Redox-induced $\eta^5 \Leftrightarrow \eta^3$ haptotropy of the fluorenyl ligand in 9-substituted η^5-fluorenylmanganesetricarbonyl complexes

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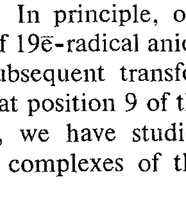
It has been shown by cyclic voltammetry in THF within the −90 to 40 °C temperature range that fluorenyl $(\eta^5\text{-9-R-C}_{13}H_8)Mn(CO)_3$ complexes (R = Bu^t (**3**) and Ph (**4**)) undergo two-electron reduction to form allyl type $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$ dianions as final products. At low temperatures complexes **3** and **4** are reduced in two one-electron steps according to the EEC-scheme. The first step is reversible and corresponds to the formation of 19ē-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$. The E^0 values for redox pairs $\mathbf{3}^{0/-\bullet}$ and $\mathbf{4}^{0/-\bullet}$ are −1.88 and −1.73 V, respectively. The further reduction of radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ at more negative potentials is accompanied by fast $\eta^5 \rightarrow \eta^3$ haptocoordination of the fluorenyl ligand to form 18ē-dianions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$. These dianions obtained by the reduction of complexes **3** and **4** by the radical anion of pyrene are stable at −80 °C and are characterized by their IR spectra. At room temperature the $\eta^5 \Leftrightarrow \eta^3$ hapticity change is a fast and reversible process occurring at the step of 19ē-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ and leading to the electron deficient 17ē-species $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{-\bullet}$, which are reduced easier than the initial complexes. As a result, complexes **3** and **4** are reduced to the corresponding dianions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$ at room temperature in one reversible two-electron step according to the ECE-scheme. Reactivities of $19e^-$-species of the isomeric η^5- and η^6-fluorenylmanganesetricarbonyl complexes are compared.

Key words: fluorenylmanganesetricarbonyl, haptotropic isomerization, electron-transfer-induced reactions, cyclic voltammetry, IR spectroscopy.

The transition from the 18-electron (18ē) to the 19-electron (19ē) configuration of metallocomplexes is accompanied by a significant increase in their reactivities.[1−3] Reactive 19ē-complexes are often metastable; therefore, identifying these species and studying the routes of their subsequent transformations are of doubtless interest for the development of the chemistry of odd-electron complexes.

We have shown previously[4] that the one-electron reduction of $(\eta^6\text{-C}_{13}H_9)Mn(CO)_3$ (**1**, where $C_{13}H_9$ is fluorenyl) to the corresponding 19ē-radical anion $\mathbf{1}^{-\bullet}$ induces the fast reaction of inter-ring haptotropic isomerization of the latter to form the radical anion $[(\eta^5\text{-C}_{13}H_9)Mn(CO)_3]^{-\bullet}$ ($\mathbf{2}^{-\bullet}$). The formation of radical anion $\mathbf{2}^{-\bullet}$ due to the isomerization of the electrogenerated radical anion $\mathbf{1}^{-\bullet}$ is confirmed by the existence of the neutral complex **2** (the yield with respect to substance >80 %)[4] in the reaction products of the preparative electroreduction of complex **1**. Since the oxidation potential of radical anion $\mathbf{2}^{-\bullet}$ is considerably more negative than the reduction potential of complex **1**, the formation of complex **2** in electrolysis occurs due to the oxidation of radical anion $\mathbf{2}^{-\bullet}$ either heterogeneously on the electrode surface or homogeneously in the near-electrode layer under the action of the initial complex **1** as an oxidant. Studying the reactivity of radical anion $\mathbf{2}^{-\bullet}$ generated directly from complex **2** by methods of cyclic voltammetry and preparative electrolysis has previously[4] been impossible, because radical anion $\mathbf{2}^{-\bullet}$ is kinetically unstable. In principle, one may try to enhance the stability of 19ē-radical anion $\mathbf{2}^{-\bullet}$ and to study the routes of its subsequent transformation by introducing substituents at position 9 of the fluorenyl ligand. In this connection, we have studied the electrochemical reduction of complexes of the general formula



2: R = H; **3**: R = Bu^t; **4**: R = Ph

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$(\eta^5\text{-9-R-}C_{13}H_8)Mn(CO)_3$ with 9-*tert*-butylfluorenyl (**3**) and 9-phenylfluorenyl (**4**) ligands, whose 19ē-radical anions are more stable, as will be shown below.

