

On the problem of stabilization of α -carbocationic centers in metallocene series. Related interconversions of permethylated α -metallocenylcarbocations and metallocenium cation-radicals of the iron sub-group

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Introduction

The discovery that thirty years ago effective stabilization of α -carbocationic centers was possible by metallocenyl groups initiated prolonged discussions on the structure of these cations, and the mechanism of their stabilization. Two alternative mechanisms have been suggested. One group of researchers has attributed stabilization to electron transfer from the iron atom to the carbocationic center via the chemical bonds. Advocates of the other hypothesis, who do not deny the first alternative, believe that the major contributor to stabilization was the direct interaction of the α -carbocationic center with the metal atom [1,2].

This problem, was not however, completely solved especially in case of primary ions which had been studied only by indirect spectral methods. The relatively low stability of the primary carbocations precludes the isolation of crystals suitable for X-ray study. Data on α -ruthenocenyl- and α -osmocenyl-carbocations are scarce [1,2].

In order to alleviate this problem some new methods and models were developed some years ago. To this end the permethylated α -metallocenylcarbocations of the metals of the iron sub-group were chosen as suitable models. On the one hand, the stability of primary ions was raised by the stabilizing effect of methyl groups, and on the other hand, it enabled the strength of interaction between the metal atom and the carbocationic center to be varied as the size and the properties of the metal atoms changed in the sub-group. We also studied the secondary aryl-substituted carbocations.

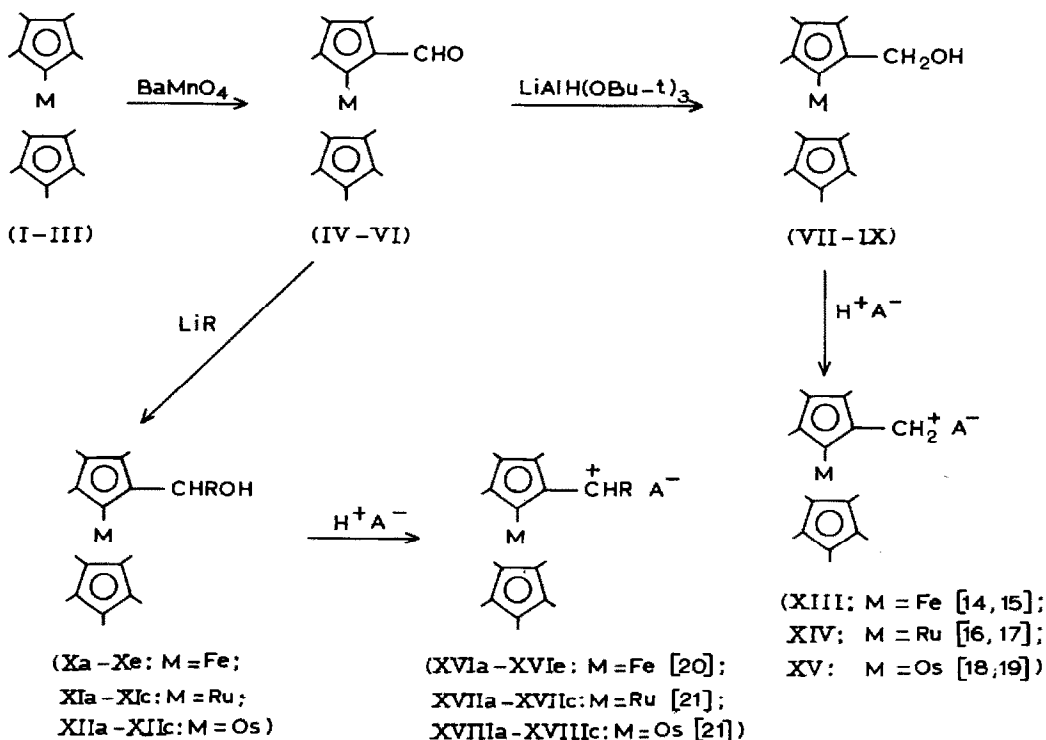
It is noteworthy that when we began this study data on permethylated metallocenes of the iron sub-group were extremely scarce. The synthesis of decamethylferrocene (I) had only been reported [3,4], and the syntheses of decamethylruthenocene (II) [5–7] and decamethylosmocene (III) [6,7] have been published in the course of the present study. Some of the properties of the complexes, such as their electro-

chemical [5,6,8–10] and chemical oxidation [7,9,11], have also been studied. Decamethylmetallocenes were used to synthesize the previously reported triple-decker sandwich complexes of the iron sub-group [12], the use of decamethylferrocene gave the first ferromagnetic organometallic compound [13].

