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The Electrochemistry of the π-Complexes and Organometallic Compounds of Transition Metals

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The results of electrochemical studies on the oxidation-reduction reactions of the π-complexes and organometallic compounds of transition metals are surveyed and described systematically. They are compared with other physicochemical properties of compounds of this class.
The bibliography includes 272 references.

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I. INTRODUCTION

The application of electrochemical methods (classical polarography, potentiometry, voltamperometry, chronopotentiometry, etc.) in the study of the oxidation-reduction reactions of the π-complexes and organometallic compounds of transition metals yields quantitative information about one of the most important properties of these compounds—their capacity to give up and accept electrons. The undoubted advantage of electrochemical methods is that they make it possible to investigate the distribution of electron density in the molecule and the relative positions of the highest occupied and lowest vacant orbitals for a number of compounds with similar structures. Such information is important for the complicated molecules of the π-complexes and organometallic compounds of transition metals with their unusual type of bonding, for which quantum-chemical calculations are still very laborious and require considerable computer time. It is useful to survey data obtained in electrochemical studies on compounds of this class, since the above properties of the complexes may be of interest for many electrochemists and chemists working on organometallic compounds. The results of the electrochemical study of the π-complexes are particularly significant for the chemistry of these compounds, since they characterise the state and behaviour of the molecules in solutions, i.e. under the conditions where the majority of chemical reactions are carried out.

The results of electrochemical studies are grouped in the present review in terms of types of complexes investigated, since the electrochemical reactions of complexes of the same type as a rule proceed via the same mechanism. Particular attention has been devoted to the problem of the location of the electronic changes in the electrochemical reactions of the complexes. Depending on the relative contribution of the ligand molecular orbital and the metal atomic orbital to the molecular orbital of the complex, it is useful to distinguish three types of location of the electronic changes in the π-complexes and organometallic compounds of transition metals: (1) in the molecular orbital of the complex to which the atomic orbital of the metal makes the main contribution; (2) in the molecular orbital of the complex to which the molecular orbital of the ligand makes the main contribution; (3) in the antibonding orbital of the localised metal–ligand σ-bond. The principal procedures used to solve the problem of the location of the electronic changes in the complexes have already been formulated in a review [1]. In many cases the properties of charged species (radical-cations and radical-anions), formed as a result of the electrochemical reactions of the complexes, have also been discussed.

Brief information concerning the electrochemical behaviour of individual representatives of the π-complexes and organometallic compounds of transition metals may be found in a number of reviews [2-4]. However, a full discussion of studies on the electrochemistry of such π-complexes and organometallic compounds has not so far been published. The present review does not include the results of electrochemical studies on the coordination compounds of transition metals and transition metal complexes with donor–acceptor ligands without at least one metal–carbon bond [for example $M(PR_3)_n$]; however, in these cases, references are given wherever necessary to the most important studies in this field. The review covers the literature up to 1975 inclusive.

II. ELECTROCHEMICAL BEHAVIOUR OF SANDWICH COMPLEXES

A characteristic feature of neutral complexes of this type is that the metal is enclosed in a stable hydrocarbon shell and that its direct contact with solvent molecules or the electrode is hindered.

1. Dicyclopentadienyl and Bisarene Complexes

Reactions involving a change in the formal oxidation state of the metal atom are characteristic of π-complexes of the sandwich type (dicyclopentadienyl and bisarene complexes). The neutral compounds $(\pi\text{-}C_5H_5)_2M$ and $(\pi\text{-}C_6H_6)_2M$ as a rule undergo reversible one-electron oxidation at the electrode with formation of the corresponding cations $[(\pi\text{-}C_5H_5)_2M]^+$ and $[(\pi\text{-}C_6H_6)_2M]^+$. These reactions have been investigated in greatest detail in relation to dicyclo-

pentadienyl compounds and, particularly, ferrocene†. The ferrocene–ferrocenium cation pair is one of the most reversible oxidation-reduction systems under homogeneous conditions. Electron exchange between the oxidised and reduced forms in this system is of the outer-sphere type and proceeds at a high rate, greatly exceeding the rate of electron exchange in rapidly exchanging systems such as, for example, $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$.[7] This means that[8,9], in the transition from the reduced to the oxidised form, there should be no significant changes in the coordination spheres and in the geometry of the complex. Indeed, X-ray diffraction studies have shown that the ferrocenium cation, like ferrocene itself, has a sandwich structure with analogous bond lengths and valence angles. Quantum-chemical calculations on ferrocene[10] and the ferrocenium cation[11,12] as well as experimental data obtained from the photoelectronic spectra of ferrocene[13,14], from magnetic susceptibility measurements[14], and from the ESR spectra of the ferrocenium cation[16,17] have shown that the highest occupied molecular orbital of ferrocene, from which an electron is removed on oxidation, is the weakly bound orbital of the e_{2g} type formed mainly by the $3d$ orbitals of iron (d_{xy}, $d_{x^2-y^2}$).

It has been shown by classical polarography at platinum[18–23] and dropping mercury electrodes[21–25] (in aprotic[22,23,26] and protic[21,25,27] media), chronopotentiometry[28–30], oscillographic and a.c. polarography[31–33], and potentiometry[34,35], using for each method standard criteria of the reversibility of the electrochemical reactions, that the electrode reactions involving the oxidation of ferrocene and the reduction of ferrocenium consist in the reversible transfer of a single electron‡. However, it has been observed that the electrode reaction of ferrocene in many organic solvents may be complicated by the subsequent chemical reaction (overall *EC* mechanism) due to the instability of the resulting ferrocenium cation in these solvents[37,39].

The electrochemical behaviour of heavier ferrocene analogues—ruthenocene and osmocene—differs by a number of characteristic features. Ruthenocene undergoes irreversible electrochemical oxidation at a platinum electrode[23,29,40] with abstraction of two electrons. The most probable product is $[(C_5H_5)_2Ru]^{2+}$; however, it has not been possible to isolate salts of this cation owing to their instability§. The oxidation of osmocene at a platinum electrode involves the stepwise abstraction of two electrons[23,29]. The electrochemically irreversible removal of the first electron leads to the formation of a singly-charged cation, which has been isolated in the form of the salt $(C_5H_5)_2OsBF_4$. The observed differences in the behaviour of ferrocene ruthenocene, and osmocene are probably caused by the differences in their electronic structures¶. In conformity with the higher Lewis basicity of ruthenocene and osmocene compared with ferrocene[23], the former two compounds give rise to waves at the dropping mercury electrode (DME) due to the reactions of these metallocenes with the mercury anode[23,41]†:

$$2(C_5H_5)_2M + Hg \rightleftarrows [(C_5H_5)_2M]_2Hg^{2+} + 2e \quad ;$$
$$M = Ru, Os .$$

The electronic changes at the metal atom take place also in the oxidation-reduction reactions of cobaltocene (d^9) and nickelocene (d^{10}). The reversible ($k_S = 0.98$ cm s^{-1})[43] one-electron oxidation of cobaltocene[25,43–45] and its derivatives[46,47] to the cobaltocenium cation proceeds very readily. Because of this, it is more convenient to employ as the depolariser in electrochemical studies the stable cobaltocenium cation rather than the neutral cobaltocene. The cation gives rise to a cathodic wave, whose half-wave potential $E_{1/2}$ coincides with $E_{1/2}$ for its anodic wave. It has been found that the bisindenylcobalt cation is reduced much more readily[44,48] than the cobaltocenium cation, as has been observed for bisindenyliron complexes[49].

The one-electron reversible oxidation of nickelocene in aprotic[50] and protic[21,51,52] media leads to the formation of the nickelocenium cation. It has been observed by voltamperometry that the cation undergoes further oxidation to $[(C_5H_5)_2Ni]^{2+}$, which reacts extremely readily with nucleophiles[53,54].

