Reviews

Permethylated metallocenes as suitable models for the preparation of onium mono- and dications

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Permethylated metallocenes of the iron subgroup (M = Fe, Ru, Os) have been considered as suitable models for preparing onium mono- and dications. EHM MO calculations of the charge distribution in monocations of the type $(C_5Me_5MC_5Me_4CH_2)^+$, homoannular dications of the type $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$, and heteroannular dications of the type $[(C_5Me_4CH_2)_2M)]^{2+}$ indicate that the positive charge is mostly localized at the metal atom (M = Ru, Os and, to a lesser degree, Fe). This fact was confirmed by X-ray structural studies and the data of IR, ^{1}H, and ^{13}C NMR spectroscopy, and electrochemistry. The reactivity of the monocations, in particular, interconversion of the odd-electron (17- and 19-electron) metallocenium radical cations and 18-electron metallocenyl carbocations has been studied. A M—C(α) σ-bond (M = Ru, Os) is realized in the mono- and dications. It has been suggested that the metallocenyl carbocations (M = Ru, Os) are in fact metallonium or metallocenonium cations (or dications).

Key words: onium mono- and dications, carbocations, permethylated metallocenes, EHM MO calculations, X-ray structural studies, IR and NMR spectra.

Introduction

It is known that cationic onium species can be prepared from organic compounds incorporating heteroatoms (E) with lone electron pairs.

R_n—E + R'^+ → R_n—E—R′]$^+$, E = N, P, O, S, *etc.*

In the chemistry of organic derivatives of transition metals, the problem of the formation of onium compounds has been scarcely considered so far. All of the existing data involves the generation of the products of protonation of the metal atom in solution,[1] for example,

$$\mathrm{CpFeCp + H^+ \rightarrow [CpFe(H)Cp]^+}$$

or the preparation of carbocations stabilized by a

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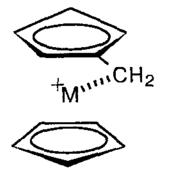
metallocomplex fragment, for example, type **1** α-metallocenyl carbocations (see Refs. 2, 3):



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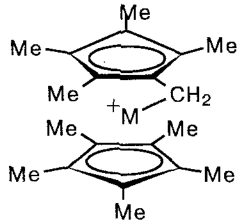

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We were first to assign this type of complexe to onium compounds using permethylated compounds **2*** as examples (see Refs. 4, 5).

In the present work we have surveyed the results of our studies on the preparation and determination of the structure of onium mono- and dications.

Onium monocations

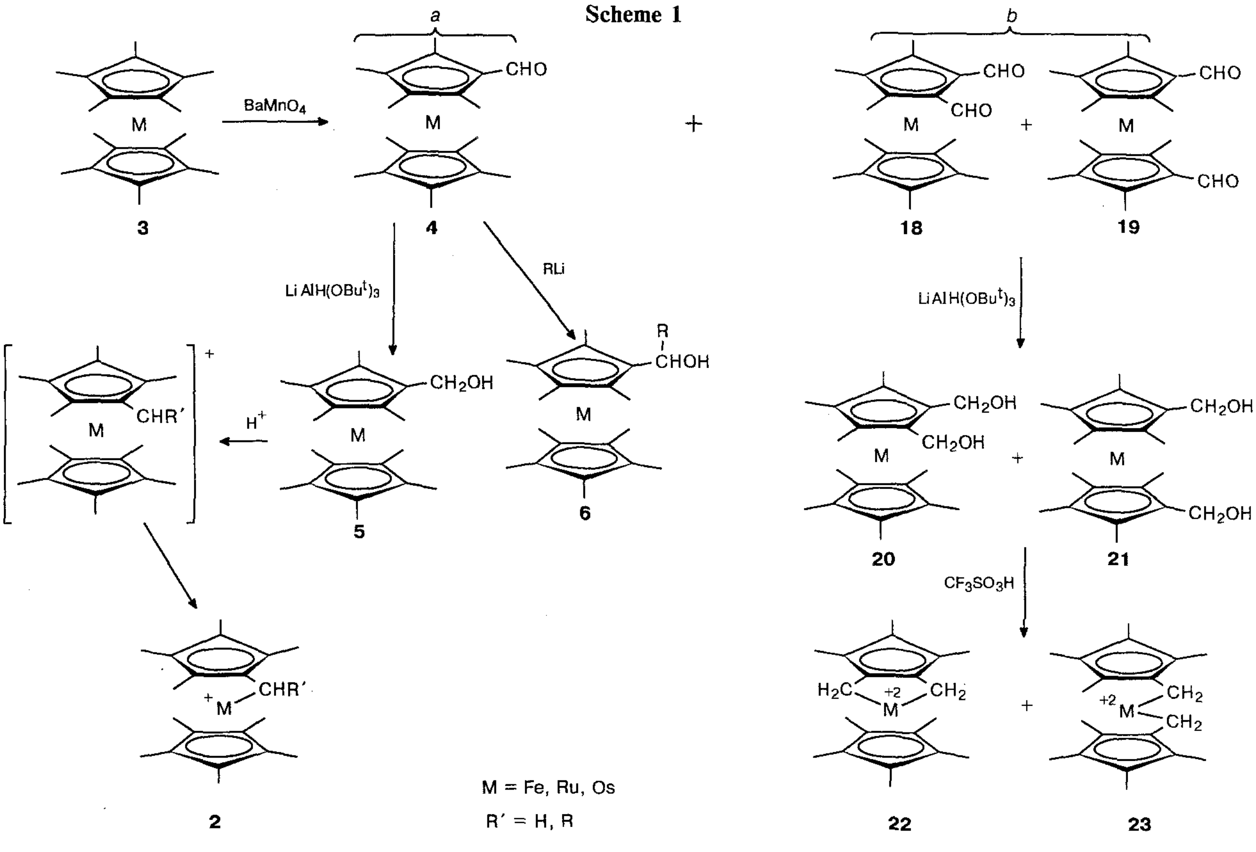
The discovery of the substantial stabilizing effect of the ferrocenyl group on the neighboring carbocation center became the subject of prolonged speculation about the structure of α-metallocenyl carbocations and the mechanism of their stabilization.[2,3]

