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Dications of the Type 1,1′-$[(C_5Me_4CH_2)_2M]^{2+}$ and $[1,2\text{-}(CH_2)_2C_5Me_3MC_5Me_5]^{2+}$ for the Iron Subgroup. ^1H NMR Spectra and Determination of Possible Rotamers for the 1,1′-Dications

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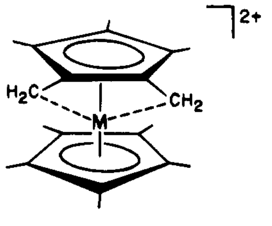
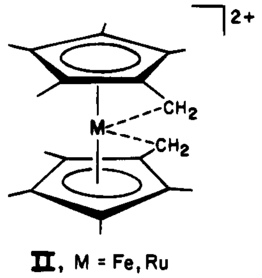
The syntheses, temperature-dependent nuclear magnetic resonance studies, and calculation of the electronic structure of the 1,1′-dications derived from decamethylmetallocenes (M = Fe, Ru, Os) are reported. It is possible to synthesize these dications in a mixture with their 1,2-isomers. The proton NMR spectra indicate substantial interaction of the carbocation centers with the metal and a definite conformational preference for a *gauche* conformation. This geometrical preference is predicted by approximate molecular orbital calculations of the extended Hückel type, with a calculated barrier to internal Cp-ring rotation close to the observed one of 7.8 kcal/mol for M = Os.

Introduction

We have recently demonstrated the ability of ruthenium and osmium atoms in metallocenes to stabilize not only one α-carbocation center but also two such centers in the homoannular dications **I**.[1] Donor−acceptor interaction between unshared electron pairs on the metals and carbocation acceptor orbitals is responsible for this stabilization.[1]



I, M = Ru, Os



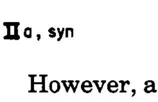
II, M = Fe, Ru

In this contribution we not only continue investigation of the properties of permethylated Ru- and Os-containing ions **I** and **II** but also expand our study to Fe-containing analogs. The main goal of the present investigation is to compare the properties of 1,2- and 1,1′-dications. The less stable dications **II**, in contrast to monocations of the type $(C_5Me_5MC_5Me_4CH_2)^+$, may also exhibit a new type of conformational nonrigidity arising from the electrostatic repulsion of two CH_2 groups or from an orbital effect depending on specific donor−acceptor orbital interactions.

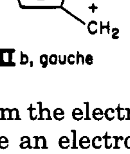
Discussion

It is known that the barrier to internal rotation of cyclopentadienyl rings in neutral metallocenes is very low: for ferrocene ≈ 1 kcal/mol, for ruthenocene ≈ 8.1 kcal/mol, and slightly higher for osmocene.[2] Methyl substitution in the cyclopentadienyl rings does not appear to influence significantly these barriers.

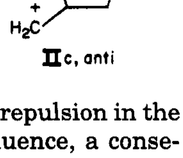
Suppose we define the relative rotation of the two CH_2^+ substituents (seen in projection along the axis passing through the centers of the Cp rings) by the angle ϕ. One might expect that, for the 1,1′-dications **II**, due to electrostatic repulsion the *anti*-rotamer **II** ($\phi = 180°$) should be more stable than *syn*- ($\phi = 0°$) and *gauche*- ($\phi = 90°$) rotamers.



IIa, syn



IIb, gauche



IIc, anti

However, aside from the electrostatic repulsion in the ions, there should be an electronic influence, a consequence of donor−acceptor interaction between unshared electron pairs on the metal atom with vacant orbitals of electron-deficient carbon atoms.[3] The stability and structure of the monocations $(C_5Me_5MC_5Me_4CH_2)^+$

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1994.

[1] Kreindlin, A. Z.; Fedin, E. I.; Petrovskii, P. V.; Rybinskaya, M. I.; Minyaev, R. M.; Hoffmann, R. *Organometallics* **1991**, *10*, 1206.

[2] Doman, T. N.; Landis, C. R.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 7264.

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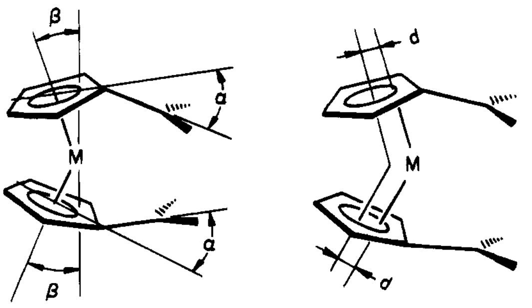

Figure 1. Definition of the geometrical parameters in dications of type **II**.

