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Reactions of ferricinium salts with Lewis bases

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A reaction of the ferricinium radical cation with Lewis bases leads to substitution in the cyclopentadienyl ring with the formation of ferrocene derivatives only when the radicals are formed from the Lewis bases in the process of the reaction.

Key words: ferricinium radical cation, Lewis bases, redox disproportionation, substitution in cyclopentadienyl ring, intermediate complexes, quantum chemical calculations, density functional theory (DFT), B3LYP functional.

It is known that ferricinium salts are convenient, mild oxidants ($E_{1/2}$ = 0.31—0.47 V (saturated calomel electrode (s.c.e.)),[1,2] $E_{1/2}$ = 0.34 V (90% aqueous EtOH, s.c.e.)[3]) and they are frequently used for the generation of radical products.[4—6] In addition, ferricinium cation in the presence of various neutral (diethylamine, Py, DMF, DMSO, hexametapol, 1,10-phenanthroline, 2,2´-bipyridine) or charged (Cl^-, Br^-, OH^-) Lewis bases is reduced to ferrocene.[7—14]

In many cases, for example for Cl^- and OH^-, thermodynamic description of the direct reduction process does not seem possible, since the oxidation potential of a proposed donor (a Lewis base) is too high. For Cl^- and OH^- anions in acetonitrile it is 2.24 and 0.92 V (MeCN, Ag/AgCl), respectively.[15] In some cases, substitution in cyclopentadienyl ring takes place in addition to reduction to ferrocene. For example, the reaction of ferricinium cation with CN^- anion leads to the formation of cyanoferrocene.[9]

To sum up, two questions are principal for the reactions of the ferricinium radical cation with Lewis bases proceeding with the redox transformations: 1) which cases are responsible for substitution in cyclopentadienyl ring with the formation of ferrocene derivatives and 2) how the reduction of the ferricinium radical cation to ferrocene takes place in the reactions occurring "against a potential" with oxidation-resistant bases?

Experimental

The reactions of Lewis bases as azole sodium salts, sodium alkoxides (NaOR, R = Me, Et) and amides ($NaNR_2$, R = H, Et, Pr^i) with ferricinium hexafluorophosphate in THF, dichloromethane, acetonitrile, and acetone solutions were studied.[16—19] Ferricinium hexafluorophosphate was obtained according to the known procedure.[20] Azole sodium salts were synthesized from the corresponding heterocycles and sodium hydride in THF under argon. Traces of the starting heterocycle were removed by decanting a benzene solution after reflux of the heterocycle salts. Precipitates were dried *in vacuo*.

Reactions were carried out on a preparative scale under argon or in the sealed tubes directly in the resonator of an ESR spectrometer in the temperature region from –80 to +40 °C. ESR spectra were recorded on a ERS-221 (ZWG DDR) spectrometer in the X-region with the HF-modulation 100 kHz. The reactants, ferricinium salt and bases, were taken in equimolar ratios. The ESR studies were performed both in the presence of a spin trap (Bu^tNO) and without it. Elemental analysis of compounds obtained was performed in the Laboratory of Microanalysis of INEOS RAS. Melting points were measured in open capillaries and were not corrected. Mass spectra (EI, 70 eV, injection temperature 80—220 °C) were recorded on a Varian CH-8 instrument.

Quantum chemical calculations for ferrocene, ferricinium radical cation, pyrazolide anion, pyrazolyl radical, pyrazole, hydroxy anion, hydroxyl radical, and intermediates of their reactions were performed in the framework of density functional theory (DFT) with the B3LYP functional.[21—23] Optimization of geometric structures of molecular systems was performed using procedures given in the works[24,25] and the GAUSSIAN-98 program[26] on a SC760D minisupercomputer. For calculations of enthalpies of the processes in the gaseous phase, the calculated total energies were used, as well as corrections for the energy of zero vibrations of the corresponding molecules, ions, and radicals.