The available information about the electrochemical behaviour of the dicyclopentadienyl complexes of other metals is limited. It has been shown that[55,56] $[(C_5H_5)_2V]^{2+}$ combines with a single electron and is reversibly reduced to $[(C_5H_5)_2V]^+$, which has two unpaired electrons. Two reduction waves were obtained on the polarogram of $[(C_5H_5)_2Nb]^+$, while $[(C_5H_5)_2Ta]^{3+}$ does not undergo polarographic reduction. In an aqueous alcoholic medium, $[(C_5H_5)_2Rh]^+$ gives rise to a cathodic wave, while $[(C_5H_5)_2.Ir]^+$ is not reduced under these conditions[51,52]. The electrochemical reduction of the dicyclopentadienylvanadium complexes with chelating ligands L of different types has been investigated in greater detail. It has been shown[57–59] that the reduction at a mercury electrode proceeds via the *EC* mechanism:

$$[(C_5H_5)_2V^{IV}L]^+ + e \rightleftarrows [(C_5H_5)_2V^{III}L]^0 \quad ;$$
$$[(C_5H_5)_2V^{III}L]^0 \xrightarrow{k} [(C_5H_5)_2V^{III}] + L \quad .$$

The electrochemical behaviour of sandwich bisarene complexes has been studied in relation to bisbenzenechromium (d^6). It has been shown[26,60–62] that it is readily oxidised to the cation $[(\pi\text{-}C_6H_6)_2Cr]^+$ (d^5). The electrode reaction is reversible under all the conditions investigated (aprotic medium[26,44,60,63,64] or protic medium[61,62,65–73]). There is a possibility of further oxidation of $[(\pi\text{-}C_6H_6)_2Cr]^+$ at a platinum electrode[74]:

$$[(\pi\text{-}C_6H_6)_2Cr]^+ - 2e \rightarrow Cr^{3+} + 2C_6H_6 \quad .$$

† A brief description of the electrochemical properties of the ferrocene–ferrocenium cation system as well as other biscyclopentadienyl compounds can be found in a number of reviews on the chemistry of metallocenes[5,6].

‡ However, there is a brief communication[36], unsupported by sound evidence, concerning the equilibrium $[(C_5H_5)_2Fe]_2^+ \rightleftharpoons (C_5H_5)_2Fe + [(C_5H_5)_2Fe]^+$ and the electrochemical irreversibility of the $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ system.

§ The chemical oxidation of ruthenocene by $FeCl_3$ or Br_2 leads to the formation of the stable salts $[(C_5H_5)_2RuCl].FeCl_4$ and $[(C_5H_5)_2RuBr]Br_3$. The introduction of halogens into the inner coordination sphere apparently stabilises the +4 formal oxidation state of ruthenocene[23].

¶ It has been stated[13] that the ionisation energies of the highest occupied orbitals of ruthenocene and osmocene are similar (7.25 and 7.23 eV) and that the energies of the orbitals of the e_{2g} and a_{1g} types in ruthenocene are much smaller (0.18 eV) than in ferrocene (0.35 eV). The highest occupied orbital in osmocene is apparently the a_{1g} orbital (and not e_{2g} as in ferrocene).

† It was suggested initially[42] that ruthenocene and osmocene are oxidised to the corresponding cations at the DME.

Polarograms of $[(\pi\text{-}C_6H_6)_2Cr]^+$ at the dropping mercury electrode in aqueous solutions frequently exhibit adsorption prewaves associated with the low solubility of the reduced form of the complex, namely $(C_6H_6)_2Cr$.[66,70-73] Measurements of the electrocapillary curves for the cation $[(\pi\text{-}C_6H_6)_2Cr]^+$ showed that the reduction proceeds in the adsorbed layer[71]. The area occupied by a single cation $[(C_2H_5C_6H_5)_2Cr]^+$ is 19.2 Å^2.[72] The diffusion coefficients of $[(C_6H_6)_2Cr]^+I^-$ have been measured in various media[44,61]. The differences between the half-wave potentials $E_{1/2}$ for the reduction of two structurally similar non-coordinated ligands (C_6H_6 and $C_6H_5-C_6H_5$) and their complexes with a chromium atom have been used to estimate the relative contribution of the atomic orbital of the metal and the molecular orbitals of the ligands to the molecular orbital of the bisarene complex, where electronic changes occur during the oxidation-reduction reaction[65]. The coefficient C_2^2 for the mixing of the atomic orbital of the metal and the molecular orbital of the ligand in the molecular orbital of the complex in which electronic changes take place during the oxidation-reduction process was calculated from the formula

$$(E^1_{1/2} - E^2_{1/2})_{\text{complex}} = C_2^2 (E^2_{1/2} - E^1_{1/2})_{\text{ligand}} .$$

It was found to be 0.15, which implies that the contribution of the ligand orbital to the molecular orbital of the complex where electronic changes take place during the oxidation of bisbenzenechromium is not more than 15% and this orbital is therefore mainly the atomic orbital of chromium.

The electrochemical properties of the bisarene complexes of other Group VIB metals have been inadequately investigated owing to their low stability. It has been noted that the reversible oxidation of $(\pi\text{-}C_6H_6)_2Mo$ proceeds with somewhat greater difficulty ($E_{1/2} = -0.71$ V) than that of $(\pi\text{-}C_6H_6)_2Cr$ ($E_{1/2} = -0.80$ V).[62] Although the available data are clearly insufficient, they nevertheless indicate that the abstraction of an electron from sandwich compounds of transition metals becomes more difficult on going from downwards in isostructural and isoelectronic series of the Periodic System.

It has been shown that the bisareneiron complexes, which exist in the form of dications, and their heteroanalogue bisthiopheniron are reduced in two stages[75]:

$$[\pi\text{-}L_2Fe]^{2+} + e \rightleftarrows [\pi\text{-}L_2Fe]^+ \rightarrow [\pi\text{-}L_2Fe] .$$

(L = tetramethylthiophen, mesitylene, and hexamethylbenzene).

Sandwich compounds with two different ligands possess electrochemical properties similar to those of their homoligand analogues. Reversible one-electron reactions at the electrode, proceeding with a change in electron density mainly in the metal atom, are also characteristic of these substances. A study of the polarographic behaviour of the cations $[\pi\text{-}C_5H_5Fe\text{-}\pi\text{-arene}]^+$ (arene = C_6H_6, biphenyl, naphthalene, anthracene, or phenanthrene) in an aprotic medium has shown[76,78] that the product of the reversible one-electron reduction is a neutral complex of formally univalent iron. The complexes of other metals have been little investigated. It is known only that the reduction of $[\pi\text{-}C_5H_5CrC_7H_7]^+$ in an aprotic medium also proceeds reversibly with addition of one electron[79], while the reversible one-electron oxidation of $\pi\text{-}C_5H_5VC_7H_7\text{-}\pi$ leads to the formation of the unstable cation $[\pi\text{-}C_5H_5.VC_7H_7]^+$.[80,81]

2. Sandwich π-Complexes and Their Cations as Standard Oxidation-reduction Systems

The $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ and $(C_5H_5)_2Co/[(C_5H_5)_2Co]^+$ systems have been suggested[82-87] and widely used (see the relevant references in the papers by Duschek and Gutmann[88] and Coetzee and Campion[89]) as standards to which the potentials measured in various media are referred. Their use as standard systems is based on Strehlow's hypothesis that the free energies of solvation of the above metallocenes and their cations are the same in different solvents. The above redox pairs have considerable advantages over familiar systems such as Rb/Rb^+ and Cs/Cs^+. Metallocenium cations are even larger than heavy alkali metal ions and the charged atom is located between two cyclopentadienyl rings, which hinders their solvation. However, subsequent studied showed[31,38,89] that the wide-scale employment of the $(C_5H_5)_2Fe/[(C_5H_5)_2.Fe]^+$ system as a standard is hindered by a number of limitations. It has been found that, owing to the specific interaction of $[(C_5H_5)_2Fe]^+$ with water, the hypothesis that $\Delta G_{(C_5H_5)_2Fe} = \Delta G_{(C_5H_5)_2Fe^+}$ does not hold in water and water-organic solvent mixtures as well as formamide. Furthermore, owing to the instability of $[(C_5H_5)_2Fe]^+$ in organic solvents, the $(C_5H_5)_2Fe/[(C_5H_5)_2Fe]^+$ system does not yield satisfactory results in potentiometric measurements in the majority of organic solvents. Thus the ferrocene–ferrocenium cation system is not an ideal standard system and its employment is possible only in relatively similar organic solvents in polarographic and voltamperometric measurements. The $(C_5H_5)_2Co/[(C_5H_5)_2.Co]^+$ system is probably likewise not ideal owing to its negative standard potential (for example, -0.98 V in acetonitrile). According to Gutmann and coworkers[90,91] the larger radius of $[(C_6H_6)_2Cr]^+$ compared with that of $[(C_5H_5)_2M]^+$ and the absence of specific interactions with water make the $(C_6H_6)_2Cr/[(C_6H_6)_2Cr]^+$ system more promising for these purposes than the two previous ones.

