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Sandwich and bent sandwich complexes. Electrochemical studies

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ABBREVIATIONS

AC	acetone
a.c.	alternative current
AO	atomic orbital
bipy	2,2′-bipyridyl
Bu	butyl

Cb	carborane ligand (η^5-(3)-1,2-$C_2B_9H_{11}^{2-}$)
Cb′	carborane ligand (η^6-(4)-1,6-$C_2B_{10}H_{12}^{2-}$)
CD	cyclodextrin
CHT	cycloheptatrienyl cation (η^7-C_7H_7)$^+$
COD	cyclo-octadiene
COT	cyclo-octatetraene
Cp	cyclopentadienyl anion (η^5-$C_5H_5^-$)
Cp*	pentamethylcyclopentadienyl anion (η^5-$C_5Me_5^-$)
CV	cyclic voltammetry
d.c.	direct current
DME	dimethoxyethane
DMF	dimethylformamide
dmit	1,3-dithiol-2-thiono-4,5-dithiolato dianion
DMSO	dimethyl sulphoxide
ESR	electron spin resonance
ETIR	electron-transfer-induced reaction
Et	ethyl
Flu	fluorenyl anion (η-$C_{13}H_9^-$)
HOMO	highest occupied molecular orbital
Hex	hexyl
GC	glassy carbon
Ind	indenyl anion (η-C_9H_7)$^-$
IR	infrared
k_c	standard heterogeneous charge transfer rate constant
LTV	low-temperature voltammetry
LUMO	lowest unoccupied molecular orbital
Me	methyl
MeCN	acetonitrile
MO	molecular orbital
NMR	nuclear magnetic resonance
PC	propylene carbonate
Ph	phenyl
PhCN	benzonitrile
phen	1,10-phenanthroline
Pr	propyl
py	pyridine
SCE	aqueous saturated calomel electrode
THF	tetrahydrofuran
Tol	toluene
UME	ultramicroelectrode
UV–VIS	ultraviolet–visible spectroscopy

A. INTRODUCTION

Electrochemical studies with transition metal sandwich complexes began to develop soon after the synthesis of ferrocene in 1951 [1]. Since then, a large number of sandwich complexes has been investigated by electrochemical methods. The application of polarography, cyclic voltammetry (CV) and other transient and preparative electrochemical methods has made it possible to obtain important information about the oxidation–reduction properties of these organometallic complexes, i.e. about the reactivity of sandwich complexes in redox reactions. Electrochemical studies, in particular CV, in addition to providing redox potentials, in many cases provide mechanistic insights into electronic and structural changes and sometimes also provide hints to hitherto unknown redox forms of the sandwich complexes or products of their further reactions. This information is extremely important for a correct understanding of the mechanisms of many reactions involving sandwich complexes, the selection of optimum conditions for their chemical and electrochemical synthesis, and the solution of important structural problems in the chemistry of the large class of complexes considered, especially those which are unstable. Furthermore, electrochemical studies provide valuable information about the distribution of electron density in the sandwich complexes and about the relative disposition of the frontier molecular orbitals (HOMO and LUMO).

Since the publication of the most recent reviews [2–5] on the electrochemistry of sandwich complexes, more than five years have elapsed and there has been no systematic consideration made with bent sandwich complexes of the Cp_2ML_n type in which L is a two-electron ligand (Cl, H, CO, alkyl, aryl, etc.). There has been a significant increase in the number of publications during recent years on the electrochemistry of sandwich and bent sandwich complexes, especially using modern electrochemical techniques such as low-temperature voltammetry and ultramicroelectrodes. Individual studies in this field have been mentioned in reviews [6,7] and monographs [8–10].

The main aim of the author is to trace the principal characteristic features of the variation of the redox properties of sandwich and bent sandwich complexes as a function of the nature of the metal and its formal oxidation state and to find a parameter which determines the reactivity of these complexes in redox reactions rather than simply accumulate factual data. The properties of the primary products of the electrochemical reactions of sandwich and bent sandwich complexes are also examined in a number of instances. The present review does not include studies which deal with previous surveys [2–8], except for cases which have been subjected to a repeated, more accurate analysis.

B. ELECTROCHEMICAL REACTIONS OF SANDWICH COMPLEXES

"Sandwich" is organometallic jargon for complexes in which a metal atom forms a complex with two planar and parallel, or nearly parallel, sets of aromatic π-

ligands of the type η^5-$C_5H_5^-$ (Cp$^-$), η^6-C_6H_6, η^7-$C_7H_7^+$ (CHT), η^8-$C_8H_8^{2-}$ (COT), etc. The bonding between the metal and the ligands results from overlapping of the d orbitals of the metal and the π orbitals of the ligands [11–14]. A characteristic feature of sandwich complexes is that their metal atom is surrounded by two bulky ligands and that its direct contacts with solvent molecules are hindered. The latter prevents the appearance of specific solvation effects. As a result, solvation effects in the redox reactions of sandwich complexes are determined mainly by the electrostatic component, which is approximately the same for isostructural complexes bearing equal charges [9,15,16]. For this reason it is possible to compare the standard potentials of the redox reactions of sandwich complexes measured in various solvents. As a rule, the electron transfer reactions of sandwich complexes are not complicated by subsequent chemical reactions of the electrochemically generated species with solvent molecules.

Quantum chemical consideration of sandwich complexes has shown [11–14] that the metal AOs make the dominant contribution to their HOMO and LUMO on which the changes of electron density are localized as a result of the electron transfer reactions (redox orbitals). Reactions occurring with a change in the formal oxidation state of the metal are therefore characteristic of sandwich complexes.

(i) *Metallocenes*

Reversible one-electron reactions of the scheme

$$Cp_2M^{2+} \underset{IP_4}{\overset{e(E_4^0)}{\rightleftarrows}} Cp_2M^+ \underset{IP_3}{\overset{e(E_3^0)}{\rightleftarrows}} Cp_2M \underset{IP_2}{\overset{e(E_2^0)}{\rightleftarrows}} Cp_2M^- \underset{IP_1}{\overset{e(E_1^0)}{\rightleftarrows}} Cp_2M^{2-} \tag{1}$$

are characteristic of the majority of metallocenes. The electron transfer reactions in these systems are of the outer-sphere type [2,3,15,16] and the reversibility of the electrode reactions of the majority of the compounds of this kind suggests that the transition from the oxidized to the neutral forms and further to the reduced forms does not entail dramatic changes in the coordination sphere and geometry of the complexes, at least in the time scale of voltammetric measurements.

Depending on the nature of the metal and solvent, the possibility for the electrochemical generation of members of the redox series (1) and their stability, especially the stability of Cp_2M^{2+}, Cp_2M^- and Cp_2M^{2-}, change dramatically. In recent years, it has become possible to generate and identify the majority of the products of the redox reactions of metallocenes which are, in principle, possible. This is a result of the employment of solvents which are extremely stable at the high anodic potential ($E > 3$ V SCE, e.g. SO_2 [17]) and high cathodic potential ($E < -3$ V SCE, e.g. DME [18], THF [19]) regions, in which the reactive members of the redox series (1) are most stable, and also of the use of low-temperature measurements [19,20] and CV with ultramicroelectrodes [21]. 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 [22,23]. It has been shown [24], using CV in THF in the temperature range from −90 to −70°C, that the corresponding substituted titanocene, zirconocene and hafnocene are formed as a result of the two-electron electrochemical reduction of pentamethyl- and *t*-butyl-substituted metallocene dichlorides. These unstable Group IVB metallocenes reduce reversibly to the corresponding anions Cp_2M^- [24] (see Sect. D).

Among the Group VB metallocenes, only vanadocene has been thoroughly investigated. It has been demonstrated by means of polarography and CV at platinum and mercury electrodes in THF solution [25–27] that Cp_2V undergoes one-electron reversible reduction with formation of the Cp_2V^- anion, which is stable on the time scale of CV, and one-electron reversible oxidation with formation of Cp_2V^+ cation. Further oxidation of Cp_2V^+ to the dication Cp_2V^{2+} takes place irreversibly, which is believed [25,26] to be associated with transition from the sandwich to bent sandwich structure (EC scheme, where E and C represent the electrochemical and chemical steps respectively) 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 instability [28]. Our attempts [29] to generate niobocene and tantalocene by two-electron electroreduction of the corresponding Cp_2MCl_2 complexes in THF medium at −90 to +20°C were unsuccessful because coordinatively unsaturated intermediate Cp_2MCl complexes react with the starting metallocene dichlorides with formation of dimers $[Cp_2MCl(\mu\text{-}Cl)_2MCp_2]$ (see Sect. D).

The electrochemistry of Group VIB metallocenes has been studied in detail in relation to Cp_2Cr. It has been shown by means of CV at a platinum electrode that chromocene is reduced reversibly in THF or MeCN solutions to the Cp_2Cr^- anion [25,26]. Preparative electrolysis at the limiting current for Cp_2Cr reduction does not, however, make it possible to obtain and characterize the Cp_2Cr^- anion in solution because of its low stability. It has also been shown [25,26,30] that chromocene can undergo reversible one-electron oxidation to the stable Cp_2Cr^+ cation.

Unstable molybdocene and tungstocene (lifetime ca. 10^{-2} s at room temperature) species have been generated and identified by means of high speed CV in DMSO [31,32] and LTV techniques in THF solutions [33] in the two-electron reduction of the corresponding metallocene dichlorides. The formal standard potentials of the redox couples $Cp_2Mo^{0/+}$ and $Cp_2W^{0/+}$ are equal to −1.25 and −1.48 V, respectively. (All the potentials in this review are quoted relative to SCE.) These are the most readily oxidizable of the known metallocenes. If $E^0 = -0.68$ V is adopted for the $Cp_2Cr^{0/-}$ redox couple [25], one may conclude that, within the framework of a single sub-group of the Periodic System, an increase in atomic number of the metal facilitates the abstraction of an electron from the corresponding metallocene and not conversely, as postulated in earlier reviews [2,3].

Among the Group VIIB metallocenes, only the manganese compound is known at present, although manganocene cannot be described as a sandwich complex because of its ionic character [34]. A substituted analogue of this compound, Cp_2^*Mn, in which the metal–ring bond is covalent and which has the sandwich structure, has been described [35]. It has been shown by means of CV at a platinum electrode that permethyl manganocene is reduced in MeCN medium to the $Cp_2^*Mn^-$ anion and is oxidized to the $Cp_2^*Mn^+$ cation [35]. Both processes are electrochemically reversible, though the stabilities of the products have not been reported.

Like molybdocene and tungstocene, rheniocene is unstable. These metallocenes are formed by photolysis of the corresponding hydrides Cp_2MH in a low-temperature argon matrix and their sandwich structure has been demonstrated by IR spectroscopy [36–38]. Recently, it has been shown [39] that rheniocene can also be generated by means of CV at a mercury electrode in THF solutions by two-electron reduction of the dimer $Cp_2Re{-}ReCp_2$ with a change of hapticity accompanying electron transfer according to the scheme:

$$Cp_2Re{-}ReCp_2 \xrightarrow{2e} 2[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)Re]^-$$

$$[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)Re]^- \xrightarrow{-e} Cp_2Re$$

The value of E^0 for the $Cp_2Re^{0/+}$ redox couple is -1.06 V.

Ferrocene, the first of the metallocenes synthesized, is undoubtedly the most thoroughly investigated representative of the Group VIIIB metallocenes. The $Cp_2Fe^{0/+}$ redox couple is one of the most highly reversible systems. Numerous studies have been devoted to it [1–10]. In recent years, it has been possible to show, using solvents stable at high cathodic and anodic potentials, that ferrocene can be oxidized to the dication and reduced to the anion. In $AlCl_3$ – 1-butylpyridinium chloride melts (1:1, mol.), the $Cp_2^*Fe^+$ cation undergoes reversible one-electron oxidation at glassy carbon to the stable $Cp_2^*Fe^{2+}$ dication, which has been characterized by means of UV–VIS [40]. The electrochemical behaviour of the ferrocenium cation and its permethylated analogue has also been investigated in liquid sulphur dioxide [17(b)]. It has been shown by means of CV at a platinum electrode that the reversible one-electron oxidation of Cp_2Fe^+ leads to the formation of the unstable dication Cp_2Fe^{2+}, which decomposes with blocking of electrode surface by polymeric decomposition products. The reversible one-electron oxidation of $Cp_2^*Fe^+$ under these conditions results in the formation of a high-spin dication $Cp_2^*Fe^{2+}$ ($\mu = 2.73$ B.M.), which is stable at −30°C. Cp_2Fe oxidizes reversibly to the Cp_2Fe^+ cation at a conventional size platinum electrode in toluene/$Bu_4NBF_4 \cdot 3Tol$ medium [41(a)].

The high purity of the solvent and electrochemical measurements at temperatures within the range −45° to −30°C have made it possible [18,19,41] to observe the reversible one-electron reduction of ferrocene at platinum and GC electrodes in DMF and DME media to the relatively unstable Cp_2Fe^- anion. It has also been shown that an increase in temperature leads to the occurrence of the two-electron reduction of ferrocene via the ECE scheme involving the formation of an unidentified intermediate X [41(b)]:

$$Cp_2Fe \overset{e}{\rightleftharpoons} Cp_2Fe^- \longrightarrow X \xrightarrow{e} 2Cp^- + Fe^0$$

In order to elucidate the nature of X, a study has been made on the electrochemical reduction of substituted ferrocenes in DMF and THF under a carbon monoxide atmosphere [42]. It is possible to identify the unstable $CpFe(CO)_2^-$ anion, which reacts with MeI to form $CpFe(CO)_2Me$ or is oxidized at a platinum electrode to the radical $CpFe(CO)_2\cdot$, which rapidly dimerizes with formation of the $[CpFe(CO)_2]_2$ complex with Fe – Fe bond. These data have led to the conclusion that the intermediate X is a $CpFe\cdot - Cp^-$ mixture.

It has been noted [18] 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 $Cp_2Fe^{0/+}$ redox couple ($k_e > 10^{-1}$ cm s^{-1}). According to Ito et al. [18], this difference is due to the increase in internal reorganization energy of 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 (hapticity change), which makes it possible to retain the energetically most favourable closed-shell 18-electron configuration of the metal atom in the Cp_2Fe^- anion. It is notable that this is not the only possible explanation for the decrease in the k_e value on passing from the $Cp_2Fe^{0/+}$ to the $Cp_2Fe^{0/-}$ redox system. 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 the value of k_e.

A more accurate study of the kinetics of heterogeneous electron transfer is possible using fast-scan CV at a UME due to the minimization of the ohmic drop and charging current (see ref. 43 and the references cited therein). Using these techniques, it is possible to measure the heterogeneous electron transfer reactions with k_e values exceeding 2 cm s^{-1} [44,45] and the value of k_e for the $Cp_2Fe^{0/+}$ redox couple is equal now to ca. 1 cm s^{-1} [43]. Other advantages of the UME are connected with the possibility for electrochemical measurements without supporting electrolyte (a situation when single electrogenerated ions exist) and/or in low polar medium (benzene, etc.). Undistorted voltammograms for ferrocene have been achieved in CO_2 under supercritical conditions with water and Hex_4NClO_4 added [46].

The kinetics of the heterogeneous electron transfer involving substituted ferrocenes and Cp_2Co^+ ions in MeCN solutions at semiconductor (p-InP)/electrolyte interface have been investigated by means of CV [47]. The above semiconductor is characterized 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 $(RCp)_2Fe^{0/+}$ (RCp = substituted cyclopentadienyl) redox reaction potential lies within this region, whereas irreversible electrode reactions are characteristic of acylated ferrocenes and Cp_2Co^+, whose redox potentials correspond to the limits of this region or are outside its limits. Furthermore, irreversible electrode reactions also become characteristic of complexes of the first type (with E^0 values lying outside the forbidden gap) when the potential at which the polarization of the electrode changes moves outside the limits of the gap.

The oxidation of ferrocenecarboxylic acid in the presence of β-CD has been investigated by means of CV in a pH 9.2 aqueous solution in which the ferrocene is present as an anion (FCA^-) [48]. The binding of FCA^- by β-CD is indicated by the change in UV–VIS absorption spectrum and the appearance of induced circular dichroism. The latter data show that FCA^- is complexed by β-CD in a configuration with the Cp–Fe–Cp axis parallel to that of the β-CD cavity. In slow-scan-rate CV, β-CD causes a decrease in the peak current and a positive shift in the peak potential for FCA^- oxidation. Each of these effects was quantitatively evaluated, giving a formation constant (K) for the [FCA^-(β-CD)] complex of $2200\ M^{-1}$ at 20°C and $\Delta H = -2.8$ kcal mol^{-1}, $\Delta S = 5$ cal K^{-1} mol^{-1}. No binding of the oxidized form of FCA^- by β-CD could be detected. Fast-scan-rate studies revealed that the inclusion complex is oxidized via the CE scheme in which the complex first dissociates to FCA^- and β-CD followed by oxidation of the free FCA^-. The quantitative evaluation of the data gave $2.1 \times 10^4\ s^{-1}$ for the dissociation rate constant, and variable-temperature studies yielded an activation enthalpy for dissociation of 15 kcal mol^{-1}. Significantly, no direct oxidation of [FCA^-(β-CD)] at the electrode could be detected.

