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The electrochemistry of sandwich and bent sandwich transition metal complexes

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ABSTRACT. The result of electrochemical studies of homo- and hetero-ligand sandwich as well as bent sandwich biscyclopentadienyl complexes of transition metals are surveyed and described systematically. The existence of a linear relation between the redox potentials of these complexes and the gas-phase ionisation potentials of the corresponding metals and their ions is demonstrated. The electrochemical reactions catalysed by sandwich and bent sandwich complexes and the possibilities of the electrochemical synthesis of the above complexes and metal complex catalysts based on them are examined.
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I. Introductions

Electrochemical studies on sandwich complexes (SC) of transition metals began to develop soon after the synthesis of ferrocene in 1951.[1] During the period which has elapsed since then, a large number of SC have been investigated by electrochemical methods. The application of polarography, cyclic voltammetry, and other methods have made it possible to obtain important information about the oxidation-reduction properties of these compounds in the condensed phase, i.e. about the reactivity of the SC in oxidation-reduction reactions. This information is extremely important for the correct understanding of the mechanisms of many reactions involving SC, the selection of optimum conditions in their synthesis and electrochemical synthesis, and the solution of important structural problems in the chemistry of the large class of complexes considered. Furthermore, the electrochemical methods provide valuable information about the distribution of electron density in the molecule and about the relative disposition of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals.

Since the publication of the last reviews[2,3] on the electrochemistry of SC more than 10 years have elapsed and there has been so far no systematic consideration of bent sandwich complexes (BC) of the type Cp_2ML_n ($Cp = \eta^5\text{-}C_5H_5$ = cyclopentadienyl). There has been a significant increase in the number of publications in recent years on the electrochemical investigation of SC and BC. Individual studies in this field have been mentioned in reviews[4,5] and monographs.[6–8]

The author's aim has been to trace the principal characteristic features of the variation of the oxidation-reduction properties of SC and BC as a function of the nature of the metal and of its formal oxidation state and to find a parameter, common to SC and BC, which determines the reactivity of these complexes in oxidation-reduction reactions rather than the greatest possible accumulation of factual data.

The properties of the primary products of the electrochemical reactions of SC and BC are also examined in a number of instances. The review does not include studies dealt with in previous surveys[2,3] with the exception of cases which have been subjected to a repeated, more accurate analysis.

II. Electrochemical reactions of sandwich complexes

Sandwich complexes constitute a class of organometallic compounds in which the metal atom is located between two plane-parallel (or approximately parallel) aromatic π-ligands of the type $\eta^5\text{-}C_5H_5^-$, $\eta^6\text{-}C_6H_6$, $\eta^7\text{-}C_7H_7^+$, $\eta^8\text{-}C_8H_8^{2-}$, etc. The bond between the metal and the ligand is formed as a result of the overlap of the *d* orbitals of the metal and the π orbitals of the ligand. A characteristic feature of the SC is that their metal atom is surrounded by two bulky ligands and that its direct contact with solvent molecules is difficult. The latter prevents the appearance of specific solvation effects. As a result, the solvation effects in the redox reactions of SC are determined mainly by the electrostatic component, which is approximately the same for isostructural complexes bearing equal charges.[7,9,10] This makes it possible to investigate and compare electron transfer reactions in the series of SC in various solvents. The transfer reactions are usually uncomplicated by chemical reactions of the electrochemically generated species with the solvent molecules.

Quantum-chemical study of SC has shown[11-13] that the atomic orbitals (AO) of the metal make the main contribution to their HOMO and LUMO on which the changes of electron density as a result of the occurrence of oxidation-reduction reactions are localised (redox orbitals). Reactions occurring with a change in the formal oxidation state of the metal are therefore characteristic of SC.

1. Metallocenes

Reversible one-electron reactions according to the scheme

$$Cp_2M^{2+} \overset{e}{\rightleftarrows} Cp_2M^{+} \overset{e}{\rightleftarrows} Cp_2M \overset{e}{\rightleftarrows} Cp_2M^{-} \qquad (1)$$

are characteristic of the majority of compounds of this kind. The electron transfer in these systems is of the outer-sphere type[2,3] and the reversibility of the electrode reactions of the majority of metallocenes suggest that the transition from the oxidised form to the neutral form and further to the reduced form does not entail significant changes in the coordination sphere and geometry of the complexes, at least during the electrochemical measurements.

Depending on the nature of the metal and the solvent, the possibility of the electrochemical generation of members of the redox series (1) and their stability, especially the stability of Cp_2M^{2+} and Cp_2M^-, change significantly. As a result of the employment of solvents which are extremely stable in the anodic and cathodic potential regions, in which the reactive members of the redox series (1) are most stable, only in recent years has it been possible to identify the majority of the products of the redox reactions of metallocenes, which are possible in principle. We shall consider the electrochemical behaviour of metallocenes belonging to different Groups in the Periodic System.

Group IVB elements do not form stable metallocenes with a plane-parallel disposition of the rings.[14,15] Among the Group VB metallocenes, only vanadocene has been thoroughly investigated. It has been demonstrated by polarographic and cyclic voltammetric methods at Hg and Pt electrodes[16-18] that Cp_2V undergoes one-electron reversible reduction in tetrahydrofuran (THF) with the formation of the metastable anion Cp_2V^- and one-electron reversible oxidation with formation of the cation Cp_2V^+. Further oxidation of Cp_2V^+ to the dication Cp_2V^{2+} takes place irreversibly, which is believed[16,17] to be associated with the transition in the Cp_2V^{2+} generation stage from the plane-parallel to the bent sandwich structure (*EC*-process, where *E* and *C* represent respectively the electrochemical and chemical stages) as a result of the interaction with solvent molecules or other suitable ligands.

The electrochemical behaviour of the vanadocene analogues Cp_2Nb and Cp_2Ta has not been investigated because of their metastability.[19,20]

The electrochemistry of Group VIB metallocenes has been studied in detail in relation to Cp_2Cr. It has been shown by cyclic voltammetry at the Pt electrode[16,17] that chromocene is reduced reversibly in THF or acetonitrile to the Cp_2Cr^- anion with transfer of one electron. Preparative electrolysis at the limiting current Cp_2Cr reduction potentials does not, however, make it possible to obtain and characterise the Cp_2Cr^- anion in solution because of its low stability. It has also been shown that chromocene can undergo reversible one-electron oxidation to the unstable cation Cp_2Cr^+.[16,17,21]

Molybdenocene and tungstocene, whose stability is low (lifetime $\sim 10^{-2}$ s), have been generated and identified by cyclic voltammetry involving two-electron reduction of the corresponding metallocene dichlorides.[22,23] The potentials of the redox couples Cp_2Mo^0/Cp_2Mo^+ and Cp_2C^0/Cp_2M^+ are respectively −1.25 and −1.48 V.† These are the most readily oxidisable metallocenes among all those known. If E^0 = −0.68 V is adopted for the Cp_2Cr^0/Cp_2Cr^+ redox couple,[16] one may conclude that, within the framework of a single subgroup of the Periodic System, an increase in the atomic number of the metal facilitates the abstraction of an electron from the corresponding metallocene and not conversely, as had been postulated earlier in a review.[2]

†All the potentials in this review are quoted relative to the aqueous saturated calomel electrode.

Among the biscyclopentadienyl complexes of Group VIIB metals, only the manganese compound is known at present, although manganocene cannot be included among metallocenes because of its ionic character.[24] A substituted analogue of this compound [$(C_5Me_5)_2Mn$], in which the metal–ring bond is covalent and which has the metallocene structure, has been described.[25] It has been shown by cyclic voltammetry at a Pt electrode[25] that permethylmanganocene is reduced in acetonitrile to the $(C_5Me_5)_2Mn^-$ anion with transfer of one electron and is oxidised to the cation $(C_5Me_5)_2Mn^+$. Both processes are electrochemically reversible but the stability of the products has not been reported.

Like molybdenocene and tungstocene, rheniocene belongs to the class of relatively unstable metallocenes. These metallocenes are formed by the photolysis of the corresponding hydrides Cp_2MH in low-temperature matrices and their sandwich structure has been demonstrated by IR spectroscopy.[26-28] Rheniocene can be generated by cyclic voltammetry at a Hg electrode in THF by the two-electron reduction of the dimer $Cp_2Re-ReCp_2$ with the subsequent oxidation of the anion $[CpRe(\eta^3\text{-}C_5H_5)]^-$ formed under these conditions.[29] E^0 = −1.06 V for the Cp_2Re^0/Cp_2Re^+ redox couple.

Ferrocene, the first of the metallocenes synthesised, is undoubtedly the most thoroughly investigated representative of the Group VIIIB metallocenes. The Cp_2Fe^0/Cp_2Fe^+ redox couple is one of the most highly reversible systems. Numerous studies have been devoted to it.[2,3] In recent years, it has been possible to show, using solvents stable at high cathodic and anodic potentials, that ferrocene can be oxidised to the dication and can be reduced to the anion. In $AlCl_3$/1-butylpyridinium chloride melts (in 1 : 1 molar proportions), the $(C_5Me_5)_2Fe^+$ cation undergoes reversible one-electrochemical reduction at a carbon glass electrode to the stable dication $(C_5Me_5)_2Fe^{2+}$, which has been characterised by UV spectroscopy.[30] The electrochemical behaviour of the ferrocenium cation and of its permethylated analogue has also been investigated in liquid sulphur dioxide.[31] It has been shown by cyclic voltammetry at a Pt electrode that the reversible one-electron oxidation of Cp_2Fe^+ leads to the formation of the unstable dication Cp_2Fe^{2+}, the decomposition products of which partly block the electrode. The reversible one-electron oxidation of the decamethyl analogue under these conditions results in the formation of the high-spin dication $(C_5Me_5)_2Fe^{2+}$ (magnetic moment μ = 2.73 B.M.), which is stable at −30 °C.

