

## Preparation of stable $\alpha$ -(nonamethylmetallocenyl)- $\alpha$ -hydroxycarbocations and their transformations<sup>1</sup>

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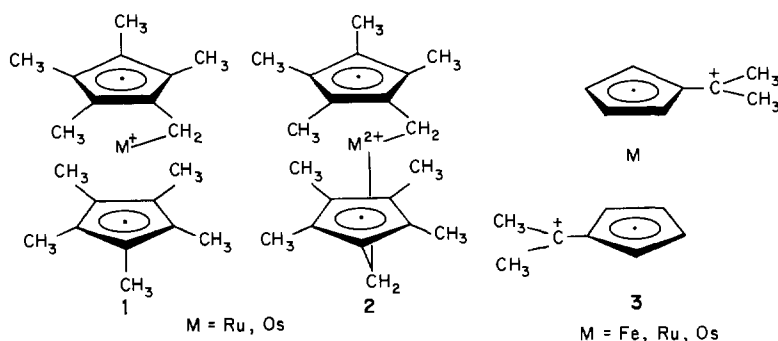
### Abstract

It has been shown that the structure of  $\alpha$ -(nonamethylmetallocenyl)- $\alpha$ -hydroxycarbocations (M = Fe, Ru, Os), prepared by protonation of formylnonamethylmetallocenes with HBF<sub>4</sub> and CF<sub>3</sub>COOH, depends on the nature of the metal and anion and is determined by the relative basicities. The Fe-containing salts have an open fulvenoid structure with an interionic hydrogen bond O–H...X irrespective of the nature of anion (X = BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>COO<sup>-</sup>). The Ru- and Os-containing salts, in which the metal atoms are more basic than Fe, have, in the case of the weakly basic BF<sub>4</sub><sup>-</sup> anion, a cyclic structure with an intramolecular M...HO hydrogen bond, while in the case of the more basic X = F<sup>-</sup> or CF<sub>3</sub>COO<sup>-</sup> anions they are transformed to the open fulvenoid structure with an interionic hydrogen bond OH...X, the structure of which has been established by an X-ray diffraction study of C<sub>5</sub>Me<sub>5</sub>RuMe<sub>4</sub><sup>+</sup>CH–OH...F<sup>-</sup>. When the Fe-containing salts are kept in polar solvents or stored in the solid state for a long time they are entirely converted into paramagnetic salts of formylnonamethylferrocenium, the structure of which was confirmed by the oxidation of formylnonamethylferrocene using AgBF<sub>4</sub>. © 1997 Published by Elsevier Science S.A.

**Keywords:** Formylnonamethylmetallocene; Iron; Ruthenium; Osmium; Crystal structure; Hydrogen bonds; O-protonation

### 1. Introduction

Recently, using ruthenium and osmium metallocenes, we have investigated mono- and dicationic species of types [C<sub>5</sub>Me<sub>5</sub>MC<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>]<sup>+</sup> (1) [1–5] and [CH<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>MC<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>]<sup>2+</sup> (2) [6,7] and have shown that they are actually onium compounds, the positive charge of which is localized mainly on the metal atom. The investigation of dicationic species of type [CMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>MC<sub>5</sub>H<sub>4</sub>CMe<sub>2</sub>]<sup>2+</sup> (3) [8] has shown that they are dicarbocations with localization of positive charges mainly on carbon atoms of the CMe<sub>2</sub> groups.

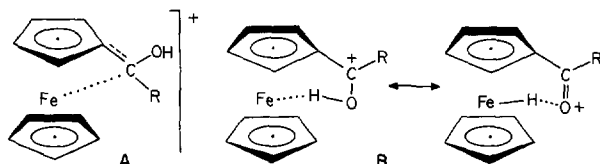


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<sup>1</sup> Dedicated to the memory of Professor Yu.T. Struchkov.

It was interesting to study the structure of monocations for  $\alpha$ -carbocation centers in which substituents different from the H atom and Me group were situated, in particular the OH group [9]. The interest in these complexes was caused mainly by the fact that introduction to the carbocation center of an electron-donating OH substituent capable of forming hydrogen bonds could essentially change the structure and properties of the resulting cations compared with cations (1) [9].

The OH derivatives were obtained by protonation of formylmetallocenes. It should be noted that previously the problem of protonation of  $\alpha$ -carbonyl derivatives of metallocenes has been studied only on the example of ferrocene derivatives with nonmethylated Cp rings. Based on the  $^1\text{H}$  NMR spectra, two alternative structures were suggested [10,11] for unstable products: structure (A) in which the metal participates in stabilization of the carbocation center and structure (B) containing a hydrogen bond with a metal atom.