The oxidation of ferrocene has been investigated by means of CV in aqueous medium in the presence of α-, β- and γ-CDs [49]. The complexation of ferrocene by cyclodextrins gives rise to a positive shift of the peak potential for Cp_2Fe oxidation and a decrease of the voltammetric peaks due to a smaller value for the diffusion coefficient of the resulting inclusion complexes. In dilute solutions ($[Cp_2Fe] \cong 10^{-4}$ M; $[CD] \leq 10^{-2}$ M), the compositions of inclusion complexes (guest:host) are 1:2 (α-CD), 1:1 (β-CD) and 2:1 (γ-CD). A stoichiometric 1:1 inclusion complex of Cp_2Fe/γ-CD has been prepared recently by Harada et al. [50], and docking calculations of ferrocene complexation with CDs have been made [51]. Surprisingly, the possibility for formation of a 2:1 stoichiometric guest:host complex has not yet been discussed. For these reasons, the formation of the [$(Cp_2Fe)_2$(γ-CD)] inclusion complex in dilute solutions is very interesting. The logarithms of the formation constants for ferrocene–CD complexes were estimated to be 3.51 (β-CD) and 2.19 (γ-CD) [49]. Azaferrocene is complexed by β-CD with 1:1 stoichiometry ($\log K = 2.57$) [49]. The electrochemical behaviour suggests that ferrocene and azaferrocene are oxidized in their free form after the dissociation of inclusion complexes at the surface and/or into the thin electrode layer [48,49].

The electrochemical behaviour of the heavier ferrocene analogues, ruthenocene and osmocene, has a number of characteristic features. Ruthenocene undergoes irreversible two-electron oxidation at a platinum electrode in MeCN with the formation of a dication [2–10]. Under the same conditions, Cp_2^*Ru is oxidized reversibly to a stable cation which has been characterized by means of EPR spectroscopy ($e_{2g}^3a_{1g}^2$ electronic configuration), however its subsequent oxidation is irreversible [52]. The stepwise two-electron oxidation of ruthenocene, which is irreversible at each step, has been observed by means of CV in the $AlCl_3$/1-butylpyridinium chloride melt (with a molar ratio in excess of unity) at the GC electrode [53].

The oxidation of osmocene is characterized by the stepwise abstraction of the two electrons, which is irreversible at each step [2–10]. The preparative one-electron chemical oxidation of Cp_2Os leads to the $[Cp_2Os{-}OsCp_2]^{2+}$ dimeric dication with a metal–metal bond [54]. The difference in the electrochemical oxidation of ferrocene, ruthenocene and osmocene is associated, according to Gale et al. [40(a)], with the fact that, with an 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 charge cations becomes preferable. On the basis of the comparative study of the electrochemical oxidation of Cp_2^*M ($M = Fe$, Ru and Os) to the corresponding cations in MeCN solutions, it has been noted [55] that the variation of the $E_{1/2}$ values for the oxidation of the metallocenes investigated in the sequence $Fe < Os < Ru$ parallels the variation of the ionization potentials of the complexes and the atomic ionization energies of the corresponding metals. 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].

Using LTV (−60°C) in combination with UME techniques (20 μm Pt) in THF medium, it has been shown that Cp_2Ru and Cp_2Os are reduced to the corresponding anions at $E_{1/2} = -3.48$ V (Ru) and -3.44 V (Os) [56] (Fig. 1). These values are the most negative among the experimentally measured potential values [57]. The reductions of ruthenocene and osmocene are slow charge transfer processes due to electron transfer at the antibonding HOMO [56].

One-electron oxidation of Cp_2Os is irreversible down to −80°C, forming a dimeric dication $[Cp_2Os]_2^{2+}$ [56(a)]. The irreversible two-electron reduction of this cation is accompanied by Os–Os bond rupture and osmocene formation. A highly reactive Cp_2Os^+ cation (lifetime ca. 1 ms) has been noted in the study of Cp_2Os oxidation by means of fast-scan CV at a platinum ultramicroelectrode (10 μm) in THF medium at room temperature [56(b)].

The cobaltocenium cation, isoelectronic with ferrocene, results from the reversible one-electron oxidation of cobaltocene [2–10,58,59]. Cobaltocene can also undergo reversible one-electron reduction to the Cp_2Co^- anion [58–61]. In aqueous

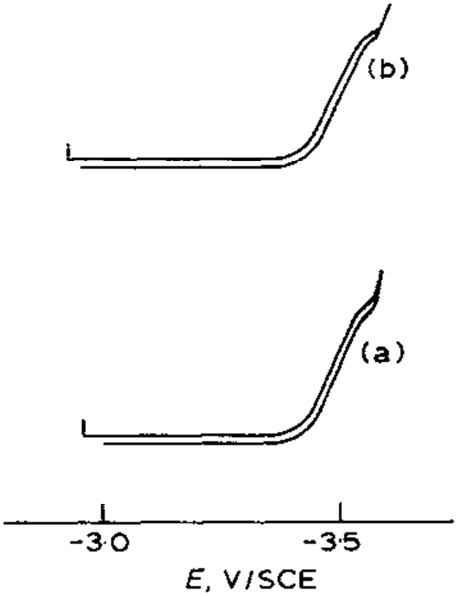
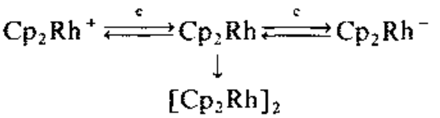


Fig. 1. Steady-state voltammograms of (a) Cp_2Ru and (b) Cp_2Os in THF/0.04 M Bu_4NPF_6 at a microdisc platinum electrode ($r_o = 20$ μm) at −60°C (according to Kukharenko et al. [56]).

solutions, Cp_2Co is stable in an alkaline medium (pH > 7), while in an acidic medium it is protonated at the ligand with formation of cyclopentadiene(cyclopentadienyl)cobalt. This is oxidized chemically at pH < 4 by a proton from the medium, with hydrogen evolution and formation of Cp_2Co^- [59]. It has been suggested [61] that, in acidic media, the $(\eta\text{-}C_5H_4COOR)_2Co^+$ cations 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 [61].

The electrochemical behaviour of the heavier cobaltocene analogue, rhodiocene, has also been investigated [62]. It has been shown by means of polarography and CV at mercury and platinum electrodes that the Cp_2Rh^+ cation is reduced in MeCN medium in accordance with the scheme:


$$\begin{tikzcd} Cp_2Rh^+ \arrow[r, shift left, "e"] & Cp_2Rh \arrow[l, shift left] \arrow[r, shift left, "e"] \arrow[d] & Cp_2Rh^- \arrow[l, shift left] \\ & {[Cp_2Rh]_2} & \end{tikzcd}$$

The intermediate rhodiocene is unstable under the conditions of controlled-potential electrolysis and dimerizes. The 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 the most readily reduced among the known metallocenes, is the last metal in the Periodic System among the class of metallocenes investigated [25,26]. However, the mechanism of this process is fairly complex. Under the conditions of the preparative electrochemical reduction of Cp_2Ni, a series of products is formed, one of which has been identified as $CpNi(\eta^3\text{-}C_5H_7)$ [26]. At reduced temperature (−58°C) in DMF, nickelocene undergoes one-electron reduction to the stable Cp_2Ni^- anion and the electrode reaction is characterized by a slow charge transfer step. According to Geiger and co-workers [26], this is associated with the fact that the electron transfer is accompanied by solvation and/or structural changes (transition to the "slipped sandwich structure"). The electrochemically generated Cp_2Ni^- anion reacts with carbon monoxide [63] via a CEC scheme with decomposition of the sandwich structure:

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

Apart from reduction, the oxidation of nickelocene, which is electrochemically reversible, has been investigated. Thus, one-electron oxidation of Cp_2Ni in THF, DMF and MeCN solutions at a platinum electrode [25,26] and in the $AlCl_3$/1-butylpyridinium chloride melt at GC [64] leads to the formation of the Cp_2Ni^+ cation. The subsequent oxidation of Cp_2Ni^+ in MeCN at a platinum electrode [65] and in the melt mentioned above [64] is also reversible and is accomplished by the formation of the Cp_2Ni^{2+} dication, which has been characterized by UV–VIS [64]. The Cp_2Ni^{2+} dication reacts extremely readily with nucleophiles.

The oxidative electrochemistry of Cp^*_2M (M = Co, Ni and Cr) with formation of the corresponding $Cp^*_2M^+$ cations and $Cp^*_2Ni^{2+}$ dication has been studied by Robbins et al. [66].

Recently [19], using LTV and UME techniques in a THF medium, it has been shown that Cp_2Co^- and Cp_2Ni^- anions at $E < -3.1$ V are reduced to the corresponding Cp_2M^{2-} dianions (or reduced with simultaneous electron transfer and bond rupture; concerted mechanism) which are unstable even at −100°C.

In liquid sulphur dioxide medium the Cp_2Co^+ cation reversibly oxidizes to the Cp_2Co^{2+} dication stable in the time scale of the CV method [67]. It is of interest that the potential working range of SO_2 in the anodic region reaches ca. +5 V (SCE) [17]. In the past, a standard solvent for anodic oxidation was MeCN. However, due to its nucleophilicity, it is less suitable for the detection of reactive intermediates. In 1979, Tinker and Bard showed [17(a)] that liquid SO_2 was an excellent solvent for the reversible generation of reactive cations because of its low nucleophilicity and its ability to solvate ionic as well as covalent substrates. For these reasons, sulphur dioxide is quite suitable for the study of electro-oxidation processes accompanied with generation of strong electrophiles.

TABLE 1

Classification of the experimentally detected metallocenes and their ions in terms of the electronic configuration of the metal in Cp_2M complexes ($M = Cp_2M$)

d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Ti^{a}	Ti^{-a}	V^{-}	Cr^{-}	Mn^{-b}	Fe^{-}	Co^{-}	Co^{2-a}	Ni^{2-a}
Zr^{a}	Zr^{-a}	Cr	Mn^{b}	Fe	Ru^{-a}	Rh	Ni^{-}	
Hf^{a}	Hf^{-a}	Mn^{+b}	Re	Ru	Os^{-a}	Ni		
V^{+}	V	Re^{+}	Fe^{+}	Os	Co			
	Cr^{+}	Fe^{2+}	Ru^{+}	Co^{+}	Rh			
			Os^{+}	Rh^{-}	Ni^{-}			
			Co^{2+}	Ni^{2+}				

[a] Detected by means of LTV and/or UME techniques.
[b] Cp_2^*M.

Thus, five redox states from dication to dianion were, for the first time, experimentally detected for Cp_2Co [19,67] and Cp_2Ni [19]. The LTV and UME techniques are seen to expand the potential working region, which is not observed at traditional temperatures and electrodes because of supporting electrolyte discharge. Extensive experimental data have been accumulated. Together with the $Cp_2M^{0/+}$ redox couples known previously, the possibility for the $Cp_2M^{0/-}$, $Cp_2M^{-/2-}$ and $Cp_2M^{+/2+}$ redox transients has been demonstrated for a series of metallocenes. The experimentally detected forms of the metallocenes are shown in Table 1.

In previous studies [10,25] this table appeared as an inverted triangle whose height was determined by the number of the known metallocenes and their ions with the d^6 electronic configuration, associated with the high stability of these 18-electron closed-shell complexes. The form of Table 1 has changed significantly now due to the intensive investigations of metastable early transition metal metallocenes and highly reactive Cp_2M^{-}, Cp_2M^{2-} and Cp_2M^{2+} ions.

(ii) Bis(arene)metals

Redox reactions involving a change in the formal oxidation state of the metal are characteristic of all homo- and hetero-ligand sandwich complexes as well as of the metallocenes [2,4,7,10].

The metal in bis(arene) complexes is formally zero-valent and $(\eta^6\text{-arene})_2M^{0/+}$ redox couples are therefore characteristic of these compounds. Examples of such systems are provided by the (arene)$_2$Cr complexes (arene = C_6H_6 and their substituted derivatives, C_6Me_6, Ph–Ph, etc.) [68–74], $(C_6H_6)_2Mo$ [2,3], etc.).

The electrochemical behaviour of the $(C_6H_6)_2Fe^{2+}$, $(C_6Me_6)_2Fe^{2+}$ [75], $(C_6Me_6)_2Ru^{2+}$ [76], and $(C_6Me_6)_2Co^{2+}$ cationic complexes [77] has been also investigated. It has been shown by means of polarography and CV at Hg and GC electrodes in protic and aprotic media that all these complexes undergo multi-step electrochemical reduction, reversible at each step, according the scheme:

$$(\text{arene})_2\text{M}^{2+} \overset{e}{\rightleftharpoons} (\text{arene})_2\text{M}^{+} \overset{e}{\rightleftharpoons} (\text{arene})_2\text{M} \qquad (2)$$

It has been shown for the $(C_6Me_6)_2Ru^{2+}$ dication [76(a)] that the replacement of CH_2Cl_2 by the more strongly coordinated MeCN leads to greater changes in the relative solvation energy (E_s) in the $(\text{arene})_2Ru^{2+/+/0}$ redox reactions, as a result of which the dication is electrochemically reduced to the neutral complex in a single two-electron step. It is interesting that the reduction of $(C_6Me_6)_2Ru^{2+}$ is described by the EEC scheme, where the chemical step represents the hapticity change from $(\eta^6\text{-arene})_2Ru$ to $(\eta^6\text{-arene})Ru(\eta^4\text{-arene})$. According to Pierce and Geiger [76(b)], who studied this system in MeCN by means of fast-scan CV with digital simulations, two-electron consecutive reduction of $(C_6Me_6)_2Ru^{2+}$ to $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_6Me_6)$ is described by the EE scheme in which the hapticity change from η^6 to η^4 occurs simultaneously with the transfer of the second electron.

Here it is also appropriate to consider the fundamental problem of redox reactions, the problem of one- or multi-step transfer of two electrons. If a redox reaction of this type is represented by the scheme

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

it is evident that $\Delta E^0 = E_1^0 - E_2^0$ reflects the change in the gas-phase ionization 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, moreover, the change in the ΔE_S value in the transition from A^+ (A^-) to A^{2+} (A^{2-}). The value of 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 transition from the multi-step ($1e^- + 1e^-$) mechanism to the apparently single step ($2e^-$) mechanism, as happens in the case considered above [76]. 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 a structural change in the sandwich complexes (the ECE scheme). The AO of the metal usually makes the main contribution to the HOMO and LUMO of the sandwich complexes, as a result of which both the HOMO and LUMO have the d character. This leads to a relatively weak electronic influence of the substituents in the π-ligands on E_1^0 and E_2^0 values [78]. For example, E^0 changes only by approximately 0.2 V for the $(C_6H_{6-x}Me_x)Cr(CO)_3^{0/-}$ redox couples when the value of x changes from 0 to 6 [79,80]. 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 criterion for their occurrence) are only observed for a few sandwich and half-sandwich complexes. As an example, one may quote the reduction of (arene)Cr$(CO)_3$ complexes [80], where the operation of the 2e$^-$ mechanism is a consequence of the $\eta^6 \rightarrow \eta^4$ hapto isomerization of the arene ligand in the anion radical intermediate. In the case of these complexes, the structural changes occurring at the step involving the formation of one-electron reduction products lead to species which are reduced more readily than the initial complexes (ECE). On the other hand, a real 2e$^-$ process is characteristic of the reduction of Cp(η^6-C_6Me_6)Ir^{2+} dications [81] and, following hapticity change, lead to the formation of stable closed-shell 18-electron species (EEC).

The (arene)$_2$Cr$^{0/+}$ redox couples together with ferrocene [82] have been recommended by IUPAC as internal standards and "pilot" ions for comparison of $E_{1/2}$ potential values measured in different solvents or by different authors. The greater radius and spherical shape of the molecule, the solubility of both redox forms, the high reversibility of the redox reaction, the virtual absence of specific solvation effects as a consequence of the shielding of the metal by bulky ligands, and the insignificant change in the electrostatic component of the ΔE_S value in the transition from one solvent to another (as a consequence of the low surface charge of the complexes), make the (arene)$_2$Cr$^{0/+}$ redox systems, along with transition metal heteropolyanions [83] and tris-bipyridine complexes [84] very promising as standard redox systems [16].

There are data indicating the possibility of the adsorption of the (arene)$_2$Cr$^+$ cation at the surface of a mercury electrode in an aqueous medium [85]. It has been suggested that the adsorption is caused by 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 surface, and the influence of the background electrolyte anion.

The LTV and UME techniques have been employed to study one-electron oxidation of (arene)$_2$Cr$^+$ (arene = PhH and Ph–Ph) cations, in a THF medium, to the corresponding dications which are stable in the temperature range from -90 to -70°C within the CV time scale [86]. Earlier, such dications were known only for $(C_6Me_3H_3)_2Cr$ [87] and (η-phen)$_2$Cr [88].

Bis(toluene)titanium is reversibly reduced in THF medium to the corresponding anion containing the metal in formal oxidation state -1 [86]. This result is of particular importance since it shows the possibility for generation of anion bis(arene) complexes of the early transition metals (having unoccupied bonding MOs) with the formal oxidation state -1 stable at least on the CV time scale.

