Synthesis and electrochemical properties of mono- and (\pm) -1,2-dialkylferrocenes and alkylferrocenium hexafluorophosphates in aqueous and micellar media

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Simple methods have been developed for the preparation of a series of *n*-alkylferrocenes $H(CH_2)_nFc$ (n = 3, 5-8, or 12) based on Friedel—Crafts acylation of ferrocenes followed by reduction of the corresponding ketones with Zn amalgam. The properties of $H(CH_2)_nFc$ and the corresponding ferrocenium ions in micellar aqueous solutions and the behavior of water-soluble cations $H(CH_2)_nFc^+$ in the absence of micelles were studied by cyclic voltammetry. In all cases, the formal redox potentials of ferrocenes (E°) increase linearly as *n* increases up to 8. Whether micelles are present or not, the corresponding correlation equation has the following form: $E^{\circ} = \alpha + \beta n$, where $\beta \approx 29$ mV in all cases. The synthesis of (\pm)-1-ethyl-2-methylferrocene from racemic α -dimethylaminoethylferrocene is reported.

Key words: alkylferrocenes, alkylferrocenium cations; synthesis; cyclopalladation, micellar media; electrochemistry.

Recently, we have demonstrated that the use of a micellar pseudophase is promising for solubilization of ferrocene in aqueous solutions. In this case, ferrocene retains its ability for electrochemical coupling with glucose oxidase in the presence of D-glucose.¹ In practice, this effect provides high catalytic currents in micellar glucose oxidase—D-glucose—ferrocene systems, which is a result of the following sequence of transformations:

$$E(ox) + S \rightarrow E(red) + P, \tag{1}$$

 $E(red) + 2 HFc^+ \rightarrow E(ox) + 2 HFc, \qquad (2)$

$$2 \text{ HFc} - 2 \text{ e} \rightarrow 2 \text{ HFc}^+. \tag{3}$$

Here, E(ox) is the native oxidized enzyme; S is a substrate (D-glucose), which transforms to the product P (gluconolactone); E(red) is the reduced enzyme; and HFc is a ferrocene molecule. According to our preliminary data, the charge on the micelle can affect substantially the efficiency of stage (2) because the enzyme in the oxidized and reduced forms is a polyampholyte. A prerequisite for the manifestation of this electrochemi-

cal effect is the presence of an *n*-alkyl radical bonded to ferrocene, which provides the contact between the ferrocenium cation and the positively or negatively charged micellar globule. In this connection, there was a need to carry out syntheses of a series of related alkylferrocenes and homoannular asymmetrical 1,2-dialkylferrocenes and to study their electrochemical properties both in aqueous and micellar media. In this work, we report the methods for the preparation of *n*-alkylferrocenes, (\pm) -1-ethyl-2-methylferrocene, and the corresponding ferrocenium cations, and describe some of the redox properties of these compounds determined by cyclic voltammetry in micellar media and in the absence of micelles.

Results and Discussion

Synthesis of alkylferrocenes $H(CH_2)_nFc$. The most convenient method for the synthesis of alkylferrocenes is the reduction of acyl derivatives obtained by direct Friedel—Crafts acylation of ferrocene (Eq. (4)). Gener-

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ally, acyl halides and acid anhydrides in the presence of $AlCl_3$ or other Lewis acids are used as acylating agents.² When aluminum chloride is used as a catalyst, diketone forms along with monoketone almost without exception. When a permanent excess of ferrocene is retained in the reaction mixture³ and (as we have established) when the reaction is carried out at reduced temperature, the yield of diketone can be reduced to a minimum.



 $R = Bu, C_6H_{13}, C_7H_{15}, C_{11}H_{23}$

Ferrocene was acylated at 0 °C by slow addition of a solution of a complex of the corresponding acid chloride RCOCI with AICl₃ (in a molar ratio of 1:1) in dichloromethane to an equimolar amount of ferrocene in the same solvent. The complex of RCOCI with AlCl₃ was prepared by gradual addition of powdered AlCl₃ to a solution of acyl chloride in CH₂Cl₂. The rate of dissolution of AlCl₃ decreases as the length of R in acyl chlorides increases, which apparently reflects a decrease in the rate of complex formation between these reagents. A small amount of a disubstitution product forms along with the major product (monoacylferrocene). The content of diacylferrocene decreases as the length of the hydrocarbon radical increases so that in the case of dodecanoyl chloride only dodecanoylferrocene forms, and nonconsumed ferrocene remains in trace amounts.

