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Generation of $[1,2\text{-}(CH_2)_2C_5Me_3MC_5Me_4CH_2\text{-}1']^{3+}$ (M = Ru, Os) trications and determination of their structures by comparing NMR-spectra with density-functional method calculations

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Abstract

A general method for generating $[1,2\text{-}(CH_2)_2C_5Me_3MC_5Me_4CH_2]^{3+}$ trications, where M = Ru (**4a**) and Os (**4b**), from the salts of monocations $[C_5Me_5MC_5Me_4CH_2]^+An^-$ (**1a**,**b**, $An^- = BF_4$) by the action of dioxygen in a solution CF_3SO_3H superacid is presented. The energy characteristics of **4a** and **4b** have been calculated. NMR-spectra have been registered and analyzed. Conclusions received from NMR data for solutions of trications were compared with DFT calculation results of them in the gaseous phase. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Monocations; Dications; Trications; Generation of trications; Metallonium cations; Ruthenium; Osmium; NMR-spectra; Calculations by ab initio density-functional method

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1. Introduction

Methods for synthesizing metallonium[1] $[CH_2C_5Me_4MC_5Me_5]^+$ (**1**) monocations and $[1,2\text{-}(CH_2)_2C_5Me_3MC_5Me_5]^{2+}$ (**2**) and $[(CH_2C_5Me_4)_2M]^{2+}$ (**3**) dications based on decamethylmetallocenes of the iron subgroup metals have been developed by us in previous studies [1–9]. The ease of forming the dications and their high thermodynamic stability [5] suggested that trications of analogous structure could be generated, because the transition metals in the metallocenes have three lone electron pairs (d_{xy}, $d_{x^2-y^2}$, d_{z^2}).

The first Ru-containing $[1,2\text{-}(CH_2)_2C_5Me_3RuC_5Me_4CH_2]^{3+}$(**4a**) trication was recently generated from $(C_5Me_5)_2Ru$ or the salt of the monocation **1a** (M = Ru) by the action of dioxygen in CF_3SO_3H superacid solution [10]. It turned out that the same method is useful for the generation of the Os-containing $[1,2\text{-}(CH_2)_2C_5Me_3OsC_5Me_4CH_2]^{3+}$ trication (**4b**) [11].

In this communication, a general method for generating trications **4a** and **4b** will be described and their structures will be discussed by comparing their NMR-spectra with the results of density-functional calculations of the geometry and energy characteristics of these species.

2. Results and discussion

The investigation of methods for oxidizing decamethylmetallocenes has shown that the most simple and promising is that based on the use of strong proton acids. This method was suitable for generating trications **4a** and **4b** in CF_3SO_3H solution using dioxygen as the oxidizing agent at room temperature. However, the best results in generating trication **4** were obtained by oxidizing the tetrafluoroborates of monocations [M = Ru(**a**); M = Os(**b**)] **1** instead of $(C_5Me_5)_2M$ under the same conditions. The reaction was monitored by ^1H-NMR-spectra. Salts **1** in CF_3SO_3H solution form the

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[1] The strong donor–acceptor interaction of the CH_2^+ group with a lone electron pair of the metal atom forms onium cations, which we call metallonium cations.

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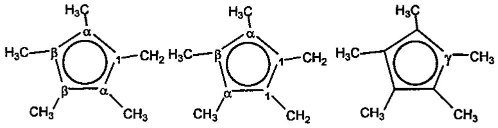
Table 1
The data of ^{1}H-NMR spectra of ruthenium and osmium cationic complexes in CF_3SO_3H [a]

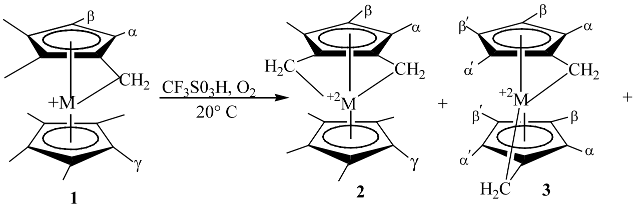
Cation	Chemical shift of protons (δ, ppm)					
	C_5Me_5 (γ)	C_5Me_{5-n} $(CH_2)_n$, $n = 1, 2$				
		α,α'-CH_3	β,β'-CH_3	CH_2^{AB}		$\Delta\delta_{AB}$
1a	1.96	1.71	2.04	4.56 s		–
2a	2.31	2.18	2.51	4.82 d	5.27 d [b]	0.45
4a	–	2.28	2.47	5.50 s		–
		2.33	2.59 (3H)	5.03 d	5.51 d [c]	0.48
1b	1.87	1.56	1.82	4.36		–
2b	2.57	2.14	2.57	4.90 d	5.52 d [d]	0.62
4b	–	2.22	2.74	5.53 s		–
		2.52	3.06 (3H)	5.06 d	5.69 d [e]	0.63