Previously this problem has been mostly studied with nonmethylated α-metallocenyl carbocations, among which no sufficiently stable primary carbocations were known. Therefore the investigation could be carried out only by spectroscopic methods, which did not enable the unambiguous determination of the structure. Despite the fact that for secondary and tertiary carbocations, such as diferrocenyl[6] and ferrocenyl(diphenyl) carbocations,[7] X-ray structural study was carried out, the effects of the electronic and steric factors of the substituents at the carbocation center could not be ignored in the interpretation of the results obtained. Cais *et al.*[6] have noted previously that the X-ray structural data obtained by them do not solve the problem of the mechanism of stabilization of the carbocationic center. The structure of the primary carbocations therefore still remained to be investigated.

We began to study this problem using permethylated α-metallocenyl carbocations of the iron subgroup metals (Fe, Ru, Os) as examples. This allowed us to obtain stable primary cations in which the nature of the metal, and thus the size of the metal atom, varied. In addition, we obtained secondary carbocations (this has been considered previously[4,5,8,9]).

The cations were prepared according to Scheme 1, which involves oxidation of decamethylmetallocenes (**3**) to aldehydes (**4**), reduction of the latter to give primary carbinols[4,5] (**5**), and the reaction of compounds **4** with organolithium compounds to afford secondary car-

Scheme 1



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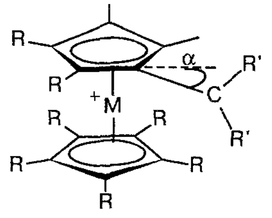
* In the schemes hereinafter the Me groups are not shown.

Table 1. The M—C(α) bond lengths and the angles α of the inclination of the CR'_2 groups to the metal atom in salts **2** (according to X-ray structural data)



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R	R′	M	M—C(α)/Å	Angle α/deg	Reference
Me	H	Os	2.244	42.5	11
Me	H	Ru	2.270	40.3	10
H	Ph	Os	2.387	38.4	8
H	Ph	Ru	2.482	34.0	15
H	Ph	Fe	2.715	20.7	7

Table 2. The energy and charge characteristics of the $[C_5R_5MC_5R_4CH_2]^+$ complexes

R	M	q(M)	q(C)	$q(CH_2)$	E^{theor}/eV*	E^{exp}/V**
H	Fe	0.25	0.28	0.36	1.28	—
	Ru	1.48	−0.02	0.04	1.68	—
	Os	0.85	0.06	0.12	1.93	—
Me	Fe	0.10	0.23	0.31	1.33	1.43
	Ru	1.35	−0.25	−0.13	2.52	>2.16
	Os	0.84	−0.20	−0.08	3.32	>2.34

Note. The MO calculation was carried out using the previously described method.[15]

* $\Delta E^{theor} = E_{LUMO} - E_{HOMO}$.