The results obtained have shown that reliable conclusions may be obtained only on the basis of investigation of stable cations, in particular of permethylated metallocenyl cations. Therefore, for the protonation we used the permethylated formylmetallocenes (4) containing all iron-group metals, since it was known that the stability of this class of compounds increases in the sequence  $\text{Fe} < \text{Ru} < \text{Os}$  [12–14]. (Preliminary results have been published in Ref. [9].)

## 2. Results and discussion

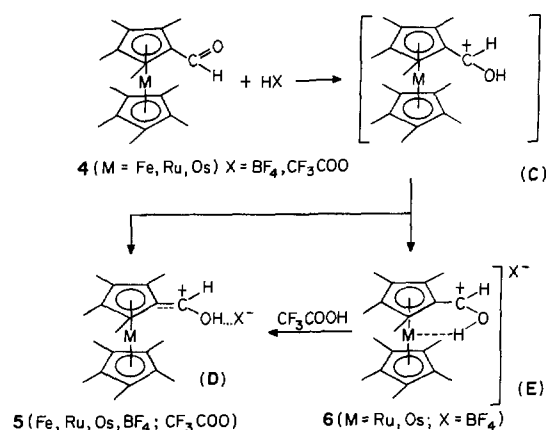
We have studied the protonation of (4) by the action of such protic acids as  $\text{HBF}_4 \cdot \text{OEt}_2$  and  $\text{CF}_3\text{COOH}$  [9]. The reaction of (4) with excess of  $\text{HBF}_4 \cdot \text{OEt}_2$  in anhydrous ether yielded relatively stable products as dark-violet, beige and gray powders for Fe, Ru and Os derivatives respectively. Elemental analysis showed that the compounds prepared were actually the adducts of starting aldehydes with  $\text{HBF}_4$ .

An examination of the IR spectra of both solid adducts and their solutions in  $\text{CH}_2\text{Cl}_2$  indicates the absence of  $\nu_{\text{CO}}$  absorption of the aldehyde group ( $1600\text{--}1645\text{ cm}^{-1}$ ) and the appearance of lower-frequency bands ( $1570\text{--}1540\text{ cm}^{-1}$ ) typical of protonated carbonyl compounds [15]. In addition, the new bands ( $\nu = 1000\text{--}1100\text{ cm}^{-1}$ ) characteristic of the  $\text{BF}_4$  anion appear. It turned out that all the compounds contained hydrogen bonds, and the character of the Fe-containing complex was significantly different from the Ru- and Os-products.

The IR spectrum of solid freshly prepared Fe-containing adduct ( $X = \text{BF}_4$ ) exhibits a  $\nu_{\text{OH}}$  band at  $3500\text{ cm}^{-1}$ . We assign this band to vibrations of the OH group bonded by an interionic hydrogen bond of the  $\text{OH} \dots \text{F} \text{BF}_3^-$  type. This conclusion is based on recording the spectra of solutions of adducts in  $\text{CH}_2\text{Cl}_2$  and studying their concentration dependence. As the concentration of adduct decreases, the intensity of the  $\nu_{\text{OH}(\text{free})}$  absorption band at  $3600\text{ cm}^{-1}$  increases. At the same time, the spectra of freshly prepared Ru- and Os-containing adducts, both in the solid state and in solution, exhibit intense bands in the region of  $3280\text{--}3220\text{ cm}^{-1}$ . Their intensities do not depend on the concentration of the solution. No bands due to  $\nu_{\text{OH}(\text{free})}$  appear, even when the concentration diminishes from  $10^{-1}$  to  $10^{-3}\text{ mol l}^{-1}$ . This indicates that the formation of  $\text{M} \dots \text{H}\text{--}\text{O}$  intramolecular hydrogen bonds with Ru and Os is more favorable than with Fe, which is in agreement with the data obtained previously for metallocenylmethanols [15].

Based on these data, it may be assumed that the protonation of aldehydes 4 ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) yields intermediate species (C) (see Scheme 1), which are further converted into different products depending on the nature of the metal atom. The structure of the products obtained was confirmed by an examination of the NMR spectra of all adducts and by an X-ray diffraction study of the Ru-containing complex.

Thus, the Fe-containing aldehyde (4,Fe) affords adduct (5,Fe, $\text{BF}_4$ ) with an open structure of type (D) with an interionic hydrogen bond, while the Ru- and Os-containing adducts (6,Ru, $\text{BF}_4$ ; 6,Os, $\text{BF}_4$ ) are characterized by type (E) with a cyclic structure and an intramolecular hydrogen bond. This is caused by an increase in the basicity of the metal atom in going from the top to the bottom of the iron subgroup.