[a] The labeling for the proton atoms in complexes.
[b] $^2J_{HH} = 2.0$ Hz.
[c] $^2J_{HH} = 1.9$ Hz.
[d] $^2J_{HH} = 2.7$ Hz.
[e] $^2J_{HH} = 2.3$ Hz.



protonated products $[C_5Me_5M(H)C_5Me_4CH_2]^{2+}$, which can be identified directly for M = Os in the first step by a ^{1}H-NMR-technique (see Section 3). Completion of the reaction was judged by the absence of changes in the ratio of products upon the addition of new portions of dioxygen. Trications **4** were the main reaction products. In addition, small amounts of the previously described dications **2** and **3** were found (see the NMR-spectra in Tables 1 and 2).

NMR-monitoring indicated that cations **1**–**3** are precursors of trication **4**. This fact together with the NMR-data agree with the structure **4** (Scheme 1).



+ $[1,2\text{-}(CH_2)_2C_5Me_3MC_5Me_4CH_2\text{-}1']^{3+}$
4

Trications **4** are sufficiently stable in CF_3SO_3H solution at 20 °C. However, **4a** decomposes upon addition of CD_3NO_2 to the CF_3SO_3H solution, whereas the more stable **4b** is unreactive to this solvent. The salts **4a** and **4b** have not been isolated in free state, because they are very sensitive to hydrolysis.

The determination of structure of trications **4a** and **4b** at first sight presented no serious problems because their ^{1}H-NMR-spectra (see Table 1) are similar to that of $CH_2C_5Me_4$ and $1,2\text{-}(CH_2)_2C_5Me_3$ fragments in precursors **1** and **2** with the signals shifted downfield. Trications **4** do not contain the C_5Me_5 ring. Thus, in accordance with the ^{1}H-NMR-spectra, the species formed upon oxidation contain three CH_2-groups. The proton signals of these CH_2-groups are deshielded compared with those for dications **2a** and **2b**.

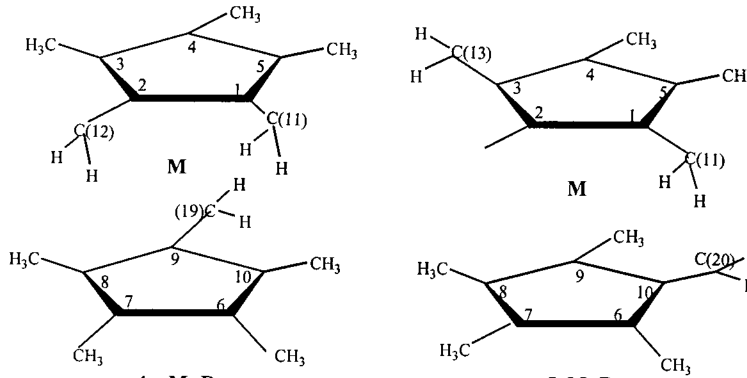
For comparison, the NMR-spectra of **1a**, **1b** and **2a**, **2b** have also been included in the Tables 1 and 2. The appearance of signals for the three CH_2-groups as two doublets and one singlet indicates that trications **4** have a plane of symmetry. The identical differences $\Delta\delta_{AB}$ for trications **4** and dications **2a** and **2b** (Table 1) is also consistent with the 1,2-position of the CH_2-groups in the $C_5Me_3(CH_2)_2$-fragment of trications **4**.

