# Organometallic Chemistry

## Electron-transfer induced haptotropic isomerization of fluorenylmanganesetricarbonyl complexes: electrocatalytic and chain mechanisms

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The electrochemical reduction of $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ (**1**, where $C_{13}H_9$ — fluorenyl) has been studied in THF by cyclic voltammetry and preparative controlled potential electrolysis. One-electron reduction of **1** to the corresponding 19-electron radical anion $\mathbf{1}^{\bullet-}$ is accompanied by the haptotropic isomerization of the latter to the radical anion $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet-}$ ($\mathbf{2}^{\bullet-}$), which is oxidized at the electrode to neutral complex **2**. Electron-transfer induced isomerization **1** → **2** is an electrocatalytic process with current efficiency of 600 %, which can be also promoted by catalytic amounts ($\leq$20 %) of the chemical reducing agents (benzophenone radical anion or sodium amalgam). If the reaction is chemically induced, the radical anion $\mathbf{2}^{\bullet-}$ is oxidized by initial complex **1**; as a result the electron-transfer induced isomerization **1** → **2** proceeds by a chain mechanism. The influence of the electronic state ($18e^-/19e^-$) of $\eta^6$- and $\eta^5$-fluorenyl complexes on the position of the equilibrium of the intra-ring haptotropic isomerization reaction is discussed.

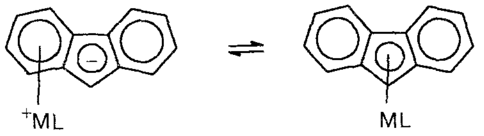
**Key words:** fluorenylmanganesetricarbonyl, haptotropic rearrangements, electron-transfer induced reactions, electrocatalysis, cyclic voltammetry.

The reaction of inter-ring haptotropic isomerization of fluorenyl complexes of cyclopentadienyliron and chromiumtricarbonyl may be induced either thermally[1] or by electrochemical reduction of the initial 18-electron ($18\bar{e}$) complexes to the corresponding $19\bar{e}$-radical-ions.[2,3] The rate of the isomerization induced by the electrochemical method is several orders of magnitude higher than that induced thermally. In the case of the thermal isomerization of $18\bar{e}$-complexes the equilibrium [Eq. (1); ML = $Fe(\eta^5\text{-}C_5H_5)$, $Cr(CO)_3{}^-$] is shifted to

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1805—1809, October, 1994.

the $\eta^5$-isomer, while in the case of the electrogenerated 19$\bar{e}$-state the $\eta^6$-isomer predominates in the equilibrium mixure.[2,3]

At present there are no criteria that allow one to predict the position of the equilibrium of type 1 inter-ring haptotropic rearrangements based on the nature of the polycyclic aromatic ligand, the migrating ML-group, or the electronic state of the complex.



(1)

**1** **2**

For the example of 18$\bar{e}$-chromiumtricarbonyl complexes of the fluorenyl anion and its carbo- and heterocyclic analogs it was shown[4] that the proportion of $\eta^5$-isomer in the equilibrium mixture increases with the increase in $\pi$-electron density in the five-membered ring of the polycyclic ligand. This allows one to propose that the driving force of rearrangement (1) in the 18$\bar{e}$-state is the tendency of the electrophilic ML-group to occupy the position with the maximum electron density in the fluorenyl ligand.[1]

