Preparation and properties of stable protonation products of permethylmetallocenecarbaldehydes (M = Fe, Ru, Os)

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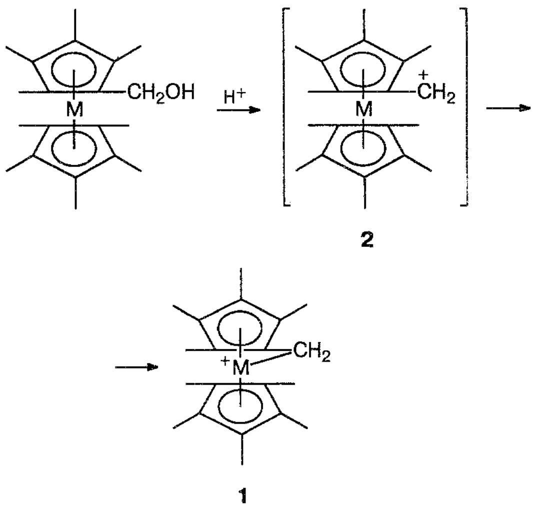
The products of *O*-protonation of metallocenecarbaldehydes $C_5Me_5MC_5Me_4CHO$ (M = Fe, Ru, Os) with HBF_4 and CF_3COOH were obtained for the first time, the adducts $[C_5Me_5MC_5Me_4CH(OH)]^+BF^-$ being isolated in a pure state. The structures of the adducts depend on the nature of the metal and the anion and are governed by the correlation between their basicities. For example, the Fe-containing adducts have an open fulvenoid structure with an interionic hydrogen bond irrespective of the nature of the anion X (X = BF_4^-, CF_3COO^-). In the case of the Ru- and Os-containing adducts in which the metal atoms are more basic than iron, the competition between the metal atom and the anion for the formation of a hydrogen bond with the OH group is clearly manifested in the IR and ^1H NMR spectra. In the presence of the weakly basic BF_4^- anion, a cyclic structure with an intramolecular M...HO hydrogen bond is formed, while in the presence of a more basic F^- or CF_3COO^- anion, it transforms to the open fulvenoid structure with an interionic hydrogen bond. The structures of the compounds obtained were determined by IR and ^1H NMR spectra, and the structure of the $(C_5Me_5RuC_5Me_4CHOH)^+...F^-$ salt was proved by X-ray diffraction analysis.

Key words: nonamethylmetallocenecarbaldehydes, iron, ruthenium, osmium, molecular structure, intramolecular hydrogen bond, interionic hydrogen bond, *O*-protonation.

Previously, by protonation of alcohols $C_5Me_5MC_5Me_4CH_2OH$ we obtained cations of the type $[C_5Me_5MC_5Me_4CH_2]^+$ (M = Fe, Ru, Os), among which ruthenium and osmium compounds proved to be especially stable.[1,2] ^1H NMR and X-ray diffraction studies[3,4] of these compounds showed that these cations are actually onium compounds, in this particular case, metallonium or metallocenonium compounds (**1**), rather than carbocations (**2**), since the unshared electron pairs of the ruthenium and osmium atoms interact with the carbocation center so effectively that an $M-CH_2$ σ-bond is formed, and the positive charge is almost entirely localized on the metal atom (according to extended Hückel MO calculations[5]) (Scheme 1).

In the case of the Fe-containing cation, this intramolecular interaction of the carbocation center with the metal is appreciably weaker, and the orange cation **2** is transformed into paramagnetic green bis-radical-cation (**3**) on storage in the solid state or in solution due to an intramolecular redox process *via* intermediate unstable biradical-cation (**4**)[6] (Scheme 2).

Scheme 1



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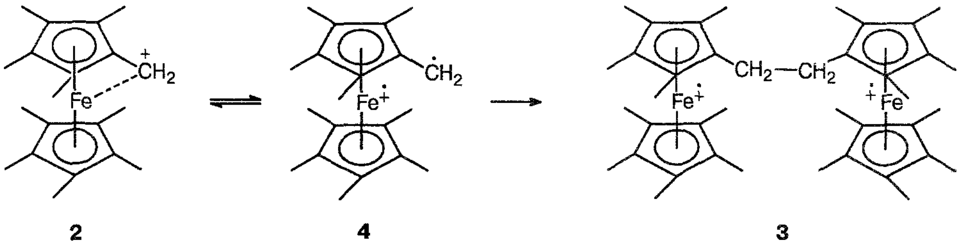
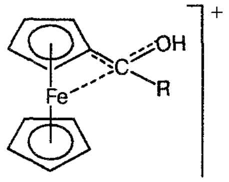
Scheme 2

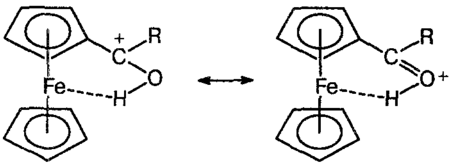


Results and Discussion

In the present work, we obtained for the first time the products of protonation of nonamethylmetallocenecarbaldehydes of iron group metals (M = Fe, Ru, Os) and studied their properties. The interest in these complexes was caused most of all by the fact that introduction to the carbocation center of an electron-donating OH substituent capable of forming H-bonds could essentially change the structures and properties of the resulting cations compared with cations **1**. Previously, the problem of protonation of metallocenes has been studied only in relation to α-carbonyl derivatives of ferrocene with nonmethylated Cp rings. Based on the ^{1}H NMR spectra, two alternative structures were suggested[7,8] for the unstable products: a structure in which the metal participates in the stabilization of the carbocation center (**A**) and a structure incorporating a hydrogen bond with the metal atom (**B**).