** ΔE^{exp} is the experimental value derived from electrochemical data[17] on the $(C_5H_5MC_5H_4CPh_2)^+$ cations.

binols[8,9] (**6**). The corresponding cations **2** were prepared by treating carbinols with protic acids[4,5,8,9] (Scheme 1, route *a*).

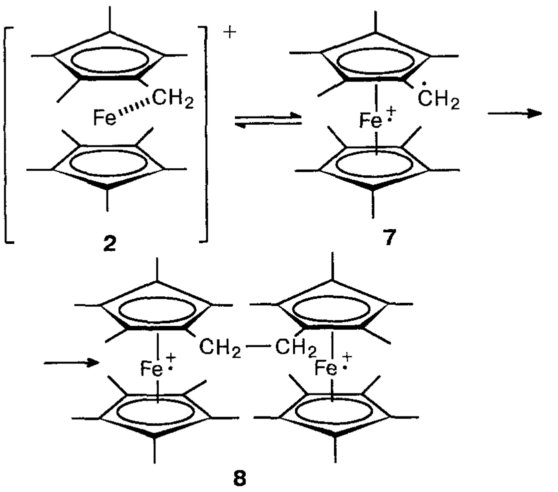
Among the primary cations compounds of ruthenium and osmium were found to be especially stable.[10,11] An X-ray structural study of these cations showed that the interaction of the carbocationic center with a lone electron pair (LEP) of the metal is so efficient that a $M—CH_2$ σ-bond is formed. Table 1 presents the lengths of the M—C(α) bonds in cations **2** (M = Ru, Os). It can be seen that they differ little from the lengths of normal M—C covalent σ-bonds for these metals, which are equal to 2.18 (Ru—C)[12] and 2.22 (Os—C)[13] Å. The existence of M—C(α) σ-bonds for M = Ru and Os indicates the formation of onium compounds. In general, they may be called metallonium compounds or in this particular case, the metallocenonium compounds. As a consequence of the formation of the σ-bonds, the positive charge should be almost entirely transferred from the carbon atom to the metal (in other words, we may speak of the formation of a metallacyclopropenylium cation as a fragment of the onium cation[14]). This is supported by EHM MO calculations of the charge characteristics of the $(C_5R_5MC_5R_4CH_2)^+$ cations (where M = Ru, Os, R = H, Me) (Table 2).[15]

Thus, among the cations stabilized by a metallocenyl fragment, we found Ru- and Os-containing species that are in fact real onium compounds, rather than carbocations. The "coordination number" of the metal atom in these species, like those of any heteroatom in onium compounds, is increased by unity, or, in other words, a sort of increase in "hapticity" ($\eta^5 \rightarrow \eta^6$) occurs.

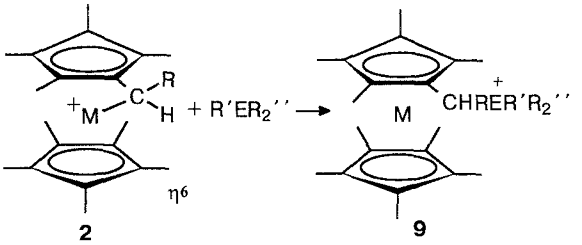
It is quite obvious that the occurrence of the M—C(α) σ-bond is the extreme case of the stabilization of the carbocation center by a metal atom. The intermediate situations, when this bond is extended and the positive charge partially remains at the exocyclic carbon atom, C(α), are also possible. At the same time, one should keep in mind that the examples we have considered are specific onium compounds, which are formed by an intramolecular interaction between the C(α) cationic center and the metal. It is impossible to draw a border line between a real onium compound and an α-metallocenyl carbocation, and intermediate cases may be assigned to both onium compounds and carbocations. It is of interest to note that in all of the α-metallocenyl carbocations studied by X-ray diffraction analysis, the C(α) carbocation center was tilted towards the metal by the angle α. This is observed even in those cases where the α-carbocation center is efficiently stabilized by electron-donating groups. For example, in $(CpFeC_5H_4)_2CH^+$, the α angles are 19.9° and 17.9° and in $CpFeC_5H_4CH^+C_3H_2$, α is 6.3° (see Refs. 6 and 16, respectively). In the $CpFeC_5H_4C^+Ph_2$ cation (see Ref. 7), which is an analog of the Re and Os derivatives studied by us, the α angle is 20.7° (see Table 1), which indicates substantial donor-acceptor interaction of the α-carbocationic center with a LEP of the metal.

