Organometallic Chemistry

Adduct of nonamethylferrocenecarbaldehyde with HBF_4 and its transformations

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Some reactions of the adduct of nonamethylferrocenecarbaldehyde with HBF_4, $[Me_5C_5FeC_5Me_4CH^+(OH)]BF_4^-$, and its transformation into the paramagnetic complex $[Me_5C_5Fe^{+\cdot}C_5Me_4CH{=}O]BF_4^-$ were studied. The structure of the complex was established from the chemical properties, the data from IR spectroscopy, mass spectrometry, and ^1H, ^{13}C, and ^{19}F NMR spectroscopy and confirmed by independent synthesis.

Key words: nonamethylferrocenecarbaldehyde, ferrocenyl carbocations, formylnonamethylferrocenium tetrafluoroborate.

Recently,[1] we have obtained rather stable adducts of nonamethylmetallocenecarbaldehydes of the iron subgroup with strong acids (HBF_4 and CF_3CO_2H).

$$Me_5C_5MC_5Me_4CH{=}O + HX \rightarrow [Me_5C_5MC_5Me_4CH^+(OH)]X^-$$

M = Fe, Ru, Os; X = BF_4, CF_3CO_2

Analysis of the spectral data of these adducts demonstrated that the structure of the ferrocene derivatives differs somewhat from that of the Ru and Os analogs.[1] In addition, the Fe-containing adduct manifested some chemical peculiarities, for example, it transformed readily into a paramagnetic compound. It is this transformation that we studied in detail in this work.

Results and Discussion

Protonation of nonamethylferrocenecarbaldehyde (**1**) with HBF_4 gave violet crystals of adduct (**2**). Based on the IR and ^1H NMR spectra of this adduct and a comparison of these spectra with those of the Ru-containing analog, whose structure had been established by X-ray structural analysis, we suggested that adduct **2** could have a fulvenoid structure with an interionic $OH...FBF_3$ hydrogen bond.[1] In this structure, the rotation of the $CH^+(OH)$ group about the C—C bond should be hindered, which would result in nonequivalence of the methyl groups in the substituted Cp ring observed in the ^1H and ^{13}C NMR spectra (Table 1, Fig. 1).

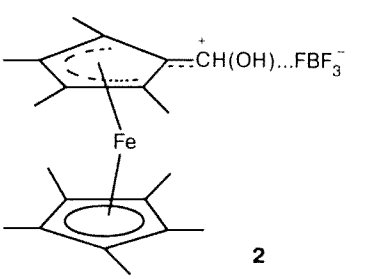

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Table 1. Parameters of the spectra of compounds **1**—**3**, and **6**

Compound	Solvent for NMR	NMR spectrum, δ			IR spectrum, ν/cm^{-1}
		^{1}H	^{13}C	^{19}F (two signals, 1 : 4)	
1	$CDCl_3$	9.98 (1 H, CHO); 1.98 (6 H, 2 CH_3); 1.79 (6 H, 2 CH_3); 1.65 (15 H, 5 CH_3)	195.5 (CHO); 86.17 (2 C); 82.74 (2 C); 72.76 (1 C, $\underline{C}_5Me_4$); 80.65 (5 C, $\underline{C}_5Me_5$); 9.32 (5 CH_3, $C_5\underline{Me}_5$); 9.41 (2 CH_3); 8.86 (2 CH_3, $C_5\underline{Me}_4$)		1040, 1360, 1390, 1670 (C=O); 2930—3000; 3420—3520
2	CD_2Cl_2	8.92 (1 H, $^+$CH(OH)); 1.93 (3 H, 1 CH_3); 1.90 (3 H, 1 CH_3); 1.86 (3 H, 1 CH_3); 1.71 (3 H, 1 CH_3); 1.58 (15 H, 5 CH_3)	186.47 ($^+$CH—OH); 97.27, 82.81, 83.26, 77.73, 72.38 (5 C, $\underline{C}_5Me_4$); 86.63 (5 C, $\underline{C}_5Me_5$); 9.96, 9.31, 8.97, 8.52 (4 CH_3, $C_5\underline{Me}_4$); 8.97 (5 CH_3, C_5Me_5)	−75.35; −75.45	
3 (method *A*)	CD_2Cl_2	−20.18 (2 CH_3); −31.60 (2 CH_3); −41.24 (5 CH_3)		−76.80; −76.86	1040, 1070 (BF_4); 1400, 1480, 1640 (C=O); 2940—2950; 3440—3460
3 (method *C*)	CD_2Cl_2	−20.31 (2 CH_3); −31.89 (2 CH_3); −41.43 (5 CH_3)		−76.89; −76.95	1040, 1070 (BF_4); 1400, 1490, 1690 (C=O); 2860 2910, 3400—3450
6	CD_2Cl_2	−37.0 (10 CH_3)		−76.26; −76.32	1040, 1070 (BF_4); 1400 1480, 2930, 2980, 3460

