Conformational analysis of the $[(C_5H_4CR'R'')_2M]^{2+}$ dications ($M = Ru, Os$) as a tool for determining their onium or dicarbocation structure

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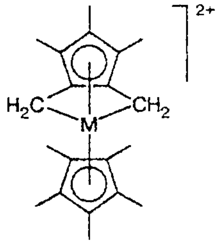
The $[(Me_2CC_5H_4)_2M]^{2+}$ and $[(Me(H)CC_5H_4)_2M]^{2+}$ dications (M = Ru, Os) were generated and their precursors, dicarbinols, were synthesized. ^1H NMR spectral analysis showed that the former dications have a dicarbocation structure. For the $[(Me(H)CC_5H_4)_2M]^{2+}$ dications, the energies of both the onium and dicarbocation structures are close, and compounds of both types can be simultaneously observed in solution.

Key words: onium dications, dicarbocations, metallocenes, EHT MO calculations, NMR spectra, conformational analysis.

Previously, we have shown that the metal atoms of permethylated ruthenocenes and osmocenes can effectively stabilize two carbocation centers in type **1** and **2** dications due to the donor-acceptor interaction with two lone electron pairs of the metal atoms, resulting in the formation of a $M-CH_2$ σ-bond, and nearly complete localization of the positive charge on the metal atoms.[1—3]



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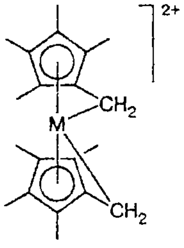

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This conclusion was drawn on the basis of the MO calculations of the geometry of dications **1** and **2** and the charge distributions on the metal atoms and CH_2 groups in these dications[1—3] (Table 1), as well as on the basis of calculations of the potential energy curves for internal rotation of Cp rings for the *syn*-, *gauche*-, and *anti*-conformers of the type **2** heteroannular dications of the iron subgroup metals. The calculations showed that only *gauche*-rotamers correspond to energy minima, while the *syn*- and even the *anti*-rotamers correspond to energy maxima (Fig. 1). On the basis of the calculations it was possible to conclude that the interaction between the metal and the carbocation centers is most effective in the case of the *gauche*-conformer and the dication has the structure of onium compounds, whereas the dicarbocation structure is more characteristic of the *anti*-conformers.

Theoretical prediction of the onium structure for the *gauche*-conformers of dications **2** was confirmed experimentally by studying their ^1H NMR spectra.[1,2] The possibility of the formation of onium dications was first proposed by Olah;[4] however, he failed to detect these species in the form of ER_4^{2+} dications (E = O, S, *etc.*) even using spectral methods.

Table 1. Calculated geometric parameters, charges on the methylene carbon atom $[q(CH_2)]$ and on the metal atom $[q(M)]$, and activation barriers to internal rotation (ΔE/kcal mol^{-1}) of dications **2** [2]

Parameter	*gauche*-Conformer			*anti*-Conformer		
	Fe	Ru	Os	Fe	Ru	Os
α^a/deg	30	40	40	26	30	30
β^b/deg	5	0	0	0	0	0
d^c/Å	0.3	0.3	0.3	0.2	0.3	0.25
φ^d/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
ΔE	0	0	0	13.3	15.5	9.4

[a] α is the angle of inclination of the $C(1)-C_{exo}$ bond to the plane of the cyclopentadienyl ring. [b] β is the angle between the Cp ring planes. [c] *d* is the shift of the perpendicular dropped from the M atom to the Cp ring plane from the ring center. [d] Angle φ is defined relative to the *syn*-conformation, for which φ = 0°.

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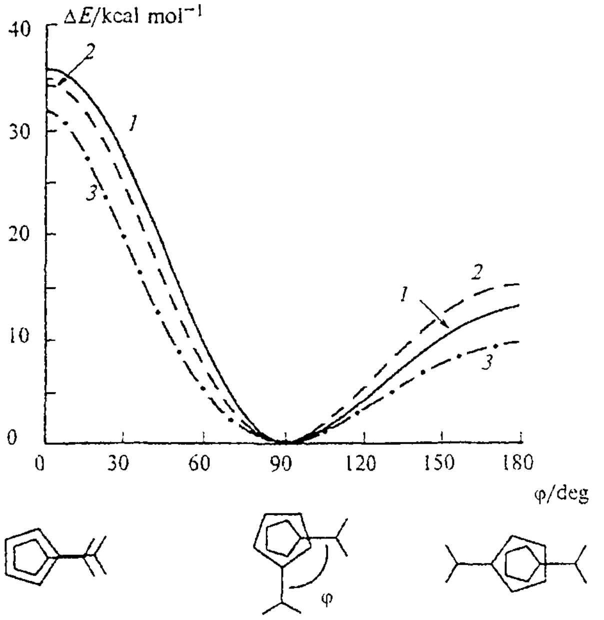


Fig. 1. Calculated potential energy curves for internal rotation for dications 2 (M = Fe (*1*), Ru (*2*), and Os (*3*)).