A



B

The use of permethylated metallocenecarbaldehydes made it possible to expect that more stable protonation products would be obtained, and the study of this process using compounds of all the iron group metals could provide more definite information concerning their structures.

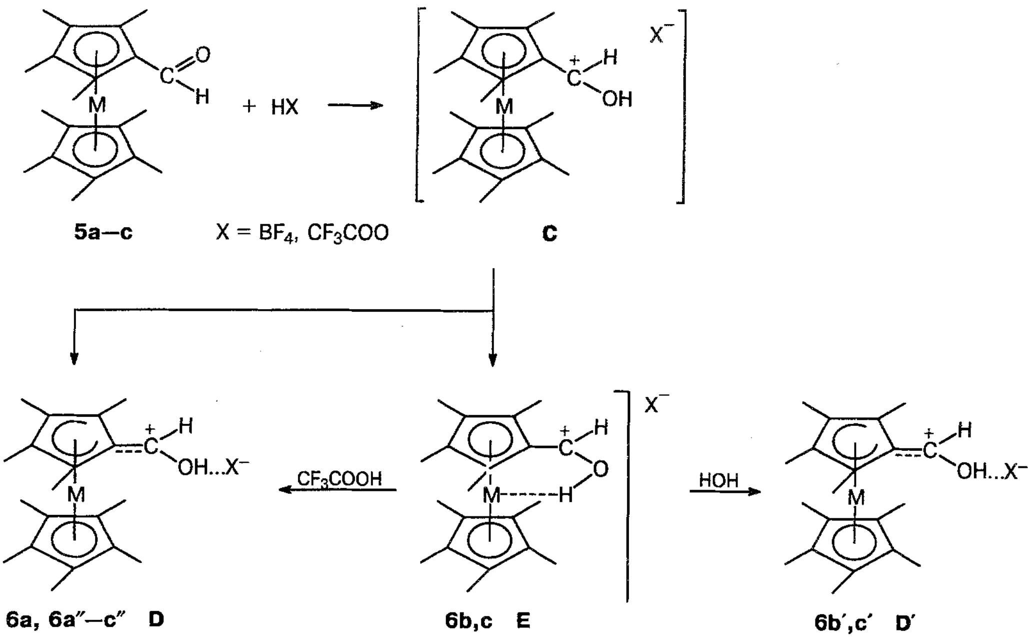
We studied interaction of nonamethylmetallocenecarbaldehydes (**5a—c**) (Scheme 3) with acids, such as $HBF_4 \cdot OEt_2$ and CF_3COOH. The reactions of **5a—c** with excess $HBF_4 \cdot OEt_2$ in anhydrous ether yielded relatively stable products as dark-violet, beige, and grey powders for Fe, Ru, and Os derivatives (**6a—c**), respectively. Elemental analysis showed that the compounds synthesized are actually the adducts of the starting aldehydes with HBF_4.

An examination of the IR spectra of both solid samples of compounds **6a—c** and their solutions in CH_2Cl_2 indicates the absence of νCO absorption of aldehydes (1660—1645 cm^{-1}) and the appearance of lower-frequency bands (1570—1540 cm^{-1}) typical of protonated carbonyl compounds.[9]

The IR spectrum of solid freshly prepared Fe-containing adduct **6a** exhibits a νOH(bound) band at 3500 cm^{-1}. We assign this band to vibrations of the OH groups bound by an interionic hydrogen bond of the $OH...BF_4^-$ type. This conclusion is based on recording the spectra of solutions of **6a** in CH_2Cl_2 and studying their concentration dependence. As the concentration of the adduct decreases, the intensity of this band decreases and the intensity of the νOH(free) adsorption band at 3600 cm^{-1} increases. At the same time, the spectra of freshly prepared Ru- and Os-containing adducts **6b,c** both in the solid state and in solution exhibit intense bands in the region of 3280—3220 cm^{-1}. Their intensities do not depend on the concentration of the solution. No bands due to νOH(free) appear, even when the concentration diminishes from 10^{-1} to 10^{-3} mol L^{-1}, which indicates the presence of M...HO intramolecular hydrogen bonds in these adducts. In other words, the formation of intramolecular hydrogen bonds with ruthenium and osmium is more favorable than with iron, which is in agreement with the data obtained previously for metallocenylmethanols.[9]

Based on these data, one may assume that the protonation of aldehydes **5a—c** yields an intermediate species **C** (see Scheme 3), which is further converted into different products depending on the nature of the metal atom. The Fe-containing aldehyde affords adduct **6a** with an open structure of type **D** and an interionic hydrogen bond, while the Ru- and Os-containing adducts **6b** and **6c** are characterized by a type **E** cyclic structure with an intramolecular hydrogen bond, which is caused by the increase in the basicity of the metal atom on going from top to bottom of the subgroup.