Adduct **2** is fairly stable in the presence of HBF_4 or in dry CH_2Cl_2 in an atmosphere of argon. In basic solvents, adduct **2** transforms rapidly into the initial aldehyde. For example, when aqueous MeOH or THF was added, this transformation occured in CH_2Cl_2 under the action of $NaBH_4$ (in CH_2Cl_2/MeOH or THF) or anhydrous Et_3N.

Solid adduct **2** is preserved under an atmosphere of argon at 0 to −5 °C for several days. After prolonged storage even under these conditions, adduct **2** transforms irreversibly into the paramagnetic complex (**3**), as can be seen from the analysis of the ^{1}H NMR spectrum (see below). In polar anhydrous solvents, for example, in $MeNO_2$, MeOH, or THF, this transformation occurs within several hours.

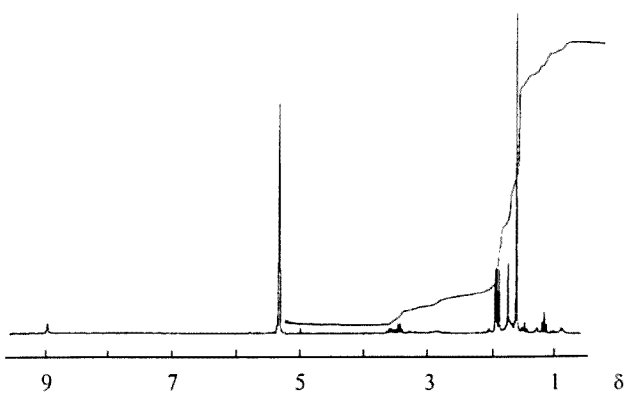


Fig. 1. ^{1}H NMR spectrum of the adduct $[Me_5C_5FeC_5Me_4CH^+(OH)]BF_4^-$ (**2**) in CD_2Cl_2.

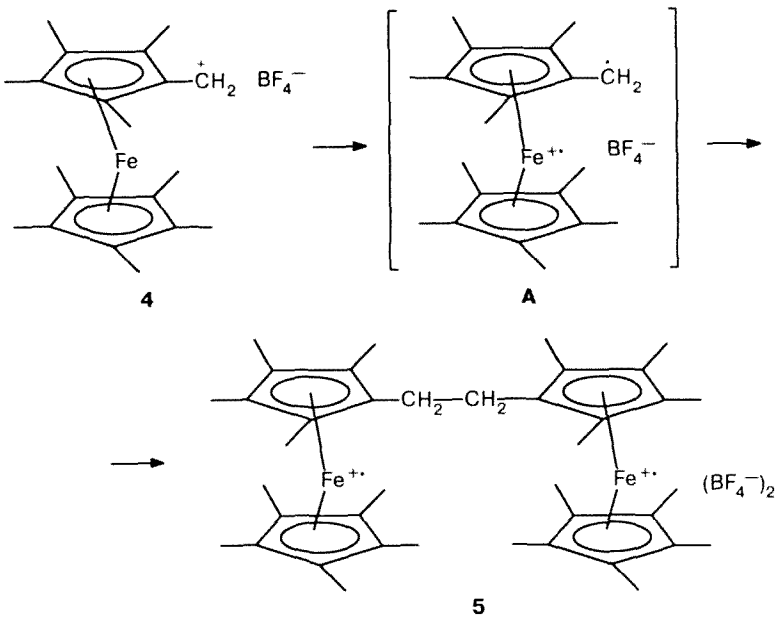
The formation of paramagnetic complexes has been observed previously for many ferrocenyl carbocations. It has been demonstrated that the cations transform into biradical cations, which then dimerize to form paramagnetic compounds.[2—5] For example, the paramagnetic dimer (**5**) was isolated from the diamagnetic complex (**4**)[4,5] (Scheme 1).

