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Single-, double-, and triple-charged cations based on iron-subgroup decamethylmetallocenes

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Methods for the synthesis and structures of metallocenylmethyl cations are considered using stable permethyl derivatives as examples. The simplest and most convenient procedure for the preparation of mono-, di-, and trications involves oxidation of permethylmetallocenes (M = Ru or Os) with oxygen in the presence of strong protic acids. Based on the results of physicochemical studies (X-ray diffraction analysis, ^{1}H and ^{13}C NMR spectroscopy) and quantum-chemical calculations (density functional theory), a resonance hybrid with contributions of the metallonium (onium), carbocationic, and fulvene structures was proposed for the description of the structures of these cations.

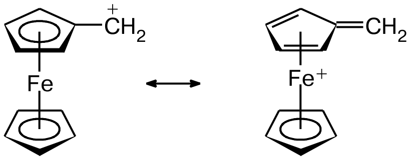
Key words: metallocenylmethyl cations, metallonium cations, carbocations, permethylmetallocenes, iron, ruthenium, osmium, synthesis, quantum-chemical calculations, X-ray diffraction analysis, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy.

Introduction

Carbenium ions are the important subject of research in theoretical, preparative, and industrial organic chemistry. However, carbocations containing organometallic fragments at the α position were not adequately studied. Among these compounds, the metallocenylmethyl cations are of special interest. The chemistry of these cations attracted attention shortly after the discovery of ferrocene when the ferrocenyl fragment was shown to have a high ability to stabilize the carbocationic center.[1,2]

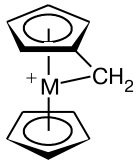
The ferrocenylmethyl cation $[C_5Me_5FeC_5Me_4CH_2]^+$, which is the simplest representative of cationic complexes, appeared to be rather unstable and its salts were not isolated in the solid state. Its structure was proposed based on the data from kinetic studies of the solvolysis of its derivatives, stereochemistry of the resulting products, spectroscopic characteristics, and results of X-ray diffraction analysis for cations (secondary and tertiary) substituted at the α-carbocationic center, such as $[C_5Me_5FeCPh_2]^+$ and $[(C_5Me_5FeC_5Me_4)_2CH]^+$.[3,4] X-ray diffraction study of these cations confirmed the presence of a through-space interaction between the Fe and C_α^+ atoms, which is manifested in the deviation of the exocyclic C—C_α^+ bond from the plane of the Cp ring toward the metal atom. However, the available results of investigations did not provide unambiguous evidence for the mechanism of stabilization and the bonding character because this process is influenced by the substituents at the α-carbocationic center. These substituents can exert not only electronic but also steric effects on this center. Many hypotheses were proposed[1,2] based on the available data on the structures and mechanism of stabilization of the carbocationic centers in cations. After an extensive discussion, two hypotheses were formulated. According to one hypothesis, stabilization occurs *via* the electron transfer from the metal atom to the carbocationic center through the ligand. The structure of this cation is described by the resonance hybrid[1] (Scheme 1).

Scheme 1



An alternative description of the structure involves the direct through-space interaction between the metal atom and the carbocationic center.

According to a more recent hypothesis,[5] this cation is described by the "specific" resonance hybrid **A** with particular contributions of several structures, *viz*., metallonium (onium) **A**´, carbocationic **A**″, and fulvene **A**´´´ structures



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† Deceased.

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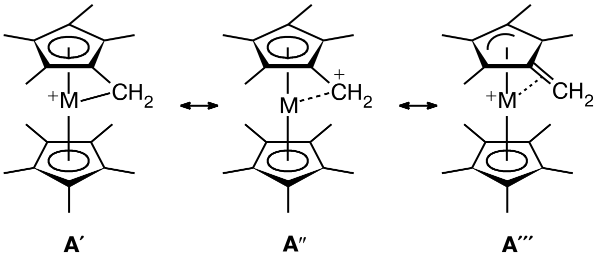
(Scheme 2). (The possibility of the occurrence of the structures **A**´—**A**´´´ will be considered below.)

Scheme 2



Investigations of these primary cations were of considerable interest. Their structures can be studied not only by indirect spectroscopic methods but also by direct X-ray diffraction analysis. Because of this, the permethylated metallocenylmethyl cations $Cp^*MC_5Me_4CH_2^+$ (**1**) of all iron-subgroup metals (M = Fe (**1a**), Ru (**1b**), Os (**1c**); Cp* = C_5Me_5) were chosen as suitable model compounds. The presence of nine Me groups facilitates stabilization of these cations. Studies[6,7] of complexes of all iron-subgroup metals made it possible to follow the changes in the properties depending on the nature of the metal atom because not only the size of the metal atom but also its basicity and nucleophilicity vary in the subgroup of the Periodic system from the top down.

More recent detailed studies discovered other unique characteristic features of these models. It appeared that stabilization of the carbocationic centers in these compounds can occur with the involvement of one, two, or even three lone pairs of the metal atom, which made it possible to prepare both mono- and polycharged cations.

Methods for the synthesis of iron-subgroup monocations 1*

Three-step synthesis. A method was developed for the preparation of salts with cations **1** (Scheme 3) based on oxidation of iron-subgroup decamethylmetallocenes to aldehydes (**2**) followed by their reduction with $LiAlH(OBu^t)_3$ or organolithium compounds LiR to primary alcohols (**5**) or secondary alcohols (**6—9**), respectively. The corresponding cations **1** and **10—12** were prepared from alcohols **5—9** under the action of protic acids (Scheme 3, path *a*).[8—16]

Permethylated ruthenocene and osmocene primary cations **1b,c** proved to be the most stable.[14,15] Salts with less stable ferrocene cation **1a** are, in turn, much more stable than $CpFeC_5H_4^+An^-$. Salts **1a** were isolated in the solid state and characterized by elemental analysis. Their solutions were also studied by ^1H and ^{13}C NMR spectroscopy.[8] However, these salts rapidly undergo redox transformations upon storage to give the coupling products $[Cp^*Fe^{+\bullet}C_5Me_4CH_2]_2An^-{}_2$.[13] For this reason, crystals suitable for X-ray diffraction analysis were isolated only for a salt with the bulky $\{B[C_6H_3(CF_3)_2\text{-}3,5]_4\}^-$ anion.[16]

The three-step procedure developed for the synthesis of monocations **1a—c** is universal because it allows one to prepare salts with all iron-subgroup cations. In particular, the advantage of this procedure is that it made it possible to synthesize difficultly accessible previously unknown functional derivatives of permethylated metallocenes, *viz.*, aldehydes $Cp^*MC_5Me_4CHO$ (**2**), the corresponding alcohols (**6a—c**, **7a—c**, **8a—c**, **9a,b**), and their derivatives.[8—16] Homoannular (**3a—c**) and heteroannular dialdehydes (**4a—c**), which were obtained according to this procedure as by-products of oxidation of $Cp_2{}^*M$, were transformed into diols **13a—c** and **14a—c** and further into dications **15a—c** and **16a—c**, respectively, following the same Scheme 3 (path *b*)[17,18] (see below).

Synthesis of monocations 1b and 1c by one-electron oxidation of Cp^*_2M (M = Ru or Os). A procedure for the synthesis of the salt with Ru-containing cation **1b** by oxidation of Cp^*_2Ru with silver salts AgAn (An^- = $CF_3CO_2^-$ or BF_4^-) was proposed[19,20] virtually simultaneously with the three-step method developed by us. The initially formed $[Cp^*_2Ru]^{+\bullet}$ radical cation is rather unstable and undergoes disproportionation to give cation **1b** and the starting decamethylruthenocene. Later on, it was found[21] that Cp^*_2Os also can undergo analogous transformations under the action of silver salts. However, the $[Cp^*_2Os]^{+\bullet}$ radical cation undergoes disproportionation much slower than the ruthenium-containing analog.*

One-electron oxidation is of preparative interest because this reaction can be performed as a one-pot procedure thus readily producing salts with cations **1b** and **1c**. More recently, it was found[22] that this procedure is virtually universal for all ruthenocenes and osmocenes containing the CHR´R″ substituents in the Cp rings, *i.e.*, for compounds of the $LMC_5R_4CHR'R''$ type (M = Ru, Os; L = Cp, Cp*, η^5-C_9H_7 (indenyl); R, R´, R″ = H, Me). It was demonstrated[22] that oxidation of LRuCp* (L = Cp, Cp*, η^5-C_9H_7) with $AgBF_4$ or $Ph_3C^+BF_4^-$ afforded the $[LMC_5R_4CH_2]^+BF_4^-$ salts and oxidation of its indenyl derivative gave rise to the product of its haptotropic rearrangement $[\eta^6\text{-}C_9H_8RuCp^*]^+BF_4^-$ (Scheme 4).