To reduce the yield of diacylation products, we used acid anhydrides as softer acylating agents (Eq. (5)). Previously, the use of acetic and propionic anhydrides in the synthesis of monoacylferrocenes has been reported.^{4,5} We found that, as in the case of the reaction with RCOCl, it is advantageous to carry out acylation with acid anhydrides under conditions of a permanent excess of ferrocene.

HFc + {RCOCI, AICI₃}
$$\xrightarrow{CH_2CI_2}$$
 RCOFc + RCOOH (5)
R = Et, C₅H₁₁

Reduction of RCOFc to alkylferrocenes proceeds readily by the Clemmensen reaction, *i.e.*, by treatment of ketones with amalgamated zinc in the presence of HCl in a water—organic solvent system.^{3,6,7} Usually, this reaction requires heating over a long period. In the case of monoacylferrocenes, reduction proceeds at room temperature in several minutes.

RCOFc $\xrightarrow{Zn/Hg, HCI/HOAc}$ H(CH₂)_nFc (6)

$$R = Et, Bu, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_{11}H_{23}$$

All the compounds obtained were characterized by IR spectra. Alkylferrocenes were additionally characterized by ¹H NMR spectra. The IR spectra of monoacyl-ferrocenes show stretching vibrations of the carbonyl group at 1690 cm⁻¹. In addition, the IR spectra of acyl- and alkylferrocenes show skeletal vibrations of the unsubstituted Cp ring in the regions of 1000 and 1100 cm⁻¹.

The ¹H NMR spectra of all monoalkylferrocenes contain triplets of the methyl group at 0.9 ppm and of the methylene group bonded to the Cp ring at 2.3 ppm and multiplets of other methylene protons of the hydrocarbon chain in the region of 1.2-1.5 ppm. The unsubstituted Cp ring gives a singlet at 4.09 ppm. Generally, the signals of two protons of the substituted ring overlap with the signal of the unsubstituted Cp ring, and two other protons form a poorly resolved doublet at 4.04 ppm.

Synthesis of (±)-1-ethyl-2-methylferrocene (7). Synthesis of dialkylferrocenes, particularly, of homoannular ferrocenes, is more complex than the synthesis of monoalkylferrocenes. To date, only the methods for preparing 1,2-dialkylferrocenes have been developed. These methods are based on regioselective lithiation of α -dimethylaminoalkylferrocenes, in which coordination of the dimethylamino group by the lithiating agent directs the attachment of the lithium atom at the adjacent position of the ferrocene nucleus.⁸ The reaction of a lithium derivative with a suitable electrophile yields 1,2-dialkylferrocenes after transformation of functional groups to alkyl groups. Cyclopalladation of α -dimethylaminoalkylferrocenes, which also occurs at position 2 of ferrocene, is an alternative to lithiation. The C-Pd bond in the products that formed exhibits high reactivity.9 Presently, cyclopalladated compounds are customary reagents in the synthetic organic chemistry.^{10,11} In some cases, cyclopalladation is more favorable, because it proceeds in high yields and does not require an inert atmosphere.^{10,11} The last-mentioned approach, whose fundamentals were developed by Troitskava and Sokolov,^{12,13} was used for the preparation of 7. The sequence of transformations is shown in Scheme 1. The first stage (cyclopalladation) of α -dimethylaminoethylferrocene (1) with $PdCl_4^{2-}$ in the presence of NaOAc is followed by carbonylation of complex 2 under the action of carbonyl monoxide in MeOH. The ester group in ester 3 was transformed to the methyl group by reduction with $LiAlH_4$ in the presence of $AlCl_3$. The dimethylamino group in amine 4 was transformed to the hydroxy group in two stages. Deoxygenation was carried out with NaBH₄ in the presence of CF₃COOH.