Scheme 1.

The <sup>1</sup>H NMR spectra of adducts **5** and **6** (Table 1) were recorded for freshly prepared samples, since they were different from those kept for some time. The signals of the protons of <sup>+</sup>CH group of <sup>+</sup>CH(OH) fragment were assigned on the basis of the number of methyl signals and the ratio between their integral intensities. The presence of a signal at δ 8.93 ppm of the CH group and four signals of nonequivalent methyl groups in the same Cp ring of the Fe-containing adduct allows structure (**5**, Fe, BF<sub>4</sub>) of type (**D**) to be attributed to the protonation product; this is also in agreement with the existence of an interionic hydrogen bond (according to the data of IR spectroscopy).

For freshly prepared Ru- and Os-containing adducts **6** (X = BF<sub>4</sub>) in CD<sub>2</sub>Cl<sub>2</sub> solution the signals for <sup>+</sup>CH–OH groups have been observed at δ = 8.07 ppm (M = Ru) and 8.09 ppm (M = Os) and two methyl signals (α and β) of corresponding intensity in both cases. This allows one to assign these adducts to the molecules with an intracyclic hydrogen bond of type (**E**) (according to the IR spectra). Even after a few minutes, the <sup>1</sup>H NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> solution, along with signals cited above, show that new CH-proton signals at δ = 8.44 (M = Ru) and 8.56 ppm (M = Os) and four signals with the corresponding intensities due to the protons of the nonequivalent methyl groups begin to grow; this is indicative of type (**D**) with the open structure (see Table 1). The intensity of the proton signals for cations of type (**E**) decreases.

The nonequivalence of methyl groups in open structures of type (**D**) is caused by the fact that the <sup>+</sup>CH(OH) fragment in these compounds (see Scheme 1) lies virtually in the Cp-ring plane, which is confirmed by X-ray diffraction data for the Ru-containing complex (**5**, Ru, F), as will be seen below.

The <sup>+</sup>CH(OH) fragment in cyclic structure (**E**) is rotated in such a way that an intramolecular hydrogen bond is formed with the metal atom. In this case, the α and α' as well as β and β' methyl groups are equivalent in pairs.

Table 1  
<sup>1</sup>H NMR data for compounds **4** and **5** (δ ppm)

Compound	Functional group (1H)	C <sub>5</sub> Me <sub>5</sub> (15H)	C <sub>5</sub> Me <sub>4</sub> (12H)
<b>4</b> , M = Fe <sup>a</sup>	9.98 CHO	1.54	1.88(6H); 1.72(6H)
<b>5</b> , M = Fe, X = BF <sub>4</sub> <sup>a</sup>	8.93 CH(OH)	1.59	1.94(3H); 1.92(3H); 1.91(3H); 1.72(3H)
<b>5</b> , M = Fe, X = CF <sub>3</sub> CO <sub>2</sub> <sup>b</sup>	8.55 CH(OH)		1.62(27H)
<b>4</b> , M = Ru <sup>a</sup>	9.61 CHO	1.63	1.89(6H); 1.70(6H)
<b>5</b> , M = Ru, X = BF <sub>4</sub> <sup>a</sup>	8.09. CH(OH)	1.67	1.80(6H); 1.72(6H)
<b>5</b> , M = Ru, X = F <sup>a</sup>	8.44 CH(OH)	1.68	1.94(3H); 1.82(3H); 1.78(3H); 1.66(3H)
<b>5</b> , M = Ru, X = CF <sub>3</sub> CO <sub>2</sub> <sup>b</sup>	7.84 CH(OH)	1.69	1.89(6H); 1.81(3H); 1.48(3H)
<b>4</b> , M = Os <sup>a</sup>	9.69 CHO	1.73	1.97(6H); 1.74(6H)
<b>5</b> , M = Os, X = BF <sub>4</sub> <sup>a</sup>	8.07 CH(OH)		1.79(27H)
<b>5</b> , M = Os, X = F <sup>a</sup>	8.56 CH(OH)	1.78	1.96(3H); 1.86(3H); 1.81(3H); 1.67(3H)
<b>5</b> , M = Os, X = CF <sub>3</sub> CO <sub>2</sub> <sup>b</sup>	7.89 CH(OH)	1.83	1.94(3H); 1.87(3H); 1.81(3H); 1.51(3H)

Solvent: <sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>; <sup>b</sup> CD<sub>3</sub>NO<sub>2</sub>.

The  $^1\text{H}$  NMR spectra of cyclic adducts **6** ( $\text{Ru}, \text{BF}_4$ ) of type **(E)** each exhibit two signals of methyl group protons of the substituted Cp ring.