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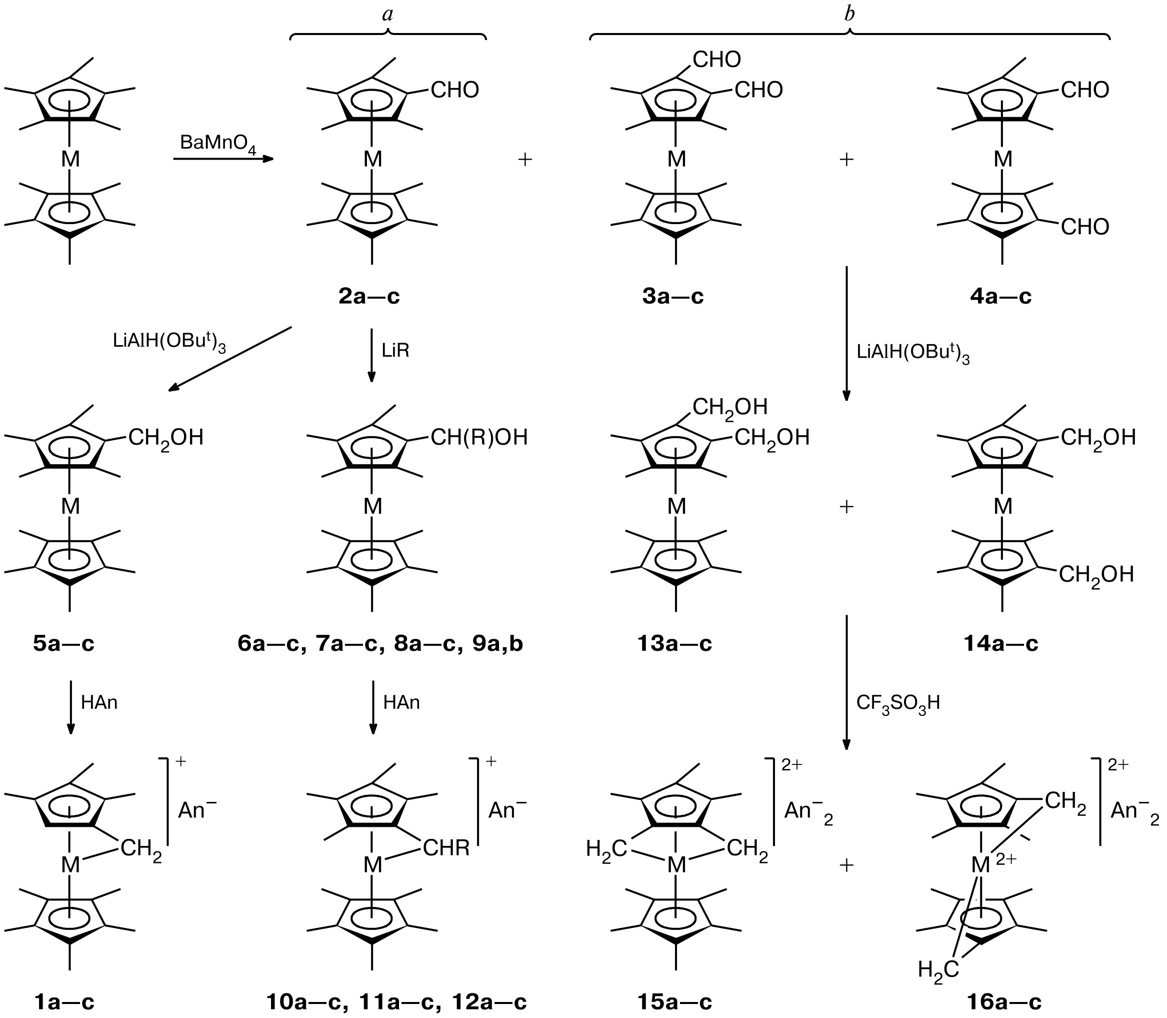
* The word combinations "synthesis of cations" and "preparation of cations" are used for brevity. In actuality, salts with the corresponding cations are obtained. Analogously, the cations mentioned in the text are sometimes illustrated by the formulas of the corresponding salts rather than cations.

* In the study,[21] such properties, as high stability and inability to undergo the transformation into cation **1c**, were erroneously ascribed to the $[Cp^*_2Os]^{+\bullet}$ radical cation.

Scheme 3



M = Fe (**a**), Ru (**b**), Os (**c**); R = Ph (**6**, **10**), $C_6H_2Me_3$ ≡ Mes (**7**, **11**), C_6F_5 (**8**, **12**), Me (**9**)

An is an anion

Scheme 4

$$2\ \eta^5\text{-}C_9H_7RuCp^* + 2\ AgBF_4 \longrightarrow$$

$$\longrightarrow 2\ [\eta^5\text{-}C_9H_7RuCp^*]^{+\bullet}BF_4 \longrightarrow$$

$$\longrightarrow [\eta^5\text{-}C_9H_7RuC_5Me_4CH_2]^+BF_4^- +$$

$$+ [\eta^5\text{-}C_9H_7Ru(H)Cp^*]^+BF_4^- \longrightarrow$$

$$\longrightarrow [\eta^6\text{-}C_9H_8RuCp^*]^+BF_4^-$$

The presence of an acceptor group in the metallocene molecule, such as the aldehyde (CHO) or metal-cluster ($Os_3(\mu\text{-}CO)(CO)_{10}(\mu\text{-}H)$) fragment, does not hinder oxidation and disproportionation to form a mixture of products consisting of substituted cations[23] (Scheme 5).

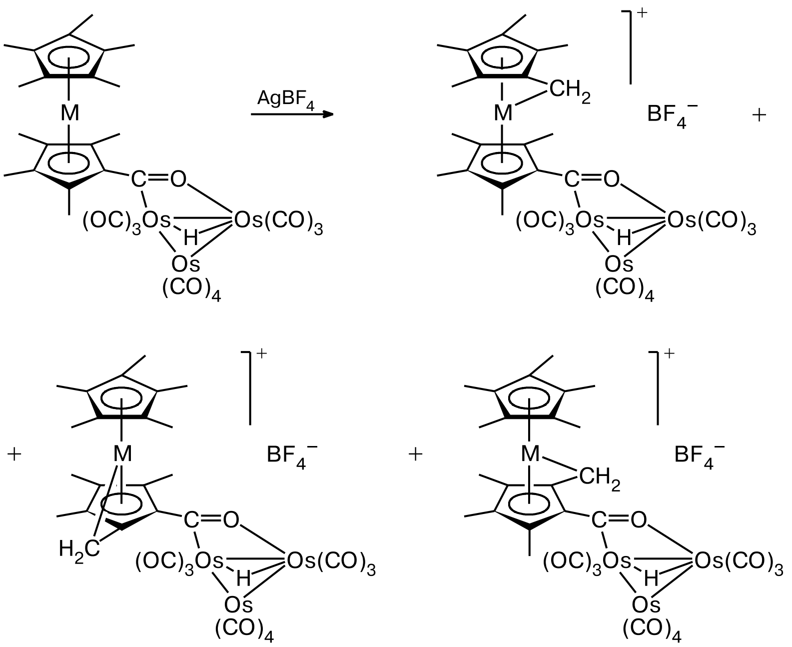
However, this procedure is unsuitable for the synthesis of Fe-containing cation **1a** because oxidation of Cp^*_2Fe with silver salts is terminated at the step of formation of the $Cp^*_2Fe^{+\bullet}$ radical cation, which does not react with nucleophiles. An ingenious preparative procedure was proposed[24] for the synthesis of cation **1a** from $Cp^*_2Fe^{+\bullet}$. This procedure involves the reaction of the radical cation with strong base (MeONa) followed by the transformation of the resulting ether $Cp^*FeC_5Me_4CH_2OMe$ (the yield was 50—60%) into cation **1a** under the action of strong acids.

Electrochemical oxidation. Investigations of electrochemical oxidation of decamethylruthenocene and -osmocene made it possible to propose the detailed mechanism of one-electron oxidation. According to the data from cyclic voltammetry, reversible one-electron

Scheme 5

$Cp^*MC_5Me_4CHO + AgBF_4 \longrightarrow$

$\longrightarrow [Cp^*MC_5Me_3(CHO\text{-}2)CH_2\text{-}1]^+BF_4^- + [(C_5Me_4CHO\text{-}1')M(C_5Me_4CH_2\text{-}1]^+BF_4^-$



M = Ru, Os

oxidation giving rise to the 17-electron $Cp^*{}_2M^{+\bullet}$ radical cations is typical of all $Cp^*{}_2M$. The ability of metallocenes to be oxidized changes[25] in the following $Cp^*{}_2M$ series ($E^{\mathrm{Ox}}{}_{1/2}$/V): $Cp^*{}_2Fe$ (0.12) < $Cp^*{}_2Os$ (0.58) < < $Cp^*{}_2Ru$ (0.73).

The examination of a possible scheme of electrochemical oxidation of decamethylmetallocenes and their indenyl analogs (**A**) showed[26,27] that the electrochemically generated 17-electron $Cp^*{}_2M^{+\bullet}$ radical cations (**B**) (M = Ru or Os) are involved in rapid reactions with nucleophiles to form the 19-electron $[Cp^*{}_2M(Nu)]^{n+\bullet}$ species (n = 0, 1) (**C**) followed by the reactions of these odd-electron intermediates to give permethylated cations **1b,c**. Unfortunately, the electrochemical procedure is inapplicable as a preparative method for the synthesis of salts **1b,c** because of the problems associated with the separation of two salts, *viz.*, the reaction product and supporting electrolyte.

Oxidation method based on photolysis of decamethylmetallocenes in a proton-containing medium. The examination of various conditions for oxidation of decamethylmetallocenes in the presence of strong protic acids CF_3COOH, HBF_4, or HPF_6 revealed very interesting properties of these compounds. Decamethylmetallocenes of Group VIII elements are rather strong Lewis bases capable of reacting with protic acids to form protonation products, *viz.*, cationic hydrides $[Cp^*{}_2MH]^+$ (M = Fe, Ru, or Os). The presence of hydride protons can be detected by ^1H NMR spectroscopy from the signals at δ ranging from −2 to −16 (Table 1).

Studies by ^1H NMR and IR spectroscopy[28–31] provided qualitative evidence for an increase in basicity of metallocenes and their permethylated derivatives in the series Fe < Ru < Os. Quite recently,[32] numerous experimental and theoretical conclusions about the increase in

Table 1. The ^1H chemical shifts (δ) of the CH (in the Cp and Cp* fragments) and MH groups in the ^1H NMR spectra of various hydride complexes

Complex	δ		
	MH	Cp	Cp*
$[Cp_2FeH]^+$	−2.70	4.25	—
$[Cp^*{}_2FeH]^+$	−3.70	—	1.67
$[Cp_2RuH]^+$	−6.96	5.59	—
$[CpRuCp^*H]^+$	−7.60	5.12	2.10
$[Cp^*{}_2RuH]^{+\,a}$	−8.33	—	1.88
$[Cp_2OsH]^+$	−14.15	5.52	—
$[Cp^*{}_2OsH]^{+\,b}$	−15.63	—	1.97

[a] $\Delta H = -19.0$ kcal mol^{-1}.

[b] $\Delta H = -26.6$ kcal mol^{-1}.

basicity of Group VIII metallocenes in the above-mentioned series were confirmed by quantum-chemical calculations using the density functional theory (DFT).

Photolysis of solutions of the $[Cp^*{}_2MH]^+$ complexes generated by protonation of permethylmetallocenes afforded cations **1b,c**. The highest yield of cation **1b** (up to 90%) was achieved by performing photolysis of $Cp^*{}_2Ru$ in a mixture of CF_3SO_3H and oleum for 3 h. Under analogous conditions, cation **1c** was generated from $Cp^*{}_2Os$ in 82% yield upon irradiation for 15 h, which indicates that $[Cp^*{}_2OsH]^+$ is more stable than the Ru-containing analog. Cation **1c** was also prepared in high yield by photolysis of the pre-synthesized $[Cp^*{}_2OsH]^+PF_6^-$ salt in neutral solutions (CH_2Cl_2 or MeCN). Photolysis of solutions of $Cp^*{}_2M$ (M = Ru or Os) in acids was examined by ^1H NMR monitoring, which made it possible to detect intermediates, *viz.*, the $[Cp^*{}_2M]^{+\bullet}$ radical cations.