It is known[5,6] that in the reduction of sandwich and half sandwich complexes of transition metals the unpaired electron is localized on the molecular orbital, whose main contribution comes from the atomic orbital of the metal. For this reason, the electrophilic properties of the migrating ML-group in the 19$\bar{e}$-state of the complex should decrease. Since the transition to the 19$\bar{e}$-state is accompanied by migration of the ML-group to a position with lower electron density, it is possible to assume that the nature of the most thermodynamically stable isomer ($\eta^5$ or $\eta^6$) is determined by the congruence of the electrophilic properties of the migrating group and the electron density of the five- or six-membered fragment of the fluorenyl ligand. This hypothesis is in agreement with the principle of hard and soft acids and bases.[7] According to this principle, coordination at a position with high electron density should correspond to a strong electrophile and vice versa. Therefore, the decrease in the electrophilic properties of the ML-group in the transition to the 19$\bar{e}$-state should be accompanied by migration of this group to a position with lower electron density, *i.e.*, to the six-membered ring of the fluorenyl ligand. However, if the electrophilicity of the ML-group were high enough even in the transition to the 19$\bar{e}$-state of the complex, one would expect that the $\eta^5$-isomer would be the most thermodynamically stable in the 18$\bar{e}$- and 19$\bar{e}$-states.

Such behaviour should be characteristic of isomeric $\eta^5$- and $\eta^6$-fluorenylmanganesetricarbonyl complexes for which,[8] as for the corresponding chromiumtricarbonyl[1] and ironcyclopentadienyl[1] analogs, the reaction of haptotropic rearrangement (1) is typical. Besides this, in the nucleophilic substitution of halides in $(\eta^6\text{-}C_6H_5X)ML^+$ complexes (where X = halide, ML = $Cr(CO)_3^-$, $Fe(\eta^5\text{-}C_5H_5)$, $Mn(CO)_3$), the reactivity changes in the following series[9]: $Cr(CO)_3^- < Fe(\eta^5\text{-}C_5H_5) \ll Mn(CO)_3$, *i.e.*, of these $d^6$-organometallic fragments the manganesetricarbonyl group exhibits the most electrophilic properties. In connection with this, we have studied the reactivity of $\eta^5$- and $\eta^6$-fluorenylmanganesetricarbonyl complexes in the reaction of inter-ring haptotropic rearrangement induced by electron transfer.

## Results and Discussion

The cyclic voltammograms (CVA) of isomeric complexes $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ (**1**) and $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ (**2**) in THF in the region of cathode potentials are practically identical (Fig. 1, curves *1* and *3*): at the voltammogram of the each isomer the irreversible diffusive peak *A* is observed ($Ip \cdot \upsilon^{-1/2}$ = const, where *I*p is the peak height, $\upsilon$ is the rate of linear sweep of the potential). The height of peak *A* is comparable with the height of the one-electron peak of the oxidation of ferrocene, all other conditions being the same. However, the oxidation of complexes **1** and **2** is observed at different potentials (peaks *A'* and *B'*, respectively). In addition, along with peak *A* on the CVA of the $\eta^6$-isomer of **1** the cathode peak *B* with a very small height is observed at more positive potentials (Fig. 1, inset). The ratio of peak heights *B* : *A* increases as $\upsilon$ increases (in the interval of 0.02—0.5 V $s^{-1}$) and/or as the temperature drops (in the interval 20÷−70 °C), but it always remains significantly less than unity. If the potential of the electrode is kept at the peak *B* potential with the subsequent sweep of the potential to the anode region, peak *A'* of oxidation of the $\eta^5$-isomer appears in the anodic part of the CVA of complex **1** along with peak *B'* of the oxidation of the $\eta^6$-isomer (Fig. 1, curve *2*). The potentials of the anodic and cathodic peaks of complexes **1** and **2** ($E_p$) observed on the CVA are given in Table 1. The anodic peaks of the low height marked on Fig. 1 by an asterisk are detected only at the potential of peak *A*. They are probably connected with the oxidation of the products of irreversible reduction at the potential of this peak. The nature of these products was not studied in this work.

Preparative electroreduction of the $\eta^6$-isomer **1** at the potential of peak *B* is accompanied by the formation of the $\eta^5$-isomer **2**. This follows from the appearance of peak *A'* on the anodic branch of the CVA and the absorption bands of complex **2** in the carbonyl region of the IR spectrum (2018, 1934 $cm^{-1}$; *cf.* Ref. 8) of the catholyte solution. According to the data of voltammetric and IR monitoring, the complete conversion of the $\eta^6$-isomer **1** to the $\eta^5$-isomer **2** is reached only after the consumption of 0.17 F $mol^{-1}$, which corresponds to a current efficiency of 600 %.