The methyl groups of  $\text{C}_5\text{Me}_5$  rings are observed in the  $^1\text{H}$  NMR spectra of all these compounds as one signal with an intensity corresponding to 15 protons.

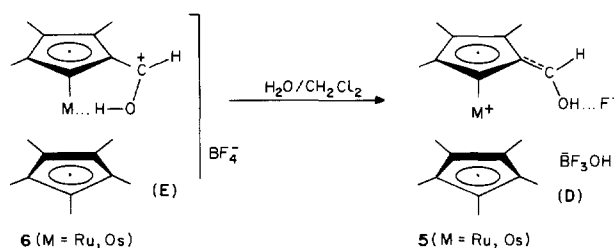
As was cited above, the cyclic Ru- and Os-containing adducts of type **(E)** are irreversibly converted in solution into the open compounds of type **(D)** with interionic hydrogen bonds. This transformation can be observed clearly in the  $^1\text{H}$  NMR spectra. For example, when the spectrum of the adduct ( $\text{6}, \text{Ru}, \text{BF}_4$ ) was recorded in  $\text{CD}_2\text{Cl}_2$  1 h after preparation of solution, the ratio of cyclic **(E)** to open structure **(D)** was 3:1 and 335 h later this ratio was 1:3. The conversion of cyclic Os-containing cation ( $\text{6}, \text{Os}, \text{X} = \text{BF}_4$ ) to the open structure occurs slowly. Moreover, it should be noted that the conversion of cyclic cations **(E)** to the open **(D)** occurs faster in open tubes and with an increase in solvent polarity.

The reason for these transformation became clear when a crystal of Ru-containing compound was grown and studied by X-ray diffraction analysis. The result of this study was somewhat unexpected, since we found that the crystal prepared from cyclic ( $\text{6}, \text{Ru}, \text{BF}_4$ ) contained  $\text{F}^-$  anion, rather than  $\text{BF}_4^-$  anion. Details of the X-ray data were published in Ref. [9]. These data showed that the crystal obtained contained molecules in which the cationic fragment had an open fulvenoid structure of type **(D)** with an  $\text{OH} \dots \text{F}^-$  interionic hydrogen bond. The  $\text{CH}_\alpha(\text{OH})$  fragment lies practically in the Cp-ring plane. This result makes it possible to conclude that there is no  $\text{Ru} \dots \text{C}_\alpha$  direct interaction (the  $\text{Ru} \dots \text{C}_\alpha$  distance is 3.174 Å). The formation of the crystal containing a fluorine anion, and irreversible changes observed in  $^1\text{H}$  NMR spectra when solutions of the samples are kept in open tubes, allow one to conclude that the type **(E)** cyclic structure is converted into the type **(D)** open structure, and the  $\text{BF}_4^-$  anions are hydrolyzed to yield  $\text{F}^-$  anion and  $\text{BF}_3\text{OH}^-$  (see Scheme 2). Hydrolysis of salts containing  $\text{BF}_4^-$  anions is possible [16]. However, one may believe that, in the case of adducts ( $\text{6}, \text{Ru}, \text{Os}, \text{BF}_4$ ) (structure **E**), the conversion of  $\text{BF}_4^-$  in organic solvents is promoted by the formation of the  $\text{OH} \dots \text{F}^-$  interionic hydrogen bond (structure **D**); this would be stronger than the  $\text{OH} \dots \text{M}$  intramolecular hydrogen bond, since in an aprotic solvent the  $\text{F}^-$  anion can successfully compete as a base with the metal atom, unlike the  $\text{BF}_4^-$  anion which only forms a weak coordination bond [17] or interionic hydrogen bond. The crystal containing the  $\text{OH} \dots \text{F}^-$  hydrogen bond might have been more stable and more suitable for X-ray diffraction analysis than a crystal with participation of the  $\text{BF}_3\text{OH}^-$  anion. In addition, it cannot be ruled out that an open fulvenoid structure of type **(D)** is thermodynamically more favorable than the cyclic structure of type **(E)**.

The idea that the hydrolysis of  $\text{BF}_4^-$  anion occurs with simultaneous transformation of cyclic form **(E)** to open **(D)** ( $\text{M} = \text{Ru}, \text{Os}$ ) is confirmed by the IR spectra of the crystals of the Ru-containing salt ( $\text{6}, \text{Ru}, \text{BF}_4$ ) grown for X-ray study. It turned out that the IR spectra of this sample exhibited neither a  $\nu_{\text{OH}(\text{bound})}$  adsorption band at  $3280 \text{ cm}^{-1}$  typical of an  $\text{O}-\text{H} \dots \text{Ru}$  intramolecular hydrogen bond nor a broad intense band in the  $1100-1000 \text{ cm}^{-1}$  region corresponding to the  $\text{BF}_4^-$  anion. The  $\nu_{\text{OH}(\text{bound})}$  band shifts to the region in which  $\nu_{\text{CH}}$  vibrations are manifested ( $3000-2800 \text{ cm}^{-1}$ ), which is caused by the formation of a strong  $\text{O}-\text{H} \dots \text{F}^-$  hydrogen bond.