The high purity of the solvent and electrochemical measurements at temperatures between −45° and −30 °C made it possible[32,33] to observe the reversible reduction of ferrocene to the relatively unstable anion Cp_2Fe^- at Pt and carbon glass electrodes in dimethylformamide (DMF) or dimethoxyethane. It has also been shown that an increase in temperature leads to the occurrence of the two-electron reduction of ferrocene via the *ECE*-mechanism involving the formation of an unidentified intermediate X:[32]

$$Cp_2Fe \overset{e}{\rightleftarrows} Cp_2Fe^- \rightarrow X \overset{e}{\rightarrow} 2Cp^- + Fe^0.$$

In order to elucidate the nature of X, a study has been made of the electrochemical reduction of substituted ferrocenes in DMF and THF under a CO atmosphere.[34] It is possible to identify the unstable anion $CpFe(CO)_2^-$, which interacts with MeI to form $CpFe(CO)_2Me$ or is oxidised at a Pt electrode to the radical $CpFe(CO)_2^{\cdot}$, which rapidly dimerises to the complex $[CpFe(CO)_2]_2$ with an Fe–Fe bond. These data led to the conclusion that the intermediate X is the $CpFe^{\cdot}$ + Cp^- mixture.

It has been noted[33] that the formal rate constant for the heterogeneous electron transfer to the ferrocene molecule ($k_e \cong 10^{-3}$ cm s^{-1}) is much lower than the analogous constant for the Cp_2Fe^0/Cp_2Fe^+ couple ($k_e > 10^{-1}$ cm s^{-1}). According to the authors,[33] this difference is due to the increase in the internal reorganisation energy on formation of Cp_2Fe^- as a result of the transition of one of the Cp rings from the planar η^5-conformation to the non-planar η^4-conformation, which makes it possible to retain the energetically most favourable 18-electron configuration of the metal atom in the anion. It is notable that this is not the only possible explanation of the decrease in k_e on passing from the Cp_2Fe^0/Cp_2Fe^+ redox system to Cp_2Fe^0/Cp_2Fe^-. In contrast to its oxidation, when ferrocene is reduced an electron is transferred to an antibonding MO which should undoubtedly entail an increase in the process activation energy and hence a decrease in k_e.

The kinetics of the heterogeneous electron transfer involving substituted ferrocenes and the Cp_2Co^+ ion in acetonitrile at a semiconductor (*p*-InP)/electrolyte interface have been investigated by cyclic voltammetry.[35] The above semiconductor is characterised by the presence of a forbidden gap and also a potential range at the limits of which the composition of the oxide layers changes as a result of electrode reactions involving the material of the electrode. Reversible electrode reactions are characteristic of alkylated ferrocenes, whose $Cp^*_2M^0/Cp^*_2M^+$ redox transition potential (Cp* is a substituted cyclopentadienyl) lies within this region, whereas irreversible electrode reactions are characteristic of the acylated ferrocene and Cp_2Co^+, whose potentials E^0 correspond to the limits of this region or are outside its limits. Furthermore, irreversible electrode reactions become characteristic also of complexes of the first type (with potentials E^0 lying outside the forbidden gap) when the potential at which the polarisation of the electrode changes moves outside the limits of the gap.

The electrochemical behaviour of heavier ferrocene analogues—ruthenocene and osmocene—has a number of characteristic features. Ruthenocene undergoes irreversible two-electron oxidation at a Pt electrode in acetonitrile, forming probably the dication.[2,3] Under the same conditions, the permethylated ruthenocene is oxidised reversibly to a stable cation which has been characterised by EPR spectroscopy ($e^3_{2g}a^2_{1g}$ electronic configuration), but its subsequent oxidation is irreversible.[36] The stepwise two-electron oxidation of Cp_2Ru, which is irreversible at each stage, has been observed by cyclic voltammetry in the $AlCl_3$/1-butylpyridinium chloride melt (with a molar ratio in excess of unity) at a carbon glass electrode.[37]

The oxidation of osmocene is characterised by the stepwise abstraction of two electrons, which is irreversible at each stage.[2,3] The preparative one-electron oxidation of Cp_2Os leads to the formation of a cation, which has been isolated as the salt $Cp_2Os^+BF_4^-$.[2] The difference in the electrochemical behaviour of ferrocene, ruthenocene, and osmocene is associated with the fact, according to Gale et al.,[30] that, with increase in the atomic number of the metal, the stability of the half-occupied d_5 electronic configuration of the singly charged cation diminishes and the formation of doubly charged cations becomes preferable. It is also noteworthy that the redox reactions of Cp_2Ru and Cp_2Os should be studied on solid electrodes, since on mercury these reactions are complicated by the formation of the corresponding organomercury compounds $(Cp_2M)_2Hg$.[2,3]

The cobaltocenium cation, formed as a result of the reversible one-electron oxidation of cobaltocene, is an isoelectronic analogue of ferrocene.[2,3,38,39] Cobaltocene can also undergo reversible one-electron reduction to the Cp_2Co^- anion.[38–41] In aqueous solutions, Cp_2Co^- is stable in an alkaline medium (pH > 8), while in an acid medium it is protonated at the ligand with formation of cyclopentadiene(cyclopentadienyl)cobalt, which is in its turn oxidised chemically at pH < 4 by the protons of the medium with liberation of H_2 and the formation of Cp_2Co^+.[39] It has been suggested that in acid media the $(C_5H_4COOR)_2Co^+$ (R = H or Me) ions can undergo electrochemical reduction at the substituent with formation of the corresponding aldehyde and alcohol derivatives. In non-aqueous media, the electrochemically generated Cp_2Co^- is protonated by phenols at the ligand with formation of $CpCo(\pi\text{-}C_5H_6)$ but without the formation of the hydride.[41]

The electrochemical behaviour of the heavier cobaltocene analogue—rhodiocene—has also been investigated.[42] It has been shown by polarographic and cyclic voltammetric methods at Hg and Pt electrodes that the Cp_2Rh^+ cation is reduced in acetonitrile in accordance with the scheme

$$Cp_2Rh^+ \overset{e}{\rightleftarrows} Cp_2Rh \overset{e}{\rightleftarrows} Cp_2Rh^-$$
$$\downarrow$$
$$(Cp_2Rh)_2$$

The intermediate rhodiocene is unstable under the conditions of preparative electrolysis and dimerises. Irreversible electrochemical oxidation of the dimer is accompanied by the regeneration of the Cp_2Rh^+ cation. There are no reliable data for the redox reactions of iridiocene and its ions.

Nickelocene, which is reduced most readily among all the known metallocenes, is the last as regards the position of the metal in the Periodic System among the class of metallocenes investigated.[16,17] However, the mechanism of this process is fairly complex. Under the conditions of the preparative electrochemical reduction of Cp_2Ni, a series of products are formed, one of which has been identified as $CpNi(\eta^3\text{-}C_5H_7)$.[17] At a reduced temperature (–58 °C) in DMF, nickelocene undergoes one-electron reduction to the anion Cp_2Ni^-, which is stable under these conditions, the electrode reaction being characterised by a slow charge-transfer stage. According to the author,[17] this is associated with the fact that the electron transfer is accompanied by a change in the solvation shell and/or in the structure of the complex (transition to a "slipped sandwich structure"). The electrochemically generated Cp_2Ni^- reacts with carbon monoxide[43] via the *CEC*-mechanism with decomposition of the sandwich structure:

$$Cp_2Ni^- \rightarrow Cp^- + CpNi \xrightarrow{CO,e} [CpNi(CO)]^- \xrightarrow{3CO} Cp^- + Ni(CO)_4.$$

Apart from the reduction reaction, the electrochemical oxidation reactions of nickelocene, which are electrochemically reversible, have been investigated. Thus the one-electron oxidation of Cp_2Ni in THF, DMF, and acetonitrile at a Pt electrode[16,17] and in the Al/1-butylpyridinium chloride melt at a carbon glass electrode[44] lead to the formation of the Cp_2Ni^+ cation. The subsequent oxidation of Cp_2Ni^+ in acetonitrile at a Pt electrode[45] and in the melt mentioned above[44] is also reversible and is completed by the formation of the Cp_2Ni^{2+} dication, which has been characterised by UV spectroscopy.[44] The dication interacts extremely readily with nucleophiles.

Thus extensive experimental data have accumulated on the redox reaction of metallocenes. Together with the Cp_2M^0/Cp_2M^+ redox transition known previously, the possibility of the Cp_2M^0/Cp_2M^- and Cp_2M^+/Cp_2M^{2+} redox transitions has been demonstrated for a series of metallocenes. The experimentally established forms of the metallocenes are presented in Table 1.

In earlier studies,[8,16] a similar Table resembled in its form an inverted triangle whose height was determined by the number of the known metallocenes or their ions with the d^6 electronic configuration, which is associated with the high stability of these 18-electron complexes. By virtue of the vigorous investigations the metastable metallocenes derived from the transition metal at the beginning of the series and the highly reactive Cp_2M^- and Cp_2M^{2+} ions, the form of Table 1 has changed significantly at the present time.

Table 1. Classification of the experimentally detected metallocenes and their ions in terms of the electronic configuration of the metal in Cp_2M.

d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
V^+	V Cr^+ Mo^+ W^+	V^- Cr Mo W Mn^{+} * Re^+ Fe^{3+} Ru^{3+}	Cr^- Mn^* Re Fe^+ Ru^+	Mn^-,* Fe Ru Co^+ Rh^+ Ni^{2+}	Fe^- Co Rh Ni^+	Co^- Rh^- Ni	Ni^-

*Data for $(C_5Me_5)_2Mn$ are presented.