The detailed study of these reactions provided information valuable for the further development of the chemistry of the permethylmetallocenylmethyl cations. It appeared that protonation of $Cp^*{}_2M$ (M = Ru or Os) in a solution in CF_3SO_3H in the presence of a small amount of oleum did not cease at the step of formation of monocations **1b,c** and could proceed further to form dications prepared previously according to Scheme 3 (path *b*). These results gave impetus to a radically new line of investigation associated with the synthesis and studies of di- and trications (see below).

Structures and mechanism of stabilization of the carbocationic center in monocations 1a—c. In X-ray diffraction studies, not only the structures of salts with monocations **1a—c** were determined but also valuable information on the mechanism of stabilization of the carbocationic centers was obtained. The structures of cations **1a—c** are shown in Fig. 1. The principal characteristics, which most clearly reflect the differences in their properties and geometry, are given in Table 2. It is appropriate to use the M—C(11)H_2 bond lengths and the angles (α) of deviation of the C(1)—C(11) bond from the plane of the ring toward the metal atom as such structural characteristics. The angles α in cations **1b** and **1c** (40.3 and 41.8°, respectively) are rather large, whereas the M—C(11) distances are among the shortest bonds known for complexes of this type.[14,15] In contrast to these cations, the Fe—C(11)H_2 bond length in the Fe-containing analog is 2.567 Å and the angle α is only 23.6°.[16]

Table 2. Principal parameters obtained in X-ray diffraction studies of cations **1a—c**, **10b**, and **12c**

Parameter	1a	1b	1c	10b	12c
Bond/Å					
M—C(11)	2.567	2.270	2.224	2.512	2.406
M—C(1)	1.968	2.066	2.069	2.097	2.094
C(1)—C(11)	1.37	1.401	1.426	—	1.411
Angle α/deg	23.6	40.3	41.8	30.9	35.4

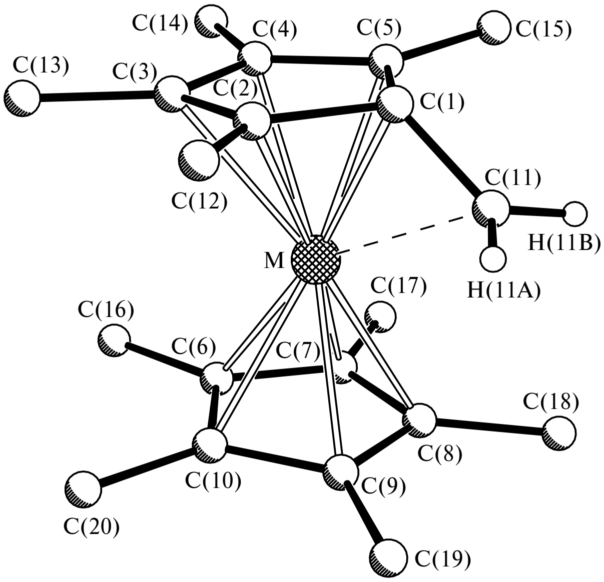


Fig. 1. Structure of nonamethylmetallocenylmethyl cations **1a—c**.

With the aim of elucidating the effect of the substituents on the character of the M—C(11) interaction, the structures of two cationic complexes, *viz.*, $[Cp^*RuC_5Me_4CHPh]^+BF_4^-$ (**10b**) (Fig. 2) and $[Cp^*OsC_5Me_4CHC_6F_5]^+PF_6^-$ (**12c**), were studied (Fig. 3, see Table 2).[34] As can be seen from Table 2, the introduction of the substituent leads to an increase in the Os—C(11) bond length (by 0.182 Å; *cf.* complexes **12c**

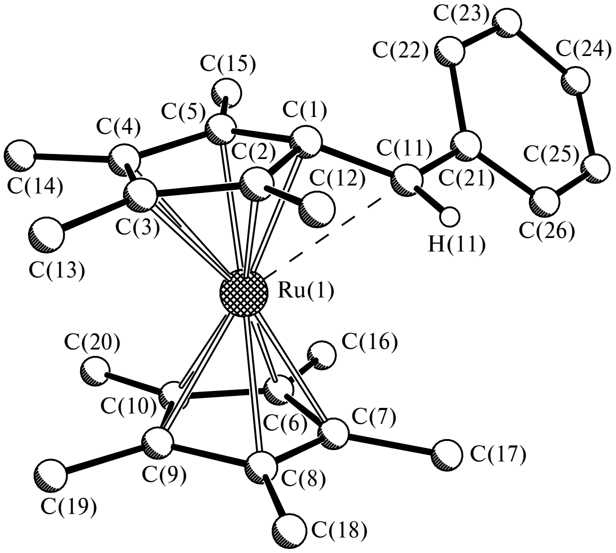


Fig. 2. Structure of nonamethylruthenocenyl(phenyl)methyl cation **10b**.

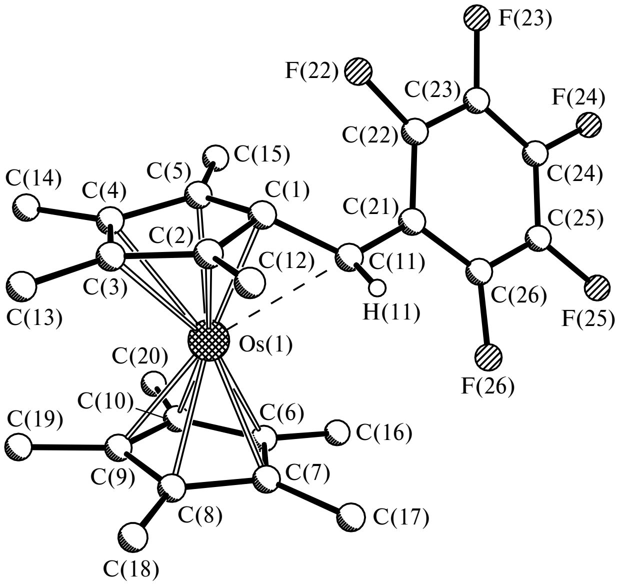
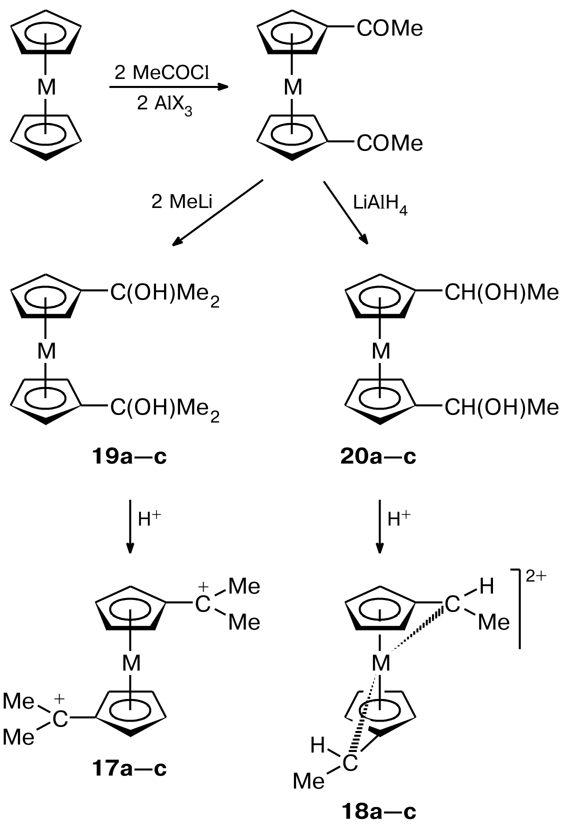


Fig. 3. Structure of nonamethylosmocenyl(pentafluorophenyl)methyl cation **12c**.

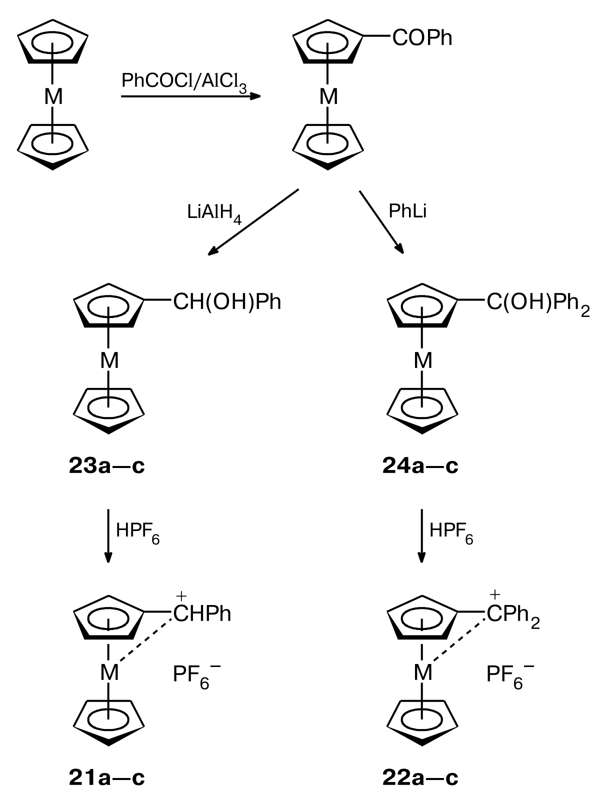
and **1c**), an increase in the Ru—C(11) bond length (by 0.242 Å; *cf.* complexes **10b** and **1b**), and a decrease in the inclination angles α (by 6.4 and 9.4° for the Os- and Ru-containing cations, respectively). It was of interest to study cationic complexes containing even more sterically hindered carbocationic centers, *viz.*, tertiary cations. However, since the synthesis of tertiary permethylated carbinols, which are precursors of the corresponding cations, presented substantial difficulties, we prepared unmethylated mono- and dimethyl derivatives **17a—c** and **18a—c**, respectively, (Scheme 6) and also mono- and diphenyl derivatives **21a—c** and **22a—c**, respectively (Scheme 7). Compounds **22b,c** were studied by X-ray diffraction analysis (Fig. 4, Table 3).[35,36] Monophenyl- (**21a—c**), monomethyl- (**18a—c**), and dimethyl cations (**17a—c**) were investigated by NMR spectroscopy.