(iii) Metallocarboranes

As in other sandwich complexes of this type, the transition metal is bonded to dicarbolyl ligands by π-bonds [89–91]. The study of the electrochemical behaviour (d.c. and a.c. polarography, CV and controlled-potential electrolysis, etc.) of the dicarbolyl complexes of iron [90], cobalt [58,90], rhodium [62], nickel [58,90], palladium [92], copper [92], and gold [92] in aprotic solvents showed that, in contrast to the cyclopentadienyl ligand, the dicarbolyl ligand (Cb) stabilizes the metal in both high and low oxidation states. The overall scheme for the redox reactions of these complexes can be represented as

$$\mathrm{Cb_2M} \overset{e}{\rightleftharpoons} \mathrm{Cb_2M^-} \overset{e}{\rightleftharpoons} \mathrm{Cb_2M^{2-}} \overset{e}{\rightleftharpoons} \mathrm{Cb_2M^{3-}} \qquad (3)$$

The only exception from this series of metallocarboranes is $\mathrm{Cb_2Pt}$, which has been shown by means of CV in DMSO and DMF media to undergo reversible two-electron reduction to the $\mathrm{Cb_2Pt^{2-}}$ dianion with subsequent quasi-reversible one-electron reduction to the $\mathrm{Cb_2Pt^{3-}}$ trianion at more cathodic potentials [93]. The two-electron character of the $\mathrm{Cb_2Pt^{0/2-}}$ electrode reaction is probably associated with the transfer of the first electron to the antibonding LUMO and/or with the solvation effects of the highly coordinating solvent in which the measurements were performed.

Titanium, vanadium and chromium complexes, as well as those of manganese, iron and cobalt, with another dicarbolyl ligand (Cb′) have also been synthesized and characterized electrochemically [94,95]. The reversible redox transitions

$$\mathrm{Cb'_2M^-} \overset{e}{\rightleftharpoons} \mathrm{Cb'_2M^{2-}} \overset{e}{\rightleftharpoons} \mathrm{Cb'_2M^{3-}} \qquad (4)$$

are also characteristic of these complexes. Metallocarboranes can also be recommended as standard redox systems although they are less frequently available.

Comparison of the redox properties of the small metallocarboranes with those of metallocenes and large metallocarborane clusters have been made by Geiger and Brennan [58(c)].

(iv) Other homo-ligand sandwich complexes

Using CV and controlled-potential electrolysis at a platinum electrode, bis(azaboralinyl)metal complexes $[\eta^5\text{-C}_3\text{H}_3\text{B(Me)NR}]_2\text{M}$ (R = H, Et, Bu or $\mathrm{SiMe_3}$; M = Co or Fe) in THF and $\mathrm{CH_2Cl_2}$ media undergo reversible one-electron oxidation to the corresponding cations whose stabilities depend on the nature of R and M [96]. Bis(borinato)metals, $(\eta^6\text{-C}_5\text{H}_5\text{BR})_2\text{M}$ (R = Me, Ph; M = V, Cr, Fe, Co), have been studied by means of CV under the same conditions [97]. The $(\mathrm{C_5H_5BR})_2\mathrm{M}^{+/0/}$ redox couples are typical for these complexes. The borinato ligands are stronger electron acceptors but weaker electron donors than the $\mathrm{Cp^-}$ ligand.

Bis(cyclo-octatetraene)uranium, $(\eta^8\text{-COT})_2\text{U}$, is oxidized in THF, MeCN, benzonitrile and $\mathrm{CH_2Cl_2}$ solutions at mercury, platinum and GC electrodes at temperatures below 10°C in a single reversible two-electron wave to the dication via the ECE scheme. 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 oxidizable cation [98]. With temperature increase or with scan rate decrease, the electrochemically generated dication can be observed to react with the initial "uranocene", forming the dimeric dication $(COT)_4U_2^{2+}$, which is capable of irreversible one-electron oxidation with elimination of the COT ligand and the formation of $COT_3U_2^{3+}$.

(v) Mixed-ligand sandwich complexes

The hetero-ligand sandwich complexes are similar in their electrochemical properties to their homo-ligand analogues. They are also characterized by the reversible consecutive one-electron reactions, which proceed with a change in the formal oxidation state of the metal. It has been established by means of polarography, CV and preparative electrolysis in non-aqeuous media that the following redox reactions are possible:

$$[CpMCb]^+ \overset{e}{\rightleftarrows} [CpMCb] \overset{e}{\rightleftarrows} [CpMCb]^- \overset{e}{\rightleftarrows} [CpMCb]^{2-}$$

M = Fe [58(a)], Co [65] and Ni [90]

$$[CpMCb']^- \overset{e}{\rightleftarrows} [CpMCb']^{2-} \overset{e}{\rightleftarrows} [CpMCb']^{3-}$$

M = Fe [64], Co [94] and Ti [95]

$$[CpM(arene)]^{2+} \overset{e}{\rightleftarrows} [CpM(arene)]^+ \overset{e}{\rightleftarrows} [CpM(arene)] \overset{e}{\rightleftarrows} [CpM(arene)]^-$$

M = Fe [2,77], Co [81], Ir [99] and Rh [100]

$$[(\eta^8\text{-COT})TiCb] \overset{e}{\rightleftarrows} [(\eta^8\text{-COT})TiCb]^- \qquad \text{(ref. 95)}$$

$$[(\eta^8\text{-COT})TiCp]^+ \overset{e}{\rightleftarrows} [(\eta^8\text{-COT})TiCp] \qquad \text{(ref. 101)}$$

$$[(\eta^5\text{-L})Ti(\eta^8\text{-COT})] \overset{e}{\rightleftarrows} [(\eta^5\text{-L})Ti(\eta^8\text{-COT})]^-$$

L = Ind and Flu [101]

$$[(\eta^7\text{-CHT})MCp]^+ \overset{e}{\rightleftarrows} [(\eta^7\text{-CHT})MCp]$$

M = V [102] and Cr [103].

The complexes $(\eta^6\text{-}C_6H_6)M(\eta^6\text{-}Et_2C_2B_4H_4)$, where M = Fe or Ru, undergo reversible one-electron oxidation to the corresponding M(III) monocations, determined by means of CV measurements. A bis(ferrocenecarborane) complex of biphenyl shows two reversible oxidations. This is the first evidence for the reversible oxidation of the

Fe(II) or Ru(II) arene complexes and further establishment of the ability of *nido*-$R_2C_2B_4H_4^{2-}$ ligands to stabilize the oxidation states of the arene–transition-metal π-complexes [58(b)].

Study of the electrochemical synthesis of η^4-arene metal 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 isomerization (the postulated key stage in the catalytic hydrogenation of arenes [104]), ligand substitution reactions [105], and isomerization of complexes [106], by means of polarography, CV, and controlled-potential electrolysis, showed [81] that, in non-aqueous media (CH_2Cl_2, MeCN, DMF etc.), the complex $[Cp^*M(C_6Me_6)]^{2+}$ was reduced in two one-electron steps when M = Rh, whereas with M = Ir it was reduced in one two-electron step, to the corresponding neutral complexes. These consist, according to ^1H NMR data, of compounds having the $(\eta^5\text{-}Cp^*)M(\eta^4\text{-}C_6Me_6)$ structure. It has been suggested that the $\eta^6 \rightleftarrows \eta^4$ hapto isomerization (the lower limit of the reaction rate constant is estimated as $10^3\ s^{-1}$; stabilization energy is ca. 9 kcal mol^{-1}), leading to the thermodynamic stabilization of these complexes, takes place in the step 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 closed-shell complex. The $\eta^6 \rightleftarrows \eta^4$ hapto isomerization is facilitated passing from 3d metals to 4d and 5d metals. It has been shown for the redox transitions

$$[Cp^*Rh(C_6Me_6)]^{2+} \underset{E^{2+/+}}{\overset{e}{\rightleftarrows}} [Cp^*Rh(C_6Me_6)]^{+} \underset{E^{+/0}}{\overset{e}{\rightleftarrows}} [Cp^*Rh(C_6Me_6)]$$

that an increase in Gutmann's donor number for the solvent from 0 to 30 lowers the value of $\Delta E^0 = E^{2+/+} - E^{+/0}$ from 0.37 to 0.09 V as a result of the greater influence of the solvation effects on the $E^{2+/+}$ value, but hardly affects the kinetics of the hapto isomerization.

The oxidative cleavage of polyolefin cobalt sandwich complexes [(COT)CoCp] and [(COD)CoCp] in strongly (MeCN) and weakly (CH_2Cl_2) coordinating solvents has been investigated electrochemically [107]. In MeCN solution, these complexes undergo irreversible electrochemical oxidation accompanied by the cleavage of the polyolefin–metal bond, which can be described by the scheme (L = COD or COT):

$$\begin{aligned} &LCoCp \xrightarrow{-e} [LCoCp]^+ \xrightarrow{3\,MeCN} L + [CpCo(MeCN)_3]^+ \\ &\xrightarrow{-0.5\,e} 0.5Cp_2Co^+ + 0.5Co^{2+} + 3MeCN \end{aligned} \tag{5}$$

On the other hand, in CH_2Cl_2 the transfer of the first electron is reversible, while the $[LCoCp]^+$ cation is more stable (it has been characterized by its ESR spectrum where L = COD), although it does undergo further reaction according to scheme (5). The possibility of the isomerization 1,5-COD$\rightleftarrows$1,3-COD in the $[LCoCp]^+$ cation has been discussed [107].

In order to investigate the possibility of electrochemically carrying out the reaction involving the abstraction of a hydride ion from $[CpM(\eta^6\text{-}C_7H_8)]^+$ (M = Fe or Ru; $\eta^6\text{-}C_7H_8 = \eta^6$-cycloheptatriene) accompanied by its conversion into $[CpM(\eta^7\text{-}CHT)]^{2+}$ sandwich complexes, which is possible in principle, by means of CV in MeCN medium, a study has been made on the electrochemical oxidation of the $[CpM(\eta^6\text{-}C_7H_8)]^+$ cations [108]. Despite the fact that the electrochemical oxidation does indeed involve the coordinated cycloheptatriene with its conversion into η^7-CHT^+, the passivation of the electrode by the products of the decomposition of the complexes prevents the preparative electrochemical synthesis of $[CpM(CHT)]^{2+}$. At $E < -1$ V, the complexes $[CpM(CHT)]^{2+}$ undergo one-electron irreversible reduction.

The redox properties of mono- and disphosphaferrocenes have been investigated [109] in CH_2Cl_2, MeCN, DMF and other aprotic solvents. Like ferrocene, these sandwich complexes undergo reversible one-electron reduction to relatively stable anions and one-electron oxidation to cations whose stability depends significantly on the nature of the solvent. Analysis of the ESR spectra of the phosphaferrocenium cations showed that the unpaired electron is predominantly localized on the metal atom. The character of the change in the redox properties on passing from Cp_2Fe to phosphaferrocenes (the anodic shift of the E^0 values at reduction and oxidation are respectively 0.39 and 0.19 V) is due to the change in the energy of the frontier (redox) orbitals on replacement of the CH group in the Cp ligand by a phosphorus atom.

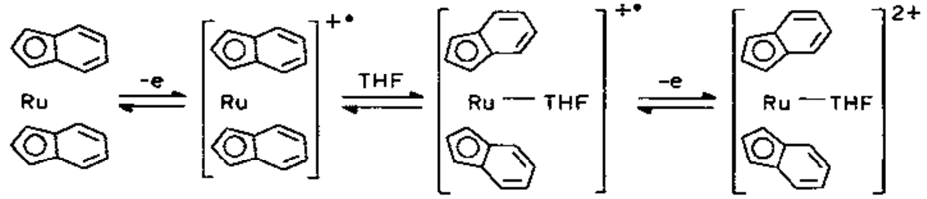
Similar changes in the energy of the frontier orbitals are also characteristic of azaferrocene. This π-complex reduces to the corresponding radical anion at less negative potentials [110] and oxidizes to the radical cation at more positive potentials [49,110] than does ferrocene. An electrogenerated radical cation of azaferrocene is unstable in MeCN and aqueous media and is likely to polymerize with formation of an electrochemically active polymeric film [49.110].

The formal potentials (ΔE_f^0) and the observed standard rate constants, k_s, of the electrode reactions for 21 ferrocenephanes (substituted 1 an 1,1′-ferrocene) in MeCN, PC, MeOH, iso-PrOH, DMF and DMSO were determined by means of CV [111]. The correlative equations $Q = f$ (acidity and/or basicity of solvent) where $Q = \Delta E_f^0$ or $\log k_s$, Gutmann's donor (DN) and acceptor (AN) numbers and Reinchardt–Krygovski's B_{KT} and E_T^N parameters were presented. Two-parameter equations $\Delta^x E_f^0 = a_x E_T^N + b_x B_{KT} + \text{const}_x$ and equations of the type $\log^x k_s = b_x B_{KT} + \text{const}_x$, agree best with the experimental results. The entropy substituent constants $\sigma_{p,s}$ for 1,3-R-$2^{\text{tia}}_{\text{oxa}}$-[3]-ferrocenephane and 1,1-methylo (or ethylo)hydroxy ferrocenephanes were determined independently of the solvent. The amphoteric properties of the ferrocenephane cation have been observed [111].

The redox reactions of the iron sandwich complexes with polyaromatic hydrocarbon ligands (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) were investigated by means of CV in aprotic media [112(a)].

In THF medium, dibenzoferrocene oxidizes to the corresponding radical cation, stable on the CV time scale at −70°C, and reduces to the radical anion [CpFe(η^5-Flu)]$^{\cdot}$, which rearranges to [CpFe(η^6-Flu)]$^{-\cdot}$ even at −80°C [113]. The one-electron electrochemical and chemical oxidation of [CpFe(η^5-Flu)] in THF and MeCN media is accompanied by the fast reaction of a generated radical cation with the initial compound, with formation of a triple-decker complex [114,115] (for more details see Sect. F).

The redox behaviour of π-indenyl complexes of general formula [(η^5-Ind)M(η^5-L)] (M = Ru, η^5-L = η^5-Ind, Cp and Cp*; M = Os, η^5-L = η^5-Ind) has been studied by means of CV (platinum and mercury electrodes) and preparative electrolysis in the temperature range −85 to +20°C in THF and CH_2Cl_2 media [116]. The complexes were shown to be capable of reversible one-electron oxidation to the corresponding radical cations whose stability and reactivity depend on the nature of both a metal and the second aromatic π-ligand, η^5-L, and the solvent nucleophilic properties. The [(η^5-Ind)M(η^5-Ind)]$^{+\cdot}$ (M = Ru, Os) complexes were characterized with ESR spectra. Fast reversible interconversion 17e$\rightleftarrows$19e of the sandwich to the bent sandwich structure is characteristic of [(η^5-Ind)M(η^5-L)]$^{+\cdot}$, even with such relatively weak nucleophiles as THF and leads to the formation of bent sandwich 19-electron radical cations [(η^5-Ind)M(η^5-L)(THF)]$^{+\cdot}$ which undergo reversible one-electron oxidation to the corresponding [(η^5-Ind)M(η^5-L)(THF)]$^{2+}$ dications.



18e 17e 19e 18e

The electrochemical behaviour of the Cp*Co(dmit) complex has been investigated in MeCN medium and redox couples [Cp*Co(dmit)]$^{-/0/+/2+}$ have been observed [117].

The standard potentials of the redox reactions of the majority of homo- and hetero-ligands sandwich complexes have been summarized elsewhere [32,118–120].

(vi) Dinuclear and polynuclear sandwich complexes

It has been shown by means of CV [121] that {(η^{10}, μ^2-$C_{10}H_8$)[(η^6-C_6R_6)Fe]$_2$}$^{2+}$ dications (R = H or Me: $C_{10}H_8$ = fulvalene), designated henceforth by A^{2+}, in aprotic media are capable of the electron transfer reactions

$$A^{2+} \xrightleftharpoons{e} A^{+} \xrightleftharpoons{e} A \xrightleftharpoons{e} A^{-} \xrightleftharpoons{e} A^{2-}$$

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

The redox properties of mono- and dimetallic cyclophane complexes of ruthenium [76,122] and iron [123] in aprotic media (THF, CH_2Cl_2, AC, DMF etc.) have been investigated by means of CV, chronoamperometry and preparative electrolysis. Together with $\eta^6 \rightleftarrows \eta^4$ hapto isomerization of the arene ligand, accompanying the two-step reduction of the dications $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}CP)]^{2+}$ (CP = cyclophanes) [76,122], the $[(CpFe)_2(\eta^6\text{-}CP)]^{2+}$ is reduced via two steps with similar potentials [123]. This electrode reaction leads to the formation of relatively unstable [Fe(2+)Fe(1+)] and [Fe(1+)Fe(1+)] complexes, which decompose with liberation of free cyclophanes and formation of CpFe(solvent)$_n$ species which disproportionate to Cp_2Fe and Fe^0. It has been suggested [123(a)] that the low stability of the neutral cyclophane complexes compared with the corresponding CpM(arene) complexes is due to the lower degree of overlapping of the orbitals of the CP ligand and AO of the metal as a result of the steric hindrances 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 and RuRu [124]. In PhCN medium, the complex with M^1M^2 = FeFe undergoes oxidation, specific with respect to the ferrocene fragments, in two reversible one-electron steps, which indicates the absence of appreciable interactions between these fragments. Such interaction is also absent from the complex with M^1M^2 = FeRu, which undergoes a quasi-reversible one-electron oxidation specific with respect to the ferrocene moiety and irreversible two-electron oxidation specific with respect to the ruthenocene moiety. For M^1M^2 = RuRu, both metallocene fragments probably interact with each other, resulting in quasi-reversible two-electron oxidation of the corresponding complex at potentials displaced negative by 0.54 V compared with Cp_2Ru oxidation potentials. Analysis of the ^1H spectra of the oxidation products has led to the conclusion that the oxidation involves only one of the ruthenocene moieties [124(a)].