At the same time, one should note that the introduction of substituents, such as two phenyl groups, at C(α) when there are no methyl substituents in the cyclopentadienyl ring, caused the M—C(α) bond to lengthen and the inclination angle to decrease compared with that in $C_5Me_5M^+C_5Me_4CH_2$ (M = Ru, Os). However, these changes are not as significant as one would have expected (see Table 1). Comparison of these data makes it possible to evaluate the approximate $Fe—CH_2$ bond length and the angle α for $[C_5Me_5FeC_5Me_4CH_2]^+$ (**2**). This cation was insufficiently stable for an X-ray study to be carried out. Relying on the X-ray structural data for the $[CpFeC_5H_4CPh_2]^+$ ion (see Table 1), it may be suggested that the $Fe—CH_2$ bond in **2** must be somewhat shorter than 2.71 Å (~2.5—2.6 Å) and the inclination angle α must be greater than 20.7° (~25—30°). But, since the length of a Fe—C covalent σ-bond varies over the range 2.00—2.10 Å (see Ref. 17), one may infer that in the iron-containing ion, this bond is very much extended compared with the Ru- and Os-containing cations, and a substantial part of the positive charge must remain at the CH_2 group.* The latter is consistent with the results of EHM MO calculations[15] (see Table 2). This fact and the smaller energy gap, $\Delta E_{\text{teor}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ (see Table 2), for Fe-containing cations are probably responsible for the fact that redox processes readily occur in these cations. For example, a singlet-triplet transition of the $[C_5Me_5FeC_5Me_4CH_2]^+$ (**2**) cation affords diradical cation **7**, which is irreversibly doubled to give the paramagnetic diradical dication **8** (see Ref. 18) (Scheme 2).

Scheme 2



Scheme 3



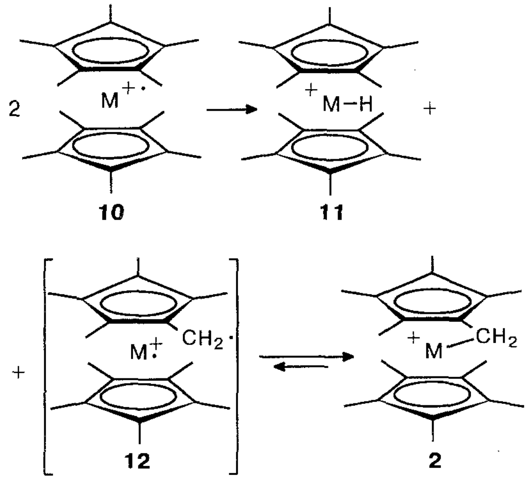
2: M = Os, R = H;
9a: M = Ru, E = P, R = R′ = R′′ = Ph;
9b: M = Os, E = P, R = H, R′ = Ph, R′′ = Me;
9c: M = Os, E = N, R = H, R′ = R′′ = Me

The type **2** cations enter into reactions of "onium exchange" or quaternization (Scheme 3) of tertiary phosphines and amines like normal onium compounds (to give tertiary ammonium or phosphonium salts **9**); it may probably be assumed that this reaction occurs with a kind of transfer of the reaction center (with cleavage of the M—C(α) σ-bond).

The clear-cut tendency of the Ru- and Os-containing ions to form onium cations apparently accounts for the reaction of the odd-electron radical cations of decamethylruthenocenium[21] and decamethylosmocenium that readily occurs.[22]

This reaction was discovered by Koelle[21] for the ruthenium-containing ion **10**. It was shown to occur in the presence of stoichiometric amounts of chloride ions. We found[22]** that a similar disproportionation is also characteristic of the osmium-containing cations **10** and that this process is accelerated in the presence of nucleophiles and solvating solvents (such as acetonitrile and THF). A scheme for this conversion has been proposed, according to which a decamethylmetallocenium ion can act both as a donor of radical hydrogen (possibly as a 19-electron species, $[(C_5Me_5)_2MNu]^{\cdot n+}$, $n = 0, 1$) and as its acceptor (possibly as a 17-electron species, $(C_5Me_5)_2M^{+\cdot}$). Consequently, apart from the protonated metallocene **11**, a biradical species **12** is formed, which is readily converted into the much more stable metallocenium diamagnetic cation (Scheme 4).