Scheme 6



M = Fe (**a**), Ru (**b**), Os (**c**)

Scheme 7



M = Fe (**a**), Ru (**b**), Os (**c**)

Table 3. Principal parameters obtained in X-ray diffraction studies of cations **22a—c**

Parameter	**22a***	**22b**	**22c**
Bond/Å			
M—C(11)	2.715	2.482	2.387
M—C(1)	2.009	2.098	2.088
C(1)—C(11)	1.416	1.421	1.459
Angle α/deg	20.7	34.0	38.4

* See Ref. 3.

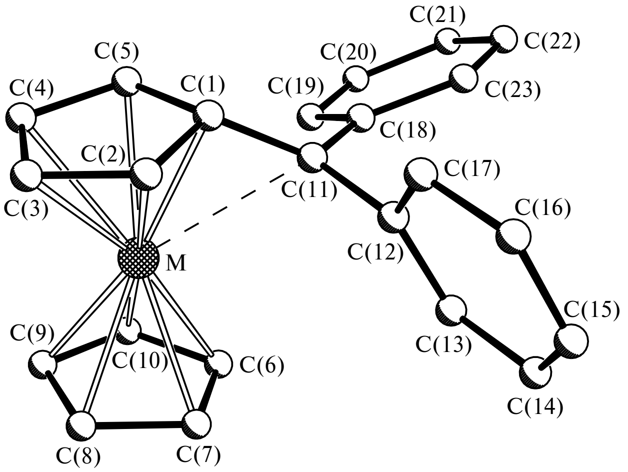


Fig. 4. Structure of metallocenyl(diphenyl)methyl cations **22b,c**.

Compared to the primary cations, the introduction of two Ph substituents at the carbocationic center leads to an increase in the Os—C(11) bond length (by 0.163 Å; *cf.* complexes **22c** and **1c**), an increase in the Ru—C(11) bond length (by 0.212 Å; *cf.* complexes **22b** and **1b**), and a decrease in the inclination angle α (by 3.4 and 6.3° for the Os- and Ru-containing cations, respectively). These data unambiguously demonstrate that the substituents at the carbocationic center and in the Cp ring have rather substantial effects on the structural characteristics.*

As can be seen from Tables 2 and 3, the Fe—C(11) bond lengths are larger than the Ru—C(11) bond lengths, which, in turn, are larger than the Os—C(11) bond lengths in all seven cations studied by us, *viz.*, in primary **1a—c**, secondary **10b**, **12c**, and tertiary cations **22b,c** (as well as in cation **22a**).[3] It should be noted that systematic X-ray diffraction studies of salts with cations of all iron-subgroup metallocenes (M = Fe, Ru, or Os) were carried out for the first time.

A comparison of the ^{1}H and ^{13}C NMR spectra of monocations **1a—c** and alcohols **5a—c**, which are their precursors, demonstrated that the transformations of the alcohols into the corresponding cations lead to downfield shifts of the resonances for all nuclei. This is indicative of the appearance of a positive charge in the molecule, the largest shifts being observed for the resonances of the ^{1}H and ^{13}C nuclei of the CH_2 groups (Table 4). In addition, the shielding of the nuclei of these groups in cations **1a—c** substantially increases in the series Fe, Ru, Os[8,10,11] (see Table 4).

Table 4. The ^{13}C chemical shifts (δ) of the CH_2 groups in the ^{13}C NMR spectra and their changes ($\Delta\delta$) on going from alcohols $Cp^*MC_5Me_4CH_2OH$ (**5a—c**) to monocations **1a—c**

M	δ		Δδ
	1a—c	**5a—c**	
Fe	90.7	41.5	49.2
Ru	74.7	53.9	20.8
Os	55.4	56.7	−1.3

Analogous changes in the shielding of the ^{13}C nuclei of the CHR^+ groups were also observed[37—39] for the secondary permethylated phenyl-substituted cations in the $[Cp^*MC_5Me_4CHPh]^+An^-$ compounds (**10a—c**) and their unmethylated analogs in the $[CpMC_5H_4CHPh]^+An^-$ complexes (**23a—c**) and also for the secondary cations containing the C_6F_5 substituent in the $[C_5Me_5MC_5Me_4CHC_6F_5]^+An^-$ complexes (**12b,c**).

An analogous situation was observed[39] for the tertiary cations of the $[CpMC_5H_4CPh_2]^+An^-$ compounds (**22a—c**). The shift δ decreases in the series Fe, Ru, Os. Analogous changes in shielding of the protons of the CHR^+ groups occur in the ^{1}H NMR spectra of the primary and secondary cations studied by us.[8,10,11,37—39]

The investigations revealed the general regularities of the changes in the ^{1}H and ^{13}C NMR spectroscopic parameters of the salts with primary, secondary, and tertiary monocations of all iron-subgroup metallocenes depending on the nature of the metal atom. Thus, the shielding of the C(11) nuclei and H atoms of the C(11)H group increases substantially in the iron subgroup from the top down due to strengthening of the interaction between the C(11) and metal atoms.

The calculations of the electronic structures and geometry of the $[C_5R_5MC_5R_4CH_2]^+$ cations (R = H, Me; M = Fe, Ru, Os) with the use of the extended Hückel theory (EHT) demonstrated[40] that the positive charge in cations **1b,c** is localized primarily on the metal atom. In cation **1a**, only a small portion of the positive charge (0.10) is localized on the Fe atom. Hence, the MO calculations of the geometric parameters and charges agree both with the results of X-ray diffraction analysis of the salts with permethylated primary cations **1a—c** and the NMR spectroscopic data. According to the results of the same calculations,[40] the M—C(11) Mulliken bond order increases in the series Fe (0.01) < Ru (0.16) < Os (0.22).

The studies of the primary cations by three physical methods provided rather convincing evidence that the structures of these cations can be described by the "specific" resonance hybrid **A** with particular contributions of the limiting forms, *viz.*, metallonium **A´** and carbocationic **A″** structures. The metallonium structure **A´** is stabilized primarily through a strong interaction of the lone pair of the metal atom with the unoccupied orbital of the C atom and a strong donor-acceptor $M^+—CH_2$ bond accompanied by a virtually complete positive-charge transfer from the carbocationic center to the metal atom.

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* The electronic and steric effects of aryl substituents were discussed in detail in the previous study (see Ref. 34).

This bond length is close to the M—CH$_2$ σ-bond length. The structure **A´** occurs primarily in cations **1b** and **1c**. In the carbocationic form **A″**, the positive charge is localized predominantly on the $^+$CH$_2$ group. Its through-space interaction with the metal atom is rather weak. The M—$^+$CH$_2$ bond is substantially elongated and its length is much larger than the length of the standard M—C σ-bond. Hence, the form **A″** makes the major contribution to the structure of Fe-containing cation **1a**. It should be taken into account that, unlike the classical resonance, the structures under consideration are characterized not only by electron transfer but also by a change in the geometry.

The conclusions made are valid both for the crystal phase and solutions where cations interact with anions and/or the solvent. The DFT quantum-chemical calculations of the geometry of cations **1a—c** in the gas phase demonstrated that the phase transition leads to substantial changes in the lengths of the donor-acceptor M$^+$—CH$_2$ σ-bonds and the inclination angles α, whereas the calculated parameters of the C—H, Cp—Cp, and M—Cp bonds in the sandwich fragment are virtually identical with those determined by X-ray diffraction analysis (XRD) (Table 5).[41] Thus, the Fe—CH$_2$ bond length in cation **1a** decreases from 2.567 Å in the solid phase to 2.324 Å in the gas phase, and the angle α is even larger than the corresponding angles in cations **1b** and **1c**. At the same time, the bond lengths in cations **1b,c** in the gas phase are smaller than those in the crystals. The absolute value $\Delta = |d_{\mathrm{XRD}} - d_{\mathrm{DFT}}|$ decreases in the series Fe > Ru > Os.

Hence, the M—CH$_2$ bond in cation **1a** in the gas phase is stronger than that in the crystal and all three cations in the gas phase can be described by the structure **A´**. Conceivably, these differences result from the fact that the structure of the cation in the gas phase is influenced only by the electronic effect of the metal atom (nucleophilicity) and its size. It is known that the nucleophilicity of the metal atom increases in the subgroup from the top down resulting in a decrease in the M—CH$_2$ bond length in the series Fe > Ru > Os. At the same time, the smaller radius of the Fe atom as compared to those of the Ru and Os atoms must lead to a change in the distances in the series Fe < Ru ≃ Os (covalent radii, Å: Fe, 1.34; Ru, 1.49; Os, 1.50), which is manifested as the absence of a monotonic change in the d_{DFT} distances determined for cations **1a—c** in the gas phase. In the crystals, an increase in the nucleophilicity in the subgroup from the top down has a dominant role, and the above-mentioned decrease in the M—CH$_2$ distances is observed. Hence, it was demonstrated for the first time[41] that the donor-acceptor M—CH$_2$ σ-bond and the inclination angles α in cations **1a—c** are very sensitive to a change in the phase state. Later, analogous results (the differences between d_{XRD} and d_{DFT} for the [CpRuC$_5$H$_4$CH$_2$]$^+$ cation) were obtained also in the study.[42]

Table 5. The M—CH$_2$ bond lengths (d/Å) according to the results of X-ray diffraction analysis (XRD) and DFT calculations for monocations **1a—c**

Cation	d		$\Delta d = d_{\mathrm{XRD}} - d_{\mathrm{DFT}}$
	XRD	DFT	
1a	2.567	2.324	+0.243
1b	2.270	2.410	–0.140
1c	2.244	2.341	–0.097

Properties of cations 1a—c. The properties of cations **1a—c** are most pronounced in reactions with nucleophilic reagents. Hydrolysis of the salts containing these cations with an aqueous solution of KOH proceeded[20,33] at 20—40 °C for 2—5 h (Scheme 8).

Scheme 8

$$\underset{\mathbf{1a,b}}{[\mathrm{Cp^*M}(\eta^6\text{-}\mathrm{C_5Me_4CH_2})]^+\mathrm{An}^-} + \mathrm{KOH} \longrightarrow$$

$$\longrightarrow \mathrm{Cp^*M}(\eta^5\text{-}\mathrm{C_5Me_4CH_2OH})$$

M = Fe, Ru

Cationic compounds are convenient synthons for the preparation of various functional derivatives. Thus, the reactions of [Cp*FeC$_5$H$_4$CHR]$^+$ and [C$_5$HMe$_4$FeC$_5$Me$_4$CH$_2$]$^+$ with amines and other nucleophiles[43,44] and the reactions of [Cp*MC$_5$Me$_4$CH$_2$]$^+$An$^-$ with alkoxides or thiophenol[20] were studied (Scheme 9).