2. Homo- and hetero-ligand sandwich complexes with other π-ligands

Redox reactions involving a change in the formal oxidation state of the metal are characteristic of all the homo- and hetero-ligand SC as well as metallocenes.[2,5,8,46]

Diarenemetals. The metal in these neutral complexes is formally zerovalent and $(arene)_2M^0/(arene)_2M^+$ transitions are therefore characteristic of these compounds. Examples of such systems are provided by the $(arene)_2Cr$ complexes (where arene = C_6H_6, C_6Me_6, $C_6H_5-C_6H_5$, etc.)[2,47,48] and $(C_6H_6)_2Mo$.[2]

The electrochemical behaviour of the cationic complexes $(C_6H_6)_2Fe^{2+}$, $(C_6Me_6)_2Fe^{2+}$,[49] $(C_6Me_6)Ru^{2+}$,[50] and $(C_6Me_6)Co^{2+}$ [51] has also been investigated. It has been shown by polarographic and cyclic voltammetric methods at Hg and carbon glass electrodes in proton-donating and aprotic media that all of these complexes undergo multistage electrochemical reduction, reversible at each stage, according to the scheme

$$(arene)_2M^{2+} \overset{e}{\rightleftharpoons} (arene)_2M^{+} \overset{e}{\rightleftharpoons} (arene)_2M.$$

It has been shown for $(C_6Me_6)Ru^{2+}$ [50] that the replacement of CH_2Cl_2 by the more strongly coordinated acetonitrile leads to a greater change in the relative solvation energy (E_S) in the $(arene)_2Ru^{2+}$ transition, as a result of which the dication is electrochemically reduced to the neutral complex in a single two-electron stage. It is of interest that the reduction of $(C_6Me_6)Ru^{2+}$ is described by the *EEC*-scheme, where the chemical stage represents the transition from $(\eta^6\text{-arene})_2Ru$ to $(\eta^6\text{-arene})Ru(\eta^4\text{-arene})$. Here it is appropriate to consider also the fundamental problem of oxidation-reduction reactions—the problem of the consecutive or multistage transfer of two electrons. If an oxidation-reduction reaction of this type is represented by the scheme

$$A \pm e \overset{E_1^0}{\rightleftharpoons} A^{-(+)} \pm e \overset{E_2^0}{\rightleftharpoons} A^{2-(2+)},$$

it becomes evident that the quantity $\Delta E^0 = E_1^0 - E_2^0$ reflects the change in the gas-phase ionisation potential I_D in the transition from A to A^+ (for oxidation) or the change in the electron affinity in the transition from A to A^- (for reduction) and, furthermore, the change ΔE_S in the transition from $A^+(A^-)$ to $A^{2+}(A^{2-})$. The quantity ΔE^0, which is significantly smaller than ΔI_D, is determined by the greater solvation energies of A^{2+} and A^{2-} compared with A^+ and A^-. As a result, solvation effects can lead to a transition from the multistage ($1e^- + 1e^-$) mechanism to the apparently single-stage ($2e^-$) mechanism, as happens in the case considered above.[50] On the other hand, the true two-electron transfer, determined by the fact that the transfer of the second electron is energetically more favourable than that of the first, is observed only when the transfer of the first electron is accompanied by structural changes in the SC (*ECE*-process). The AO of the metal usually make the main contribution to the HOMO and LUMO of the sandwich complexes, as a result of which the HOMO and the LUMO have the *d* character. This leads to a relatively weak electronic influence of the substituents in the π-ligands on the quantities E_1^0 and E_2^0.[52] For example, E^0 changes only by approximately 0.2 V for the $(C_6H_{6-x}Me_2)Cr(CO)_3/C_6H_{6-x}Me_x)Cr(CO)_3^-$ redox couples in the transition from $x = 0$ to $x = 6$.[53,54] It is therefore difficult to suppose that the introduction of substituents into the π-ligand can induce the $1e^- + 1e^- \rightarrow 2e^-$ transition. Explicit reversible two-electron processes (the difference between the potentials of the cathodic and anodic peaks on cyclic voltammograms, amounting to 30 mV, can serve as an electrochemical sign of their occurrence) are observed only for certain SC and semi-sandwich complexes. As an example, one may quote the reduction of $(arene)Cr(CO)_3$,[54] where the operation of the $2e^-$ mechanism is a consequence of the $\eta^6 \rightarrow \eta^4$ haptoisomerisation of the arene ligand in the radical-anion stage. An analogous $2e^-$ process, accompanied by a change in the hapto-binding of the ligand, is also characteristic of the reduction of $Cp(\eta^6\text{-}C_6Me_6)Ir^{2+}$.[55] In all these cases, the structural changes occurring in the stage involving the formation of the one-electron reduction products lead to species which are reduced more readily than the initial complexes.

The $(arene)_2Cr^0/(arene)_2Cr^+$ redox couples together with ferrocene[56] have been recommended by IUPAC as internal standards and "pilot" ions for the comparison of the potentials $E_{1/2}$ measured in different solvents. The greater radius and spherical shape of the molecule, the solubility of both redox forms, the high reversibility of the redox reaction, the virtually complete absence of specific solvation effects as a consequence of the shielding of the metal by bulky ligands, and the insignificant change in the electrostatic components of ΔE_S in the transition from one solvent to another [as a consequence of the low surface charge of the complexes], make the $(arene)_2Cr^0/(arene)_2Cr^+$ systems, together with transition metal heteropolyanions[57] and tris(bipyridyl) complexes,[58] more promising as standard redox systems than the metallocenes.[10]

There are data indicating the possibility of the adsorption of $(arene)_2Cr^+$ on a Hg electrode in an aqueous medium.[59] It has been suggested that the adsorption is due to the positive charge of the complex, the "squeezing out" effect, the presence of an unpaired electron, the π-electronic interaction of the cation with the electrode, and the influence of the supporting electrolyte anion.

Metallocarbaboranes. As in other SC, in these complexes the transition metal is linked to dicarbaboryl ligands by π-bonds.[60,61] The study of the electrochemical behaviour (d.c. and a.c. polarography, cyclic voltammetry, and preparative electrolysis) of the dicarbaboryl complexes of iron,[60] cobalt,[38,60] rhodium,[42] nickel,[38,60] palladium,[62] copper[62] and gold[62] in aprotic media showed that, in contrast to the Cp ligands, the dicarbaboryl ligand [Cb = η^6-(3)-1,2-$C_2B_9H_{11}$] stabilises the metal in both the highest and lowest oxidation states. The overall scheme for the redox reactions of these complexes can be represented in the following form:

$$Cb_2M \overset{e}{\rightleftarrows} Cb_2M^- \overset{e}{\rightleftarrows} Cb_2M^{2-} \overset{e}{\rightleftarrows} Cb_2M^{3-}$$

The only exception in the series of dicarbaboryl complexes is platinum dicarbaboride, which has been shown [by cyclic voltammetry in dimethyl sulphoxide (DMSO) and DMF] to undergo the reversible two-electron Cb_2Pt^0/Cb_2Pt^{2-} transition with the subsequent quasi-reversible Cb_2Pt^{2-}/Cb_2Pt^{3-} transition at more cathodic potentials.[63] The two-electron character of the Cb_2Pt^0/Cb_2Pt^{2-} electrode process is probably associated with the transfer of the first electron to the antibonding LUMO and possibly with the solvation effects of the highly coordinating solvents in which the measurements were performed.

Ti, V, and Cr complexes, as well as Mn, Fe, and Co complexes, with another dicarbaboryl ligand $Cb^- = \eta^6$-(4)-1,6-$C_2B_{10}H_{12}$ have also been synthesised and characterised electrochemically.[64,65] The reversible redox transitions

$$Cb'_2M^- \overset{e}{\rightleftarrows} Cb'_2M^{2-} \overset{e}{\rightleftarrows} Cb'_2M^{3-}$$

are characteristic of these complexes too. Metallocarbaboranes can also be recommended as standard redox systems, although they are less readily available.

Other homoligand sandwich complexes. It has been shown by voltammetric and coulometric methods at Pt electrodes that bis(azaboralinyl)metal complexes [η^5-$C_3H_3B(Me)NR]_2M$ (R = H, Et, Bu, or $SiMe_3$; M = Co or Fe) in THF and CH_2Cl_2 undergo reversible one-electron oxidation to the corresponding cations, whose stability depends on the nature of R and M.[66]

Bis(cyclo-octatetraene)uranium $(COT)_2U$ is oxidised in THF, acetonitrile, benzonitrile, and CH_2Cl_2 at Hg, Pt, and carbon glass electrodes at temperatures below 10 °C in a single reversible two-electron stage to the dication via the *ECE*-mechanism, according to which the transfer of the first electron leads to the formation of the unstable cation $(COT)_2U^+$, which undergoes rapid structural and/or solvation changes with formation of a new more readily oxidisable cation.[67] With increase in temperature or with decrease in the rate of scanning of the potential, the electrochemically generated dication reacts with the initial "uranocene", forming the dimeric dication $(COT)_4U_2^{2+}$, which is capable of irreversible one-electron oxidation with elimination of cyclo-octatetraene and the formation of $(COT)_3U_2^{3+}$.