Synthesis of the salts of permethylated α -metallocenylcarbocations

In order to carry out a systematic study of the salts of permethylated α -metallocenylcarbocations, a convenient general procedure for their synthesis from decamethylmetallocenes (I–III) was required. We suggested a method based on the oxidation of the methyl groups in I–III to give the aldehydes IV–VI. Reaction of the latter with $\text{LiAlH}(\text{O}i\text{Bu}-t)_3$ or organolithium compounds leads to the primary, VII–IX, or secondary, X–XII, carbinols respectively. The carbinols were then converted to the primary XIII–XV or secondary XVI–XVIII carbocations by treatment of acids (Scheme 1).

The technique [22] described previously for α -[n]-ferrocenophanone synthesis was used to oxidize with barium manganate the metallocenes I–III to the aldehydes IV–VI. The reactivity of the Me group in oxidation reactions decreases in the order $\text{Fe} > \text{Ru} > \text{Os}$ [18]. Reduction of aldehydes IV–VI with LiAlH_4 leads to mixtures of initial metallocenes I–III and the carbinols VII–IX, although the separation of such



Scheme 1. a: R = 2,4,6- $\text{C}_6\text{H}_2\text{Me}_3$; b: R = Ph; c: R = C_6F_5 ; d: R = $\text{PhCr}(\text{CO})_3$; e: R = $\alpha\text{-C}_{10}\text{H}_7$. I, IV, VII: M = Fe; II, V, VIII: M = Ru; III, VI, IX: M = Os.

mixtures presents certain difficulties. Use of $\text{LiAlH}(\text{O}i\text{Bu-t})_3$ instead of LiAlH_4 in the reduction of aldehydes yields pure primary carbinols. Reaction of aldehydes IV–VI with organolithium compounds including the sterically hindered $\text{C}_6\text{H}_2\text{Me}_3\text{Li}$ gives secondary carbinols X–XII in good yields.

All the primary and secondary carbinols synthesized give cations with strong acids (CF_3COOH , $\text{CF}_3\text{SO}_3\text{H}$, HBF_4 , HPF_6). Ruthenium- and osmium-containing primary carbinols VIII and IX give the corresponding cations even with weak acid such as acetic acid in presence of the stabilizing BPh_4^- -anion [14–21]. Which testifies to high stability.

Structure of α -nonamethylmetallocenylcarbocations and mechanism of stabilization of α -carbocationic center

The Ru- and Os-containing cations [18,19] can be obtained even under the action of weak acetic acid, a fact which attests to their high stability. Their salts (with the anions BF_4^- , PF_6^- and Bh_4^-) are not changed after prolonged storage in air at room temperature. X-Ray study of these cations could thus be carried out. The salts, XIV and XV, are the first of the primary metallocene carbocations to be structurally characterized.

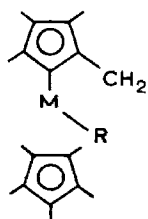
An X-ray study of the complex XV was carried out in cooperation with Struchkov and Yanovsky [19]. The displacement of the $\alpha\text{-CH}_2$ group from the plane of the cyclopentadienyl ring towards the metal atom (the $\text{C}(\text{Cp})\text{-C}_\alpha$ bond dips towards the Cp ring by 41.8°), and the $\text{Os}\dots\text{C}_\alpha$ distance of 2.244 Å, (in ref. 23 the length of the Os–C bond is given as 2.22 Å) confirm the formation of a covalent Os– C_α bond. Thus the C_α atom in the Os-containing cation XV in fact loses its carbenium character, the positive charge is delocalized so that it is mainly concentrated about the metal atom which then acts as a specific onium center*.

An X-ray study of the nonamethylruthenocenylcarbocation hexafluorophosphate (XIV) [16,17] has shown the inclination angle of $\alpha\text{-CH}_2$ -group is significantly smaller (14.4°) than in the Os-analogue furthermore, the $\text{Ru}\dots\text{C}_\alpha^+$ distance of 2.603 Å is 0.4 Å longer than of the covalent Ru–C bond length of ~ 2.2 Å [24]. Thus although the metal atom– $\alpha\text{-CH}_2$ interaction in Ru-containing derivatives is lower than that in the Os-containing analogues even this interaction ensures stabilization of the carbocationic center. Thus to describe the Os- and possibly also the Ru-containing cations as carbocations is rather incorrect. However, the term is still used owing to historical tradition, and because of the absence of the general name for the whole group.

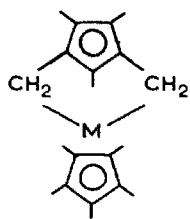
In discussing the structural data for Os- and Ru-containing cations it is emphasized that despite the significant tilt of the $\alpha\text{-CH}_2$ group towards the metal atom, the metallocene structure is preserved. Slight displacement (0.2 Å) of the Os atom from the center of the cyclopentadienyl ring is only observed. It is also noteworthy that the C– C_α distances in Os (XV) [19] and Ru-containing (XIV) [17] complexes, 1.426 and 1.424 Å respectively, are markedly shorter than the other nine C–Me distances, while the bond lengths in the five-membered cycle are typical of such complexes (Table 1).