Results and Discussion

The cathodic diffusion-controlled peak *A* ($I_p \cdot \upsilon^{-1/2}$ = const, where I_p is the height of the peak and υ is the rate of linear scanning of the potential) is observed on the cyclic voltammograms (CVA) of the complex $(\eta^5\text{-9-Bu}^t\text{-}C_{13}H_8)Mn(CO)_3$ (**3**) at ~20°C (Fig. 1, curve *1*). The height of peak *A* is double that of the one-electron oxidation peak of ferrocene or decamethylferrocene under the same conditions, which indicates a two-electron character of the electrodic process. The reversibility of the reduction of complex **3** follows from the existence of the corresponding equally high anodic response *A*' (I_p^a/I_p^c = 1, where I_p^a and I_p^c are the heights of the anodic and cathodic peaks, respectively). An increase in temperature from 20 to 40 °C results in a decrease in the value of $\Delta E_p = E_p^a - E_p^c$ (where E_p^a and E_p^c are the potentials of the anodic and cathodic peaks, respectively) from 60 to 45 mV. A decrease in temperature within the 20 to −80 °C range is accompanied by decrease in the height of peak *A* down to that of the one-electron peak at $t \le -80$ ° and by the appearance of the new cathodic irreversible peak *B* at more negative potentials. In addition, the pronounced irreversible peak *C* (Fig. 1, curve *2*) appears on the anodic branch of the CVA at these temperatures. It should be mentioned that peak *C* is not observed on the anodic branch of the CVA when the direction of scanning is changed, until reaching the potential range of peak *B* (Fig. 1, curve *2*, dotted line). Potentials of the cathodic and anodic peaks (E_p) observed on the CVA of complex **3** at different temperatures are presented in Table 1. In addition to the reduction, complex **3** can also be irreversibly two-electronically oxidized (E_p = 1.26 V, SCE), which is not studied in this work.

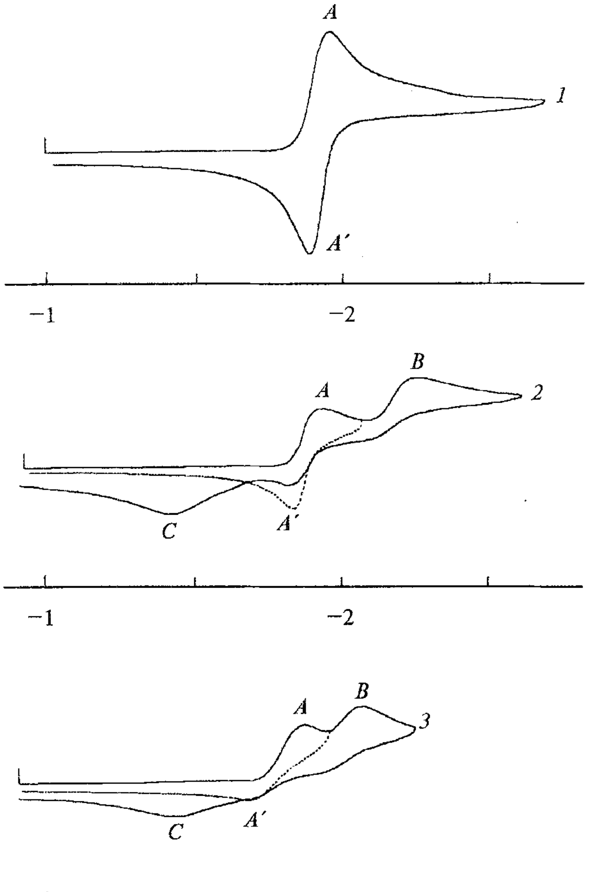


Fig. 1. Cyclic voltammograms of complexes **3** (*1, 2*; $1.1 \cdot 10^{-3}$ mol L^{-1}) and **2** (*3*; $1.2 \cdot 10^{-3}$ mol L^{-1}) in a THF/0.05 *M* Bu_4NPF_6 solution on the Pt-electrode at υ = 0.2 V s^{-1} and 20°C (*1*) and −80°C (*2, 3*). The heights of the peaks at different temperatures are normalized to the height of the one-electron peak of oxidation of decamethylferrocene under other equal conditions.