Undoubtedly the generation of the first obtained type **1** and **2** onium dications is made possible by the great ability of the transition metal atom to localize the positive charge and the high electron-releasing effect of the permethylcyclopentadienyl rings, as well as by intramolecular cyclization resulting in onium chelate cycles.

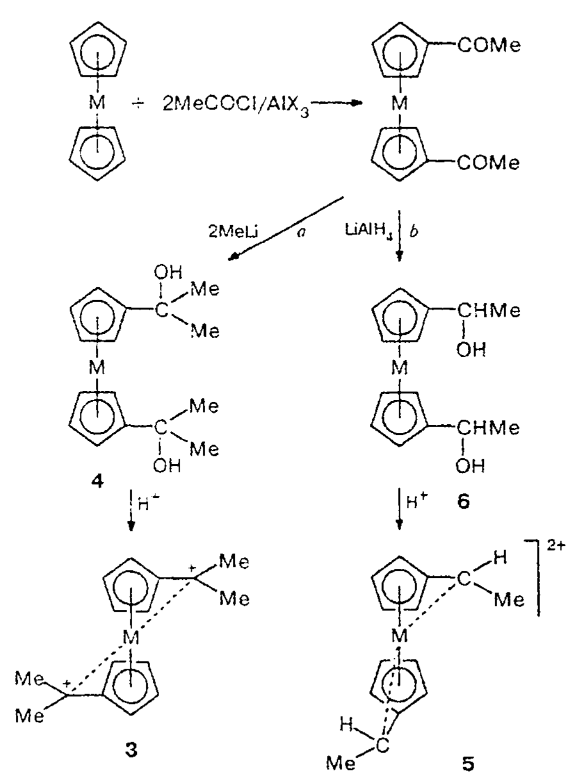
In this work, we attempted to generate dications of another type, which have the *anti*-conformation in solution (see below) and a dicarbocation structure in which the positive charge is localized on the α-carbon atoms; dications of an intermediate type have also been considered.

Results and Discussion

Dications **3** were generated (Scheme 1) as model dications, in which the positive charges are mostly localized on the α-carbon atoms. Unlike onium dications **2**, dications **3** contain two methyl groups at each of the α-carbon atoms, while the cyclopentadienyl rings have no methyl substituents.

Such a model should favor the dicarbocation structure. It is obvious that the donor-acceptor interaction of the metal atom with the carbocation centers in a dicarbocation derivative is weaker than that in onium compounds **2**. Calculations for $[(C_5H_4CH_2)_2M]^{2+}$ showed[2] that weakening of the donor-acceptor interaction is characteristic of the *anti*-conformers. This is indicated primarily by the fact that the bond between the α-carbocation center and the cyclopentadienyl ring is tilted less with respect to the plane of the cyclopentadienyl ring (see Table 1). Along with the weakened donor-acceptor interaction, the electrostatic repulsion of the two carbocation centers as well as the presence of the substituents at these centers should also favor the *anti*-conformers. Actually, the presence of the two methyl substituents at the α-carbocation centers hampers their interaction with the metal atom and, hence, also helps to weaken the donor-acceptor interaction with the metal. The absence of the methyl substituents in the ring results in a decrease in the electron density on the metal atom, which has the same effect, *i.e.* it weakens the donor-acceptor interaction. Thus, the chosen dications **3** meet the requirements of the dicarbocation structure.

Scheme 1



The first generated dication of this type (a ferrocene derivative[5]) played an important role in choosing the

Table 2. ¹H NMR data of dicarbinols **4** in CD_2Cl_2 at 20 °C (δ, *J*/Hz)

M	δ_{Me} (s, 6 H)	$\delta_{H(2,5)(3,4)}$[a] (t, 2 H, $J_{1,1}$ = 1.6)	$\delta_{H(3,4)(2,5)}$[a] (t, 2 H, $J_{1,1}$ = 1.6)
Fe	1.50	4.16	4.20
Ru	1.43	4.55	4.77
Os	1.46	4.69	4.84

[a] Exact assignment of the signals to H(2), H(5) and H(3), H(4) atoms is difficult.

model dications **3**. Its ^{1}H NMR spectrum contained one singlet of the methyl protons, which indicated the *anti*-conformation of dication **3** (M = Fe).