Mixed-ligand sandwich complexes. The heteroligand SC resemble in their electrochemical properties their homoligand analogues. They too are characterised by reversible one-electron reactions, which proceed with a change in the formal oxidation state of the metal. It has been established by polarographic, cyclic voltammetric, and preparative electrolysis methods in non-aqueous media that the redox transitions

$$[CpMCb]^+ \overset{e}{\rightleftarrows} CpMCb \overset{e}{\rightleftarrows} [CpMCb]^- \overset{e}{\rightleftarrows} [CpMCb]^{2-},$$
M = Fe (Ref.38), Co (Ref.45), Ni (Ref.60);

$$[CpMCb']^- \overset{e}{\rightleftarrows} [CpMCb']^{2-} \overset{e}{\rightleftarrows} [CpMCb']^{3-},$$
M = Fe (Ref.64), Co (Ref.64), Ti (Ref.65);

$$[(arene)MCp]^{2+} \overset{e}{\rightleftarrows} [(arene)MCp]^+ \overset{e}{\rightleftarrows} (arene)MCp \overset{e}{\rightleftarrows} [(arene)MCp]^-,$$
M = Fe (Refs.2, 51), Co (Ref.55), Ir (Ref.68), Rh (Ref.69);

$$(COT)\,TiCb \overset{e}{\rightleftarrows} [(COT)\,TiCb]^- \text{ (Ref.65)};$$

$$(COT)\,TiCp \overset{-e}{\rightleftarrows} [(COT)\,TiCp]^+ \text{ (Ref.70)};$$

$$(\eta^5\text{-L})\,Ti\,(COT) \overset{e}{\rightleftarrows} [(\eta^5\text{-L})\,Ti\,(COT)]^-,$$
L = indene, fluorene (Ref.70);

$$(\eta^5\text{-}C_7H_7)\,MCp \overset{-e}{\rightleftarrows} [(\eta^5\text{-}C_7H_7)\,MCp]^+,$$
M = V (Ref.71), Cr (Ref.72).

are possible. The study of the electrochemical synthesis of η^4-arenemetal complexes by the electrochemical reduction of the corresponding η^6-arene complexes as well as the electrochemical investigation of $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation—the postulated key stage in the catalytic hydrogenation of arenes,[73] ligand substitution reactions,[74] and isomerisation of complexes[75]—by polarography, cyclic voltammetry, and preparative electrolysis showed[55] that in non-aqueous media (CH_2Cl_2, acetonitrile, DMF, etc.) the complex $[(C_5Me_5)M(C_6Me_6)]^{2+}$ is reduced in two one-electron stages when M = Rh, whereas with M = Ir it is reduced in one two-electron stage, to the corresponding neutral complexes which consist, according to ^1H NMR data, of compounds having the structure $(\eta^5\text{-}C_5Me_5)M(\eta^4\text{-}C_6Me_6)$. It has been suggested that the $\eta^6 \rightarrow \eta^4$ hapto-isomerisation ($k \cong 10^3$ s^{-1}; stabilisation energy ~38 kJ mol^{-1}), leading to the thermodynamic stabilisation of these complexes, takes place in the stage involving the transfer of the second electron and is accompanied by the transition from the relatively unstable 20-electron complex to the stable 18-electron complex. The $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation is facilitated on passing from 3*d* metals to 4*d* and 5*d* metals. It has been shown for the redox transitions

$$[(C_5Me_5)\,Rh\,(C_6Me_6)]^{2+} \overset{e}{\rightleftarrows} [(C_5Me_5)\,Rh\,(C_6Me_6)]^+ \overset{e}{\rightleftarrows} (C_5Me_5)\,Rh\,(C_6Me_6)$$

that an increase in the Gutman's donor number of the solvent from 0 to 30 lowers $\Delta E^0 = E^{2+}/E^+ - E^+/E^0$ from 0.37 to 0.09 V as a result of the greater influence of the solvation effects on E^{2+}/E^+, but hardly affects the kinetics of the hapto-isomerisation. The oxidative cleavage of polyolefin cobalt SC (COT)CoCp and (COD)CoCp (whhere COD = cyclo-octadiene) in strongly (acetonitrile) and weakly (CH_2Cl_2) coordinating solvents has been investigated electrochemically.[76] In acetonitrile, these complexes undergo irreversible electrochemical oxidation accompanied by the cleavage of the polyolefin–metal bond, which can be described by the scheme

$$LCoCp \xrightarrow{-e} [LCoCp]^+ \xrightarrow[(A^+)]{+aMeCN} L + [CpCo\,(MeCN)_3]^+ \xrightarrow{-0.5e} \rightarrow 0.5Cp_2Co^+ + 0.5Co^{2+} + 3MeCN,$$
L = COT, COD. (2)

On the other hand, in CH_2Cl_2 the transfer of the first electron is reversible, while the A^+ cation is more stable (it has been characterised by its EPR spectrum in relation to the compound where L = COD), although it does undergo further reaction according to formula (2). The possibility of the isomerisation 1,5-COT ⇄ 1,3-COT in the cation A^+ has been discussed.

In order to investigate the possibility of carrying out electrochemically the reaction involving the abstraction of a hydride ion from $[CpM(\eta^6\text{-}C_7H_8)]^+$ (where M = Fe or Ru; $\eta^6\text{-}C_7H_8$ = η^6-cycloheptatriene) accompanied by its conversion into $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$, which is possible in principle, by the cyclic voltammetric method in acetonitrile, a study has been made of the electrochemical oxidation of $[CpM(\eta^6\text{-}C_7H_8)]^+$.[77] Despite the fact that the electrochemical oxidation does indeed involve the coordinated cycloheptatriene with its conversion into $\eta^7\text{-}C_7H_7^+$, the passivation of the electrode by the products of the decomposition of the complexes prevents the preparative electrochemical synthesis of $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$. It has also been noted that, for $E < -1$V, the complexes $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$ undergo one-electron reduction, specific with respect to the method, which is, however, electrochemically irreversible.

The redox properties of mono- and di-phosphaferrocenes have been investigated[78] in CH_2Cl_2, $H_2\overline{COCOOCH}Me$, acetonitrile, DMF, and other non-aqueous solvents. Like ferrocene, these SC undergo reversible one-electron reduction to relatively unstable anions and one-electron oxidation to cations, whose stability depends significantly on the nature of the solvent. Analysis of the EPR spectra of the phosphaferrocenium cations permitted the conclusion that the unpaired electron is predominantly localised on the metal atom. The character of the change in the redox properties on passing from Cp_2Fe to phosphaferrocenes (the anodic shifts of E^0 on reduction and oxidation are respectively 0.39 and 0.19 V) is due to the change in the energy of the redox MO on replacement of the CH group in the Cp ligand by the phosphorus ligand.

The standard potentials of the redox reaction of the majority of homo- and hetero-ligand SC have been compiled in tables in a number of communications.[23,79,80]

Dinuclear sandwich complexes. It has been shown by cyclic voltammetry[81] that the dications $\{(\eta^{10},\mu^2\text{-}C_{10}H_8)[(\eta^6\text{-}C_6R_6)Fe]^2\}^{2+}$ (R = H or Me; $C_{10}H_8$ = fulvalene), designated henceforth by B^{2+}, are capable of the redox transitions

$$B^{2+} \overset{e}{\rightleftarrows} B^{+} \overset{e}{\rightleftarrows} B^{0} \overset{e}{\rightleftarrows} B^{-} \overset{e}{\rightleftarrows} B^{2-}$$

which are separated on the potential scale, with the intermediate formation of the mixed-valence complexes [Fe(2+) Fe(1+)](B^+) and [Fe(1+) Fe(0)](B^-). The complexes B^+ and B^0 have been characterised in terms of their magnetic susceptibility and also by EPR and NMR spectra. The electron exchange between the Fe nuclei in B^+ takes place at a rate $> 10^9$ s^{-1} at 4.2 K, the fulvalene ligand being involved in this process.

The oxidation-reduction properties of monometallic and dimetallic cyclophane complexes of ruthenium[50,82] and iron[83] in non-aqueous media (THF, CH_2Cl_2, CH_3COCH_3, DMF, etc.) have been investigated by cyclic voltammetry, chronoammetry, and preparative electrolysis. Together with the $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation of the arene ligand, accompanying the multistage two-electron reduction of the dications $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}L)]^{2+}$ (L = cyclophanes),[50,82] the complex $[(CpFe)_2(\eta^6\text{-}L)]^{2+}$ is reduced via two stages with similar potentials.[83] This process leads to the formation of the relatively unstable [Fe(2+)Fe(1+)] and [Fe(1+)Fe(1+)] complexes, which decompose with ejection of the cyclophanes and the formation of the solvated CpFe fragment, which disproportionates to ferrocene and Fe^0. It has been suggested[83] that the low stability of the neutral cyclophane complexes compared with CpM(arene) is due to the smaller degree of overlap of the orbitals of the cyclophane ligand and the AO of the metal as a result of the steric strain in the cyclophane structure.

We shall now consider metallocenophanes having the general formula $[(\eta^5\text{-}C_5H_4)CH_2]_2M^1M^2$, where M^1M^2 = FeFe, FeRu, or RuRu.[84]. In benzonitrile, the compound with $M^1 = M^2$ = Fe undergoes oxidation, specific with respect to each of the ferrocene fragments, in two reversible one-electron stages, which indicates the absence of appreciable interactions between these fragments. Such interaction is also absent from the complex with M^1 = Fe and M^2 = Ru, which undergoes a quasi-reversible one-electron oxidation specific with respect to the ferrocene fragment and irreversible two-electron oxidation specific with respect to the ruthenocene fragment. For $M^1 = M^2$ = Ru, both metallocene fragments probably interact strongly with one another, as a consequence of which the complex undergoes quasi-reversible two-electron oxidation at potentials displaced to the cathodic region by 0.54 V compared with the ruthenocene oxidation potentials. Analysis of the ^1H NMR spectra of the oxidation products has led to the conclusion that the oxidation involves a single ruthenocene fragment.[84]

The electrochemistry of bis(fulvalene)dimetal complexes $(C_{10}H_8)_2M_2$ (M = V, Cr, Fe, Co, or Ni) has been investigated in acetonitrile.[85] It has been shown by cyclic voltammetry at a Pt electrode that most of these complexes are capable of redox transitions:

$$(C_{10}H_8)_2M_2^0 \overset{-e}{\rightleftarrows} [(C_{10}H_8)_2M_2]^+ \overset{-e}{\rightleftarrows} [(C_{10}H_8)_2M_2]^{2+}.$$

Redox transitions with a change in the formal oxidation state of the metal are also characteristic of triple decker SC[86-88] and there is a significant increase in the number of possible redox transitions as a result of the increase in the numbers of metal atoms.