Scheme 4



Later we observed an analogous transformation of the η^5-indenyl-η^5-pentamethylcyclopentadienylruthenium **13** radical cation (see Ref. 24), which disproportionated to give the diracial-cation species (**14**) and the protonated metallocene (**15**). Particle **14** is converted into the diamagnetic onium cation (**16**), whereas the

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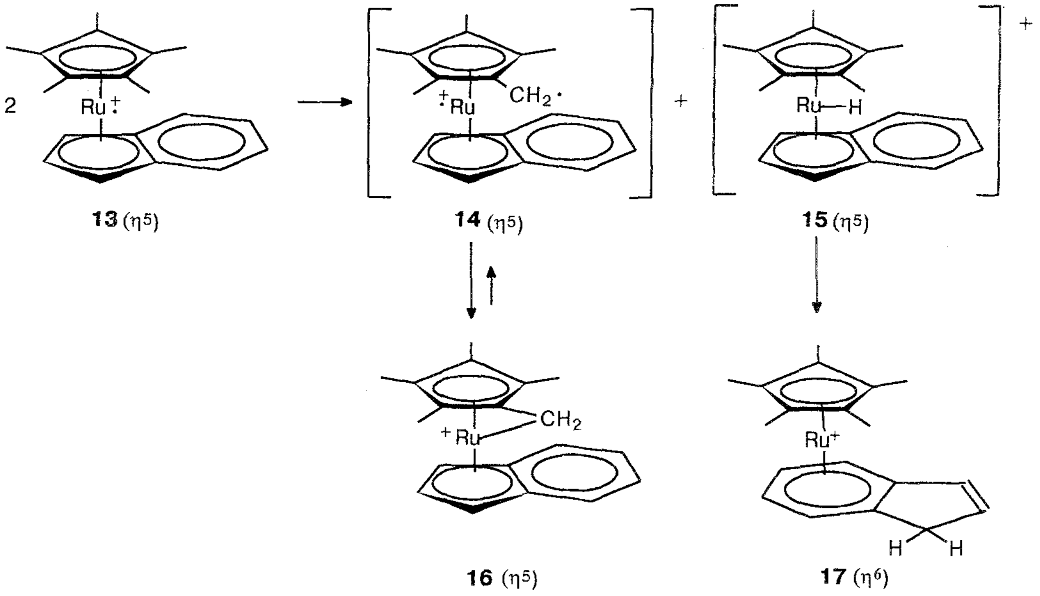
* Analogous inferences may be made based on the study of the type **2** cations under consideration by NMR spectroscopy[19] and electrochemistry.[20]

** It should be noted that Miller *et al.*[23] drew the wrong conclusion that the decamethylosmocenium atom cannot be converted into the type **2** cation.

Scheme 5



protonated metallocene **15** undergoes a $\eta^5 \rightarrow \eta^6$ haptotropic shift to give the (η^6-indene)(-η^5-pentamethylcyclopentadienyl)ruthenium cationic complex (**17**) (Scheme 5).

One should note that metal atoms in metallocenes possess various basicities, therefore, protonated metallocenes that should also be regarded as onium compounds, have different stabilities. For example, $[(C_5Me_5)_2Ru{-}H]^+$ readily loses hydrogen bound to the metal atom, while the $[(C_5Me_5)_2Os{-}H]^+$ cation can be isolated in the idividual state.[25] As was shown above, the unstable cation **15** tends to undergo a haptotropic shift.

The basicity of the metal atom in metallocenes varies in the sequence Fe < Ru < Os. Therefore, metallocenylcarbinols of the general formula $C_5R_5MC_5R_4CR'R''OH$ can form intramolecular hydrogen bonds of O—H...M type (see Refs. 26, 27), and the strength of these bonds will vary in the same order.

Metallocenes are also able to form intermolecular hydrogen bonds of the M...H—O type with weak OH acids, such as phenols *p*-X—C_6H_4OH (where X = H, F, or NO_2).[28] It is of interest that the formation of the protonation product in the reaction with trifluoroacetic acid is also preceded by the formation of an intermolecular hydrogen bond:[29]

$$(C_5R_5)_2M + HOCOCF_3 \rightleftarrows (C_5R_5)_2M...H{-}OCOCF_3 \rightleftarrows$$

$$\rightleftarrows [(C_5R_5)_2M{-}H]^+\ {}^-OCOCF_3\ ,$$

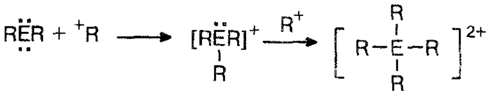
$$R = H, Me$$

The ease of this process increases in the order: $(Cp)_2Ru < (Cp)_2Os < (C_5Me_5)_2Ru < (C_5Me_5)_2Os$.[29]

Onium dications

The metal atoms in metallocenes of the iron subgroup have three LEP, d_{xy}, $d_{x^2-y^2}$ and d_{z^2}, located at the $(a'_{1g})^2(e_{2g})^4$ levels. Therefore, an attempt was undertaken to prepare homoannular $[1,2\text{-}(CH_2)_2{-}C_5Me_3MC_5Me_5]^{2+}$ and heteroannular $1,1'\text{-}[(CH_2{-}C_5Me_4)_2M]^{2+}$ dications and to study the efficiency of the donor-acceptor interaction of two of the LEP of the metal with two carbocationic centers. The idea to synthesize these dications belongs to Prof. R. Hoffmann (Cornell University, USA), who studied the problem of the formation of conformers in the case of 1,1'-heteroannular dications.