3. An Electrode Reversible with Respect to the Ferrocenium Cation

The high rate of electron exchange between the oxidised and reduced forms of the ferrocene–ferrocenium cation system as well as the virtual insolubility of ferrocene and its derivatives in aqueous solutions made it possible to devise an electrode reversible with respect to ferrocenium cations[92] derived from both unsubstituted ferrocene and its derivatives[93]. In the study of the properties of the ferrocene–ferrocenium electrode, the following galvanic cells were used:

$$Pt \mid \underline{Fe\,(C_5H_5)\,(C_5H_4R)},\ Fe\,(C_5H_4R)\,(C_5H_5)^+X^- \mid \underline{KCl},\ \underline{Hg_2Cl_2} \mid Hg.$$

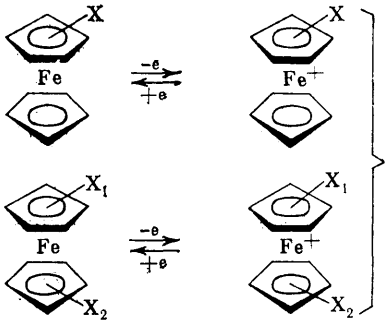
The ferrocene–ferrocenium electrode has been employed to investigate the properties of the ferrocenium cation in solutions: thermodynamic stability in aqueous solutions[94], hydrolytic decomposition[95], complex formation[96,97], and determination of the heat of hydration[98,99].

A perchlorate electrode[100], retaining the perchlorate response in solutions containing oxidants and reductants, has been devised on the basis of alkylferrocenes and the corresponding alkylferrocenium perchlorates.

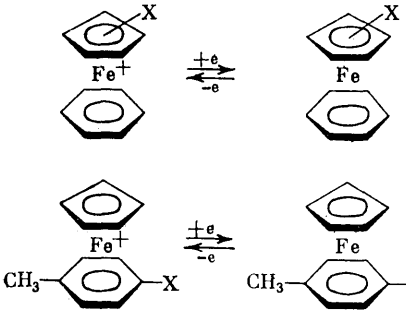
4. The Electronic Effects of Substituents in the Oxidation-reduction Reactions of π-Complexes of the Sandwich Type

Electrochemical methods have been used successfully to investigate the nature of the electronic influence of substituents on the reaction centre (the transition metal atom) in oxidation-reduction reactions [29,34,35,101-108]. This problem has been investigated in greatest detail in the following reaction series: monosubstituted ferrocenes [108], heteroannular disubstituted ferrocenes [108], arenecyclopentadienyliron cations with substituents in the arene or cyclopentadienyl ring [76], and bisbenzenechromium derivatives [109]. In all cases, systematic correlation analysis with different sets of substituent constants σ showed that the best linear relation is observed when Taft's σ_π^0 constants are used. Furthermore, the additivity of the influence of substituents, located in different rings of the molecule, on the oxidation potential of the metal atom was demonstrated for heteroannular disubstituted ferrocenes [108] and alkyl derivatives of bisbenzene chromium [109].

The results obtained led to the hypothesis that the nature of the influence of substituents in the above reaction series‡ differs from the influence of substituents in classical aromatic systems by the fact that there is no direct polar conjugation of the substituent with the reaction centre and that mainly the overall inductive component of the total polar influence of substituents is transmitted to both the metal atom and to the other ring. If the substituent is separated from the ferrocenyl nucleus by a methylene group (π-C_5H_5Fe–π-C_5H_4–CH_2–X), preventing the conjugation of X with the five-membered ring, a satisfactory linear relation is observed between E_f^0 and the inductive constants σ_i of the corresponding substituents. The observed relation has been used successfully to determine the σ_i for metallocenyl groups and other polyatomic groups [X = π-$C_5H_5FeC_5H_4$, π-$C_5H_5Fe^+$–π-C_5H_4, π-C_5H_5Ru–π-C_5H_4, π-$C_5H_4Mn(CO)_3$, or π-$C_6H_5Cr(CO)_3$] [1§].



$E_f^0 = (+0.50\sigma_n^0 - 0.272)$v;



$E_{1/2} = (+0.52\sigma_n^0 - 1.39)$v;

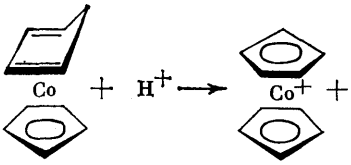
$E_{1/2} = (+0.515\sigma_n^0 - 1.42)$v.

5. Electrochemical Properties of Biferrocenyls

The electrochemical oxidation of biferrocenyl (π-C_5H_5Fe–π-C_5H_4)$_2$ and biferrocenylene (π-C_5H_4Fe–π-C_5H_4)$_2$ proceeds in two one-electron stages [30,113-116]. The first oxidation stage is reversible [30] and leads to a mixed valence Fe(III)–Fe(II) compound [117]. The electron transfer reaction Fe(II)*–Fe(III) ⇌ Fe(III)*–Fe(II) takes place in the resulting monocation between the oxidised and neutral ferrocenyl nuclei [114,115]. The second electron is apparently abstracted irreversibly [30], which corresponds to the oxidation of the second ferrocenyl nucleus with formation of the Fe(III)–Fe(III) dication. The introduction of a bridge group between the two ferrocenyl nuclei of biferrocenyl and biferrocenylene leads to an appreciable decrease of the difference between the potentials of the first and second oxidation stages. When X = $-CH_2-CH_2-$, $-Hg-$, $-(CH_3)_2C-C(CH_3)_2-$, or $-CH{=}CHC_6H_4CH{=}CH-$, biferrocenyl is oxidised in a single two-electron stage [114]. When X = $-C{\equiv}C-$, the oxidation proceeds in two stages with similar values of $E_{1/2}$. [118] It has been shown that compounds with metal atoms in different oxidation states can be formed when π-arenebis-(π-cyclopentadienyliron) dications are reduced at the dropping mercury electrode [119].

6. Electrochemical Reduction of Neutral π-Complexes of the Sandwich Type

Together with oxidation, electrochemical reduction reactions have been observed for neutral metallocenes (cobaltocene and nickelocene) [22]. In an aprotic medium (1,2-dimethoxyethane) [43] or in an alkaline medium at pH > 11, [47] cobaltocene undergoes reversible electrochemical reduction (k_S = 0.3 cm s^{-1}, $E_{1/2}$ = −1.89 V) (n = 1) to the previously unknown anion (π-$C_5H_5)_2Co^-$ containing the cobalt atom in the formal +1 oxidation state. In a more acidic medium (pH < 8) or acetonitrile, the anion formed reacts with a proton of the solvent, forming π-C_5H_5Co–π-C_5H_6. [120] A decrease of pH to 0–1 results in an increase of the height of the reduction wave owing to the catalytic evolution of hydrogen [120]:



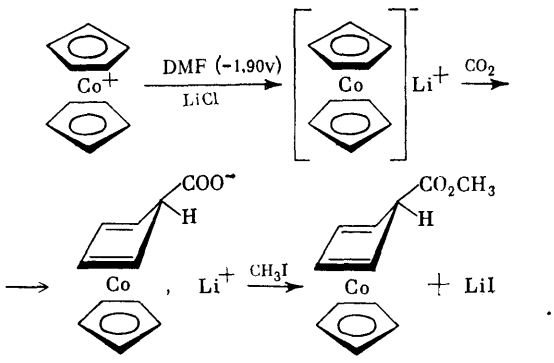
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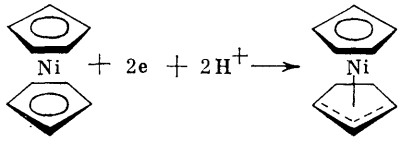
‡ A similar type of influence of substituents has been found in "non-electrochemical" reaction series [110] and reflects a general property of the metal–π-ligand bond, namely its ability to transmit mainly the inductive component of the total polar influence of substituents in the direction of the metal atom and other ligands.

§ The oxidation-reduction potentials of the ferrocene–ferrocenium cation system have been correlated with other physicochemical parameters of ferrocene derivatives (absorption maxima in ultraviolet spectra [111], S_N1 solvolysis rate constants [112], etc.