The presence of the OH group at the carbocation center of adduct **2** may substantially affect the stabilization of intermediate biradical cations of type **A**.

We failed to grow a single crystal of compound **3**. Its structure was established by chemical methods, by comparing the spectral data for compounds **1**—**3**, and by determing the molecular weight of **3**.

In the ^{1}H NMR spectra of a solution of complex **3** in CD_2Cl_2, the signals of the Me group in the region of δ 1.5—2 typical of adduct **2** (see Figs. 1 and 2) are absent, and three broad signals ($\Delta\nu_{1/2} \geq 100$ Hz) appear in the region of δ −20 to −41 (in the ratio of 2 : 2 : 5,

Scheme 1



see Table 1) typical of paramagnetic derivatives of ferrocene (ferrocenium radical cations[5]). These signals were assigned to the Me groups based on a comparison with the spectrum of permethylferrocenium tetrafluoroborate $[(Me_5C_5)_2Fe^{+\cdot}]BF_4^-$ (**6**), which has one broad signal at δ −37 in the ^1H NMR spectrum. It is evident from the ratio of the signals of the Me groups of complex **3** that this compound, like the initial aldehyde **1**, contains pairs of nonequivalent Me groups (see Table 1).

The IR spectrum of complex **3** has bands at 1690 cm^{-1} (C=O) and 1070 cm^{-1} (BF_4^-)[6,7] (see Table 1).

As in the case of compounds **2** and **6**, the presence of the BF_4^- anion in complex **3** is confirmed by the ^{19}F NMR spectra. All these spectra have two signals (in the ratio of 1 : 4) in the range of δ −75 to −77 (see Table 1). The occurrence of two signals agrees with the known data and is, apparently, associated with the spin-spin coupling of the ^{19}F atoms with the ^{10}B and ^{11}B boron isotopes (1 : 4).[6*]

The molecular weight of complex **3** (445 (±5%)) was determined by the sedimentation equilibrium method[8] for three concentrations in the range of 3—5 g L^{-1}. Figure 3 shows the gradient curve of the compound under study for C = 5 g L^{-1}. The shape of the curve is typical of the equilibrium distribution of a monodisperse compound, *i.e.*, it is fairly safe to say that the compound under study contains no admixtures with different molecular weights (for example, dimers).

The FAB mass spectrum of complex **3** has an intense peak at m/z (I_{rel} (%)) 340 $[427-BF_4]^+$ (100), which

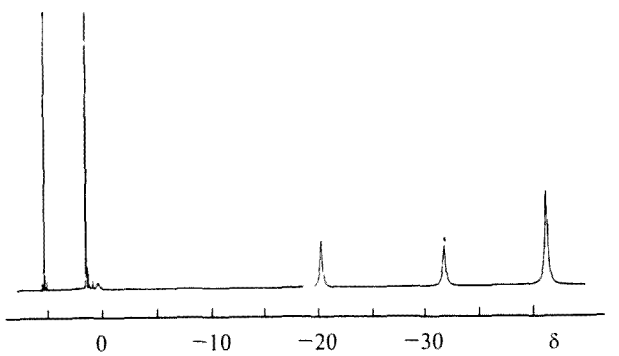


Fig. 2. ^1H NMR spectrum of the paramagnetic complex $[Me_5C_5Fe^{+\cdot}C_5Me_4CH{=}O]BF_4^-$ (**3**) in CD_2Cl_2.

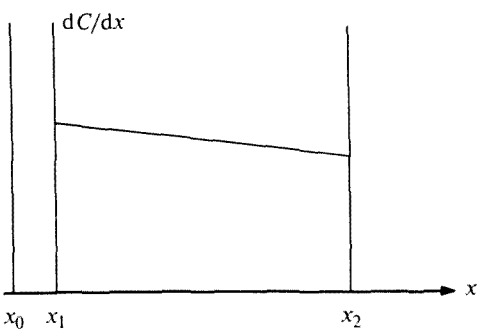


Fig. 3. Sedimentation curve of the equilibrium distribution of complex **3** in a CH_2Cl_2 solution with concentration C = 5 g L^{-1} (see the Experimental section); x is the distance from the axis of rotation; x_0 is the distance to the air—solvent interface; x_1 is the distance to the air—solution interface; x_2 is the distance to the solution—cell-bottom interface.