G. A. Olah[30] was the first to suggest that it is possible to generate onium dications involving two LEP of the same heteroatom using compounds of nontransition metals, such as oxygen, sulfur, *etc.*, as examples.



$$R\ddot{E}R + {}^+R \longrightarrow [R\ddot{E}R]^+ \xrightarrow{R^+} \left[\begin{matrix} & R & \\ R- & E & -R \\ & R & \end{matrix}\right]^{2+}$$

$$\qquad\qquad\qquad\quad\ \ |\ R$$

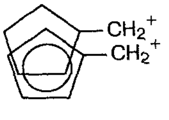
However, the calculations carried out by him showed that these species are rather thermodynamically unfavorable. Their formation could not be detected even by spectroscopy. The models proposed by us had a number of advantages that allowed us to hope that the onium dications could be obtained. First, the transition metal atoms in these compounds possess a higher ability to localize the positive charge than the above-mentioned heteroatoms of nontransition elements E. Second, the presence of permethylated cyclopentadienyl rings should also be beneficial for stabilization of the dications. Third, the favorable chelate-type metallacycles formed by intramolecular cyclization might play a considerable role in the stabilizaton of metallonium dications.

In fact, the synthesis of 1,2- and 1,1′-dications from decamethylmetallocenes (M = Fe, Ru, Os) was carried out according to the same Scheme 1 using route *b*.

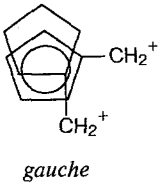
Scheme 1 indicates that oxidation of the iron subgroup decamethylmetallocenes **3** affords dialdehydes (**18**) and (**19**), which react with $LiAlH(OBu^t)_3$ to give carbinols (**20**) and (**21**). The latter are converted to dications (**22**) and (**23**) through the action of acids. However, one should keep in mind that the major product of the first step is monoaldehyde **4** (yield ~60 %), which can be easily separated from the mixture of 1,2- and 1,1′-dialdehydes (the yield of the mixture is 3—5 %). Only the main product, 1,2-dialdehyde **18**, can be isolated pure from the mixture of 1,2- and 1,1′-dialdehydes. Reduction of compound **18** followed by treatment with CF_3SO_3H gave 1,2-dication **22**, whose structure has been confirmed by ^1H and ^{13}C NMR spectra.[31] The spectral data will be considered below.

1,1′-Dialdehyde **19** cannot be isolated in the pure state. Therefore, 1,1′-dication **23** generated from **19** was studied using the unseparated mixture of 1,2- and 1,1′-dications. Since the individual 1,2-dications (M = Ru, Os) **22** have been comprehensively studied by us using ^1H NMR spectra,[31] their presence in the mixture with 1,1′-dications **23** did not hamper the study of the latter. Furthermore, the investigation of this mixture proved to be rather useful, since it allowed us to compare the behavior of these cations under identical conditions.

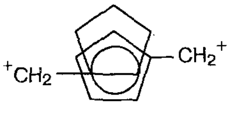
When we began this study, we believed the dications to be considerably less stable than the monocations and that the positive charge would remain partially at the carbon atoms of the methylene groups. Therefore, it was assumed that, because of electrostatic repulsion, of the three possible extreme cases of rotamers (*syn*, *gauche*, and *anti*) with rotation angles Φ = 0, 90, and 180°, respectively, only the *anti*-rotamer (Φ = 0°) would exist.



syn
Φ = 0°



gauche
Φ = 90°



anti
Φ = 180°

However, apart from the electrostatic repulsion, the structure of these ions should be considerably affected by the electronic factors caused by the donor-acceptor interaction between the LEP of the metal and the vacant orbitals of the electron-deficient carbon atoms of the CH_2 groups, as has already been shown for the monocations. Therefore, it was important to first evaluate the role of the donor-acceptor interaction in the dications and to find out, which of the possible rotamers it favored. For this purpose, R. Hoffmann and R. M. Minyaev carried out EHM calculations of the dicationic species and determined the potential energy curves for the rotation of the cyclopentadienyl rings.[32]

The calculations afforded somewhat unexpected results: the *gauche*-rotamers (Φ = 90°) possess the minimum energy, whereas the *syn*- (Φ = 0°) and *anti*-rotamers (Φ = 180°) correspond to the heights of the energy barriers. It should be noted that the ruthenium dication has the highest *anti*-barrier.