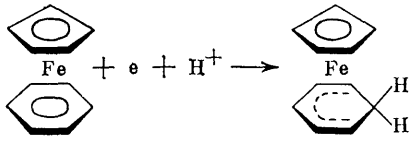
The high reactivity of $(\pi\text{-}C_5H_5)_2Co^-$ has been used in electrochemical syntheses [121]:



The anion $[(C_5H_5)_2Co]^-$ completes the series of cobalt complex $[(C_5H_5)_2Co]^+$ (d^8), $(C_5H_5)_2Co$ (d^9), and $[(C_5H_5)_2Co]^-$ (d^{10}) isoelectronic with the analogous nickel compounds: $[(C_5H_5)_2Ni]^{2+}$ (d^8), $[(C_5H_5)_2Ni]^+$ (d^9), and $(C_5H_5)_2Ni$ (d^{10}). A cathodic wave is also observed on the polarogram of neutral nickelocene. By analogy with chemical reduction, it is suggested [22] that in this case the reduction proceeds via the ligand in accordance with the following mechanism:



A reaction via the ligand has also been suggested in the reduction of neutral $\pi\text{-}C_5H_5Fe\text{-}\pi\text{-}C_6H_6$: [76]



7. Electrochemical Properties of Dicarbollyl π-Complexes

Like the dicyclopentadienyl compounds, the dicarbollyl complexes of transition metals, having the general formulae $(\pi\text{-}B_9C_2H_{11})_2M$ and $(\pi\text{-}B_9C_2H_{11})M(\pi\text{-}C_5H_5)$ [122] and the sandwich structure, undergo oxidation-reduction reactions, which lead to a change in the formal oxidation state of the metal atom. The study of the electrochemical behaviour of the dicarbollyl complexes of iron [123], cobalt [123-125], nickel [53,123,124,126,127], palladium [126,128], gold, and copper [128] showed that, in contrast to the π-cyclopentadienyl ligand, the π-dicarbollyl ligand stabilises the metal in both the highest and lowest oxidation states. Thus a series of electrochemically reversible one-electron transitions have been observed for the dicarbollyl complexes of cobalt, nickel, and palladium:

$$Co^{IV} \underset{+1.57\ V}{\rightleftharpoons} Co^{III} \underset{-1.36\ V}{\rightleftharpoons} Co^{II} \underset{-2.24\ V}{\rightleftharpoons} Co^{I} \quad ;$$

$$Ni^{IV} \underset{+0.18\ V}{\rightleftharpoons} Ni^{III} \underset{-0.56\ V}{\rightleftharpoons} Ni^{II} \underset{-2.10\ V}{\rightleftharpoons} Ni^{I} \quad ;$$

$$Pd^{IV} \underset{-0.47\ V}{\rightleftharpoons} Pd^{III} \underset{-0.71\ V}{\rightleftharpoons} Pd^{II} \quad .$$

It is interesting that isomeric dicarbollyl complexes, differing in the positions of the carbon atoms in the plane with the metal atom, have half-wave potentials $E_{1/2}$ differing by a very large amount (up to 0.5 V).

As for the ferrocene–ferrocenium cation system, the rate constants for electron transfer between the oxidised and reduced forms, namely $[(B_9C_2H_{11})_2Fe]^{2-}$ and $[(B_9C_2H_{11}).Fe(C_5H_5)]^-$, are high [129]. Owing to the large bulk of the dicarbollyl ligand, an arrangement of molecules in the transition states of these compounds of the "sitting on top" type is unlikely. One can therefore assume that, in both dicarbollyl complexes and in the ferrocene–ferrocenium system, the molecules in the transition state are arranged "side by side". It is useful to express the data described in Section II in terms of a scheme (see Table below) including only electrochemically reversible oxidation-reduction systems.

III. ELECTROCHEMICAL REACTIONS OF THE FUNCTIONAL GROUPS OF THE LIGAND BOUND IN THE π-COMPLEX

Apart from the electrochemical reactions involving the metal atom, fairly numerous reactions with participation of the functional groups of the ligand bound in the π-complex are known. The study of these reactions proved fruitful from the standpoint of the quantitative estimation of the electronic influence of metallocenes as substituents and in the study of the problem of the influence of coordination on the reactivity of ligands bound in π-complexes.

The numbers of electrons around the metal atom.

16e		17e		18e		19e		20e
$[CpVC_7H_7]^+$	$\underset{}{\overset{+0.18V}{\rightleftharpoons}}$	$CpVC_7H_7$						
		$[CpCrC_7H_7]$	$\underset{}{\overset{-0.70V}{\rightleftharpoons}}$	$CpCrC_7H_7$				
		$[(C_6H_6)_2Cr]^+$	$\underset{}{\overset{-0.80V}{\rightleftharpoons}}$	$(C_6H_6)_2Cr$				
		$[Cp_2Fe]^+$	$\underset{}{\overset{+0.31V}{\rightleftharpoons}}$	Cp_2Fe				
				$[CpFeC_6H_6]^+$	$\underset{}{\overset{-1.46V}{\rightleftharpoons}}$	$CpFeC_6H_6$		
				$[(C_6H_6)_2Fe]^{2+}$	$\underset{}{\overset{-0.30V}{\rightleftharpoons}}$	$[(C_6H_6)_2Fe]^+$		
				$[Cp_2Co]^+$	$\underset{}{\overset{-0.80V}{\rightleftharpoons}}$	Cp_2Co	$\underset{}{\overset{-1.90V}{\rightleftharpoons}}$	$[Cp_2Co]^-$
				$[Cp_2Ni]^{2+}$	$\underset{}{\overset{+0.75V}{\rightleftharpoons}}$	$[Cp_2Ni]^+$	$\underset{}{\overset{+0.01V}{\rightleftharpoons}}$	Cp_2Ni

Cp = cyclopentadienyl

The electrochemical reactions of the functional groups in the coordinated ligand proceed mainly via mechanisms similar to those which have been established for the analogous substituents in aromatic rings. In accordance with its electronic properties, the metal-containing group alters only the potential of the electrochemical reaction of the substituent, which permits conclusions concerning the electronic effects of the metal-containing group. The polarographic reduction of acyl derivatives of π-complexes has been investigated in greatest detail. It has been demonstrated [130-132] that the mechanism of the polarographic reduction of the acetyl derivatives of ferrocene [$(\pi$-$C_5H_5)Mn(CO)_3$ and π-$C_6H_6Cr(CO)_3$] and benzene in a protic medium are identical. The results led to the conclusion that the ferrocenyl group is more electropositive than C_6H_5 and is close to pyrrole on the electron affinity scale, while $(CO)_3MnC_5H_4$- and $(CO)_3CrC_6H_5$- are more electronegative than phenyl. The results of the polarographic reduction of $(CO)_3Cr(C_6H_5COCH_3)$ in an aprotic medium lead to the analogous conclusion about the electronic properties of the $C_6H_5Cr(CO)_3$ groups [133].

The σ constants (σ_p, σ_m, σ_p^0, and σ_m^0), characterising quantitatively the electronic influence of ferrocenyl as a substituent, have been calculated [134] on the basis of the correlation between the half-wave potentials $E_{1/2}$ for the reversible one-electron reduction of the C=C bond in the chalcones $C_5H_5FeC_5H_4CH{=}CHCOC_6H_4X$ (*m*, *p*), $C_5H_5FeC_5H_4$. .$COCH{=}CHC_6H_4X$ (*m*, *p*), $C_6H_5CH{=}CHCOC_6H_4X$ (*m*, *p*), and $C_6H_5COCH{=}CHC_6H_4X$ (X = OCH_3, CH_3, F, Cl, Br, or $CNC_5H_4FeC_6H_5$). It was first shown [130,135-139] that ferrocenyl-containing chalcones are reduced in the same way as aromatic chalcones. The polarographic reduction of ferrocenyl aldehydes [139,140] and of nitrogen-containing derivatives of acetylferrocenes of the type $C_5H_5FeC_5H_4CR{=}NA$ [135] also proceed analogously to the reduction of the corresponding benzene derivatives. In conformity with the electron-donating properties of the ferrocenyl group, the half-wave potentials $E_{1/2}$ for these derivatives are displaced towards negative potentials.

It has been established for the quinone complexes of rhodium and iridium [141] that the polarographic reduction of the coordinated quinones proceeds with greater difficulty than that of the free quinones. The half-wave potentials $E_{1/2}$ for the first reversible one-electron quinone waves are displaced towards more negative values by 0.9, 1.1, 0.6, and 0.3 V as a result of the coordination to the RhC_5H_5-π, IrC_5H_5-π, RhC_9H_7-π-indenyl, and Rh(acac) groups respectively. The ligands combined with the metal atom have been arranged in a series in terms of their donating capacity on the basis of the results obtained: π-$C_5H_5 > \pi$-$C_9H_7 >$ acac.