Scheme 9

$$[\mathrm{Cp^*MC_5Me_4CH_2}]^+\mathrm{An}^- + \mathrm{MeONa} \longrightarrow$$

$$\longrightarrow \mathrm{Cp^*MC_5Me_4CH_2OMe}$$

M = Fe, Ru, Os

$$[\mathrm{Cp^*MC_5Me_4CH_2}]^+\mathrm{An}^- + \mathrm{PhSH} \longrightarrow$$

$$\longrightarrow \mathrm{Cp^*MC_5Me_4CH_2SPh}$$

M = Fe

The C—O and C—S bonds in the resulting ethers and thioesters are readily cleaved under the action of acids giving rise to the starting cationic compounds. Salts containing these cations react also with amines and phosphines to form ammonium and phosphonium salts, respectively[12] (Scheme 10).

Hence, the reactions of cationic compounds with nucleophiles enable one to extend the spectrum of func-

Scheme 10

$$[Cp^*MC_5Me_4CHR]^+An^- + ER'R''_2 \longrightarrow$$

$$\longrightarrow Cp^*MC_5Me_4CH(R)E^+R'R''_2$$

M = Os, R = H, E = P, R′ = Ph, R″ = Me;
M = Os, R = H, E = N, R′ = R″ = Me;
M = Ru, R = H, E = P, R′ = R″ = Ph;
M = Ru, R = H, E = P, R′ = Ph, R″ = Me;
M = Os, R = H, E = P, R′ = R″ = Ph

tional derivatives of permethylated metallocenes prepared by us.

Generation of the homo- and heteroannular dications $[C_5R_5MC_5R_3(CR'R''-1,2)_2]^{2+}$ (15a—c) and $[M(C_5R_4CR'R'')_2]^{2+}$ (16a—c)

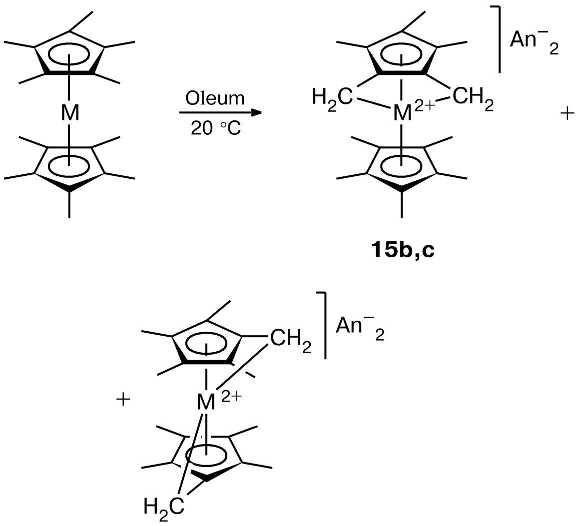
Three-step synthesis of iron-subgroup dications. The first procedure for the preparation of dications was based on transformations of the minor products of oxidation of Cp^*_2M with barium manganate. As mentioned above, these reactions afford monoaldehydes as the major reaction products along with a mixture of 1,2- and 1,1′-dialdehydes **3** and **4** (see Scheme 3, path *b*). This mixture can be readily separated from monoaldehydes **2a—c**. Reduction of the dialdehydes to alcohols **13a—c** and **14a—c** followed by the treatment of the latter with CF_3SO_3H gave rise to dications **15a—c** and **16a—c**, respectively.[17,18]

This method was used for the preparation of homo- and heteroannular cations of all iron-subgroup metals. Secondary and tertiary cations devoid of the methyl substituents in the ring and containing substituents at the carbocationic center were synthesized[45] according to Scheme 6.

Hence, the three-step syntheses of all primary, secondary, and tertiary dications of permethylated iron-subgroup metallocenes and those devoid of the methyl substituents in the ring were performed with the use of conventional procedures employed in organic chemistry. Nevertheless, the presence of a transition-metal atom made it possible to develop unique one-step (one pot) procedures for the synthesis of organometallic multicharged cations, which are virtually unknown in the classical organic chemistry.

One-pot synthesis of Ru,Os-containing dications 15b,c and 16b,c. When developing a procedure for the preparation of the $[Cp^*MC_5Me_4CH_2]^+$ monocations (**1b,c**) by photolysis of protonated decamethylmetallocenes under an inert atmosphere, it was found that the addition of a small amount of oleum to CF_3SO_3H led to the formation of dications **15b,c** and **16b,c** in yields of up to 3—5% along with the major reaction products, *viz.*, monocations **1b,c** (Scheme 11). It appeared that the reaction can be directed to either monocations or a mixture of dications by varying the ratio between CF_3SO_3H and oleum. With the aim of preparing dications as the major products, we examined the reactions of decamethylmetallocenes with oleum or a mixture of oleum and sulfuric acid.[46] The optimum results were obtained under the action of oleum on decamethylmetallocenes.

Scheme 11



15b,c

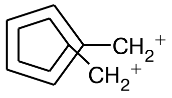
16b,c

The dications are generated from Cp^*_2Ru and Cp^*_2Os with different rates. Thus, a mixture of dications **15b** and **16b** was obtained immediately after dissolution of Cp^*_2Ru in oleum at room temperature, whereas dications **15c** and **16c** were prepared from a mixture of Cp^*_2Os and oleum under the same conditions only after 8 days. To accelerate the latter process, the solution was heated at 50 °C for 2—3 h or the reaction mixture was irradiated with UV light for 20 h. It should be noted that the reactions of the salts containing monocations **1b,c** (An = PF_6) with oleum proceeded at room temperature in a similar fashion in the case of the Ru- and Os-containing cations to give directly mixtures of dications **15b,c** and **16b,c**.

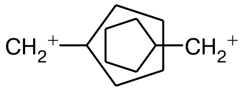
Unlike the reaction of Cp^*_2Ru in the presence of CF_3SO_3H, which gave rise to the monoprotonation product, *viz.*, cationic hydride $[Cp^*_2RuH]^+$, the reaction of Cp^*_2Os with CF_3SO_3H afforded cationic dihydride $[Cp^*_2OsH_2]^{2+}$. The reactions of the Os-containing derivatives differ from those of the Ru-containing analogs in that they afforded the $[Cp^*Os(H)(C_5Me_4CH_2)]^{2+}$ dication (protonated monocation), which was detected as an intermediate in the synthesis of dications under the action of oleum both on Cp^*_2Os and monocation **1c**. The reactions of Cp^*_2Ru with oleum gave dication **15b** and an analog of heteroannular dication **16b′** as the final products. The ^{1}H NMR spectrum of this dication differs from the spectrum of dication **16b**, which was prepared by protonation of the corresponding carbinol. Based on the ^{1}H and ^{13}C NMR spectroscopic data and the results of chemical transformations of dication **16b´**, the $[(\eta^1:\eta^3\text{-}CH_2C_5Me_4)Ru(\eta^2\text{-}H_2)(\eta^1:\eta^5\text{-}CH_2C_5Me_4)]^{2+}$ structure was presumably assigned to this dication.[46]

Study of the structures of dications. In the absence of acid, dications **15a—c** and **16a—c** are very sensitive to nucleophilic reagents and moisture due to which attempts to isolate their salts in pure form failed. The NMR spectroscopy and quantum-chemical calculations proved to be the most informative methods for the determination of their structures. The ^{1}H and ^{13}C NMR spectroscopic data made it possible to perform conformational analysis of the heteroannular 1,1´-dications.[18]

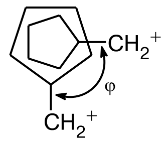
Three conformers, *viz.*, *syn*, *gauche*, and *anti*, are theoretically possible for the heteroannular dications.



syn



anti

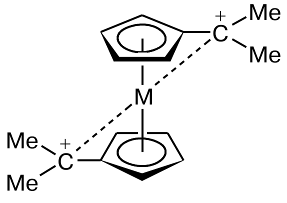


gauche

With the aim of obtaining preliminary estimates of the role of the donor-acceptor interaction of the metal atom in dications **16a—c** with unoccupied orbitals of the CH_2 group and resolving the question of which possible rotamer offers the optimum interaction, we carried out MO (EHT) calculations of the potential energy curves of the rotation of the $C_5Me_4CH_2$ ligands around the axis linking the metal atom and the center of the C_5Me_4 ring. The results of calculations demonstrated that the *gauche* rotamers ($\varphi = 90°$) correspond to the energy minimum, whereas the *syn* ($\varphi = 0°$) and *anti* rotamers ($\varphi = 180°$) belong to the tops of the corresponding energy barriers. The ^{1}H NMR spectra of individual 1,2-dications **15a—c**, which were recorded in $CF_3SO_3H—CD_2Cl_2—MeNO_2$ solutions, completely confirmed their structures.[17,18] Thus, the ^{1}H NMR spectrum of dication **15b** has three singlets with the integral intensity ratio of 6 : 15 : 3 in the region of signals for the protons of the Me groups, the spectrum of dication **15a** has two singlets (21 : 3), and the spectrum of dication **15c** has two singlets (6 : 18). The spectrum of each of dications **16a—c** has four singlets with equal intensities (α-, α´- and β-, β´-Me) in the region of signals for the protons of the Me groups.[18] The signals for the protons of the CH_2 groups of dications **15a—c** and **16a—c** are observed as doublets of the AB spin system. The nonequivalence of the protons of the CH_2 groups in 1,1´-isomers **16b,c** and the fact that they give two doublets of the AB system as well as the presence of four signals of the α-, α´- and β-, β´-Me groups may indicate that solutions contained the *gauche* rotamers and that the latter have onium structures. The spectra of the *anti* rotamers with the symmetry plane would show singlets of the CH_2 groups (the A_2 spin system) and two signals of the α- and β-Me groups. It should be emphasized that the signals of 1,1´-dications **16a—c** and the signals of 1,2-dications **15a—c** are shifted downfield compared to the analogous signals of the monocations. The temperature dependence of the ^{1}H NMR spectra demonstrates that 1,2-homoannular dications **15b,c** are more stable than 1,1´-heteroannular dications **16b,c**, which is in agreement with the results of calculations (see below[18]).