Examples of such systems are

$$[CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2+} \overset{e}{\rightleftarrows} [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{+} \overset{e}{\rightleftarrows}$$
$$\rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{0} \rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{-} \overset{e}{\rightleftarrows}$$
$$\rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2-} \quad \text{(Ref.87)}$$

and

$$[CpCo(COT)]^{2+} \overset{e}{\rightleftarrows} [CpCo(COT)]^{+} \overset{e}{\rightleftarrows} [CpCo(COT)]^{0} \overset{e}{\rightleftarrows} [CpCo(COT)]^{-} \text{ (Ref.88).}$$

The behaviour of other polynuclear SC in redox reactions has been described in a number of communications.[2-8,61,86,89-91]

In concluding the consideration of the oxidation-reduction reactions of SC, we may note that the author's aim was not the unrealistic task of providing exhaustive information about all the investigations in this large field. In particular, the question of the electronic effects of substituents on the redox properties of SC, with which one can become acquainted from other publications,[2-6,90] has been hardly dealt with. Whenever possible, later studies are quoted in which earlier publications on the same topic are mentioned. The author's aim was to demonstrate that the quantitative characteristics of the oxidation-reduction reactions of the class of complexes considered are determined primarily by the nature of the metal atom involved. The discovery of a quantitative relation between the redox properties of SC and the corresponding metals would make it possible, without resorting to additional physicochemical studies, to estimate beforehand, from tabulated data for metals, the redox properties of the corresponding complexes. This problem of

predicting the reactivities of metal complexes from the properties of the metal involved (even for individual classes of complexes and individual types of reactions) is of fundamental importance.

3. Linear relations between the redox potentials of sandwich complexes and the gas-phase ionisation potentials of metals

A model has been proposed[79] permitting the estimation of the contribution of the energies of the *d* orbitals of the metal to the redox orbitals of the complexes. This model has been used to discover the trends in the behaviour of the redox potentials of octahedral and pseudo-octahedral complexes, in particular metallocenes. However, the variation of the quantities E^0 as a function of the number of the *d* electrons of the metal, the charge of the complex, the type of the ligand environment, the character of the spreading of the redox MO, the electron pairing energy, etc. has been examined at a purely descriptive level. Attempts have been made to find a correlation between the quantities $E_{1/2}$ for metallocenes and the gas-phase ionisation potentials of metals (IP), but these were limited, since the comparison was carried out only for a single Cp_2M^0/Cp_2M^- redox transition and for a limited range of metals (V, Cr, Fe, Ni).[17] An attempt has also been made to find a correlation[16] between the potentials $E_{1/2}$ of the Cp_2M^0/Cp_2M^+ (M = V, Cr, Fe, Co, or Ni) redox transitions and the ionisation potentials of the complexes in the gas phase, but for certain metallocenes an appreciable deviation from the linear relation predicted by the equation[6,92]

$$E_{1/2} = 0.92\,I_D - 6.20.$$

was observed. Although the ionisation potentials have now been measured for a large number of SC,[13] such correlation is hardly suitable for the prediction of the redox properties, especially if one is dealing with complexes which have not yet been synthesised or which are unstable, for which the values of I_D are unknown. Furthermore there are no reliable literature data for the second, third, and subsequent ionisation potentials of the complexes, while the values of IP for the metals are readily available.[93]

A completely different approach has been proposed in studies[23,80,94] in which the existence of a linear relation between the standard potentials *of all possible redox transformations* of SC [see, for example, Eqn.(1) for metallocenes] and the IP of the corresponding metals has been established and justified. The existence of such a relation is due to the fact that the main contribution to the HOMO and LUMO of sandwich complexes comes from the AO of the metals[11-13,93] and the potentials E^0 for the electron transfer reactions in the series of SC, involving precisely the HOMO and LUMO,[2,3] should in fact reflect the change in the state of oxidation of the metal, whose measure is the IP.[23] Furthermore, the SC retain their plane-parallel structure regardless of the formal oxidation state of the metal and the solvation energy of the components of the redox couples, for example, Cp_2M^x/Cp_2M^{x-1}, depend little on the nature of the metal, since the manifestation of the effects of specific solvation is prevented by the bulky ligand environment in the SC. As a result, the solvation effects in the redox transition of SC are associated mainly with the electrostatic component E_S, which is approximately the same for equally charged isostructural complexes.[9,57,94] The change in E_S on transition from, for example, Cp_2M^x to Cp_2M^{x-1} makes approximately the same contribution to E^0 for different metals. Furthermore, the predominantly electrostatic character of the influence of E_S on the potentials E^0 for SC permits a comparison of the redox potentials of the SC measured in different solvents.[23] The set of these quantities leads to a significantly linear relation between E^0 and IP for all possible redox reactions of homo- and hetero-ligand SC.[23,80,94] However, in certain cases, for example, for individual di(arene)metal complexes,[47,48] whose redox reactions occur with electron transfer to the ligand, such a linear relation does not hold.

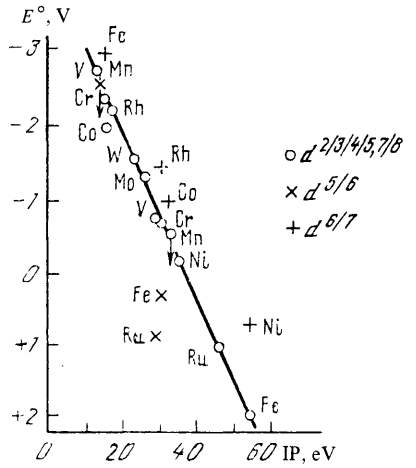


Figure 1. Dependence of E^0 for the d^x/d^{x+1} transitions in the series of metallocenes on the corresponding gas-phase ionisation potentials of the metals.[23] The values of E^0 for $(C_5Me_5)_2Mn$ are quoted in the case of manganocene; the arrows indicate the shift of E^0 taking into account the effects of the substituents.

Figs. 1 and 2 present the E^0–IP relations for metallocenes and metallocarbaboranes respectively. The parallel variation of the potentials E^0 and the corresponding IP is clearly seen (E^0 increases with IP), but certain points deviate significantly from the straight line. All these deviations refer to the redox transitions involving the most stable 18-electron configuration of the complex. The deviation of the quantities E^0 for the d^5/d^6 redox transitions in the direction of more positive potentials, which might have been expected from the IP of the metals, is not fully understood if account is taken of the order in which the redox orbitals of the metallocenes are filled with electrons. However, such deviations are characteristic only of iron subgroup metallocenes and are in all probability caused by the extraordinary stability of the metallocenes of this subgroup. As regards the d^6/d^7 redox transitions, it is clear, since in this case the electron is transferred to the antibonding e_1^* orbital of the SC,[11-13,95] that the potentials E^0 for these electronic transitions must deviate consistently in the direction of more negative potentials, because electron transfer to the given orbital requires an additional energy expenditure in order to overcome the splitting energy in the crystal field of the ligand. The splitting between non-bonding (a_{1g}) and antibonding (e_{1g}^*) orbitals can probably be estimated from the degree of deviation of the E^0 in the case of the d^6/d^7 redox transitions.

It is seen from Figs. 1 and 2 that the same slope of the E^0–IP relations, amounting to approximately 0.1 V eV^{-1}, is characteristic of SC of three different types. This makes it possible to predict the

redox properties of different SC from the IP of their metals, *provided that E^0 is known for at least one of the redox transitions of one of the complexes of the given type.* In fact, this is equivalent to the creation of a single redox scale for transition metal SC, which is especially important for SC which have been weakly characterised electrochemically, have not yet been synthesised, or are so unstable that their electrochemical investigation is impossible. This approach permits the expression of the potential of any possible redox transitions of hetero- and homo-ligand SC by the simple equation

$$E^0 = \sum_{i=1,2} a_i + 0.1 \text{ IP}.$$

The constants a_i have been calculated[23] for the principal types of π-ligands (in V): −2.08 for Cp, −0.73 for η^6-C_6H_6, +1.52 for η^7-C_7H_7, −3.61 for η^8-COT, −2.05 for Cb, and −1.70 for Cb′. Fig. 3 illustrates graphically the validity of the proposed approach (the E^0–IP relations calculated from the constants a_i found previously are shown by dashed lines).

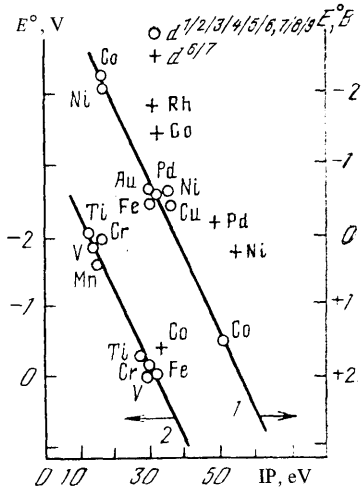


Figure 2. Dependence of E^0 for the d^x/d^{x+1} redox transitions in the series of metallocarbaboranes Cb_2M (line *1*) and Cb'_2M (line *2*) on the corresponding gas-phase ionisation potentials of the metals.[23]

The existence of a linear relation between the reactivity of SC in oxidation-reduction reactions and the ionisation potentials of the metals makes it possible to investigate systematically the regions of the thermodynamic stability of compounds of this type as a function of the nature of the metal, to understand the causes of the two-electron character of the oxidation-reduction reactions of certain complexes uncharacteristic of SC, to select the optimum conditions for the synthesis and investigation of the physicochemical characteristics of SC, to assess the possibility of the synthesis of various SC, to determine the redox properties of both relatively unstable and hitherto not synthesised SC, etc. A study has been devoted to the consideration of these questions.[23] In addition, its authors (see also Ref. 94) discuss questions associated with the application of the linear relations between E^0 and IP to the estimation of the reactivities of octahedral metal complexes in oxidation-reduction reactions and consider the factors which determine the slopes of these relations.

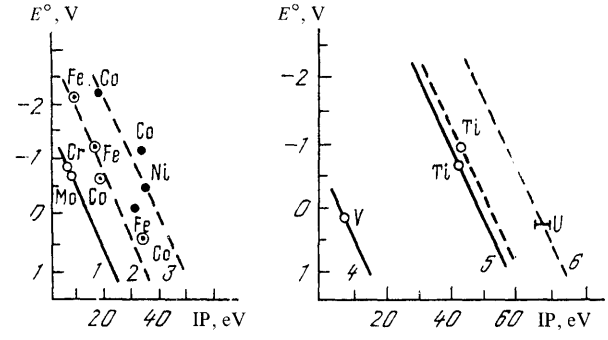


Figure 3. Dependence of E^0 on IP for the d^x/d^{x+1} redox transitions in the series of homo- and hetero-ligand sandwich complexes:[23] *1*, $(arene)_2M$; *2*, (arene)MCp; *3*, CpMCb; *4*, $CpM(C_7H_7)$; *5*, $(C_8H_8)MCb$; *6*, $(C_8H_8)_2M$. The dependences calculated from the values of a_i found previously are shown by dashed lines.