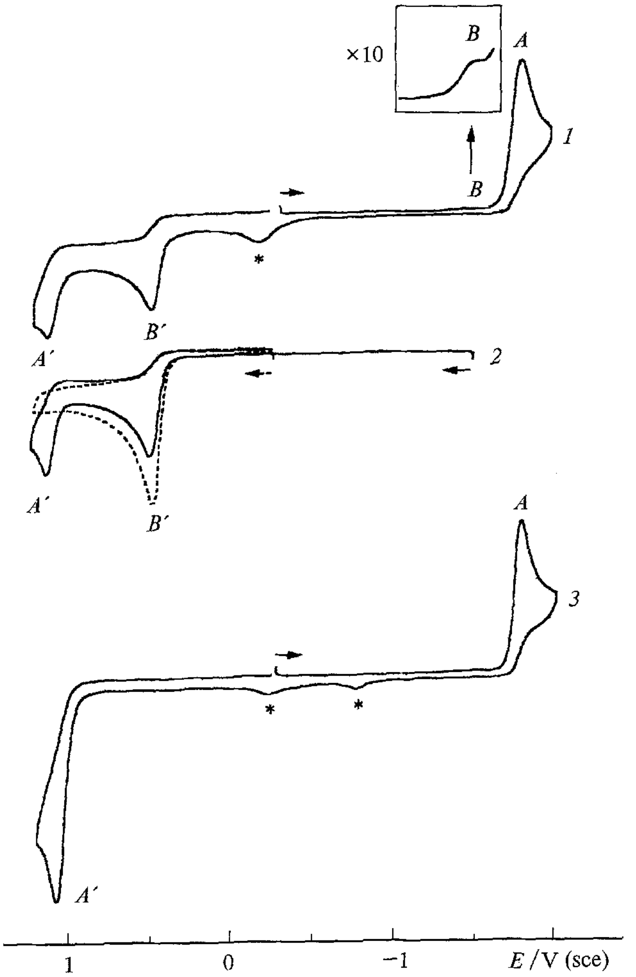


**Fig. 1.** Cyclic voltammogram of isomeric complexes **1** (*1,2*; $1 \cdot 10^{-3}$ *M*) and **2** (*3*; $1 \cdot 10^{-3}$ *M*) in THF/0.05 *M* $Bu_4NPF_6$ at the platinum electrode at $v$ = 0.2 V $s^{-1}$ and 20 °C; (the initial directions of the sweep of the electrode potential are shown by horizontal arrows; inset shows peak *B* at a 10-fold increase in sensitivity).

**Table 1.** The potentials of peaks on the cyclic voltammograms of isomeric complexes **1** and **2** in THF/0.05 M $Bu_4NPF_6$ (Pt-electrode at $v$ = 0.2 V $s^{-1}$ and 20 °C)

| Complex | Peak | $E_p$/V, sce |
|---|---|---|
| $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ (**1**) | *A* | −1.83 |
| | *B* | −1.51 |
| | *A′* | 1.08 |
| | *B′* | 0.44 |
| $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ (**2**) | *A* | −1.82 |
| | *A′* | 1.10 |

The data given above indicate that the 19ē-radical anion $\mathbf{1}^{\cdot-}$ generated at the potential of the peak *B* undergoes fast haptotropic isomerization to form $\mathbf{2}^{\cdot-}$. Since the potential of the electrode is significantly more positive than the potential of reduction of **2** (see Table 1, peak *A*), the rapid oxidation of the radical anion $\mathbf{2}^{\cdot-}$ to the corresponding 18ē-complex takes place at the electrode. Superposition of the reduction processes of the initial complex **1** and the oxidation of the forming radical anion $\mathbf{2}^{\cdot-}$ proceeding at the potential of peak *B* can account for the observed low height of this peak. Thus, the mechanism of the electroreduction of the $\eta^6$-isomer **1** is described by a catalytic $E_1CE_2$-scheme (where $E_1$ corresponds to the stage of direct electron transfer, $E_2$ — to reverse electron transfer, and C — to the reaction of inter-ring haptotropic isomerization).