The data obtained allows one to assume that the reduction of complex **3** at room temperature is described by the $E_1C_1E_2$-scheme,[5] where E_1 and E_2 are the electrochemical steps and C_1 is the reversible chemical step of transformation of the 19ē-radical anion $3^{-\bullet}$ electrogenerated at the E_1 step. At increased temperatures, the rates of the direct and back reactions of the chemical step are fairly high in the time scale of cyclic voltammetry, which results in the observation of the reversible peak *A* on the CVA of complex **3**. The value of ΔE_p of the complex studied is greater than 30 mV, which is typical, for example, of the quinone/hydroquinone system in an aqueous acidic medium[5] and is described as the ECE-process with the fast reversible chemical step. This indicates that the chemical step C_1 is the rate-determining in the $E_1C_1E_2$-process considered. Finally, the fact of a decrease, but not an increase,

Table 1. Potentials of peaks on cyclic voltammograms of complexes **3, 4** and **2** in a THF/0.05 M Bu_4NPF_6 solution (Pt-electrode at υ = 0.2 V s^{-1}) at different temperatures

Complex	Peak	E_p/V (SCE)	
		20 °C	−80 °C
3	*A*	−1.95	−1.93
	A'	−1.89	−1.83
	B	—	−2.25
	C	—	−1.41
4	*A*	−1.76	−1.76
	A'	−1.70	−1.69
	B	—	−1.97
	C	—	−1.29
2	*A*	−1.82	−1.86
	A'	—	−1.69
	B	—	−2.04
	C	—	−1.42

in the value of $\Delta E_p = 2.303RT/nF$ for peak *A* as temperature increases (see above) rejects the possibility of the two-electron reduction of complex **3** according to the simple EE-scheme.

A decrease in temperature is accompanied by the decrease in the rate of chemical step C_1 up to its complete suppression in the time scale of cyclic voltammetry. This makes it possible to observe the subsequent one-electron reduction of 19$\bar{e}$-radical anion $\mathbf{3}^{-\cdot}$ generated at the E_1 step to dianion $\mathbf{3}^{2-}$ at potentials of peak *B* (step E_3). The irreversible character of peak *B* and the appearance of peak *C* on the anodic curve of the CVA suggest that there is the fast and irreversible chemical transformation of the electrogenerated 20$\bar{e}$-dianion $\mathbf{3}^{2-}$ (step C_2). Therefore, the electroreduction of complex **3** at low temperatures is described by the $E_1E_3C_2$-scheme.[5]

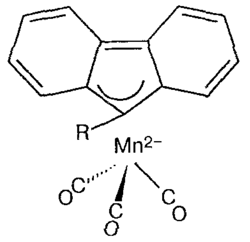
Similar electrochemical behavior is also characteristic of the complex $(\eta^5\text{-9-Bu}^t\text{-C}_{13}H_8)Mn(CO)_3$ (**4**). Potentials of the cathodic and anodic peaks on the CVA of this complex at different temperatures are presented in Table 1 (the designations of peaks observed are the same as those for complex **3**). The irreversible two-electron oxidation of complex **4** (E_p = 1.17 V, SCE) is not studied in this work.

Thus, the reduction of complexes **3** and **4** occurs *via* the same mechanism, which is described by the $E_1C_1E_2$-scheme at ~20°C and by the $E_1E_3C_2$-scheme at low temperatures.

Let us consider the possible nature of the C_2 step. It has recently been shown[6] that the two-electron reduction of the isoelectronic $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ complex, which resembles in structure complexes **3** and **4**, under the action of [K(18-C-6)]K (where 18-C-6 is 18-crown-6) in THF is accompanied by the $\eta^5 \rightarrow \eta^3$-type hapticity change (haptocoordination of the methylcyclopentadienyl ligand) to form the allyl type dianion $[\eta^3\text{-}C_5H_4Me)Mn(CO)_3]^{2-}$, which is rather stable at 0°C and is characterized by IR spectra. This allows one to assume the possibility of the similar reaction at the C_2 step, which is accompanied by the change in the type of binding of the five-membered ring of the fluorenyl ligand to the metal-containing group $Mn(CO)_3$. To check this hypothesis, we have studied the products of reduction of complexes **3** and **4** by the pyrene radical anion (E^0 = −2.1 V, SCE[7]) by low-temperature IR spectroscopy.