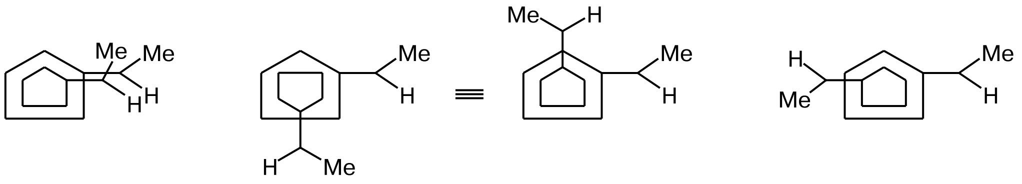
The structures of homoannular dications **15b,c** were also confirmed by ^{13}C NMR spectroscopy (**15b**, $\delta(CH_2)$ 88.4; **15c**, $\delta(CH_2)$ 71.1). These data showed that the M—C(11) interaction in dications **15b,c**, like those in all known monocations, is strengthened in the subgroup from the top down (Ru < Os) resulting in an increase in shielding. The signals for the C(11) atoms of dications **15b,c** are observed at lower field than the corresponding signals of monocations **1b,c** (**1b**, δ 74.7; **1c**, δ 55.4). Therefore, an increase in the positive charge causes downfield shifts of the resonances for the C(11) atom. The spin-spin coupling constants $^1J_{C,H}$ (**15b**, 171 Hz; **15c**, 172 Hz) are somewhat larger than the corresponding values for monocations **1b** and **1c** (164 and 166 Hz, respectively).[18]

Tertiary dications **17a—c** devoid of the Me groups in the ring belong to another limiting type of dications, which adopt an *anti* conformation in solution and possess structures of dicarbodications with the predominant localization of the positive charge on the C_α atoms.[45] It is this model that must be favorable for dicarbodications. It is quite apparent that the donor-acceptor interactions between the metal atom and the cationic centers in the dicarbocationic derivatives are weaker than those in onium compounds **16a—c**. The calculations performed for the $[M(C_5H_4CH_2)_2]^{2+}$ anion showed that weakening of the donor-acceptor interaction, which is evidenced primarily by the smaller inclination angle α, is typical of the *anti* conformers.

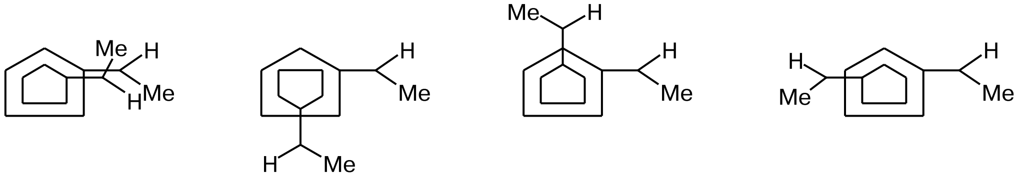


17a—c

In addition to weakening of the donor-acceptor interaction, the Coulomb repulsion between two cationic



meso Forms (*RS,SR*) of compounds **18a—c**



syn, φ = 0° *gauche*, φ = 90° *gauche*, φ = 270° *anti*, φ = 180°

Racemic forms (*RS,RS*) of compounds **18a—c**

centers and the presence of substituents, which provide steric hindrances to interactions of these centers with the metal atom and lead to weakening of the donor-acceptor interaction with the metal atom, are the major factors favorable for the *anti* conformation. The lack of the Me substituents in the Cp rings also results in a decrease in the electron density on the metal atom and causes weakening of the donor-acceptor interaction.

The studies of salts with cations **17a—c*** in solutions by ^{1}H NMR spectroscopy at different temperatures demonstrated[45] that the spectra of these cations each have one singlet for the protons of the Me groups and two triplets for the 2,5- and 3,4-protons of the Cp ring. The spectral patterns of these dications remain virtually unchanged under changes of the temperature (dication **17a** decomposes at a temperature above −30 °C, dication **17c** decomposes at a temperature above 10 °C, whereas dication **17b** is stable upon heating up to 25 °C). The presence of one singlet signal of the Me groups indicates that these groups are equivalent and the molecules adopt an *anti* conformation (Table 6). The ^{1}H NMR spectra of dications **17a—c** show that all iron-subgroup dications are characterized by dicarbodicationic structures with the predominant localization of the positive charge on the α-CMe$_2$ groups.

Secondary unmethylated derivatives are intermediates between the primary permethylated onium dications and tertiary unmethylated dicarbodications.[45] A consideration of the possible conformers of two diastereomers of secondary dications **18a—c** shows that the *meso* diastereomer (*RS*,*SR*) occurs as the only *gauche* conformer (*gauche* conformers with the rotation angles φ = 90 and 270° are identical), whereas another diastereomer, *viz.*, *rac*-(*RS*,*RS*), occurs as two different *gauche* conformers at the same angles.

Table 6. ^{1}H NMR spectroscopic data for dications **17b,c** (in CF$_3$SO$_3$H)[45]

Compound	*T* /°C	δ		
		s, 12 H, Me	t, 4 H, H(2), H(5), *J* = 2 Hz	t, 4 H, H(3), H(4), *J* = 2 Hz
17b	−60	2.394	5.902	6.465
	−30	2.415	5.915	6.472
	0	2.424	5.827	6.469
	+25	2.446	5.988	6.494
17c	−50	2.157	5.953	6.624
	−30	2.161	5.964	6.625
	−10	2.165	5.971	6.625
	+10	2.168	5.979	6.623

The ^{1}H NMR spectra of the salts with cations **18a—c** were recorded in solutions in FSO$_3$H in the temperature range from −40 to 30 °C. Each spectrum shows three doublets for the protons of the Me groups at δ 2.3—2.6. In addition to the intense doublets, this region has low-intensity doublets, which can also be assigned to the protons of the Me groups.

In the ^{1}H NMR spectra of the same cations **18b,c** recorded with the addition of a solvent (CF$_3$SO$_3$H—CD$_2$Cl$_2$—CD$_3$NO$_2$ mixture) in the same temperature range, the relative intensities of the signals remain virtually unchanged, although the signals are somewhat shifted. Apparently, the low-intensity signals whose number increases on going from acid to a solution with the addition of solvents can be assigned to signals of the Me groups of the *anti* conformers occurring as dicarbodications because the addition of solvents has a noticeable effect on the ^{1}H NMR spectra of the *anti* conformers.

---

* It should be noted that cations **17a** have been generated previously.[47,48]

Conceivably, the simultaneous presence of the *gauche* and *anti* conformers in solution indicates that dications **18b,c** with metallonium and dicarbodicationic structures are similar in energy, although the onium structure is energetically more favorable. This fact is in agreement with the results of calculations. It should also be emphasized that the ^{1}H NMR spectra of dication **18a** in a $CF_3SO_3H—CD_2Cl_2—CD_3NO_3$ solution at −20 and +25 °C have only two doublets at δ ~2, the spectral pattern being virtually unchanged under changes of the temperature. It is not improbable that Fe-containing dication **18a**, in which donor-acceptor interactions between the lone pair of the metal atom and the carbocationic centers are weaker than those in Ru- and Os-containing analogs **18b,c**, occurs as the dicarbodication whose spectra in solution have signals of only the *anti* conformers of the (*RS*,*RS*)- and (*RS*,*SR*)-diastereomers.[45]

Hence, two limiting structural types of dications, *viz.*, metallonium dications **15a—c** and **16a—c** and dicarbodications **17a—c**, were modeled by choosing the metal atom and selecting appropriate substituents in the ring and at the α-carbocationic center. The examination of these dications by ^{1}H NMR spectroscopy provided the convenient means of distinguishing their structures as metallonium compounds or dicarbodications.[18,45]

Dications **15a—c** and **16a—c**, like monocations **1a—c**, were generated also in the gas phase and then studied by mass spectrometry.[41] Since the dications were investigated only by NMR spectroscopy and mass spectrometry, the quantum-chemical DFT calculations of the molecules in the gas phase were carried out to obtain more reliable information on their structures and mechanism of stabilization of the carbocationic centers.[41] The results of calculations confirmed the assumed structures of the dications. It was demonstrated that the $M—CH_2$ distances in homoannular 1,2-dications **15a—c** are somewhat larger than those in monocations **1a—c** (Table 7).

It should be noted that the $M—CH_2$ distances in the homoannular dications decrease monotonically in the subgroup from the top down. These bonds are somewhat shorter than those in the heteroannular analogs (for example, the $Ru—CH_2$ bond length is 2.586 Å), which indicates that these bonds in the latter compounds are weaker.

Table 7. The $M—CH_2$ distances (d) and angles α in monocations **1a—c** and 1,2-dications **15a—c** calculated by the DFT method

M	d/Å		α/deg	
	1	**15**	**1**	**15**
Fe	2.324	2.504, 2.511	34.0	25.03, 24.58
Ru	2.410	2.456, 2.456	23.6	24.62, 24.30
Os	2.341	2.401, 2.395	32.4	31.24, 31.11

Trications $[1,2-(CH_2)_2C_5Me_3MC_5Me_4CH_2-1']^{3+}$ (M = Ru or Os) (25b,c)

Generation of trications. The successful preparation of dications stable in acidic media gave impetus to studies aimed at generating trications based on decamethylmetallocenes because the metal atoms involved in the latter compounds have three lone pairs capable of stabilizing three carbocationic centers. It was worthwhile to generate trications under the conditions, which have been successfully used in the one-pot syntheses of the mono- and dications with the use of strong protic acids, including superacids and oxidizing agents.

When studying the behavior of Cp^*_2Ru in a solution in CF_3SO_3H (98%) under an inert atmosphere and in air, we found that the reactions in argon afforded the protonation product $[Cp^*_2RuH]^+$ and monocation **1b** (according to the ^{1}H NMR spectroscopic data), whereas the reaction in air gave rise not only to the above-mentioned products but also to dications and a small amount of new species containing three CH_2 groups. This investigation demonstrated for the first time[49] that atmospheric oxygen in a solution of superacid can oxidize one, two, or even three Me groups of Cp^*_2Ru. All reactions were carried out at 20 °C in NMR tubes, which were filled with new portions of oxygen at certain intervals. In the generation of trications **25b,c**, Cp^*_2Ru and Cp^*_2Os also behaved differently. Studies by ^{1}H NMR spectroscopy demonstrated that monocation **1b** was completely consumed in the reaction of Cp^*_2Ru with CF_3SO_3H/O_2 after two cycles of filling of an NMR tube with oxygen. After filling with oxygen three times, the reaction mixture contained compounds **25b**, **15b**, and **16b** in 57, 21, and 22% yields, respectively. Dihydride $[Cp^*_2OsH_2]^{2+}$ was generated from Cp^*_2Os in the CF_3SO_3H/O_2 system. When O_2 was passed further, the reaction afforded dications **15c** and **16c** as the major products (62 and 34%, respectively) along with compound **25c** (4%).[50] Attempts to increase the yield of trication **25c** by further passing oxygen failed. However, this reaction starting from monocation **1c** (An = BF_4) instead of Cp^*_2Os gave rise to **25c** as the major product (**25c**, 81%; **15c**, 11%; **16c**, 8%). The use of salt **1b** instead of Cp^*_2Ru also afforded **25b** as the major product (the yield was 80%).