In a few instances, the application of electrochemical methods made it possible to demonstrate the formation of previously unknown functional derivatives of π-complexes. Thus the use of cyclic voltamperometry and of a rotating disc electrode with a ring showed [132-144] that the reduction of $C_5H_5FeC_5H_4NO_2$ at an amalgamated gold electrode in an alkaline medium proceeds via the intermediate formation of radical-anions. The reduction of the radical anion leads to the formation of previously unknown ferrocenylhydroxylamine:

$$C_5H_5FeC_5H_4NO_2 + e \rightleftarrows C_5H_5FeC_5H_4NO_2^{\cdot-} \quad ;$$

$$C_5H_5FeC_5H_4NO^{\cdot-} + 3e + 3H_2O \rightarrow C_5H_5FeC_5H_4NHOH + 4OH^- \quad .$$

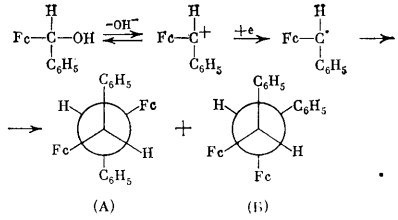
In contrast to C_6H_5NHOH, ferrocenylhydroxylamine is extremely unstable and disappears as a result of a disproportionation reaction:

$$C_5H_5FeC_5H_4NHOH + [C_5H_5FeC_5H_4NH_2OH]^+ \rightarrow$$

$$\rightarrow C_5H_5FeC_5H_4NH_2 + Fe^{2+} + C_5H_5^{\cdot} + C_5H_4NO^- + H_2O + H^+ \quad .$$

Electrochemical methods are used fairly widely for the generation of radical-anions. It has been shown that the electrolysis of a number of ferrocene derivatives (benzoyl, *p*-nitrophenyl, cyano-, nitro-, and other derivatives) [145] and of the benzoyl derivative of cyclopentadienylmanganese tricarbonyl [146] leads to radical-anions, which give rise to ESR signals. The study of the distribution of the unpaired spin density in these species showed [145] that, when both the C_6H_5 group and the ferrocenyl group are present in the same molecule, the unpaired spin density is delocalised to a larger extent over the C_6H_5 group than over the ferrocenyl group.

The electrochemical reduction of a number of other ferrocene derivatives has also been investigated [147,148]. Thus electrolysis of ferrocenylmethanol, which is involved in an equilibrium with the ferrocenylcarbonium ion in an acid medium, proceeds via a one-electron mechanism with formation of a free radical (Fc = ferrocenyl):



The radical then dimerises with formation of the stereoisomers (A) and (B). [147] In this section, it is also appropriate to quote data on the polarographic studies of the mercury derivatives R_2Hg and RHgX [R = ferrocenyl, $(CO)_3MnC_5H_4$, or $(CO)_3ReC_5H_4$], which are reduced similarly to the compounds R_2^1Hg and R'HgX (R' = alkyl or aryl) [149]:

$$\left.\begin{array}{l} R_2Hg + 2e \rightarrow Hg^0 + 2R^- \xrightarrow{+2H^+} 2RH\ (R = C_5H_5FeC_5H_4)\ ; \\ RHgX + e \rightarrow RHg^{\cdot} \\ RHg^{\cdot} + e \rightarrow Hg^0 + R^- \xrightarrow{H^+} RH \end{array}\right\} (R = C_5H_5FeC_5H_4-,\ \text{or}\ (CO)_5MC_5H_4;\ M = Mn \text{ or } Re)$$

A linear correlation is observed between $E_{1/2}$ and pK_a(RH): $E_{1/2} = (-0.07pK_a + 0.16)$ (V); $r = 0.966$. The pK_a values for ferrocene ($pK_a = 39$) and $(CO)_3MC_5H_5$ ($pK_a = 31$ for M = Mn and $pK_a = 30$ for M = Re) as CH acids were estimated from this relation [149-151].

IV. ELECTROCHEMICAL REACTIONS OF METAL CARBONYLS AND THEIR DERIVATIVES

The electrochemical behaviour of metal carbonyl complexes containing n-donor ligands bound in π- and σ-complexes is extremely varied, primarily due to the differences between their electronic structures.

1. Metal Carbonyls

In contrast to chemical reduction, which has been investigated in fair detail (see, for example, Kaska [152]), the electrochemistry of metal carbonyls has been inadequately studied. It has been shown [26] that in dimethoxyethane singly-charged metal carbonyls $M(CO)_n$ (M = Fe, $n = 5$; M = V, $n = 6$; M = Ni, $n = 4$) combine as a rule with one electron and the process is electrochemically irreversible. $Fe(CO)_5$ and $Ni(CO)_4$ form short-lived paramagnetic species giving rise to ESR signals; however, the nature of these species is obscure. In a protic medium ($C_2H_5OH-H_2O$), $Fe(CO_5)$ is reduced with addition

of two electrons and the dissociation of the M–CO bond[153]. As in the initial compound, in the product $Fe(CO)_4^{2-}$ an 18-electron shell is formed around the metal atom. The polarographic reduction of $M(CO)_6$ (M = Cr, Mo, or W) in aprotic solvents proceeds via the following irreversible electrochemical mechanism[26,154,155]:

$$M(CO)_6 + e \rightarrow [M(CO)_6]^{\mp} \xrightarrow{-CO} [M(CO)_5]^{\mp} \rightarrow \frac{1}{2}[M_2(CO)_{10}]^{2-} .$$

The one-electron reversible voltamperometric oxidation of $Cr(CO)_6$ at platinum and gold electrodes ($E_{a.p.}$ = +1.44 V relative to the Ag/Ag^+ electrode) leads to the formation of the 17-electron cation $Cr(CO)_6^+$, which gives rise to a broad signal in the ESR spectrum[154,156]. At higher anodic potentials, a further electron is removed with formation of the unstable species $Cr(CO)_6^{2+}$. The oxidation of $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$ is electrochemically irreversible and involves the abstraction of two electrons. Dinuclear carbonyls containing the M–M bond are reduced at dropping mercury[26,157,158] and platinum electrodes[159,160] with dissociation of the M–M bond and the formation of 18-electron anions of the metal carbonyls (see below for further details).

The reduction of trinuclear $Fe_3(CO)_{12}$ proceeds with addition of one electron[26]; the reaction products are unknown.

2. Metal Carbonyl Complexes with n-Donor Ligands

(a) Oxidation. Compounds having the general formula $L_nM(CO)_m$ (L = amines, phosphines, isonitriles, or carbenes¶ and M = Cr, Mo, or W) are oxidised at a platinum electrode in methylene chloride with the loss of one electron and the formation of the corresponding cations[161–164]; the process is electrochemically reversible. The cations $[Mn(CO)_6 - n(CNR)_n]^+$ and $[Cr(NO)_2(CNR)_5]^+$ are oxidised to the dications, which are capable of further oxidation[165–167]. The half-wave potentials $E_{1/2}$ depend on the electronic properties of the ligand L, the number of CO groups, and the nature of the metal atom. The successive weakening of the π-acceptor properties of L, accompanied by the corresponding increase of the σ-donor capacity, leads to a shift of $E_{1/2}$ towards lower positive potentials. A similar result is obtained when n in $[(RNC)_nM(CO)_{6-n}]$ is diminished, which is associated with the gradual substitution of the strong π-acceptor ligand CO by the less effective CNR. It has been shown for $Cr(CO)_5L$ (the L species are different phosphines) that there is a linear correlation between the values of $E_{1/2}$ for the oxidation of the complex and the ionisation potential of the free ligand L. It has been established[162] that the ease of abstraction of the electron from $[(RNC)_nM(CO)_{6-n}]$ diminishes in the sequence Cr > W > Mo.

The observed relations lead to the conclusion that both the atomic orbital of the metal and the molecular orbital of the ligand L contribute to the molecular orbital from which the electron is removed on oxidation. Studies on the ESR and Mössbauer spectra of the radical-cations generated on oxidation of the complexes CoL(CO)(NO), where L = o-phenanthroline or 2,2′-bipyridyl, in dimethoxyethane at a mercury electrode[168] have confirmed this view and have shown that the spin density is located in the molecular orbital to which predominantly s-type metal orbitals contribute together with the ligand orbitals. However, quantum-chemical calculations on molecules of the type $Cr(CO)_5L$ (L = NH_3, PH_3, or PMe_3) have shown, in contrast to electrochemical data, that the ligand orbitals do not contribute significantly to the highest occupied orbital of the complex, comprising mainly the $3d$(Cr), $2p$(C), and $2s$(O) orbitals. According to Lloyd et al.[163], this contradiction can be resolved if it is supposed that L has a long-range or indirect influence on the energy of the highest occupied orbital of the complex without a change in the relative contributions of the atomic orbitals.