Electrochemical behavior of alkylferrocenes and ferrocenium cations in the presence and in the absence of micelles. In spite of the substantial interest of researchers in the electrochemical properties of cene complexes of transition metals,¹⁴ systematic data on their behavior in aqueous solutions are unavailable. Alkylferrocenium hexafluorophosphates are sufficiently soluble in water for the study of their redox properties by



Reagents: a. Na₂PdCl₄-NaOAc/MeOH; b. CO/MeOH; c. LiAIH₄-AICl₃; d. MeI; e. H₂O-THF; f. NaBH₄-CF₃COOH

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cyclic voltammetry. Typical voltammograms obtained in this work are given in Fig. 1 using BuⁿFc and $Bu^{n}Fc^{+}PF_{6}^{-}$ as examples; the electrochemical data for other compounds are summarized in Table 1. The voltammograms for $H(CH_2)_nFc$ and $H(CH_2)_nFc^+PF_6^$ were recorded at different initial potentials, and the directions of the potential scan were different: in the former case, the scan of the potential started toward the anodic region, whereas in the latter case, the potential scan started toward the cathodic region. From Fig. 1, a, b it is clearly seen that the cyclic voltammograms recorded in the presence and in the absence of micelles of Triton X-100 differ substantially. When micelles are absent, the anodic current is substantially larger than the cathodic current, which is indicative of adsorption of poorly water-soluble n-butylferrocene on the surface of a pyrographite electrode (see Fig. 1, b). The redox behavior of $H(CH_2)_nFc^+PF_6^-$ in this system (in the absence of surfactants) is characterized by poor reversibility. However, in the presence of micelles, the adsorption peak virtually disappears, and the voltammogram as a whole takes the form typical of a reversible one-electron process (see Fig. 1, a). Therefore, surfactants do not complicate the electrochemical pattern and, moreover, efficiently protect the electrode surface against adsorption of alkylferrocenes. Note that an analogous effect of surfactants was observed for all ferrocenes and ferrocenium salts studied. The only complication was observed in micelles of sodium dodecyl sulfate in the case of alkylferrocenes with rather long alkyl chains at low rates of the potential scan. In these cases, cyclic voltammograms are complicated by the occurrence of an additional irreversible wave in the anodic region (see Fig. 1, c), which disappears in the presence of proteins, for example, glucose oxidase. Apparently, this wave can be attributed to adsorption, although this explanation cannot be considered as ultimate. It is also worthy of

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Fig. 1. Cyclic voltammograms: *a*, $Bu^{n}Fc^{+}PF_{6}^{-}$ (0.001 *M*), solubilized in a micellar solution of Triton X-100 (0.1 *M* KH₂PO₄, 0.05 *M* Triton X-100), pH 7.0, 25 °C, the rate of the potential scan was 30 mV s⁻¹; *b*, $Bu^{n}Fc^{+}PF_{6}^{-}$ (0.001 *M*) in the absence of a surfactant (0.1 *M* KH₂PO₄), pH 7.0, 25 °C, the rate of the potential scan was 30 mV s⁻¹; *c*, *n*-butylferrocene (0.001 *M*), solubilized in a micellar solution of sodium dodecyl sulfate (0.1 *M* KH₂PO₄, 0.05 *M* sodium dodecyl sulfate), pH 7.0, 25 °C, the rate of potential scan was 2 mV s⁻¹.

Table 1. Formal redox potentials E° of alkylferrocenes and alkylferricenium salts in various media at 25 °C and pH 7.0 (0.1 *M* phosphate buffer)

