Oxidation of the *exo*- and *endo*-phenylcyclohexadienyl iron complexes $Fe(\eta^5\text{-}6\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$

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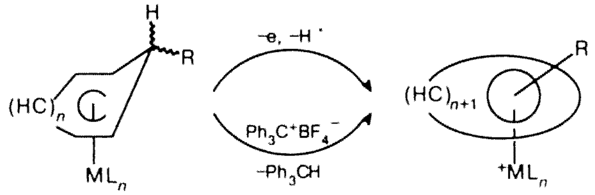
The rate of oxidatively induced homolytic scission of the $C(sp^3)-H$ bonds in the iron phenylcyclohexadienyl complexes $Fe(\eta^5\text{-}6\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ (**1**) depends on the spatial orientation of the Ph substitutent. In the case of the ($\mathbf{1}_{endo}{}^{+\cdot}$) radical cation this process, resulting in the cationic biphenyl complex $[Fe(\eta^6\text{-}C_6H_5C_6H_5)(\eta^5\text{-}C_5H_5)]^+$ ($\mathbf{2}^+$), is fast and proceeds for several minutes. In the case of the more stable radical cation ($\mathbf{1}_{exo}{}^{+\cdot}$) the formation of $\mathbf{2}^+$ is slow and takes tens minutes to complete.

Key words: iron complexes, oxidation reactions, cyclic voltammetry.

Oxidatively induced elimination of hydrogen in semi-open π-polyene (polyenyl) complexes of transition metals is an important method of expanding the coordinated polyene system by one carbon atom (Scheme 1).[1–3]

Scheme 1



Reactions of the type shown in Scheme 1, which proceed with the participation of a trityl cation, are often considered in the literature as an electrophillic attack of the Ph_3C^+ cation on the C—H bond of a complex followed by elimination of a hydride ion.[1] However, direct observation of 17-electron intermediates[4,5] and the occurrence of the reactions (Scheme 1) with the participation of one-electron oxidants having no affinity for a hydride ion,[5–7] allow one to assume that these reactions proceed *via* transfer of an electron followed by homolysis of the C—H bond at the saturated carbon atom adjacent to the polyene system. As was mentioned above, the processes (Scheme 1) are important for the purposeful modification of coordinated polyenes. Therefore, it is of interest to reveal the dependence of their pathways on the spatial orientation of the C—H and C—R bonds. The literature data available on the behavior of π-complexes in the reaction (Scheme 1) concerns, as a rule, only one of the two possible isomers (*exo*-R or *endo*-R) and, hence, cannot answer unambiguously the question under consideration. In this work, the electrochemical and chemical (by $AgBF_4$) oxidation of two isomeric η^5-phenylcyclohexadienyl complexes $Fe(\eta^5\text{-}6\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ with a definite *exo*- ($\mathbf{1}_{exo}$) and *endo*-($\mathbf{1}_{endo}$) orientation of the Ph group are studied to determine the influence of the spatial orientation of the phenyl substituent on the pathway of type (1) reactions.

Results and Discussion

Electrochemical oxidation of the $\mathbf{1}_{exo}$ and $\mathbf{1}_{endo}$ isomers was carried out on a glassy carbon electrode in CH_2Cl_2 and THF, using cyclic voltammetry (CV). The values of the potentials and the characteristics of the one-electron processes observed are presented in Table 1. As can be seen in Fig. 1, the electrochemical behavior of the $\mathbf{1}_{exo}$ and $\mathbf{1}_{endo}$ isomers is different.

Only one irreversible peak of oxidation (Fig. 1, *a*) is observed on the cyclic voltammogram of isomer $\mathbf{1}_{endo}$ in both solvents. On the reverse potential scan, reversible cathode peaks appear on the voltammograms in both solvents and coincide in potentials with those of the reduction of the $[Fe(\eta^5\text{-}C_5H_5)(C_6H_5C_6H_5)]^+$ cation ($\mathbf{2}^+$). This gives evidence for the fast (in the CV time scale) transformation of the 17-electron radical cation $\mathbf{1}_{endo}{}^{+\cdot}$ into cation $\mathbf{2}^+$ accompanied by the cleavage of the $C-H_{exo}$ bond (Scheme 2).