Reaction of sodium pyrazolide with ferricinium hexafluorophosphate. ***A.*** A mixture of ferricinium hexafluorophosphate (0.5 g, 1.5 mmol) and sodium pyrazolide (0.135 g, 1.5 mmol) in THF (75 mL) was stirred for 45 min in a Schlenk flask at room temperature. The color of the solution turned from dark blue to reddish brown. Then the solvent was evaporated *in vacuo*, the residue was extracted with freshly distilled THF and subjected to chromatography on a column with Al_2O_3. Ferrocene was eluted with hexane (yellow band), the yield was 0.11 g (38%), m.p. 173 °C (*cf.* Ref. 27: m.p. 173 °C). MS, *m/z*: 186 $[M]^+$. *N*-Ferrocenylpyrazole was eluted with THF (yellowish red band), the

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yield was 0.09 g (23%), m.p. 63 °C. Found (%): C, 62.31; H, 5.02; N, 10.87; Fe, 21.17. $C_{13}H_{12}N_2Fe$. Calculated (%): C, 61.90; H, 4.76; N, 11.11; Fe, 22.20. MS, *m/z*: 252 $[M]^+$, 225 $[M - HCN]^+$, 214 $[M - C_2N]^+$, 199 $[M - C_2N_2H]^+$, 186 $[M - C_3N_2H_2]^+$. Further elution with THF gives pyrazole (0.04 g, 39%) with m.p. 70 °C (*cf.* Ref. 28: m.p. 70 °C). The residue in the Schlenk flask left after the extraction with THF was washed with ethanol, water, and acetone and dried *in vacuo*. According to the elemental analysis data, these were coordination polymers of the composition $[Fe(C_3H_3N_2)_2]_n$. Found (%): C, 37.53; H, 3.52; N, 30.05. $C_6H_6N_4Fe$. Calculated (%): C, 37.89; H, 3.16; N, 29.47.

B. A mixture of ferricinium hexafluorophosphate (0.5 g, 1.5 mmol) and sodium pyrazolide (0.14 g, 1.5 mmol) in THF (75 mL) was stirred for 15 min at 40 °C, the solvent was evaporated *in vacuo*, the mixture was treated similarly to that in method ***A*** to isolate ferrocene (0.14 g, 50%), *N*-ferrocenylpyrazole (0.14 g, 37%), and pyrazole (0.04 g, 39%).

Reaction of sodium 3,5-dimethylpyrazolide with ferricinium hexafluorophosphate was carried out similarly to method ***B*** with the use of sodium 3,5-dimethylpyrazolide (0.18 g, 1.5 mmol) and ferricinium hexafluorophosphate (0.5 g, 1.5 mmol) to isolate ferrocene (0.12 g, 43%), *N*-ferrocenyl-3,5-dimethylpyrazole (0.17 g, 41%) with m.p. 46 °C, and 3,5-dimethylpyrazole (0.03 g, 21%) with m.p. 105 °C (*cf.* Ref. 28: m.p. 107 °C).

N-Ferrocenyl-3,5-dimethylpyrazole. Found (%): C, 64.12; H, 5.64; Fe, 20.35. $C_{15}H_{16}N_2Fe$. Calculated (%): C, 64.30; H, 5.83; Fe, 19.93. MS, *m/z*: 280 $[M]^+$, 274 $[M - 6\ H]^+$, 272 $[M - 8\ H]^+$, 270 $[M - 10\ H]^+$, 254 $[M - C_2H_2]^+$ and/or $[M - CN]^+$, 239 $[M - CH_3CN]^+$.

Reaction of sodium imidazolide with ferricinium hexafluorophosphate was carried out similarly to method ***B*** with the use of sodium imidazolide (0.14 g, 1.5 mmol) and ferricinium hexafluorophosphate (0.5 g, 1.5 mmol) to isolate ferrocene (0.03 g, 10%), *N*-ferrocenylimidazole (0.02 g, 4.7%) with m.p. 57 °C (decomp.), and coordination polymers $(Im_2Fe)_n$ (0.11 g, ~37%).

N-Ferrocenylimidazole. MS, *m/z*: 252 $[M]^+$, 225 $[M - HCN]^+$, 198 $[M - 2\ HCN]^+$, 186 $[M - C_3N_2H_2]^+$.