(where M = Ru[4a] and Os[4b]) show that the interaction of methylene groups with metal atoms is so strong that the M—CH$_2$ bond length approximates that of Ru—C and Os—C covalent bonds.[4] These facts emphasize the importance of the donor-acceptor interaction. The positive charge thus appears to be mainly localized on the metal atom, which allows one to call the monocations metallocenonium compounds (or metallonium cations).

However, the stability of the dications to hydrolysis is significantly diminished, compared to the monocations. We have shown that the compounds are easy hydrolyzed and can be obtained only in superacid media.[1] Therefore it is important to estimate the role of donor—acceptor interaction in the dications and to determine which rotamers are stabilized. To elucidate this matter we have studied variable temperature ^{1}H NMR spectra of these compounds. And we have carried out calculations of compounds of type **II** by means of approximate molecular orbital (MO) calculations of the extended Hückel (EH) type.[5]

Let us examine the calculations first. The computational parameters are specified in the Appendix. We have taken C—C and C—M bond lengths (given in the Appendix) from experimental data[3,4] and kept them constant during optimization of following parameters: angles α and β, "slipping off" distance *d*, and rotational angle ϕ. All of these are defined in Figure 1, except ϕ. ϕ is the angle of internal rotation of the Cp rings, defined in the projection of the rings (with their CH$_2^+$ groups) on the plane between them.

Calculations carried out for ions of type **II**, with and without methyl substitution in the rings, show that the introduction of methyl groups in the rings has little influence on the computational results. This is in accord with the results obtained for 1,2-dications **I**.[1] We present here the results for the 1,1′-dications. All calculations have been carried out with optimization of only four geometry parameters α, β, ϕ, and *d* in the following way: The energy minima with respect to the angle ϕ were located, then α, β, and *d* were optimized, then ϕ was recomputed, and the procedure was iterated. The same optimization scheme has been used also for *syn-*, *gauche-* and *anti-*conformations. The results are given in Table 1 and in Figure 2.

Table 1. Calculated Geometry, Charges on the Methylene Carbon [q(CH$_2$)] and Metal [q(M)], and Calculated Activation Barriers to Internal Rotation of 1,1′-Dications (II) for *gauche-* and *anti-*Conformations

	gauche			*anti*		
	Fe	Ru	Os	Fe	Ru	Os
α, deg	30[b]	40	40	26	30	30
β, deg	5	0	0	0	0	0
d, Å	0.3	0.3	0.3	0.2	0.3	0.25
ϕ,[a] deg	90	90	90	180	180	180
q(CH$_2$)	−0.12	−0.16	−0.10	0.03	−0.03	0.04
q(M)	2.09	2.24	1.75	1.73	1.79	1.31
Δ*E*,[c,d] kcal/mol	0[c]	0	0	13.3[b]	15.5	9.4[e]

[a] Angle ϕ is defined relative to the *syn*-conformation, for which ϕ = 0°. [b] The angle α calculated for the Fe-containing dication is probably overestimated {for monocation [C$_5$H$_5$FeC$_5$H$_4$CPh$_2$]$^+$, α = 20.7° (Berens, U. *J. Organomet. Chem.* **1979**, *182*, 89)}, which leads to a higher metal atom charge and, probably, to a higher barrier to internal rotation. [c] The relative energy of the *gauche*-conformation is considered to be equal to 0. [d] ΔE_{syn} = 36 (Fe), 35 (Ru), and 32 (Os) kcal/mol. [e] The experimental value of the internal rotation barrier, based on the temperature dependence of the ^{1}H NMR spectra, is 7.8 kcal/mol.

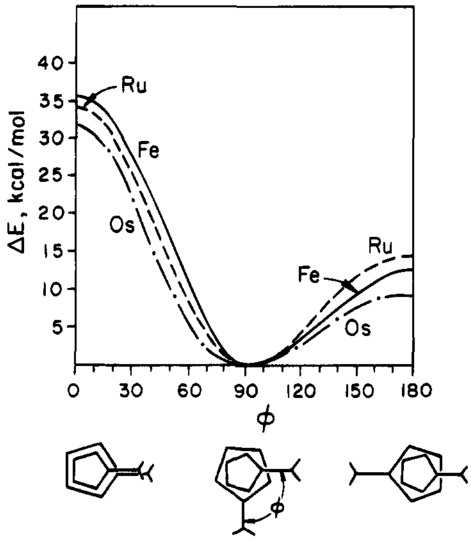

Figure 2. Calculated potential energy curves for internal rotation for **II** M = Fe, Ru, and Os.