Conditions	E°/mV (saturated calomel electrode)	∆ <i>E</i> /mV
Triton X-100	210	60
Triton X-100	195	60
Surfactant is absent	210	130
Triton X-100	170	55
Triton X-100	190	65
Surfactant is absent	100	60
Triton X-100	230	60
Triton X-100	244	52
Surfactant is absent	222	56
Triton X-100	255.5	50
Triton X-100	277	56
Surfactant is absent	222	56
Triton X-100	285.5	55
Triton X-100	304	60
Surfactant is absent	281	54
Triton X-100	315	47
Triton X-100	333	57
Surfactant is absent	291	53
Triton X-100	341	60.5
Triton X-100	362	57
Surfactant is absent	332	48
Triton X-100	365	63
Triton X-100	383.5	62
Surfactant is absent	377	60
Triton X-100	400	59
Triton X-100	407	80
Surfactant is absent	402	54.5
Triton X-100	410	65
Triton X-100	451.5	90
Triton X-100	166	58.5
	Conditions Triton X-100 Triton X-100 Surfactant is absent Triton X-100	Conditions $E^{o'}/mV$ (saturated calomel electrode)Triton X-100210Triton X-100195Surfactant is absent210Triton X-100170Triton X-100190Surfactant is absent100Triton X-100230Triton X-100244Surfactant is absent222Triton X-100255.5Triton X-100285.5Triton X-100285.5Triton X-100304Surfactant is absent281Triton X-100315Triton X-100315Triton X-100341Triton X-100362Surfactant is absent332Triton X-100365Triton X-100365Triton X-100407Surfactant is absent377Triton X-100407Surfactant is absent402Triton X-100410Triton X-100410Triton X-100451.5Triton X-100451.5Triton X-100166

Note: ΔE is the difference between the peak potentials of oxidation and reduction waves.

note that the protein improves the general view of cyclic voltammograms of ferrocenes obtained in solutions of sodium dodecyl sulfate.

It is of interest that a linear relationship occurs between the values of formal redox potentials E° and nfor $H(CH_2)_nFc$; this relationship is observed not only in micellar media but also in aqueous solutions in the absence of surfactants (Fig. 2). The values of E° were determined as the average of the peak potentials of oxidation E_{pa} and reduction E_{pc} waves. The linearity holds at least up to *n*-octylferrocene. The value of E° for *n*-dodecylferrocene demonstrates that E° cannot increase indefinitely as the *n* increases and, evidently, a limit should be found. This relationship is unusual because alkyl substituents are electron donors, and their donor properties are virtually constant and depend only slightly on the number of carbon atoms in the linear alkyl radicals. In particular, this fact is confirmed by the values of Hammett constants σ_p , which are 0.17, 0.15,



Fig. 2. Relationships between E° and the number of methylene groups (*n*) in $H(CH_2)_nFc$ and the corresponding alkylferricenium cations at pH 7.0, KH_2PO_4 (0.1 *M*), 25 °C: *I*, $H(CH_2)_nFc$ (0.001 *M*), Triton X-100 (0.05 *M*); 2, $H(CH_2)_nFc^+PF_6^-$ (0.001 *M*), Triton X-100 (0.05 *M*); 3, $H(CH_2)_nFc^+PF_6^-$ (0.001 *M*).

0.13, 0.16, 0.15, and 0.16 for the Me, Et, Prⁿ, Buⁿ, C_5H_{11} , and C_7H_{15} substituents, respectively.¹⁵ The "normal" relationship between E° and the presence of an alkyl radical is observed only in going from unsubstituted ferrocene to methylferrocene, for which E° decreases according to the inductive electron-donor effect of the methyl group (see Table 1). In other cases, the values of E° increase according to Eq. (7).

$$E^{\circ'} = \alpha + \beta n \tag{7}$$

The parameters of Eq. (7) for ferrocenes and ferrocenium cations calculated for various media are given in Table 2. It is worth noting that the increment of one methylene group (the coefficient β) is ~29 mV in all the compounds studied.