Two intense bands at 1584 and 1569 cm^{-1} are observed for the two-electron chemical reduction of complex **3** by the pyrene radical anion (THF, −80 °C) instead of the characteristic absorption bands (2008 and 1928 cm^{-1}) of carbonyl groups observed in the initial IR spectra. The observed value of the shift in absorption bands toward the long-wave region (~400 cm^{-1}) correlates with that (~350 cm^{-1}) obtained in the reduction of the complex $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ related to **3** to the dianion $[(\eta^3\text{-}C_5H_4Me)Mn(CO)_3]^{2-}$.[6] Similar changes in IR spectra also occur during the two-electron reduction of complex **4** by the pyrene radical anion. The reverse oxidation of the products of the two-electron reduction of complexes **3** and **4** by oxygen at low temperatures results in restoring the shapes of the initial spectra. According to the data of IR studies, the products of the two-electron reduction of complexes **3** and **4** above −40 to −30 °C are unstable and decompose to form unidentified products. Therefore, preliminary attempts to preparatively electroreduce initial complexes **3** and **4** at ~20°C were unsuccessful.

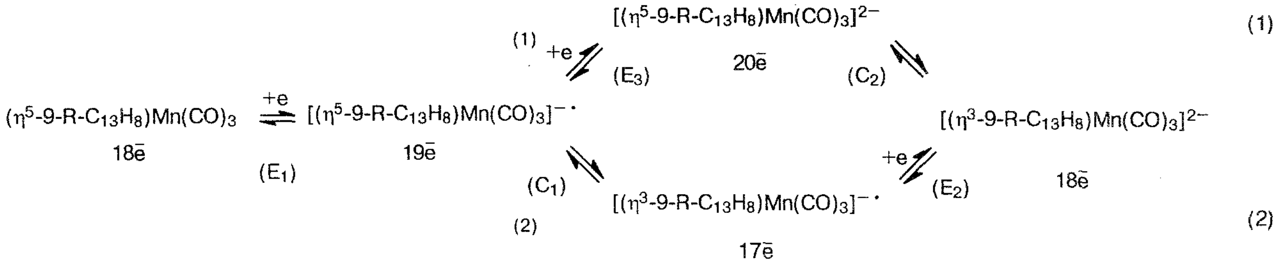
It can be assumed that at the C_2 step 20$\bar{e}$-η^5-dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$, which are electrogenerated at low temperatures at two subsequent one-electron steps, undergo rearrangement to change the type of haptocoordination of the fluorenyl ligand and to form the allyl type 18e$^-$-dianions $[(\eta^3\text{-9-R-}C_{13}H_8)Mn(CO)_3]^{2-}$ oxidized at the potentials of peak *C*. The reductive inducing of reactions of the change in haptocoordination of the π-ligand of $\eta^6 \rightarrow \eta^4$ and $\eta^5 \rightarrow \eta^3$ types is the established fact presently and is observed, *e.g.*, in the electrochemical and chemical reduction of organometallic complexes $[(\eta^5\text{-}C_5Me_5)M(\eta^6\text{-arene})]^{2+}$ (where M = Rh, Ir[8,9]), $[(\eta^5\text{-}C_9H_7)_2V(CO)_2]^+$ (where C_9H_7 is indenyl[2,10]), and $(\eta^6\text{-arene})Cr(CO)_3$.[11,12]



Now let us consider the nature of the chemical step C_1. It has previously been shown[4] that the one-electron reduction of η^5-fluorenylmanganesetricarbonyl complex **2** to the 19$\bar{e}$-state is not accompanied by the haptotropic shift of the $Mn(CO)_3$ group from the five- to six-membered ring of the fluorenyl ligand. This is caused by the strong electrophilic character of the $Mn(CO)_3$ group, due to which the coordination of this group at the site with the maximum electron density, *i.e.*, with the five-membered ring of the fluorenyl ligand, remains preferable even in the 19$\bar{e}$-state. Therefore, the C_1 step cannot be related to the inter-ring shift of the $Mn(CO)_3$ group.

