Investigation of the redox properties of polynuclear "ladder" complexes containing Cr, Mn, and Fe

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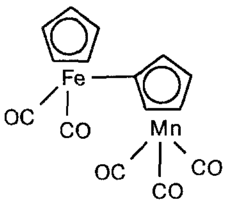
The redox potentials of new Cr, Mn, and Fe polynuclear "ladder" complexes, $(\eta^5\text{-Cp})\text{Fe(CO)}_2(\eta^1,\eta^5\text{-C}_5\text{H}_4)\text{Fe(CO)}_2(\eta^1,\eta^5\text{-C}_5\text{H}_4)\text{Mn(CO)}_3$, $(\eta^5\text{-Cp})\text{Fe(CO)}_2(\eta^1,\eta^5\text{-C}_5\text{H}_4)\text{Mn(CO)}_3$, $(\eta^5\text{-Cp})\text{Fe(CO)}_2(\eta^1,\eta^6\text{-Ph})\text{Cr(CO)}_3$, $(\eta^5\text{-Cp})\text{Fe(CO)}_2(\eta^1,\eta^5\text{-C}_5\text{H}_4)\text{Fe(CO)}_2\text{CH}_2\text{Ph}$, $(\eta^5\text{-Cp})\text{Fe(CO)}_2(\eta^1,\eta^6\text{-CH}_2\text{Ph})\text{Cr(CO)}_3$, were measured and the mechanism of their electrochemical oxidation and reduction was suggested. It was shown that the σ- or π-bonds of the bridging ligand can be cleaved selectively by applying cathodic or anodic potentials, respectively. On the basis of the obtained electrochemical data, a mechanism is suggested for the rearrangement observed when the complexes are metallated by butyllithium.

Key words: electrochemistry, complexes.

A new interesting class of polynuclear complexes of transition metals is made up of complexes with chains containing bridging cyclopentadienyl or arene ligands that are π-bonded to one metal atom and σ-bonded to another atom (so-called "ladder" complexes). "Ladder" complexes with bridging $\eta^1,\eta^5\text{-C}_5\text{H}_4$ ligands are obtained by metallation of the cyclopentadienyl ring using $(\eta^5\text{-Cp})\text{Fe(CO)}_2\text{I}$ as electrophilic agents, which allows a chain to build up by the sequential introduction of new $(\eta^5\text{-Cp})\text{Fe(CO)}_2$ fragments.[1,2] "Ladder" complexes with bridging η^1,η^6-Ph ligands can be obtained by heating $\eta^5\text{-CpFe(CO)}_2\text{Ph}$ ($\text{Cp} = \text{C}_5\text{H}_5$) with metal carbonyls, for example, with Cr(CO)_6.[3] These complexes are of special interest because they have a bridge that can transfer the electronic effects of the metal-containing fragments within the metal—σ-bond—π-system—metal moiety. Hence, such compounds can be used as models for the investigation of intramolecular charge transfer. Important information on the structure and properties of these systems may be obtained by studying their electrochemical oxidation and reduction, which allows one to simulate the behavior of polynuclear complexes in various chemical reactions.

The purpose of the present work is to investigate the electrochemical properties of bi- and trinuclear organometallic chains with Fe—Fe, Fe—Mn, Fe—Cr, and Fe—Fe—Mn metal sequences.



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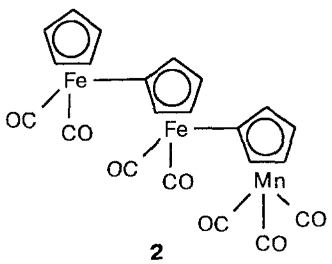

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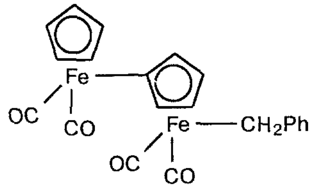

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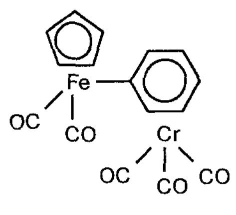

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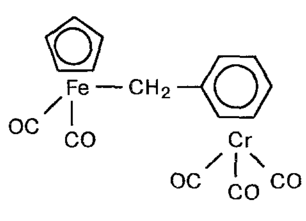

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Results and Discussion

Table 1 shows that all of the compounds studied can be oxidized and reduced within the ranges of the available potentials. However, the localizations of the electronic changes during oxidation and reduction are different. The reduction of complexes **1**—**5** seems to involve the orbitals that are localized on the Fe—C σ-bond, and the electron transfer is followed by a rapid chemical reaction to cleave the σ-bond of the bridging ligand. The oxidation of all of the polynuclear complexes except for **3** is directed primarily to the oxidation of the Mn and Cr atoms. In this process the π-bond is cleaved, whereas the bridging σ-bond remains untouched.