**Scheme 1**

$$(\eta^6\text{-}C_{13}H_9)Mn(CO)_3 \overset{+e}{\rightleftharpoons} (\eta^6\text{-}C_{13}H_9)Mn(CO)_3{}^{\cdot-} \qquad (E_1)$$

$$(\eta^6\text{-}C_{13}H_9)Mn(CO)_3{}^{\cdot-} \rightleftharpoons (\eta^5\text{-}C_{13}H_9)Mn(CO)_3{}^{\cdot-} \qquad (C)$$

$$(\eta^5\text{-}C_{13}H_9)Mn(CO)_3{}^{\cdot-} \overset{-e}{\rightleftharpoons} (\eta^5\text{-}C_{13}H_9)Mn(CO)_3 \qquad (E_2)$$

The existence of the stage of reverse electron transfer $E_2$ makes possible the catalytic haptotropic isomerization of complex **1** induced by electron transfer with a current efficiency of more than 100 %. In an ideal case, the quantity of electricity consumed in a catalytic ECE-process with an irreversible C-stage should be close to zero. The fact that the observed amount of electricity consumption (0.17 F $mol^{-1}$) necessary for the complete conversion of the $\eta^6$-isomer **1** to the $\eta^5$-isomer **2** is distinct from zero indicates that the haptotropic isomerization in 19ē-state (Eq. (1)) is reversible, although the equilibrium is significantly shifted to the right.

In principle, the reverse transfer of an electron from the forming radical anion $\mathbf{2}^{\cdot-}$ to either the electrode (heterogeneous transfer) or the initial complex **1** (homogeneous transfer), which is reduced more easily than the $\eta^5$-isomer **2** (see Table 1) can occur. Since at the potential of peak *B* the concentration of the initial $\eta^6$-isomer **1** in the layer near the electrode is negligibly small, the homogeneous transfer of an electron in the reaction of haptotropic isomerization induced electrochemically is not very probable. The homogeneous stage of the reverse transfer of an electron can be realized if a chemical reducing agent is used instead of an electrode. This allows the transition from an electrocatalytic reaction mechanism to a chain process (Scheme 2).

The reducing agent, Red, is necessary in catalytic quantities only at the stage of chain generation, $E_1$, but it is not involved in the further steps of the reaction.

We used either the radical anion of benzophenone ($E^0$ = −1.72 V, see Ref. 10) or sodium amalgam as the chain initiator. In this case no more than 20 % of the stoichiometric quantity of reducing agent (assuming one-electron reduction) was necessary to complete the con-

**Scheme 2**

$$(\eta^6\text{-}C_{13}H_9)Mn(CO)_3 + Red \rightleftharpoons (\eta^6\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet -} + Ox$$

$$(\eta^6\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet -} \rightleftharpoons (\eta^5\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet -}$$

$$(\eta^5\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet -} + (\eta^6\text{-}C_{13}H_9)Mn(CO)_3 \rightleftharpoons$$

$$\rightleftharpoons (\eta^5\text{-}C_{13}H_9)Mn(CO)_3 + (\eta^6\text{-}C_{13}H_9)Mn(CO)_3{}^{\bullet -}$$

version of **1** to **2**. The value obtained is close to the amount of electricity consumption required for the complete conversion of the $\eta^6$-isomer to the $\eta^5$-isomer in electrochemical induction.