The structure of trications **4** is also supported by the ^{13}C-NMR-data (Table 2). In the ^{13}C-NMR-spectra, the three carbon atoms of the CH_2-groups appear as triplets. Both carbon atoms of the $1,2\text{-}(CH_2)_2$ groups ($C(11)H_2$ and $C(12)H_2$, see below) with chemical shifts $\delta = 88.57$ ppm for **4a** and $\delta = 71.32$ ppm for **4b** exhibit $^1J_{CH} = 172$ Hz, which is close to that for dications **2a** and **2b** ($^1J_{CH} = 171$ Hz).The signals of the third CH_2 group ($C(19)H_2$, see below) are at 65, 66 ppm($^1J_{CH} = 157$ Hz) for **4a** and at 65.75 ppm ($^1J_{CH} = 157$ Hz) for **4b** and practically coincide. It is important to note that the last signals experience an upfield shift. Their weak sensitivity to the nature of the metal (Ru or Os) is interesting.

Table 2
The data of ^{13}C-NMR spectra of ruthenium and osmium cationic complexes [a]

Cation	Medium	Chemical shift of carbon atoms (δ, ppm)($^1J_{CH}$, Hz)							
		CH_2	α,α′-CH_3	β,β′-CH_3	γ-CH_3	Carbon atoms of the Cp* rings			
						C_1	C_α	C_β	C_γ
1a	CD_2Cl_2	74.67 t (164)	8.01	8.74	9.51	105.36	107.20	97.22	96.91
2a	CF_3SO_3H Oleum	87.25 t (171)	8.52	9.18	9.59	137.37	125.89	110.29	112.01
4a	CF_3SO_3H	65.66 (157)	9.22	10.09	–	99.50	114.01	107.16	–
		88.57 (172)	9.28	10.09		138.50	128.44	110.35	
1b	CD_2Cl_2	55.36 (166)	7.64	8.47	9.03	95.82	99.68	90.61	92.51
2b	CF_3SO_3H Oleum	70.92 (171)	9.41	10.23	10.00	134.66	115.06	105.53	107.58
4b	CF_3SO_3H	65.75 (157)	8.67	9.28	–	93.20	108.45	102.80	–
		71.32 (172)	8.71	9.47	–	135.12	116.80	106.93	–

[a] The labeling for the carbon atoms is analogous Table 1.



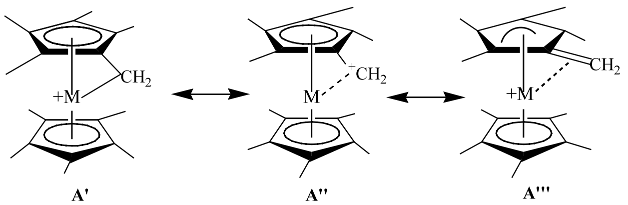
4a, M=Ru
4b, M=Os

5, M=Ru

Scheme 1.

The discussion of the ^{1}H-NMR-spectra data for trications **4a** and **4b** should take into account that, in contrast to X-ray analysis, this method is not direct and is more difficult to use for the determination of structural details and especially the mechanism of stabilization of all three carbocation CH_2-groups.

In a previous report [9] we proposed interpreting the structure of monocations **1** (where M = Fe, Ru, Os) in terms of a specific resonance hybrid A, which is determined by the contributions of metallonium form A′ and carbocation form A″. Earlier [12], another resonance form A‴ was proposed.



A′ A″ A‴

Thus, the mechanism of stabilization of carbocation CH_2-groups depends on the contributions of the form A′, A″ and A‴. It seems expedient to use the same concept in the case of trications **4**. However, for this purpose it was necessary to have an idea about the geometry of the species. To obtain these data and energy characteristics of trication **4** in the gas phase, we also calculated them by the ab initio density-functional method [4][2] and compared these results with the NMR-data. Naturally, such a comparison can be correct only if the conditions of different phase states are taken into account.

The density-functional calculations for two conformers of decamethylmetallocenes in the gas phase have shown that the eclipsed conformation is energetically more favorable than the staggered one by 1.8 kcal mol^{-1}. Therefore, the eclipsed conformation was chosen as initial one for optimizing the energies of the trications, formed from $(C_5Me_5)_2M$.

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[2] It should be noted for the calculation of cations **1**–**4** that only methods that take into account the electron correlation energy, such as the density-functional method, are useful. The Hartree–Fock method, as we have found, shows all CH_2-groups lying in the plane of the cyclopentadienyl ring [13].