Scheme 3*



5a—c X = BF_4, CF_3COO **C**

6a, 6a″—c″ D **6b,c E** **6b′,c′ D′**

M = Fe (**a**), Ru (**b**), Os (**c**)
6a: X = BF_4
6a″—c″: X = CF_3COO

6b,c: X = BF_4

6b′,c′: X = F, BF_3OH

The structure of the compounds obtained was confirmed by an examination of the ^1H NMR spectra of all of the adducts **6** and by an X-ray structural study of **6b′**. Altogether, this played an important role, since it provided information on the properties of molecules with type **D**, **D′**, and **E** structures and showed that the existence of these structures depends on the correlation between the basicities of the metal and the anion X.

The ^1H NMR spectra of the adducts were recorded in various solvents (Table 1). It should be born in mind that the spectra of freshly prepared samples of the products of protonation of aldehydes **5a—c** differ from the spectra of their solutions kept for some time and that the spectra exhibit a clear-cut dependence on the nature of the solvent and in some cases on the concentration (Table 2). The signals of the protons of the CH-group of the CH(OH) fragment were assigned on the basis of the number of methyl signals and the ratio between their integral intensities. For example, the presence of a signal at δ 8.93 and four signals of nonequivalent methyl groups in the same Cp-ring of the Fe-containing adduct allows structure **D** to be attributed to the protonation product (compound **6a**), which is also in agreement with the existence of an interionic hydrogen bond (according to the data of IR spectroscopy).

In the case of Ru- and Os-containing adducts, type **E** compounds **6b,c** with intramolecular hydrogen bonds are irreversibly converted in solution into compounds **6b′,c′** of type **D′** with an open structure and interionic hydrogen bonds, this process being accelerated when the solution is kept in an unsealed tube or as the polarity of the solvent increases. In fact, the spectra recorded even after a few minutes in a CD_2Cl_2 solution, along with the signals at δ = 8.07 (M = Ru) and 8.09 (M = Os) associated with the protons of the CH groups of the CH(OH) fragment and two signals with the corresponding intensities due to the methyl-group protons for the type **E** cyclic structure, exhibit signals of CH-group protons at δ = 8.44 (M = Ru) and 8.56 (M = Os) and four signals with the corresponding intensities due to the protons of nonequivalent methyl groups, which refer to type **D′** open structure (see Table 1). The nonequivalence of the methyl groups in structures **D** and **D′** is caused by the fact that the CH(OH) fragment in compounds **6a,b′,c′** and **6a″—c″** (see Scheme 3) lies virtually in the Cp-ring plane, which is confirmed by the X-ray diffraction data for the Ru-containing complex **6b′** (see below).

The methyl groups of the C_5Me_5 rings are manifested in the ^1H NMR spectra of all these compounds as one signal with an intensity corresponding to 15 protons. The CH(OH) fragment in cyclic structure **E** is rotated in such a way that an intramolecular hydrogen bond with the metal atom is formed. In this case, the α and α′ as well as β and β′ methyl groups are equivalent in pairs. The ^1H NMR spectra of cyclic adducts **6b,c** of type **E**

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* Hereinafter, salts **6a—c** without dashes over the letters incorporate the BF_4^- anion, **6b′,c′** contain the F^- anion, and **6a″—c″** have the CF_3COO^- anion.

