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Electrochemical and spectral study of intramolecular charge transfer in dinuclear and polynuclear ladder complexes

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The potentials of electrochemical oxidation and reduction of the polynuclear ladder complexes $Cp(CO)LM-\eta^1,\eta^5-C_5H_4Mn(CO)_2L$ (M = Fe or W(CO); L = PPh_3 or CO), $\mu-(C\equiv C)[C_5H_4(CO)_2Fe-\eta^1,\eta^5-C_5H_4Mn(CO)_3]_2$, and $MeSi[C_5H_4(CO)_2Fe-\eta^1,\eta^5-C_5H_4Mn(CO)_3]_3$ were measured, and the mechanism of these processes is proposed. The change in the electron density at the atom of one metal (Fe or W) is transferred along the σ- and π-bond chain in the cyclopentadienyl bridge to the atom of another metal (Mn) and, on the contrary, the perturbing effect of the substituent is somewhat weakened.

Key words: electrochemical oxidation and reduction; iron, tugsten, and manganese complexes; bridging cyclopentadienyl ligand.

Dinuclear and polynuclear transition metal complexes with the bridging η^1,η^5-cyclopentadienyl or η^1,η^6-arene ligands (so-called ladder complexes) are of interest as models of intramolecular charge transfer along the π-ligand—metal—σ,π-ligand—metal bond system.

Studies of the electronic structures of complex organometallic compounds by electrochemical methods allow one to quickly estimate the influence of the replacement of one or several ligands in the coordination sphere of one metal atom on the electronic properties of another metal center and the ligands coordinated to the latter metal. Earlier,[1] we have studied the electrochemical properties of a series of di-, tri-, and pentanuclear organometallic chains containing bridging ligands σ-coordinated to one of the metal atoms and π-coordinated to another metal atom.

In the present study, we investigated the electrochemical properties of new dinuclear ladder complexes **1—6**, which contain the Fe—Mn or W—Mn sequences and in which one of the CO ligands in the coordination sphere of the metal atom is replaced by PPh_3, as well as the properties of complexes **7** and **8** in which the dinuclear fragments $C_5H_4(CO)_2Fe-\eta^1,\eta^5-C_5H_4Mn(CO)_3$ are linked to each other by the acetylene or silyl bridge.

All the compounds under study proved to be electrochemically active at both anodic and cathodic potentials, the localization sites of the electronic changes for oxidation being different from those for reduction.

Oxidation of complexes **1—6** is accompanied by the appearance of several peaks in the cyclic voltammograms (CV). In most cases, the transfer of the first electron occurs reversibly and leads to a change in the oxidation state $Mn^{+/2+}$. The transfer of the second electron causes, apparently, the cleavage of the M—C σ-bond in the bridging ligand. Reduction of the $[CpFe(CO)L]^+$ and $[CpW(CO)_2L]^+$ cations can be observed (L = CO or PPh_3) on the reverse scan after the second oxidation peak. Apparently, the oxidation peak recorded at high anodic potentials corresponds to oxidation of fulvalene-type complexes that are formed. This is consistent with the fact that the potentials of the long-range redox transitions are rather similar for all the complexes under study.

Therefore, oxidation occurs with the involvement of the highest occupied molecular orbital, to which the orbitals of the metal atom π-coordinated by the bridging Cp ligand, *viz.*, the Mn atom, make the major contribution (Scheme 1).

Reduction of the complexes occurs with the involvement of the orbitals localized on the σ-bond of the bridging ligand, the electron transfer being followed by the fast cleavage of this bond (Scheme 2). This is evidenced by the fact that the first reduction peak of the complexes is irreversible. Reoxidation of the $[CpFe(CO)L]^-$ and $[CpW(CO)_2L]^-$ anions (L = CO or PPh_3) is observed on the reverse scan (see Scheme 2).