Oxidation. During the oxidation of all of the investigated complexes, several irreversible one-electron waves were observed. Only the first wave of the oxidation of complexes **1** and **2** were reversible. In order to elucidate the most probable mechanism of the oxidation of the "ladder" complexes, we compared the potentials of the first oxidation waves (E^{ox}) of complexes **4**, **5**, $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, $(\eta^5\text{-}Cp)Fe(CO)_2Ph$, and $(\eta^5\text{-}Cp)Fe(CO)_2CH_2Ph$ (see Table 1). The oxidation of σ-aryl and σ-benzyl complexes of cyclopentadienyl iron dicarbonyl proceeds irreversibly to result in the cleavage of the Fe—C σ-bond and the formation of the $[(\eta^5\text{-}Cp)Fe(CO)_2]^+$ cation. This is confirmed by the presence of the peak corresponding to the reduction of the cation ($E = -0.49$ V) in the reversed scan of the cyclic voltammogram.[4] The introduction of an electron-withdrawing $Cr(CO)_3$ group into a molecule should result in an anodic shift of the E^{ox} of a bimetallic complex, if the oxidation still occurs involving the Fe—C σ-bond. However, Table 1 shows that when a chromiumtricarbonyl group is introduced into an aryl or benzyl derivative of cyclopentadienyl iron dicarbonyl, the oxidation potentials are dramatically cathode-shifted. This is only possible if the highest occupied molecular orbital (HOMO) of the complex is made up mainly of contributions by the d-orbitals of the Cr atom. In the case of bi- and trimetallic complexes **1** and **2** containing Fe and Mn atoms, the reaction patten is similar: the Mn atom is oxidized first. However, unlike the Cr complexes, the π-bond of the bridging ligand is not cleaved after the removal of the first electron. The elimination of the chromiumtricarbonyl group during the oxidation of complex **4** is confirmed by the fact that the potentials of the second, third, and forth oxidation waves of this complex coincide with E^{ox} of the complex $(\eta^5\text{-}Cp)Fe(CO)_2Ph$ (see Table 1). Thus, it is reasonable to propose the following mechanism for the oxidation of "ladder" complexes **1**, **2**, **4**, **5**.

The above-mentioned electrochemical data attest that, during the oxidation of these complexes, the π-bond of the bridging ligand is primarily cleaved, while the σ-bond of the bridge remains untouched. Unlike complex **4**, the

Scheme 1

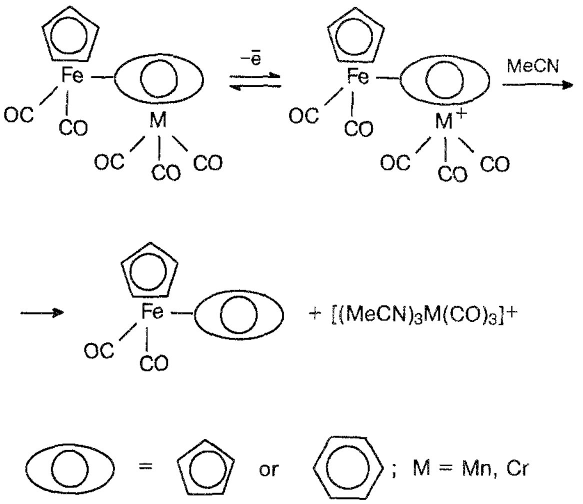


Table 1. Potentials of the oxidation (E^{ox}), reduction (E^{red}) peaks, and the frequency of the valent vibrations ν(CO) of the CO groups[8] of the "ladder" complexes **1**—**5** and the mononuclear fragments involved