Table 1. ^{1}H NMR data for compounds **5a—c** and **6a—c,b′,c′**

Compound	Solvent	δ		
		Functional group (1 H)	C_5Me_5 (15 H)	C_5Me_4 (12 H)
5a[a]	CD_2Cl_2	9.98 (C$\underline{\text{H}}$O)	1.54	1.88 (6 H); 1.72 (6 H)
6a	CD_2Cl_2	8.93 C$\underline{\text{H}}$(OH)	1.59	1.94 (3 H); 1.92 (3 H); 1.91 (3 H); 1.72 (3 H)
	CD_2Cl_2[b]	8.79 C$\underline{\text{H}}$(OH)	1.53	1.88 (6 H); 1.79 (3 H); 1.64 (3 H)
	CD_3NO_2	8.95 C$\underline{\text{H}}$(OH)	1.65	2.03 (3 H); 2.00 (3 H); 1.91 (3 H); 1.81 (3 H)
5b[a]	CD_2Cl_2	9.61 C$\underline{\text{H}}$O	1.63	1.89 (6 H); 1.70 (6 H)
6b	CD_2Cl_2[c]	8.09 C$\underline{\text{H}}$(OH)	1.67	1.80 (6 H); 1.72 (6 H)
6b′	CD_2Cl_2[c]	8.44 C$\underline{\text{H}}$(OH)	1.68	1.94 (3 H); 1.82 (3 H); 1.78 (3 H); 1.66 (3 H)
6b	CD_2Cl_2[b,d]	7.96 C$\underline{\text{H}}$(OH)	1.62	1.79 (6 H); 1.74 (6 H)
6b′	CD_2Cl_2[b,d]	8.35 C$\underline{\text{H}}$(OH)	1.64	1.88 (3 H); 1.82 (3 H); 1.59 (3 H); 1.44 (3 H)
6b	CD_3NO_2[e]	8.03 C$\underline{\text{H}}$(OH)		1.71 (27 H)
6b′	CD_3NO_2[e]	8.43 C$\underline{\text{H}}$(OH)		1.87 (27 H)
5c[a]	$CDCl_3$	9.69 C$\underline{\text{H}}$O	1.73	1.97 (6 H); 1.74 (6 H)
6c	CD_2Cl_2[f]	8.07 C$\underline{\text{H}}$(OH)		1.79 (27 H)
6c′	CD_2Cl_2[f]	8.56 C$\underline{\text{H}}$(OH)	1.78	1.96 (3 H); 1.86 (3 H); 1.81 (3 H); 1.67 (3 H)
6c	CD_2Cl_2[b,g]	7.95 C$\underline{\text{H}}$(OH)		1.74 (21 H); 1.72 (6 H)
6c′	CD_2Cl_2[b,g]	8.39 C$\underline{\text{H}}$(OH)	1.75	1.91 (3 H); 1.80 (3 H); 1.76 (3 H); 1.58 (3 H)

[a] *cf.* Lit.[4,6,10]. [b] $T = -50$ °C. [c] **6b** : **6b′** = 5 : 4. [d] **6b** : **6b′** = 3 : 2. [e] **6b** : **6b′** = 4 : 1. [f] **6c** : **6c′** = 4 : 1. [g] **6c** : **6c′** = 3 : 1.

Table 2. Proportions of salts **6b** and **6b′** or **6c** and **6c′** as a function of the concentration in CD_2Cl_2 from the data of ^{1}H NMR spectroscopy

Salt	C/mol L^{-1}	δ, C$\underline{\text{H}}$ (OH)	Ratio between the salts
6b **6b′**	0.08	8.05 8.46	6:1
6b **6b′**	0.04	8.08 8.50	3:1
6b **6b′**	0.02	8.23 8.49	3:2
6b **6b′**	0.01	8.42 8.49	1:1
6c **6c′**	0.08	8.42 8.54	3:1
6c **6c′**	0.04	8.62 8.56	2:1
6c **6c′**	0.02	8.36 8.56	3:2

exhibit each two signals of the methyl group protons (6 H, 6 H) of the substituted Cp ring. It is also noteworthy that the conversion of cyclic structure **E** into open structure **D′** was monitored by ^{1}H NMR spectroscopy using the transformations of the Ru- and Os-containing adducts as examples (Table 3, see Scheme 3). For example, when the spectrum of the products of protonation of compound **5b** was recorded in CH_2Cl_2 1 h after preparation, the **6b** to **6b′** ratio was 3 : 1, and 335 h later this ratio was 1 : 3. The conversion of **6c** into **6c′** occurs more slowly.

The reason for these transformations became clear, when a crystal of the Ru-containing compound was grown (see Experimental) and studied by X-ray diffraction analysis. The result of this study was somewhat unexpected, since we found that the crystal of **6b′** under investigation contained F^- anions, rather than BF_4^-. The crystal had a disordered structure with the population parameters $R = 0.5$ with respect to both oxygen and fluorine, and this meant that the molecule (Figs. 1 and

Table 3. Conversion of compound **6b** (0.04 mol L^{-1} in CD_2Cl_2) into compound **6b′** (from the data of ^{1}H NMR spectroscopy)

Compound	Time/h	**6b**:**6b′** ratio	δ		
			C$\underline{\text{H}}$(OH) (1 H)	C_5Me_5 (15 H)	C_5Me_4 (12 H)
6b	1	3:1	8.03	1.66	1.78 (6 H); 1.75 (6 H)
6b′			8.53	1.68	1.94 (3 H); 1.82 (3 H); 1.77 (3 H); 1.68 (3 H)
6b	168	1:2	8.25	1.66	1.78 (6 H); 1.75 (6 H)
6b′			8.49	1.68	1.94 (3 H); 1.82 (3 H); 1.78 (3 H); 1.66 (3 H)
6b	336	1:3	8.42	1.66	1.78 (6 H); 1.74 (6 H)
6b′			8.49	1.68	1.94 (3 H); 1.82 (3 H); 1.79 (3 H); 1.67 (3 H)