Reaction of sodium benzotriazolide with ferricinium hexafluorophosphate. A mixture of ferricinium hexafluorophosphate (1.0 g, 3.0 mmol) and sodium benzotriazolide (0.42 g, 3.0 mmol) in THF (100 mL) was stirred for 30 min, concentrated, and subjected to chromatography on a column with Al_2O_3. A colorless fraction, which preceded a yellow band on the column, was eluted with hexane. According to the mass spectrometric data, this fraction contains cyclopentadiene resins and tetrahydrofuran oligomers. Elution with the hexane—THF (1 : 1) yielded a fraction, from which ferrocene (0.28 g, 50%) was isolated with m.p. 172 °C (*cf.* Ref. 27: m.p. 173 °C). Further elution with THF gave a fraction corresponding to the red band on the column. After the solvent was evaporated, reddish orange crystals of *N*-ferrocenylbenzotriazole (0.37, 40%) with m.p. 113 °C were obtained. Collection of the red band was followed by collection of a colorless eluate, evaporation of the solvent from which gave benzotriazole (0.08 g, 23%) with m.p. 101 °C (*cf.* Ref. 28: m.p. 100 °C).

N-Ferrocenylbenzotriazole. Found (%): C, 63.85; H, 4.38; N, 13.51. $C_{16}H_{13}N_3Fe$. Calculated (%): C, 63.37; H, 4.29; N, 13.86. MS, *m/z*: 303 $[M]^+$, 275 $[M - N_2]^+$, 247 $[M - C_2N_2H_4{}^+]$, 218 $[M - C_4N_2H_9]^+$, 217 $[M - C_4N_2H_{10}]^+$, 186 $[M - C_6N_3H_3]^+$.

Results and Discussion

Reactions of azole salts with ferricinium hexafluorophosphate are accompanied with a rapid change of color of the reaction mixture from blue to dark red already within the first few minutes. Chromatographic separation of the reaction mixture formed after 5—75 min at 20—40 °C on Al_2O_3 showed that it contains ferrocene (a reduced form of ferricinium) (~50%), *N*-ferrocenylazole (5—40%), azole (the heterocycle itself, not its salt) (10—40%), coordination polymers $(FeL_2)_n$ (~10%), small amount of cyclopentadiene resins (~2%), and tetrahydrofuran oligomers (traces). The yields of *N*-ferrocenylazoles decrease in the order benzotriazole > pyrazole ~ 3,5-dimethylpyrazole > imidazole.

No amino- or alkoxyferrocenes are formed in the reactions of sodium amides and alkoxides with ferricinium hexafluorophosphate. Rather partial reduction to ferrocene and destruction with the formation of cyclopentadiene resins and inorganic iron compounds take place.

Studies of reactions of ferricinium hexafluorophosphate with the azole sodium salts by ESR spectroscopy showed that, irrespective of the nature of the starting azolide anion, a very broad signal ($\Delta H_{1/2} \approx 250$ mT) with the *g*-factor close to that of electron ($g = 2.0026—2.0028$) appears in the spectrum at the beginning at –80 °C, which cannot be assigned neither to the ferricinium radical cation (the signal for ferricinium is found only at very low temperatures, $g_{\|} = 4.40$ and $g_{\perp} = 1.39$),[29] nor to the azolyl radicals having a multiplet structure.[30,31] It does not correspond to an inorganic compound of Fe^{II} ($g = 3.30—3.43$ and $g = 6.58—6.86$)[32] either. Apparently, the spectrum can belong to the charge transfer complexes $[Fc^{\cdot +}\ Az^-]$ (Fc is the ferrocenyl, Az^- is the azolide anion). Intensity of this signal rapidly decreases on temperature elevation with simultaneous appearance of a signal, which is a triplet of triplets of the spin adducts of azolyl radicals if a Bu^tNO spin trap is present in the system. Parameters of the spectra of the azolyl radical spin adducts are given in Table 1. Figure 1 shows the ESR spectrum of pyrazolyl-

Table 1. Parameters of the ESR spectra of nitroxyl radicals in the Bu^tNO—AzNa system in THF at 20 °C

Radical	*g*-Factor	a_{N_1}	a_{N_2}
		mT	
$Bu^tN(O^\cdot)Pz$	2.0060	1.45	0.20
$Bu^tN(O^\cdot)Im$	2.0060	1.48	0.18
$Bu^tN(O^\cdot)Bt$	2.0060	1.38	0.15
$Bu^tN(O^\cdot)$-3,5-$(Me)_2$Pz	2.0060	1.39	0.18
$Bu^t{}_2NO^\cdot$	2.0060	1.54	—

Note. Pz is the pyrazolyl, Im is the imidazolyl, Bt is the benzotriazolyl.