Compound		E^{ox}/V	$-E^{red}$/V	ν(CO)/cm^{-1}
$(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$	**(1)**	1.06/0.98; 1.36; 2.03; 2.14	2.20	1916; 1978; 2003; 2032
$(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1,\eta^5\text{-}C_5H_4)Fe(CO)_2(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$	**(2)**	1.07/0.97; 1.32; 1.93; 2.14;	2.06; 2.19	1913; 1956; 1979; 1999; 2015; 2036
$(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1,\eta^5\text{-}C_5H_4)Fe(CO)_2CH_2Ph$	**(3)**	0.71; 0.94; 1.08; 1.57	2.10	1929; 1977; 1987; 2029
$(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1,\eta^6\text{-}Ph)Cr(CO)_3$	**(4)**	0.67; 1.13; 1.30; 2.14	2.06; 2.25	1875; 1950; 1980; 2032
$(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1,\eta^6\text{-}CH_2Ph)Cr(CO)_3$	**(5)**	0.66; 0.87; 1.54; 2.03	2.06; 2.36	1877; 1954; 2009
$(\eta^5\text{-}Cp)Fe(CO)_2Ph$	**(6)**	1.09; 1.28; 2.14	2.14	1971; 2028
$(\eta^5\text{-}Cp)Fe(CO)_2CH_2Ph$	**(7)**	0.89; 1.07; 2.05	2.31	1948; 2005
$(\eta^5\text{-}Cp)Mn(CO)_9$	**(8)**	1.29; 1.66; 2.32	2.78	1938; 2035
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	**(9)**	0.79; 1.91	2.56	1892; 1971

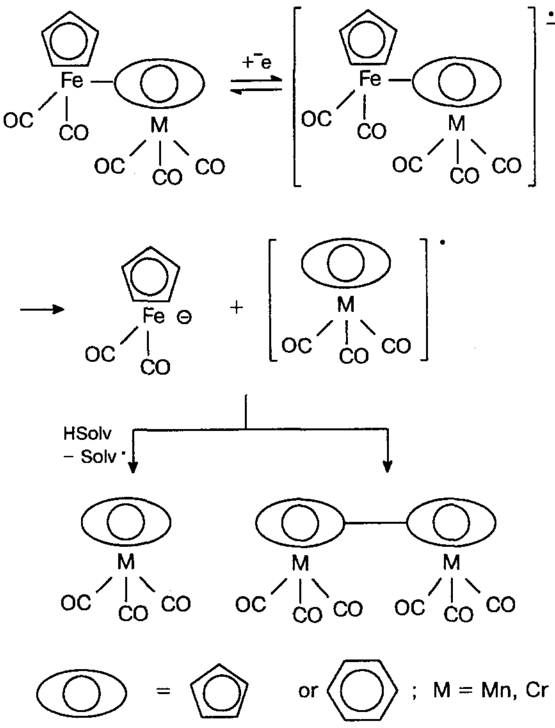
Note. Conditions: $C = 5 \cdot 10^{-4}$ mol L^{-1}, MeCN, Pt, 0.05 *M* Bu_4NBF_4, Ag/AgCl/KCl, 20 °C, 200 mV s^{-1}.

oxidation of binuclear complex **3**, which contains two Fe atoms, involves the cleavage of the Fe—benzyl σ-bond. This is associated with the fact that the ionization potential (IP) of Fe^{2+} (30.61 eV)[5] is considerably higher than the IP of the Cr^0 (6.765 eV) and Mn^{1+} (15.64 eV)[5] atoms incorporated in complexes **1**, **2**, **4**, and **5**. Therefore, in the case of complex **3**, the oxidation of the metal atom is considerably hindered. The introduction of one more donating $CpFe(CO)_2$-group attached by the cyclopentadienyl bridge facilitates the oxidation at the Fe—benzyl bond. This is confirmed by a comparison between the E^{ox} of complex **3** and $(\eta^5\text{-}Cp)Fe(CO)_2CH_2Ph$ (see Table 1).

Reduction. The reduction of all of the investigated complexes is irreversible and rather difficult to perform. It is known[6,7] that, if the benzene ring contains a substituent that can be reduced, coordination to the electron-withdrawing chromiumtricarbonyl group results in an anodic shift of the reduction potential of the substituent. In our case, the $(\eta^5\text{-}Cp)Fe(CO)_2$ group may be considered as a substituent that can be reduced. Bimetallic complexes **4** and **5** containing chromium are reduced more readily than the benzyl and aryl σ-derivatives of cyclopentadienyl iron dicarbonyl (see Table 1). This indicates that the reduction of the "ladder" complexes, unlike their oxidation, involves the participation of the σ-bond of the bridge (Scheme 2).

A peak corresponding to the oxidation of the $[(\eta^5\text{-}Cp)Fe(CO)_2]^-$ anion ($E = -0.78$ V) is observed on the reverse branch of the reduction curves of complexes **1**, **4** and **5** obtained by cyclic voltammetry. This fact also confirms the scheme proposed. During the reduction of complexes **2** and **3**, the electron transfer is also followed by the cleavage of the Fe—C σ-bond to form the same fragment, which is indicated by the existence of the same peaks ($E = -0.51$ V) on the reverse branches of the reduction curves. Since the common moiety for these compounds is a fragment containing two Fe atoms, one can conclude that in complex **3** the Fe—benzyl σ-bond is cleaved, while in complex **2** cleavage of the σ-bond of the cyclopentadienyl bridge π-bonded with the manganesetricarbonyl group occurs.