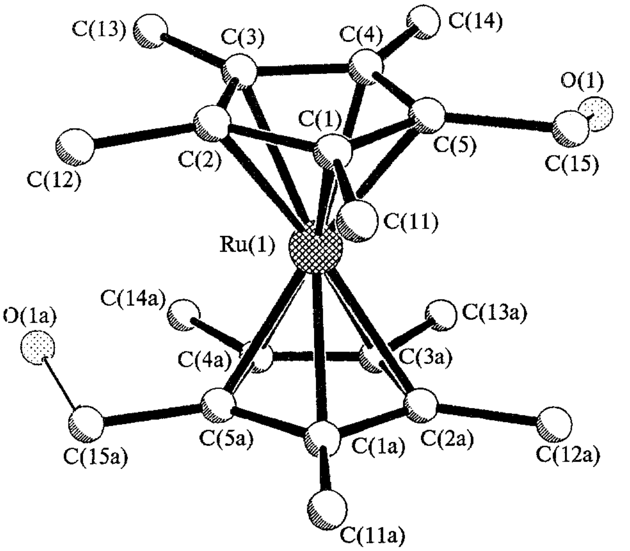


Fig. 1. Structure of the cation of the salt $[C_5Me_5RuC_5Me_4CHOH]^+F^-$ (**6b′**). The crystal has a disordered structure with population parameters being *R* = 0.5, which means that the molecule contains either O(1) or O(1a) (the absence of O means that C(15) or C(15a) belongs to a methyl group).

Table 4. Bond lengths in structure **6b′**

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—C(1)	2.171 (16)	Ru(1)—C(5)	2.140 (21)
Ru(1)—C(2)	2.188 (13)	Ru(1)—C(15)*	3.174 (19)
Ru(1)—C(3)	2.168 (14)	C(15)—O(1)	1.423 (43)
Ru(1)—C(4)	2.139 (19)		

* The Ru(1)—C(15) interatomic distance (see Results and Discussion).

2) incorporated either O(1) and F(1) or O(1a) and F(1a). The disordered structure of the crystal, which is sometimes observed in permethylated metallocene derivatives,[10] did not allow us to determine the main structural parameters to a sufficient accuracy. Nevertheless, the results obtained provide unambiguous information concerning the structure of the molecule. The cationic fragment of this molecule has an open fulvenoid structure of type **D′** with the OH...F^- interionic hydrogen bond; the C(15) atom of the CH(OH) fragment lies virtually in the Cp-ring plane and the oxygen atom deviates somewhat from this plane (by 0.38 Å). The carbon—carbon bond length in the $C\overset{\cdots}{-}C(OH)H$ group is 1.45 Å, *i.e.*, it is intermediate between the lengths of a single and a double bond (1.54 and 1.34 Å, respectively).

The C(15)—O(1) bond length is 1.42 Å, which is much larger than the C=O bond length (1.22 Å [11]) and is virtually identical to the length of a C—O single bond (1.36—1.43 Å [11]). Since the precise lengths of the C—C bonds in the Cp rings cannot be determined due to the disorder of the structure, these rings were regarded as rigid pentagons with a side of 1.42 Å and an angle of 108°. The Ru—C_{Cp} bond lengths vary from 2.14 to 2.19 Å [2.140(21)—2.188(13), Table 4]. However, the accuracy of their determination does not allow one to discuss the geometrical features of the coordination of the Cp ligand. Nevertheless, the X-ray structural study makes it possible to conclude that there is no Ru—C(15) direct interaction (the Ru—C(15) distance is 3.174 Å).

The formation of the crystal of **6b′** containing a fluorine anion and irreversible changes observed in the ^1H 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 that BF_4^- anions are hydrolyzed yielding F^- anions and BF_3OH^- (see Scheme 3). Hydrolysis of salts containing BF_4^- anions is possible,[12] but it occurs slowly even in aqueous solutions.[13] However, one may believe that in the case of adducts **6b,c** (structure **E**), the conversion of BF_4^- in organic solvents is promoted by the formation of the OH...F^- interionic hydrogen bond (structure **D′**), which is stronger than the OH...M intramolecular hydrogen bond, since in an aprotic solvent, the F^- anion can successfully compete as a base with the metal atom, unlike the BF_4^- anion, which forms only weak coordination[14] or interionic hydrogen bonds. The crystal containing the OH...F^- hydrogen bond might have been more stable and more suitable for X-ray diffraction analysis than a crystal incorporating BF_3OH^- anions, which accounts for the fact that the latter was not isolated.

In addition, it cannot be ruled out that an open fulvenoid structure of type **D** or **D′** is thermodynamically more favorable than the cyclic structure **E**. The structure of the crystals grown for the Ru-containing sample **6b′**, which corresponds to structure **D′**, was confirmed by the IR spectra. The spectra exhibit no νOH(bound) adsorption band at 3280 cm^{-1} typical of an OH...Ru intramolecular hydrogen bond and no broad intense band in the 1100—1000 cm^{-1} region corresponding to the BF_4^- anion. The νOH(bound) band shifts to the region in which νCH vibrations are manifested (3000—2800 cm^{-1}), which is caused by the formation of a strong OH...F^- hydrogen bond.