The above situation is typical for all the complexes with analogous structure, including the neutral complexes [25–33].

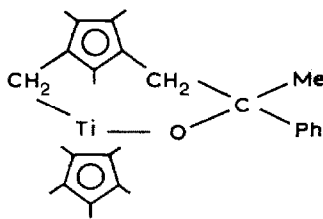
* Chemical properties of this cation have been earlier discussed [19].



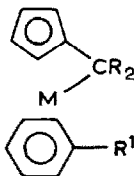
(M = Zr, R = Ph [29];
M = Hf, R = CH₂Ph [30])



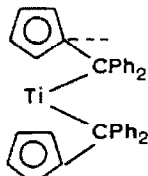
(M = Ti [27];
M = Zr [27])



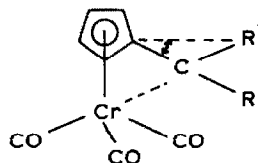
[27]



(R = Me, Ph; R¹ = H, Me;
M = Mo, W [31])



[31]



(R = R¹ = Ph [28];
R = R¹ = SMe, R = R¹ = C₃H₅;
R + R¹ = SCH₂CH₂S;
R + R¹ = SCH = CHS [32];
R = H, R¹ = OCOPh [33])

A study of the less stable Fe-containing cations presented certain difficulties. That their synthesis was possible only with strong protic acids demonstrates the lower stability of these cations in comparison to Os- and Ru-containing analogues. However in contrast to the nonmethylated α -ferrocenylcarbocations their permethylated complexes proved to be more stable and can be isolated. Freshly prepared primary α -nonamethylferrocenylcarbocation is an orange-red powder, however, when solutions or the solid are stored or recrystallization is attempted a green dimer results. The structure of this dimer will be described. All our attempts to prepare single crystals of the salts of the Fe-containing cations for the structural study were unsuccessful. Thus the Fe, and the Ru- and Os-containing cations were studied by ¹H and ¹³C NMR spectroscopy (in cooperation with P.V. Petrovsky) (Tables 2, 3). NMR spectral data for all the complexes together with the X-ray data for Ru- and Os-containing cations enabled certain conclusions to be made on structure and the character of the interaction of the α -carbocationic center with the metal atom in the case of the α -nonamethylferrocenylcarbocation as well. The increase in shielding of

Table 1

Bond lengths d(Å).

XIV	d	XV	d
C(1)–C(2)	1.426(6)	C(1)–C(2)	1.470(6)
C(2)–C(3)	1.380(6)	C(2)–C(3)	1.403(7)
C(3)–C(4)	1.410(6)	C(3)–C(4)	1.439(6)
C(4)–C(5)	1.412(6)	C(4)–C(5)	1.413(6)
C(5)–C(1)	1.432(7)	C(5)–C(1)	1.461(7)

Table 2

Chemical shifts for the ^{13}C nuclei of the $\alpha\text{-CHR}^+$ group^a

M	R			
	H	$\text{C}_6\text{H}_2\text{Me}_3$	Ph	C_6F_5
Fe	90.7 (164.7 Hz)(XIII) ^b	137.5 (XVIa)	132.1 (XVIIb)	—
Ru	74.7 (164.2 Hz)(XIV)	134.3 (XVIIa)	104.4 (XVIIb)	83.9 (XVIIc)
Os	55.4 (166.0 Hz)(XV)	102.4 (XVIIIa)	79.0 (XVIIIb)	55.7 (XVIIIc)

^a The spectra of XIII–XV, XVIIa–XVIIc and XVIIIa–XVIIIc recorded on CH_2Cl_2 solution of the freshly precipitated salts indicated the presence of cations with BF_4^- and PF_6^- anions at 25°C . The spectra of solutions of XVIa, XVIIb were determined for solutions of carbinols Xa, Xb in $\text{CH}_2\text{Cl}_2/\text{HBF}_4 \cdot \text{OEt}_2$ at -30° . ^b Values for the coupling constants $J(^1\text{H}-^{13}\text{C})$ are given in brackets.

Table 3

The values of chemical shifts for ^1H of the $\alpha\text{-CHR}^+$ group^a

M	R			
	H	$\text{C}_6\text{H}_2\text{Me}_3$	Ph	C_6F_5
Fe	5.27 (XIII)	9.31 (XVIa)	^b	7.24 (XVIc)
Ru	4.75 (XIV)	7.84 (XVIIa)	6.51 (XVIIb)	6.21 (XVIIc)
Os	4.42 (XV)	7.98(XVIIIa)	6.26 (XVIIIb)	6.15 (XVIIc)

^a The solutions of corresponding carbinols in $\text{CF}_3\text{COOH}/\text{CDCl}_3$ were measured. ^b Chemical shifts for ^1H of $\alpha\text{-CHR}$ group coincide with the values for Ph-protons in the region of 7.2–7.8 ppm.