It is difficult to interpret unambiguously the regularities observed. Apparently, the following explanation can be accepted as the first rough approximation. If alkyl

Table 2. Parameters of Eq. (7) obtained under various conditions (alkylferrocene/alkylferricenium 0.001 *M*, 0.1 *M* KH₂PO₄, pH 7.0, 25 °C)

Conditions	α/mV	β/mV
$H(CH_2)_nFc$, 0.05 <i>M</i> Triton X-100	173±3	28.0±0.5
$H(CH_2)_nFc^+PF_6^-$, 0.05 <i>M</i> Triton X-100	194±4	27±1
$H(CH_2)_nFc^+PF_6^-$	157±10	30±2

groups tend to "adhere" to a rather hydrophobic periphery of a ferrocene/ferrocenium molecule, the alkyl "interface" between the ferrocene nucleus and/or a solution/electrode surface should increase as the length of the radical increases. Therefore, the path, which is traversed by an electron in the direction from the ferrocene nucleus to the electrode surface, should increase, which requires more energy at the stage of electron transfer. The energy source is evident, namely, it is higher redox potentials or, in other words, a substantial overvoltage for normal medium-length-chain alkylferrocenes.

Experimental

Instruments and materials. The following reagents were used in this work: surfactants (sodium dodecyl sulfate (Reanal), cetyltrimethylammonium bromide (Merck), and Triton X-100 (Sigma)); AlCl₂ (Reakhim); sodium hexafluorophosphate (Aldrich), ferrocene (Reakhim), ethylferrocene (Strem Chemicals), and *n*-butylferrocene (Aldrich). Methylferrocene was prepared according to the procedure reported previously.16 The carboxylic acids used in this work (propionic, valeric, hexanoic, heptanoic, octanoic, and dodecanoic acids, Reakhim) were purified before use according to standard procedures¹⁷ and transformed to the corresponding acyl chlorides by treatment with thionyl chloride.¹⁸ Propionic and hexanoic anhydrides were prepared by the reaction of thionyl chloride with the corresponding acid taken in a molar ratio of 1:2 according to the procedure reported in the literature.¹⁹ Dichloromethane was dried with anhydrous CaCl₂. Voltammetric measurements were carried out in a three-electrode temperature-controlled 10-mL glass cell equipped with a working pyrographite (A = 1.2 ± 0.2 cm²) or a disk glassy-carbon ($A = 3.5\pm0.2$ mm²) electrode, a saturated calomel reference electrode (Radiometer), and a platinum auxiliary electrode. Triangular potential scan for the working electrode was carried out on a P-5827M potentiostat and an IPC-3 potentiostat-galvanostat (Institute of Physical Chemistry, Russian Academy of Sciences). When measurements were carried out on a P-5827M potentiostat, voltammetric curves were recorded on a flat-bed two-coordinate XY Recorder 4103 potentiometer. The ¹H NMR spectra were recorded on a Bruker CXP-200 spectrometer. The IR spectra were obtained on IR-10 (in thin films) and Specord instruments. TLC was carried out on Silufol plates.

General procedure for the acylation of ferrocenes with acyl chlorides. Carboxylic acid chloride (0.054 mol) was dissolved in CH₂Cl₂ (80 mL), and anhydrous AlCl₃ (7.2 g, 0.054 mol) was added portionwise. The mixture was shaken periodically until the aluminum chloride dissolved completely. The acylating mixture was added dropwise with intense stirring to a solution of ferrocene (10 g, 0.054 mol) in dichloromethane (50 mL) at 0 °C for approximately 2.5 h. After the addition of the acylating mixture, the reaction mixture was stirred for an additional 1 h and then poured onto ice (300 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic phases were combined, and the products were chromatographed on a column (50×3 cm) packed with Al2O3. Ferrocene, monoacylferrocene, and diacylferrocene were eluted with light petroleum, benzene, and diethyl ether, respectively. The benzene fraction was concentrated in vacuo, and the acylation product was subjected to reduction without additional purification.

Pentanoylferrocene: yield 55%, m.p. 36-38 °C, b.p. 110– 120 °C (0.01 Torr) (cf. Ref. 20: b.p. 119–121 °C (0.08 Torr)). Heptanoylferrocene: yield 50%, m.p. 24 °C. Octanoylferrocene: yield 52%, m.p. 28 °C (cf. Ref. 21: m.p. 26-27 °C). Dodecanoylferrocene: yield 86%, m.p. 36 °C (cf. Ref. 21: m.p. 36-37 °C).