The calculations gave an unexpected result. As seen from the potential energy curves for rotation shown in Figure 2, only *gauche*-rotamers with large α angles (the optimum angle ϕ is equal to 90° for all metals studied) correspond to energy minima (see Table 1). In fact, in the *gauche*-rotamers a pretty much fully formed σ-bond between metal and carbocation center is found (the lengths of M—CH$_2$ bonds obtained in our calculations are 2.43, 2.20, and 2.22 Å for Fe-, Ru-, and Os-containing dications, respectively). The *syn-* (ϕ = 0°) and *anti-*rotamers (ϕ = 180°) are maxima in the rotational energy profiles.

Where does the observed preference for the *gauche*-rotamer come from? A Walsh diagram showing how the orbital and the total energy varies with angle ϕ (Figure 3) and the associated interaction diagrams (not shown here) are instructive. The primary interactions are of cation 2p orbitals with two of the three occupied d orbitals[6] (the "t$_{2g}$" set) of the metallocene core. These orbitals are z^2, $x^2 - y^2$, and xy, approximately. We thought at first that only $x^2 - y^2$ and xy would be

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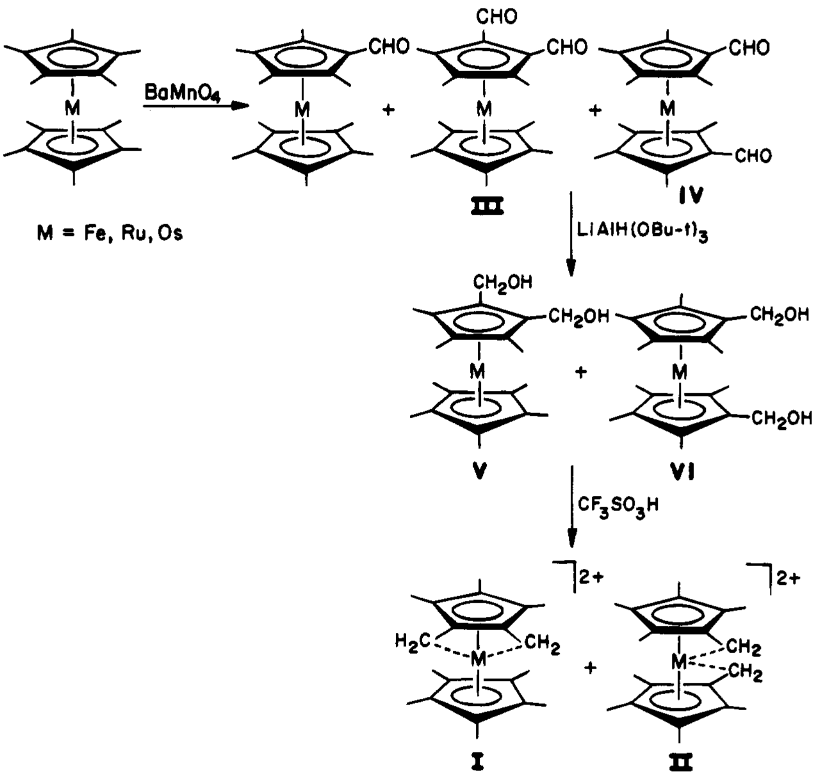
(3) For the first theoretical discussion of this important effect in the ferrocenylcarbonium ion, see: Gleiter, R.; Seeger, R. *Helv. Chim. Acta* **1971**, *54*, 1217.

(4) (a) Yanovsky, A. Y.; Struchkov, Yu, T.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *369*, 125. (b) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Yu. T.; Yanovsky, A. Y. *J. Organomet. Chem.* **1989**, *369*, 233.

(5) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872.

(6) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry, John, Wiley* & Sons: New York, 1085; pp 392–3.

Scheme 1



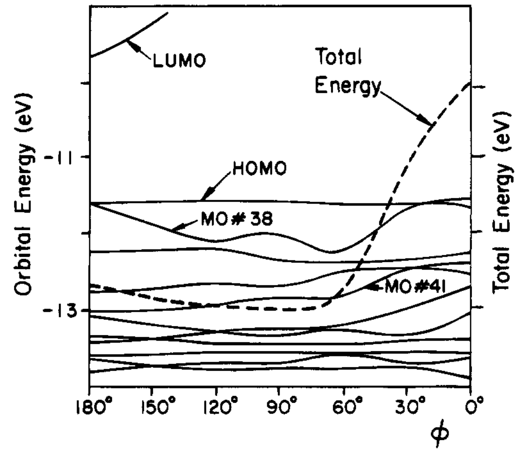


Figure 3. Computed Walsh diagram for dication **II** (M = Os) for decreasing angle ϕ. The scale for the total energy is such that each scale marking is 0.462 eV.

involved. If that were so, the idea of getting most interaction out of each empty cation p orbital interacting with a different metal electron pair would lead to an optimum ϕ of 45° (and 135°). Clearly this idea is too naive; z^2, $x^2 - y^2$, and xy combine to give two combinations which interact with the cation center p orbitals well at $\phi = 90°$ (these orbitals are shown in Figure 4) and one orbital that avoids overlap with the acceptor.