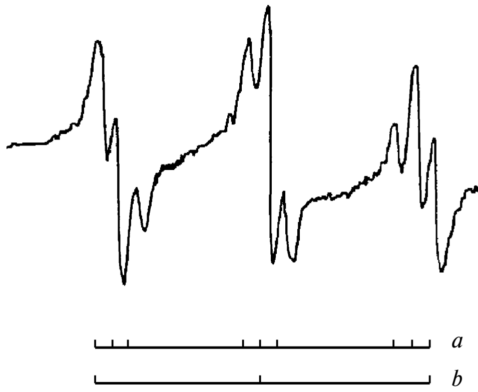


Fig. 1. The ESR spectrum of PzN(O$^\cdot$)Bu^t (*a*) and $Bu^t_2NO^\cdot$ (*b*) radicals observed in the reaction of ferricinium hexafluorophosphate with sodium pyrazolide in the presence of Bu^{t}NO in THF at 20 °C (see Table 1).

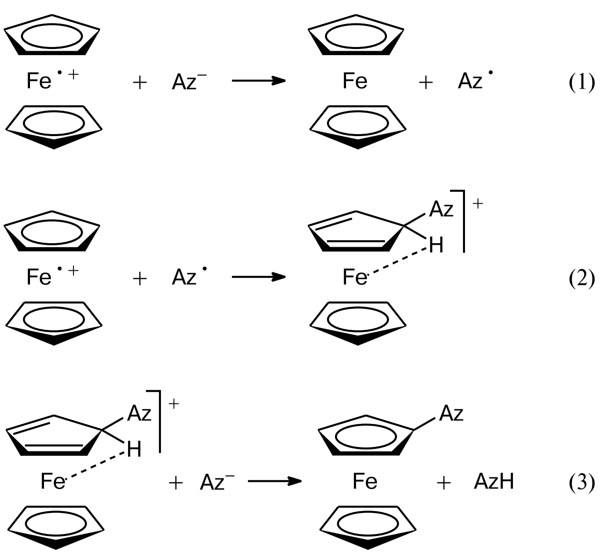
tert-butylnitroxyl radical formed in the reaction of sodium pyrazolide with ferricinium hexafluorophosphate.

Since formation of these azolyl-*tert*-butylnitroxyl radicals is also observed in the direct reaction with Bu^{t}NO,[33] the concentration ratio of azolyl-*tert*-butylnitroxyl and $Bu^t_2NO^\cdot$ radicals is of principal importance. In the reactions of ferricinium hexafluorophosphate with the azole sodium salts, the concentration of azolyl-*tert*-butylnitroxyl radicals formed is significantly higher than that of $Bu^t_2NO^\cdot$, which indicates the generation of azolyl radicals directly in the system [$Fc^{\cdot+}$ Az^-]. It should be emphasized that the use of the 2,4,5-triphenylimidazole sodium salt (lophine) in the reaction with ferricinium hexafluorophosphate leads to the formation of stable lophinyl radical ($g = 2.0036$), which can be observed directly.

A combination of chemical and spectroscopic data allows us to conclude that the reactions under study follow the mechanism of a direct reduction of the ferricinium radical cation to ferrocene with the azole anions (Scheme 1, Eq. (1)). Calculations of enthalpy of the first step in the direct generation of azolyl radicals for the pyrazolide anion showed that this process is exothermic ($\Delta H = -81.0$ kcal mol^{-1}) (Table 2).

The azolyl radicals, which came out of the cell, possess high enough reactivity and are apparently consumed in several ways. First, they can react with another ferricinium radical cation at the site of localization of the unpaired electron. The ground electron state of the ferricinium radical cation is $^2E_{2g}$ with the configuration ($a^2_{1g}\,e^3_{2g}$).[34] The thermal population of the first excited state $^2A_{1g}$ ($a^1_{1g}\,e^4_{2g}$) is significant at room temperature, since the electron transition $^2E_{2g} \rightarrow {}^2A_{1g}$ occurs at ~200 cm^{-1}, to which the kT corresponds under these conditions.[35] Depending on the electron state of ferricinium cation, either attack on the cyclopentadienyl ring or formation of the coordination Fe—N bond takes place. The first pathway leads to the replacement of the hydrogen atom and formation of

Scheme 1



N-ferrocenylazoles (see Scheme 1, Eqs (2) and (3)), the second route leads to decomposition of the ferrocene core and formation of coordination polymers $(FeAz_x)_n$. Second, the azolyl radicals which come into the solvent bulk can be terminated by entering various reactions with the solvent. Apparently, this explains appearance of tetrahydrofuran oligomers among the reaction products, which were detected by mass spectrometry.