Unlike $\mathbf{1}_{endo}$, the one-electron oxidation of $\mathbf{1}_{exo}$ to $\mathbf{1}_{exo}{}^{+\cdot}$ proceeds reversibly: the reduction peak of the $\mathbf{1}_{exo}{}^{+\cdot}$ radical cation is observed on the cathode branch of the cyclic voltammogram. However, the $i_p{}^k/i_p{}^a$ ratio is somewhat less than unity (0.87). In addition, the peak of the reduction of cation $\mathbf{2}^+$ appears during the reverse potential scan and differs from the similar peak in the

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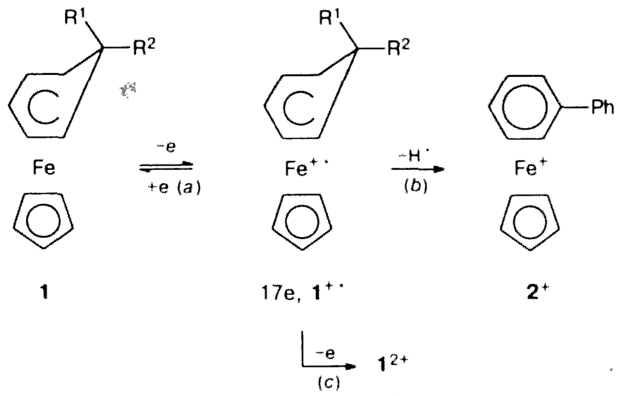
Scheme 2



1_{exo}: R^1 = Ph; R^2 = H
1_{endo}: R^1 = H; R^2 = Ph

(*a*) Reversibility only for 1_{exo}.
(*b*) Slowly for ($1_{exo}^{+\cdot}$); fast for ($1_{endo}^{+\cdot}$).
(*c*) For ($1_{exo}^{+\cdot}$).

case of $\mathbf{1}_{endo}$ by its lower intensity (Fig. 1, *b*). The result obtained provides evidence for the capability of the radical cation $\mathbf{1}_{exo}^{+\cdot}$ to break the C—H_{endo} bond (Scheme 2), but the rate of this process is significantly lower than that in the case of radical cation $\mathbf{1}_{endo}^{+}$. In the region of more positive potentials, an additional peak is observed on the cyclic voltammogram of isomer $\mathbf{1}_{exo}$ that corresponds to further oxidation of radical cation $\mathbf{1}_{exo}^{+\cdot}$ to the 16-electron dication $\mathbf{1}_{exo}^{2+}$ (Fig. 1, *c*, Scheme 2). The absence of the reverse cathodic peak on the voltammogram gives evidence for chemical irreversibility of the oxidation due to the high reactivity of the 16-electron dication $\mathbf{1}_{exo}^{2+}$. This behavior of isomer $\mathbf{1}_{exo}$ is in line with the known data,[8] according to which the oxidation of the structurally similar 2,4-pentadienyl iron complex $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}2,4\text{-}Me_2C_5H_3)$ proceeds through two one-electron steps, the first of which (0.29 V) is reversible and the second of which (1.32 V) is irreversible.

Table 1. Electrochemical characteristics of $Fe(\eta^5\text{-}6\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ complexes according to CV data ($C = 2 \cdot 10^{-3}$ mol L^{-1}, glassy carbon electrode, 0.1 *M* Bu_4NBF_4, 200 mV s^{-1}, relative to saturated calomel electrode)

Complex	Solvent					
	CH_2Cl_2		THF			
	E_{ox}/V	Process	E_{ox}/V	Process	$-E_{red}$/V	Process
$\mathbf{1}_{exo}$	0.32	Reversible 18e↔17e	0.34	Reversible 18e↔17e		
	1.24	Irreversible 17e→16e	1.20	Irreversible 17e→16e		
$\mathbf{1}_{endo}$	0.25	Irreversible 18e→17e	0.32	Irreversible 18e→17e	1.25*	Reversible
					2.08*	Reversible
$\mathbf{2}^+$					1.25	Reversible
					2.10	Reversible

* Potentials of the cathode peaks appearing after anodic polarization.