H and C nuclei of $\alpha\text{-CHR}^+$ groups on going down the sub-group is the most characteristic tendency of ^1H and ^{13}C NMR spectra of primary XIII–XV ($\text{R} = \text{H}$) and secondary XVI–XVIII cations.

The increase in shielding of ^{13}C nuclei of the $\alpha\text{-CHR}^+$ group on going from Fe to Ru to Os with the same substituents can be seen from Table 2 to be 23–32 ppm (with the exception of the pair XVIa–XVIIa where $\Delta\delta$ is 3.2 ppm *).

The increase in shielding of ^{13}C nuclei has been reported previously for nonmethylated $\text{C}_5\text{H}_5\text{MC}_5\text{H}_4\text{CHC}_5\text{H}_4\text{FeC}_5\text{H}_5$ (δ (ppm) (CH): $\text{M} = \text{Fe}$, 147.2; $\text{M} = \text{Ru}$ 116.9 [34]), $\text{C}_7\text{H}_7\text{M}(\text{CO})_3^+$ (δ (ppm) (C_7H_7); $\text{M} = \text{Cr}$ 104.7; $\text{M} = \text{Mo}$ 100.0; $\text{M} = \text{W}$ 96.9 [35]) and neutral complexes $\text{C}_5\text{Me}_5\text{MC}_5\text{Me}_3(\text{CH}_2)_2$ (δ (ppm) (CH_2); $\text{M} = \text{Ti}$ 67.6; $\text{M} = \text{Zr}$ 56.5 [29]).

The change in the ^1H shielding in $\alpha\text{-CHR}^+$ (Table 3) in general follows the same law as that for the ^{13}C nuclei of this group, i.e. an increase in the ^1H shielding is observed on going from the Fe to the Os compounds.

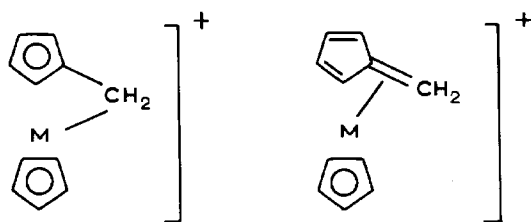
A comparison of NMR spectral and X-ray data for the Ru- and Os-containing cations reveals that the increase of ^1H and ^{13}C shielding in the $\alpha\text{-CH}_2^+$ group coincides with the strengthening of the metal atom– $\alpha\text{-CH}_2^+$ interaction and thus with the shortening of the $\text{M}-\text{C}_\alpha$ distance. Thus the interaction of the iron atom with the α -carbocationic center is weaker than with Os and Ru atoms. This

* Anomalous $\Delta\delta$ values also observed in the ^1H NMR spectra of cations with $\text{R} = \text{C}_6\text{H}_2\text{Me}_3$ are discussed below.

conclusion is in good agreement with the X-ray data on secondary and tertiary diferrocenyl- and diphenylferrocenyl-carbocations [25,26] with the Fe-C, distances of 2.69 and 2.71 Å, respectively.

The data obtained indicate that both mechanisms (electron transfer from the metal atom to the α -carbocationic center C_{α}^{+} via the chemical bonds, and the direct interaction of the metal atom with C_{α}^{+}) must be present. The contribution by each of the mechanisms is determined by the nature of the metal. The contribution by the second mechanism increases significantly in the sub-group and changes from weak for the Fe complexes, to very strong and results in the covalent M-C bond in the osmium compound. The reason for the observed phenomenon is probably the increase in size * and basicity [36,37], or more precisely the nucleophilicity, of the metal atom.

After much discussion on the structure of cationic and neutral complexes, two models that account for the metal-ligand bonding in the α -metallocenylcarbocations are generally accepted and may be represented as follows:



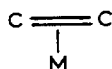
(A)

(B)

The question which of the two schemes is to be preferred [27-29,31] is academic and similar to which of the two types C and D of π -bonding in olefins is the most appropriate:



(C)



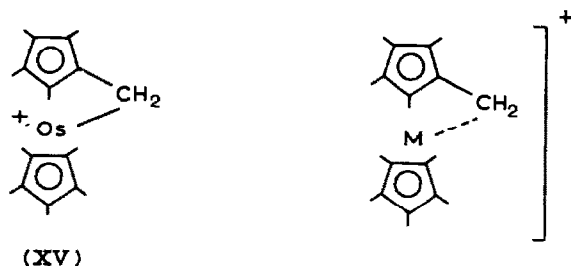
(D)