The redox reactions of σ-bridged 1,1,12,12-tetra-*n*-butyl[1,1]-stannaferrocenophane have been investigated by means of polarography, CV, coulometry and near-IR and NMR spectroscopies in CH_2Cl_2 medium [124(b)]. This complex undergoes two successive reversible one-electron oxidations to yield the mono- and then the dication. The intermolecular electron transfer in the mixed-valence cation is attributed to the d π overlap mechanism of tin atoms and cyclopentadienyl rings.

The electrochemistry of bis(fulvalene)dimetal complexes $[(C_{10}H_8)_2M_2]$ (M = V, Cr, Fe, Co and Ni) has been investigated in MeCN solutions [125(a)]. CV at a platinum electrode shows that most of these complexes are capable of redox transitions:

$$(C_{10}H_8)_2M_2 \overset{e}{\rightleftharpoons} (C_{10}H_8)_2M_2^{+} \overset{e}{\rightleftharpoons} (C_{10}H_8)_2M_2^{2+}$$

Electrochemical studies of mono- and di-iron cyclopentadienyl complexes of thianthrene (TH), phenothiazine and diphenylene dioxide at a platinum electrode in MeCN and CH_2Cl_2 solutions have been reported [125(b)]. At fast scan rates ($v > 10\ V\ s^{-1}$) at an ultramicroelectrode (25 μm diameter) in MeCN, the di-iron complexes show two Nernstian one-electron reduction waves. The small separation of the reduction waves (180 mV for the TH complex) is attributed to a moderate through-space interaction of the two CpFe centres in the dimer. At slower scan rates, some decomposition of the reduced complex is observed; the chemical step involves cleavage of the Fe–arene bond to form the free arene and a solvated CpFe(1 +) species. This CpFe(1 +) species reacts with added CO to produce $[CpFe(CO)_2]_2$, disproportionates to form ferrocene and Fe(CO) or reduces the TH complex in homogeneous solution. Digital simulations of the electrochemical data are presented in support of the assigned mechanism. The monoiron TH complex displays similar reactions, with the [CpFe(1 +)(TH)] species more stable in CH_2Cl_2 than in MeCN solutions [125(b)].

The electron transfer reactions with a change in the formal oxidation state of the metal are also characteristic of triple decker sandwich complexes [126–128] and there is a significant increase in the number of possible redox transitions as a result of the increase in the number of metal atoms. Examples of such systems are:

$$[CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2+} \overset{e}{\rightleftharpoons} [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{+} \overset{e}{\rightleftharpoons}$$

$$[CpCo(\eta^5\text{-}C_2B_3H_5)CoCp] \overset{e}{\rightleftharpoons} [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{-} \overset{e}{\rightleftharpoons}$$

$$[CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2-} \qquad \text{(ref. 127)}$$

and

$$[CpCo(\eta^8\text{-}COT)]^{+} \overset{e}{\rightleftharpoons} [CpCo(\eta^8\text{-}COT)] \overset{e}{\rightleftharpoons} [CpCo(\eta^8\text{-}COT)]^{-} \qquad \text{(ref. 128)}$$

It has been shown by means of CV [112(b)] that the reduction of the double-decker cations $[(Cp^*Fe)_2(\eta^{12}, \mu^2\text{-}L)]$ (L = biphenyl, 9,10-dihydrophenanthrene or triphenylene) to corresponding neutral complexes in aprotic media is a multi-stage process which proceeds via the intermediate formation of mixed-valence [Fe(2 +)Fe(1 +)] complexes. The redox reactions of ferrocene-substituted phosphazenes and polyphosphazenes [129] and of the ferrocene complex containing germanium octaethylporphyrine as the bridge linking the two ferrocene moieties have been investigated [130]. The redox reactions of polynuclear homo- and hetero-ligand sandwich complexes of transition metals, especially bridged dimetallocenes, bis(fulvalene) dimetal complexes, metallocenophanes and multi-decker sandwich complexes have been examined in a review [5].

Redox-active cavitand host molecules containing multiple ferrocenyl redox centres with the ferrocene moieties lining the wall of the cavitand cavity have been studied by means of CV, differential pulse voltammetry and controlled-potential electrolysis in CH_2Cl_2 and DMF media [131]. The electrochemical studies show the multiple ferrocene centres present in cavitands to undergo independent reversible one-electron oxidations in CH_2Cl_2. The addition of CH_2Cl_2 to or bubbling of CO_2 through electrochemical dimethylformamide solutions of cavitands produced no significant changes in the cyclic voltammograms (cf. refs. 48 and 49) because complexation of neutral guests near the Cp_2Fe redox centres is unlikely to perturb the electron density of the ferrocene iron atom.

The behaviour of the other polynuclear sandwich complexes in redox reactions has been described in a number of communications [2,3,6-10,132,133].

In concluding consideration of the redox reactions of sandwich complexes, 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 problem of the electronic effects of substituents on the redox properties of sandwich complexes, with which one may become acquainted from other publications [2,3,6,7,132], has hardly been 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 redox reactions of the class of complexes considered are determined primarily by the nature of the metal atom involved. The discovery of a quantitative relationship between the redox properties of sandwich complexes and the corresponding metals would make it possible, without resorting to additional physical and/or chemical measurements, 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.

C. LINEAR RELATIONSHIP BETWEEN THE REDOX POTENTIALS OF SANDWICH COMPLEXES AND THE IONIZATION POTENTIALS OF THE CORRESPONDING METALS

A model has been proposed [118] 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 E^0 values 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 frontier orbitals, the electron pairing energy etc. has been examined at a purely descriptive level. Attempts have been made to find a correlation between the $E_{1/2}$ values for metallocenes and ionization potentials of metals (IP), but these were limited, since the comparison was carried out only for a single $Cp_2M^{0/+}$ redox couple and for a limited range of metals (vanadium, chromium, iron and nickel) [26]. An attempt was also made [25] to find a correlation between the $E_{1/2}$ values of the $Cp_2M^{0/+}$ (M = V, Cr, Fe, Co and Ni) redox transitions and the ionization potentials of the complexes (I_D), but for certain metallocenes an appreciable deviation from the linear relationship predicted by the equation [134,135]

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

was observed. Although the ionization potentials have now been measured for a large number of sandwich complexes [14], such a correlation is hardly suitable for the prediction of the redox properties, especially if one is dealing with complexes which have not yet been synthesized or which are unstable, for which the I_D values are unknown. Furthermore, there are no reliable literature data for the second, third and subsequent ionization potentials of the complexes, while the IP values for the metals are readily available [136].

A completely different approach has been proposed in studies [32,33,119,137] in which the existence of a linear relationship between the standard potential values of all possible redox reactions of sandwich complexes [see, for example, eqn. (1) for metallocenes] and IP_j ($j = 1-4$) values of the corresponding metals has been established and justified. The existence of such a relationship is due to the fact that the frontier orbitals of the sandwich complexes are predominantly metal based [12–14] and the E^0 values for the electron reactions in the series of sandwich complexes, involving precisely the HOMO and LUMO [2,3], should in fact reflect the change in the oxidation state of the metal, whose measure is the IP_j value [32]. Furthermore, the sandwich complexes retain their plane-parallel structure regardless of the formal oxidation state of the metal (at least in the time scale of transient electrochemical measurements) and solvation energy of the components of the redox couples, e.g. $Cp_2M^{x/x-1}$, depend little on the nature of the metal, since the effects of specific solvation is prevented by the bulky ligand environment in the sandwich complexes. As a result, solvation effects in the redox reactions of sandwich complexes are associated mainly with the electrostatic E_s component, which is approximately the same for equally charged isostructural complexes [15,83,137]. The change of E_s value on transition from, for example, Cp_2M^x to Cp_2M^{x-1} makes approximately the same contribution to the E^0 values for different metals. Furthermore, the predominantly electrostatic character of the influence of E_s on the E^0 value for sandwich complexes permits a comparison of the standard potentials of the redox reactions of the sandwich complexes measured in different solvents [32]. The set of these quantities leads to a linear relationship between the E^0 and IP_j values for all possible redox reactions of homo- and hetero-ligand sandwich complexes [32,119,137]. However, in certain cases, e.g. for individual bis(arene)metal complexes [69,70,86] whose redox reactions occur with electron transfer to the ligand based orbitals, such a linear relationship does not hold.

Figures 2 and 3 present the E^0–IP_j relationships for metallocenes and metallocarboranes, respectively. The parallel variation of the E^0 and IP_j values is clearly seen (the E^0 values increase with an increase in the value IP_j), but certain points

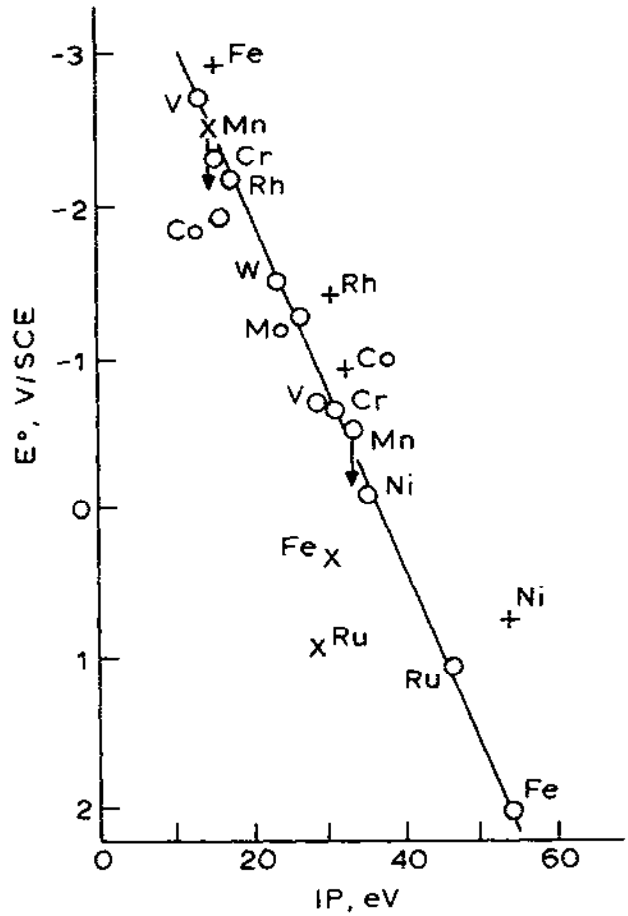


Fig. 2. Dependence of E^0 values for the $d^{x/x-1}$ transitions in the series of metallocenes on the corresponding ionization potentials of the metal. The E^0 values for Cp_2^*Mn are quoted in the case of manganocene; the arrows indicate the shift of E^0 values taking into account the effects of the substituents. (From refs. 32, 33 and 137.)

deviate significantly from the straight line. All these deviations refer to the redox couples involving the most stable 18-electron closed-shell configuration of the complexes. The deviation of the E^0 values for the $d^{5/6}$ redox transitions in the direction of more positive potentials, which might have been expected from the IP_j values, 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 these subgroups. As the electron is transferred to the antibonding e_{1g}^* orbital of the sandwich complexes [12–14,138], the E^0 values for these electron transfer reactions must deviate consistently in the direction of more

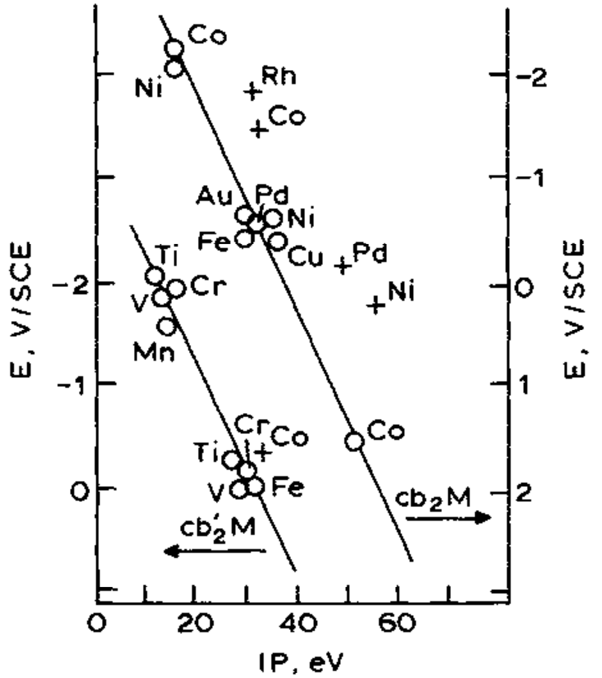


Fig. 3. Dependence of E^0 values for the $d^{x/x-1}$ redox transitions in the series of metallocarboranes Cb_2M and Cb'_2M on the corresponding ionization potentials of the metal. (From refs. 32, 33, and 137.) Legend: $+ = d^{6/7}$ and $o = d^{1/2/3/4/5/6.7/8/9}$.

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 value between non-bonding (a_{1g}) and antibonding (e^*_{1g}) orbitals can probably be estimated from the degree of deviation of the E^0 value in the case of the $d^{6/7}$ redox transitions.

It is seen from Figs. 2 and 3 that the same slope of the E^0–IP_j relationships, amounting to approximately 0.1 V eV^{-1}, is characteristic of sandwich complexes of three different types. This makes it possible to predict the redox properties of different sandwich complexes from the IP_j values of the corresponding metals, *provided that the E^0 value 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 universal redox scale for transition metal sandwich complexes, which is especially important for the sandwich complexes which have not been characterized electrochemically, have not yet been synthesized, or are so unstable that their electrochemical investigation is impossible. This approach allows the E^0 value of any possible redox reaction to be expressed:

$$E^0 \approx \sum a_i + 0.1\mathrm{IP}_j \qquad i = 1, 2 \qquad (6)$$

The values of the constants a_i have been calculated for the principal types of π-ligand (in V): -2.08 (Cp), -0.73 (η^6-C_6H_6), $+1.52$ (η^7-$C_7H_7^+$), -3.61 (η^8-COT^{2-}), -2.05 (Cb^{2-}) and -1.70 (Cb'^{2-}). Figure 4 illustrates graphically the validity of the proposed approach for other sandwich complexes.

The existence of a linear relationship between the reactivity of sandwich complexes in redox reactions and ionization potentials of the metal makes it possible to investigate systematically the regions of 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 redox reactions of certain complexes uncharacteristic of sandwich complexes, to select the optimum conditions for the synthesis and investigation of the physical/chemical characteristics of sandwich complexes, to assess the possibility of the synthesis of various sandwich complexes, to determine the redox properties of the different types of sandwich complexes, to determine the redox properties of both relatively unstable and hitherto not yet synthesized sandwich complexes, etc. A study has been devoted to the consideration of these questions [32]. In addition, its authors (see also ref. 137) discuss questions associated with the application of the linear relationships E^0 vs. IP_j to the estimation of the reactivities of octahedral metal complexes ($[M(bpy)_3]^{n+}$, $[M(phen)_3]^{n+}$, MF_6^{m-}, etc.) in redox reactions and consider the factors which determine the values of the slopes of these relationships.

Two uses for electrochemical redox potentials as valuable parameters for the prediction of molecular behaviour in homogeneous chemical reactions have been discussed by Butin et al. [120]. It has been proposed that the oxidation (E^{ox}) and reduction (E^{red}) potentials of the molecule must be taken into consideration along

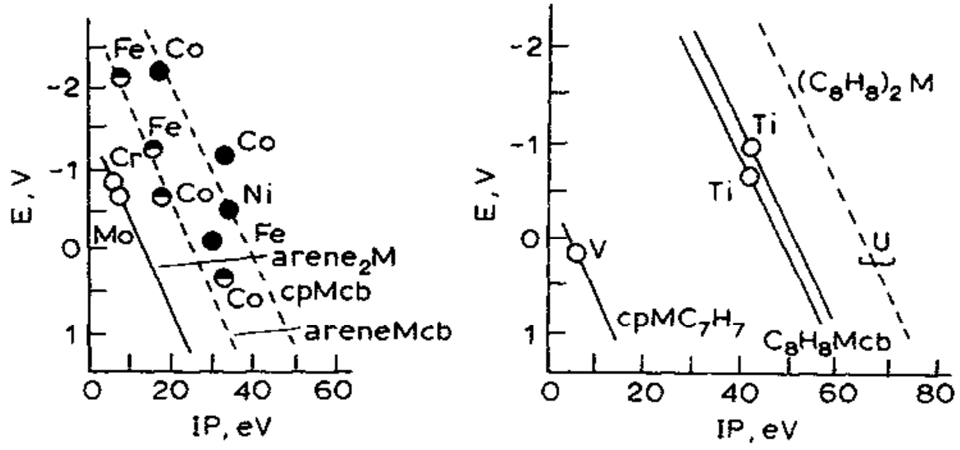


Fig. 4. Dependence of E^0 values on IP_j for the $d^{x/x-1}$ redox transitions in the series of homo- and heteroligand sandwich complexes: $(arene)_2M$, (arene)MCp, CpMCb, $CpM(C_7H_7)$, (COT)MCb, $(COT)_2M$. The dependences calculated from the a_i values found previously are shown by broken lines. (From refs. 32, 33, and 137.)

with and independently of its electron donor and electron acceptor properties. The proper terms "electrochemical gap" ($G = E^{ox} - E^{red}$), "intermolecular electrochemical gap" and "electrochemical electronegativity" ($\chi = [E^{ox} + E^{red}]/2$) are defined as a function of the E^{ox} and E^{red} values. Some properties of the sandwich complexes are analysed in these terms.