To confirm the theoretical calculations we carried out an ^1H NMR study. As was noted above, we used a mixture of 1,2- and 1,1′-dications **22** and **23**. The ^1H NMR spectra of the mixture were recorded in $MeNO_2$ or CD_2Cl_2/CD_3NO_2. It should be noted that the signals of both the 1,2- and 1,1′-dications are desheilded compared with the corresponding signals of the monocations.

The clearest spectral pattern was obtained for Ru- and Os-containing dications at room temperature. In addition to the AB-quadruplet of the methylene protons of the 1,2-isomers* (δ(Ru) = 5.21 and 4.88 and δ(Os) = 5.37 and 4.79), the ^1H NMR spectrum exhibited another quadruplet corresponding to the methylene protons of the 1,1′-isomers (δ(Ru) = 5.12, 4.99 and δ(Os) = 5.74, 5.28). The ratios between the isomers were 70 : 30 and 80 :20 for Ru and Os compounds, respectively.

The fact that the signals of the protons of the CH_2 groups of the 1,2-isomers are manifested as an AB-quadruplet is due to their different positions with respect to the symmetry plane that goes through the metal atom and the middle of the C—C bond of the ring between the CH_2 groups.

The nonequivalency of the protons of the CH_2 groups in the 1,1′-isomers, which occur as an AB quadruplet, may indicate that the solutions contain only *gauche*-rotamers, since *syn*- and *anti*-rotamers having a symmetry plane would exhibit an A_2 spin system. The *gauche*-rotamer has no symmetry plane.

The study of the temperature dependence of the ^1H NMR spectrum showed[32] that a decrease in the temperature does not cause variations in the spectral pattern. When the temperature is increased up to 80 °C, the character of the signals for the Ru-containing isomers does not change. However, it is significant that in the 70—80 °C range, the intensity of the signals associated with the 1,2-isomer decrease. After heating the

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* The C atoms of the CH_2 groups are exhibited in the ^{13}C NMR spectra of the Ru- and Os-containing dications as singlets (δ(Ru) = 88.38., $^1J_{^{13}CH}$ = 171 Hz; δ(Os) = 71.13, J_{CH} = 172 Hz) strongly desheilded compared with those in the spectra of the monocations, which is in agreement with the structure proposed for the dications.[31]

sample at 80 °C and cooling to 60 °C, the ratio of the 1,2- to the 1,1′-isomer changes from 70 : 30 to 40 : 60. Simultaneously, additional signals appear in the 4.5—4.7 ppm range, which should be assigned to the decomposition products of mostly the 1,2-isomer. This phenomenon has been reported for derivatives of ferrocenes.[33,34]

In the case of Os-containing dications, the 1,2-isomer does not decompose at 70 °C, which is in agreement with the view that the Os—ring bond is stronger. However, the doublet lines of the AB-quadruplet at δ 5.74 and 5.28 corresponding to the 1,1′-isomer coalesce already at 40 °C into two singlet lines with half-height widths of 3.7 Hz. At 70 °C, their widths amount to 10 Hz. These changes are temperature-reversible, are adequately described by the model of exchange processes occurring between the AB and A_2 spin systems, and may be attributed to an increase in the population of the *anti*-rotamer.

Fe-containing dications were the least stable. Their ^1H NMR spectra are not sufficiently resolved even at low temperatures. At −88 °C, in the region typical of CH_2-protons, two pairs of broadened singlets are exhibited at δ 4.88, 5.23 and 5.13, 5.91 corresponding to the 1,2- and 1,1′-isomers (70 and 30 %, respectively). As the temperature increases, the spectral lines of the 1,1′-isomer are gradually broadened, while the widths of the lines of the 1,2-isomer remain practically unchanged up to −30 °C. A further increase in the temperature results in the irreversible broadening of all of the lines due to decomposition of the dications and the appearance of paramagnetic impurities. The spectral pattern between −88 and −30 °C somewhat resembles the behavior of the Os-containing 1,1′-dication.