In order to choose one of the two structures C or D the $J(^1\text{H}-^{13}\text{C})$ values for α -CHR and α -CHR groups, the type of C_{α} atom hybridization and the type of bonding between the transition metal and the α -CHR group of cationic and neutral complexes, are usually taken into consideration [27,29,30,38]. However it is evident that the $J(^1\text{H}-^{13}\text{C})$ values for the Fe, Ru, Os primary cations are almost the same (164.2-166.0 Hz) (see Table 2), although the interaction in the Fe complexes differs greatly from that in Ru and Os compounds (see above). Thus in this case the $J(^1\text{H}-^{13}\text{C})$ values are not affected by fine structural changes, and so cannot be used to characterize the type of bonding in XIII-XV.

In light of the limitations of both schemes in the detailed description of the interaction between the carbocationic center and the metal atom in α -metallocenylcarbocations we decided to use for the Os-containing cation XV structure A which seems to be the more suitable. At the same time a somewhat modified scheme can

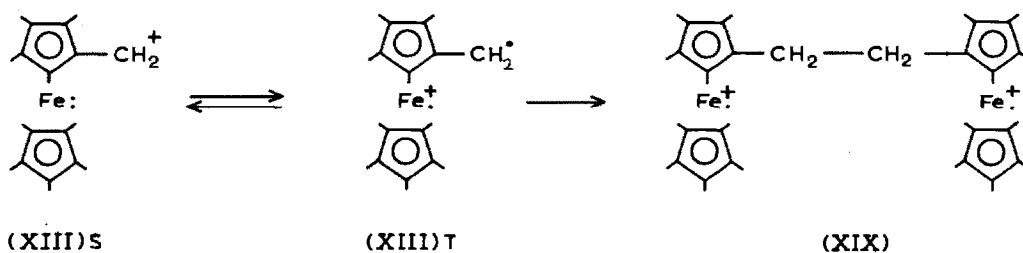
* The covalent radii of Fe, Ru, Os are 1.34; 1.49; 1.50 Å respectively, according to ref. 34.

be used for cations with a weaker $M-C_{\alpha}$ interaction:

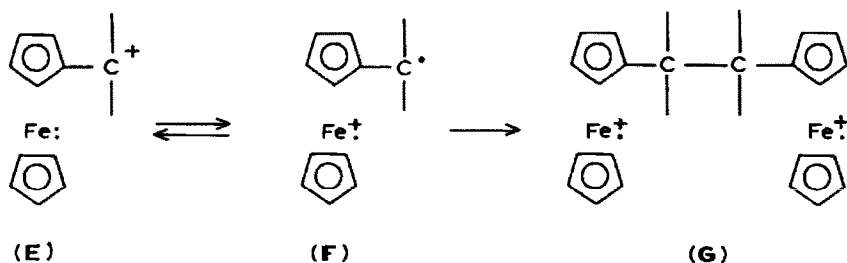


Singlet-triplet transition and related interconversions of permethylated α -metallocenyl-carbocations and metallocenium cation-radicals

It has been mentioned that unstable α -nonamethylferrocenylcarbocation undergoes dimerization when stored in solid state or as a solution and on recrystallization give a dicationic biradical, bis(nonamethylferrocenyl)ethane (XIX). Reduction of this product by NaBH_4 leads to bis(nonamethylferrocenyl)ethane. Reduction of the freshly precipitated cation XIII gives decamethylferrocene (I). Examples of such



doubling are numerous [1]. The reasons for the dimerization have been repeatedly discussed. Cais [39–42], for instance, attributed this process to an intermediate “redox-tautomeric” conversion of cation E into biradical-cation F, now referred to as the singlet-triplet transition $E \rightleftharpoons F$. The final product G is the result of dimerization of biradical-cation F.



However there is no direct experimental proof for the formation of the intermediate triplet particles F because only the products of their conversion were detected. Cais reported the absorbance of triplet particle nitrosobenzene [40] in the ESR spectra, however, in the following article [42] he suggested an alternative scheme for the formation of a paramagnetic substance without including participation of the triplet species.