Unlike transformations at low temperatures, chemical transformations that accompany the reduction of complexes **3** and **4** at room temperature (the C_1 step) occur at the step of 19$\bar{e}$-radical anions $\mathbf{3}^{-\cdot}$ and $\mathbf{4}^{-\cdot}$. The observed two-electron character of peak *A* indicates that the product formed at the C_1 step is reduced at more positive potentials than those of the reduction of the initial complex. It is quite logical to assume that this product is the electron-unsaturated 17$\bar{e}$-radical anion $[(\eta^3\text{-9-R-}C_{13}H_8)Mn(CO)_3]^{-\cdot}$. The fact that the values of oxidation potentials of 18$\bar{e}$ η^3-dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$

Scheme 1



(peak *C*) are by ~0.5 V more positive than the reduction potentials of the initial compounds (see Table 1) favors this assumption. Despite the irreversible character of peak C, the value of its potential can be used for estimating reduction potentials of 17ē-radical anions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{-\bullet}$ (the E_2 step). Therefore, one can draw the conclusion that the C_1 step is the reversible reaction changing the $\eta^5 \Leftrightarrow \eta^3$-type hapto-binding of the five-membered ring of the fluorenyl ligand at the step of 19ē-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$, which is accompanied by the formation of 17ē-radical anions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{-\bullet}$. This reaction can be classified at the *intra-ring haptotropic isomerization.* The similar reaction with the transformation of the 19ē particle to the 17ē particle due to the $\eta^5 \Leftrightarrow \eta^3$ haptoisomerization has previously been observed in the reduction of $[(\eta^5\text{-C}_9H_7)_2V(CO)_2]^+$.[2,10]

Thus, the two-electron reduction of complexes **3** and **4** results in the temperature-independent formation of the allyl type 18ē-dianions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$. These dianions are rather stable at low temperatures and can be characterized by IR spectra (see above). At ~20°C they are stable only in the time scale of cyclic voltammetry, *i.e.*, their lifetimes are several seconds. The overall scheme of reduction of complexes **3** and **4** can be presented as Scheme 1, according to which complexes **3** and **4** are quasi-reversibly reduced at low temperatures to stable 19ē-radical anions (peaks *A*/*A*′, Fig. 1). The quasi-reversible character of the electrodic reaction (ΔE_p = 100 and 70 mV at −80° C for complexes **3** and **4**, respectively, which are higher than ΔE_p = 40 mV at this temperature for the electrochemically reversible reaction[5]) is most likely caused by slowness of the electron-transfer step at low temperatures. The values of $E^0 = (E_p{}^a + E_p{}^c)/2$ for redox pairs $\mathbf{3}^{0/-\bullet}$ and $\mathbf{4}^{0/-\bullet}$ are −1.88 and −1.73 V (SCE), respectively. The further reduction of $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ results in the formation of unstable 20ē-η^5-dianions (peak *B*), undergoing rapid $\eta^5 \rightarrow \eta^3$ isomerization into 18ē-dianions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$ stable at $t < -40°$ C (Scheme 1, route (1)). The irreversible character of peak *B* even at low temperatures follows from the instability of η^5-dianions.

An increase in temperature to room temperature affects the kinetic stability of 19ē-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$, which undergo under these conditions the $\eta^5 \Leftrightarrow \eta^3$ reversible haptoisomerization to form 17ē-η^3-radical anions. These radical anions can be reduced easier than initial complexes and undergo the further one-electron reduction to 18ē-η^3-dianions at potentials of peak *A* (Scheme 1, route (2)). The $\eta^5 \Leftrightarrow \eta^3$ isomerization is the fast and reversible step, and η^3-dianions are stable in the time scale of cyclic voltammetry; therefore, the reversible pair of two-electron peaks *A*/*A*′ is observed on the CVA of complexes **3** and **4** at ~20°C.

In the range of intermediate temperatures (−50 to 0 °C), the reduction of complexes **3** and **4** occurs in parallel *via* routes (1) and (2) (Scheme 1). Both 19ē-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ and 20ē-η^5-dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ undergo $\eta^5 \rightarrow \eta^3$ isomerization. This results in the more difficultly interpreted shape of the CVA of complexes **3** and **4** at these temperatures due to overlapping of cathodic peaks *A* and *B* and anodic peaks *A*′ and *C*.

Thus, despite the fact that at different temperatures the two-electron reduction of the complexes studied occurs *via* different mechanisms, it is completed by the formation of the same products, the allyl type 18ē-dianions $[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}$. At ~20°C these dianions are unstable, cannot be obtained by preparative reduction, and are directly studied electrochemically. A decrease in temperature enhances the kinetic stability of these particles and makes it possible to observe their oxidation at potentials of peak *C*. The irreversible character of peak *C* and the absence of other additional signals except peak *A* on the cathodic branch of the CVA when the direction of scanning is changed after reaching the potential of peak *C* suggests that oxidation of η^3-dianions results in regeneration of the initial complexes (Scheme 2).