According to the calculations, the *syn*-barriers are significantly higher than the *anti*-barriers (the Ru dication has the biggest barrier). This is easy to understand from consideration of electrostatic and steric repulsions between cationic centers. Thus, the calculations indicate the possibility of appreciable donor–acceptor interaction of two unshared electron pairs on the metal with cation centers, predicting the stability of *gauche*-rotamers.

To test the theoretical predictions we have carried out experimental studies for whole iron subgroup. In order to enhance the stability of the dications our experiments use permethylated Cp-complexes rings.

Permethylated ions **II** were synthesized in a mixture with ions of type **I** as shown in Scheme 1, described earlier.[1] The synthesis proceeded by oxidation of decamethylmetallocenes to the aldehydes **III** and **IV**, with corresponding reduction to 1,2- and 1,1′-dialcohols **V** and **VI**, followed by treatment with superacid.

It should be noted that 1,2-dialdehydes **III** are dominant products in the mixture with 1,1′-dialdehydes **IV**. Only the 1,2-dialdehydes can be isolated as pure compounds.

To understand the behaviour of 1,1′-dications we had to work with mixtures containing 1,2- and 1,1′-isomers. Thus, the diols obtained contained mixtures of 1,2- and 1,1′-isomers **V** and **VI**, which when treated by superacid CF_3SO_3H were transformed into a mixture of dications **I** and **II**. The dication mixture was investigated by ^1H NMR spectroscopy in CD_2Cl_2/CD_3NO_2 solution (Figures 5–7). Since pure 1,2-dications **I** were thoroughly studied by ^1H NMR by us earlier,[1] their presence in the mixture with 1,1′-dications **II** did not hamper our investigation. Moreover, the study of the mixture was very useful, for it allowed us to observe differences in behavior of 1,2- and 1,1′-isomeric dications for the whole iron subgroup under identical conditions.

It is important to note that proton signals for 1,1′-dications, just as for 1,2-dications, are strongly shifted toward lower field in comparison with the smaller monocation signals. AB quadruplets of protons of CH_2 groups and the signals of α- and β-methyl groups of the rings are observed in the 1,1′-dication spectra, which is in accord with the structure suggested for them.

For more stable Ru- and Os-containing dications (see Figures 6 and 7) the picture found in ^1H NMR spectra at room temperature is clearer. Along with an AB

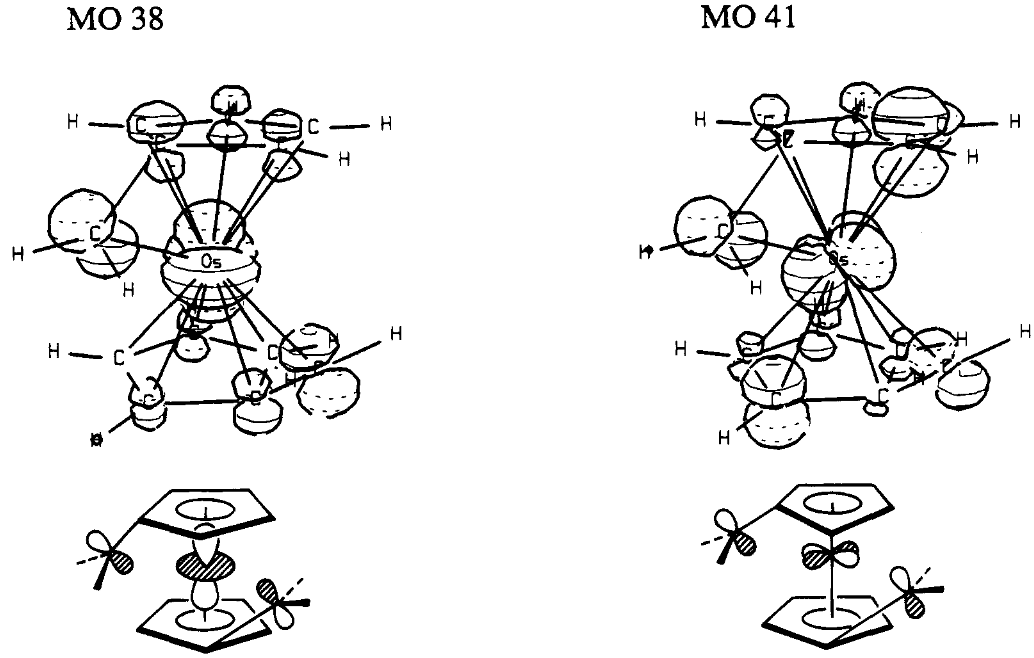


Figure 4. Contours (top) and schematic drawings (bottom) of the 38th and 41st MO. (See Figure 3.) These are mainly responsible for the stability of the *gauche*-forms of dications **II**.