To prove the involvement of cationic triplet species in the process we synthesized nonamethylferrocenylcarbocations (XVIa–XVIe) with bulky substituents at the

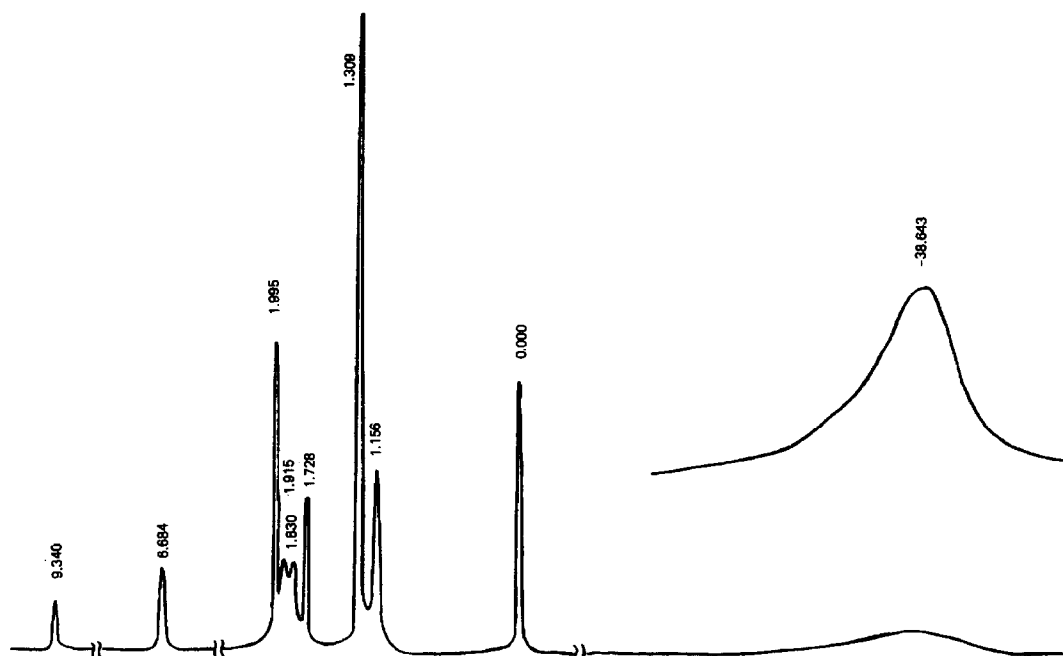
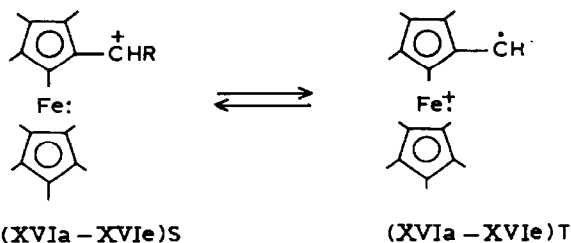


Fig. 1. ¹H NMR spectrum of XVIa.

α -C-atom which inhibits dimerization. The ¹H NMR spectra indicate that a mixture of singlet (diamagnetic) and triplet (paramagnetic) particles is formed on dissolution of the carbinols Xa–Xe in CDCl₃/CF₃COOH, or upon precipitation as tetrafluoroborates or hexafluorophosphates with subsequent dissolution in CDCl₃, CD₃CN or other similar solvents.



The ¹H NMR spectrum of such a mixture for mesitylsubstituted cations is shown in Fig. 1. Reduction of the mixtures XVI(S)–XVI(T) by NaBH₄ gives nonamethylferrocenylmethanes C₅Me₅FeC₅Me₄CH₂R; no dimeric “ethane” derivatives were found in the mass spectra of the reduction product.

The ¹H NMR spectral data also indicate that the triplet species XVI(T) in solution depends on the nature of the substituent and increases along the series as follows (content, %): C₆H₂Me₃ (15–20) < Ph, α -C₁₀H₇ (30–35) < (CO)₃CrPh (50) < C₆F₅ (70–80), thus the population of the triplet state increases together with the increase of the electron-withdrawing ability of the aryl substituents, i.e. a decrease in the stability of the α -carbocationic center facilitates the singlet \rightleftharpoons triplet transfer. These data explain, why only diamagnetic i.e. singlet, particles were found in solutions of relatively stable diferrocenylcarbocations by ¹H NMR spectroscopy [25]. In cooperation with E.I. Fedin and A.L. Blumenfeld we began a study of the salt of this cation by use of relaxation methods for solid samples. It was demon-

strated by spin-lattice relaxation techniques that even this salt contained paramagnetic species, albeit in concentrations of less than 1% [15]. The concentration of paramagnetic species in solution was naturally below the limit of ^1H NMR sensitivity.

Thus NMR spectra showed the presence of not only the singlet but also the triplet species. In our study, however, we did not attempt to characterize the equilibrium between these two forms. The problem is much more complicated; on discussing singlet-triplet transfer of the cationic forms, the migration of the anion should be taken into consideration, because sometimes this process may be the limiting factor to achievement of the equilibria [15].