It was important to synthesize dications **3** of all elements of the iron subgroup in order to compare their properties. Dications **3** (M = Fe, Ru, and Os) were obtained as shown in Scheme 1 (route *a*) from 1,1′-diacetylmetallocenes,* which were transformed into tertiary dicarbinols (**4**) by the action of MeLi. The structures of dicarbinols **4** were confirmed by the data of elemental analyses, mass spectrometry, and ^{1}H NMR spectroscopy (Table 2). A group of ion peaks with *m/z* 338—352 (the maximum intensity ion peak was *m/z* 346) and a group with *m/z* 428—442 (the maximum intensity ion peak was *m/z* 436) were detected in the mass spectra of compounds **4** for M = Ru and Os, respectively. These peaks correspond to isotopically distributed $[M]^{+\cdot}$ molecular ions and the ions formed from the latter at the expense of the loss of hydrogen. There are also groups of intense ion peaks with *m/z* 308—316 (the maximum intensity ion peak is *m/z* 312) and with *m/z* 396—405 (the maximum intensity ion peak is *m/z* 402) in the spectra for M = Ru and Os, respectively. These correspond to the ions formed from the above-mentioned fragments by elimination of two water molecules (or formed at the expense of thermal dehydration of the corresponding molecules).

The ^{1}H NMR spectra of all dicarbinols **4** contain one singlet of methyl groups in the δ ~1.5 region. Nonequivalent ring protons appear as triplets (see Table 2).

Dissolution of dicarbinols **4** in superacids (CF_3SO_3H and FSO_3H) results in the generation of dications **3**. It is important to note that the solutions are prepared by adding dicarbinols to superacid pre-cooled to −70 °C.

The ^{1}H NMR studies of the solutions were performed at temperatures from −60 to +25 °C and from −50 to +10 °C for M = Ru and Os, respectively. One singlet of the methyl protons and two signals of the 2,5- and 3,4-protons of the Cp ring are observed in the spectra (Table 3). The spectral patterns of these dications remain almost unchanged when the temperature is varied. The one singlet of methyl groups indicates their equivalence and implies the existence of *anti*-conformers (in the *gauche*-conformers, the methyl groups are nonequivalent and must appear as two singlets). The obtained spectral patterns of ruthenium and osmium dications **3** are similar to that of the iron dication **3**,[5] and one can conclude that dications **3** of all elements of the iron subgroup have a dicarbocation structure, in which the positive charge is mainly localized on the α-CMe_2 groups.

Table 3. ^{1}H NMR data of dications **3** (M = Ru, Os) in CF_3SO_3H (δ, *J*/Hz)

M	*T* /°C	δ_{Me} (s, 12 H)	$\delta_{H(2,5)}$ (t, 4 H, *J* = 2)	$\delta_{H(3,4)}$ (t, 4 H, *J* = 2)
Ru	−60	2.40	5.90	6.47
	−30	2.42	5.92	6.47
	0	2.42	5.83	6.47
	+25	2.45	5.99	6.49
Os	−50	2.16	5.95	6.62
	−30	2.16	5.96	6.63
	−10	2.17	5.97	6.63
	+10	2.17	5.98	6.62

The *anti*-conformations of dications **3** are confirmed by the following observations. The ^{1}H NMR spectra of the onium dications **2**, which we studied previously, remained nearly unchanged when being recorded in both a pure superacid and a superacid with solvent additives. The ^{1}H NMR spectra of dicarbocations **3** change on going from pure superacid to superacid with a solvent additive (Table 4). In the first case, one singlet of methyl protons is observed in the spectrum, whereas addition of the solvent results in two singlets with different intensities. If these changes were due to conversion of the *anti*-conformer into the *gauche*-conformer, then two singlets with equal intensities would be observed. The appearance of the second singlet in the spectra of **3** in a superacid with a solvent additive may be associated with the fact that solvent-separated ionic pairs of carbocations and anions appear in the solution along with close ionic pairs of the carbocations and anions, and the intensities of the signals of the former increase as the solution becomes more diluted. The MO calculations showed that in the onium compounds **1** and **2**, in which the positive charge is more delocalized than in dicarbocations, the C_α atom has no positive charge (see Table 1). For this reason, the protons at the C_α atom are only slightly affected by solvation effects, and the ^{1}H NMR spectral patterns remain nearly unchanged on going to a solution in superacid with a solvent additive. These results show that the presence of solvents has no effect on the spectra of the *gauche*-conformers, which have the structure of onium compounds, whereas their effect is great in the case of *anti*-conformers. It appeared to be useful to take into account this conclusion when performing the conformational analysis of secondary $[(C_5H_4CHMe)_2M]^{2+}$ dications (**5**) (M = Fe, Ru, Os),

Table 4. ^{1}H NMR data of dications **3** in a CF_3SO_3H—CD_2Cl_2—CD_3NO_2 mixture (δ, *J*/Hz)

M	*T* /°C	δ_{Me} (s, 12 H)		$\delta_{H(3,4)}$ (t, 4 H, *J* = 3—4)		$\delta_{H(2,5)}$ (t, 4 H, *J* = 3—4)	
Ru	−60	2.09	2.23	5.11	5.25	6.23	6.30
	+20	2.25	2.28	5.14	5.27	6.25	6.33
Os	+20	2.12	2.14	5.22	5.55	6.25	6.33

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* Previously,[6] a procedure for the synthesis of the product in 0.1% yield was described. The use of $AlCl_3$ as catalyst is unsuccessful. In this work, we proposed an improved procedure for the synthesis of 1,1′-diacetylosmocene based on acetylation of osmocene by acetyl chloride using $AlBr_3$ as the Friedel—Crafts catalyst.