The results in the work[11] are important for the understanding the mechanism of substitution in the cyclopentadienyl ring, in which the reaction of the ferricinium radical cation with the radical obtained by oxidation of a Lewis base is considered as a key step of the process. Thus (see Scheme 1, Eqs (2) and (3)), cyanoferrocene ($CN^\cdot$ instead of $Az^\cdot$), phenylferrocenyl sulfone ($PhSO_2^\cdot$ instead of $Az^\cdot$),

Table 2. Relative total energies with correction for the zero vibrations (E') and with correction for the zero vibrations and entropy members (G), as well as entropies (S) of ferrocene, pyrazole, and particles formed in their reactions

Compound	E'	G	S /cal mol^{-1} deg^{-1}
	kcal mol^{-1}		
Ferrocene	105.73	84.69	92.070
Ferricinium radical cation	106.30	84.71	93.292
Pyrazolide anion	35.52	19.08	64.674
Pyrazolyl radical	36.71	19.89	66.253
Pyrazole	44.99	28.49	65.028

Note. The total energy ($-E$/Hartreess) for ferrocene is 510.4390, for the ferricinium radical cation is 510.2030, for pyrazolide anion is 225.5698, for pyrazolyl radical is 225.4639, and for pyrazole is 226.1594.

p-tolylferrocenyl sulfide ($CH_3C_6H_4S^{\cdot}$ instead of $Az^{\cdot}$), α-cyanoisopropylferrocene ($C(CH_3)_2CN^{\cdot}$ instead of $Az^{\cdot}$) were obtained. One can consider that a direct cyanation of ferrocene[9] with liquid cyanic acid in the presence of a strong oxidant $FeCl_3$ also proceeds by the mechanism of the reaction of the ferricinium radical cation with the $CN^{\cdot}$ radical. The same mechanism operates in the direct electrochemical alkylation of ferrocene with alkyl radicals in the anode decarboxylation of the carboxylic acid anions.[36,37]

Scheme 1 seems the most probable, however, an alternative Scheme 2 of the one-electron redox process with a preliminary "activating complexation" is quite acceptable. In this case, the role of reducing agent belongs to the preliminary formed complex of the ferricinium radical cation and the azolide ion (Lewis base) rather than to the azole anion (the Lewis base in the anionic form). Then, the process proceeds according to Eq. (3). If applied to the reactions with the azole salts, this should lead to the fact that azolyl radicals are not generated in the process of formation of *N*-ferrocenylazoles and do not come out of the cells, which poorly agrees with the facts of rapid accumulation of the spin adducts $AzN(O^{\cdot})Bu^t$, comparatively low yield of *N*-ferrocenylazoles, and appearance of tetrahydrofuran oligomers.

To answer the question on the structure of the intermediate complex and on how the attack on the ferricinium radical cation takes place, we performed model quantum chemical calculations.* Figure 2 shows possible structures of the complex emerging in the reaction of the ferricinium radical cation with the pyrazolyl radical. The structures of **1a** and **1b** are formed upon the attack by the pyrazolyl radical on the cyclopentadiene ring, whereas **1c**, on the iron atom. All three intermediates correspond to the local minima on the potential energy surface, with the complex **1a** being energetically more preferable (Table 3).

Based on the data given in Tables 2 and 3, enthalpies for the reactions (2) and (3) with the formation of the intermediates **1a—c** were calculated. It turned out that all the steps of the process are exothermic:

Intermediate	$-\Delta H_{(2)}$	$-\Delta H_{(3)}$
	kcal mol^{-1}	
1a	30.7	164.5
1b	25.4	169.9
1c	14.2	181.1.

To sum up, in the reaction of the ferricinium radical cation with the azolide anions, substitution in the cyclopentadienyl ring with the formation of *N*-ferrocenylazoles occurs through the azolyl radicals, which then directly react with the ferricinium radical cation.