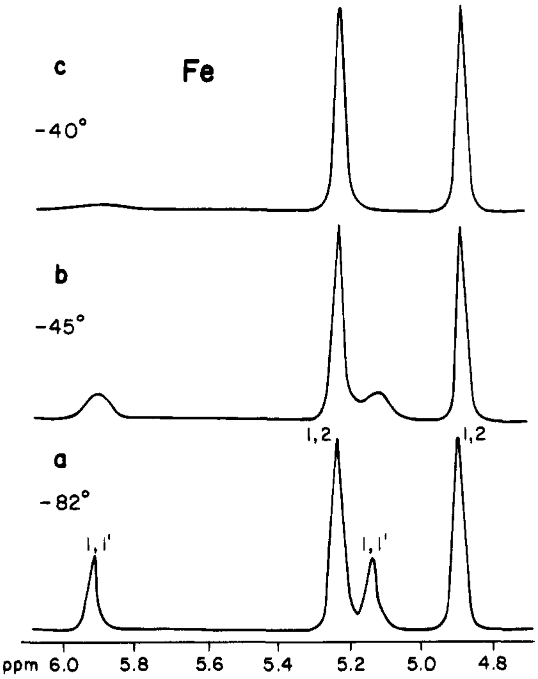


Figure 5. Part of the NMR spectrum in the range of methylene proton signals for 1,2- and 1,1′-derivatives of Fe-containing dications.

quadruplet of methylene protons at δ_{Ru} 5.21 and 4.80 ppm and δ_{Os} 5.37 and 4.79 ppm ($^2J_{^1H-^1H} = 2.5$ Hz) for 1,2-isomer, there is observed another AB quadruplet of methylene protons [δ_{Ru} 4.88 and 4.99 ppm and δ_{Os} 5.74 and 5.28 ppm ($^2J_{^1H-^1H} = 1.3$ Hz) correspondingly] for the 1,1′-isomer. The content of 1,2-dications in the mixture is equal to ≈70% and ≈80% for Ru and Os complexes (+20 °C), respectively. The appearance of CH_2 proton signals of 1,2-isomers as AB quadruplets is determined by their different location relative to the symmetry plane passing through the metal atom and the midpoint of the C—C bond of the ring in which C atoms bear methylene groups.

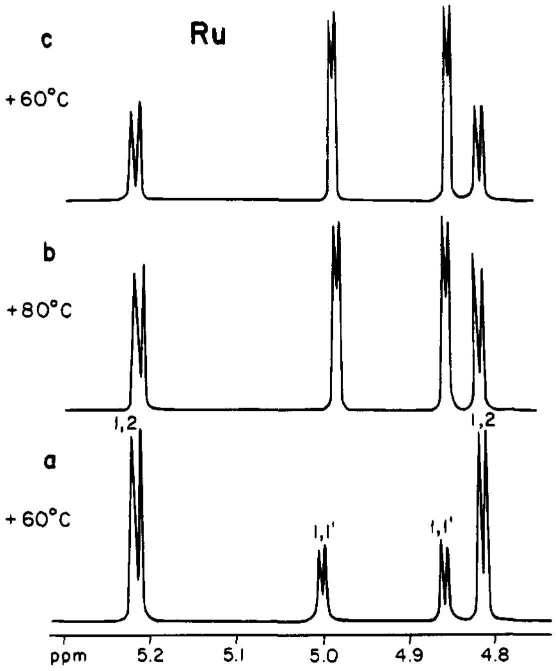


Figure 6. Part of the NMR spectrum in the range of methylene proton signals for 1,2- and 1,1′-derivatives of Ru-containing dications. (a) The signals of the 1,1′- and 1,2-isomers are essentially unchanged in the temperature interval +20 to +60 °C. (b) Starting at 70 °C, the intensity of the signals of the 1,2-isomer decreases; this may be easily seen at 80 °C. (c) After 15 min at 80 °C and cooling of the solution again to 60 °C, the ratio of 1,2-isomer:1,1′-isomer changed from 7:3 to 4:6.