Table 5. ^{1}H NMR data of dicarbinols **6** (M = Fe, Ru, Os) in CD_2Cl_2 (δ)[a]

M	δ_{Me} (d)	δ_{CH} (q)	δ_{Cp} (m)	δ_{OH}
Fe	1.36 (6.4)	4.20 (6.4)	4.12—4.20	4.46
	1.39 (6.4)	4.62 (6.4)		
Ru	1.33 (6.3)	4.39 (6.4)	4.53—4.69	—
	1.34 (6.3)	4.36 (6.4)		
Os	1.32 (6.3)	4.21 (6.3)	4.68—4.88	—
	1.34 (6.3)	4.27 (6.3)		

[a] The $J_{^1H-^1H}$/Hz values are given in parentheses.

Table 6. Partial ^{1}H NMR data of dications **5** in FSO_3H (δ, J/Hz)

M	T/°C	δ_{Me} (d, 6 H)			δ_{CH} (q, $J_{^1H-^1H}$ = 6.6—6.8)
		$J_{^1H-^1H}$ = 6.6—6.8		$J_{^1H-^1H}$ = 9.4	
Ru	−30	2.16	2.37	2.43	7.39
	0	2.26	2.38	2.45	7.51
	+30	2.28	2.38	2.46	7.33
Os	−30	2.23	2.24	2.29	7.10
	−10	2.24	2.26	2.30	7.20
	+30	2.23	2.26	2.30	7.28
	−10[a]	2.24	2.26	2.30	7.15

[a] The spectrum was recorded after cooling from +30 to −10 °C.

which are intermediates between onium dications and dicarbocations.

The generation of dications **5**, as well as the synthesis of their precursors, carbinols (**6**), were performed according to Scheme 1 (route *b*). In both cases, the presence of two chiral centers in compounds **5** and **6** results in the formation of two diastereomers. The structures of dicarbinols **6** were confirmed by the data of elemental analyses, mass spectrometry, and ^{1}H NMR spectroscopy. A group of ion peaks with *m/z* 310—322 (the maximum intensity ion peak was *m/z* 316) and a group with *m/z* 400—412 (the maximum intensity ion peak was *m/z* 402) were detected in the mass spectra for M = Ru and Os, respectively. They are isotopically distributed peaks of both the $[M]^+$ molecular ions and the ions formed from the former at the expense of the loss of hydrogen. The observed groups of ion peaks with *m/z* 294—304 (the maximum intensity ion peak is *m/z* 300) and with *m/z* 384—394 (the maximum intensity ion peak is *m/z* 390) for M = Ru and Os, respectively, correspond to the ions formed from the above mentioned fragments by the elimination of water molecules. Groups of intense ion peaks with *m/z* 274—288 (the maximum intensity ion peak is *m/z* 282) and with *m/z* 364—378 (the maximum intensity ion peak is *m/z* 372) for M = Ru and Os, respectively, correspond to the ions formed after further loss of water.

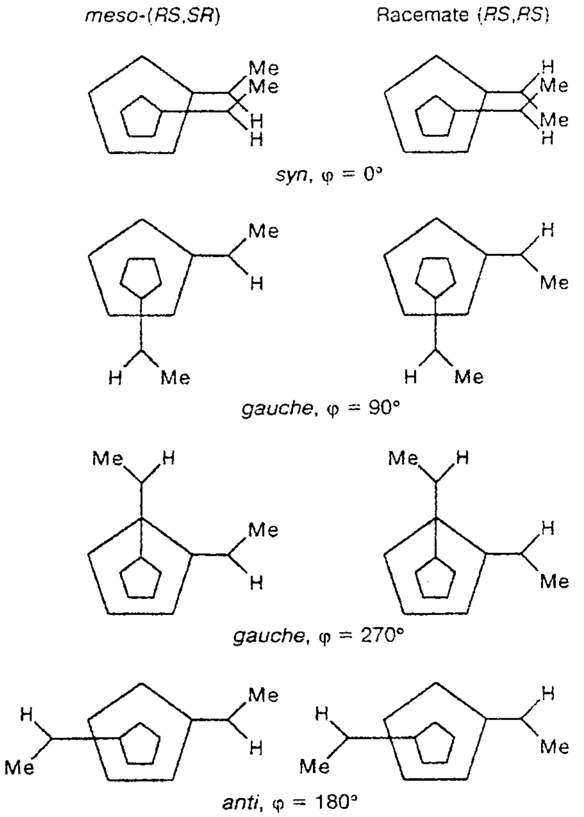

Fig. 2. The *syn*-, *gauche*-, and *anti*-conformers of diastereomers (*meso-RS,SR* and racemate *RS,RS*) of dications **5**.