This assumption is in agreement with the Mössbauer data for the complexes studied. The freshly prepared solid salt of α -mesityl- α -nonamethylferrocenylcarbocation XVIa contains an iron(II) compound corresponding to the singlet particle. A mixture of iron(II) and iron(III) compounds is found in frozen solutions of XVIa in dimethylformamide *. The amount of iron(III) compound corresponding to the triplet species, is about 20% **. This result is in qualitative agreement with the ^1H NMR data for solutions of this cation. Thus the Mössbauer spectra suggest that separation of the anion from the carbocationic center induces the singlet-triplet transfer. However, further study of this phenomenon is required.

It has been mentioned earlier that Ru- and Os-containing cations are extremely stable and diamagnetic. We failed to locate the paramagnetic centers in these cations even by spin-lattice relaxation of solid samples. The situation remains unchanged for secondary cations containing an electron-withdrawing substituent C_6F_5 in the carbocationic center; the population of the triplet state in analogous iron derivatives is about 70–80%. It confirms that the barrier of the singlet-triplet transfer in Ru and Os derivatives is much higher than in the ferrocene series and the singlet \rightleftharpoons triplet equilibrium is shifted considerably in the direction of the singlet state. This was clear from the values of oxidation-reduction potentials [10] *** and the stability data for these species. The formation of the triplet species after breaking of the strong metal- C_α bond thus reverse triplet \rightleftharpoons singlet transfer is far more likely when the triplet species is formed.

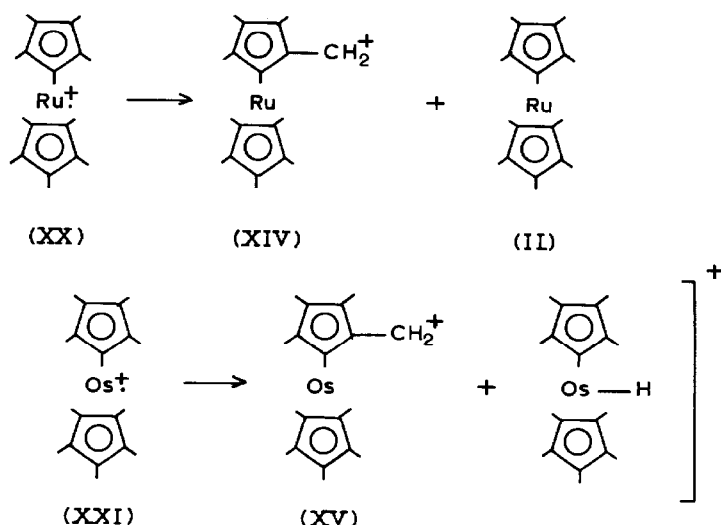
The phenomenon of singlet \rightleftharpoons triplet transfer determines the nature of the properties of the α -ferrocenylcarbocations and accounts for the related interconversion of decamethylruthenocenium (XX) and decamethyl-osmocenium (XXI) cation radicals. Koelle and coworkers [9] were the first to observe disproportionation of decamethylruthenocenium (XX) on α -nonamethylruthenocenium carbocation (XIV) and decamethylruthenocene (II) in the presence of chloride ion. We have shown that decamethyl-osmocenium (XXI) cation radical undergoes the same conversion [18].

A thorough study of these transformations has revealed that the presence of the Cl-anion is not essential. Thus decamethylmetallocenium (-ruthenicum and -osmium) (XX, XXI) disproportionate readily in acetonitrile with formation of the carboca-

* Mössbauer spectra were measured in cooperation with R.A. Manapov and coworkers in Kazan Physico-Technical Institute of the Kazan Branch of the Academy of Sciences of the USSR. The results of this work will be published latter.

** It is noteworthy that the more sensitive relaxation method can detect the triplet particles in the solid samples as well.

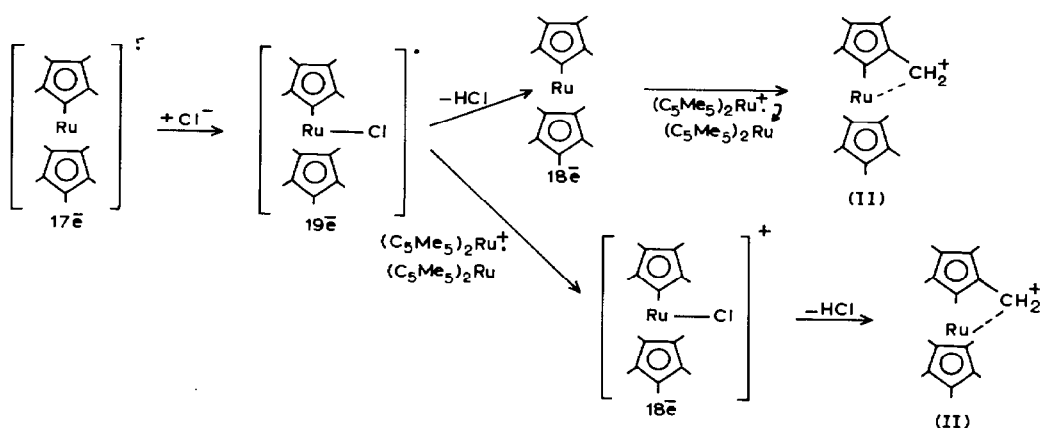
*** Oxidation-reduction potentials were measured in cooperation with L.I. Denisovich and M.G. Peterleytner.