D. 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 polymerization, hydrogenation and izomerization of olefins [139,140(a)]. The products of their reduction activate small molecules such as dinitrogen [140(b)–(d),141] and carbon oxides [140(b)–(d), 142–147] in reactions of their chemical and electrochemical reductions, etc. The catalytic activity of systems based on the Cp_2MCl_2 complexes is manifest as 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 mechanical analysis shows [13] that in both sandwich and bent sandwich complexes frontier orbitals are predominantly metal based, 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 Group IVB bent sandwich complexes, titanocene dichloride has been thoroughly investigated with respect to its electrochemical behaviour. However, despite the fact that many studies have been carried out [148–153] there has been no unanimous view until recently concerning the detailed mechanism of its reduction.

The reduction of Cp_2TiX_2 (X = Cl or Br) in THF medium has been studied by means of polarography, CV (platinum and GC electrodes), preparative electrolysis and ESR spectroscopy [148]. It has been suggested that the reduction takes place in three successive reversible one-electron steps:

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

The $[Cp_2TiX_2]^-$ anion is stable in bulk 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_2TiCl^- with the elimination of the X^- anion. The paramagnetic $[Cp_2TiX_2]^-$ and $[Cp_2TiX_2]^{2-}$ complexes have been characterized by ESR 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 also been confirmed in subsequent studies [149,150].

It has been found from cyclic voltammetric, preparative electrolysis and ESR spectroscopic data [151–153] that, although Cp_2TiCl_2 does in fact undergo electrochemically reversible reduction to the $[Cp_2TiCl_2]^-$ anion in aprotic media, the anion is unstable and rapidly loses Cl^-. This is replaced by a molecule of the solvent or another suitable ligand (L) with formation of the $Cp_2Ti(L)Cl$ complex, which is then capable of reversible one-electron oxidation to the $[Cp_2Ti(L)Cl]^+$ cation. The latter is converted into the initial Cp_2TiCl_2 complex in the presence of an excess of Cl^- ion [152]. As the electron-donating properties of L are enhanced in the sequence $THF < py < DMF$, the rate of the forward reaction

$$Cp_2TiCl_2{}^- + L \rightleftharpoons Cp_2Ti(L)Cl + Cl^- \qquad (7)$$

increases while that of the reverse reaction decreases. The complex $Cp_2Ti(THF)Cl$ has been characterized by ESR spectra [151].

The electrochemical reduction of Cp_2TiCl_2 has also been investigated in the $AlCl_3$/1-butylpyridinium chloride melt [53]. 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 the Cp_2TiX_2 complexes [154]. The electrochemically generated $Cp_2Ti(NCS)_2$ species (characterized by ESR spectroscopy) is stable in THF and CH_2Cl_2 solutions at room temperature. The irreversibility of the first reduction stage in DMF has been attributed to the irreversible dimerization of the anion, which forms a diamagnetic titanium(III) complex.

The data of Kukharenko et al. [155] generally agrees well with the results of other studies [151–153]. According to these data, the electrochemically generated $Cp_2TiCl_2^-$ anion is unstable and is rapidly but reversibly dehalogenated in accordance with eqn. (7) with the formation of Cp_2TiCl (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 subsequent one-electron reduction of Cp_2TiCl leads to the formation of the unidentified "titanocene Cp_2Ti", which is capable, according to the authors [153–155], of undergoing one-electron reduction. However, it has been suggested [153] that the product of the reduction of Cp_2TiCl is a dimeric titanium(II) complex and not the "titanocene".

Among heavier analogues of Cp_2TiCl_2, the dichlorides of zirconocene [148,155–158(a)] and hafnocene [155,156,158(a)] 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 characterized by ESR spectroscopy [156–158]. 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" [155]. At room temperature, the electrochemically generated $Cp_2MCl_2^-$ anions are apparently dehalogenated with formation of the more readily reduced monochlorides [155]. The rate of dehalogenation of $Cp_2MCl_2^-$ anions diminishes in the sequence Ti > Hf > Zr as a function of the nature of the metal, but the rate of the back reaction (7) increases in the sequence $Hf \leqslant Zr \ll Ti$ [155]. Together with dehalogenation, there is also a possibility of Cp–metal bond rupture in the zirconium- and hafnium-containing anions $Cp_2MCl_2^-$ via the reaction [156,158(a)]

$$Cp_2MCl_2^- \rightleftharpoons Cp^- + CpMCl_2$$

The electro-oxidation of $[(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(4+)(\eta^1\text{-}1,\ \eta^1\text{-}1')\text{-}(\eta^5\text{-}C_5H_4)_2Fe(2+)]$ in THF solution in the presence of traces of water gives [bis(η^5-t-butylcyclopentadienyl)(η^1-ferrocenyl)(η^1-hydroxy)-zirconium(4+)] via an electrocatalytic process with an endergonic cross-electron transfer propagation step [158(b)].

Recently [24], the intermediate formation of corresponding substituted titanocene, zirconocene and hafnocene has been detected for the first time by means of CV in a study of the mechanism of the electrochemical reduction of the corresponding pentamethyl- and t-butyl-substituted metallocene dichlorides in THF at temperatures in the range −90 to −70°C. Thus the cryoelectrochemical approach to the study of redox reactions of sandwich and bent sandwich complexes proposed by Kukharenko et al. [19–21] has made it possible to establish the fundamentally important fact of the existence of the previously unknown Group IVB metallocenes and the possibility of their reversible one-electron reduction to the corresponding anions.

The electrochemical behaviour of bridged titanocene dichlorides $[(CH_2)_x(C_5H_4)]TiCl_2$ ($x = 1$–3) and substituted titanocene dichlorides in THF has been investigated [159,160]. While the reduction mechanism is the same, the $E_{1/2}$ values 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 [159(a)] that the influence of the bridging substituents on the values of $E_{1/2}$ is due to their steric and not the inductive effect. The electronic and steric effects of the substituents in the electrochemical reduction of bis(cyclopentadienyl)titanium and zirconium dichlorides have also been studied by means of CV [159(b)].

The reversible one-electron reduction of the dialkyl derivatives of titanocene and zirconocene [Cp_2MR_2 (M = Ti and Zr; R = Me or $PhCH_2$)] in THF leads to the formation of the corresponding unstable anions, which are decomposed with the elimination of R^- or Cp^- anions [156,161–163]. In THF, {2,3-bis(methylene)bicyclo[2.2.2]octane}zirconocene undergoes one-electron reduction to the corresponding anion radical, which is relatively stable at 20°C (characterized by its ESR spectrum), but decomposes with zirconocene-diene bond rupture on raising the temperature [164]. References to other studies on the electrochemical reduction of dialkyl metallocenes may be found in refs. 6 and 7.

The $[Cp_2TiR_2]^-$ anion ($R = C \equiv CPh$), stable at −30°C, has been obtained by the reversible one-electron reduction of Cp_2TiR_2 in THF solutions. On heating to

25°C, it slowly and reversibly splits off the Cp^- anion with formation of the $CpTiR_2$ species, which reacts with the $Cp_2TiR_2^-$ anion to form $Cp_2TiR_2^-$ [165].

The Cp_2TiCl complex, 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 [166] as a model for the activation of the N=N double bond.

The electrochemistry of Group VB metallocene dichlorides has mainly 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 electrochemical reduction of these bent sandwich complexes. Thus, the following mechanism for the reduction reaction has been proposed on the basis of data for the polarographic study of Cp_2VCl_2 in THF [25]

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

It has been claimed [25] 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 vanadocene reduction wave permitted the conclusion that vanadocene is the product of the consecutive two-electron reduction of Cp_2VCl_2.

In contrast to this [27], the transfer of the first electron to Cp_2VCl_2 is accompanied by formation of the $Cp_2VCl_2^-$ anion, which, however, is extremely unstable and rapidly but reversibly splits off Cl^- with formation of the Cp_2VCl monochloride, which is in fact then reduced to vanadocene. Other data [167] confirm the validity of this conclusion.

Study of the reduction of the bis(cyclopentadienyl)vanadium complexes with different types of chelating agents showed that the product of the two-electron multistage reduction of these complexes is vanadocene [168].

A reversible one-electron wave, corresponding to the formation of the $Cp_2NbCl_2^-$ or $\{[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]NbCl_2\}^-$ anions, has been observed in the electrochemical reduction of the corresponding niobocene dichlorides in THF [169,170]. On the basis of cyclic voltammetric and preparative electrochemical reduction data [170], 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:

$$Cp_2NbCl_2 \overset{e}{\rightleftarrows} [Cp_2NbCl_2]^- \xrightarrow{Cl^-} [Cp_2NbClCl_2NbCp_2]$$

At room temperature, the one-electron reduction of niobocene dichloride leads to the formation of the $(Cp_2NbCl)_2$ dimer, while in the presence of $L = Ph_3P$ or $(PhO)_3P$, it yields $Cp_2Nb(L)Cl$ [171]. 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^- [171] results in the formation of unstable niobocene, which is destroyed in subsequent reactions. Previously, the formation of niobocene as the primary unstable product of the amalgam reduction of Cp_2NbCl_2 was suggested on the basis of the ESR data [172].

Electrochemical reduction of Cp_2MCl_2 (M = Nb, Ta), $Cp_2Nb(CO)X$ (X = H, Cl) and $CpNb(CO)_4$ complexes in argon and carbon monoxide atmospheres has been studied by means of CV and preparative electrolysis in THF solutions in the −90 to +20°C temperature range [173]. The Cp_2MCl_2 complexes have been shown to undergo a reversible one-electron reduction yielding $Cp_2MCl_2^-$ anions, which lose halogen anions reversibly with formation of highly reactive and coordinatively unsaturated Cp_2MCl monochlorides. Under argon at room temperature, the Cp_2MCl complexes are unstable and react with starting metallocene dichlorides producing mixed-valence $[Cp_2MClCl_2MCp_2]$ dimers. Electrochemical reduction of $Cp_2MCl_2^-$ anions into extremely unstable $Cp_2MCl_2^{2-}$ dianions has been observed at −60°C at very negative potentials (near Bu_4N^+ ion discharge potentials). Electrogenerated Cp_2MCl complexes react with CO with formation of $Cp_2M(CO)Cl$ complexes. Further two-electron electrochemical reduction proceeds according to the ECE scheme yielding metallocene carbonyl $Cp_2M(CO)$ intermediates and eventually $CpM(CO)_xMCp$. These dimers can undergo reversible stepwise two-electron oxidations accompanied by changes in the metal–metal bond order and irreversible reduction with loss of dimeric structure and formation of $CpM(CO)_4^-$ anions. Under argon atmospheres the $Cp_2Nb(CO)^-$ anion generated by two-electron reduction of the $Cp_2Nb(CO)Cl$ complex is protonated by Bu_4N^+ cations, yielding a stable carbonyl hydride $Cp_2Nb(CO)H$ complex capable of reversible reduction to the related anion. It is concluded that, unlike the previously studied metallocene dichlorides of Groups IV–VIB metals, the reduction of Cp_2NbCl_2 and Cp_2TaCl_2 does not lead to the formation of the corresponding metallocenes.

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 [174].

It has been established by means of CV that the dithiolene complexes $(Cp_2NbS_2C_2R_2)^+$ (R = Me or Ph) are reduced in THF in two reversible one-electron steps to a neutral compound and a monoanion, respectively. The complex $Cp_2NbS_2C_2R_2$ can be obtained by preparative electrolysis [175].

The complex $[Cp_2TaL]^+$, where L = 1,2-bis(dimethylphosphino)ethane, is oxidized in aprotic media (CH_2Cl_2, MeCN or AC) in two reversible one-electron steps to $[Cp_2TaL]^{2+}$ (characterized by its ESR spectrum) and $[Cp_2TaL]^{3+}$, respectively, according to data obtained by means of CV [176].

The polarographic study of the $Cp_2MH_mSnMe_nCl_{3-n}$ complexes (M = Ta, Mo, Re; $m = 1$ or 2; $n = 0$–3) in THF showed that the reduction is directed to the Sn(IV) atom of the parent group and the M–H bond and/or the transition metal atom is oxidized [177].

In contrast to Group IVB and VB metallocene dichlorides, the complexes Cp_2MoCl_2 and Cp_2WCl_2 are reduced in an aprotic medium to the corresponding unstable metallocenes in one two-electron step [31,32] 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) reduction waves 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 [31]. On the other hand, it leads to a marked destabilization of the $Cp_2MCl_2^-$ anions, which are rapidly and irreversibly dehalogenated with formation of Cp_2MCl complexes more readily reducible than the initial metallocene dichlorides [31]. In has been shown [167] that Cp_2M^+ cations are products of this kind. Thus, the reduction of Group VIB metallocene dichlorides proceeds via the ECE mechanism with $E^0{}_1 < E^0{}_2$.

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 [178(a)]. In MeCN, these complexes undergo reversible one-electron oxidation to the unstable cations $Cp_2MX_2^{+}$, in which the ligand is substituted by a reductive elimination reaction with ejection of the $X^{\cdot}$ atom, which results in the formation of the complexes $[Cp_2M(MeCN)X]^+$. The potentials of the $Cp_2MX_2{}^{0/+}$ 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 dimerize with formation of $[Cp_2M(\mu\text{-}SR)_2MCp_2]^{2+}$. The redox properties of the trinuclear heterometallic complex $Cp_2Ti[(\eta\text{-}C_5H_4)FeCp]_2$ have also been investigated [178(a)].

The electrochemical oxidation of complexes of the type $[Cp_2M(py)X]^+$ ($M =$ Mo, W; $X = Cl$, Br, H) to the corresponding dications has been studied in MeCN by means of CV [178(b)]. It has been shown that (i) chloride complexes are oxidized at slightly lower potentials than bromide complexes and (ii) tungsten complexes undergo oxidation at lower potentials than molybdenum complexes.

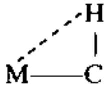
The electrochemical oxidation of the Cp_2WH_2 and $Cp_2W(Ph)H$ hydrides in MeCN has been investigated by means of CV and preparative electrolysis [179]. The above compounds undergo reversible one-electron oxidation to the corresponding unstable radical cations (lifetime from 10^{-3} to 20 s; characterized by means of ESR spectroscopy), which are stabilized either via the reduction elimination reaction

$$CpW(Ph)H^{+\cdot} \xrightarrow{H} CpWPh \rightarrow CpW + Ph^{\cdot} \xrightarrow{MeCN} PhH$$

or as a result of additive dimerization

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

The oxidation of $Cp_2WR^1R^2$ (where R^1,R^2=alkyl, aryl, Cl, Br or I) in MeCN has been studed [180]. It is suggested that the agostic interaction



takes place in the electrochemically generated $[Cp_2WR^1R^2]^+$ cations. The donor interactions of the halides (Cl > Br > I) reverse the usual electronegativity trend, probably because of unusually good d–p π-overlap. The π-donor effects of the alkyl ligands suggest a stabilizing three-electron agostic interaction in the cations, controlled by steric repulsion between the alkyl ligands and cyclopentadienyl ligands.

Data on the electrochemical behaviour of lanthanide and actinide bent sandwich complexes are extremely limited. It has been shown [181,182] that $(C_5Me_5)_2UCl_2$ undergoes reversible one-electron reduction to the anion in THF and MeCN media, but the available data on the stability of this anion are contradictory. It has been reported [183] that Cp_3UX (X = Cl or Me) undergoes reversible one-electron reduction in THF with formation of the stable Cp_3UX^- anion. Finally, it has been shown by means of CV that the reversible one-electron reduction of $(C_5Me_5)_2NpCl_2$ to the anion takes place in MeCN [184(a)]. The E^0 value of the $CpMe_2ThCl_2{}^{0/-}$ redox couple (−2.32 to −2.8 V SCE) has been estimated by means of flash photolysis [184(b)]. According to our unpublished results, Cp_2YCl does not reduce in THF up to −3 V SCE.