* Note that the transformation **2**→**3** can be followed by monitoring the changes in the ^{19}F NMR spectrum. For $AgBF_4$ δ ^{19}F (CD_2Cl_2): −76.31; −76.36.

corresponds to the $Me_5C_5FeC_5Me_4CH{=}O$ fragment, and peaks of fragmentation ions at *m/z* 312 $[340-CO]^+$ (40), 311 $[340-COH]^+$ (40), which were also observed for aldehyde **1**.[4,5]

The evidence taken as a whole and the data from elemental analysis suggest that complex **3** has the structure of formylnonamethylferrocenium $[Me_5C_5Fe^{+\cdot}C_5Me_4CH{=}O]\ BF_4^-$.

Complex **3** is stable in air and is virtually insoluble in benzene and ether and readily soluble in polar solvents (CH_2Cl_2, alcohols, acetone, nitromethane, *etc.*). In accordance with the known properties of ferrocenium derivatives,[2,9,10] complex **3** is reduced readily with triethylamine or sodium borohydride in an aqueous alcohol solution to aldehyde **1** (60—80%).

The structure of paramagnetic compound **3** was confirmed also by an independent synthesis, namely, by oxidation of aldehyde **1** with silver tetrafluoroborate in a CH_2Cl_2—MeOH mixture.

Therefore, we obtained the first stable ferrocenium derivative containing the electron-withdrawing CH=O group, namely, formylnonamethylferrocenium tetrafluoroborate **3**. Apparently, the nine electron-donor Me groups compensate for the electron-withdrawing effect of the CH=O group.

Complex **3** can be derived from adduct **2** through a redox process with the intramolecular transfer of an electron from the Fe atom to the carbocation center $CH^+(OH)$ and transformation of the intermediate carbocation to the biradical cation **B**. It can be suggested that one possible way to stabilize the radical **B** is β-elimination of the H atom from the OH group of the CH(OH) fragment, which results in formylnonamethylferrocenium **3**.

$$[Me_5C_5FeC_5Me_4CH^+(OH)]BF_4^- \longrightarrow$$
2
$$\longrightarrow [Me_5C_5Fe^{+\cdot}C_5Me_4CH^{\cdot}(OH)]BF_4^- \xrightarrow{-H}$$
B
$$\longrightarrow [Me_5C_5Fe^{+\cdot}C_5Me_4CH{=}O]BF_4^-$$
3

Analogous stabilization of the $(\overbrace{CH_2)_nC}^{}{}^{\cdot}$—OH radical through β-elimination of the hydrogen atom has been observed in the oxidation of cyclic alcohols to ketones.[11]

Therefore, the nature of the substituents at the carbocation center affects substantially the behavior of the cations. The $Me_5C_5FeC_5Me_4CH_2^+$-type cations are transformed into biradical cations of the type $Me_5C_5Fe^{+\cdot}C_5Me_4CH_2^{\cdot}$ (**A**), which are stabilized through dimerization.[4,5] The biradical cations of the type $C_5Me_5Fe^{+\cdot}C_5Me_4CH^{\cdot}(OH)$ (**B**) are stabilized through elimination of the hydrogen atom with the formation of monomeric paramagnetic complex **3**.

Experimental

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP-200SY spectrometer for 3—10% solutions of compounds in anhydrous $CDCl_3$ and CD_2Cl_2. The IR spectra (KBr pellets) were obtained on an UR-20 instrument. The FAB mass spectra were measured on a Kratos Concept instrument; *m*-nitrobenzyl alcohol was used as the matrix. The mass spectra (EI) were recorded on an MS-890 instrument (70 eV, 250 °C, direct inlet of the sample).

All syntheses were carried out under an atmosphere of argon in anhydrous solvents. Aldehyde **1** was prepared according to a known procedure.[4] Adduct **2** was obtained according to a procedure reported previously.[1]

Reaction of adduct 2 with triethylamine. Dry triethylamine (5 mg, 0.05 mmol) was added to a violet solution of **2** (10 mg, 0.025 mmol) in anhydrous CH_2Cl_2. After the violet color disappeared and the volatile compounds had been removed with a flow of argon, aldehyde **1** was extracted with benzene from the dry residue in a yield of 7 mg (85%). Compound **1** was identified by ^1H NMR and mass spectroscopy: *m/z* (I_{rel} (%)): 340 $[M]^+$ (80—90), $C_{20}H_{28}Fe$; 312 $[M-CO]^+$ (40); 311 $[M-COH]^+$ (20).