The nonequivalence of the protons of the CH_2 group for 1,1′-isomers shows up in the AB quadruplet, which indicates that *gauche*-rotamers are predominant in the solutions. In the case of the *syn*- and *anti*-rotamers an A_2 spin system would have been observed. [It should be noted that, according to the X-ray structural results for monocations $(C_5Me_5MC_5M_4CH_2)^+$ (M = Ru and Os,[3,4] the CH_2 is located in a plane parallel to cyclopentadienyl

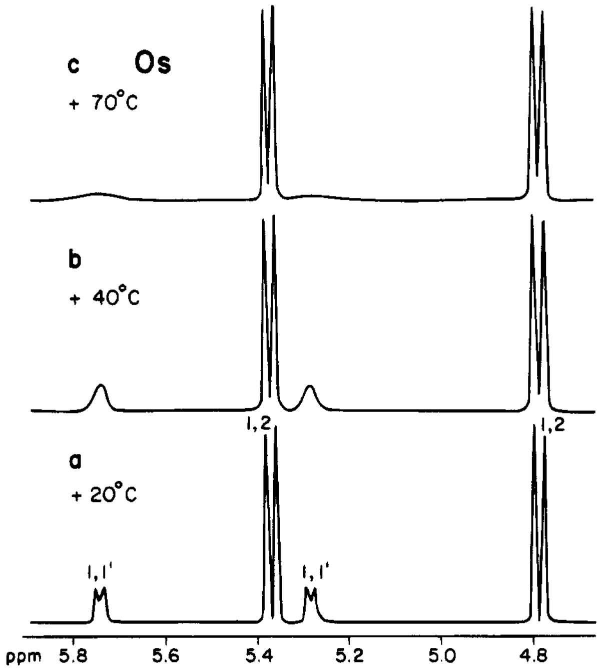


Figure 7. Part of the NMR spectrum in the range of methylene proton signals for 1,2- and 1,1'-derivatives of Os-containing dications.

rings.] Strictly speaking, fast exchange processes among all the conformers of 1,1'-isomer could result in the same quadruplet as for a *gauche*-conformer (see Figure 2). But reduction in temperature in fact does not significantly change in spectrum, which excludes the possibility of fast exchange processes and confirms the presence of only the *gauche*-rotamers in solution. [An insignificant broadening of the CH$_2$-group proton signal was observed for both 1,1'- and 1,2-isomers at sufficiently low temperature. This could be related to the increasing solvent viscosity.] The signals for Ru-containing 1,1'- and 1,2-isomers are essentially unchanged when the temperaturev is increased to +80 °C, but starting from +70 °C the intensity of the signals of 1,2-isomer decreases. After 15 min at 80 °C and cooling of the solution again to 60 °C the ratio of 1,2-isomer:1,1'-isomer was changed from 70%:30% to 40%:60% (Figure 6c). At the same time there appear new signals in the 4.5-4.7 ppm region. Apparently, these have to be assigned to decomposition products of mainly 1,2-isomers. Actually, easy abstraction of cyclopentadienyl rings containing strong electron-withdrawing substituents in the α-position, among them carbocationic groups, has been described in the literature for ferrocene derivatives.[7,8]

The iron-containing dications obtained appeared to be even less stable. We could monitor them only at low temperature. In the region typical for methylene protons, at −82 °C, two pairs of singlet signals at δ 4,88. 5.23 ppm and 5.13, 5.91 ppm assigned to the 1,2-(70%) and 1,1'-isomers (30%), respectively, were observed in the ^{1}H NMR spectrum of the Fe-containing dication mixture. Insufficiently high resolution in the spectrum of this sample did not allow us to determine the coupling constant between the methylene group protons. Gradual broadening of spectral lines of the 1,1'-isomer is observed upon increasing temperature, whereas the widths of the methylene proton signals of 1,2-isomers appear to be almost constant up to −30 °C. Further increase in temperature of the solution leads to irreversible broadening of all spectral lines, caused by dication decomposition and the appearance of paramagnetic side products, containing probably Fe(III).