The $\eta^5$-isomer is the most thermodynamically stable isomer in the 18e$^-$-state of the complexes $(C_{13}H_9)Fe(C_5H_5)$, $(C_{13}H_9)Cr(CO)_3{}^-$, and $(C_{13}H_9)Mn(CO)_3$ (see Refs. 11,4,8, respectively). Unlike the fluorenyl complexes of iron[2] and chromium[3] studied before, in which the $\eta^6$-isomer prevails in the 19ē-state, for $(C_{13}H_9)Mn(CO)_3$ complexes, as it was shown above, the most thermodynamically stable isomer in the reduced state remains the $\eta^5$-isomer. This distinction may be accounted for from the point of view of the mutual congruence of the electrophilic properties of the migrating ML-group and the electron density of the coordinated ring of the fluorenyl ligand. In a series of complexes $(\eta^5\text{-}C_{13}H_9)ML$ and $(\eta^6\text{-}C_{13}H_9)ML$ (ML = $Fe(C_5H_5)$, see Ref. 2; $Cr(CO)_3{}^-$, see Ref. 3; $Mn(CO)_3$, see Table 1) the manganese compounds are characterized by the most positive reduction potentials. This fact suggests that the $Mn(CO)_3$ group has stronger electrophilic properties than $Fe(C_5H_5)$ and $Cr(CO)_3{}^-$. Even in the 19ē-state of the complex the electrophilic properties of the $Mn(CO)_3$ group remain strong enough to keep the preferable coordination of this group at the position with the maximum electron density, *i.e.*, at the five-membered ring of the fluorenyl ligand.

For all fluorenyl complexes of iron, chromium, and manganese studied the $\eta^5$-isomer is more difficult to reduce than the $\eta^6$-isomer (see Table 1). However, only for the manganese complexes is equilibrium (1) in the 19ē-state shifted to the radical anion of the $\eta^5$-isomer, which is easier to oxidize. This allows the realization of *the electron transfer induced reaction of* $\eta^6\to\eta^5$*-isomerization in either an electrocatalytic or chain mode.* For the complexes of iron and chromium the electron transfer induced isomerization proceeds in the opposite direction: $\eta^5\to\eta^6$ (see Refs. 2,3). As the reverse transfer of the electron from the 19ē-$\eta^6$-isomer formed during the isomerization either to the electrode or to the initial $\eta^5$-complex is not possible, the reduction of the initial $\eta^5$-isomer occurs only stoichiometrically.

The influence of the electronic state of the fluorenyl complexes $(C_{13}H_9)ML$ (18ē or 19ē) on equilibrium (1) can be accounted for with the help of the thermodynamic cycle:

**Scheme 3**

$$\begin{tikzcd}
(\eta^6\text{-}C_{13}H_9)ML \arrow[r, shift left, "+e"] \arrow[d, shift left] & (\eta^6\text{-}C_{13}H_9)ML^{\bullet -} \arrow[l, shift left, "E^0{}_6"] \arrow[d, shift left] \\
(\eta^5\text{-}C_{13}H_9)ML \arrow[r, shift left, "+e"] \arrow[u, shift left, "\Delta G^0{}_{18}"] & (\eta^5\text{-}C_{13}H_9)ML^{\bullet -} \arrow[l, shift left, "E^0{}_5"] \arrow[u, shift left, "\Delta G^0{}_{19}"']
\end{tikzcd}$$

where $\Delta G^0{}_{18}$ and $\Delta G^0{}_{19}$ are the changes in the free energy of the reaction of isomerization (1) for the 18ē- and 19ē-states, and $E^0{}_6$ and $E^0{}_5$ are the reduction potentials of $\eta^6$- and $\eta^5$-isomers, respectively. Then $\Delta G^0{}_{18} - \Delta G^0{}_{19} = F\cdot(E^0{}_6 - E^0{}_5)$, or $\ln K_{18}/K_{19} = F/RT\cdot\Delta E$, where $K_{18}$ and $K_{19}$ are the corresponding constants of the equilibrium, F is the Faraday constant, and $\Delta E = E^0{}_6 - E^0{}_5$. Since for the studied complexes of iron,[2] chromium,[3] and manganese (see Table 1) the value of $\Delta E$ is positive, then it is obvious that upon the transition of the complex from the 18ē-state to the 19ē-state the constant of equilibrium (1) decreases and the degree of this decrease is determined by the value of $\Delta E$.