The possibility of transfer of a structure with an intramolecular hydrogen bond into a structure with interionic hydrogen bond has been demonstrated previously in relation to the hydrolysis of protonated 2-formylnorbornadienecyclopentadienylrhodium hexafluorophosphate[15] (Scheme 4) as well as for a number of other instances.[16]

When aldehydes **5a—c** are dissolved in CF_3COOH, protonation products **6a″—c″** are formed; these compounds were studied by ^1H NMR spectroscopy. In the case of Ru- and Os-containing compounds, these spectra can be assigned rather easily, and they indicate that in each case only one product was formed. Along with the signals of the protons of the CH group and methyl

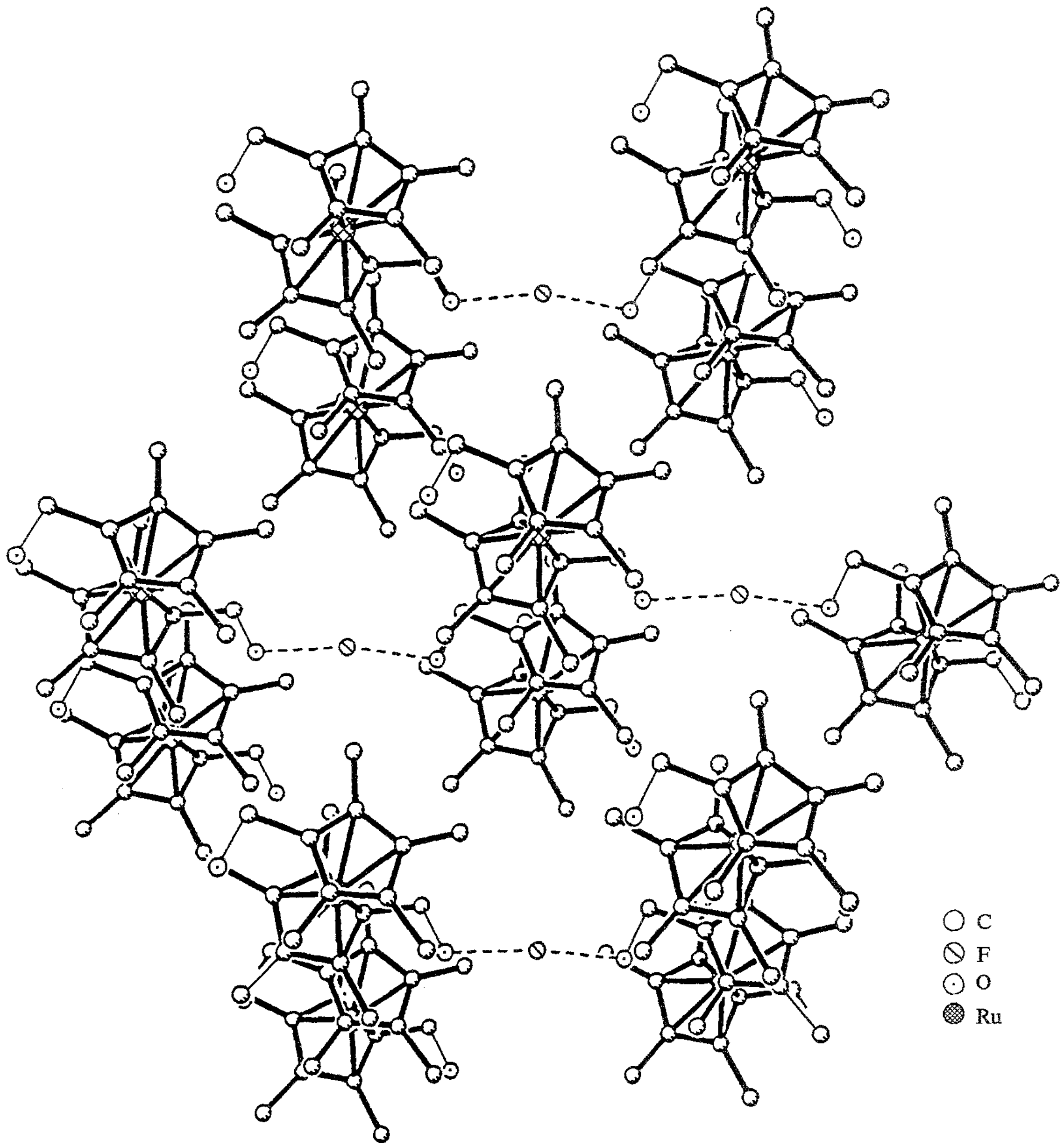
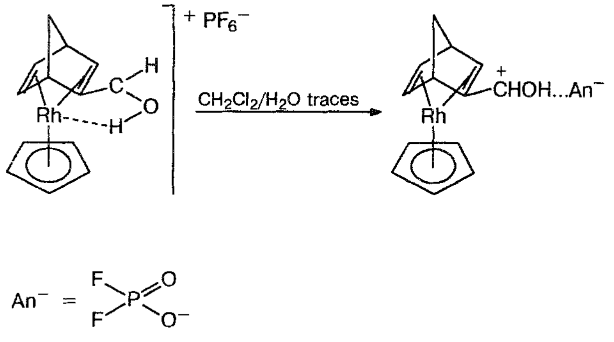


Fig. 2. Fragment of packing of the salt $[C_5Me_5RuC_5Me_4CHOH]^+F^-$ (**6b′**).