The electrochemical oxidation of complexes with chelating diphosphine ligands, namely $M(CO)_2(DPE)_2$ and $M(CO)_2(DPM)_2$, where M = Mn, Cr, Mo, or W, DPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and DPM = $(C_6H_5)_2PCH_2P(C_6H_5)_2$, proceeds with the successive elimination of two electrons and the formation of cations and dications respectively; the stereochemistry of the electrochemical reactions has been investigated[169,170]. The available information concerning the oxidation of other complexes with n-donor ligands is limited. It has been shown, for example, that the oxidation of $M(CO)_3$(triarsine)† in a $C_2H_5OH-C_6H_6$ mixture at mercury and platinum electrodes proceeds with the elimination of two electrons and the formation of a dication[171]. In this section, it is also appropriate to mention the oxidation of the carbonyl hydride complexes $M(H)(CO)L_3$ (M = Rh or Ir and L = PPh_3).[172] The reversible oxidation of $Ir(H)(CO)L_3$ in acetonitrile at a platinum electrode leads to the formation of a fairly stable cation containing the metal in the unusual +2 oxidation state:

$$Ir(H)(CO)L_3 \rightleftarrows Ir(H)(CO)L_3^+ .$$

The oxidation of $Rh(H)(CO)L_3$ is irreversible. Owing to the instability of the Rh–H bond, the cation formed reacts further via the following mechanism:

$$Rh(H)(CO)L_3^+ \rightarrow M(CO)L_3^+ + {}^1/_2H_2 .$$

(b) Reduction. Octahedral chromium, molybdenum, and tungsten complexes $L_1M(CO)_5$ (L_1 = pyridine or quinoline) and $L_2M(CO)_4$ (L_2 = ethylenediamine or 2,2′-bipyridyl) and the tetrahedral cobalt and iron complexes $L_2Co(CO)(NO)$ and $L_2Fe(NO)_2$ (L_2 = o-phenanthroline or 2,2′-bipyridyl) are as a rule reduced in two electrochemically reversible one-electron stages with formation of radical-anions and dianions[60,168,173]. The reduction proceeds at less negative potentials than the reduction of the non-coordinated ligand L and in the case of the chromium, molybdenum, and tungsten complexes also at less negative potentials than the corresponding unsubstituted metal carbonyl. The radical-anions formed give rise to an ESR signal and exhibit an enhanced chemical stability compared with the radical-anions of the non-coordinated ligand. It has been concluded[168,173] on the basis of the similarity of the hyperfine splitting constants for the ESR spectra of the radical-anions of the complexes and the non-coordinated ligands that the electron occupies on reduction the antibonding π-orbital of the ligand L; the infrared spectra of the radical-anions showed that the addition of the electron does not lead to a change in the symmetry of the molecule. The absence of an ESR signal from the spectrum of the dianion showed that it exists in the singlet state. Analysis of the ESR, infrared, Mössbauer, and NMR spectra of the radical-anions and dianions led to a conclusion concerning the distribution of spin and charge densities in these species (for a more detailed treatment, see below).

¶ The M–C bond is present in carbenes.

† Triarsine = methylbis-(3-propyldimethyl)arsine.

The reduction of cobalt carbonyl nitrosyl complexes $Co(NO)(CO)L_{n-3}$ ($L = EPh_3$; E = P, As, or Sb) and iron carbonyl nitrosyl complexes $Fe(NO)_2(CO)_nL_{n-2}$ ($L = PPh_3$) (the formal degree of oxidation of the metal in the complexes is −1) in acetonitrile at the DME has been investigated[174-177]. Brief information concerning the electrochemical behaviour of other substituted carbonyl compounds can be found in a number of reports[26,60,179,180]. The reduction proceeds as a rule irreversibly and the reaction products have not been identified. The reduction of metal carbonyl compounds with an M—M bond and bridging phosphorus- and sulphur-containing ligands is discussed below.

3. Complexes Containing Hydrocarbon Ligands Bound in π-Complexes

(a) Complexes with two-electron ligands. The reduction reactions of the bipyramidal complexes (olefin)$Fe(CO)_4$ and carbonyl complexes with *n*-donor ligands (see the previous section) have much in common. The electrochemically reversible addition of one-electron to (olefin)$Fe(CO)_4$ leads to fairly stable radical-anions, where the unpaired electron is located in the antibonding π*-orbital of the olefin ligand[26,60,178]; the distribution of spin and charge densities in the radical-anions formed has been investigated by ESR, infrared spectroscopy, and Mössbauer spectroscopy (see below).

The cationic olefin complexes of platinum $[Pt(NH_3)_2.(RCH{=}CH_2)Cl]ClO_4$ (R = H, CH_3, CH_2OH, or C_6H_5) have been reduced at the dropping mercury electrode[181]. It was found that these complexes are reduced more readily than the initial amine complex $[Pt(NH_3)_3Cl]^+$.

(b) Complexes with three-electron π-allyl ligands. The electrochemical behaviour of π-allyl complexes $(\pi\text{-}C_3H_5MX)_2$ of platinum group metals, where the formal oxidation state of the metal is +2, is determined by the well known ease of reduction of these metal ions M^{2+} and of their chloride complexes. Pd^{2+} and Pt^{2+} ions ions are reduced even with metallic mercury without the application of a potential difference[182,183]. The study of the reduction of $(\pi\text{-}C_3H_5PdX)_2$ (X = halogen) at the DME showed[183-186] that these compounds react with the mercury of the electrode:

$$(\pi\text{-}C_3H_5PdX)_2 + Hg \rightarrow Pd^0 + 2C_3H_5HgX \quad .$$

The waves observed on the polarogram correspond to the reduction of C_3H_5HgX. The diffusional nature of the waves shows that the preceding chemical reaction of the π-allyl complexes of palladium with mercury proceeds so fast that its rate does not affect the electrode reduction of C_3H_5HgX. The results suggest that the coordination of Pd^{2+} to the π-allyl ligand has little influence on the capacity of Pd^{2+} for reduction.

The electrochemical reduction of $\pi\text{-}(C_3H_5M)(CO)_3X$ (M = Fe or Ru) leads to the dissociation of the M—X bond (see Section V). $\pi\text{-}C_3H_5Fe(CO)_2NO$ and $\pi\text{-}C_3H_5Co(CO)_3$, which do not contain π-bonds, behave differently. The addition of two electrons leads to the dissociation of the π-bond between the allyl ligand and the metal atom[187,188]:

$$\pi\text{-}C_3H_5Fe(CO)_2NO + 2e \rightarrow [Fe(CO)_2NO]^- + C_3H_5^- \xrightarrow{+H^+} CH_2{=}CH{-}CH_3 \quad ;$$

$$\pi\text{-}C_3H_5Co(CO)_3 + 2e \rightarrow Co(CO)_3^- + C_3H_5^- \xrightarrow{H^+} C_3H_6 \quad .$$

(c) Complexes with four-electron ligands. The polarographic reduction of $(\pi\text{-diene})Fe(CO)_3$ at the dropping mercury electrode in aprotic media proceeds via the successive addition of two electrons, as was observed for the free diene ligand[189]. The first electrochemically reversible stage leads to the formation of a radical-anion, which gives rise to an ESR signal in the case of complexes with cyclic dienes[190]. In view of the identity of the polarographic characteristics of $(\pi\text{-diene})Fe(CO)_3$ and the free dienes, it was concluded that the electronic changes occurring on reduction of the complexes are localised in the antibonding π*-orbital of the diene ligand.

(d) Complexes with five-electron ligands. The electrochemical properties of monocyclopentadienylmetal carbonyls have been inadequately investigated. It has been shown[26,60,149] that $\pi\text{-}C_5H_5M(CO)_3$ (M = Mn or Re) and some of their derivatives are reduced at the DME, but the number of electrons added and the reaction products are unknown. The complexes $\pi\text{-}C_5H_5V(CO)_4$, $\pi\text{-}C_5H_5Co(CO)_2$, $\pi\text{-}C_5H_5W(CO)_2NO$, and $\pi\text{-}C_5H_5NiNO$ are reduced with addition of one electron, but the formation of a short-lived anion has been demonstrated only for the last two compounds[191].