The calculations of trications **4a** and **4b** were performed with consideration of the NMR spectra data. The hypothetical isomeric trication [1,3-$(CH_2)_2C_5Me_3$-$RuC_5Me_4CH_2$-1′]$^{3+}$ (**5**) has also been calculated to compare its geometry with that of **4a**. The structures of these ions are given in Scheme 1. Table 3 lists the results of calculating the full energies (E, in a.u. of energy), some interatomic distances (in Å), and dihedral angles and α-angles (α-angles of the tilt of CH_2-groups from the plane of cyclopentadienyl rings) (in °).

Table 3
Results of calculations for trications **4a**, **4b** and **5**

Parameters	**4a**	**4b**	**5**
Bond distances			
M–C(1)	2.202	2.217	2.714
M–C(2)	2.338	2.217	2.427
M–C(3)	2.740	2.667	2.191
M–C(4)	2.939	2.938	2.419
M–C(5)	2.649	2.644	2.672
M–C(6)	2.451	2.463	2.393
M–C(7)	2.419	2.490	2.553
M–C(8)	2.317	2.335	2.543
M–C(9)	2.238	2.218	2.293
M–C(10)	2.309	2.316	2.228
M–C(11)	2.442	2.431	3.804
M–C(12)	2.925	2.435	3.518
M–C(13)	–	–	2.459
M–C(19)	2.950	2.768	3.417
M–C(20)	–	–	2.815
C(1)–C(2)	1.514	1.517	1.490
C(1)–C(5)	1.480	1.474	1.502
C(1)–C(11)	1.418	1.428	1.392
C(2)–C(3)	1.476	1.478	1.476
C(2)–C(12)	1.395	1.428	1.501
C(3)–C(4)	1.474	1.470	1.500
C(3)–C(13)	1.498	1.503	1.421
C(4)–C(5)	1.460	1.479	1.448
C(4)–C(14)	1.495	1.493	1.507
C(5)–C(15)	1.502	1.502	1.499
C(6)–C(7)	1.479	1.483	1.464
C(6)–C(10)	1.465	1.470	1.496
C(6)–C(16)	1.502	1.502	1.499
C(7)–C(8)	1.471	1.466	1.462
C(7)–C(17)	1.503	1.502	1.506
C(8)–C(9)	1.497	1.504	1.484
C(8)–C(18)	1.503	1.509	1.499
C(9)–C(10)	1.504	1.503	1.498
C(9)–C(19)	1.403	1.411	1.503
C(10)–C(20)	1.506	1.507	1.400
Bond angles			
M–C(1)–C(11)	81.74	80.51	133.14
M–C(11)–C(1)	63.17	64.09	31.38
M–C(2)–C(12)	100.10	80.70	–
M–C(12)–C(2)	51.89	63.96	–
M–C(3)–C(13)	–	–	82.87
M–C(13)–C(3)	–	–	62.15
M–C(9)–C(19)	105.96	96.94	–
M–C(19)–C(9)	46.82	52.68	–
M–C(10)–C(20)	–	–	99.23
M–C(20)–C(10)	–	–	51.37
α(1)	20.8	27.2	2.5
α(2)	11.7	26.2	–
α(3)	–	–	24.9
α(9)	13.4	20.4	–
α(10)	–	–	16.6
γ	12.9	5.7	15.7
The total energy, −E (a.u.)	870.5845	867.7329	870.5823

In considering the geometry of trications **4a** and **4b** it should first of all be noted that they preserve in general the sandwich structure, although it is more distorted than for the mono- and dication structures [14].

The fact that the lengths of the ordinary covalent bonds C_{ring}–C_{ring}, C(1)–C(11), C(2)–C(12) and C(9)–C(19) do not differ significantly from those in the mono- and dications is important. The distortion results in the shortening of the M–C(1), M–C(2) and M–C(9) bonds compared with the bonds of the metal atoms to the other carbon atoms of this ring. The lengths of the bonds M–C(11), M–C(12), M–C(19) increase in comparison with **2** and **3**, whereas the α tilt angles decrease. The markedly distorted sandwich structure of the trications results in an increase of the dihedral angles between the five-membered rings: for **4a**, 12.9°; **4b**, 6.3°; for **1b**, 6.8°; **2b**, 4.3°. The interatomic M–CH_2 distances and tilt α-angles in trications **4a** and **4b** show that the characteristics of the Ru-containing cation differ substantially from those of the osmium analogue.