For the second one-electron step in Scheme 2, the measured and presented above values of E^0 are more negative than the values of the potential of peak *C*. Therefore, this peak should correspond to the two-

Scheme 2

$$\underset{18\bar{e}}{[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{2-}} \xrightleftharpoons{-e} \underset{17\bar{e}}{[(\eta^3\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{-\bullet}} \rightleftharpoons \underset{19\bar{e}}{[(\eta^5\text{-9-R-C}_{13}H_8)Mn(CO)_3]^{-\bullet}} \xrightleftharpoons{-e} \underset{18\bar{e}}{(\eta^5\text{-9-R-C}_{13}H_8)Mn(CO)_3}$$

electron process. Peak *C* is shorter than the expected two-electron peak (Fig 1, curve *2*), which is typical of pulse electrochemical methods, in particular, of cyclic voltammetry when generation of a particle due to the EC- and/or EEC-process occurs upon direct run of the potential scanning and the registration is performed with reverse potential scanning, and potentials of generation and registration differ considerably, while the scanning rate is relatively low. This is caused by a decrease in the near-electrodic concentration of registered particles (in this case, η^3-dianions) due to partial diffusion from the electrode deep in solution during the scanning time from the generation potential (peak *B*) to the registration potential (peak *C*).

It should be mentioned that when Scheme 2, describing the process of low-temperature oxidation of η^3-dianions at potentials of peak C, is considered from right to left, it is adequate to the mechanism of reduction of complexes **3** and **4** at ~20°C *via* route (2) presented in Scheme 1. Therefore, the temperature effect on the mechanism of reduction of complexes studied is determined in fact by the difference in stabilities of $19\bar{e}$-radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ at different temperatures.

In addition to the temperature factor, the kinetic stability of $19\bar{e}$-radical anions of η^5-fluorenylmanganesetricarbonyl complexes depends on substituents at position 9 of the fluorenyl ligand and, as shown in this work, it increases substantially on going from the nonsubstituted complex **2** to its substituted analogs **3** and **4**. It can be assumed that the presence of bulky substituents at the five-membered rings of complexes **3** and **4** results in steric hindrances for the interaction between radical anions and dianions of these complexes, which are strong nucleophiles, and electrophilic admixtures, whose trace amounts are inevitably present in solution, and/or cations of the base electrolyte. Therefore, radical anions and dianions of complexes **3** and **4** are kinetically more stable, which allows one to observe reactions of their intra-ring haptoisomerization.

It has been shown previously[4] that the irreversible one-electron peak *A* is observed at room temperature on the CVA of complex **2** (Fig. 1), which indicates the kinetic instability of the electrogenerated $19e^-$-radical anion $\mathbf{2}^{-\bullet}$. Nevertheless, at ≤ −80 °C the shape of the CVA curve of the nonsubstituted complex **2** is qualitatively similar to the CVA curve of complexes **3** and **4** (Fig. 1, curve *3*). Therefore, the mechanism of reduction of complex **2** at low temperatures also can be described by route (1) of Scheme 1. At ~20°C the electrogenerated radical anion $\mathbf{2}^{-\bullet}$ is unstable in the time scale of cyclic voltammetry and decays to form electrically inactive products.

It is quite probable that the process of the redox-induced change in the type of $\eta^5 \rightarrow \eta^3$ haptocoordination, due to which the $20e^-$-particles generated gain stable $18e^-$-configurations because the hapticity of the π-ligand decreases, is typical of many complexes containing η^5-cyclopentadienyl type ligands. In addition to η^5-indenyl complexes, which are characteristic of $\eta^5 \rightarrow \eta^3$ isomerization due to the "indenyl effect",[13] the fact that there are only few experimentally proved examples of reductive inducing $\eta^5 \rightarrow \eta^3$ haptoisomerization reactions for complexes with other η^5-ligands[6] is probably related to the kinetic instability both of intermediate reduction products (the corresponding $19e^-$-radical particles) and $18\bar{e}$-η^3-complexes.