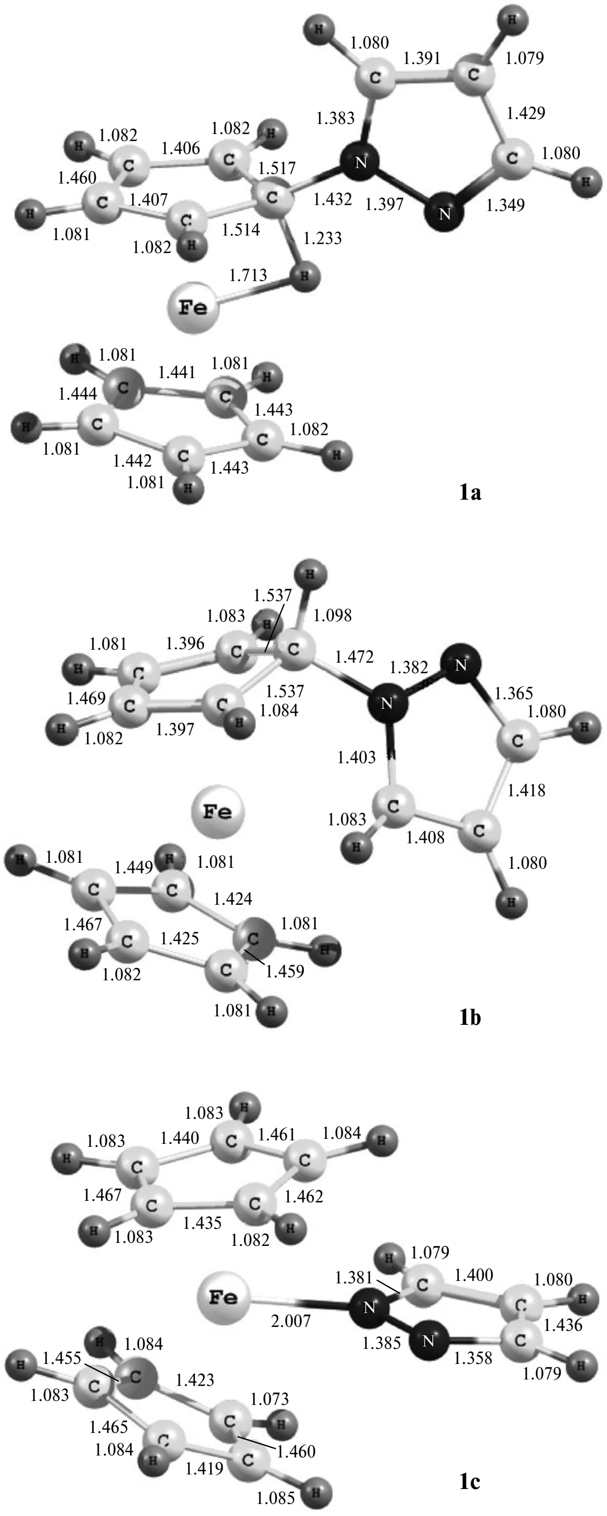


Fig. 2. The intermediate cationic complexes **1a—c** formed in the reaction of the ferricinium radical cation with the pyrazolyl radical (see Scheme 1, Eq. (2)).

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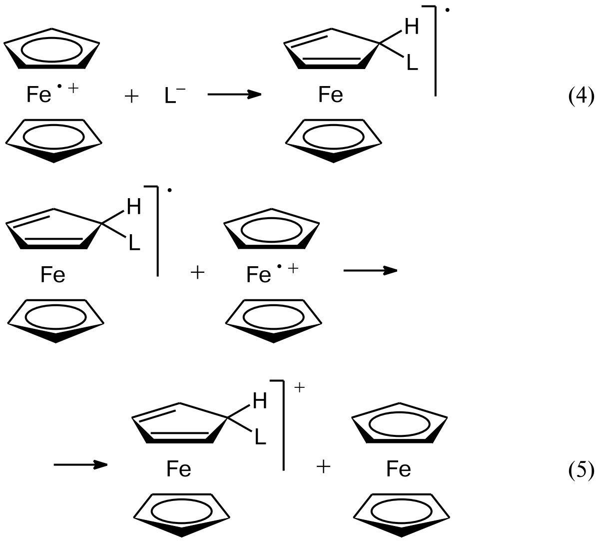
* Quantum chemical calculations for compounds, their intermediates and transformations were carried out for the gaseous phase. This puts certain limits on the use of these data for the description of the processes proceeding in solutions. Nevertheless, it is considered reasonable to use these calculated data, since they agree with the results of the studies of the process obtained by chemical and spectroscopic methods.