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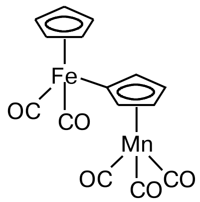

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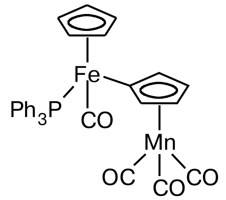

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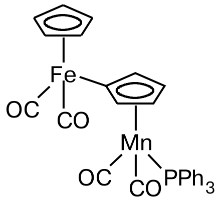

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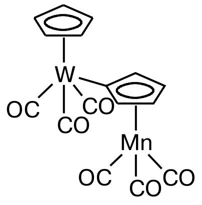

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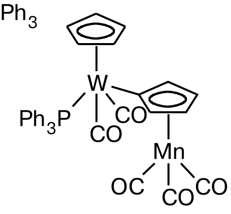

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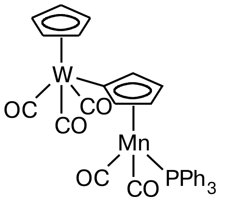

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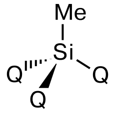

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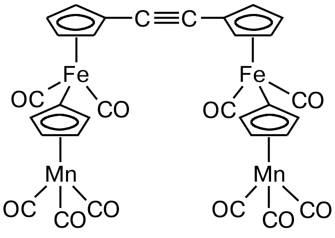

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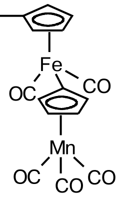
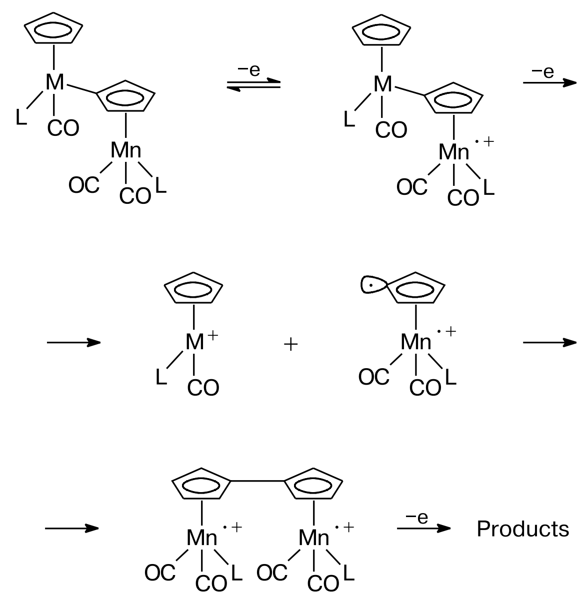
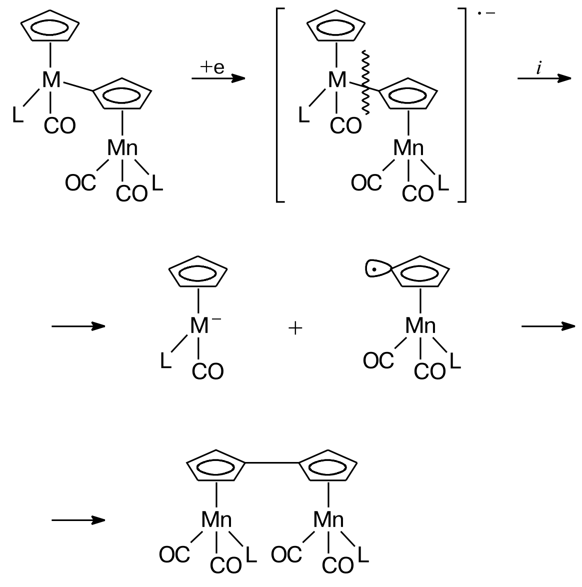
Q = 

Scheme 1



M = Fe, W(CO); L = CO, PPh_3

Scheme 2



i. Rapidly.

M = Fe, W(CO); L = CO, PPh_3

The measured oxidation and reduction potentials are given in Table 1.

As can be seen from Table 1, the replacement of the π-acceptor ligand CO by the σ-donor ligand PPh_3 has a much stronger effect on the oxidation potentials of the dinuclear complexes than on their reduction potentials; these potentials vary within the ranges of 470 and 200 mV, respectively. In the case of $CpFe(CO)_2Ph$, the replacement of one CO group by PPh_3 leads to a slight change in the reduction potential accompanied by the cleavage of the Fe—Ph σ-bond (*cf.* −1.96 and −2.01 V relative to the saturated calomel electrode (SCE)).[2] The same tendency is observed for the bridged dinuclear complexes, *e.g.*, E^{Red} is slightly shifted to cathodic potentials (see Table 1). If the replacement by the donor ligand occurs at the Mn atom, the shift of the potential is less pronounced compared to that caused by the replacement of the ligand at the Fe or W atom, *i.e.*, the transfer through the bridging Cp ligand leads to a "damping" of the electronic effect of one reaction center on another center. On the contrary, the oxidation potentials of the dinuclear complexes are more sensitive to the replacement of the ligand at the Mn atom comapred to those at the Fe (W) atom. This is quite reasonable taking into account that oxidation occurs at the Mn atom.