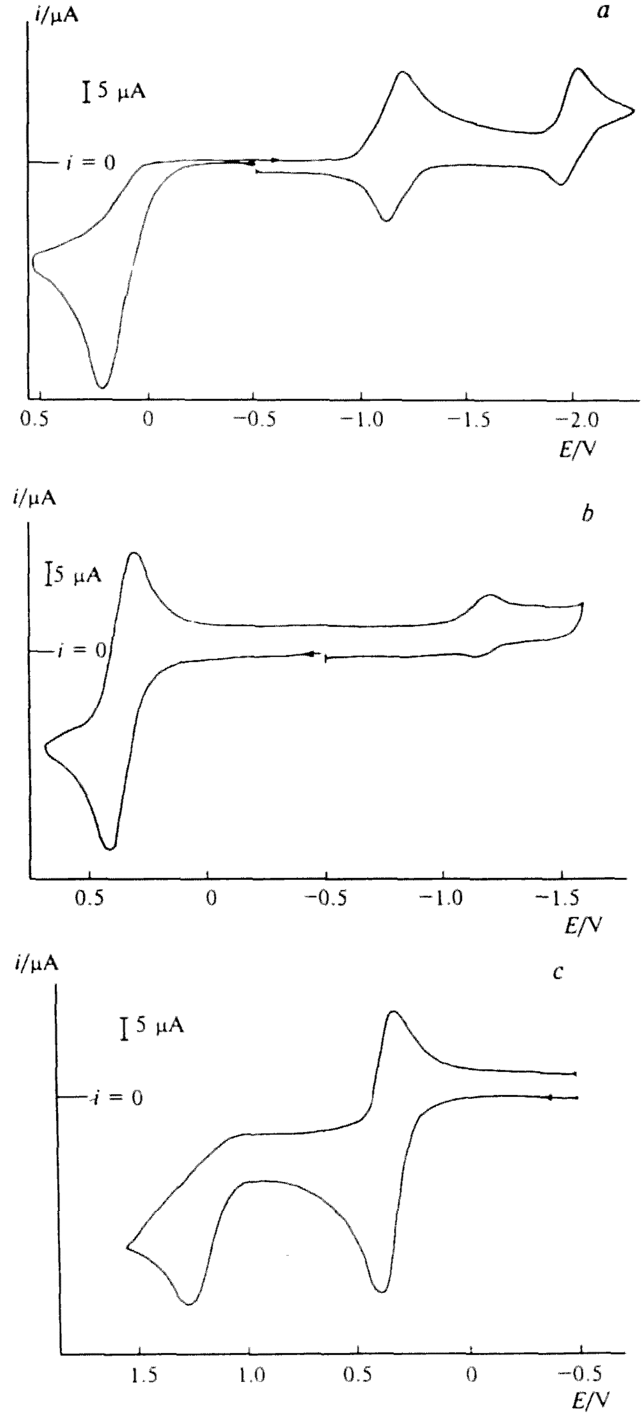


Fig. 1. Cyclic voltammograms (glassy carbon electrode, CH_2Cl_2, 0.1 *M* Bu_4NBF_4, relative to saturated calomel electrode, 200 mV s^{-1}): *a*, $Fe(\eta^5\text{-}endo\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ complex ($\mathbf{1}_{endo}$); *b*, $Fe(\eta^5\text{-}exo\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ complex ($\mathbf{1}_{exo}$), oxidation to $\mathbf{1}_{exo}^{+\cdot}$; *c*, $Fe(\eta^5\text{-}exo\text{-}PhC_6H_6)(\eta^5\text{-}C_5H_5)$ complex ($\mathbf{1}_{exo}$), oxidation to $\mathbf{1}_{exo}^{2+}$.