III. Electrochemical behaviour of bis(cyclopentadienyl) bent sandwich complexes

The enhanced interest in the mechanism of the electrochemical reduction of metallocene dichlorides is due to the fact that these compounds are components of catalytic systems used for the polymerisation, hydrogenation, and isomerisation of olefins,[96,97] while the products of their reduction activate small molecules such as molecular nitrogen,[98] and CO,[99–104] promote the reduction of the latter, etc. The catalytic activity of systems based on the complexes Cp_2MCl_2 is manifested as a rule for low oxidation states of the metal, so that the study of the mechanism of the reduction of these complexes is an important task.

Quantum-chemical analysis[12] shows that in both BC and SC the AO of the metal makes the main contribution to the HOMO and LUMO of the complexes, so that compounds of this type can also evidently undergo redox reactions with a change in the formal oxidation state of the metal, i.e. with a change in the electron density mainly on the metal atom.

Among the BC of Group IVB metals, titanocene dichloride has been most thoroughly investigated (as regards electrochemical properties). However, despite the fact that many studies have been carried out,[105–111] until recently there has been no unanimous view concerning the detailed mechanism of its reduction.

The reduction of Cp_2TiX_2 (X = Cl or Br) in THF has been investigated by polarography, cyclic voltammetry (Pt and carbon glass electrodes), preparative electrolysis, and EPR spectroscopy.[105] It has been suggested that the reduction takes place in three reversible one-electron stages:

$$Cp_2TiX_2 \overset{e}{\rightleftarrows} [Cp_2TiX_2]^- \overset{e}{\rightleftarrows} [Cp_2TiX_2]^{2-} \overset{e}{\rightleftarrows} [Cp_2TiX_2]^{3-}.$$

The $Cp_2TiX_2^-$ anion is stable in solution and can be obtained on a preparative scale, while the $Cp_2TiX_2^{2-}$ dianion is unstable and is converted under these conditions into Cp_2TiX^- with elimination of X^-. The paramagnetic $Cp_2TiX_2^-$ and $Cp_2TiX_2^{2-}$ complexes have been characterised by EPR spectra. The conclusion that the stage involving the transfer of the first electron is electrochemically and chemically reversible and that the $Cp_2TiX_2^-$ anion is stable in solution in the absence of moisture and oxygen has been confirmed also in subsequent studies.[106,107]

It has been found from cyclic voltammetric, preparative electrolysis, and EPR spectroscopic data[108–110] that, although Cp_2TiCl_2 does in fact undergo electrochemically reversible reduction to the $Cp_2TiCl_2^-$ anion in an aprotic medium, the anion is unstable and rapidly loses Cl^-, which is replaced by a molecule of the solvent or another suitable ligand (L) with formation of the complex $Cp_2Ti(L)Cl$. The complex $Cp_2Ti(L)Cl$ is in its turn capable of reversible one-electron oxidation to $Cp_2Ti(L)Cl^-$, which is converted into the initial Cp_2TiCl_2 in the presence of an excess of Cl^-.[109] As the electron-donating properties of L are enhanced in the sequence THF < Py < DMF, the rate of the forward reaction

$$Cp_2TiCl_2^- + L \rightleftarrows Cp_2Ti(L)Cl + Cl^- \qquad (3)$$

increases while that of the reverse reaction falls. The complex $Cp_2Ti(THF)Cl$ has been characterised by EPR spectroscopy.[108]

The electrochemical reduction of Cp_2TiCl_2 has also been investigated in the $AlCl_3$/1-butylpyridinium chloride melt.[37] It has been suggested that the product of the first reversible one-electron stage is the complex $Cp_2Ti[Al_2Cl_7]$ with two Ti–Cl–Al bridge bonds.

The replacement of Cl^- by the more electronegative ligand NCS^- greatly facilitates the reduction of Cp_2TiX_2.[111] The electro-chemically generated $Cp_2Ti(NCS)_2^-$ (characterised by EPR spectroscopy) is stable under these conditions in THF and CH_2Cl_2 at room temperature. The irreversibility of the first reduction stage in DMF has been attributed to the irreversible dimerisation of the anion, which forms a diamagnetic dimeric titanium(III) complex.

The data of Kukharenko et al.[112] in the main agree well with the results of other studies.[108–110] According to these data, the electro-chemically generated $Cp_2TiCl_2^-$ anion is unstable and is rapidly but reversibly dehalogenated in accordance with Eqn.(3) with formation of Cp_2TiCl_3.‡ The subsequent one-electron reduction of Cp_2TiCl leads to the formation of the unidentified "titanocene Cp_2Ti", which is capable according to the authors,[110–112] of undergoing one-electron reduction. However, it has been suggested[110] that the product of the reduction of Cp_2TiCl is a dimeric titanium(II) complex and not the "titanocene".

Among heavier analogues of Cp_2TiX_2, the dichlorides of zirconocene[105,112–115] and hafnocene[112,113,115] have been investigated in electrochemical reduction processes. In THF, these metallocene dichlorides undergo reversible one-electron reduction with formation especially at reduced temperatures (from –40° to –20 °C), of extremely stable $Cp_2MCl_2^-$ anions, which have been characterised by EPR spectroscopy.[113–115] The $Cp_2ZrCl_2^-$ and $Cp_2HfCl_2^-$ anions undergo further irreversible one-electron reduction in the region of extremely cathodic potentials (from –2.95 to –3.05 V) probably to the "corresponding metallocenes".[112] At room temperature the electrochemically generated $Cp_2MCl_2^-$ anions are apparently dehalogenated with formation of the more readily reduced mono-chlorides.[112] The rate of dehalogenation of $Cp_2MCl_2^-$ diminishes in the sequence Ti > Hf > Zr as a function of the nature of the metal, but the rate of the reverse reaction (3) increases in the sequence Hf $\lesssim$ Zr $\ll$ Ti.[112] Together with dehalogenation, there is also a possibility of the destruction of the zirconium- and hafnium-containing anions $Cp_2MCl_2^-$ via the reaction[113,115]

$$Cp_2MCl_2^- \rightleftarrows Cp^- + CpMCl_2.$$

The electrochemical behaviour of bridged titanocene dichlorides $(CH_2)_x(C_5H_4)_2TiCl_2$ (x = 1–3) and substituted titanocene dichlorides in THF has been investigated.[116,117] While the reduction mechanism is the same, the potentials $E_{1/2}$ for the reduction of the bridged monochloride complexes are displaced towards more cathodic values by 0.05–0.3 V compared with the non-bridged analogues. It has been suggested[116] that the influence of the bridging substituents on $E_{1/2}$ is due to their steric and not the inductive effect.

The reversible one-electron reduction of dialkyl derivatives of titanocene and zirconocene—Cp_2MR_2 (R = Me or $PhCH_2$)—in THF leads to the formation of corresponding unstable anions, which are destroyed with the elimination of R^- or Cp^-.[113,118–120] In THF, {2,3-bis(methylene)bicyclo[2.2.2]octane}zirconocene undergoes one-electron reduction to the corresponding radical-anion, which is relatively stable at 20 °C (characterised by its EPR spectrum), but decomposes with the dissociation of the zirconocene–diene bond on raising the temperature.[121] References to other studies on the electrochemical reduction of dialkylmetallocenes may be found in other reviews.[4,5]

The $Cp_2TiR_2^-$ anion, stable at –30 °C, has been obtained by the reversible one-electron reduction of Cp_2TiR_2 (R = C≡CPh) in THF. On heating to 25 °C, it slowly and reversibly splits off Cp^- with formation of $CpTiR_2$, which reacts in its turn with $Cp_2TiR_2^-$ to form $CpTiR_2^-$.[122]

Cp_2TiCl, generated electrochemically in THF, reacts with benzo[*c*]cinnoline (RN=NR) to form the dinuclear complex $Cp_2Ti(Cl)N(R)N(R)(Cl)TiCp_2$. This reaction has been considered[123] as a model for the activation of the N=N double bond.

The electrochemistry of Group VB metallocene dichlorides has been investigated in relation to vanadium and niobium compounds. However, there is no unanimous view in the literature concerning the detailed mechanism of the stability of the products of the electro-chemical reduction of these BC. Thus, the following mechanism for the reduction reaction has been proposed on the basis of data for the polarographic reduction of Cp_2VCl_2 in THF:[16]

$$Cp_2VCl_2 \overset{e}{\rightleftharpoons} [Cp_2VCl_2]^- \overset{e}{\rightleftarrows} [Cp_2VCl_2]^{2-} \xrightarrow{-2Cl^-} Cp_2V.$$

It has been claimed[16] that the $[Cp_2VCl_2]^-$ anion is stable and can be obtained by preparative electrochemical reduction. The agreement of the values of $E_{1/2}$ for the third wave on the Cp_2VCl_2 polarogram and the vanadocene reduction wave permitted the conclusion that vanadocene is the product of the two-electron reduction of Cp_2VCl_2.

In contrast to this, it has been concluded[18] that the transfer of the first electron to Cp_2VCl_2 is accompanied by the formation of the $Cp_2VCl_2^-$ anion, which, however, is extremely stable and rapidly but reversibly splits off Cl^- with formation of the monochloride Cp_2VCl, which is in fact reduced to vanadocene. Other data[124] confirm the validity of this conclusion.

‡Here and henceforth the coordinated solvent molecule is not shown for the sake of simplicity in the formulae of the monochloride complexes Cp_2MCl.