The electrochemical data agree well with the data on metallation of complexes containing the PPh_3 ligand.

Earlier,[3] we have demonstrated that metallation of the dinuclear complex $Cp(CO)_2FeC_5H_4Mn(CO)_3$ (**1**)

Table 1. Oxidation peak potentials (E^{Ox}), reduction peak potentials[a] (E^{Red}), and CO stretching frequencies[b] ν(CO) of complexes **1—8**

Compound[c]	E^{Ox}	$-E^{\mathrm{Red}}$	ν(CO)/cm^{-1}	
	V		$M(CO)_nL$	$Mn(CO)_nL$
$Cp(CO)_2FeC_5H_4Mn(CO)_3$ (**1**)	1.07, 1.32, 1.93	2.20	2032, 1978	2003, 1916
$Cp(CO)LFeC_5H_4Mn(CO)_3$ (**2**)	0.75, 1.35, 1.95	2.40	1932	1998, 1906
$Cp(CO)_2FeC_5H_4Mn(CO)_2L$ (**3**)	0.6, 1.25, 2.05	2.35	2025, 1971	1914, 1848
$Cp(CO)_3WC_5H_4Mn(CO)_3$ (**4**)	1.06, 1.36, 1.63, 1.96	2.22	2033, 1940	2007, 1923
$Cp(CO)_2LWC_5H_4Mn(CO)_3$ (**5**)	0.98, 1.52, 1.75, 2.05	2.45	1940, 1885	2003, 1913
$Cp(CO)_3WC_5H_4Mn(CO)_2L$ (**6**)	0.85, 1.39, 2.02	2.20	2022, 1945	1920, 1877
μ-$C_2[C_5H_4(CO)_2FeC_5H_4Mn(CO)_3]_2$ (**7**)	1.08, 1.38, 2.18	2.20	2029, 1976	2003, 1918
$MeSi[C_5H_4(CO)_2FeC_5H_4Mn(CO)_3]_3$ (**8**)	1.12, 1.36, 1.92	[d]	2033, 1982	2004, 1918

[a] Conditions: MeCN, a Pt electrode, 0.05 *M* Bu_4NPF_6, Ag/AgCl/KCl, 20 °C, 200 mV s^{-1}.

[b] CH_2Cl_2 as the solvent.

[c] L = PPh_3.

[d] A weakly pronounced peak at a potential <—2.3 V.

with Bu^nLi (THF, –78 °C) occurs selectively and exclusively at the Cp ring coordinated to the Fe atom, and we have isolated the monodeuterium derivative $DC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$ by treatment of the lithium derivative with D_2O.

Under the same conditions, no metallation of the $Cp(CO)PPh_3FeC_5H_4Mn(CO)_3$ complex (**2**) occurs. The mononuclear complex $Cp(CO)(PPh_3)FePh$ does not undergo metallation as well.[4] This is attributed to the fact that the strong electron-donating ligand PPh_3 at the Fe atom substantially decreases the CH-acidity of the Cp ligand. Metallation of the $Cp(CO)_3FeC_5H_4Mn(CO)_2PPh_3$ complex (**3**), in which the electron-donating ligand PPh_3 is far removed from the reaction center (Cp ring), gives rise to the lithium derivative. Treatment of the latter with D_2O affords the monodeuterium derivative $DC_5H_4(CO)_2FeC_5H_4Mn(CO)_2PPh_3$.

The complexes, in which the dinuclear Fe—Mn fragments are linked to each other by the acetylene (complex **7**) or silyl (complex **8**) bridges, are of particular interest. The properties of the acetylene and polyyne spacers have been studied in sufficient detail. For example, electrochemical oxidation of two ferrocene fragments in the CpFe(η^5-C_5H_4—C≡C—C_5H_4-η^5)FeCp complex was demonstrated[5] to occur successively, although the potential difference is ~130 mV, which is typical of weakly interacting biferrocenes.

For complex **7**, the first oxidation peak at anodic potentials corresponds to two weakly resolved successive electron transfers, the potential difference between which is as small as 60 mV.