The calculation of **4b** pointed out that the interatomic distances M–C(11)H_2 and M–C(12)H_2 in the gas phase are quite short and equal to 2.431 and 2.435 Å with tilt angles $\alpha_1 = 27.2°$ and $\alpha_2 = 26.2°$ (for comparison, the M–CH_2 bond in monocation **1b** is equal to 2.224 Å, $\alpha = 41.8°$ and, in dication **2b**, M–C(11)H_2, 2.401 Å, $\alpha_1 = 31.24°$; M–C(12)H_2, 2.232Å, $\alpha_2 = 31.11°$) [14]. Consequently the C(11)H_2 and C(12)H_2-groups in trication **4b** form direct (metallonium) bonds to the metal atom, which may be described by the form A′ in both cases.

In contrast, the third C(19)H_2 group gives a weak M–C(19)H_2 bond, which is stretched to 2.768 Å with $\alpha_3 = 20.4°$. Therefore, the resonance hybrid A in the case of the trication with the M–C(19)H_2 bond is dominated by the contribution of the A″ and especially the A‴ forms. The increase in the contribution of A‴ is supported by the very short length of the C(9)–C(19)H_2 bond (1.411 Å) compared with the C(1)–C(11)H_2 and C(2)–C(12)H_2 bonds, which are equal to 1.428 Å. Therefore, the structure of the trication in the gas phase may be described by formula **4b**, which contains a fulvene fragment[3].

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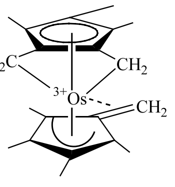
[3] It should be noted that the dotted line in formula **4** signifies a weak bond.

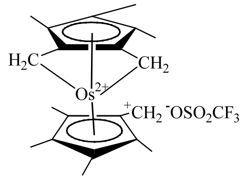


4b (M = Os)

The presence of the fulvene fragment in **4b** is accordance not only with the short C(9)–C(19)H_2 bond but also with the C_{ring}–C_{ring} bonds, the lengths of which are characteristic of the fulvene ring.

The ^{1}H-NMR-spectrum is consistent with the structure of the trication **4b**. In CF_3SO_3H solution the three signals of the CH_2-groups can be seen with $\delta = 5.06$ ppm (d), 5.69 ppm (d) (AB-system) and 5.53 ppm (s).

The ^{13}C-NMR-spectrum is the most informative and shows that the C(19)H_2 group has the signal shifted upfield at $\delta = 65.75$ ppm ($^1J_{CH} = 157$ Hz) compared with those of the C(11)H_2 and C(12)H_2 groups ($\delta =$ 71.32 ppm, $^1J_{CH} = 172$ Hz). This indicates that the C(19)H_2 group is noticeably different from the other two and points to a different type of stabilization of this group by the metal atom, which is in accordance with the structure **4b**. Therefore, the C(19)H_2 group is stabilized by the metal atom not by direct interaction, but mainly by electron donation from the metal atom through the fulvene ligand. It should be noted that the reported chemical shifts for CH_2-groups of fulvene complexes $[\{Me_3P)_3Rh(C_5Me_4CH_2)\}^+Cl^-]$ ($^{13}\delta_{CH2}$ 73.4 ppm) are similar [15]. However, in discussing the structure of the Os-containing trication, the carbocationic contribution A″ and the ability of the C^+(19)H_2 group to be stabilized by the CF_3SO_3-anion with the formation of a tight ion pair (complex **4b**′) or the $CF_3SO_2OCH_2$-σ-bound (complex **4b**″) should be kept in mind.



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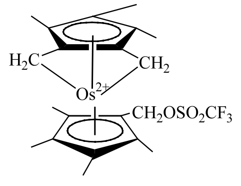


4b′ *4b″*

However, the signal of the C(19)H_2 group in the ^{13}C-NMR-spectrum of **4b**′ should be deshielded compared with the signals of the C(11)H_2 and C(12)H_2 groups.