Scheme 2



Thus, the analysis of the cyclic voltammograms obtained in the electrochemical study of bridged polynuclear complexes **1—5** allows one to conclude that in the studied compounds, which consist of mutually influencing moieties united as a common system, the locations of the electronic changes are different for oxidation and reduction. Applying a cathode or anode potential makes possible the selective cleavage of the σ- and π-bonds of the bridging ligand, respectively.

Correlation between the electrochemical and the spectral data. It is interesting to compare the obtained electrochemical data with the spectral characteristics of the "ladder" complexes, *e.g.*, with the frequency of the CO group valent vibrations. This value is a "spectral indicator" of the electronic effect of the fragments that are π- or σ-bonded with the metal atom. Previously[8] the vibrational spectra of "ladder" complexes containing Cr, Mn, and Fe have been studied, and the observed bands were assigned to different metal-carbonyl fragments. The longest-wave band in the spectra of complexes **1**, **2**, **4**, and **5** corresponds to degenerate (*E*) vibrations of the carbonyl groups attached to the Cr and Mn atoms. Therefore, the frequency of this band should reflect the influence of the remainder of the molecule on the electron density at the atoms of these metals. Since the oxidation of complexes **1**, **2**, **4**, and **5** also involves the orbitals of these atoms, it is reasonable to expect that there is a linear correlation between E^{ox} and ν(CO). Figure 1 shows that this correlation is observed in fact, and depending on the location of the electronic changes (d-orbitals of Cr and Mn for complexes **1**, **2**, **4**, **5**, $(\eta^5\text{-}Cp)Cr(CO)_3$, $(\eta^5\text{-}Cp)Mn(CO)_3$), or the Fe—C σ-bond (complex **3**, $(\eta^5\text{-}Cp)Fe(CO)_2Ph$, $(\eta^5\text{-}Cp)Fe(CO)_2CH_2Ph$)) the experimental points are located on two virtually parallel lines. This correlation attests that the mechanism proposed for the oxidation of the studied "ladder" complexes is valid.

Correlation between the electrode and homogeneous chemical reactions. One can explain the unusual rearrangements observed during metallation of "ladder" complexes based on the known mechanism of their reduction. As was shown previously,[9] when complex **4** is treated successively with butyl lithium and benzyl chloride, a compound with connected cyclopentadienyl and the benzene rings is formed (Scheme 3).

It is possible that the elimination of the proton from the cyclopentadiene ring is followed by the transfer of an

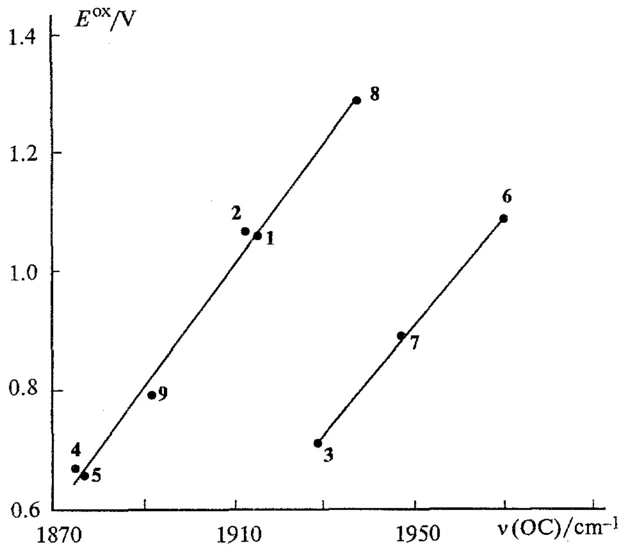
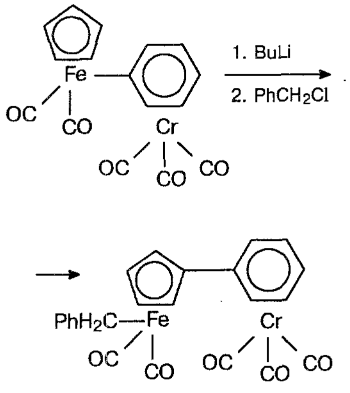


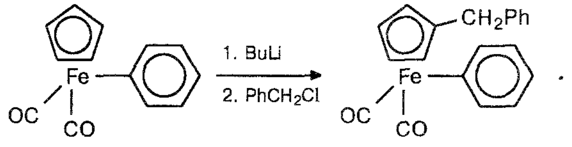
Fig. 1. Dependence of the oxidation potential (E^{ox}) on the frequency of the valent vibrations ν(CO) of the "ladder" complexes and the mononuclear fragments involved (the numbers of the points correspond to the numbers of the compounds in Table 1).