Thus, unlike the $\eta^6 \Leftrightarrow \eta^5$ *inter-ring* haptotropic rearrangement (see Ref. 4), which is induced by electron transfer and is characteristic of η^6-fluorenylmanganesetricarbonyl complexes, the reductive activation of η^5-fluorenylmanganesetricarbonyl complexes causes the $\eta^5 \Leftrightarrow \eta^3$ *intra-ring* haptoisomerization. The intra-ring haptoisomerization can occur at the steps both of $19\bar{e}$-radical anions and $20\bar{e}$-dianions.

The driving force of the inter-ring haptotropic rearrangement is the tendency of the electrophilic metal-containing group to occupy the coordination site with the polydentate π-ligand with optimum nucleophilic properties, as has previously been shown for manganese,[4] iron,[14,15] and chromium[16] fluorenyl π-complexes. This haptotropic rearrangement occurs without change in the electron configuration of the complex. The driving force of the $\eta^5 \Leftrightarrow \eta^3$ intra-ring haptoisomerization is the tendency of the complex to change its electron state ($19\bar{e} \rightarrow 17\bar{e}$ or $20\bar{e} \rightarrow 18\bar{e}$) by "removing" electrons from boundary antibonding orbitals due to a decrease in the hapticity of the π-ligand.

Experimental

Electrochemical measurements were carried out in a dry argon atmosphere in THF preliminarily purified by the ketyl method and distilled directly into an evacuated and filled with Ar electrochemical cell according to the previously described procedure.[17] A 0.05 *M* solution of Bu_4NPF_6 was used as the supporting electrolyte. Tetrabutylammonium hexafluorophosphate was preliminarily dehydrated by fusing *in vacuo*. Low-temperature electrochemical measurements were carried out in a cell that was thermostated with ethanol cooled with liquid nitrogen in a Dewar flask.

All potentials were measured relative to an aqueous saturated calomel electrode (SCE) by referring the potential of the reference electrode (Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the studied solution in the cell by a bridge filled with the solution of the supporting electrolyte, to the potential of the redox-transition decamethylferrocene$^{0/+}$ (E^0 = 0.00 V, SCE in THF).

A disk platinum electrode 1 mm in diameter, which had been sealed in glass and polished with a diamond paste (grain size ≤1 μm), was used as the working electrode. Cyclic voltammograms were recorded by a PAR 175 signal generator and a PAR 173 potentiostat with compensation of ohmic losses.

Preparative electrolysis at controlled potential was carried out using a PAR 173 potentiostat and a PAR 179 coulometer on an electrode of the platinum net in a two-chamber glass cell, whose cathodic and anodic spaces were separated by a porous glass filter. The depth of electrolysis was controlled at regular intervals by voltammetric and IR monitoring.

All syntheses were performed in an atmosphere of dry argon using anhydrous solvents. A usual incandescent lamp (200 W) was used for irradiation. The progress of reactions was controlled by TLC on Silufol plates and by IR spectra. Silpearl silica gel (40 to 100 μm) (Sklo Union, Czech Republic) was used for column chromatography. IR spectra at room temperature were recorded on a Specord 75 IR spectrometer, while IR spectra at low temperatures were recorded on a Specord M 82 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-200 instrument with working frequencies of 200.13 and 50.31 MHz, respectively (CD_2Cl_2, TMS as the internal standard).

Initial 9-phenylfluorene and 9-(*tert*-butyl)fluorene were synthesized by the known procedures (Refs. 18 and 19, respectively).

The complex (η^5-9-Bu^t-$C_{13}H_8$)Mn(CO)$_3$ (**3**) was prepared in a 41 % yield by the procedure similar to that used previously[20] for preparing nonsubstituted η^5-fluorenylmanganesetricarbonyl and was isolated as large orange crystals, m.p. 196°C (from hexane). IR (hexane, ν/cm^{-1}): 2019, 1942, 1937 (C≡O). ^{1}H NMR (δ, ppm): fluorenyl: 8.18 (m, 2 H); 7.99 (m, 2 H); 7.27 (m, 4 H); 1.85 (s, 9 H, 3 CH_3). ^{13}C NMR (δ, ppm): 226.03 (2 CO); 216.02 (1 CO); fluorenyl: 127.82; 126.10; 125.61; 124.30; 106.54; 94.46; C_9 91.11; $\underline{C}Me_3$ 34.92; CH_3 32.24.