Acylation of ferrocene with hexanoic anhydride. The reaction was carried out for 3 h analogously to the procedure described above with the use of hexanoic anhydride (12.8 g, 0.06 mol), AlCl₃ (16 g, 0.12 mol), and ferrocene (11 g, 0.06 mol) in dichloromethane (120 mL). Ferrocene (3.2 g, 0.017 mol) and hexanoylferrocene (8.7 g, 0.031 mol, 51%) were isolated by chromatography on a column (50×3 cm) packed with Al₂O₃ as described above, m.p. 33-34 °C (*cf.* Ref. 21: b.p. 161–163 °C (1.5 Torr), n_D^{20} 1.5843).

Acylation of ferrocene with propionanhydride. A mixture of propionanhydride (9.7 g, 0.07 mol) and aluminum chloride (12 g, 0.09 mol) was dissolved with stirring in CH_2Cl_2 (100 mL). A solution of ferrocene (13.9 g, 0.07 mol) in CH_2Cl_2 (60 mL) was added to the mixture, and the mixture was stirred for 30 min. Subsequent workup of the reaction mixture was carried out analogously to the synthesis described above. The yield of propionylferrocene was 60%, m.p. 37-38 °C (cf. Ref. 22: m.p. 38-39 °C).

General procedure for the reduction of acylferrocenes. A solution of $HgCl_2$ (1.3 g, 0.005 mol) in water (22 mL) was added to zinc dust (17 g, 0.26 g-at.), and then concentrated HCl (3 mL) was added. The mixture was vigorously shaken for 5 min. After sedimentation, the aqueous layer was decanted. A solution of acylferrocene (0.012 mol) in glacial acetic acid (24 mL) and concentrated HCl (18 mL) were added immediately to the zinc amalgam that resulted. The mixture was shaken for several minutes until the solution became colorless. Then water was added (100 mL). The precipitate was filtered off and washed with diethyl ether until the solvent became colorless. The compound isolated from the organic phase was chromatographed on a column (15×2 cm) packed with Al₂O₃; alkylferrocene was eluted with light petroleum. The yields and characteristics of the compounds that obtained are given below.

<u>*n*-Propylferrocene:</u> yield 61%, b.p. 135 °C (28 Torr) (*cf.* Ref. 22: b.p. 106–107 °C (5 Torr)). ¹H NMR, δ : 1.01 (t, Me); 1.58 (sextet, CH₂Me); 2.38 (t, CpCH₂); 4.11 (d, C₅H₄); 4.15 (s, Cp). IR, v/cm⁻¹: 3075, 2930, 1100, 990.

<u>*n*-Pentylferrocene:</u> yield 47%, m.p. 17 °C, n_D^{18} 1.5690 (cf. Ref. 22: n_D^{20} 1.5711). ¹!1 NMR, δ : 0.91 (t, Me); 1.3? (m, (CH₂)₂); 1.52 (m, CpCH₂CH₂); 2.28 (t, CpCH₂); 4.06 (d, C₅H₄); 4.10 (s, Cp). IR, v/cm⁻¹: 3080, 2935, 1110, 1005.

<u>*n*-Hexylferrocene:</u> yield 72%, $n_D^{25,5}$ 1.5510 (*cf.* Ref. 21: n_D^{20} 1.5602). ¹H NMR, δ : 0.89 (t, Me); 1.29 (m, (CH₂)₃); 2.32 (t, CpCH₂); 4.04 (d, C₅H₄); 4.07 (s, Cp). IR, v/cm⁻¹: 3090, 2940, 1100, 1000.

<u>*n*-Heptylferrocene:</u> yield 81%, m.p. 20.2–20.5 °C, n_D^{26} 1.5538. ¹H NMR, δ : 0.90 (t, CH₃); 1.29 (s, (CH₂)₄); 1.51 (m, CpCH₂CH₂); 2.32 (t, CpCH₂); 4.05 (d, C₅H₄); 4.09 (s, Cp). IR, v/cm⁻¹: 3090, 2920, 1100, 1000.