The possibility of transformation of a molecule with an intramolecular hydrogen bond into a compound with an interionic hydrogen bond has been demonstrated previously in connection with protonated 2-formylinorbornadiene-cyclopentadienylrhodium hexafluorophosphate [18], the  $\text{PF}_6^-$  anion of which was also hydrolyzed.

When aldehydes **4** ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) are dissolved in  $\text{CF}_3\text{COOH}$ , protonation products are also formed; these compounds were studied by  $^1\text{H}$  NMR spectroscopy. These spectra confirmed that all compounds formed have the open structure of type **(D)** only. Along with the proton signals of the CH groups and methyl groups of the  $\text{C}_5\text{Me}_5$ -ring, signals corresponding to the protons of the four ( $\alpha$ ,  $\alpha'$ ,  $\beta$  and  $\beta'$ ) methyl groups of the substituted Cp ring are observed. This makes it possible to assign the structure of complexes **5** ( $\text{Fe}, \text{Ru}, \text{Os}, \text{CF}_3\text{COO}^-$ ) of type **(D)**, in which the OH group forms a hydrogen bond with the  $\text{CF}_3\text{COO}^-$  anion (see Table 1). It is of interest that the same situation is observed in the  $^1\text{H}$  NMR spectra of cyclic Ru- and Os-containing tetrafluoroborates **6** when  $\text{CF}_3\text{COOH}$  is added to their solutions in  $\text{CD}_2\text{Cl}_2$  or  $\text{CD}_3\text{NO}_2$ . Instead of signals corresponding to the cyclic adducts **6**, only signals



Scheme 2.

Table 2  
 $^{13}\text{C}$  NMR data for salts **5** of type (D)  $\text{C}_5\text{Me}_3\text{MC}_5\text{Me}_4\text{C}(\text{H})\text{OH} \dots \text{X}^-$

Compound	$\delta$ (ppm)
<b>5</b> , M = Fe, X = $\text{BF}_4^-$	186.47 (CHOH); 97.27, 82.81, 83.26, 77.73, 72.38 ( $\text{C}_5\text{Me}_4$ ); 9.96, 9.31, 8.97, 8.52 ( $\text{C}_5\text{Me}_5$ ); 86.63 ( $\text{C}_5\text{Me}_5$ ); 8.97 ( $\text{C}_5\text{Me}_5$ )
<b>5</b> , M = Ru, X = F, $\text{BF}_3\text{OH}^-$ <sup>a</sup>	169.28 (CHOH); 98.50, 98.31, 88.31, 88.21, 79.63 ( $\text{C}_5\text{Me}_4$ ); 10.56, 8.97, 8.85, 8.77 ( $\text{C}_5\text{Me}_5$ ); 90.72 ( $\text{C}_5\text{Me}_5$ ); 9.40 ( $\text{C}_5\text{Me}_5$ )
<b>5</b> , M = Os, X = F, $\text{BF}_3\text{OH}^-$ <sup>a</sup>	120.06 (CHOH); 96.31, 95.80, 88.32, 85.73, 79.80 ( $\text{C}_5\text{Me}_4$ ); 10.20, 8.48, 8.48, 7.61 ( $\text{C}_5\text{Me}_5$ ); 90.93 ( $\text{C}_5\text{Me}_5$ ); 8.59 ( $\text{C}_5\text{Me}_5$ )

<sup>a</sup> It should be noted that the  $^{13}\text{C}$  NMR spectra of Ru- and Os-containing complexes are not sensitive to the presence of two different anions.

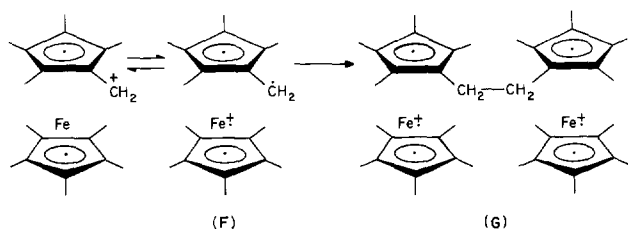
of the trifluoroacetates **5** (M = Ru, Os; X =  $\text{CF}_3\text{COO}^-$ ) were detected. In this case the transformation of **6** into **5**, among other reasons, may be due to the fact that the  $\text{OH} \dots \text{OCOCF}_3^-$  hydrogen bond is stronger than the  $\text{OH} \dots \text{M}$  bond involving Ru and Os atoms.