In summary it should be noted that the experimental data obtained are in good agreement with the results of EHM calculations, which predicted that in the case of the 1,1′-isomers, only the *gauche*-rotamers are thermodynamically stable; the fact that the barrier to the transition to the *anti*-rotamer is higher for the Ru-containing ion than for Os-containing ion is also consistent with the EHM calculation.

The stability of the *gauche*-rotamer indicates that the interaction with the carbocation centers involves not the pure $d_{x^2-y^2}$ and d_{xy} LEP of the metal atom (in this case, the conformer with a rotation angle Φ of 45° would be the most stable), but the LEP located in the hybrid orbitals built of all three of the LEP, $d_{x^2-y^2}$, d_{xy}, and d_{z^2}.

The fact that the *gauche*-rotamer considerably predominates even at elevated temperatures attests that the donor-acceptor interaction between the metal and carbocation centers in the dications is rather efficient; the relatively high stability of the *gauche*-rotamer experimentally confirms the suggestion that the positive charge in these cations is actually located at the metal atom, rather than at the CH_2 groups, since in the opposite case, due to electrostatic repulsion of the two CH_2 groups, the *anti*-rotamers would have been observed.

Table 3. Calculation of the geometry of the dications, the charges q at the metal and the CH_2 group, and the X-ray data for the monocations

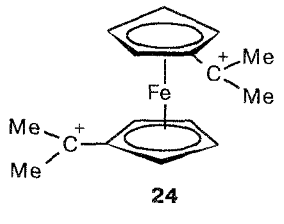
Parameter	1,1′-Dication *gauche*-rotamer		Monocations	
	Ru	Os	Ru	Os
α/deg	40.0	40.0	40.3[a]	41.8[a]
$M-CH_2$/Å	2.200	2.22	2.27[a]	2.24[a]
q_M	2.24	1.75	1.48[b]	0.85[b]
q_{CH_2}	−0.16	−0.10	−0.02[b]	0.06[b]

[a] See Refs. 6—8. [b] See Ref. 9.

The dications have not been yet isolated in the crystalline state, since they are readily hydrolized during isolation. For example, partial hydrolysis of $[Ru(C_5H_4CPh_2)]^{2+}(CF_3SO_3)_2^-$ yields the hydroxy substituted cation $[HOCPh_2C_5H_4RuC_5H_4CPh_2]^+$, which has been studied by X-ray diffraction analysis.[14] To determine the geometry of the initial cations as well as the charges (q) on the metal (M) and the CH_2 groups, an EHM calculation has been carried out (Table 3).[32]

Comparing the calculated data for the dications with the X-ray structural data for the monocations, one may note that the inclination angles α and the $M-CH_2$ distances for the dications differ little from the corresponding parameters in the monocations. As shown by the calculations, the positive charges are also almost entirely located at the metal, while at the carbon atoms, the charge is nearly zero. It should also be noted that the $M-CH_2$ σ-bond may occur only in the case of *gauche*-conformers. As was mentioned above, the lengths of the $M-CH_2$ σ-bonds for M = Ru and Os are equal to 2.18 and 2.22 Å (see Refs. 12 and 13, respectively).

Thus, all of the experimental data and the results of the calculations indicate that the dications of the metallocene series prepared by us are the first stable onium dications, which, unlike the onium dications of nontransition metals (E = O, S, *etc*), were detected by NMR spectra. The formation of these metallonium dications is undoubtedly made possible by the high ability of the metal atom to localize positive charge and by the high electron-donating properties of the permethylated cyclopentadienyl rings. The formation of a favorable chelate-type metal-containing ring is also of importance for the stabilization of the metallonium dications.



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In conclusion it should be noted that permethylated metallocenes proved to be suitable models for generating the first stable onium dications. The conclusion concerning the formation of the onium dications is also supported in this case by the fact that Pittman,[35] who generated the first analogous type **24** dication, observed only one singlet for the protons of the methyl groups at C(α) in the ^{1}H NMR spectrum, which attests that this dication exists in solution only as the *anti*-rotamer. The presence of the *anti*-rotamer indicates first of all that the positive charge is substantially localized at the C(α) atom. Therefore, Pittman's dication may be considered to be a dicarbocation, rather than an onium compound. Our preliminary results show that in the case of the Ru and Os analogs of "Pittman's cations", similar phenomena are observed. It is likely that one *anti*-rotamer for each of the two diastereomers has been observed previously[36] for $Ru(C_5H_4CH^+Ph)_2$ in a DSO_3F (or HSO_3F, or H_2SO_4) solution.

In summary it should be noted that the results obtained by us and reported in the literature indicate that a smooth transition (a sort of continuum) exists between carbocations and onium cations for both mono- and dications.

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