The ^{1}H NMR spectra of each of the diastereomers of carbinols **6** (M = Fe, Ru, and Os) contain signals of the methyl groups in the δ 1.3 region, quadruplets of the CH groups in the δ ~4.3 region, and multiplet signals of the protons of the Cp rings (Table 5).

Consideration of the possible conformers for the diastereomers of dications **5** shows that the *meso*-diastereomer (*RS,SR*) has only one *gauche*-rotamer (if the angles of rotation of the rings are equal to φ = 90° and 270°, then the *gauche*-rotamers coincide), whereas the other diastereomer, the (*RS,RS*) racemate, has two different *gauche*-rotamers at the same angles (Fig. 2). In this case, one could expect that using the ^{1}H NMR spectra one would successfully assign the proton signals for each of the diastereomers, as well as determine which of the conformers is present in the solution.*

The solutions for ^{1}H NMR analysis of dications **5** were prepared by adding dicarbinols **6** (M = Ru, Os) to FSO_3H cooled to −70 °C. The ^{1}H NMR spectra were recorded at temperatures from −30 to +30 °C. In each case, three doublets of the methyl protons in the δ 2.1—2.5 region and a quadruplet of the CH protons in the

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* The retention of the optical configuration of the α-carbocation center in metallocenylmonocarbocations has been repeatedly noted in the literature.[7]

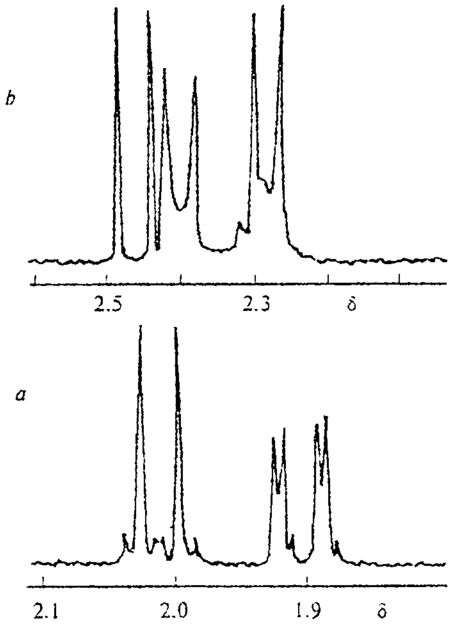

Fig. 3. ^{1}H NMR spectra of dications 5 (M = Ru) in CF_3SO_3H with a solvent additive (*a*) and in the pure FSO_3H at 0 °C (*b*).

δ 7.3—7.5 region from one of the diastereomers are observed. Quadruplets of the CH protons of the other diastereomer overlap with the signals of the CH protons of substituted cyclopentadienyl rings, which appear as complex multiplets in the δ 5—7 region. For this reason, the signals were assigned to a specific conformation and diastereomer taking into account the signals of the methyl protons (Table 6). In addition to the intense doublets (Fig. 3), low-intensity doublets are observed in the same region; they also can be assigned to the methyl protons.

The ^{1}H NMR spectra of dications 5 (M = Ru, Os) recorded in a superacid with a solvent additive (a $CF_3SO_3H—CD_2Cl_2—CD_3NO_2$ mixture*) in the same temperature interval (Table 7)** are somewhat shifted but their relative intensities remain nearly unchanged. This made it possible to assign the intense signals to the *gauche*-conformers. In particular, the low-field doublet was assigned to the methyl protons of *meso*-(*RS*,*SR*)-diastereomers and the two high-field doublets with equal intensities were assigned to the methyl protons of the (*RS*,*RS*)-racemates. The low-intensity signals, the number of which increases on going from the pure superacid to a solution with a solvent additive (see Fig. 4), can likely be assigned to the signals of the methyl groups of *anti*-conformers with the dicarbocation structure. As was already mentioned above, the solvent additive has a pronounced effect on the ^{1}H NMR spectra of *anti*-conformers. The number of these signals for the two *anti*-conformers of the *meso*- and racemic forms should double because of partial transformation of a close ionic pair into a solvent-separated pair, *i.e.*, four doublets with different intensities should be observed in the spectrum. In fact, the number of low-intensity signals of *anti*-conformers in the presence of a solvent is larger than that in a superacid without a solvent. However, some of them are likely overlapped with the much more intense signals of the *gauche*-conformers.