According to quantum mechanical calculations [13], the structure of the frontier orbitals of the bent sandwich complexes Cp_2MCl_2 and Cp_2MCl_2 is, qualitatively, virtually the same with different metals. 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 $E_{1/2}$ values for Group IVB and VB bis(cyclopentadienyl)metal chloride complexes, the characteristic reactions of which are one-electron reductions and oxidations, are also linearly related to the corresponding IP_j values of the metals. This has been confirmed by Kukharenko and co-workers [137,155]. Thus it is seen from the relationship between $E_{1/2}$ and IP_j presented in Fig. 5 that the $E_{1/2}$ values for metallocene dichloride [137] fit satisfactorily on the line not only for the reversible $Cp_2MCl_2^{0/-}$ 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 $Cp_2MCl_2^-$ species and the $Cp_2MCl_2^{2-}$ dianions formed as the primary reduction products of the $Cp_2MCl_2^-$ anions. The specific linear relationship also exists for Cp_2MCl monochlorides, which differ somewhat in their structure (Fig. 5). The same figure shows by a broken line the analogous relationship for metallocenes. Evidently the value of the slope for all three relationships is virtually the same (ca. 0.1 V eV^{-1}). This is probably associated with retention of the dominant contribution of the AO of the metal to the redox orbitals of both sandwich and bent sandwich complexes and with similar changes in solvation energies in the redox transitions of

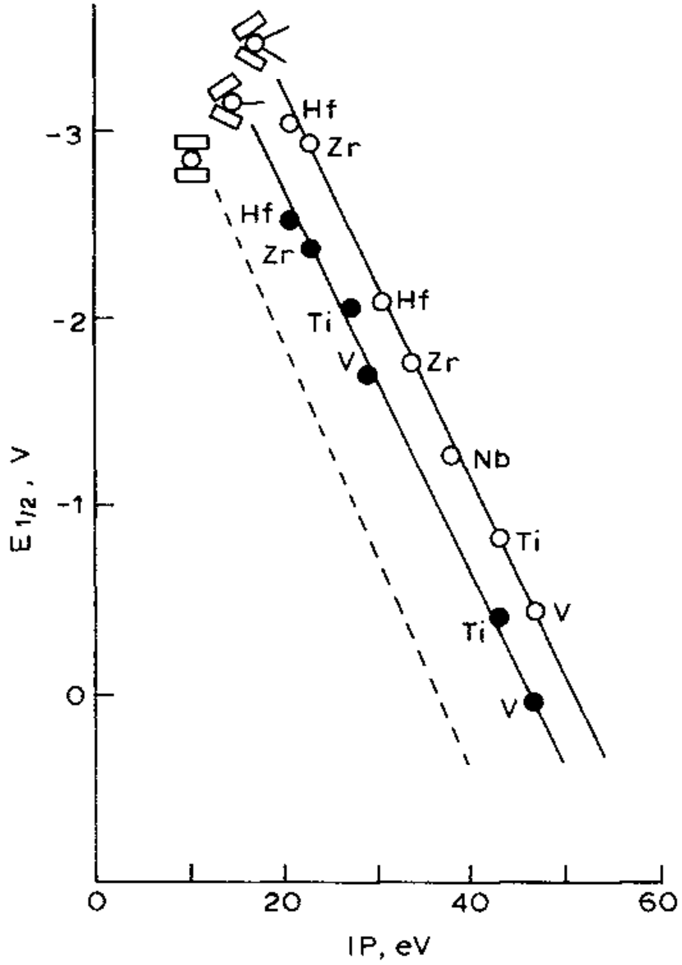
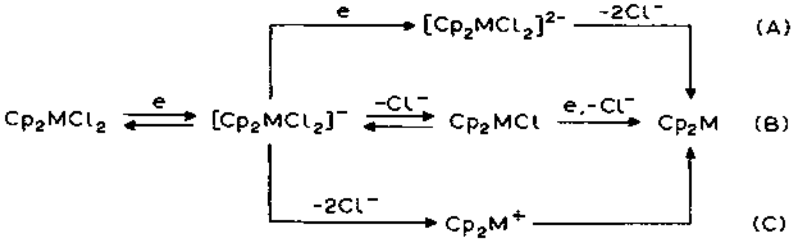


Fig. 5. Linear dependences of the half-wave potentials of the complexes Cp_2MCl_2 (○) Cp_2MCl (●), and Cp_2M (broken line) with the ionization potentials of the corresponding metals. (From refs. 33, 137, and 140(c).)

the complexes of all three types. On the other hand, the discrepancy in the linear relationships for complexes of different types is due to the energy differences between the corresponding frontier orbitals of the complexes, which are associated with differences in the angles of inclination between the cyclopentadienyl rings and with the presence of electron-donating Cl^- ligands [137,155].

A uniform mechanism for the electrochemical reduction of the Group IVB–VIB metallocene dichlorides has been proposed on the base of the linear relationships $E_{1/2}$ vs. IP_j established by Kukharenko et al. [24,137] and consideration of the character of the redox orbitals of the complexes. It can be presented schematically as:



Pathway (A) is realized for M = Zr and Hf at low temperature, pathway (B) for M = Ti, V, Zr, and Hf at room temperature and pathway (C) for M = Mo and W. When metallocenes whose lifetime is comparable with the time scale of the electrochemical method are formed (M = V, Mo, and W), the subsequent reduction of the anions to relatively unstable dianions becomes possible [31,32]. In the case of metallocene dichlorides of Groups IVB and VB, the electrogenerated monochlorides couple with formation of corresponding reducible dimers [137,173].

E. SANDWICH AND BENT SANDWICH COMPLEXES AS CATALYSTS OF CHEMICAL AND ELECTROCHEMICAL REACTIONS. ELECTROCHEMICAL SYNTHESIS OF SANDWICH AND BENT SANDWICH COMPLEXES AND METAL COMPLEX CATALYSTS BASED THEREON

After consideration of the electrochemical reactions of sandwich complexes and metallocene dichlorides we deal briefly with the catalytic activity of their electrochemically generated derivatives in relation to small molecules and other substrates and with the problem of electrosynthesis of sandwich, bent sandwich complexes and metal complex catalysts based thereon.

(i) Catalytic activity

The products of the electrochemical reduction of metallocene dichlorides frequently activate inert molecules, especially CO [142–146,186,187], CO_2 [185], N_2 [141], etc. in redox reactions, are inserted into the C–H bond [187] and participate in reactions involving the oxidative addition of olefins with formation of metallocycles [188], i.e. play an important or even a key 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 "unusual" valence states including unstable states, leads to considerable possibilities for investigation of reactivities of the low-valence products of the reduction of sandwich and bent sandwich complexes in reactions with different substrates.

The products of 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% [150]. However, the one-electron reduction product of Cp_2TiCl_2 in carbon monoxide atmosphere may be the 17-electron complex $Cp_2Ti(CO)Cl$ and not the 19-electron anion $[Cp_2Ti(CO)Cl_2]^-$ [146]. This is confirmed by the fact that the significantly more stable $Cp_2MCl_2^-$ anions (M = Zr or Hf) do not react with CO [146,155].

It is of interest to investigate the possibility of electrochemically induced insertion of CO in the metal–carbon bond in the alkyl derivatives of metallocenes with formation of corresponding acyl complexes (e.g. M–Alk → M–COAlk), because a reaction of this kind was observed [189(a)] in the electrochemical reduction of $CpFe(CO)_2Me$ in THF in the presence of Ph_3P. The acyl complex $CpFe(CO)(Ph_3P)$-(COMe) was formed as the product. The mechanism of oxidatively induced migratory insertion of carbon monoxide for $CpFe(CO)(Ph_3P)Me$ with evidence for a 19-electron intermediate $[CpFe(CO)(Ph_3P)(Nu)Me]^{+\cdot}$ (produced from electrochemically generated $[CpFe(CO)(Ph_3P)Me]^{+\cdot}$ radical cation and nucleophile, Nu = py) and $[CpFe(CO)(Ph_3P)(Nu)(COMe)]^+$ as final product has been studied by means of transient electrochemical techniques [189(b)].

The interaction of the electrochemically generated "titanocene" with dinitrogen has been briefly mentioned [153]. 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, the electrochemical reduction of N_2 to NH_3 was claimed [190] with a current yield of approximately 2%. However, the dinitrogen fixation was not confirmed by a blank experiment (argon) and by experiments with $^{15}N_2$.

It was shown by means of CV and preparative electrolysis that the complexes Cp_2VL (L = CO or HexNC) undergo reversible one-electron reduction in THF to the corresponding anions, which rapidly decompose to the metal, L and Cp^- anion, probably via the intermediate formation of CpVL [191,192].

In the presence of proton donors (phenols, diethylbarbituric acid, etc.) in non-aqueous media (THF, DMF, DMSO, etc.), vanadocene catalyses the amalgam reduction of carbon monoxide to C_1–C_4 hydrocarbons [142–146]. The $[Cp_2V(CO)]$ behaves as a catalyst–substrate complex, which undergoes one-electron reduction during the catalytic cycle to form the $[Cp_2V(CO)]^-$ anion. This undergoes subsequent protonation and reduction to form the methyl complex Cp_2V–Me. Protolysis of this intermediate leads to the formation of methane and chain growth takes place as a result of insertion of the CO molecule 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 (endergonic electron transfer) [145]. This reaction has been considered as an electrochemical analogue of the Fischer–Tropsch synthesis which takes place at room temperature and atmospheric carbon monoxide pressure. Other metallocenes Cp_2M (M = Nb, Mo or W) [146] also form reducible carbonyl complexes, which can be observed polarographically, for example in the case of M = Mo and W [31]. However, the deactivation of the unstable metallocenes during the catalytic process prevents their use as catalysts for the conversion of carbon monoxide to hydrocarbons.

Electrochemical reactions of complexes of bis(fulvalene) divanadium with CO and MeCN taking place with change in the formal oxidation state, have been examined [125]. The redox reactions of unbridged and of tetramethylethanediyl bridged chromocene carbonyl complexes and corresponding chromocenes and their ions with carbon monoxide have been studied by means of CV in THF medium [193]. The reactivity of these electrogenerated carbonyl complexes towards proton donors with potential formation of hydrocarbons has not been studied.

Sandwich complexes as electron transfer reagents (redox catalysts) have been used in biological systems (substituted ferrocenes; electrochemistry of redox proteins) [194(a)], in photo-electrochemical system for hydrogen evolution from water (Cp_2Co) [194(b)], in electrochemical reduction of $(PhO)_3PO$, which takes place at very negative potentials ($Cp_2Fe^{0/-}$ redox couple) [194(c)], etc.

(ii) Electrosynthesis

The principal methods for the synthesis of sandwich and bent sandwich complexes involve the interaction of the cathodically generated carbanions with the transition metal cations formed at "sacrificial" anodes [10,195]. Bis(cyclopentadienyl) derivatives of manganese, iron, cobalt and other transition metals [195] and the dicarbolyl complexes of iron, cobalt and nickel [195,196], etc. were recently obtained by this method. Carbonyl complexes of cyclopentadienyl derivatives of manganese, iron, cobalt, titanium and vanadium are formed when the Cp^- ligand is generated by electrochemical reduction of cyclopentadiene (CpH) in an aprotic medium and/or in a carbon monoxide atmosphere under conditions when transition metal ions are generated anodically [10,195].

The mechanism of the generation of carbanions is the principal problem in the electrochemical synthesis of sandwich and bent sandwich complexes. Bukhtiarov et al. have suggested [197,198(a)–(c)] that generation of the Cp^-, Flu^-, and Ind^- anions in the reduction of corresponding C–H acids (CpH, FluH, and IndH) proceeds via intermediate formation of corresponding radical anions (e.g. $CpH^{-\cdot}$). The authors also claim [197,198(a)–(c)] that the transition metal electrodes (Pt, Ni, Fe, Co, Cu) activate C–H acid reduction. In my opinion, this is erroneous since, according to our data, CpH is not reduced on mercury and platinum electrodes and the potentials of FluH and IndH reduction to the corresponding anion radicals do not depend on the electrode material [198(d)]. The main medium used here [197,198(a)–(c)] is MeCN, which is catalytically reduced to the $MeCN^{-\cdot}$ anion radical, yielding the strong base $NCCH_2^-$ upon H atom ejection (see, for example, ref. 198(b)); in the case of DMSO as solvent, the strong base $MeS(O)CH_2^-$ is also generated. It is evident that this electrochemically generated strong base abstracts a proton from the C–H acids with formation of the corresponding anions (e.g. Cp^-), which produce sandwich complexes in further bulk reactions with anodically generated metal cations.

A review [199] has been devoted to the synthesis of sandwich complexes with cyclo-olefin ligands. The review also covers reactions involving the introduction of functional groups into sandwich complexes. These include the electrophilic addition of alkyl halides and CO_2 to the electrochemically generated metallocene anions with formation of mono-substituted metallocene complexes or via anodic substitution of a hydrogen atom in ferrocene by alkyl and alkylcarboxy substituents which are obtained by the anodic decarboxylation of the anion of monocarboxylic and dicarboxylic acids and the monoesters of the dicarboxylic acid. Individual examples for the introduction of functional groups into ferrocene and other sandwich complexes can be found in a number of communications [6,7,200].

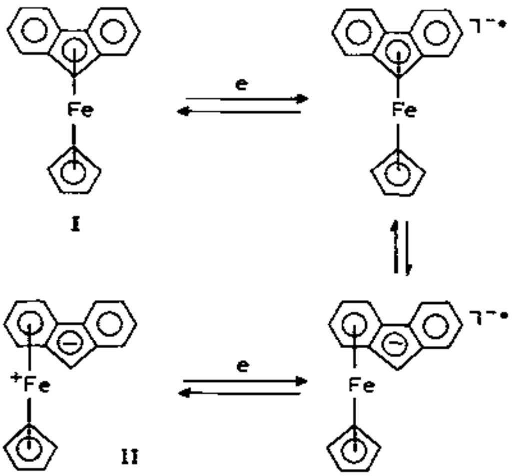
Another review [201] deals with the chemical synthesis of various complexes from metallocenes, including catalysts for the cyclo-oligomerization and trimerization of alkynes and nitriles and also for the hydrogenation of alkenes and arenes. The key stage in these reactions is the reduction of Cp_2M by an alkali metal to the Cp_2M^- anion with subsequent substitution of one or both Cp ligands by an olefin, an arene, a phosphyne, CO, N_2, etc. The reduction by an alkali metal can be replaced by electrochemical reduction, which makes it possible to extend significantly the scope of the electrochemical synthesis of metal complex catalysts for chemical and/or electrochemical reactions.

F. ELECTRON TRANSFER-INDUCED REACTIONS OF SANDWICH AND BENT SANDWICH COMPLEXES

In the last decade, there has been a sharp growth in the number of studies concerning the use of sandwich complexes 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 catalyzed by iron sandwich complexes as well as ligand substitution, cis–trans isomerization, chelation and demetallation reactions and those involving the migration, insertion of carbon monoxide in carbon–metal bonds in metal complexes and organometallic compounds etc., induced by charge transfer, have been considered elsewhere [202–204]. The main interest, of course, is connected with electron-transfer induced reactions (ETIR).

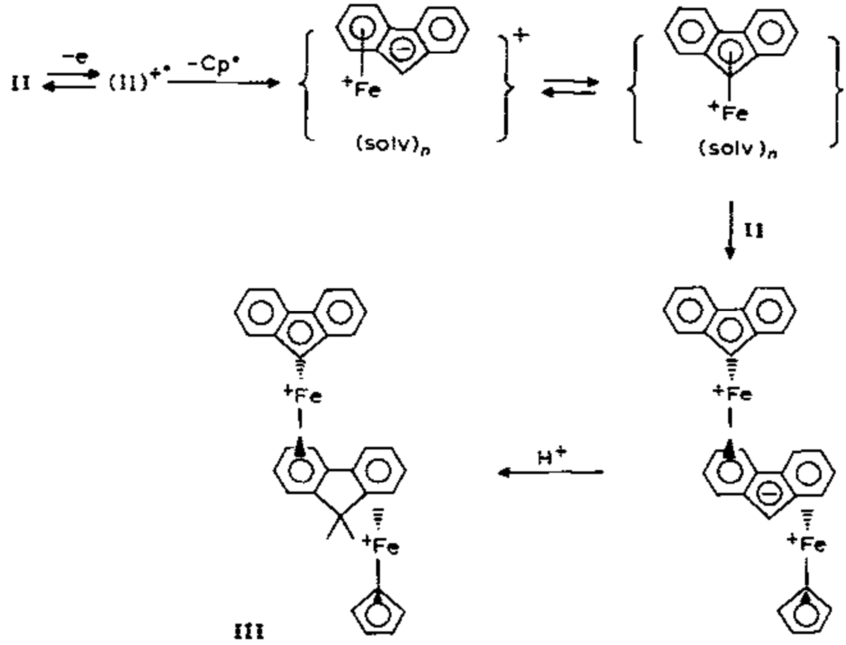
There are some papers connected with redox-induced hapticity changes. Thus, Geiger and co-workers [205] demonstrated that the two-electron consecutive reduction of the rhodium arene complexes of the formula $[(\eta^6\text{-Me}_nC_6H_{6-n})RhCp^*]^{2+}$ ($n=0$–6) in AC solutions is accompanied by hapticity change with formation of the corresponding Rh(I+) complexes with η^4-bonded arene and this has been confirmed by X-ray crystallographic data [205(a)] and ^1H NMR spectra [205(b)] for the hexamethylbenzene complex. The results demonstrate that, when a metal complex undergoes a two-electron-transfer-induced change from η^6- to η^4-arene hapticity, the one-electron intermediate can retain the planar arene structure, even if this results in a 19-electron configuration.

Another interesting application of ETIR is the first evidence of a rapid and reversible intramolecular inter-ring $\eta^5 \rightleftarrows \eta^6$ haptotropic rearrangement of isomeric fluorenyl(cyclopentadienyl)iron complexes induced by electrochemical generation of their 19-electron radical anions in THF medium [113]:

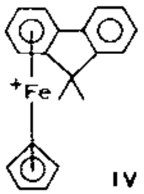


This hapticity change is reversible and the equilibrium is shifted to the side of the $II^{-\cdot}$ radical anion; lowering of the temperature to −70°C favours this shifting to an even greater degree.

The one-electron chemical and electrochemical oxidation in THF or MeCN media of isomer II to the 17-electron radical cation induced the following reactions with formation of triple-decker sandwich complex III as a final product [115]:

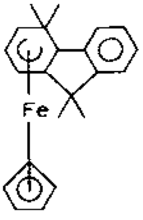


Further examples of ETIR for complexes I, II, IV and V with hapticity changes and their interconversions are described in the literature [113–115].



IV

V



Other examples of electrochemically induced hapticity changes for a series of sandwich and bent sandwich complexes can be found in refs. 39, 76, 80, 81, 107, 122, and 123.