It is interesting to point out that some broadening of the lines of the 1,1'-isomer with increasing temperature, which was not observed for the Ru-containing dication, appears in the spectrum of the Os-containing 1,1'-cation. The mixture of Os-containing dications was investigated in the temperature range from +20 to +70 °C (see Figure 7). Among the three metals, the Os-containing dications have the strongest metal−ring bond. Indeed, in this case the decomposition of the 1,2-dication is not detected even at +70 °C. However, as in the case of the Fe-containing analogue, the CH$_2$-proton signals of the osmium 1,1'-dication undergo strong broadening with increasing temperature. Thus, at +40 °C, the doublets of the AB quadruplet with δ 5.74 and 5.28 ppm coalesce into two singlet lines with widths at half maximum of 3.7 Hz. Further increase of the temperature of the solution under study leads to an increase of the width of these lines; at +70 °C the widths are equal to 10 Hz. It should be pointed out that all of the spectral changes for the 1,1'-isomer are reversible and are adequately described by exchange processes occurring between AB and A$_2$ spin systems. They can thus be related to the increase of *anti*-rotamer content. The barrier observed, ≈7.8 kcal/mol, is in reasonable agreement with the theoretical estimate of 9.4 kcal/mol (Table 1). It is also important to note that the lines in the spectrum of the 1,2-isome are broadened not more than 0.2 Hz upon raising the temperature to +70 °C and the process starts at +40 °C.

Summing up all the experimental results obtained, we find that they correspond well with the EH calculations, which predict for the 1,1-isomers thermodynamic stability of only the *gauche*-rotamer. The higher energy barrier to rotation in the Ru-containing *anti*-rotamer is also in accord with the theoretical results (see Figure 2).

Thus the considerable prevalence of the *gauche*-rotamer, even at the high temperature, provides evidence of a quite effective donor−acceptor interaction of the carbocation centers with the metal atom.

Experimental Section

The ^{1}H NMR analysis was performed on a Bruker WP-200 SY (200.13 MHz). Oxiation of decamethylmetallocenes (M = Fe, Ru, Os) was carried out by a method described earlier.[1] From 5.0 mmol of C$_5$Me$_5$MC$_5$Me$_5$, after chromatographic separation of monoaldehydes, a mixture of 1,2- and 1,1'-dialdehydes (**III** and **IV**) with yields of 5% for M = Fe and of 4% for M = Ru and Os was obtained.

^{1}H NMR (CDCl$_3$) of a mixture of **III** and **IV** [pure 1,2-dialdehydes and 1,2-dicarbinols of Ru and Os were obtained and characterized in ref 1] are as follows. *M* = *Fe*: for 1,2-dialdehyde (**III**), δ = 2.10 (s, 6H, α-Me), 1.85 (s, 3H, β-Me), 1.63 (s, 15H, γ-Me) [γ-Me = methyl protons of C$_5$Me$_5$ rings] 10.28 (s, 2H, CHO); for 1,1'-dialdehyde (**IV**), δ = 1.97 (s, 6H, α-Me), 1.76 (s, 6H, β-Me), 10.01 (s, 2H, CHO). *M* = *Ru*: for 1,2-dialdehyde (**III**), δ = 2.02 (s, 6H, α-Me), 1.77 (s, 3H, β-Me), 1.66 (s, 15H, γ-Me), 9.94 (s, 2H, CHO); for 1,1'-dialdehyde (**IV**),

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[7] Nesmeyanov, A. N.; Sazonova, V. A.; Zudkova, G. I.; Isaeva, L. S. *Izv. AN SSSR* (*Ser. Chem.*) **1966**, *16*, 2017.

[8] Nesmeyanov, A. N.; Sazonova, V. A.; Drozd, V. N. *Dokl. AN SSSR* **1964**, *154*, 1393.

[9] Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

δ = 1.93 (s, 6H, α-Me), 1.71 (s, 6H, β-Me), 9.74 (s, 2H, CHO). *M* = *Os*: for 1,2-dialdehyde (**III**), δ = 2.07 (s, 6H, α-Me), 1.82 (s, 3H, β-Me), 1.76 (s, 15H, γ-Me), 9.94 (s, 2H, CHO); for 1,1′-dialdehyde (**IV**), δ = 2.03 (s, 6H, α-Me), 1.78 (s, 6H, β-Me), 9.72 (s, 2H, CHO).

After reduction of a 0.5 mmol mixture of 1,2- and 1,1′-dialdehydes (**III** and **IV**) by $LiAlH(OBu\text{-}t)_3$ by the method presented earlier,[1] a mixture of 1,2- and 1,1′-diols (**V** and **VI**) with yields of 90−93% was obtained.