The study of the reduction of the biscyclopentadienylvanadium complexes with different types of chelating agents showed that the product of the two-electron multistage reduction of these complexes is vanadocene.[125]

A reversible one-electron wave, corresponding to the formation of the $Cp_2NbCl_2^-$ anion, has been observed in the electrochemical reduction of niobocene dichloride in THF.[126,127] On the basis of cyclic voltammetric and preparative electrochemical reduction data, it has been suggested[127] that the electrochemical reduction of Cp_2NbCl_2 proceeds via the *ECE*-mechanism and is completed by the formation of a dimeric μ-chloride complex, which is stable at −30 °C:

$$Cp_2NbCl_2 \overset{e}{\rightleftharpoons} Cp_2NbCl_2^- \xrightarrow{-Cl} Cp_2NbCl \xrightarrow{+Cp_2NbCl_2^-} [Cp_2NbClCl_2NbCp_2]^-.$$

At room temperature, the one-electron reduction of niobocene dichloride leads to the formation of $(Cp_2NbCl)_2$, while in the presence of L = Ph_3P or $(PhO)_3P$ it yields $Cp_2Nb(L)Cl$.[128] The subsequent one-electron reduction of $(Cp_2NbCl)_2$ is accompanied by the rapid dissociation of the anion generated to Cp_2NbCl and Cp_2NbCl^-; it has been suggested that the dehalogenation of Cp_2NbCl^- [128] results in the formation of metastable niobocene, which is destroyed in subsequent reactions. Previously the formation of niobocene as the primary metastable product of the amalgam reduction of Cp_2NbCl_2 was detected by EPR.[129]

The reversible one electron oxidation of niobocene dichloride in THF leads to the preparation of the unstable $Cp_2NbCl_2^+$ cation, which is converted into Cp_2NbCl^+ as a result of the reductive elimination of the chlorine atom.[130]

It has been established by cyclic voltammetry that the dithiolene complexes $(Cp_2NbS_2C_2R_2)^+$ (R = Me or Ph) are reduced in THF in two reversible one-electron stages to a neutral compound and a monoanion respectively. The complex $Cp_2NbS_2C_2R_2$ can be obtained by preparative electrolysis.[131]

The complex $[Cp_2TaL]^+$, where L = 1,2-bis(dimethylphosphino)-ethane, is oxidised in an aprotic medium (CH_2Cl_2, acetonitrile, or acetone) in two reversible one-electron stages to $[Cp_2TaL]^{2+}$ (characterised by its EPR spectrum) and $[Cp_2TaL]^{3+}$ respectively according to data obtained by cyclic voltammetry.[132]

In contrast to Group IVB and VB metallocene dichlorides, the complexes Cp_2MCl_2 (M = Mo or W) are reduced in an aprotic medium to the corresponding unstable metallocenes in one two-electron stage, [22,23] because the first electron in the Group IVB and VB complexes is transferred to a non-bonding orbital, while in the Group VIB metallocene dichloride the analogous transfer is to an antibonding MO. On the one hand, this entails a cathodic shift of the Cp_2MCl_2 (M = Mo or W) wave relative to the first reduction waves of the Group IVB and VB complexes, since the electron is transferred to an antibonding MO whose energy is significantly higher[12] and, on the other hand, it leads to marked destabilisation of the $Cp_2MCl_2^-$ form, which is rapidly and irreversibly dehalogenated with formation of an M(III) complex more readily reducible than the initial metallocene dichloride.[22] It has been shown[124] that Cp_2M^+ is a product of this kind. Thus the reduction of Group VIB metallocene dichlorides proceeds via the *ECE*-mechanism with $E^0 < E_2^0$.

The electrochemical oxidation of the complexes Cp_2MX_2 (M = Mo or W; X = Cl, Br, I, or SR, where R = alkyl) has been investigated.[133] In acetonitrile, these complexes undergo reversible one-electron oxidation to the metastable cations $Cp_2MX_2^+$, in which the ligand is substituted by a reductive elimination reaction with ejection of X$^{\cdot}$, which results in the formation of the complexes $[Cp_2M(MeCN)X]^+$. The potentials of the $Cp_2MX_2^0/Cp_2MX_2^+$ redox couples depend only on the nature of M and not X, which has led to the hypothesis that the oxidation involves a non-bonding MO of the complexes to which the main contribution comes from the AO of the metal. The electrochemically generated cations $[Cp_2MSR]^+$ can also dimerise with formation of $[Cp_2M(\mu\text{-}SR)_2MCp_2]^{2+}$. The redox properties of the trinuclear heterometallic complex $Cp_2Ti[(C_5H_4)FeCp]_2$ have also been investigated.[133]

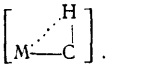
The electrochemical oxidation of the hydrides Cp_2WH_2 and $Cp_2W(Ph)H$ in acetonitrile has been investigated by cyclic voltammetry and preparative electrolysis.[134] The above compounds undergo reversible one-electron oxidation to the corresponding unstable radical-cations (lifetime from 10^{-3} to 20s; characterised by EPR spectroscopy), which are stabilised either via the reductive elimination reaction

$$Cp_2W(Ph)H^{+\cdot} \xrightarrow{-H^+} Cp_2WPh \rightarrow Cp_2W + Ph^{\cdot} \xrightarrow{MeCN} PhH,$$

or as a result of the additive dimerisation

$$Cp_2WH_2^{+\cdot} \xrightarrow{-H^+} Cp_2WH \xrightarrow{Cp_2WH_2} (Cp_2W)_2H_3 \xrightarrow{-e} (Cp_2W)_2H_3^+.$$

The oxidation of $Cp_2WR^1R^2$ (where R^1, R^2 = alkyl, aryl, or Cl) in acetonitrile has been studied.[134] It is suggested that the agostic interaction



takes place in the electrochemically generated cations $[Cp_2WR^1R^2]^+$.

Data on the electrochemical behaviour of lanthanide and actinide BC are extremely limited. It has been shown[136,137] that $(C_5Me_5)_2UCl_2$ undergoes reversible one-electron reduction to the anion in THF and acetonitrile, but the available data on the stability of this anion are contradictory. It has also been reported[138] that Cp_3UX (X = Cl or Me) undergo reversible one-electron reduction in THF with formation of the stable anion Cp_3UX^-. Finally it has been shown by cyclic voltammetry that the reversible one-electron reduction of $(C_5Me_5)_2NpCl_2$ to the anion takes place in acetonitrile.[139]

According to quantum-chemical calculations,[12] the structure of the frontier MO of the bent sandwich complexes Cp_2MCl_2 and Cp_2MCl is qualitatively virtually the same for different metals and the dominant contribution of the metal AO to the redox orbitals of the complexes is retained in all cases. One can therefore expect that the potentials $E_{1/2}$ for the Group IVB and VB biscyclodienylmetal chloride complexes, the characteristic reactions of which are one-electron reduction and oxidation, are also linearly related to the corresponding IP of the metals. This has been confirmed.[94,112] Thus it is seen from the relation between $E_{1/2}$ and IP presented in Fig. 4 that the values of $E_{1/2}$ for the metallocene dichloride complexes[112] fit satisfactorily on the straight line not only for the reversible $Cp_2MCl_2^0/Cp_2MCl_2^-$ redox couples but also for the irreversible $Cp_2MCl_2^-$ reduction reactions of the anions. This is due to the retention of the bent sandwich structure in the Cp_2MCl_2 and $Cp_2MCl_2^-$ complexes and the $Cp_2MCl_2^{2-}$ dianion formed as the primary reduction product of the latter. A specific linear relation exists also for the monochlorides Cp_2MCl, which differ somewhat in their structure (Fig. 4). The same figure shows by a dashed line the analogous relation for metallocenes. Evidently the slopes of all three relations are virtually the same ($\sim$0.1 V eV^{-1}), which is

probably associated with the retention of the dominant contribution of the AO of the metal to the SC and BC redox orbitals and with the similar changes in solvation energies in the redox transitions of the complexes of all three types. On the other hand, the discrepancy between the linear relations for complexes of different types is due to the energy differences between the corresponding redox orbitals of the complexes, which are associated with the differences in the angles of inclination between the cyclopentadienyl rings and with the presence of the electronegative Cl^- ligands.[94,112]

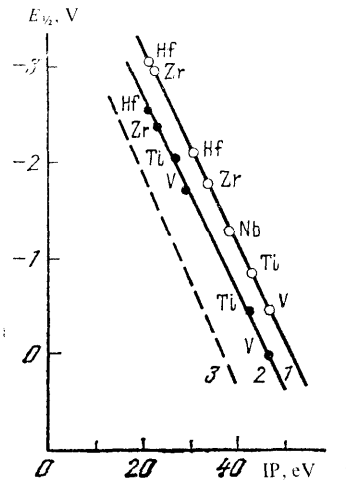
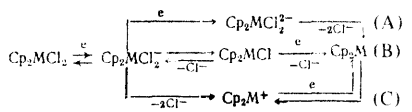


Figure 4. Linear dependences of the half-wave potentials of the complexes Cp_2MCl_2 (line *1*), Cp_2MCl (line *2*), and Cp_2M (line *4*) on the ionisation potentials of the corresponding metals in the gas phase according to Kukharenko et al.[112]

A single mechanism for the electrochemical reduction of the Group IVB–VIB metallocene dichlorides has been proposed on the basis of the linear relation between $E_{1/2}$ and IP established by Kukharenko et al.[112] and the consideration of the character of the redox MO of the complexes. It can be represented schematically as follows:



Pathway A obtains for M = Zr and Hf at a reduced temperature, pathway B for M = Ti and V and M = Zr and Hf at room temperature, and pathway C for M = Mo and W. When metallocenes whose lifetime is comparable to the time of the electrochemical measurement are formed (M = V, Mo, or W), their subsequent reduction to relatively unstable anions becomes possible.[22,24]

In conclusion of the consideration of the electrochemical reactions of the biscyclopentadienyl complexes, we shall deal briefly with the reactivities of the electrochemically generated species in relation to small molecules and certain other substrates. The products of the electrochemical reduction of metallocene dichlorides frequently activate inert molecules, especially CO,[99–103,140,141] CO_2,[140] and N_2,[98] in oxidation-reduction reactions, are inserted in the CH bond,[142] and participate in reactions involving the oxidative addition of olefins with formation of metallocycles,[143] i.e. play an important role in many synthetic reactions. So far there have been comparatively few studies of this kind, but the relative ease of the electrochemical generation of species in non-standard valence states, including unstable states, leads to considerable possibilities for the investigation of the reactivities of the low-valence products of the reduction of SC and BC in reactions with different substrates.