Thus, we were first to show that the structures resulting from protonation of permethylformylmetallocenes **4** are determined not only by the nature of metal, but also by the nature of the anion that can successfully compete with the metal atom for the formation of a hydrogen bond. Thus, the Fe-containing adducts have an open fulvenoid structure with an interionic hydrogen bond irrespective of the nature of the anion X (X =  $\text{BF}_4^-$ ,  $\text{CF}_3\text{COO}^-$ ). In the case of the Ru- and Os-containing adducts, in which metal atoms are more basic than iron, the competition between the metal atom and the anion for formation of a hydrogen bond with the OH group is clearly manifested in the IR and  $^1\text{H}$  NMR spectra. In the presence of the weakly basic  $\text{BF}_4^-$  anion, a cyclic structure with an intramolecular  $\text{M} \dots \text{H}-\text{O}$  hydrogen bond is formed, while in the presence of a more basic X ( $\text{F}^-$ ,  $\text{CF}_3\text{COO}^-$ ) anion, it transforms to the open fulvenoid structure with an interionic hydrogen bond  $\text{O}-\text{H} \dots \text{X}^-$ . It is noteworthy that the participation of the OH group in the hydrogen bond formation entirely suppresses the ability of the  $\overset{+}{\text{C}}\text{H}(\text{OH})$  carbocation center to interact with a metal atom, whereas the unsubstituted  $\overset{+}{\text{C}}\text{H}_2$  center possesses this ability, as we have shown previously using cations **1** and **2** as examples [1,2].

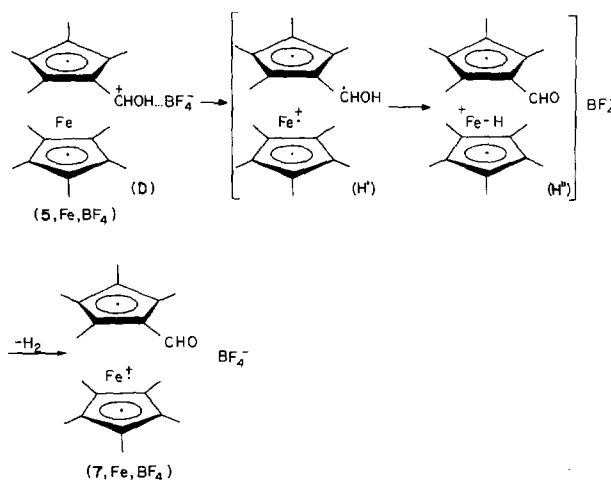
It should be noted that the  $^{13}\text{C}$  NMR spectra are less informative than the  $^1\text{H}$  NMR spectra. As has been shown, the cyclic cation **6** (Ru,Os, $\text{BF}_4^-$ ) of type (E) is very easily converted to the open structure of type (D). Therefore, we present the  $^{13}\text{C}$  NMR spectra only for stable open-complexes of type (D). In the case of Ru- and Os-containing ions, they are formed due to hydrolysis of cyclic borofluorides (see Table 2).

In studying the protonated Fe-containing products **5**, we also observed a change when these adducts (M = Fe, X =  $\text{BF}_4^-$ ,  $\text{CF}_3\text{COO}^-$ ) were kept in polar solvents or stored in the solid state. They were converted entirely into green-colored paramagnetic cations, as was shown by  $^1\text{H}$  NMR spectroscopy [19]. In a polar solvent such as  $\text{CH}_3\text{OH}$ , along with the transformation to the green product, we observed deprotonation of **5** to aldehyde **4** (M = Fe).

Previously it has been published that  $\alpha$ -ferrocenylcarbocations are converted by a redox process to cation-biradicals (F), which couple to form the paramagnetic salts of ferrocenium. For example, salt (G) is formed [20].