In order to confirm the oxidative cleavage of the C—H bond of the cyclohexadienyl ligand with the formation of cation $\mathbf{2}^+$, we also carried out also the chemical oxidation of the $\mathbf{1}_{exo}$ and $\mathbf{1}_{endo}$ isomers by a dioxane complex of silver tetrafluoroborate, $AgBF_4 \cdot 3C_4H_8O$ (CH_2Cl_2, 20 °C). In the case of $\mathbf{1}_{endo}$ the reaction is fast and leads to cation $\mathbf{2}^+$ due to the elimination of the H atom from position 6 of the cyclohexadienyl ligand (Scheme 2). The cationic complex $\mathbf{2}^+$ was also obtained in the oxidation of $\mathbf{1}_{exo}$ under the same conditions. In line with the CV data, the reaction was slower than in the case of $\mathbf{1}_{endo}$ and was completed in approximately 1 h. The yields of $\mathbf{2}^+$ were equal to 35 % in the case of $\mathbf{1}_{exo}$ and to 76 % in the case of isomer $\mathbf{1}_{endo}$. No $[Fe(\eta^5\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)]^+$ cation was found in the products of the oxidation of the $\mathbf{1}_{exo}$ and $\mathbf{1}_{endo}$ isomers. The appearance of this cation would give evidence competing cleavage of the carbon—carbon bond with the elimination of phenyl radical. Examples of similar cleavage of C—C bonds have been considered in Ref. 9.

Thus, this work showed that the oxidatively induced homolytic scission of the C—H bond in the $\mathbf{1}_{exo}$ isomer proceed more readily than in the $\mathbf{1}_{endo}$ isomer. Nevertheless, the rate of hydrogen elimination, even in the case of isomer $\mathbf{1}_{exo}$, is sufficient so that on the preparative time scale (tens minutes, hours) the same diphenyl cation $\mathbf{2}^+$ forms as in the oxidation of $\mathbf{1}_{endo}$. When the time of the oxidation is limited, this result can be used for the quantitative separation of isomer $\mathbf{1}_{exo}$ from the mixture of $\mathbf{1}_{exo}$ and $\mathbf{1}_{endo}$ isomers. The observed differences in the rates of the cleavage of the $C—H_{exo}$ and $C—H_{endo}$ bonds in the $17e^-$-complexes of $\mathbf{1}^{+\cdot}$ may be caused by the fact that the $C—H_{exo}$ bond is oriented parallel to the π-electron system of the dienyl fragment and is therefore more reactive than $C—H_{endo}$. It is also possible that the cleavage of the $C—H_{endo}$ bond is a two-step process involving the [1,5] sigmatropic shift of the hydrogen atom followed by cleavage of the $C(6)—H_{exo}$ bond. At the present time, there is no evidence for the [1,5] sigmatropic shift in the $17\bar{e}$-complex $\mathbf{1}_{exo}{}^{+\cdot}$.

Experimental

All reactions were carried out in an atmosphere of purified argon in absolute solvents. The ^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer in CD_2Cl_2. Electrochemical measurements were conducted on a PI-50-1 potentiostat. Glassy carbon was the working electrode, a platinum net was the auxiliary electrode, and a saturated calomel electorde was used as the reference electrode. The velocity of potential scanning was 200 mV s^{-1}, the base electrolyte was Bu_4NBF_4.

Complexes **1** were prepared according to procedures described previously.[10]

The oxidation of the $\mathbf{1}_{endo}$ and $\mathbf{1}_{exo}$ complexes with the $AgBF_4$ tridioxanate. An equimolar amount of $[AgBF_4 \cdot 3(C_4H_8O_2)]$ was added with stirring to solutions of 0.20 g (0.73 mmole) of complex $\mathbf{1}_{exo}$ or $\mathbf{1}_{endo}$ in CH_2Cl_2. When the reaction was completed (for $\mathbf{1}_{exo}$ after 1 h and for $\mathbf{1}_{endo}$ after 10 min), water was added to the reaction flask and the mixture was thoroughly stirred. After separation, the organic layer was filtered off from a silver residue, CH_2Cl_2 was removed in a vacuum, and the raw residue was twice reprecipitated by ether from dichloroethane. As a result, complex $\mathbf{2}^+$ was obtained in 35 % yield in the case of $\mathbf{1}_{exo}$ and in 76 % yield in the case of the $\mathbf{1}_{endo}$ isomer. M.p. and the ^1H NMR spectrum of the complex obtained corresponded exactly to the literature data.[11,12]

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