For the Si-containing complex (**8**), no separation of the peaks was observed, which could be evidence that the Mn^+ atoms of each propeller blade are successively oxidized. The first oxidation peak current of complex **8**, which corresponds to the three-electron transfer, and the fact that the oxidation potential of complex **8** is similar to that of complex **1** suggest that oxidation of the Mn atoms of all three propeller blades occurs virtually simultaneously. We failed to obtain clear reduction peaks at cathodic potentials because reduction of the Si-containing complex occurs at high negative potentials.

These data provide evidence that the MeSi-containing bridge, which links three η^5-$C_5H_4Fe(CO)_2$(η^1,η^5-C_5H_4)$Mn(CO)_3$ fragments, serves as a poor conductor of the electronic effects. Oxidation of the Mn atom in one fragment gives rise to a positive charge, which, however, has almost no effect on the oxidation potentials of the other Mn atoms. Because of this, the cyclic voltammogram shows one three-electron peak.

The electrochemical data can be compared with the CO stretching frequencies, which also provide evidence for the electron density distribution in the molecules of the complexes in question. Earlier, we have demonstrated[6] that the ν(CO) frequencies of ladder di- and trinuclear carbonyl complexes containing the Fe—Fe, Fe—Mn, Fe—Fe—Mn, Fe—Fe—Cr, W—Fe—Cr, *etc.* sequences are sensitive to changes in the electron density at the metal atoms.

The CO stretching frequencies for complexes **1—8** are given in Table 1. The assignment of the observed bands to ν(CO) vibrations of particular metal carbonyl fragments, which is presented in Table 1, was made according to an approach proposed in our earlier study.[6] The replacement of the CO group at the Mn atom by the electron-donating PPh_3 ligand (complexes **3** and **6**) decreases ν(CO) at the Mn atom by ~90 cm^{-1}, whereas ν(CO) for the groups at the Fe (complex **3**) and W (complex **6**) atoms decreases to a lesser extent (by ~7 cm^{-1}). The introduction of the PPh_3 ligand into the coordination sphere of the Mn atom also leads to a slight increase in the electron density at the Fe or W atom, *i.e.*, as in the previously studied complexes, the electronic effect is transferred from the atom of one metal to the atom of another metal through the bridging Cp ligand. A comparison of the ν(CO) frequencies of complexes **1** and **2** and of complexes **4** and **5** shows that the replacement of the CO group at the Fe (complex **2**) and W (complex **5**) atom by Ph_3P leads to a substantial (by 70 cm^{-1}) decrease in ν(CO) at these metal atoms and to a slight (by ~5 cm^{-1}) decrease in ν(CO) at the Mn atom, *i.e.*, the electronic effect in these complexes is also transferred from the Fe or W atom to the Mn atom through the bridging Cp ligand.

The influence of the nature of the metal atom on the ν(CO) frequencies can be seen from a comparison of the IR spectra of complexes **1** and **4**. The ν(CO) frequencies of the groups at the Mn atom of complex **4** are 4—7 cm^{-1} higher than the corresponding frequencies of complex **1**, which indicates that the electron-donating ability of the $CpW(CO)_3$ fragment, which causes a decrease in the ν(CO) frequency, is slightly lower than that of the $CpFe(CO)_2$ fragment.

Therefore, the spectroscopic data agree well with the results of electrochemical studies. The results obtained by both methods reflect the same tendency, *i.e.*, an increase in the electron density at the atom of one metal (Fe or W) is transferred along the chain of σ- and π-bonds in the Cp bridge to the atom of another metal (Mn). This effect is less pronounced in the opposite direction (from Mn to Fe or W). It should be noted that the total estimation of the electronic perturbations introduced into the molecule due to the replacement of one CO ligand by PPh_3 at any metal center, which was calculated as $(\Delta E^{\mathrm{Ox}} + |\Delta E^{\mathrm{Red}}|)$ or $\Delta\nu(\mathrm{CO})_{\mathrm{Fe(W)}} + \Delta\nu(\mathrm{CO})_{\mathrm{Mn}}$, gave similar values regardless of at which metal atom the ligand is replaced.

The ν(CO) frequencies for complexes **1**, **7**, and **8** (see Table 1) are virtually identical, *i.e.*, the introduction of several identical η^5-$C_5H_4Fe(CO)_2(\eta^1,\eta^5$-$C_5H_4)Mn(CO)_3$ fragments, which are linked to each other by the acetylene or silyl bridge, into one molecule has virtually no effect on their properties.