<u>*n*-Octylferrocene</u>; yield 84%, b.p. 173–180 °C (5 Torr), $n_D^{17.5}$ 1.5520 (*cf.* Ref. 21: b.p. 154–155 °C (1 Torr), n_D^{20} 1.5490). ¹H NMR, δ : 0.89 (t, Me); 1.29 (m, (CH₂)₅); 2.31 (t, CpCH₂); 4.05 (d, C₅H₄); 4.09 (s, Cp). 1R, v/cm⁻¹: 3100, 2925, 1105, 1000.

<u>*n*-Dodecylferrocene;</u> yield 90%, m.p. 36 °C (*cf.* Rcf. 21: m.p. 35–36 °C). ¹H NMR, δ : 0.91 (t, Me); 1.20 (m, (CH₂)_{*n*}); 2.33 (t, CpCH₂); 4.05 (d, C₅H₄); 4.08 (s, Cp). IR, v/cm⁻¹: 3095, 2950, 1110, 1000.

Preparation of alkylferrocenium hexafluorophosphates. Synthesis was carried out according to the procedures described previously.²³ Alkylferrocene $(3 \cdot 10^{-4} \text{ mol})$ was dissolved in concentrated H₂SO₄ (1 mL), kept at room temperature for 1 h, and poured into water (5 mL). The solution was filtered off, mixed with a saturated NaPF₆ solution (1 mL), and cooled at $-5 \,^{\circ}$ C for 1 h. The crystals that formed were filtered off and washed with cold water. The yields of alkylferrocenium salts were 30–70% depending on the substituent in alkylferrocene.

Methyl 2-(α -dimethylaminoethyl)ferrocenecarboxylate (3). Compound 1 (7.8 g, 0.0303 mol) (see Ref. 24) was transformed to cyclopalladated complex 2 under the action of Na₂PdCl₄ in the presence of NaOAc in MeOH.

A stream of CO was passed through a suspension of 2 (11.27 g, 0.0283 mol) in MeOH (60 mL) for 3.5 h. Metallic palladium was filtered off, and methanol was evaporated. The residue was treated with a solution of Na₂CO₃ and extracted with benzene. The benzene solution was dried with MgSO₄ and concentrated in vacuo. The residue was chromatographed on a column with silica gel (elution with a 10:1 heptanetriethylamine mixture). Two fractions of diastereoisomers were collected: R^*R^* diastereoisomer (3a) and R^*S^* diastereoisomer (3b) in yields of 0.3 and 5.2 g, respectively (the total yield was 61.7%). ¹H NMR (CDCl₃), δ: <u>diastereoisomer</u> 3a: 1.30 (d, 3 H, CHMe); 2.42 (s, 6 H, NMe2); 3.78 (s, 3 H, COOMe); 3.99 (q, I H, CHMe); 4.14 (s, 5 H, Cp); 4.33, 4.47, 4.75 (all s, 3 H, all C₅H₃); diastereoisomer 3b: 1.43 (d, 3 H, CHMe); 2.02 (s, 6 H, NMe₂); 3.72 (s, 3 H, COOMe); 4.08 (s, 5 H, Cp); 4.32 (s, 2 H), and 4.74 (s, 1 H, C₅H₃); 4.40 (q, 1 H, C<u>H</u>Me).

1-(α-Dimethylaminoethyl)-2-ethyl/ferrocene (4). AlCl₃ (1.65 g, 0.012 mol) was added with stirring to a suspension of LiAlH₄ (0.94 g, 0.025 mol) in anhydrous ether (50 mL) under an argon atmosphere. After 15 min, a solution of 3 (5.2 g, 0.0165 mol) in ether (20 mL) was added dropwise to the reaction mixture. The course of the reaction was monitored by TLC. After 50 min, a suspension of the same amounts of LiAlH₄ and AlCl₃ in ether was added to the reaction mixture. The mixture was stirred additionally for 30 min and guenched with water. The organic layer was separated. A solution of Na_2CO_3 was added to the aqueous layer, and extraction with ether was carried out. The combined ether layers were washed with water, dried with MgSO₄, and evaporated. The mixture was separated by chromatography on a column with silica gel. The first fraction was eluted with hexane. The second and third fractions were eluted with a 5:1 hexane-triethylamine mixture. Compounds 7, 4, and 1-CH₂OH-2-{CH(NMe₂)CH₃}Fc were obtained in yields of 0.15, 3.08, and 0.4 g, respectively; the total yield was 81.3%. ¹H NMR (CDCl₃), δ: amine 4: 1.44 (d, 3 H, CHMe); 1.95 (s, 3 H, Me); 2.06 (s, 6 H, NMe₂); 3.60 (q, I H, CHMe); 3.98 (s, 5 H, C₅H₅); 4.03 (s, 2 H), and 4.06 (s, 1 H, C₅H₃). <u>1-CH₂OH-2-{CH(NMe₂)CH₃}Fc</u>: 1.23 (d, 3 H, CH<u>Me</u>); 2.09 (s, 6 H, NMe₂); 2.52 (q, 1 H, C<u>H</u>Me); 4.04 (s, 5 H, C₅H₅); 4.03 (s, 1 H), and 4.09 (s, 2 H, C₅H₃); 3.71 and 3.77 (AB system, 2 H, CH₂).