Attempts to isolate salts with trications **25b,c**, like salts with dications **15b,c** and **16b,c**, in pure form were unsuccessful because these salts are unstable in the absence of strong acid. The mechanism of transformations of Cp^*_2M and monocations **1b,c** into **15b,c**, **16b,c**, and **25b,c** under the above-mentioned conditions remains an open question. It should be emphasized that ^{1}H NMR monitoring revealed protonation products, such as $[Cp^*_2RuH]^+$ as well as $[Cp^*_2OsH_2]^{2+}$ and $[Cp^*Os(H)C_5Me_4CH_2]^{2+}$, which were further oxidized to **1b**, **15b,c**, **16b,c**, and **25b,c** *via* the intermediate

Scheme 12

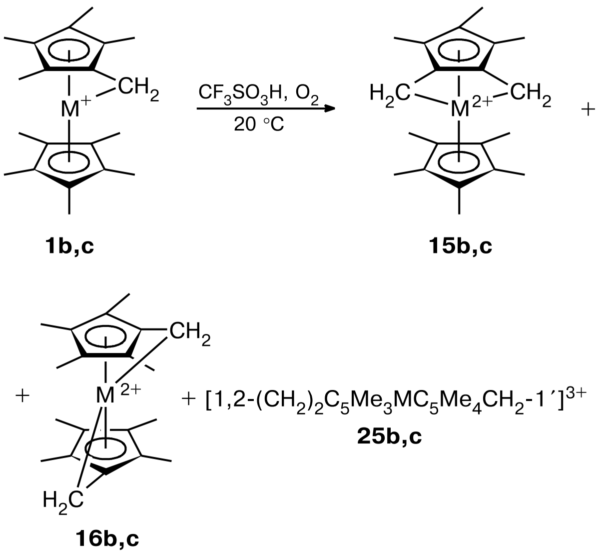


Table 8. ^{1}H and ^{13}C NMR spectroscopic data for the CH_2 groups of monocations **1b,c**, dications **15b,c**, and trications **25b,c**

Compound	δ (*J*/Hz)	
	^{1}H	^{13}C
1b	4.75 (s)	74.6 (t, $^1J_{C,H}$ = 164)
1c	4.42 (s)	55.4 (t, $^1J_{C,H}$ = 167)
15b	4.82 (d, $^2J_{H,H}$ = 1.9); 5.27 (d, $^2J_{H,H}$ = 1.9)	88.4 (t, $^1J_{C,H}$ = 170)
15c	4.90 (d, $^2J_{H,H}$ = 2.4); 5.52 (d, $^2J_{H,H}$ = 2.4)	71.1 (t, $^1J_{C,H}$ = 172)
25b	5.03, 5.51 (both d, 2 H each, $^2J_{H,H}$ = 1.9); 5.50 (s, 2 H)	65.7 (t, 1 C, $^1J_{C,H}$ = 157); 88.6 (t, 2 C, $^1J_{C,H}$ = 170)
25c	5.04 (d, 2 H, $^2J_{H,H}$ = 2.3); 5.49 (s, 1 H); 5.66 (d, 2 H, $^2J_{H,H}$ = 2.3)	65.8 (t, 1 C, $^1J_{C,H}$ = 157); 71.3 (t, 2 C, $^1J_{C,H}$ = 172)

17-electron $Cp^*{}_2M^{+\bullet}$ radical cations and the corresponding $[Cp^*MC_5Me_4CH_2]^{2+\bullet}$ radical dications.

In conclusion, it should be noted that other examples of such oxidation reactions are lacking in the literature. Oxidation of methane with oxygen[51] in concentrated H_2SO_4 to methanol and its derivatives in the presence of Pt complexes is the only process similar to the reactions under investigation.

Structures of trications 25b,c determined from NMR spectroscopic data and results of calculations using the density functional theory.[5] The determination of the structures of trications **25b,c** presented no serious difficulties because their ^{1}H NMR spectra (Table 8)* are similar to the spectra of the $CH_2C_5Me_4$ and $1,2\text{-}(CH_2)_2C_5Me_3$ fragments in monocations **1b,c** and 1,2-dications **15b,c**, respectively. The presence of three methylene groups in these molecules was unambiguously proved by ^{1}H and ^{13}C NMR spectroscopy (see Table 8). The ^{1}H NMR spectra of these cationic species each have three signals for the protons of the CH_2 groups with equal intensities. The fact that these signals are observed as two doublets and one singlet with equal intensities indicates that these species have a symmetry plane and contain no Cp* rings. The similarity of $\Delta\delta_{AB}$ for **15b** and **25b** (0.45 and 0.48) and the equality of these values for **15c** and **25c** (0.62) are also consistent with the 1,2-positions of the CH_2 groups in the $C_5Me_3(CH_2)_2$ fragment of the trications.

In the ^{13}C NMR spectra, two signals for the C atoms of the CH_2 groups (with the intensity ratio of 2 : 1) are observed as two triplets (see Table 8). Hence, the ^{13}C NMR spectroscopic data also confirmed the presence of three CH_2 groups in the structures of **25b,c**.

At the same time, the ^{13}C NMR spectra of these compounds have some characteristic features, which call for a special discussion. On going from carbinols **5b,c** to monocations **1b,c** and then to dications **15b,c** (see Table 8), the resonances of the CH_2 groups are substantially shifted downfield and the spin-spin coupling constants slightly increase. In the spectra of **25b,c**, the chemical shifts and the spin-spin coupling constants for the signals of the CH_2 groups of the $\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2$ ligand are virtually equal to those observed in the spectra of the dications. The signals of the CH_2 groups of the $\eta^6\text{-}C_5Me_4CH_2\text{-}1'$ ligand are shifted upfield, the chemical shift for the signal of this group for Ru-containing trication **25b** being intermediate between the chemical shifts of neutral carbinol **5b** and monocation **1b**. The spin-spin coupling constants for this group are also smaller than those for **1b,c**. In addition, the chemical shifts for the mono- and dications decrease substantially on going from Ru to Os (increase in shielding), whereas the signals of the CH_2 groups of the $\eta^6\text{-}C_5Me_4CH_2\text{-}1'$ ligand for the Ru- and Os-containing complexes are virtually equal.

The results of DFT calculations confirmed the possibility of the existence of these molecules.[5] The enthalpies of formation (ΔH) of compounds **1b**, **15b**, and **25b** from $Cp^*{}_2Ru$, **1b**, and **15b** are −232.2, −124.5, and −13.6 kcal mol^{-1}, respectively. However, these trimethylene species, which contain the metal atom with three lone pairs and three positively charged CH_2 groups, can be stabilized in the gas phase and solution through different mechanisms.

As mentioned at the beginning of the present review, the structures of monocations **1a—c** should be described by the "specific" resonance hybrid **A** with contributions

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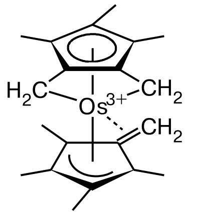
* In addition to the spectroscopic data for trications **25b,c**, Table 8 gives the above-discussed ^{1}H and ^{13}C spectroscopic data for monocations **1b,c** and dications **15b,c** for comparison.

of the metallonium (**A′**), carbocationic (**A″**), and fulvene forms (**A‴**),[5] the mechanism of stabilization of the carbocationic centers being dependent on these contributions. It is reasonable to apply these concepts to trications **25b,c**.

Previously,[6,7] we have noted that the structures **A′** and **A‴** are mere two equivalent ways of describing the same mono- and dicationic complexes (studied by us) or their neutral analogs, *viz.*, the mono- and dimethylene complexes (studied by other researchers). In our opinion, the data available in the literature (results of physicochemical methods among which are X-ray diffraction analysis, NMR spectroscopy, and quantum-chemical calculations) gave no way of unambiguously distinguishing the structures **A′** and **A‴**.[6,7] However, the data obtained in the NMR spectroscopic studies and the results of DFT calculations of the geometry of the trications (trimethylene species) allow one to distinguish the proposed structures necessary for the discussion of the observed phenomena. To obtain independent information on the geometry of the trications, we carried out DFT calculations. The results of these calculations showed that trications **25b,c** in the gas phase can be described as cationic species, which retain a sandwich structure, but their geometry is more distorted (compared to monocations **1a—c** and dications **15b,c** and **16b,c**). The carbocationic centers can be stabilized through two mechanisms.[5]

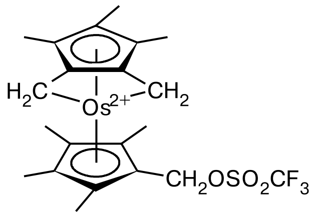
In trication **25c**, the $C(1)H_2$ and $C(2)H_2$ groups are stabilized through the direct interactions with the metal atom (the $Os—CH_2$ bond lengths are 2.41 and 2.435 Å, respectively, and the angles α are 27.2 and 26.2°, respectively). Consequently, the $C(1)H_2$ and $C(2)H_2$ groups form metallonium bonds. In both cases, the structures of the fragments thus formed can be described by the form **A′**. Unlike these groups, the bond of the third group with the metal atom, *viz.*, $Os—C(1')H_2$, is elongated (2.768 Å) and the angle α is 20.4°. In other words, the form **A″** and, particularly, the form **A‴** make the major contributions to the resonance hybrid of the fragment formed by this bond. An increase in the contribution of the form **A‴** was confirmed by the fact that the $Cp—C(1')H_2$ bond length (1.428 Å) is smaller than the lengths of the bonds formed by the $C(1)H_2$ and $C(2)H_2$ groups with the ring. Consequently, the structure of this trication in the gas phase can be described by formula **25c** containing the fulvene fragment **A‴** and can be represented as a π complex of the tricationic fragment $[1,2\text{-}(CH_2)_2C_5Me_3Os]^{3+}$ with the fulvene ligand $C_5Me_4CH_2\text{-}1'$.