An electrochemical study of an oxidatively induced ring slippage in the 17-electron $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]$ complex was reported by Trogler and co-workers [206]. Oxidation of $(\eta^5\text{-arene})_2V$ (where arene = Ind, Cp or Cp*) under a carbon oxide atmosphere provides a convenient route to $[(\eta^5\text{-arene})_2V(Co)_2]^+$ complexes. The cyclic voltammograms of the indenyl compound shows two reversible one-electron reduction waves. Reduction of the 18-electron $[(\eta^5\text{-Ind})_2V(CO)_2]^+$ cation leads directly to the 17-electron $[(\eta^3\text{-Ind})(\eta^5\text{-Ind})V(CO)_2]$. A lower limit for the η^3-to-η^5 ring slip rate constant is estimated to be $10\ s^{-1}$ at $-32°C$. Reduction of the cationic Cp and Cp* analogues were irreversible and showed no evidence for ring-slipped intermediates.

The electron-transfer chemistry of the 20-electron complex $(C_6Me_6)_2Fe$ and 19-electron complex $[(C_6Me_6)Fe(\eta^5\text{-}C_6Me_6H)]$ have been studied [207]. There is mild C–H bond activation via superoxide and functionalization of the exocyclic methylenes in the resulting complexes $[(C_6Me_6)Fe(\eta^4\text{-polyene})]$. This study is an example of how ETIR can be used in the hydrocarbon activation problem.

The electrochemically induced reversible insertion of ruthenium atoms into an eight-carbon chain in the anodic two-electron oxidation of the pseudo-triple-decker complex $Cp_2Ru_2(COT)$ in AC or CH_2Cl_2 solutions generates a pseudo-triple-decker dimetallacycle, which has been viewed as a key intermediate in the formation of cyclo-octatetraenes from alkynes and accounts in part for the interest in flyover-type molecules [208].

Other examples of ETIR in sandwich, bent sandwich and multi-decker sandwich complexes and their synthetic applications may be found in refs. 189, 201, 209, and 210 and reviews [211–214].

Thus, the redox activation of 18-electron complexes with closed-shell electron configurations greatly expands the synthetic possibilities for the modification of sandwich complexes, preparation of new sandwich and bent sandwich complexes, and metal complex catalysts based on them, etc. The high reactivity of 17- and 19-electron complexes (compared with their 18-electron analogues) follows for both thermodynamic and kinetic reasons. If the excitation of 18-electron complexes is connected with electron transfer between bonding and antibonding frontier orbitals, then the excitation of odd (17,19) electron complexes involves electron transfer between bonding (17-e) or antibonding (19-e) orbitals, respectively. Thus the excitation energy and the difference in reactivity for the ground and excited states of these odd-electron complexes are less than for their 18-electron analogues. Due to this high reactivity, the 17- and 19-electron complexes undergo some typical reactions, which hardly occur, or occur very slowly, with their 18-electron precursors.

G. CONCLUDING REMARKS

In conclusion, the use of solvents which are stable in regions of extremely anodic and cathodic potentials, and low-temperature and ultramicroelectrode techniques has greatly expanded our knowledge about possible redox reactions of sandwich and bent sandwich complexes. Besides the establishment of a linear relationship between the standard potentials of the redox reactions of sandwich and bent sandwich complexes and the ionization potentials of the corresponding metals, it has been possible to find a convenient parameter for the estimation of the reactivity of these types of complexes in redox reactions. The mechanisms of electrode reactions involving sandwich and bent sandwich complexes have been studied in fair detail. On the other hand, there exist promising aspects of this field in which there are still many unsolved problems. These include the electrochemistry of sandwich and bent sandwich complexes of the actinides and lanthanides, the reactivity of intermediates of redox reactions of sandwich and bent sandwich complexes in relation to reagents of different kinds (electrophiles, nucleophiles, small molecules, etc.), and the electrochemical synthesis of sandwich and bent sandwich complexes and of the metal complex catalysts based on them. The study of electrode reactions of sandwich and bent sandwich complexes in the absence of supporting electrolytes by means of UME and LTV techniques is also of interest (see, for example, ref. 215). This will permit an even more significant expansion of the potential working range (from -4 to $+5$ V SCE) and will make it possible to generate and identify species with "unusual" formal oxidation states and also to avoid the undesirable interaction of the species generated with components of the supporting electrolytes. Using the UME technique, the time scale of voltammetric measurements has been decreased by several orders of magnitude in the last decade and cyclic voltammograms recorded at scan rates in the 10^6 V s^{-1} range have been reported [216–218]. Low-temperature studies (cryoelectrochemistry) are very promising to make it possible to identify many unstable intermediates [219] in the electrochemical reactions of sandwich and bent sandwich complexes and to investigate their properties. The coupling of spectro-electrochemistry, UME and LTV techniques has proved to be a powerful tool in getting a better electrochemical and spectroscopic characterization of the species involved in the electrode mechanisms of sandwich and bent sandwich complexes. Finally, the development of new examples of electron transfer-induced reactions (as a synthetic tool) in the series of sandwich and bent sandwich complexes appears to be important for their modification.

NOTE ADDED IN PROOF

A comprehensive review on the electrochemistry of symmetrical sandwich complexes has recently been published by Geiger [220].

Redox reactions of sandwich and bent sandwich complexes with electron changes localized on the metal-based, π-bond or σ-bond orbitals have been discussed [221]. Main attention is focused on the correlation of the redox potentials of these organometallic complexes with the reactivity of their electrochemical reaction products and the analogy between electrochemical and chemical reactions.

(i) Sandwich and related complexes

The oxidation of ferrocene at a platinum electrode in DMF, EtOH, PC and their aqueous solutions was studied by means of CV [222(a)]. The electrode reaction may be described as quasi-reversible one-electron charge transfer, followed by slow decomposition of the oxidized species.

One-electron oxidation of ferrocene has been used as a model system for studying solvent effects in heterogeneous charge-transfer kinetics [222(b)]. The energy dependences of the electronic state densities of the reactant in several non-aqueous solvents (MeCN, MeOH, acetic anhydride, AC, DMSO and DMF) have been investigated. The energy dependence of the state density of ferrocene has shown non-Gaussian distribution characterized by two reorganization energies. The reorganization energy corresponding to the main peak of the distribution function has been found to be correlated with the donor number of the solvents, indicating the presence of a new inner-shell reorganization based on the donor–acceptor interaction. Both types of reorganization process have been attributed to the solvation sites peculiar to the shape of the ferrocene molecule.

The CV of Cp_2Fe and Cp_2^*Fe was studied at high temperature and pressure in a small cell in which the pressure and temperature could be varied independently [223]. Both compounds showed well-defined electrochemical behaviour under supercritical conditions ($T > 230$°C). The diffusion coefficient of Cp_2Fe was measured at 280°C as a function of pressure, and the experimental results were correlated to the values derived from the Stokes–Einstein relation.

The redox reactions of ferrocene derivatives containing a crown ether cavity have been studied by means of CV [224]. The redox properties of the ferrocene fragments do not change upon binding of an ether unit of the molecule with Na^+ and K^+ ions.

The coordination of alkaline-earth (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) and lanthanide (Eu^{3+}, Tb^{3+} and Dy^{3+}) metal cations by cryptand-containing ferrocene units has been examined by CV in MeCN medium [225]. The data are used to deduce the value of the equilibrium constant (K) for the association of oxidized cryptand with the range of metal cations and a linear correlation between $\ln K$ values and the ratio of ionic radius/ionic charge is reported.

The redox chemistry of ferrocene and ruthenocene bis(aza-crown ethers) and related compounds amide bond linkages between the metallocene redox centre and aza-15-crown-5(1,4,7,10-tetraoxa-13-azacyclopentadecane) and aza-18-crown-6-(1,4,7,10,13-pentaoxa-16-azacycloctadecane) is described in ref. 226. A sodium cation forms 1 : 2 stoichiometric complexes with the ferrocene bis(aza-crown ethers), whereas potassium produces a 1 : 1 intramolecular sandwich complex with the former and a 1:2 complex with the latter. Electrochemical investigations reveal that binding of Na^+ and K^+ guest cations at the respective aza-crown ether coordination sites results in shifts of the ferrocene oxidation wave to more positive potentials. The lithium ion produces analogous electrochemical effects with these two compounds, however, ^{13}C NMR results suggest this cation coordinates exclusively to the respective amide carbonyl oxygen donor atoms. This rationalization is supported by model ferrocene bis(tertiary amide) derivatives which exhibit redox-responsive behaviour to Li^+ while being electrochemically insensitive to Na^+ and K^+.

The mono- and bis-metallocene calix[4]arene hydrophobic receptor molecules have been studied by means of CV and coulometry in MeCN medium [227]. Electrochemical study reveals that bis-ferrocene calix[4]arenes undergo reversible two-electron oxidations at 0.90 V (SCE) suggesting that both ferrocene moieties are oxidized in one step. The cobalticinium analogue exhibits a reversible one-electron reduction at -0.45 V.

The equilibrium complexation constants of mono-substituted ferrocenes $CpFeC_5H_4X$ ($X=CH_2NMe_2$ and COOH) with α-, β- and γ-cyclodextrins were measured by CV in aqueous phosphate buffer solution (pH 7) [228,229]. The most stable 1 : 1 inclusion complexes are formed in the case of β-CD. The binding constants, K, of dimethylaminomethylferrocene and ferrocenecarboxylate with β-CD are equal to $(4.7 \pm 0.3) \times 10^3$ and $(2.1 \pm 0.3) \times 10^3\ M^{-1}$, respectively. Both the increase and decrease of the inner cavity size by one glucose unit results in a ca. 100-fold decrease in stability of the corresponding inclusion complexes. The ferrocenes inside the inner cavities of α- and β-CDs are no longer substrates for glucose oxidase and do not bring about catalytic current in the enzyme (α-D-glucose)–ferrocene system. This shows that ferricinium ions, like the ferrocene, form inclusion complexes, which, however, can not oxidize the reduced form of the flavoprotein. L-Lysine oxidase has been demonstrated to enhance effectively the electrochemical response of ferrocenes similar to glucose oxidase. The results obtained are briefly discussed in relation to the immunoenzyme analysis.

The reversible one-electron oxidation of the η^5-$C_5H_4Fe(\eta^5$-$C_5H_4)Zr$-$(\eta^5$-C_5H_4Bu-$t)_2$ complex in THF solution is directed to the ferrocene fragment and results in formation of the $[\eta^5$-$C_5H_4Fe(\eta^5$-$C_5H_4)Zr(\eta^5$-C_5H_4Bu-$t)_2]^+$ cation [230]. This cation reacts with water with formation of $[\eta^5$-$C_5H_4Fe(\eta^5$-$C_5H_4)Zr$-$(OH)(\eta^5$-C_5H_4Bu-$t)_2]^+$, which is reduced by its precursor in the near electrode layer to the neutral complex. The reaction is catalytic with endoergic cross-electron transfer.

The redox-reactions of bridged ferrocenes, *syn, syn-, syn, anti*-CpFeLFeCp and *all-syn*-CpFeLCpFeLFeCp (where L = 4,8-ethano-2,4,6,8-tetrahydro-*s*-indacene dianion), have been studied by means of CV [231]. In the voltammograms of these complexes, which contain rigid bent bridges between the cyclopentadienylmetal fragments, the separate waves indicate that the ferrocene units oxidize at different potentials. These potentials depend on the number of bridges and Cp_2Fe^+ fragments next to the ferrocene unit under study. The separation of potentials reflects the metal–metal interaction.

Electrochemical study of the ferrocenyl compounds, containing two hypervalent silicon substituents ($-SiOMe_3$ and $-Si(cat)_2$, where $catH_2$ = catechol) in different cyclopentadienyl rings, showed a significant reduction in the Fe(II)/Fe(III) redox potential when the silicon atom was penta-coordinated, in contrast to the small increase in this potential in ferrocenes bearing tetra-coordinated silicon substituents [232].

The redox reactions of the α-metallocenylmethyl cations, $C_5H_5MC_5H_4\overset{+}{C}Ph_{3-n}$ (where M = Fe, Ru and Os; $n = 1$–3), were studied by means of CV and preparative electrolysis in CH_2Cl_2 solutions [233]. These complexes reduce in two one-electron reversible steps to the $C_5H_5MC_5H_4\dot{C}Ph_{3-n}$ carbon-based radical and C_5H_5-$MC_5H_4\bar{C}Ph_{3-n}$ carbanion, respectively. The oxidation of ferrocenyl-containing complexes is directed towards the metallocene fragment.

The electrochemical behaviour of the metallocenyl-containing trinuclear osmium clusters, $[C_5R_5MC_5H_4C(=O)Os_3(CO)_{10}(\mu_2\text{-}H)]$ (where R = H or Me; M = Fe, Ru and Os), was studied by CV [234]. It was shown that oxidation of the complexes was directed towards the metallocene fragments whereas their reduction was towards the $Os_3(CO)_{10}$ fragment.

The synthesis of octamethylferrocene derivatives for functionalization of electrode surfaces has been described [235(a)]. Reaction of the (octamethylferrocenyl)-methyl carbocation with surface-confined nucleophiles such as NH_2 or SH [electrode surface derivatized by $(MeO)_3Si(CH_2)_3NH_2$ or $(MeO)_3Si(CH_2)_3SH$] is a convenient way to attach octamethylferrocene derivatives to electrode surfaces, including platinum and indium tin oxide. These modified electrodes can be used in electro- and bioelectro-catalysis.

Another type of ferrocene derivative has been prepared for functionalization of electrode surfaces [235(b)]. The syntheses and electrochemical properties of new mono- and diferrocenyl bipyridyl ligands containing trans conjugated olefinic linkages between the ferrocene redox centres and the 4,4′-substituted bipy moieties are described. The corresponding ruthenium(2+) complexes have been prepared and one complex, $[RuL(bipy)_2]^{2+}$ (where L-4,4′-bis(ferrocenylvinyl)-2,2′-bipyridine), undergoes electrochemical polymerization to produce an electrochromic polymer film. The electrochemical data indicate that ferrocene moieties and the ruthenium atoms in the above complexes do not interact electrochemically with one another either inductively through the conjugated system or through space.

The formation of organic thin films containing redox-active ferrocenyl moieties by controlled-potential electrolysis (oxidation) of aqueous solutions of surfactants with ferrocenyl moiety and an organic compound incorporated in micelles or in a dispersed organic pigment with use of the surfactants has been examined [235(c)].

The electrochemical and spectroelectrochemical behaviour of $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$, where P is the dianion of octaethylporphyrin or tetraphenylporphyrin and Fc is a ferrocenyl group, are described in ref. 236. The $(P)Ge(C_6H_5)(Fc)$ complexes provide the first example of metalloporphyrins which contain two different σ-bonded axial groups. Neutral $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$ were characterized by ^1H NMR, UV–VIS and IR spectroscopy. $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$ have Soret band molar absorptivities which are about only half that of other $(P)Ge(R)_2$ species, indicating a delocalization of positive charge from the ferrocenyl group onto the porphyrin macrocycle. Both complexes can be reversibly reduced at the porphyrin π-ring system. The first oxidation of $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$ involves the σ-bonded ferrocenyl groups and occurs at potentials much more negative than for oxidation of free ferrocene under the same experimental conditions. The singly electro-oxidized $(P)Ge(Fc)_2$ complexes exhibit an interaction between the ferrocenyl redox centres. The porphyrin macrocycles of $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$ can also be oxidized and this electrode reaction is followed by a cleavage of one σ-bonded ferrocenyl group.

The electrochemistry of phosphaferrocenes and reactivity of their electrogenerated ions towards nucleophiles have been studied [237].

The redox chemistry of ferrocenylphosphines, their transition metal complexes [238] and heteropolymetallic complexes of 1,1′-bis(diphenylphosphino)ferrocenes (dppf), $(dppf)MCl_2$ (where M = Co, Ni, Pd, Pt, Zn, Cd and Hg) [239], have been studied by means of CV in aprotic media. The data indicate that the ferrocenyl moiety in these complexes undergoes a strong stabilization toward oxidation.

The intermolecular electron transfer in the σ-bridged 1,1,12,12-tetrabutyl[1,1]stannaferrocenophane cation has been studied by means of CV and near-IR spectroscopy and has been attributed to the d-π overlap mechanism of the tin atoms and the cyclopentadienyl rings [240].

The 1,2,3-trithia[3]ferrocenophane and related compounds show a well-defined reversible one-electron oxidation wave Fe(II)/Fe(III) in CV [241]. The [3]ferrocenophanes with sulphur and/or selenium atoms in the bridge show unusually high oxidation $E_{1/2}$ values which have not been observed either in [3]ferrocenophane or in 1,1′-bis(methylchalcogeno)ferrocenes. The effect of chalcogen atoms at the 1,3-positions in the bridge on the positive shift of the $E_{1/2}$ potentials is larger than that at the 2-position. Two kinds of electron-attracting effect of chalcogen atoms at 1,3-positions in the bridge are proposed: an inductive electron-attracting effect ('through-bond' effect) and the interactions between the d orbitals of iron and chalcogen atoms ("through-space" interaction). The role of the sulphur atom at the 2-position in the bridge is to stabilize the electron attracted by the sulphur atoms at the 1,3-positions by conjugation of the three sulphur atoms.

The ESR spectra of deprotonated and subsequently oxidized cations of toluene-diphenylmethane-, fluorene-, triphenylmethane-, hexamethylbenzenecyclopentadienyl iron and dications of diphenylmethane-, fluorene- and triphenylmethane-bis-cyclo-pentadienyl iron have been investigated [242(a)]. The nature of the oxidation products depends on the structure of the arene and changes from carbon-centred paramagnetic to the metal-centred one. The mechanism of unpaired electron delocalization is discussed in terms of limiting structures which involve different oxidation states for the iron atoms.