The complex (η^5-9-Ph-$C_{13}H_8$)Mn(CO)$_3$ (**4**) was prepared in a 47 % yield by the procedure used previously[21] for preparing nonsubstituted η^5-fluorenylmanganesetricarbonyl and was isolated as large orange crystals, m.p. 128 °C (from hexane). IR (hexane, ν/cm^{-1}): 2023, 1948, 1942 (C≡O). ^{1}H NMR (δ, ppm): fluorenyl: 8.17 (m, 2 H); 7.89 (m, 2 H); 7.31 (m, 4 H); 7.57 (m, 5 H, Ph). ^{13}C (δ, ppm): 225.67 (3 CO); fluorenyl: 131.43; 129.29; 125.28; 123.94; 106.78; 94.21; C_9 83.16; Ph 133.58; 128.47; 128.21; 125.52. The structure of complex **4** is confirmed by the data of X-ray diffraction analysis, the results of which will be published elsewhere.

Low-temperature reduction of complexes 3 and 4 by the pyrene radical anion. In a typical experiment, a titrated solution of a two-fold excess (0.05 mmol) of pyrene radical anion (preliminarily prepared by the reduction of pyrene by Na metal) in THF was added to a frozen with liquid nitrogen solution of 0.025 mmol of complex **3** or **4** in 25 mL of THF in an Ar atmosphere. After increasing the temperature to −80 °C, the reaction mixture under Ar pressure was transferred into a cell (CaF_2) preliminarily filled with Ar and thermostated at −80 °C, and IR spectra were recorded. For comparison, spectra of the initial complex **3** or **4** were recorded under the same conditions but without a reducing agent.

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References

1. D. Astruc, *Chem. Revs.*, 1988, **88**, 1189.
2. *Organometallic Radical Processes*, Ed. W. C. Trogler, Elsevier, Amsterdam, 1990.
3. V. V. Strelets, *Coord. Chem. Rev.*, 1992, **114**, 1.
4. S. V. Kukharenko, L. N. Novikova, V. V. Strelets, N. A. Ustynyuk, and A. I. Yarmolenko, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1805 [*Russ. Chem. Bull.*, 1994, 1710 (Engl. Transl.)].
5. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, 1980.
6. S. Lee and N. J. Cooper, *J. Am. Chem. Soc.*, 1991, **113**, 716.
7. C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker, Inc., N. Y., 1970.
8. W. J. Bowyer and W. E. Geiger, *J. Am. Chem. Soc.*, 1985, **107**, 5657.
9. W. J. Bowyer, J. W. Merkert, W. E. Geiger, and A. L. Rheingold, *Organometallics*, 1989, **8**, 191.
10. G. A. Miller, M. J. Therien, and W. C. Trogler, *J. Organomet. Chem.*, 1990, **383**, 271.
11. S. N. Milligan and R. D. Rieke, *Organometallics*, 1983, **2**, 171.
12. R. D. Rieke, W. P. Henry, and J. S. Arney, *Inorg. Chem.*, 1987, **26**, 420.
13. A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 441; M. E. Rerek, L.-N. Ji, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 1983, 1208.
14. S. V. Kukharenko, V. V. Strelets, N. A. Ustynyuk, L. N. Novikova, M. G. Peterleitner, and L. I. Denisovich, *Metalloorg. Khim.*, 1991, **4**, 299 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
15. L. N. Novikova, B. A. Mazurchik, N. A. Ystynyuk, S. V. Kukharenko, and V. V. Strelets, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 319 [*Russ. Chem. Bull.*, 1994, 136 (Engl. Transl.)].
16. S. V. Kukharenko, L. N. Novikova, V. V. Strelets, and N. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 48 [*Russ. Chem. Bull.*, 1994, 41 (Engl. Transl.)].
17. S. V. Kukharenko, G. L. Soloveichik, and V. V. Strelets, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1020 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, 926 (Engl. Transl.)].
18. F. Ullmann and R. Wurstemberger, *Ber. Dtsch. Chem. Ges.*, 1904, **37**, 73.
19. F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, 1956, **34**, 991; P. M. G. Bavin, *Anal. Chem.*, 1960, **32**, 554.
20. P. M. Treichel and J. W. Johnson, *Inorg. Chem.*, 1977, **16**, 749.
21. R. B. King and A. Efraty, *J. Organomet. Chem.*, 1970, **23**, 527.

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