Scheme 3



electron to the aromatic ring bonded with the chromiumtricarbonyl group, which in turn causes the cleavage of the Fe—C σ-bond. In this case, the radicals formed can recombine with a cage to give a rearrangement product resembling that of the Stevens rearrangement (Scheme 4).

When using (η^5-Cp)Fe(CO)$_2$Ph instead of complex **4**, the treatment of the complex with BuLi and PhCH$_2$Cl results in the introduction of a benzyl radical at the cyclopentadienyl ring to prevent the rearrangement:[9]



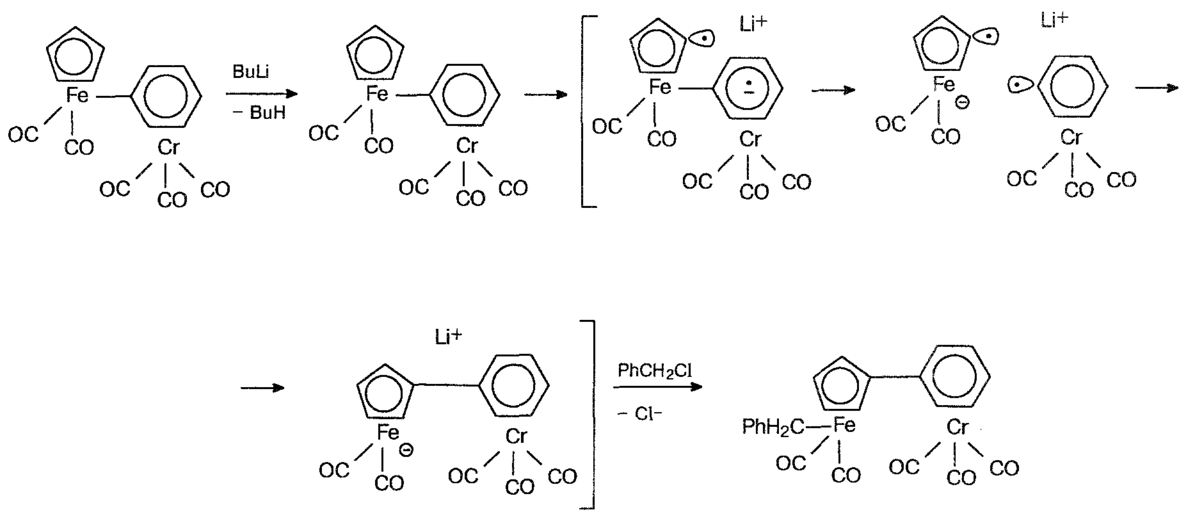
In this case, BuLi also acts as a base and eliminates the proton from the cyclopentadienyl ring to form an anion, which enters the nucleophilic substitution reaction with PhCH$_2$Cl. Since the (η^5-Cp)Fe(CO)$_2$Ph is less readily reduced than complex **4** and the electrophilicity of the aromatic ring non-bonded with the chromiumtricarbonyl ring is substantially lower, electron transfer does not occur in this case, and the normal product of nucleophilic substitution is formed.

The results obtained show that investigating the electrochemical behavior of organometallic compounds is beneficial for the elucidation of the mechanisms of homogeneous chemical reactions.

Experimental

The electrochemical measurements were carried out on an SVA-1B-M voltammetric system with stationary and rotating platinum electrodes with a 0.05 *M* solution of Bu$_4$NBF$_4$ in anhydrous MeCN as the supporting electrolyte at 20 °C. Plati-

Scheme 4



num was used as the auxiliary electrode, and a silverchloride electrode was used as the reference electrode. Oxygen was removed from the cell by a current of dry argon. The voltammetric curves were registered by cyclic voltammetry with sweep rates of the potential of 50, 100, 200, and 500 mV s^{-1}. The rate of electrode rotation varied from 480 to 3450 cycles per minute. The ohmic losses were taken into account. Pure grade MeCN was purified by stirring over CaH_2 for 24 h followed by filtration. Then 5 g of KNO_3 and 10 ml of concentrated H_2SO_4 were added, and the mixture was boiled for 3 h and distilled. After this, MeCN was refluxed for 2 h over P_2O_5 and again distilled to collect the fraction with b.p. 81—82 °C (760 Torr). The complexes under study were prepared according to procedures described previously.[1—3, 10] The constants were in agreement with the published data.

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