Experimental

The electrochemical oxidation and reduction potentials were measured on an IPC-Win digital potentiostat/galvanostat connected to a personal computer. The voltammetric curves were recorded by cyclic voltammetry on a stationary Pt electrode at a potential scan rate of 200 mV s^{-1} using 0.05 *M* $Bu^n{}_4NPF_6$ as the supporting electrolyte in acetonitrile at 20 °C in a 10 mL electrochemical cell. Oxygen was removed from the cell by purging with dry argon. The measured potentials were corrected for ohmic losses. Platinum served as the auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode.

The IR spectra (solutions in CH_2Cl_2) were recorded on a Nicolet Magna IR 750 Fourier-transform spectrometer at 2 cm^{-1} resolution. The ^1H NMR spectra (C_6D_6) were measured on a Bruker AMX-400 spectrometer (400.13 MHz).

Tetrahydrofuran (chemical purity) was distilled over sodium benzophenone ketyl under Ar immediately before use. Acetonitrile (chemical purity) was stirred over CaH_2 for 12 h, distilled, refluxed over P_2O_5 for 2 h, and again distilled, the fraction with the b.p. of 81—82 °C (760 Torr) being collected.

The $Cp(CO)_2FeC_5H_4Mn(CO)_3$,[7] $Cp(CO)PPh_3FeC_5H_4Mn(CO)_3$,[8] $Cp(CO)_2FeC_5H_4Mn(CO)_2PPh_3$,[9] $Cp(CO)_3WC_5H_4Mn(CO)_3$, $Cp(CO)_2PPh_3WC_5H_4Mn(CO)_3$, $Cp(CO)_3WC_5H_4Mn(CO)_2PPh_3$,[10] μ-$C_2[C_5H_4(CO)_2FeC_5H_4Mn(CO)_3]_2$,[11] and $MeSi[C_5H_4(CO)_2FeC_5H_4Mn(CO)_3]_3$[12] complexes were synthesized according to known procedures. All reactions were carried out under dry argon.

The reaction of η^5-cyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienyldicarbonyltriphenylphosphinemanganese, $Cp(CO)_2FeC_5H_4Mn(CO)_2PPh_3$ (3), with Bu^nLi and D_2O. A 1.6 *M* Bu^nLi solution in hexane (0.4 mL, 0.6 mmol) was added to a solution of $Cp(CO)_2FeC_5H_4Mn(CO)_2PPh_3$ (0.1 g, 0.16 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h, and D_2O (0.5 mL) was added. The reaction mixture was stirred at −78 °C for 30 min, and then the temperature was gradually raised to ~20 °C. The solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockmann activity II). η^5-Monodeuterocyclopentadienyldicarbonyliron-η^1,η^5-cyclopentadienyldicarbonyltriphenylphosphinemanganese was eluted with a 1 : 1 benzene—hexane mixture. The yield of $DC_5H_4(CO)_2FeC_5H_4Mn(CO)_2PPh_3$ was 0.03 g (30%). ^1H NMR, δ: 4.10 (2 H, CpMn); 4.27 (4 H, C_5H_4DFe); 4.43 (2 H, CpMn); 7.17 (10 H, Ph); 7.84 (5 H, Ph).

The reaction of η^5-cyclopentadienylcarbonyltriphenylphosphineiron-η^1,η^5-cyclopentadienyltricarbonylmanganese, $Cp(CO)PPh_3FeC_5H_4Mn(CO)_3$ (2), with Bu^nLi and D_2O. A 1.6 *M* Bu^nLi solution in hexane (1 mL, 1.6 mmol) was added to a solution of $Cp(CO)PPh_3FeC_5H_4Mn(CO)_3$ (0.6 g, 1 mmol) in THF (50 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h, and D_2O (1 mL) was added. The reaction mixture was stirred at −78 °C for 30 min, and then the temperature was gradually raised to ~20 °C. The solvent was removed, and the residue was chromatographed on Al_2O_3 (Brockmann activity II). η^5-Cyclopentadienylcarbonyltriphenylphosphine-iron-η^1,η^5-cyclopentadienyltricarbonylmanganese was eluted with a 1 : 1 benzene—hexane mixture. The yield of the starting complex **2** was 0.55 g (92%). ^{1}H NMR, δ: 3.72, 4.25, and 4.31 (all, 1 H each, CpMn); 4.32 (5 H, CpFe); 4.43 (1 H, CpMn); 7.06 (8 H, Ph); 7.40 (6 H, Ph). The ratio of the signals CpFe : CpMn = 5 : 1.

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