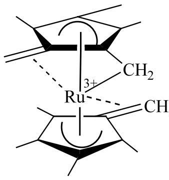
The formula **4b**″ seems to be more compatible with the NMR-data, than **4b**′, because the chemical shift of δ_{CH2}-group in the ^{13}C-NMR-spectrum of **4b**″ should be very shielded and close to that of the CH_2-group in a compound such as $C_5Me_5OsC_5Me_4CH_2OH$ ($\delta_{CH2} =$ 56.7 ppm). Besides, there are some objections against the structure **4b**′ and **4b**″. They are the following:

1. Complex **4b**″ is a dication (analog of **2b**). It is not clear, why the excess of O_2 does not promote further oxidation of the methyl groups, as occurred in the case of **2b**.
2. The addition of CD_3NO_2 to the reaction products does not change the NMR-spectra and the dissociation of the $CF_3SO_2O^-CH_2{}^+$-group has not been observed.

In conclusion, we find that structure **4b** is most attractive for the complex prepared by the oxidation of **1b** in CF_3SO_3H solution.

The interpretation of the structure of the Ru-containing trication is very complicated. The calculation showed that a short Ru–C(11)H_2 bond equal to 2.442 Å with $\alpha_1 = 20.8°$ is formed in the gas phase due to the strong interaction of the metal atom with only one CH_2-group (C(11)H_2). The two other C(12)H_2 and C(19)H_2 groups in different cyclopentadienyl rings are bonded and form rather elongated Ru–CH_2 bonds (Ru–C(12)H_2 = 2.925 Å, Ru–C(19)H_2 = 2.950 Å. Their tilt α-angles ($\alpha_2 = 11.7°$, $\alpha_3 = 13.4°$) are significantly less than α_1.

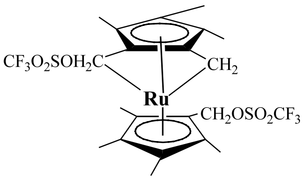
This indicates that the Ru-containing complex is less stable that **4b**. Thus, in terms of the resonance hybrid A, this is a trication in the gas phase in which one C(11)H_2 group is stabilized mainly by direct interaction with the metal atom (form A, metallonium bond) and two other groups (C(2)H_2 and C(19)H_2) with participation mainly of form A‴ with the formation of fulvene fragments. In accordance with this interpretation, the Ru-containing trication in the gas phase may be described by the structure **4a**′.



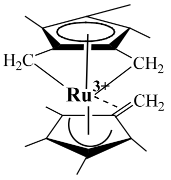
4a′

However, the Ru-containing complex, prepared in CF_3SO_3H solution, has, based on ^{1}H- and ^{13}C-NMR-spectra, the structure **4a**, similar to the structure of the Os-containing trication **4b**. Indeed, the ^{1}H-NMR-spectrum of trication **4a** has three signals for CH_2-groups with $\delta = 5.03$ (d), 5.51 (d) (AB-system), 5.50 (s) ppm. In the ^{13}C-NMR-spectrum, there are two signals with $\delta = 88.57$ ppm ($^1J_{CH} = 172$ Hz) and 65.66 ppm ($^1J_{CH} =$ 157 Hz). The different structures of the Ru-containing trication in the gas phase and in CF_3SO_3H solution indicate that the length of the M–C(12)H_2 bond is changed by a change of the phase state. In our earlier paper [14], we paid attention to the special properties of donor–acceptor M^+–CH_2-bonds, formed by the interaction of the p-orbital of carbocationic CH_2^+ groups with the lone electron pairs of metal atoms. The lengths of these bonds, in contrast with the covalent C–C and M–C_{ring} bonds, vary over wide limits upon transfer from one phase state to another. It is also possible that the less stable trication **4a** is more sensitive to a change of the phase state.

Finally, it should be noted that structures with two $-^{+}CH_2O^{-}SO_2CF_3$ (**4a″**) or $CH_2OSO_2CF_3$(**4a‴**) for the Ru-containing complex in CF_3SO_3H solution are incorrect because they should have NMR-spectra different from that of **4a**. This also provides evidence against the formation of structures **4a′** and **4a″**, as in the case of the Os-containing complex.