 $1-\alpha$ -(Hydroxyethyl)-2-ethylferrocene (6). Amine 4 (3.08 g, 0.0114 mol) was transformed to methiodide 5.²⁵ A solution of 5 in 50% aqueous THF (100 mL) was boiled for 2 h. After cooling, the reaction mixture was poured into water and extracted with ether. The ethereal solution was washed with water, dried with MgSO₄, and concentrated. Alcohol 6 was recrystallized from *n*-hexane. The yield was 1.03 g. An additional crop of compound 6 was obtained from the mother liquor in a yield of 0.6 g. The total yield was 08.8%.

1-Ethyl-2-methylferrocene (7). NaBH₄ (0.86 g, 0.0228 mol) was added to a solution of 6 (1.03 g, 0.0042 mol) in CH₂Cl₂ (40 mL) under an argon atmosphere. The reaction mixture was cooled to $0 \circ C$, CF₃COOH (6.3 mL) was added to

the mixture, and the solution was stirred for 20 min. Then NaBH₄ (0.86 g) and CF₁COOH (6.3 mL) were added sequentially, and the mixture was stirred for 15 min. Oxidation to ferrocenium occured, as evidenced by the blue color of the solution. The course of the reaction was monitored by TLC (hexane was used as an eluent). After completion of the reaction, the reaction mixture was poured onto ice, and a 10% Na₂CO₃ solution (300 mL) was added. In this case, ferrocenium cation was not reduced. Therefore, Na₂SO₃ was added portionwise, and the mixture was vigorously shaken until the aqueous phase became virtually colorless. Simultaneously, the organic phase developed a typical orange color. The organic layer was separated, washed with water, dried with MgSO₄, and concentrated. The residue was dried in a desiccator over P₂O₅ and paraffin. Compound 7 was obtained in a yield of 0.75 g (78%). Analogously, compound 7 was obtained from 6 (0.6 g) in a yield of 0.5 g (89%). The combined product was distilled in vacuo, b.p. 105-106 °C (4 Torr), ¹H NMR (CDCl₁), δ: 1.13 (t, 3 H, CH₂Me); 1.97 (s, 3 H, Me); 2.34 and 2.39 (AB system, 2 H, CH₂); 3.93 (s, 1 H); 4.02 (7 H, Cp, C₅H₃).

Preparation of solutions for electrochemical studies. *A.* Alkylferrocenes. Alkylferrocene $(3 \cdot 10^{-5} \text{ mol})$ was dissolved in ethyl alcohol (5 mL). An aliquot of the resulting solution (0.5 mL) was added to a phosphate buffer (pH 7.0, 0.1 *M* KH₂PO₄, 2.5 mL) containing (or without) Triton X-100 (0.05 *M*).

B. Ferrocenium salts. Alkylferrocenium hexafluorophosphate $(5 \cdot 10^{-6} \text{ mol})$ was dissolved in a phosphate buffer (pH 7.0, 0.1 *M* KH₂PO₄, 5 mL) containing (or without) Triton X-100 (0.05 *M*). The prepared solutions were used directly for electrochemical measurements.

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