^{1}H NMR ($CDCL_3$) of a mixture of **V** and **VI** are as follows. *M* = *Fe*: for 1,2-diol (**V**), δ = 1.65 (s, 15H, Y-Me), 1.68 (s, 3H, β-Me), 1.78 (s, 6H, α-Me), 3.79 and 3.99 (ABq, 4H, $^2J_{HH}$ = 2.1 Hz, CH_2); for 1,1′-diol (**VI**), δ = 1.71 (s, 6H, α-Me), 1.85 (s, 6H, β-Me), 3.85 and 4.06 (ABq, 4H, $^2J_{HH}$ = 2.5 Hz, CH_2). *M* = *Ru*: for 1,2-diol (**V**), δ = 1.62 (s, 15H, γ-Me), 1.64 (s, 3H, β-Me), 1.77 (s, 6H, α-Me), 3.83 and 4.03 (ABq, 4H, $^2J_{HH}$ = 1.3 Hz, CH_2); for 1,1′-diol (**VI**), δ = 1.67 (s, 6H, α-Me), 1.79 (s, 6H, β-Me), 3.79 and 4.12 (ABq, 4H, $^2J_{HH}$ = 1.2 Hz, CH_2). *M* = *Os*: for 1,2-diol (**V**), δ = 1.79 (s, 16H, γ-Me), 1.71 (s, 3H, β-Me), 1.78 (s, 15H, α-Me), 4.02 and 4.04 (ABq, $^2J_{HH} \leq 7$ Hz, 4H, CH_2); for 1,1′-diol (**VI**); δ = 1.81 (s, 6H, α-Me), 1.85 (s, 6H, β-Me), 3.95 and 4.01 (ABq, $^2J_{HH}$ = 4 Hz, 4H, CH_2).

^{1}H NMR spectra of a mixture of 1,2- and 1,1′-dications (**I** and **II**) measured upon dissolving diols (**V** and **VI**) in CF_3SO_3H and CD_2Cl_2/CD_3NO_2 are as follows. *M* = *Fe*: for 1,2-dication (**I**), δ = 2.36 (s, 3H, β-Me), 1.85 (s, 21H, α-Me + γ-Me), 5.23 and 4.88 (ABq, 4H, CH_2); for 1.1′-dication (**II**), δ = 2.28 and 2.12 (s, 6H, β- and β'-Me), 1.88 and 1.45 (s, 6H, α- and α'-Me), 5.91 and 5.13 (ABq, 4H, CH_2). [It should be noted that ^{1}H NMR spectrum of the Fe dications was measured at −70 °C. At −30 °C the proton signals of the methyl groups of 1,1′-dications (**II**) (M = Fe) coalesce into a single signal with δ = 2.02 ppm.] *M* = *Ru*: for 1,2-dication (**I**), δ = 2.32 (s, 3H, β-Me), 2.12 (s, 15H, γ-Me), 2.00 (s, 6H, α-Me), 5.21 and 4.80 (Aq, 4H, CH_2); for 1.1′-dication (**II**), δ = 2.22 and 2.20 (s, 6H, β- and β'-Me), 1.82 and 1.79 (s, 6H, α- and α'-Me), 4.88 and 4.99 (ABq, 4H, CH_2). *M* = *Os*: for 1,2-dication (**I**), δ = 2.25 (s, 18H, β- and γ-Me), 1.80 (s, 6H, α-Me), 5.37 and 4.79 (ABq, 4H, CH_2); for 1,1′-dication (**II**), δ = 2.51 and 2.09 (s, 6H, β- and β'-Me), 1.99 and 1.82 (s, 6H, α- and α'-Me), 5.74 and 5.28 (ABq, 4H, CH_2).

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Table 2. Atomic Parameters Used in the Calculations

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	c_1[a]	c_2[a]
H	1s	−13.60	1.300			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
Fe	4s	−9.10	1.900			
	4p	−5.32	1.900			
	3d	−12.60	5.320	2.00	0.5505	0.6260
Ru	5s	−7.73	2.080			
	5p	−4.44	2.040			
	4d	−11.23	5.380	2.30	0.5340	0.6365
Os	6s	−8.17	2.452			
	6p	−4.81	2.429			
	5d	−11.84	5.571	2.416	0.6372	0.5598

[a] Contracted coefficients used in the double-ζ expansion.

Appendix

All the calculations are of the extended Hückel type[5] and are performed with use of the CACAO program.[9] The atomic parameters for H, C, Fe, Ru, and Os are chosen from the literature[5,10,11,12] and are listed in Table 2. The C−C bond lengths of cyclopentadienyl rings in the iron, ruthenium, and osmium dications are chosen to be equal to 1.42, 1.43, and 1.45 Å, respectively. The distances from the metal to the center of the cyclopentadienyl ring in the iron, ruthenium, and osmium dications are equal to 1.66, 1.76, and 1.86 Å, respectively. All the C−H bond lengths are equal to 1.08 Å.

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(10) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(11) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3340.

(12) Tuan, D. F.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 871.