The addition of one electron to the cationic complexes $[\pi\text{-}C_5H_5Fe(CO)_2L]^+$ ($L = CO$ or PPh_3) apparently leads to the formation of the dimer $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, the reduction of which gives rise to the second wave on the polarograms[60].

The one-electron oxidation of cyclopentadienylmanganese and cyclopentadienylrhenium tricarbonyls at a platinum electrode proceeds with much greater difficulty than, for example, the reduction of ferrocene under analogous conditions; cyclopentadienylrhenium tricarbonyl is oxidised at more positive potentials than cyclopentadienylmanganese tricarbonyl[192]. The replacement of carbonyl groups by the more strongly electron-donating phosphine ligands leads to a significant cathodic shift of the oxidation potentials and to an increase of the stability of the cation formed[193]:

$$\pi\text{-}C_5H_5M(CO)_2L \underset{+e}{\overset{-e}{\rightleftarrows}} [\pi\text{-}C_5H_5M(CO)_2L]^+ (M{=}Mn \text{ or } Re;\ L{=}PR_3) \quad .$$

The cationic nitrosyl complexes $[\pi\text{-}C_5H_5Mn(NO)LL']^+$ (L and L′ are Lewis bases such as PR_3 and amines) are oxidised to the dications[194]. The change in $E_{1/2}$ reflects the change in the π-acceptor properties of the Lewis bases as ligands.

The polarographic behaviour of π-cyclopentadienylmetal complexes with chelating ligands has been investigated in greater detail. It has been found that π-cyclopentadienyldithiolenemetal complexes are as a rule reduced reversibly in dimethoxyethane (with the addition of one electron and the formation of radical-anions, which give rise to an ESR signal[26,60,179]. The half-wave potentials $E_{1/2}$ of $\pi\text{-}C_5H_5MS_2C_4F_6$ depend on the nature of the metal atom and increase in the sequence Fe < Co < Ni (from left to right in Mendeleev's Table) and in the cobalt subgroup Co < Rh < Ir (from above downwards (see also McCleverty[195]). The anionic complexes $[\pi\text{-}C_5H_5MS_4C_4(CN)_4]^-$ (M = Ti, Mo, or W) are oxidised to neutral species at a platinum electrode in CH_2Cl_2 solution[196].

A detailed study of π-cyclopentadienylnitrosyldithiolenemanganese complexes showed that those with 1,2-dithiolenes are capable of reversible oxidation and reduction to radical-cations and radical-anions respectively. The complexes of 1,1-dithiolenes are capable of one-electron reduction only, while dithiocarbamates and thioxanthates

are capable of one-electron oxidation [194,196-198]. The paramagnetic species have been characterised by their ESR spectra.

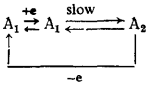
(e) Arenemetal carbonyl complexes. It follows from chemical data‡ that (π-arene)$Cr(CO)_3$ complexes are oxidised with greater difficulty than (π-arene)$_2$.Cr. Indeed, the complexes (π-C_6H_5X)$Cr(CO)_3$ are oxidised at a platinum electrode in CH_2Cl_2 in two electrochemically reversible stages at fairly considerable positive potentials [199,200]. The values of $E_{1/2}$ for the first waves are sensitive to the nature of the substituent in the benzene ring (X = alkyl or NR_2). A linear relation has been observed between $E_{1/2}$ for the first wave of (π-C_6H_5X)Cr.$(CO)_3$, on the one hand, and the $E_{1/2}$ and the ionisation potentials of the non-coordinated ligand C_6H_5X, on the other, the half-wave potentials $E_{1/2}$ of the complexes being less sensitive to structural changes in the arene bound in the complex than the $E_{1/2}$ of the free ligand. There is also a linear relation between $E_{1/2}$ for the first wave and the ionisation potentials of the complexes. The observed relations indicate the involvement of the orbitals of the arene ligand in the highest occupied molecular orbital from which the electron is removed on oxidation. The problem of the degree of involvement of the metal orbitals in this molecular orbital remains obscure [cf. the above discussion of the oxidation of $LM(CO)_5$].

The half-wave potential $E_{1/2}$ for the oxidation of the π-cycloheptatriene complex (π-C_7H_8)$Cr(CO)_3$ is close to $E_{1/2}$ for its isomer (π-$C_6H_5CH_3$)$Cr(CO)_3$. It has been found that the *exo*- and *endo*-isomers of $RC_7H_7Cr(CO)_3$ (R = Ph or CN) differ significantly (by approximately 70 mV) in their capacities for oxidation [200]. The reversible one-electron oxidation of (π-$C_6Me_{6-n}H$)$Cr(CO)_2$(PhC≡CPh) to the corresponding cations proceeds at potentials lower by 0.8 V than for (π-arene)$Cr(CO)_3$, which reflects the more pronounced σ-donor and weaker π-acceptor properties of the acetylene ligand compared with CO. [201]

The polarographic reduction of (π-C_6H_6)$Cr(CO)_3$ proceeds in a single two-electron stage with formation of a dianion [26,202]. The intermediate formation of the radical-anion has been demonstrated by electrolysis at a controlled potential. The polarograms of (π-arene)$Cr(CO)_3$ (arene = diphenyl or naphthalene) as well as those of the non-coordinated aromatic hydrocarbons show one-electron reversible waves corresponding to the reduction to the radical-anions. As in the reduction of metal carbonyl complexes with π-olefinic and n-donor ligands, the electron apparently occupies in this case the antibonding π^*-orbital of the aromatic hydrocarbon ligand. The observed shift of the $E_{1/2}$ for the complexes relative to the $E_{1/2}$ for the free ligands towards more positive potentials by 600–700 mV is consistent with the available data [199] showing a decrease of electron density in the aromatic ring on coordination to the $Cr(CO)_3$ group.

It has been noted that the reduction of the cationic arene complexes $[1,3,5\text{-}(CH_3)_3C_6H_3Mn(CO)_3]^+$ and the cycloheptatrienyl complexes $[\pi\text{-}C_7H_7Cr(CO)_3]^+$ and $[(\pi\text{-}C_7H_6OMe)Cr.(CO)_3]^+$ proceeds readily [26,200], but the nature of the process and the reaction products have not been investigated in detail.

(f) Complexes obtained on interaction of acetylenes with metal carbonyls. The complexes obtained when acetylenes react with metal carbonyls contain π-linked organic ligands of various types; cyclobutadiene, cyclopentadiene, quinone, tropone, and other ligands, containing as a rule several metal atoms and carbonyl groups. Many of these compounds undergo reversible electrochemical reduction at the dropping mercury electrode with formation of radical-anions and then dianions [190]. The stability of the radical-anions varies within wide limits. Studies of the individual radical-anions showed that, despite the electrochemical reversibility of the process demonstrated by triangular voltamperometry, the half-wave potentials $E_{1/2}$ for their oxidation do not agree with the half-wave potentials for the reduction of the initial complex. The electrochemical oxidation of the radical-anions nevertheless restores the initial state. The authors believe that the discrepancy between $E_{1/2}$(ox) and $E_{1/2}$(red) is due to the slow change in the structure of the radical-anion§:



The foregoing data are of interest from the standpoint of the investigation of the properties of organometallic radical-anions.

4. General Conclusions Concerning the Electrochemical Reactions of Metal Carbonyls and Their Derivatives

The results of electrochemical studies on the majority of metal carbonyl complexes with π-linked or n-donor ligands have shown that these undergo both oxidation and reduction reactions. The reduction processes have been investigated in greater detail. The reversible stepwise addition of two electrons leads to the formation of radical-anions and then dianions. The agreement of the hyperfine splitting constants for the radical-anions of the complexes and the non-coordinated ligands shows that the electron is located in the antibonding π^*-orbital of the ligand. The absence of splitting by the nitrogen of the NO group in the radical-anions $L_2Co(NO)CO$ and $L_2Fe(NO)_2$ (see subsection 2 above) shows that the spin density of the unpaired electrons belonging to L_2 is not transmitted via the metal atom to the other ligands. The infrared spectra of the radical-anions confirmed this conclusion and, together with the NMR spectra of the dianions, showed that a major proportion of the charge density in the radical-anion and the dianion is concentrated in the $M(CO)_n$ group. Thus, in contrast to organic compounds, the distribution of spin and charge densities in the radical-anions of the complexes may not be the same. While the spin density is concentrated at the ligand L, the charge density is largely concentrated at the metal atom and the carbonyl groups. The study of the Mössbauer spectra of the radical-anions of iron-containing complexes showed that charge transfer proceeds via σ-bonds [203].