4a‴



4a

For comparison with **4a**, we have also calculated the hypothetical Ru-containing trication **5**. It turned out that this trication is less stable than **4a** (the difference between their full energies is 1.4 kcal mol^{-1}). For structure **5**, the Ru–C(13) distances are 2.459 Å; Ru–C(20), 2.815 Å; and Ru–C(11), 3.804 Å. This shows the presence of one strong Ru–C(13) interaction and one weak Ru–C(20) interaction, and the complete absence of a Ru–C(11) interaction. The $C(11)H_2$ group is situated practically within the plane of the cyclopentadienyl ring (angle $\alpha = 2.5°$) and consequently is carbocationic in character. In this case only carbocation form A″ contributes to the resonance hybrid A. It is interesting to note that the trication **5** resembles the anti-conformation for the heteroannular Ru-containing dication **3** [14].

For estimating the thermodynamics of formation of polycharged-cations of the following formula: $[C_5Me_n(CH_2)_{5-n}MC_5Me_m(CH_2)_{5-m}]^{(10-m-n)+}$, we consider the hypothetical processes of H_2 cleavage by the action of a proton on a neutral molecule of decamethylmetallocene or the cation with a smaller positive charge. For the sake of simplicity, we restrict our consideration to the case of zero temperature, the enthalpies of the processes depending only on the changes in full energies. For such an estimation, we use the results of calculations from the present and previous papers [14]. The formation of the monocation **1a** ($n = 5$, $m = 4$) results in the elimination of energy equal to -232.2 kcal mol^{-1}; of 1,2-dication **2a** ($n = 5$, $m = 3$) from the monocation, -124.5 kcal mol^{-1}, and of trication **4a** from 1,2-dication **2a**, -13.6 kcal mol^{-1}. We have also calculated the ruthenium tetracation ($n = 3$, $m = 3$) using the BLYP/LanL2DZ density-functional method and have received a value for the full energy equal to -869.3230 a.u. The calculation of the enthalpy of formation of the tetracation from trication **4a** results gives a value of $+60.3$ kcal mol^{-1}, i.e. the process of formation should be followed by the absorption of energy. These estimates suggest that the tetracation forms with the consumption of energy if the trication forms with a small energy gain. Consequently, it can hardly be synthesized. This demonstrates the very important role of unpaired electrons of transition metals in stabilization of carbocation centers.

3. Experimental

NMR-spectra were measured on a Bruker AMX-400 spectrometer (400.13 and 100.61 MHz for ^{1}H and ^{13}C, respectively). C_6D_6 was used as an external standard for acid solutions (δ C_6D_5H 7.25 and 127.96 ppm for ^{1}H and ^{13}C, respectively).

The calculations for trications, formed from decamethylmetallocenes of ruthenium and osmium in the gas phase, were made within the framework of the density-functional theory (BLYP) [16,17] using the program GAUSSIAN-98 [18] on supercomputer CRAY J-90 (National Energy Research Supercomputer Center, Berkeley, California, USA). Geometrical structures of ions were optimized using the Dunning-Hay bi-exponential atomic basis set and pseudo-potentials LanL2 for ruthenium and osmium atoms [19]. A similar level of calculations was used successfully by one of the authors in a previous study of the geometrical and electronic structure of heavy metal complexes [20,21].

*3.1. Generation of trications **4***

Salts of cation **1** (An = BF_4) [2] were oxidized in CF_3SO_3H solution in a 0.7 ml NMR tube (for monitoring) that was treated with portions of dioxygen at regular intervals. ^{1}H-NMR-monitoring demonstrates at first the formation of the protonated product **1**, which may be easy identified in the case of Os-containing complex $[C_5Me_5M(H)C_5Me_4CH_2]^{2+}$ (δ, ppm: 2.57s (15H, C_5Me_5); 2.17s, 2.31s, 2.51s, 2.98s (3H × 4, α- and β-Me); 5.17s, 5.79s (2H, CH_2); -15.40s (1H, OsH). The end of the reaction was judged by the absence of changes in the ratio of products upon the addition of a new portion of dioxygen (ca. three portions). The ratio of products is: 4:2:3 (for **4a**) = 57:21:22% and 4:2:3 (for **4b**) = 81:11:8%.

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