Scheme 4



groups of the unsubstituted Cp ring, signals corresponding to the protons of the four (α, α′, β, and β′) methyl groups of the substituted Cp ring are recorded, which makes it possible to assign the structure of complexes **6b″** and **6c″**, in which the OH group forms a hydrogen bond with the CF_3COO^- anion, to these products (see Scheme 3 and Table 5). It is of interest that the same situation is observed in the ^1H NMR spectra of Ru-containing (**6b,b′**) or Os-containing (**6c,c′**) adducts when CF_3COOH is added to their solutions in CD_2Cl_2 or CD_3NO_2. Instead of the signals corresponding to two adducts, only signals of one trifluoroacetate [**6b″** (M = Ru) or **6c″** (M = Os)] were detected. These results imply first of all that cations **6b** and **6c** can be easily

Table 5. ^{1}H NMR spectra of the products of protonation of aldehydes **5a—c** and the exchange of BF_4^- for CF_3COO^- anions in compounds **6a—c** through the action of trifluoroacetic acid

Starting compound	Solvent	Reaction product	δ		
			C<u>H</u>(OH) (1 H)	C_5Me_5 (15 H)	C_5Me_4 (12 H)
5a*	CD_2Cl_2	**6a″**	8.55		1.54 (27 H)
6a*	CD_3NO_2	**6a″**	8.54		1.62 (27 H)
5b	CD_3NO_2	**6b″**	7.84	1.69	1.89 (6 H); 1.81 (3 H); 1.48 (3 H)
6b,b′	CD_2Cl_2	**6b″**	7.81	1.68	1.88 (3 H); 1.86 (3 H); 1.79 (3 H); 1.47 (3 H)
5c	CD_3NO_2	**6c″**	7.89	1.83	1.94 (3 H); 1.87 (3 H); 1.81 (3 H); 1.51 (3 H)
6c,c′	CD_3NO_2	**6c″**	7.99	1.84	1.95 (3 H); 1.89 (6 H); 1.53 (3 H)

* The spectra were recorded over a period of 20 min after mixing the reactants in an argon atmosphere.

converted into **6b″** and **6c″**. The ease of this transformation, among other reasons, may be due to the fact that the OH...$OCOCF_3^-$ hydrogen bond is stronger than the OH...M bond incorporating Ru or Os atoms. In the case of the Fe-containing cation resulting from dissolution of **5a** in CF_3COOH, the ^{1}H NMR spectrum exhibits, along with the signals of the CH-group protons, a singlet corresponding to all 27 protons of the methyl groups of the substituted and unsubstituted Cp rings. Similar ^{1}H NMR spectra are recorded for Ru-containing adducts **6b** and **6b′** in CD_3NO_2, and for one of the Os-containing adducts **6c** in CD_2Cl_2 (see Table 1).

Thus, we were first to show that the structures of products resulting from the protonation of nonamethylmetallocenecarbaldehydes **5a—c** are determined not only by the nature of the metal, but by the nature of the anion that can successfully compete with the metal atom for the formation of a hydrogen bond.

It is noteworthy that the participation of the OH group in the hydrogen bonds entirely suppresses the ability of the $^+$CH(OH) carbocation center to interact with a metal atom, whereas an unsubstituted $^+CH_2$ center possesses this ability, as we have shown previously using cations **1** as examples.[1,2]

The presence of the OH group at the α-carbocation center in the protonation intermediate **C** (see Scheme 3) also has an effect on the redox transformation of Fe-containing salts **6a,a″**. When these adducts are kept in polar solvents or stored in the solid state, they are entirely converted into green-colored paramagnetic complexes that differ from dimer **3**, as shown by ^{1}H NMR spectroscopy.[6] A study of their structure is in progress.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200.13 MHz, tetramethylsilane as the internal standard). IR spectra were measured on Specord M-80 and Specord M-82 spectrophotometers with concentrations of salts of 10^{-2}—10^{-4} mol L^{-1} and d = 0.01 to 0.4 cm using CD_2Cl_2 or CH_2Cl_2 as the solvents. All the syntheses were carried out under argon in anhydrous solvents, which were distilled immediately prior to use. Nonamethylmetallocenecarbaldehydes **5a—c** were synthesized by known procedures.[4,6,10]

Salt 6a. Aldehyde **5a** (0.14 g, 0.4 mmol) was placed into a flask equipped with a reflux condenser and a magnetic stirrer and filled with argon, and 40 mL of Et_2O was siphoned into it. $HBF_4 \cdot Et_2O$ (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 it was 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_2O and dried *in vacuo* to give **6a**. Yield 0.16 g (93 %). Found (%): C, 56.16; H, 6.62; B, 3.00; Fe, 12.50. $C_{20}H_{29}BF_4FeO$. Calculated (%): C, 56.11; H, 6.82; B, 2.53; Fe, 13.04. Salt **6a** is converted with time into a green-colored paramagnetic complex.