Thus, the transition of the complex from 18ē-state to the 19ē-state for the fluorenylmanganesetricarbonyl complexes and for the ironcyclopentadienyl analogs is accompanied by a decrease in the equilibrium constant of inter-ring haptotropic rearrangement (1). The stronger electrophilic character of the $Mn(CO)_3$ group, as compared to $Fe(C_5H_5)$ and $Cr(CO)_3{}^-$, causes a significant shift of equilibrium (1) of $(C_{13}H_9)Mn(CO)_3$ in the direction of the $\eta^5$-isomer in the 18ē- and 19ē-states. This, in turn, allows the electron transfer induced reaction of haptotropic **1**→**2** isomerization to occur either by an electrocatalytic or chain mechanism.

## Experimental

Complexes **1** and **2** were obtained according to the known procedures.[8]

The electrochemical measurements were performed in an atmosphere of dry Ar in THF. The THF was purified by the ketyl method and then distilled directly into an evacuated electrochemical cell which was then filled with Ar as described earlier.[12] The supported electrolyte was a 0.05 *M* solution of $Bu_4NPF_6$, which was dehydrated by fusing *in vacuo*. The electrochemical measurements at low temperatures were carried out in a cell termostatted by ethanol cooled with liquid nitrogen in a Dewar flask.

All potentials were measured relative to a saturated calomel electrode (sce). The potential of the reference electrode (Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution under investigation by a bridge with the supported electrolyte, was referred to the potential of the redox transition of ferrocene$^{0/+}$ ($E^0$ = 0.44 V, sce).

A disk platinum electrode sealed in glass and polished with a diamond paste (grain size 1 μm) was used as the working electrode. The cyclic voltammograms were recorded using a PAR 173 potentiostat with compensation of ohmic losses and a PAR 175 signal generator.

IR spectra were recorded using a Specord 75 IR spectrometer.

Electrolysis at the controlled potential was carried out with a PAR 173 potentiostat on a of platinum gauze electrode in a two chamber glass cell in which catholyte and anolyte were separated by a porous glass filter. The progress of the electrolysis was monitored by voltammetry and by periodic registration of the IR spectra of the catholyte solution.

**Reduction of ($\eta^5$-$C_{13}H_9$)Mn(CO)$_3$ by the radical anion of benzophenone.** The corresponding aliquot of a titrated solution of $Na^+Ph_2CO^{\bullet -}$ in THF (prepared by reduction of benzophenone by Na metal) was added with stirring using a microsyringe to a solution of 0.024 g (0.08 mmol) of **1** in 20 mL of THF under Ar. The reaction mixture was kept for 10 min and then the IR spectrum was recorded. This procedure was repeated until **1** was completely converted to **2**. The total quantity of reducing agent necessary for complete conversion of **1** to **2** in three independent experiments was 18±1 % of the stoichiometric quantity (assuming one-electron reduction). In the absence of a reducing agent no change in the IR spectrum of the initial solution was observed.

**Reduction of ($\eta^6$-$C_{13}H_9$)Mn(CO)$_3$ by a sodium amalgam.** Three mL of 0.033 % sodium amalgam (0.6 mmol Na) was added with vigorous stirring to a solution of 0.18 g (0.59 mmol) of **1** in 30 mL of THF under Ar. When conversion of **1** to **2** was complete (IR data), the content of sodium in the amalgam was determined by reverse titration. In a typical experiment the complete conversion of **1** to **2** required 0.12 mmol of Na in the amalgam, which is 20 % of the stoichiometric quantity (assuming one-electron reduction).

This work was supported in part by the Russian Foundation for Basic Research (Project No. 93-03-05209) and the International Science Foundation (Grant No. REV 000).

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*Recieved July 3, 1994*