Table 7. Partial ^{1}H NMR data of dications 5 in a $CF_3SO_3H—CD_2Cl_2—CD_3NO_2$ mixture (δ)

M	T/°C	δ_{Me} (d, 6 H, $^3J \approx 6.5$ Hz)					
Ru	−40	1.86[a,b]	1.87[a,b]	1.93[a,c]	1.99[a,c]	2.01[b,d]	2.01[c,d]
	−30	1.87	1.89	1.86	—	2.01	—
	−20	1.89	1.90	—	2.01	2.02	—
	−10	1.91	1.92	—	—	2.03	—
	0	1.92	1.93	1.91	2.02	2.04	—
	+10	1.94	1.96	1.93	2.26	2.05	2.06
	+20	1.95	1.95	1.94	2.04	2.05	2.07
	+30	1.96	1.96	1.95	2.04	2.06	2.07
	−40[e]	1.86	1.87	1.99	—	2.01	—
Os	−30	1.84	1.85	—	—	1.97	—
	0	1.88	1.88	—	—	1.98	—
	+20	1.90	1.90	—	—	2.00	—
Fe	−20	2.15[c]	2.18[c]	6.92 (q, 2 H)[f]	7.13 (q, 2 H)[f]		
	+20	2.17	2.21	6.99 (q, 2 H)	7.17 (q, 2 H)		

[a] (*RS*,*RS*)-Diastereomer. [b] *gauche*-Conformers. [c] *anti*-Conformers. [d] (*RS*,*SR*)-Diastereomer. [e] After cooling from +30 to −40 °C. [f] The signals of the C<u>H</u>Me groups.

Concluding the discussion of the ^{1}H NMR spectra of dications 5 in a pure superacid or in a superacid with solvent additives it is important to note that varying temperature has little effect on the general spectral pattern and the observed changes are temperature-reversible. Only slight changes in the chemical shifts and Δδ values are observed, particularly for the (*RS*,*RS*)-diastereomer (Figs. 3,4). Unfortunately, the compounds decompose at temperatures above +30 °C. At the same time, the simultaneous presence of *gauche*- and *anti*-conformers in solution may indicate that dications 5 with the onium structure and with the dicarbocation structure have similar energies, though the former is more energetically favorable, which is in agreement with the calculations (see Table 1 and Fig. 1).

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* Resolution of the spectra in pure FSO_3H is better than in CF_3SO_3H; however, because of the poor miscibility of the solvents CD_2Cl_2 and CD_3NO_2 with FSO_3H, the spectra in superacids with a solvent additive were recorded in CF_3SO_3H.

** In Table 7, the parameters of the resonance signals of the Me groups are given. The signals of Cp rings and C<u>H</u>(Me) groups (M = Ru, Os) are complex multiplets in the δ 5—7 region. The signals of *gauche*-conformers of both diastereomers are observed at all temperatures studied. The signals of *anti*-conformers partly coincide and are overlapped with the above signals and therefore are not discernible at any temperature. Their assignment to the (*RS*,*SR*)- and (*RS*,*RS*)-diastereomers is ambiguous.

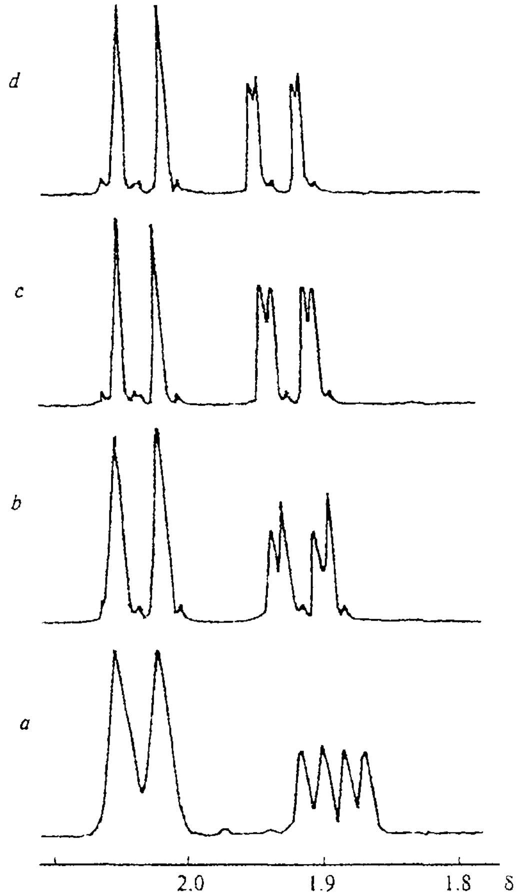

Fig. 4. ^1H NMR spectra of dications 5 (M = Ru) in CF_3SO_3H with a solvent additive at −40 (*a*), −10 (*b*), +10 (*c*), and +30 (*d*) °C.

It also should be noted that only two doublets in the δ ~2 region and two quadruplets in the δ ~7 region are recorded in the ^1H NMR spectra of dication 5 (M = Fe) in the solution of superacid with the solvent additive at −20 °C and +25 °C (see Table 7), and the spectral pattern remains nearly unchanged as the temperature changes. The donor-acceptor interaction of lone electron pairs of the metal atom with the carbocation centers in the Fe-containing dication is weaker than that in the Ru- and Os-containing analogs.[2,3,8] Hence, it cannot be ruled out that the Fe-containing dication is a dicarbocation, for which only *anti*-conformers of the (*RS,RS*)- and (*RS,SR*)-diastereomers are observed in the solution. Thus, by selecting appropriate substituents in the ring and at the α-carbocation center, we succeeded in modeling two extreme types of these compounds: onium dications 1 and 2 and dicarbocations 3; the onium cations (metallonium ions) were detected for the first time. ^1H NMR analysis of dications of these types is a convenient tool for assigning their structures to that of onium compounds or dicarbocations.

