110(2)
Radiation	λ(Mo-Kα)	λ(Mo-Kα)
Space group	$P2_1/c$	$P2_1/n$
a/Å	15.3727(14)	8.8296(18)
b/Å	9.7033(9)	21.144(4)
c/Å	15.7535(15)	13.648(3)
β/deg	95.745(2)	95.736(4)
V/Å^3	2338.1(4)	2535.3(9)
Z	4	4
d_{calc}/g cm^{-3}	1.515	2.019
μ/cm^{-1}	7.14	50.90
Absorption correction	SADABS program	
T_{min}/T_{max}	0.667/0.928	0.513/0.928
F(000)	1096	1496
Scanning mode	φ-ω	φ-ω
$2θ_{max}$/deg	60	60
Number of independent reflections (R_{int})	6842 (0.0612)	7380 (0.0610)
R_1 (based on F for reflections with $I > 2σ(I)$)	0.0503 (4241 reflections)	0.0459 (5170 reflections)
wR_2 (based on F^2 for all reflections)	0.1199	0.1142
Number of parameters in the refinement	449	356
Weighting scheme	$w^{-1} = σ^2(F_o^2) + (αP)^2 + βP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
α	0.0635	0.0620
β	0	0
GOF	0.881	1.002

Experimental

The experimental X-ray data were collected on an automatic Bruker SMART diffractometer. The principal crystallographic characteristics and the details of X-ray data collection and refinement are given in Table 4. Both structures were solved by the direct method and refined by the least-squares procedure based on F^2_{hkl} with anisotropic thermal parameters for nonhydrogen atoms. The positions of the H atoms in **1b** were located from the difference Fourier maps and refined isotropically. The positions of the H atoms in **1c**, except for the H(11) atom at the C(11) atom, were placed in geometrically calculated positions and refined using the riding model.

All calculations were carried out with the use of the SHELXTL-97 program package.[11]

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