Scheme 2



Let us consider the cases when anionic Lewis bases are not directly oxidized to radicals. To explain the mechanism of this type of reactions, a concept of "activating complexation" has been suggested,[38] which consists in the following (Scheme 3). If donor L (for example, a Lewis base in the anionic form L$^-$) cannot directly reduce acceptor Fc$^{\cdot +}$, then a complex is formed, which plays the role of the reducing agent.

Scheme 3

$$L^- + Fc^{\cdot +} \not\longrightarrow L^{\cdot} + Fc$$

$$L^- + Fc^{\cdot +} \longrightarrow FcL^{\cdot}$$

$$FcL^{\cdot} + Fc^{\cdot +} \longrightarrow FcL^+ + Fc$$

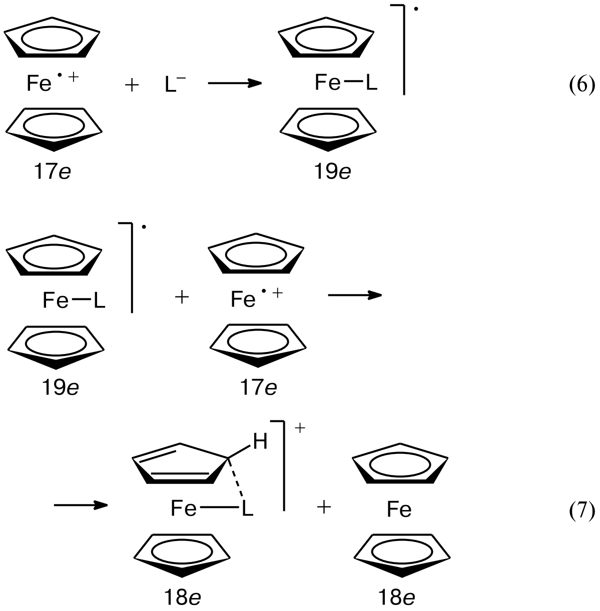
As a rule, the Lewis bases used are quite simple molecules (ions) with the localized σ-bonds and without π-electron system of conjugation. Therefore, abstraction of an electron leads to a strong change in the charge on the key atom, which is energetically unfavorable. Conversely, a complex formed acquires donor properties and readily donates electron.

Such a scheme is characteristic of a Lewis base in the anionic form. An important example is the reduction of ferricinium salts in alkaline medium, when L$^-$ = OH$^-$. Due to the thermodynamic reasons mentioned at the beginning of the paper, the hydroxide ion cannot be directly oxidized to a radical with the ferricinium radical cation, but their complexation takes place to furnish ferricinium hydroxide, which can be isolated.[7] Its reaction with the ferricinium salt leads to the rapid reaction (7) with the formation of ferrocene[7] (Scheme 4).

Table 3. Relative total energies (E) with correction for the zero vibrations (E') and with correction for the zero vibrations and entropy members (G), as well as entropies (S) of the intermediates **1a—c**

Form	E	E'	G	S/cal mol^{-1} deg^{-1}
	kcal mol^{-1}			
1a	0.00	0.00	0.00	113.203
1b	4.21	5.34	4.94	116.662
1c	16.80	16.55	16.27	117.182

Scheme 4



The cation formed in (7) reacts with the Lewis bases to be decomposed to the inorganic iron complexes: Fe(OH)$_3$ is formed with alkalis,[7,13] [Fe(SCN)$_6$]$^{3-}$ anion is formed with NH$_4$SCN,[10] [FeCl$_4$]$^-$ and [FeBr$_4$]$^-$ anions are formed with Cl$^-$ and Br$^-$, respectively.[10,12] In the work,[12] it was shown that decomposition of the ferricinium cation results in disproportionation to initially form Fe^{II} coordination complexes, which in the secondary processes are oxidized with the starting ferricinium cation to Fe^{III} complexes. Therefore, finally the greater part of the ferricinium is reduced to ferrocene, whereas the inorganic iron compounds formed are the Fe^{III} complexes.