Recent data[9] of an X-ray study of 1,1′-$Fe(C_5H_4BBr_2)_2$ (7) (an analog of 3)*, which showed that this molecule has the *anti*-conformation in crystal, are in agreement with the results of investigating dications 5. The X-ray analysis of 1,1′,3,3′-$M[C_5H_3(BBr_2)_2]$ (M = Fe, Ru, and Os),[10] the ^{11}B NMR spectra of these compounds, those of 7 and its Ru- and Os-analogs,[9,10] as well as quantum-chemical calculations of 1,1′-$Fe(C_5H_4BH_2)_2$ by the density functional method[11] unambiguously show that the M—B* interaction increases in the series Fe < Ru < Os (though to a significantly lesser extent than the M—C^+ interaction),[9,10] while the energies of the *gauche*- and *anti*-conformers for diborylated ferrocene are nearly equal.[11]

Experimental

^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer at 200.13 MHz for ketones and carbinols in a solution of $CDCl_3$. Mass spectra were recorded on a Kratos MS-890 instrument at 70 eV and at an ionizing chamber temperature of 250 °C. Reduction of $(C_5H_4Ac)_2M$ by $LiAlH_4$ and its interaction with MeLi were performed according to standard procedures. In most cases the substances were crystallized from a benzene—hexane mixture (1 : 5). 1,1′-Diacetylferrocene was synthesized according to previously published procedures.[12,13]

1,1′-Diacetylosmocene. MeCOCl (4 g, 51 mmol) and $AlBr_3$ (13.4 g, 50 mmol) in 100 mL of CH_2Cl_2 were added to a solution of osmocene (1.6 g, 5 mmol) in 50 mL of anhydrous CH_2Cl_2 over a period of 1 h under an Ar atmosphere. The refluxing mixture was stirred for 24 h, cooled, and poured onto ice. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with water, dried with Na_2SO_4, and evaporated. The reaction mixture was separated on a column with Al_2O_3. Unreacted osmocene (0.8 g, 2.5 mmol) was eluted with petroleum ether and a petroleum ether—benzene mixture (1 : 5), acetylosmocene (yield 0.45 g, 1.24 mmol, 25%) was eluted with a benzene—ether mixture (4 : 1), and 1,1′-diacetylosmocene (yield 0.1 g, 0.25 mmol, 10% with respect to the reacted osmocene) was eluted with a chloroform—ether mixture (1 : 1), m.p. 149—151 °C (*cf.* Ref. 6: m.p. 148—152 °C). MS: a group of peaks with *m/z* 401—408 (the maximum intensity ion peak with *m/z* 406) $[M]^{+\cdot}$ and a group of peaks with *m/z* 330—337 (the maximum intensity ion peak with *m/z* 335 $[M-Me-2\ CO]^+$. Found (%): C, 41.55; H, 3.50; Os, 47.24. $C_{14}H_{14}O_2Os$. Calculated (%): C, 41.57; H, 3.49; Os, 47.03. ^1H NMR, δ: 2.12 (s, 6 H, Me); 5.00 (t, 4 H, H(3, 4), *J* = 1.6 Hz); 5.28 (t, 4 H, H(2, 5), *J* = 1.6 Hz). ^1H NMR spectrum of $(C_5H_5)OsC_5H_4Ac$, δ: 2.22 (s, 3 H, Me); 4.79 (s, 5 H, C_5H_5); 4.94 (t, 2 H, H(3, 4), *J* = 1.6 Hz); 5.23 (t, 2 H, H(2, 5), *J* = 1.6 Hz).

1,1′-Diacetylruthenocene was synthesized following a procedure analogous to that described previously[8] from ruthenocene (1.16 g, 5 mmol), MeCOCl (1.67 g, 20 mmol), and $AlCl_3$ (2.7 g, 20 mmol). Chromatography on Al_2O_3 (Brockmann II activity) analogous to that of 1,1′-diacetylosmocene resulted in isolation of $(C_5H_4Ac)_2Ru$ (yield 0.49 g, 1.6 mmol, 31%).

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* The neutral boron atom has six electrons and is considered to be an isoelectron analog of carbocation systems.[9—11]

M.p. 148—149 °C (*cf.* Ref. 6: m.p. 149—150 °C). ^{1}H NMR, δ: 2.15 (s, 3 H, Me); 4.76 (t, 4 H, H(3, 4), *J* = 1.6 Hz); 5.05 (t, 4 H, H(2, 5), *J* = 1.6 Hz).