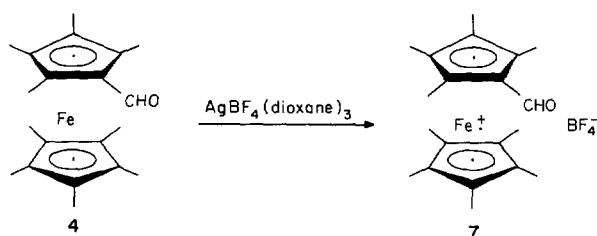
However, the presence of the OH group at the  $\alpha$ -carbocation center in the protonated intermediate (C) (see Scheme 1) may influence the redox process of the Fe-containing cation. Certainly, it turns out that the paramagnetic salt has a monomer structure. This was shown by determination of the molecular mass by two methods. Molecular mass  $M = 445 \pm 5\%$  was determined by the sedimental equilibrium method [21] for three concentrations in the interval  $3-5 \text{ g l}^{-1}$ . FAB mass-spectroscopy of this salt gave  $m/z$  ( $I_{\text{relat.}}\%$ ): 340 [ $427 - \text{BF}_4$ ] $^+$  (100), corresponding to  $\text{Me}_5\text{C}_5\text{FeC}_5\text{Me}_4\text{CHO}$  (**4**) and signals of ion fragments  $m/z$  312 [ $340 - \text{CO}$ ] $^+$  (40); 311 [ $340 - \text{COH}$ ] $^+$  (40), which were observed for aldehyde **4** (M = Fe) [20].



Scheme 3.

Therefore, the results obtained have shown that the paramagnetic complex is a monomer with the possible structure of the formylnonamethylferrocenium salt  $[C_5Me_5Fe^+C_5Me_4CHO]BF_4^-$  (7). The presence of C=O and BF<sub>4</sub><sup>-</sup> anion was confirmed by IR spectroscopy ( $\nu_{CO}$  1690 cm<sup>-1</sup>,  $\nu_{BF_4}$  1070 cm<sup>-1</sup>), corresponding to known data for this group.

The structure of salt 7 was proved by its reduction to aldehyde 4 (M = Fe) using NaBH<sub>4</sub> or N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> [22,23] and by its direct synthesis by the oxidation of aldehyde 4 (M = Fe) using AgBF<sub>4</sub>.



The formation of 7 from protonated aldehyde 5 (Fe, BF<sub>4</sub>) is shown in Scheme 3. We suppose that cation-biradical (H') eliminates a hydrogen atom (probably through intermediate H'') with formation of end product 7. Therefore, the presence of the OH group at the  $\alpha$ -carbocation center influences strongly the behavior of the intermediate cation-biradical (H') compared with cation-biradical F [20].

### 3. Experimental

Mass spectra were measured with an AEI-MS spectrometer, NMR spectra were recorded with a Bruker WP-200SY spectrometer (<sup>1</sup>H 200.13 MHz and <sup>13</sup>C 50.31 MHz) with TMS as internal standard. IR spectra were measured on Specord M-80 and Specord M-82 spectrophotometers with concentrations of salts of 10<sup>-2</sup> to 10<sup>-4</sup> mol l<sup>-1</sup> and  $d = 0.01$  to 0.4 cm using CD<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub> as solvent. The compounds were prepared under argon in anhydrous solvents, which were distilled immediately prior to use. Formylnonamethylmetallocenes 4 were synthesized by known procedures [9].

#### 3.1. Synthesis of 5 (M = Fe, X = BF<sub>4</sub>)

Aldehyde 4 (M = Fe) (0.14 g, 0.4 mmol) was placed in a flask equipped with a reflux condenser and a magnetic stirrer and 40 ml of Et<sub>2</sub>O was added to it. HBF<sub>4</sub>·Et<sub>2</sub>O (0.4 ml) was added to the resulting red solution. The dark-violet mixture thus obtained was stirred for 2 h at 20 °C and for 1 h at 0–5 °C, and then kept at this temperature for 3 h without stirring until precipitation was completed. The solvent was decanted, and the dark-violet precipitate

was washed with 30 ml of Et<sub>2</sub>O and dried in vacuum to give **5** (M = Fe, X = BF<sub>4</sub>). Yield 0.16 g (93%). Anal. Found: C, 56.16; H, 6.62; B, 3.00; Fe, 12.50. C<sub>20</sub>H<sub>29</sub>BF<sub>4</sub>FeO. Calc.: C, 56.11; H, 6.82; B, 2.53; Fe, 13.04%.

### 3.2. Salts **5** (M = Ru, Os; X = BF<sub>4</sub>)

These were prepared similarly to **5** (M = Fe; X = BF<sub>4</sub>) from **4** (M = Ru (0.2 g, 0.52 mmol); M = Os (0.15 g, 0.32 mmol)) over a period of 0.5 h at 20 °C. Yield of **5** (M = Ru, X = BF<sub>4</sub>) 0.23 g (94%). Anal. Found: C, 49.93; H, 6.08; B, 2.32; Ru, 21.46. C<sub>20</sub>H<sub>29</sub>BF<sub>4</sub>ORu. Calc.: C, 50.75; H, 6.18; B, 2.29; Ru, 21.34%. Yield of **5** (M = Os, X = BF<sub>4</sub>) 0.17 g (96%). Anal. Found: C, 40.42; H, 5.51; F, 15.46; Os, 30.97. C<sub>20</sub>H<sub>29</sub>BF<sub>4</sub>OOS · H<sub>2</sub>O · HF. Calc.: C, 40.00; H, 5.37; F, 15.82; Os, 31.67%.