To answer the question on the structure of the intermediate complex and on how the attack on the ferricinium radical cation occurs, we performed model (see above) quantum chemical calculations. Figure 3 shows possible structures of the radical emerging it the reaction of the ferricinium radical cation with hydroxide ion. All three intermediates **2a—c** correspond to the minima on the potential energy surface, with the radical **2c** being the

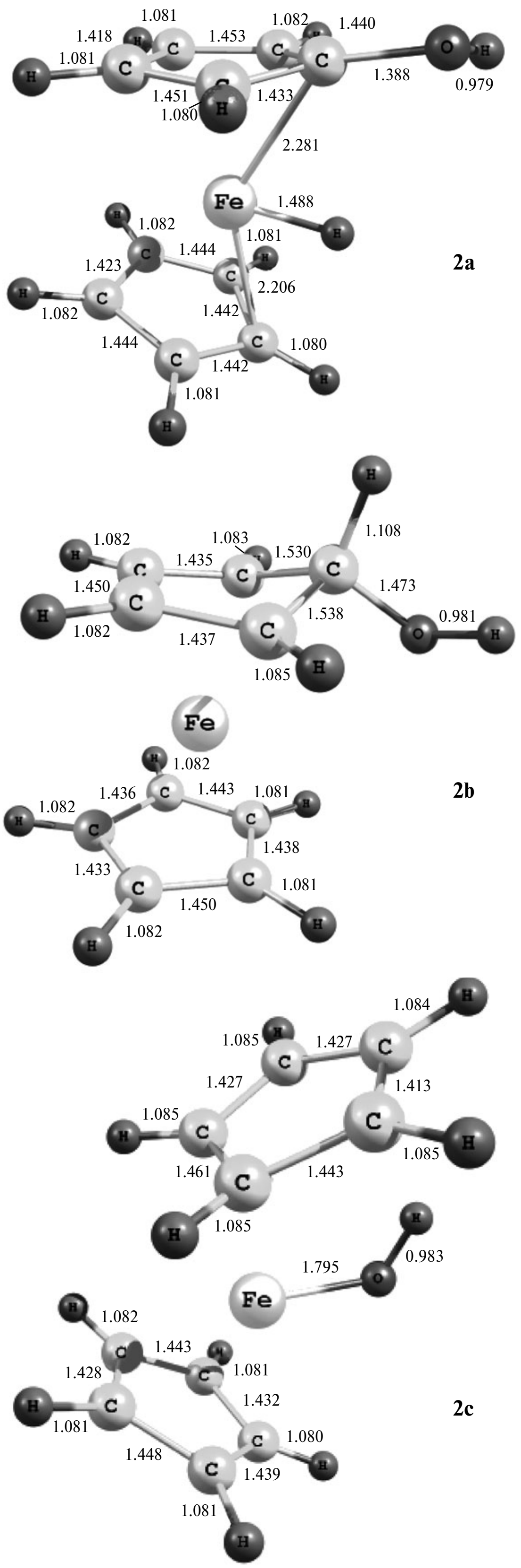


Fig. 3. The intermediate radical complexes **2a—c** formed in the reaction of the ferricinium radical cation with the hydroxide ion (see Scheme 4, Eq. (6)).

Table 4. Relative total energies (E) with correction for the zero vibrations (E') and with correction for the zero vibrations and entropy members (G), as well as entropies (S) of the intermediates **2a—c**

Form	E	E'	G	S/cal mol^{-1} deg^{-1}
	kcal mol^{-1}			
2a	26.58	25.80	25.12	106.617
2b	5.13	6.80	6.36	104.737
2c	0.0	0.0	0.0	102.173

most stable (Table 4). From this it follows that the attack of the ferricinium radical cation by the anion having small size can proceed at the iron atom to form the iron-centered intermediate complex.

In conclusion, the reactions of the ferricinium radical cation with Lewis bases lead to the substitution in the cyclopentadienyl ring with the formation of ferrocene derivatives only in such cases when the Lewis bases are transformed to radicals in the course of the reaction, which then directly react with the ferricinium radical cation. Formation of radicals from the bases can occur by oxidation either directly with ferricinium salts, or with strong oxidants introduced into the reaction medium, for example, Cu^{2+} or Fe^{3+} salts, or electrochemically.

When the Lewis bases are not oxidized, reduction of the ferricinium radical cation follows apparently the scheme of "activating complexation" involving a complex of the ferricinium radical cation with the base with further electron transfer to another ferricinium radical cation. During this process, some ferricinium radical cations are reduced to ferrocene, whereas some by further reaction with the Lewis base are transformed to the iron coordination compound.

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