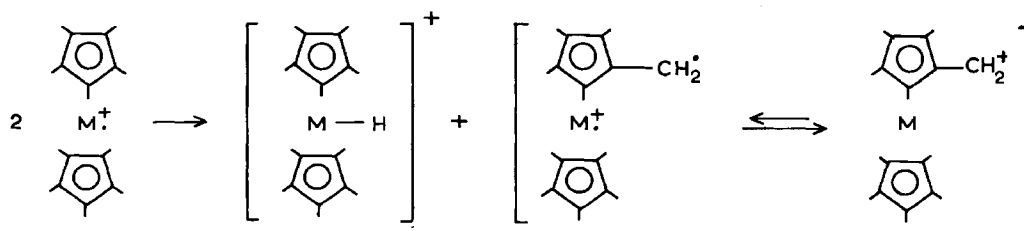
tions XIV, XV and metallocenes II, III. Whereas permethylsoscenium (XXI) gives protonated osmocene, in addition to the products already mentioned.

Similar conversions were observed for decamethylmetallocenes in the presence of oxidizing agents such as Ag^+ , Ph_3C^+ . Use of this method converts decamethylruthenocene (II) completely into the carbocation, however decamethyl-osmocene (III) gives a mixture of carbocation XV and protonated osmocene [18]. The salt of the protonated osmocene has been previously described [6]. Its formation was confirmed by ^1H and ^{13}C NMR spectroscopy.

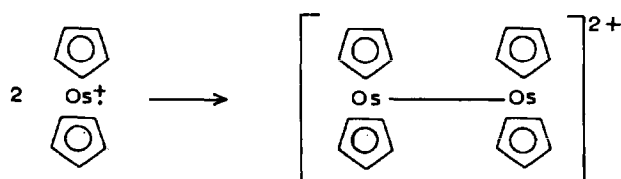
A complicated scheme that involves chloride has been suggested [9] for the transformation of the paramagnetic cation-radical of decamethylruthenocenium into the diamagnetic nonamethylruthenocenylicarbocation:



However, if involvement chloride in disproportionation is regarded as not essential to formation of the protonated decamethylsoscene, we suggest the following hypothetical scheme for the mechanism of the process. This scheme incorporates the singlet \rightleftharpoons triplet transfer of α -carbocations analogous to that observed by us for the ferrocene series.



According to this scheme part of the cation-radicals act as acceptors whereas the other, as donors of H[•]. In the first case metal atoms take up H[•] to give a protonated decamethylsmocene whereas in the second case methyl groups release H[•] and are thus transformed into the triplet species which are readily transferred onto the singlet cations*. Decamethylruthenocene being a weaker base readily releases a proton under such conditions. High reactivity of osmocenium salt as a radical has been confirmed [43] by its rapid dimerization to a dication with an Os–Os bond:



Methyl groups in the permethylated osmocenium hinder such dimerization and the active radical is probably stabilized by release of the radical hydrogen from the methyl group. In addition the formation of the protonated decamethylsmocene may involve participation of hydrogen radicals present in the medium.

Conclusion

The study of permethylated α -metallocenylcarbocations of the iron sub-group proved fruitful for elucidating the structure of these cations, the mechanism by which the α -carbocationic center is stabilized and for the study of singlet \rightleftharpoons triplet transfer in these cations.

Recent data on neutral fulvene complexes [25–33] (see above) point to the same problems as in case of α -metallocenylcarbocations. This fact clearly demonstrates that at present a more general problem should be discussed. The stabilization of an α -carbocationic center by a metallo complex fragment should be regarded as part of a more general problem of the stabilization of any coordinatively nonsaturated center in α -position to this fragment. Not only the cation, but also the radical, the carbenium, and even the anionic centers may act as such. Thus prospects for development in this field are broad.

* *Note added in proof.* In a recent publication (D. O'Hare, J.C. Green, T.P. Chadwick, J.S. Miller, *Organometallics*, 7 (1988) 1335) on the synthesis and crystal structure of $[\text{Me}_5\text{C}_5\text{OsC}_5\text{Me}_5]^+ \text{BF}_4^-$ transformation of this osmocenium salt in the ^1H NMR spectrum recorded, in CH_3CN was not mentioned. We observed this transformation by monitoring the ^1H NMR spectrum in CD_3CN with periodical registration. In CH_3CN the signals of the methyl groups of cyclopentadienyl rings are obscured by that of the solvent.

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