The products of the electrochemical reduction of titanocene dichloride react with CO to form $[Cp_2Ti(CO)Cl_2]^-$ and $Cp_2Ti(CO)_2$, the current yield of the latter amounting to approximately 100%.[107] However, it has been suggested[103] that the product of the one-electron reduction of Cp_2TiCl_2 in a CO atmosphere is the 17-electron complex $Cp_2Ti(CO)Cl$ and not the 19-electron anion $[Cp_2Ti(CO)Cl_2]^-$. This is confirmed by the fact that the significantly more stable $Cp_2MCl_2^-$ anions (M = Zr or Hf) do not react with CO.[103,112]

It is of interest to investigate the possibility of the electrochemically induced insertion of CO in the metal–carbon bond in the alkyl derivatives of metallocenes, because a reaction of this kind has been observed[144] in the electrochemical reduction of $CpFe(CO)_2Me$ in THF in the presence of Ph_3P and the acyl complex $CpFe(CO)(Ph_3P)(COMe)$ was formed as the product.

The interaction of the electrochemically generated "titanocene" with molecular nitrogen has been briefly mentioned.[110] A cathodic shift of the second reduction wave of bridged titanocene dichlorides, attributed to the electrochemical reduction of unidentified hydride and dinitrogen complexes of "titanocene", was observed in THF in the presence of N_2 and H_2. Finally, it has been claimed[145] that the products of the electrochemical reduction of Cp_2TiCl_2 in THF or methanol catalyse the electrochemical reduction of N_2 to NH_3 with a current yield of approximately 2%. However, the fixation of nitrogen was not confirmed by a blank experiment (Ar) and by experiments with $^{15}N_2$.

It has been shown by cyclic voltammetry and preparative electrolysis that the complexes Cp_2VL (L = CO or $C_6H_{11}NC$) undergo reversible one-electron reduction in THF to the corresponding anions, which rapidly decompose to the metal, L, and Cp^-, probably via the immediate formation of CpVL.[146,147]

In the presence of proton donors (phenols, diethylbarbituric acid) in non-aqueous media (THF, DMF, and DMSO, etc.), vanadocene catalyses the amalgam reduction of CO to C_1–C_4 hydrocarbons.[99–103] $Cp_2V(CO)$ behaves as a catalyst-substrate complex, which undergoes one-electron reduction during the catalytic cycle to the $Cp_2V(CO)^-$ anion, as a result of the subsequent protonation and reduction of which the methyl complex Cp_2VMe is formed. The protolysis of this intermediate leads to the formation of methane and chain growth takes place as a result of the insertion of CO in the V–Me bond. As a consequence of the rapid subsequent protonation of the $[Cp_2V(CO)]^-$ anion, the transfer of the first electron to the catalyst-substrate complex takes place against the standard potential gradient.[102] This reaction has been considered as a kind of electrochemical analogue of the Fischer–Tropsch reaction which takes place at room temperature and atmospheric CO pressure. It has been noted[103] that other metallocenes Cp_2M (M = Nb, Mo, or W) also form reducible carbonyl complexes, which can be observed polarographically, for example in the case of M = Mo and W.[22]

However, the deactivation of the unstable metallocenes during the catalytic process prevents their use as catalysts of the conversion of CO into hydrocarbons.

The electrochemical reactions of the complexes of bis(fulvalene)-divanadium with CO and acetonitrile, which take place with a change in the formal oxidation state, have been examined.[85]

IV. Electrochemical synthesis of sandwich and bent sandwich transition metal complexes and of metal complex catalysts based on them

The principal methods of synthesis of SC and BC involve the interaction of the cathodically generated carbanions with the transition metal cations formed on the dissolving anode.[8,148] Bis(cyclopentadienyl) derivatives of manganese, iron, and cobalt[148] and the dicarbaboryl complexes of iron, cobalt, and nickel[148,149] have been obtained recently by this method. The carbonyl complexes of the cyclopentadienyl derivatives of manganese, iron, cobalt, titanium and vanadium are formed when Cp^- is generated by the electrochemical reduction of cyclopentadiene in an aprotic medium and under a CO atmosphere under conditions where transition metal ions are generated anodically.[8,148]

A review[150] has been devoted to the synthesis of SC with cycloolefin ligands and to the reactions involving the introduction of functional groups into SC by the electrophilic addition of alkyl halides and CO_2 to the electrochemically generated metallocene anions with formation of monosubstituted metallocene compounds or via the anodic substitution of hydrogen atoms in ferrocene by alkyl or alkylcarboxy-groups, which are obtained by the anodic decarboxylation of the anions of monocarboxylic and dicarboxylic acids and the half esters of dicarboxylic acids. Individual examples of the introduction of functional groups into the ferrocene and other SC can be found in a number of communications.[4,5,151]

A review[152] has been devoted to the chemical synthesis from metallocenes of various complexes, including catalysts for the cyclooligomerisation and trimerisation of alkynes and nitriles and also for the hydrogenation of alkenes and arenes. The key stage in these reactions is the reduction of Cp_2M by an alkaline metal to the Cp_2M^- anion with subsequent substitution of one or both Cp ligands by an olefin, an arene, a phosphine, CO, N_2, etc. The reduction by an alkali metal can be fully replaced by electrochemical reduction, which makes it possible to expand significantly the scope of the electrochemical synthesis of metal complex catalysts.

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In conclusion one should note that the use of solvents which are stable in the regions of extremely anodic and cathodic potentials greatly expanded our ideas about the possible oxidation-reduction reactions of sandwich and bent sandwich complexes and the establishment of a linear relation between the standard potentials of the redox reaction of complexes of this class and the gas-phase ionisation potentials of the corresponding metals made it possible to find a convenient parameter for defining the reactivity of the SC and BC in oxidation-reduction reactions. The mechanisms of the electrode reactions involving SC and BC have been studied in fair detail. On the other hand, there exist a series of promising aspects of this field in which there are still many unsolved problems. These include the electrochemistry of the BC of the actinides and lanthanides, the reactivity of intermediates in the redox reactions of SC and BC in relation to reagents of different kinds (electrophiles, nucleophiles, small molecules, etc.), and the electrochemical synthesis of SC and BC and of the metal complex catalysts based on them. The study of the electrode reactions of SC and BC in the absence of supporting electrolytes by means of the technique using ultramicroelectrodes is also of interest.[153] This will permit an even more significant expansion of the working range of potentials (from −4 to +5 V) and will make it possible to generate and identify species with an unusual formal oxidation state of the metal and also to avoid the undesirable interaction of the species generated with the components of the supporting electrolyte. Finally, low-temperature studies (cryoelectrochemistry), which will probably make it possible to identify many metastable intermediates in the electrochemical reactions of SC and BC and to investigate their properties, are promising.

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During the preparation of the present review, there has been a sharp growth of the number of studies concerning the use of SC as promoting agents for reactions involving electron transfer from the electrode to different kinds of inorganic and organic substrates. The reduction reactions of oxygen, the nitrate ion, and carbonyl and other organic compounds catalysed by iron SC as well as ligand substitution, *cis–trans* isomerisation, chelation, and demetallation reactions and reactions involving the migration insertion of carbon monoxide in a carbon–metal bond in metal complex and organometallic compounds, induced by charge transfer in catalysis by SC, have been considered in a number of reviews.[154–156]

The oxidation-reduction reactions of the iron SC with polyaromatic hydrocarbons (L = biphenyl, naphthalene, phenanthrene, triphenylene, pyrene, perylene, and caronene), having the general formula $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-}L)]^+$ (R = H or Me) have been investigated.[157] It has been shown by cyclic voltammetry[158] that the reduction of the double decker dinuclear cations $\{[(\eta^5\text{-}C_5Me_5)Fe]_2\text{-}(\eta^{12}, \mu^2\text{-}L\}^{2+}$ (L = biphenyl, 9,10-dihydrophenanthrene, or triphenylene) to the corresponding neutral complexes in non-aqueous solvents is a multistage process which proceeds via the intermediate formation of mixed valence [Fe(1+)Fe(2+)] complexes. The redox reactions of ferrocene-substituted phosphazenes and polyphosphazenes[159] and of the diferrocene complex containing germanium octaethylporphyrinate as the bridge linking the two ferrocene fragments have been investigated.[160] The oxidation-reduction reactions of polynuclear homo- and hetero-ligand SC of transition metals, especially bridged dimetallocenes, bis(fulvalene)-dimetal complexes, metallocenophanes, and multidecker SC have been examined in a review.[161]

On the basis of a comparative study of the electrochemical oxidation of $(C_5Me_2)_2M$ (M = Fe, Ru, or Os) to the corresponding cation in acetonitrile, it has been noted[162] that the variation of the potentials $E_{1/2}$ for the oxidation of the metallocenes investigated in the sequence Fe < Os < Ru parallels the variation of the ionisation potentials of the complexes and the atomic ionisation energies of the corresponding metals. It has been shown[163] by cyclic voltammetry in THF at temperatures in the range −90 to −70 °C that the cobaltocene and nickelocene anions are capable of subsequent one-electron reduction with formation of the unstable Cp_2M^{2-} dianions at potentials more cathodic than −3 V. Under analogous conditions, the formation of the corresponding substituted titanocene and

zirconocene derivatives has been detected in a study of the mechanism of the electrochemical reduction of pentamethyl- and t-butyl-substituted titanocene and zirconocene dichlorides.[164] Thus the cryoelectrochemical approach to the study of the oxidation-reduction reactions of SC and BC proposed by Kukharenko and co-workers[163,164] has made it possible to expand the redox series (1) for metallocenes by yet another member (Cp_2M^{2-}) and also to establish the fundamentally important fact of the existence of the previously unknown Group IVB metallocenes.

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