The 3d level order of the iron atom in its d^5, d^7 and d^9 arenecyclopentadienyl complexes was determined by ESR spectra analysis [242(b)]. The relationship between the g-factor anisotropy and the chemical structure of the d^7 complexes is discussed. Paramagnetic complexes of the Fe(I)–Fe(II) mixed-valence systems are the reduction products of arene-bis-cyclopentadienyliron dications.

The electrochemistry of the novel macromolecular organometallic polymer poly[(μ-η^6,η^6-naphthalene)chromium] is delineated through study of its (bis(η^6-naphthalene)-chromium) precursor and an oligomeric model ((μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium) in order to observe the degree of intervalence charge transfer between chromium sites in the multinuclear species [243]. Theoretical studies have indicated that the multi-decker sandwich compound poly[(μ-η^6,η^6-naphthalene) chromium] should be an electrical conductor in its oxidized state; no electrical conductivity is observed in the zero-valent state. The inferred mechanism of the ligand exchange process of bis(η^6-naphthalene)chromium in THF through an η^2-THF, η^4,η^6-intermediate is supported by the CE mechanism of the $Cr^{0/+}$ couples observed by the Nicholson and Shain method kinetic analysis in (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium). The cyclic voltammetry of bis(η^6-naphthalene)chromium and (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium) in THF, and bis-(η^6-naphthalene) chromium and poly [(μ-η^6,η^6-naphthalene)chromium] in ethylenediamine is described to delineate the electrochemical behaviour of chromium compounds incorporating η^6-naphthalene and μ-η^6,η^6-naphthalene moieties. In addition to the various kinetic processes, characteristic $Cr^{0/+}$ and relatively unusual $Cr^{+/2+}$ couples were observed; ligand (naphthalene)$^{0/-/-2}$ redox couples were also observed. While the second reduction of the μ-η^6,η^6-naphthalene moiety was inhibited by the first reduction; mixed valence interaction between the metal sites was not observed electrochemically.

The mononuclear and binuclear cationic complexes $[Cp^{*}Ru(\eta^6\text{-arene})]^+$ (A^+) and $[(Cp^{*}Ru)_2(\eta^6,\eta^6\text{-arene})]^{2+}$ (B^{2+}, where arene = naphthalene, phenanthrene, anthracene, chrysene, pyrene, triphenylene, fluorene, bifluorene, biphenyl and 4,4′-biphenyl) have been studied by means of CV in CH_2Cl_2 and PC solutions [244]. The lower aromaticity in polyaromatics compared with that in non-annelated arenes obviously facilitates electrochemical reduction of the above cations. All compounds show a first reduction potential that is considerably more positive compared with free arene [244(a)]. The above complexes form one ($A^{+/0}$) or two ($B^{2+/+/0}$) redox couples. Two features are noteworthy in the cyclic voltammograms [244(b)]. One is the relative stability of the B^+ monocations derived from the bis complexes and the neutral complexes A derived from the mono complexes. The second point to be noticed is the separation of the two reduction waves in bis complexes and displacement of the first reduction towards more positive potentials when mono and bis complexes are compared, which can be taken as a measure for the interaction of the two Cp*Ru groups over the π-system.

Binuclear complexes of polyaromatics have been synthesized in order to examine their electron transfer (ET) chemistry and the stereoelectronic consequences of ET [244(c)]. The electrochemistry of complexes bearing two $(Fe(II)Cp)^+$ units shows a single two-electron wave for diphenyl in DMF at a mercury electrode at −30°C, two close one-electron waves for dihydrophenanthrene and four one-electron waves with pyrene, triphenylene and phenanthrene. Since reduced states are not stable, Fe(II)Cp* analogues were made. The diphenyl complex now has two one-electron reduction waves and the X-ray crystal structures of both the mono-reduced (average valence on the Mössbauer time scale) and the bi-reduced complexes show that chemical coupling intervenes in the course of the second ET to give the new bicyclohexadienylidene ligand. Delocalized mixed valence Fe(I)Fe(II) complexes are obtained for all the polyaromatics under study. Chemical coupling after two-electron reduction tolerated in dihydrophenanthrene is inhibited in phenanthrene, triphenylene and pyrene for which bis-reduced complexes are $38e^-$ biradicals, as $[Fe(\text{fulvalene})_2C_6H_6]$ (R = H, Me), but with much more spin density on the aromatic ligand than in the latter.

The series of bis(η^6-hexamethylbenzene) (η^6,η^6-$[2_n]$cyclophane)diruthenium-(2+,2+) tetracation complexes (where the $[2_n]$cyclophanes are $[2_2]$ (1,4)-, $[2_2]$ (1,3)-, 4,7,13,16-tetramethyl-$[2_n]$ (1,4)-4,5,7,8-tetramethyl-$[2_2]$ (1,4)- and $[2_3]$ (1,3,5)cyclophanes) has been prepared and their electrochemistry has been studied by means of CV in acetone, PC and CH_2Cl_2 [245]. These 4+ diruthenium complexes undergo two-electron irreversible reduction to give the corresponding dication $[2_n]$cyclophane derivatives in which each of the cyclophane ligands now has two cyclohexadienyl anion decks connected by a new carbon–carbon bond. The assignment of structures to these two-electron reduction products is based on ^1H and ^{13}C NMR spectral analyses, electrochemical studies, X-ray photoelectron data and a single-crystal X-ray analysis of $[2_z]$ (1,4)cyclophane derivative. A theoretical analysis of these dication diruthenium complexes and their formation is presented.

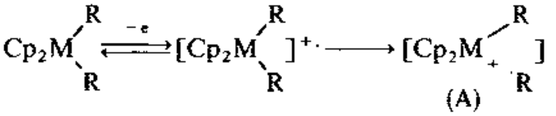
The bis(η^6-hexamethylbenzene) (η^6,η^6-polycyclic aromatic)diruthenium-(2+,2+) tetracation complexes (where polycyclic aromatic ligands are phenanthrene, 9,10-dihydrophenanthrene, Ph–Ph, 3,3′, 5,5′-tetramethylbiphenyl, 4,5,9,10-tetrahydropyrene and triphenylene) have been synthesized and their electrochemical properties measured by means of CV and coulometry in PC [246]. A two-electron reduction of each of these 4+ diruthenium complexes had led to the isolation and characterization of each of their corresponding dication diruthenium complexes. On the basis of analyses of their ^{1}H and ^{13}C NMR spectra, structural assignments have been made. Although the reduction product of the phenanthrene derivative is a mixed-valence ion having Ru(0) and Ru(2+) sites, all of the other complexes above undergo two-electron reduction by changing the biphenyl moiety of their polycyclic aromatic ligand into two cyclohexadienyl anions joined by a carbon–carbon double bond. It has been concluded [246], that there is a strong similarity between the 4+ diruthenium complexes of polycyclic aromatic ligands and the corresponding complexes of $[2_n]$cyclophanes [245]. In both series, the general behaviour is that two-electron reduction causes the attached ligand to change from a bis(arene) structure to a bis(cyclohexadienyl anion) system.

(ii) Bent sandwich and related complexes

Catalytic oxidation of PPh_3 by the electrogenerated $[(\eta^5\text{-}Me_3SiC_5H_4)_2\text{-}NbCl_2]^+$ cation has been studied by means of CV and preparative electrolysis in THF solution in the presence of water as an oxygen atom source [247]. The Ph_3PO oxide is the product of catalytic oxygenation of phosphine.

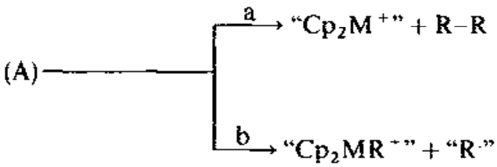
Electrochemical oxidation of Cp'_2NbHL [where $Cp' = C_5H_4SiMe_3$; $L = P(OMe)_3$] yields Cp'_2NbHL^+ and $Cp'_2NbL_2^{2+}$, which have been characterized by ESR spectroscopy [248]. These species represent the first niobium(IV) monocationic hydride and dicationic niobocene complexes.

The d^0 bis(cyclopentadienyl)dialkyl complexes of titanium and zirconium readily react with one-electron oxidants or are electrochemically oxidized (MeCN or CH_2Cl_2) to give products arising from either alkyl radical expulsion or formal reductive elimination [249]. Thus, bulk electrochemical oxidation of titanacyclobutanes, $Cp_2\underline{TiCH_2CR^1(R^2)CH_2}$ (where R^1,R^2 = different combinations of H, Me, i-Pr or *t*-Bu) results in the formation of the respective cyclopropanes, $\underline{CH_2CR^1(R^2)CH_2}$. Oxidation of the stereospecifically deuterated titanacyclobutanes led to the stereospecific formation of cyclopropanes with a high degree of retention of the configuration (>15/1 retention/inversion). This stereoselectivity requires either (i) that the oxidatively induced reductive elimination is concerted or (ii) if stepwise, that subsequent cleavage pathways leading to product are faster than C–C bond rotations if any intermediates are formed by Ti–C bond homolysis (i.e. very short-lived intermediates). The plausible mechanism for oxidation of d^0 Group IV complexes involves metal–carbon bond homolysis after oxidation of the metal–ligand bond to form the radical cation pair (A):



$$\mathrm{Cp_2M}\begin{smallmatrix}\mathrm{R}\\ \mathrm{R}\end{smallmatrix} \overset{-e}{\rightleftharpoons} [\mathrm{Cp_2M}\begin{smallmatrix}\mathrm{R}\\ \mathrm{R}\end{smallmatrix}]^{+\cdot} \longrightarrow \underset{(A)}{[\mathrm{Cp_2M}^{+}\begin{smallmatrix}\mathrm{R}\\ \mathrm{R}\end{smallmatrix}]}$$

The observed reaction products would then result from a competition between intramolecular S_H2 coupling (path a) and cage escape (path b) of this intermediate



Diphenylzirconocene oxidizes with the formation of biphenyl, while diphenyltitanocene gives predominantly benzene as well as some biphenyl under similar conditions. It is suggested [249] that this oxidation chemistry may find important synthetic application as a new route from Ti and Zr metallacycles to hetero- and carbocycles.

The electrochemical behaviour of cationic 1,3-diaryltriazenido complexes of molybdocene, $[\mathrm{Cp_2Mo}(p\text{-}\mathrm{R^1C_6H_4NNN}\text{-}p\text{-}\mathrm{C_6H_4R^2})]^+$ (where $R^1 = R^2 =$ H, F, Me, OMe; $R^1 =$ H, $R^2 +$ Me, OMe; $R^1 =$ Me, $R^2 +$ OMe), in MeCN has been studied by means of CV and constant potential electrolysis at platinum electrodes [250]. The complexes undergo two reversible one-electron reductions to species which are stable on the CV time scale, but the uptake of electrons appears to be followed by loss of the triazenido ligand. The oxidative electrochemistry of the complexes can be rationalized in terms of disproportionation occurring after the first one-electron oxidation. Both reduction and oxidation potentials show good linear correlations with σ^+ Hammett parameters, providing evidence for the mesomeric influence of ligand R^1 and R^2 substituents on the metal orbitals involved in the redox processes.

The electrochemistry of metalla-crown ether complexes, $[\mathrm{Cp_2M}(4\text{-thiobenzo-}15\text{-crown-}5)_2]$ (where M = Mo or W), was studied by CV in DMF and MeCN solutions [251]. These complexes undergo reversible oxidation, the $E_{1/2}$ values of which are quite sensitive to the presence of alkali metal cations ($\mathrm{Li^+}$, $\mathrm{Na^+}$ and $\mathrm{K^+}$; $\Delta E = 100$–120 mV) in solution.

Cycloheptatrienylcyclopentadienyltitanium $\mathrm{CpTi}(\eta^7\text{-}\mathrm{C_7H_7})$ exhibits by CV in THF a one-electron reversible reduction [252]. The 17-electron paramagnetic radical anion produced, $[\mathrm{CpTi}(\eta^7\text{-}\mathrm{C_7H_7})]^{-\cdot}$, was fully characterized by ESR and the magnetic parameters were determined by studies on liquid and frozen solutions. The UV–VIS spectra of both the neutral compound and radical anion were measured and interpreted according to a molecular orbital scheme. The structure of the radical anion was determined by proton electron nuclear double resonance spectroscopy (ENDOR) at 30 and 100 K whereby it was shown that the geometry of the parent neutral molecule was preserved upon one-electron reduction.

Electrolysis in the cavity of the ESR spectrometer was used to study in situ the species generated by the electroreduction of Cp_2TiX_2 (where X = Cl, Br, and I) in THF medium [253]. Careful analysis of the spectra showed that the only species formed were the respective Ti(III) solvated monohalides. It was concluded that the radical anion $[Cp_2TiX_2]^{-}$ formed upon the electron addition by electrolytic reduction was rapidly followed by halide cleavage, therefore it was not detectable as such by ESR. The role of residual water present in the purified THF is discussed.

(iii) Electrochemical synthesis and electron transfer-induced reactions

The electroxidation of a "sacrificial" cobalt anode in the undivided cell in the presence of C_5H_4R (where R = H, Et, i-Pr and Ph) and phenylacetylene in wet MeCN medium (0.5 v/v % H_2O) results in cyclopentadienyl cobalt tetraphenylbutadiene complexes, $[(\eta^5\text{-}C_5H_4R)Co\{\eta^4\text{-}PhHC{=}C(Ph)C(Ph){=}CPhH\}]$ [254].

The electrochemical oxidation of Cp_2Fe in the presence of $(EtO)_2PHS$ in MeCN solution results in thiophosphorylation of ferrocene with formation of $CpFeC_5H_4P(S)(OEt)_2$ (yield 11%) [255].

A series of four pseudo-triple-decker complexes $[(\eta^5\text{-}C_5R_5)_2M_2(\eta\text{-}C_8H_8)]$ (M = Co or Rh, R = H or Me) undergoes a chemically reversible two-electron oxidation [256]. The neutral complexes have the two metals on either side of a tub-shaped cyclo-octatetraene bridging ligand, whereas the dication have a twisted bridging C_8 ring which has two planar C_4 fragments. The two dicobalt complexes $Cp_2Co_2(\mu\text{-}C_8H_8)$ and $Cp^*_2Co_2$ $(\mu\text{-}C_8H_8)$ display quasi-reversible couples with $E^0 = +0.10$ V (SCE), $k_e > 2 \times 10^{-2}$ cm s^{-1} and $E^0 = -0.22$ V, $k_e = 4.6 \times 10^{-3}$ cm s^{-1}, respectively, in CH_2Cl_2. This conclusion is based on the data from CV, controlled potential coulometry, d.c. polarography and rotating ring–disc voltammetry experiments. Similar studies on the dirhodium complex $Cp_2Rh_2(\mu\text{-}C_8H_8)$ (**I**) show a more complex voltammetric behaviour. The oxidation wave for $\mathbf{I}^0/\mathbf{I}^{2+}$ redox couple is over 0.5 V positive of the reduction wave for $\mathbf{I}^{2+}/\mathbf{I}^0$ with CV peak potentials of ca. +0.43 V for the former and −0.11 V for the latter. This couple is described by a square scheme in which the electron-transfer reactions are experimentally separable from the tub ⇄ twist isomerizations. A rate of ca. 2 s^{-1} was measured for the twist → tub isomerization by CV, double potential step chronocoulonometry and ring–disc voltammetry. The slower isomerization of the ruthenium complex is consistent with larger rearrangement energies for ruthenium–olefin bonds as compared with cobalt–olefin bonds. The two-electron oxidation wave of **I** separated into two one-electron waves, the first being reversible, in low-temperature CV experiments in CH_2Cl_2. When combined with fast-scan CV on the reduction of $\mathbf{I}^{2+}$, these experiments show that the chemically reversible couple for tub-**I** $-2e^- \rightleftarrows$ twist-$\mathbf{I}^{2+}$ proceeds in both directions via EEC mechanisms. This result is compared with other two-electron transfers with associated geometric changes.

Oxidation of the pseudo-triple-decker complex $[Cp_2Ru_2(\mu\text{-cyclo-}C_8H_8)]$ (**II**) proceeds by a two-electron process at ambient temperatures to give a stable dication $[Cp_2Ru_2(\mu\text{-cyclo-}C_8H_8)]^{2+}$ ($\mathbf{II}^{2+}$) [257]. Whereas the bridging C_8H_8 moeity of **II** is a cyclo-octatetraene ring, the C_8H_8 group in $\mathbf{II}^{2+}$ is an open chain, so that the dication is a flyover complex. Insertion of both metal atoms into a C–C bond of the cyclo-octatetraene is thus observed as a consequence of the redox process. The flyover dication is efficiently reduced back to the original complex **II**. Thus, **II** and $\mathbf{II}^{2+}$ form a chemically reversible couple in which two-electron transfer leads to insertion and de-insertion of two metal atom into C–C bond. The overall process is similar to those suggested regarding the metal-catalyzed cyclo-oligomerization of alkynes. The mechanism of the reaction was studied by means of CV, bulk coulometry and other electrochemical methods. At low temperatures, the two-electron oxidation wave of **II** becomes a one-electron wave owing to the stability of the monocation of **II**. At higher temperatures, $\mathbf{II}^+$ isomerizes to the flyover monocation, which is then oxidized to **II**. The lifetime of the $\mathbf{II}^+$ monocation is ca. 50 ms at 15°C. The overall mechanism for the reaction $\mathbf{II} \rightleftarrows \mathbf{II}^{2+} + 2e^-$ appears to follow an ECE–EEC route.

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