### 3.3. Transformation of diamagnetic adduct **5** (M = Fe, X = BF<sub>4</sub>) into paramagnetic formylnonamethylferrocenium tetrafluoroborate **7**

#### 3.3.1. In the solid state

96 mg (0.23 mmol) of salt **5** (M = Fe, X = BF<sub>4</sub>) under argon was allowed to stand for 480–720 h at 0–5 °C. The color of the crystals changed from dark-violet to dark-green. The crystals that formed were washed with C<sub>6</sub>H<sub>6</sub>, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and precipitated with C<sub>6</sub>H<sub>6</sub>, to give 67 mg (70%) of **7** (M = Fe, X = BF<sub>4</sub>). Anal. Found: C, 56.09; H, 6.74; F, 16.72; Fe, 13.55. C<sub>20</sub>H<sub>28</sub>BF<sub>4</sub>FeO. Calc.: C, 56.24; H, 6.61; F, 17.79; Fe, 13.06%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): –20.27 (2CH<sub>3</sub>), –31.76 (2CH<sub>3</sub>), –41.32 (5CH<sub>3</sub>).

#### 3.3.2. In CH<sub>3</sub>OH solution

A solution of 10 mg (0.023 mmol) of cation **5** (M = Fe, X = BF<sub>4</sub>) in 3 ml of dry CH<sub>3</sub>OH was allowed to stand 15–20 h at room temperature. The color of the solution changed from violet to brown-green. The solvent was evaporated, the residue was then washed with C<sub>6</sub>H<sub>6</sub> and dried to give 9 mg (72%) of salt **7**. Spectral data as above. From benzene solution 1 mg of aldehyde **4** (M = Fe) was isolated.

#### 3.3.3. In CH<sub>3</sub>NO<sub>2</sub> solution

Complex **5** (M = Fe, X = BF<sub>4</sub>) transformed completely in **7** over 12 h (in CF<sub>3</sub>CO<sub>2</sub>H: 2 h).

### 3.4. Reduction of salt **7** (as prepared above) to aldehyde **4** (M = Fe)

#### 3.4.1. By NaBH<sub>4</sub>

To salt **7** (4.5 mg, 0.01 mmol) in C<sub>2</sub>H<sub>5</sub>OH (1.5 ml) and H<sub>2</sub>O (0.1–0.2 ml) was added powdered NaBH<sub>4</sub> (13.5 mg, 0.3 mmol). After 1 h the solvents were evaporated. The dry residue was extracted by THF, the filtrate was evaporated in vacuum. The red product was aldehyde **4** (M = Fe) identified by IR-, <sup>1</sup>H NMR- and mass-spectroscopy: *m/z* (*I*<sub>relat.</sub> %) [M]<sup>+</sup> 340 (90).

#### 3.4.2. By N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

To the solution of salt **7** (13.6 mg, 0.03 mmol in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (5 mg, 0.5 mmol) was added. After disappearance of the violet color the solvent was removed. The dry residue was extracted with C<sub>6</sub>H<sub>6</sub> to give 7 mg (63%) aldehyde **4** (M = Fe), identified as above.

### 3.5. Oxidation of aldehyde **4** (M = Fe) to salt **7**

To a solution of AgBF<sub>4</sub> · (1,4-dioxane)<sub>3</sub> (107.5 mg, 23.5 mmol) in dry CH<sub>3</sub>OH (1.5 ml) was added a solution of aldehyde **4** (M = Fe) (47.5 mg, 14 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (3 ml). After 3 h the filtrate was evaporated. The green crystals were washed with C<sub>6</sub>H<sub>6</sub> and dried to give 56.6 mg (94%) of paramagnetic salt **7**. This was precipitated as above. Anal. Found: C, 56.28; H, 6.64; F, 17.62. C<sub>20</sub>H<sub>28</sub>BF<sub>4</sub>FeO. Calc.: C, 56.24; H, 6.61; F, 17.79%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): –20.31 (2CH<sub>3</sub>), –31.89 (2CH<sub>3</sub>), –41.43 (5CH<sub>3</sub>).

The salt **7** with NaBH<sub>4</sub> or N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> was transformed to aldehyde **4** (M = Fe) as above.

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