Salt 6b was prepared similarly to **6a** from **5b** (0.2 g, 0.52 mmol), Et_2O (25 mL), and $HBF_4 \cdot Et_2O$ (0.4 mL) over a period of 0.5 h at −20 °C. The resulting beige precipitate was

Table 6. Main bond angles in structure **6b′**

Angle	φ/deg
C(1)—Ru(1)—C(2)	38.0(2)
C(2)—Ru(1)—C(3)	38.0(2)
C(2)—Ru(1)—C(4)	64.1(5)
C(1)—Ru(1)—C(5)	38.4(3)
C(3)—Ru(1)—C(5)	64.5(5)
Ru(1)—C(1)—C(11)	124.4(4)
Ru(1)—C(1)—C(5)	69.6(5)
Ru(1)—C(2)—C(12)	125.0(5)
Ru(1)—C(3)—C(2)	71.7(3)
Ru(1)—C(3)—C(4)	69.6(5)
Ru(1)—C(4)—C(14)	123.1(3)
Ru(1)—C(5)—C(1)	72.0(4)
Ru(1)—C(5)—C(15)	123.1(4)
C(1)—Ru(1)—C(3)	63.9(4)
C(1)—Ru(1)—C(4)	64.4(5)
C(3)—Ru(1)—C(4)	38.5(3)
C(2)—Ru(1)—C(5)	64.1(5)
C(4)—Ru(1)—C(5)	38.8(4)
Ru(1)—C(1)—C(2)	71.6(4)
Ru(1)—C(2)—C(1)	70.3(4)
Ru(1)—C(2)—C(3)	70.2(4)
Ru(1)—C(3)—C(13)	124.3(5)
Ru(1)—C(4)—C(3)	71.9(4)
Ru(1)—C(4)—C(5)	70.7(4)
Ru(1)—C(5)—C(4)	70.6(3)
C(5)—C(15)—O(1)	103.9(23)

Table 7. Atomic coordinates ($\times 10^4$) in structure **6b′**

Atom	x	y	z	U_{eq}/Å^2
Ru(1)	0	0	0	6(1)
C(1)	494(15)	987(9)	2500(24)	96(7)
C(11)	375	2123	2340	219(24)
C(2)	1676	422	2864	96(8)
C(12)	3066	838	3168	156(14)
C(3)	1354	−594	2898	123(12)
C(13)	2331	−1473	3246	238(27)
C(4)	−30	−657	2556	215(24)
C(14)	−815	−1616	2467	221(25)
C(5)	−561	320	2310	75(5)
C(15)	−1938	590	1930	254(36)
O(1)	−2682(53)	−313(27)	1314(74)	155(19)
F(1)	−4949(35)	−529(24)	1245(51)	117(10)

separated, washed with Et_2O, and dried to give **6b**. Yield 0.23 g (94 %). Found (%): C, 49.93; H, 6.08; B, 2.32; Ru, 21.46. $C_{20}H_{29}BF_4ORu$. Calculated (%): C, 50.75; H, 6.18; B, 2.29; Ru, 21.34.

Salt 6c was prepared similarly to **6a,b** from **5c** (0.15 g, 0.32 mmol), Et_2O (8 mL), and $HBF_4 \cdot Et_2O$ (0.3 mL). The resulting grey precipitate was separated, washed with Et_2O, and dried to give **6c**. Yield 0.17 g (96 %). Found (%): C, 40.42; H, 5.51; F, 15.46; Os, 30.97. $C_{20}H_{29}BF_4OOs \cdot H_2O \cdot HF$. Calculated (%): C, 40.00; H, 5.37; F, 15.82; Os, 31.67.

X-ray structural study of salt 6b′. A crystal of salt **6b′** was grown in a CH_2Cl_2—C_6H_6 (1:5) mixture by slow evaporation of a solution containing products of protonation of aldehyde **5b** with HBF_4. Crystals of **6b′** are monoclinic, at −80 °C a = 10.959(7), b = 13.504(9), c = 7.556(9) Å, β = 116.88(6)°, V = 997.4(5) Å^3, d_{calc} = 1.350 g cm^{-3}, Z = 2, space group C_m. Unit cell parameters and intensities of 1072 independent reflections were measured on a Rigaku AFC-75 diffractometer (−80 °C, Mo-Kα radiation, graphite monochromator, $2\theta/\omega$-scanning, $5.0 < 2\theta < 53.0°$). Allowance for absorption was made using azimuthal scanning curves.

The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for the Ru atom and in the isotropic approximation for the other atoms. Cyclopentadienyl rings and C atoms attached to them were refined as "rigid" groups. The populations of the positions of the O and F atoms were taken to be 0.5. Attempts to solve the structure in C_2 or $C2/m$ space groups were unsuccessful. The final residual factors R = 0.052, R_w = 0.062, s = 0.88 for 1007 reflections with $I > 3\sigma(I)$.

All the calculations were carried out using a SHELXTL-PLUS program (Version 4.2).[17] Bond lengths and angles and atomic coordinates are listed in Tables 4, 6, and 7.

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