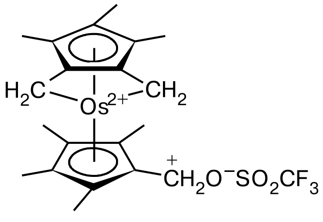
25c

The above-described ^1H and ^{13}C NMR spectra do not contradict the proposed structure **25c**. Thus the fact that the ^{13}C NMR spectrum has two different signals (at high and low field) with the intensities of 1 C and 2 C, respectively, is actually indicative of different types of stabilization of these groups by the metal atom.

Besides, when discussing the structure of the Os-containing trication, account must be taken of the contribution of the carbocationic form **A″** and the ability of the $^+CH_2$ group to be stabilized by the $CF_3SO_3^-$ anion giving rise to a tight ion pair (complex **25c‴**) or the σ bond (complex **25c″**, the formation of ester).



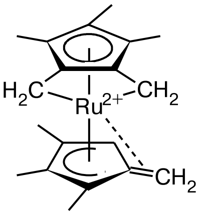
25c″



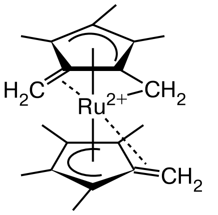
25c‴

If structure **25c‴** were typical of the Os-containing trication, the opposite ^{13}C NMR spectral pattern would be expected, *viz.*, the signal of the $C(1')H_2$ group with a lower intensity would be shifted downfield relative to the signal of two other groups, $C(1)H_2$ and $C(2)H_2$. In this case, the downfield shift of the signal of the CH_2 group would be attributed to a positive charge on this group, whereas an interaction with the Os atom is absent.

The structure of Ru-containing trication **25b** was more difficult to interpret. According to the results of calculations, the short $Ru—C(1)H_2$ (2.442 Å) bond and the inclination angle $\alpha_1 = 20.8°$ indicate that only one CH_2 group interacts with the metal atom in the gas phase. Two other groups, *viz.*, $C(2)H_2$ and $C(1')H_2$, which are bound to different cyclopentadienyl rings, form rather elongated $Ru—C(2)H_2$ (2.925 Å) and $Ru—C(1')H_2$ (2.950 Å) bonds, and their angles α (11.7 and 13.4°, respectively) are much smaller than the angle α_1. This is evidence that Ru-containing complex **25b** is less stable than osmium analog **25c**. Hence, the $C(1)H_2$ group in the Ru-containing trication in the gas phase is stabilized through the direct interaction with the metal atom (form **A′**, the metallonium bond), whereas two other groups, *viz.*, $C(2)H_2$ and $C(1')H_2$, are stabilized primarily through the fulvene fragments (form **A‴**), which corresponds to structure **25b′**.

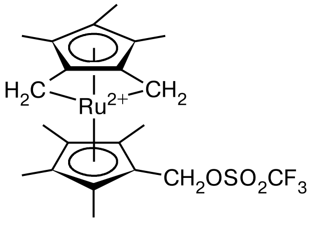


25b

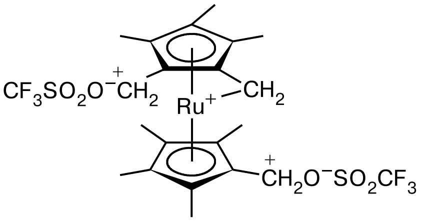


25b′

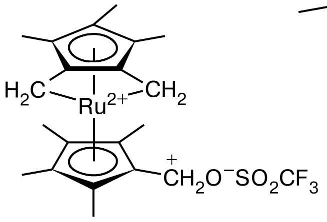
However, according to the ^{1}H and ^{13}C NMR spectra (see Table 8), Ru-containing cation **25b** generated in CF_3SO_3H is structurally analogous to Os-containing trication **25c**. The fact that cation **25b** has different structures in the gas phase and in a CF_3SO_3H medium indicates that the length of the donor-acceptor M—C(2)H_2 bond must change upon the phase-state transition. This possibility has been already noted[41] in the comparison of the structures of monocations **1a—c** in the gas phase and crystalline state. It appeared that the length of the donor-acceptor M^+—CH_2 bond can vary over a wide range (contrary to the Cp—Cp and Cp—M covalent bonds) on going from one phase to another. Hence, it is not inconceivable that less stable Ru-containing trication **25b′** is more sensitive to the phase transition than **25c** and this trication is transformed into **25b** (analog of **25c**) on going from the gas phase to solution.



25b″

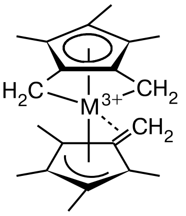


25b‴

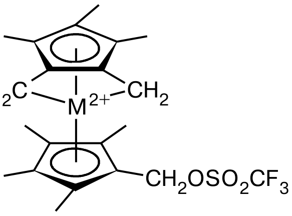


25b⁗

The structure of the Ru-containing trication in solution can be described by structures **25b″**, **25b‴**, and **25b⁗**. The existence of structures **25b‴** and **25b⁗** (formation of tight ion pairs) is highly improbable for the reasons discussed above for the Os analog. Recall that the ^{1}H and ^{13}C NMR spectra unambiguously indicate that the Ru- and Os-containing trications in solutions have identical structures. These trications are characterized by the presence of two groups, *viz.*, C(1)H_2 and C(2)H_2, involved in strong interactions with the metal atom and by the presence of one C(1′)H_2 group whose interaction with the metal atom is much weaker (if ever occurs) as evidenced by the fact that the chemical shift δ(CH_2) of this methylene group is independent of the nature of the metal atom.



25b,c

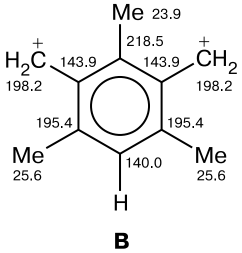


25b″,c″

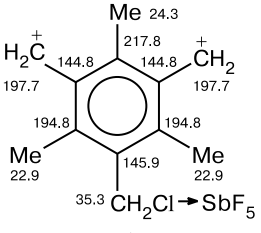
The upfield shift of the signal of this CH_2 group is indicative of either the absence of the positive charge on this group or another type of stabilization of the positive charge, for example, through the formation of a strongly polarized covalent bond (ester). The shifts δ(CH_2) of 5.50 and 65.7 ppm and $^1J_{CH}$ = 157 Hz are typical of the CH_2 groups, which are noncoordinated to the metal atom but are bound to two acceptor substituents, *viz.*, [M^{2+}] and OSO_2CF_3.

Therefore, of all the structures proposed for the description of trications **25b,c**, only **25b,c** and **25b″,c″** are consistent with the NMR spectroscopic data.

As discussed above, the chemical shifts in the ^{13}C NMR spectra depend on the nature of the metal atom and the charge of the complex. Thus, the signals of the dications are shifted downfield relative to those of the monocations (and the latter are shifted downfield compared to their neutral precursors, *viz.*, carbinols). An analogous situation was observed for a series of organic carbenium ions. It should be noted that attempts to generate a trication from trichloride 1,3,5-$(ClCH_2)_3C_6Me_3$-2,4,6 and SbF_5 gave rise to the dication **B′** whose ^{1}H and ^{13}C spectroscopic characteristics are analogous to those of the dication **B** prepared under the same conditions from dichloride 1,3-$(ClCH_2)_2C_6HMe_3$-2,4,6.[52] In the trichloride, the



B



B′

Note. The chemical shifts in the ^{13}C NMR spectra are given.

C—Cl bond in the third CH_2Cl group was not cleaved under the action of SbF_5. Based on the fact that the chemical shifts for the C atoms of the CH_2^+ groups and aromatic ring in the ^{13}C NMR spectrum of the molecule **B** are virtually equal to those observed in the spectrum of the molecule **B**´ and taking into account that the CH_2Cl group is retained, it was concluded[52] that the desired trication was not generated.

Evidently, there is no complete analogy between the organic carbenium ions in which the carbocationic centers cannot interact with the metal atom, on the one hand, and organometallic cations, on the other hand. However, it is necessary to take into consideration the data obtained previously in the treatment of the structures of trications **25b,c**.[52]

It cannot be stated with assurance that changes in the NMR spectra on going from the dications to trications are analogous to those observed in the NMR spectra for the carbinol—monocation—dication series without performing the corresponding calculations (if they are possible). However, based on the spectroscopic characteristics of the trimethylene species (the presence of three CH_2 groups in the molecule) and the bond lengths determined from the DFT calculations, structures **25b,c** can be assigned to the trications in the gas phase and, probably, in solution. At the same time, according to the results of NMR spectroscopy, the fact that the species occurring in solution can, in principle, have the structures of triflate dications **25b″,c″** must not be ruled out.

* * *

The studies started with the primary permethylmetallocenylmethyl cations $[Cp^*MC_5Me_4CH_2]^+$ (where M are iron-subgroup metals) with the aim of elucidating the structures and the mechanism of stabilization of the carbocationic centers in these cations, made it possible not only to solve the problem at hand but also enables us to substantially extend the knowledge of the properties and synthetic possibilities of permethylmetallocenes as well as of their oxidation reactions giving rise to mono-, di-, and trications.

Several procedures were developed for the preparation of cations, among which the one-pot synthesis with the use of strong protic acids, including superacids, is the simplest and most convenient. Under particular conditions, permethylruthenocene and -osmocene proved to be capable of being oxidized to the monocations under the action of different-strength acids. In superacids in combination with oxidizers (oxygen, oleum), these permethylmetallocenes can be oxidized to di- and trications. It is easy to find the conditions under which oxidation can be terminated at any step. As a result, it was demonstrated for the first time that the Me groups in permethylruthenocene and -osmocene are readily subjected to CH-activation under the conditions of the oxidation reaction. The oxidation reactions open up a simple and convenient approach to the previously unavailable functional derivatives of permethylmetallocenes using the reactions of the metallocenylmethyl cations with nucleophilic reagents.

A comparison of the physicochemical characteristics (results of X-ray diffraction analysis, ^1H and ^{13}C NMR spectroscopic data) with the results of quantum-chemical DFT calculations for these mono-, di-, and trications made it possible to describe their structures as a "specific" resonance hybrid with contributions of the metallonium (onium), carbocationic, and fulvene structures.

The preparation and studies of the permethylmetallocenylmethyl cations gave impetus to a new line of investigation, which is not limited only to iron-subgroup complexes but can be extended by the involvement of permethylcyclopentadienyl complexes of other transition metals.

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