General procedure for reduction of $(C_5H_4Ac)_2M$ (M = Fe, Ru, and Os). A solution of 1,1′-diacetylmetallocene in a mixture of anhydrous Et_2O and anhydrous C_6H_6 was added with stirring to $LiAlH_4$ (0.4 g, 10 mmol) in anhydrous Et_2O over a period of 0.5 h at 20 °C. Then the mixture was stirred for an additional 2 h and decomposed by adding ether saturated with water followed by careful addition of H_2O. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with water, dried with Na_2SO_4, and evaporated.

Starting from $(C_5H_4Ac)_2Fe$ (0.3 g, 1.1 mmol), $(C_5H_4Ac)_2Ru$ (0.32 g, 1.0 mmol), and $(C_5H_4Ac)_2Os$ (0.4 g, 0.99 mmol) carbinols **6** were prepared: 0.26 g (87%) for M = Fe, 0.27 g (85%) for M = Ru, and 0.35 g (86%) for M = Os, m.p. 68—69 °C (*cf.* Ref. 14: m.p. 69—72 °C), 71—73 °C, and 73—75 °C, respectively. Found (%): C, 52.87; H, 5.73. $C_{14}H_{18}O_2Ru$. Calculated (%): C, 52.65; H, 5.68. Found (%): C, 41.78; H, 4.57; Os, 46.32. $C_{14}H_{18}O_2Os$. Calculated (%): C, 41.46; H, 4.44; Os, 46.56.

General procedure for the synthesis of dicarbinols 4. A two-fold excess of a 1 *M* ethereal solution of MeLi obtained from MeI and Li was added to a solution of $(C_5H_4Ac)_2M$ (1 mmol) in anhydrous Et_2O (100 mL); the mixture was stirred for 1 h and then decomposed with a saturated aqueous solution of NH_4Cl. The organic layer was separated, the aqueous layer was extracted with ether, and the combined ethereal extracts were washed with water, dried with Na_2SO_4, and evaporated.

Starting from $(C_5H_4Ac)_2Fe$ (0.3 g, 1.1 mmol), $(C_5H_4Ac)_2Ru$ (0.32 g, 1.0 mmol), $(C_5H_4Ac)_2Os$ (0.4 g, 0.99 mmol), and MeLi (4 mL, 4 mmol) dicarbinols **4** were prepared: 0.28 g (85%) for M = Fe, 0.29 g (83%) for M = Ru, and 0.36 g (82%) for M = Os; m.p. 121—122 °C (*cf.* Ref. 15: m.p. 124—124.2 °C), 120—122 °C, and 123—125 °C, respectively. Found (%): C, 55.08; H, 6.34. $C_{16}H_{22}O_2Ru$. Calculated (%): C, 55.32; H, 6.38. Found (%): C, 44.32; H, 5.04; Os, 42.73. $C_{16}H_{22}O_2Os$. Calculated (%): C, 44.02; H, 5.08; Os, 43.57.

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References

1. A. Z. Kreindlin, E. I. Fedin, P. V. Petrovskii, R. M. Minyaev, and R. Hoffmann, *Organometallics*, 1991, **10**, 1206.
2. M. I. Rybinskaya, A. Z. Kreindlin, P. V. Petrovskii, R. M. Minyaev, and R. Hoffmann, *Organometallics*, 1994, **13**, 3903.
3. M. I. Rybinskaya, A. Z. Kreindlin, R. Hoffmann, and R. M. Minyaev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1701 [*Russ. Chem. Bull.*, 1994, **43**, 1605 (Engl. Transl.)].
4. G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 767.
5. C. U. Pittmann, *Tetrahedron Lett.*, 1967, 3619.
6. M. D. Raush and V. Mark, *J. Org. Chem.*, 1963, **28**, 3225.
7. W. E. Watts, *J. Organomet. Chem. Libr.*, 1979, **7**, 399.
8. E. G. Gal'pern, N. P. Gambaryan, A. Z. Kreindlin, M. I. Rybinskaya, I. V. Stankevich, and A. A. Chistyakov, *Metalloorg. Khim.*, 1992, **5**, 831 [*Organomet. Chem. USSR*, 1992, **5**, 401 (Engl. Transl.)].
9. B. Wrackmeyer, U. Dorfler, W. Millus, and M. Herberhold, *Polyhedron*, 1995, **14**, 1425.
10. A. Appel, H. Noth, and M. Schmidt, *Chem. Ber.*, 1995, **128**, 621.
11. A. Appel, F. Jakle, T. Priermeier, R. Schmid, and M. Wagner, *Organometallics*, 1996, **15**, 1188.
12. M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.*, 1960, **82**, 76.
13. G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 1958, 692.
14. P. J. Graham and R. V. Lidsey, *J. Org. Chem.*, 1961, **26**, 1671.
15. R. Piemschneider and D. Helm, *Chem. Ber.*, 1956, **89**, 155.

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