Reaction of adduct 2 with aqueous MeOH. Aldehyde **1** was obtained by treating a solution of adduct **2** (12 mg) in dichloromethane (1 mL) with an aqueous methanol solution (1 : 3) in a yield of 50%.

Formylnonamethylferrocenium tetrafluoroborate (3). ***A.*** Violet crystals of adduct **2** (96 mg, 0.23 mmol) were stored under an atmosphere of dry argon at 0—5 °C and transformed into a green solid compound in 20—30 days. The residue was washed with benzene, dried, and dissolved in CH_2Cl_2. The solution was filtered. Green needle-like crystals of tetrafluoroborate **3** (67 mg, 70%) were precipitated with benzene from the filtrate. For analytical purposes, the residue was reprecipitated once more. Found (%): C, 56.09; H, 6.74; F, 16.72; Fe, 13.55. $C_{20}H_{28}BF_4FeO$. Calculated (%): C, 56.24; H, 6.61; F, 17.79; Fe, 13.06.

B. When violet adduct **2** (10 mg, 0.023 mmol) was dissolved in anhydrous methanol (3 mL), a green-brown solution formed. After 15—25 h, the solvent was evaporated. Aldehyde **1** (2 mg) was extracted with benzene from the mixture of red and green crystals that formed. The green crystals (9 mg, 72%), which are insoluble in benzene, are complex **3**.

C. A solution of aldehyde **1** (47.5 mg, 14 mmol) in CH_2Cl_2 (3 mL) was added portionwise to a solution of $AgBF_4 \cdot (dioxane)_3$ (107.5 mg, 23.5 mmol) in anhydrous methanol (1.5 mL). A black precipitate of silver metal formed immediately, and the solution gradually developed a green color. After 3 h, the solution was decanted from the precipitate and filtered. The solvent was evaporated at 20 °C. The green precipitate was washed with benzene and dried *in vacuo*. Complex **3** was obtained in a yield of 56.6 mg (94%). For analytical purposes, the product was twice reprecipitated with benzene from CH_2Cl_2.

Decamethylferrocenium tetrafluoroborate (6) was obtained from decamethylferrocene and $AgBF_4 \cdot (dioxane)_3$ in a similar manner. The yield of green-blue crystals was 94%. Found (%): C, 58.08; H, 7.37; F, 18.52; Fe, 13.61. $C_{20}H_{30}BF_4Fe$. Calculated (%): C, 58.14; H, 7.32; F, 18.40; Fe, 13.52.

Reduction of formylnonamethylferrocenium tetrafluoroborate (3) (prepared from adduct **2**). ***A.*** A solution of complex **3** (4.5 mg, 0.01 mmol) and $NaBH_4$ (13.5 mg, 0.3 mmol) in ethanol (1.5 mL) and water (0.1—0.2 mL) was kept for 30—40 min.

The solution changed color from green to yellow. After the removal of the solvents, the residue was extracted with THF. Aldehyde **1** was obtained in a yield of 3.2 mg (91%).

B. Similarly, aldehyde **1** was obtained from a solution of complex **3** (13.6 mg, 0.03 mmol) in CH_2Cl_2 (2 mL) and dry triethylamine (38 mg, 0.38 mmol) in a yield of 7 mg (63%).

Determination of the molecular weight of complex 3 (prepared from adduct **2**) (Fig. 3). Experiments were carried out on a model 3180 analytical ultracentrifuge (MOM, Hungary) in a 12-mm two-compartment cell with Philpot—Swensson optics (the angle was 70°). The rotor temperature was 25±0.1 °C; the rate of rotation was 50000 rpm. Dichloromethane was used as the solvent. The concentrations of the solvents were 3—5 g L^{-1}. To decrease the time necessary to establish the equilibrium concentration, the height of the solution and solvent columns in the cell were decreased from 12 to 3 mm. The time required for equilibration did not exceed 3 h. The specific partial volume ($\bar{v}$ = 0.688 cm^3 g^{-1}) and the solvent density (ρ_0^{25} = 1.317 g cm^{-3}), which are necessary for calculating the molecular weight from the sedimentation data, were determined picnometrically.

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