It is noteworthy that, compared with their reduction, the electrochemical oxidation of the complexes has been inadequately investigated. There are virtually no data for the kinetics of the electrochemical processes.

V. ELECTROCHEMICAL REACTIONS OF COMPLEXES CONTAINING σ-BONDS

Together with the complexes examined in the previous sections, studies have been made on a large number of compounds containing σ-bonds of different types: M–M,

‡ See A.R. Siedle, J.Amer.Chem.Soc., 97, 5931 (1975).

§ The nature of the rearrangement is so far obscure.

M–halogen, and M–C. It has been shown that, as a rule, these compounds are reduced or oxidised with participation of the σ-bond, while π- and donor–acceptor bonds are electrochemically inactive.

1. METAL COMPLEXES WITH AN M–M σ-BOND

Compared with compounds containing M–X and M–C σ-bonds, complexes with an M–M bond have a wide variety of structures, as a result of which various types of electrochemical reactions are characteristic of these substances.

Electrochemical Reactions Involving the Dissociation of the M–M σ-Bond

(a) Homodimetallic compounds. Complexes of this type are reduced polarographically in a single irreversible two-electron stage with dissociation of the M–M σ-bond and formation of an 18-electron metal carbonyl anion [157,158,204,205]:

$$L_nM{-}ML_n + 2e \rightarrow 2[L_nM]^- \quad ;$$

$L_nM = C_5H_5M(CO)_3$, (M = Cr, Mo or W), $(CO)_5M$, (M = Mn or Re); $C_5H_5M(CO)_2$, (M = Fe or Ru), $(CO)_4Co$ or C_5H_5NiCO .

It has been shown [206] that the anions $M(CO)_5^-$ (M = Mn or Re) enter into the following chemical reaction under the conditions of electrolysis:

$$M(CO)_5^- + M_2(CO)_{10} \rightarrow [M_3(CO)_{14}]^- + CO \ .$$

The reduction of complexes of Group VI–VIII metals becomes more difficult on moving from above downwards in the Periodic Table. For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, this is satisfactorily consistent with the higher Re–Re bond energy (ΔH = 2.22 eV) compared with the Mn–Mn bond energy (ΔH = 0.96 eV). [207] It has been stated [157] that in the remaining compounds the bond energy also increases with increasing atomic number down the Group in the Periodic System. In those cases where the M–M bond energy is low, as happens for $[\pi\text{-}C_3H_5Fe(CO)_3]_2$, dissociation with formation of a monomeric radical takes place at room temperature when the solution is diluted [208] and the polarographed solution contains radical species, which are reduced at the electrode [209]. For other homodimetallic compounds, the dissociation energy is not sufficiently small to enable the detection of paramagnetic species in the solution, but it has been shown for $Mn_2(CO)_{10}$ [210] that many reactions may proceed via the initial homolytic dissociation of the M–M bond. One can therefore suppose that, in the polarographic reduction of compounds with an M–M bond, there is also homolytic dissociation of the reduced bond with formation of a pair of radicals having a half-filled orbital to which the electron is transferred.

The electrochemically irreversible oxidation of homodimetallic compounds at a platinum electrode also proceeds with the dissociation of the M–M bond [156,211,212]

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 - 2e \xrightarrow{L} [\pi\text{-}C_5H_5Fe(CO)_2L]^+ \quad ;$$

L = CH_3CN, acetone, Cl^-, or $S(C_2H_5)_2$.

$$Mn_2(CO)_{10} - 2e \rightarrow 2Mn(CO)_5^+ \xrightarrow{CH_3CN} 2(CO)_5Mn{-}N{\equiv}\overset{+}{C}{-}CH_3 \ .$$

(b) Heterodimetallic compounds ($L_nM{-}M'R_3$). The majority of compounds of this class [L_nM = $C_5H_5M(CO)_3$ (M = Cr, Mo, or W), $(CO)_5M$ (M = Mn or Re), $C_5H_5Fe(CO)_2$, or $(CO)_4Co$; M′ = Sn or Pb; R = CH_3 or C_6H_5] are reduced polarographically with addition of one electron at potentials intermediate between the reduction potentials of the related homodimetallic compounds [157]. The addition of one electron results in the formation of an anion of the homodimetallic compound, which is reduced at less negative potentials to a radical, which dimerises at the limiting current potentials for the first wave with formation of a homodimetallic compound, identifiable by the appearance of the corresponding wave on the polarogram. The polarographic reduction of $\pi\text{-}C_5H_5FeCO.(SiCl_3)H$ and $\pi\text{-}C_5H_5Fe(CO)_2SiCl_3$ has also been investigated [213].

(c) Polymetallic compounds. Symmetrical mercury derivatives containing two M–Hg bonds are reduced polarographically in a single two-electron irreversible stage with dissociation of the M–Hg bonds and formation of a pair of metal carbonyl anions [157,158,204,205]:

$$L_nM{-}Hg{-}ML_n + 2e \rightarrow 2[L_nM]^- + Hg \quad ;$$

$L_nM = C_5H_5M(CO)_3$, (M = Cr, Mo, or W), $C_5H_5Fe(CO)_2$; or $(CO)_5Mn$.

The reduction proceeds at more positive potentials than the reduction of the corresponding $(L_nM)_2$. Owing to the non-equivalence of the Hg–Cl and M–Hg bonds, the asymmetric mercury derivatives M–Hg–Cl are reduced in two stages. The first wave is of the one-electron type and corresponds to the dissociation of the Hg–Cl bond. The mercury radical formed dimerises at the limiting current potentials for the first wave with formation of the compound $(L_nM)_2Hg$, which is reduced in the second stage.

The trimetallic complexes $[\pi\text{-}C_5H_5(CO)_3Mo]_2Sn(CH_3)_2$ and $[\pi\text{-}C_5H_5(CO)_2Fe]_2Sn(CH_3)_2$ are reduced in a single two-electron irreversible stage with dissociation of the Mo–Sn and Fe–Sn bonds and formation of the metal carbonyl anion [157]. The complexes $[\pi\text{-}C_5H_5Mo(CO)_3]_2Sn[Fe(CO)_2.C_5H_5\text{-}\pi]_2$, containing four metal–metal bonds, are reduced in several stages, each of which corresponds to the rupture of one of the M–M bonds [157].

(d) The nucleophilic properties of the metal-containing anions $[L_nM]^-$. It follows from the foregoing that the reduction of homo-, hetero-, and poly-metallic compounds results as a rule in the formation of the metal carbonyl anions $[L_nM]^-$. The nucleophilicity of the $[L_nM]^-$ anion is a parameter which determines quantitatively its reactivity in relation to electrophiles. The study of the electrochemical behaviour of these anions permitted the determination of their nucleophilic properties [214]. It has been found that the anions $[L_nM]^-$ give rise to distinct oxidation waves at a platinum electrode; the variation of the current with the $[L_nM]^-$ concentration is linear. Polarographic study of the kinetics of the reaction of $[L_nM]^-$ with alkyl halides RX showed that the reaction is described by the equation for second-order kinetics. The rate constants k_2', adjusted to conform to k_2 for the anion $[(CO)_4CO]^-$, have been adopted as a measure of the nucleophilicity of $[L_nM]^-$.

It has been established that the nucleophilicity of $[L_nM]^-$ varies in parallel with $E_{1/2}$ for its oxidation. Thus the possibility of one-electron transfer from $[L_nM]^-$ to the substrate (Sub),

$$[L_nM]^- + Sub \rightarrow [L_nM]^{\cdot} + Sub^{\cdot -} \quad ,$$
$$\downarrow$$
$$^1/_2L_nM{-}ML_n$$

is related to $E_{1/2}$ for the oxidation of $[L_nM]^-$ and hence to its nucleophilicity. The problem of the relation between

$E_{1/2}$ for the oxidation of $[L_nM]^-$ and $E_{1/2}$ for the reduction of the substrate and of the possibility of one-electron transfer reactions between them has been examined [215].

The determination of $E_{1/2}$ for the reduction of compounds with an M–M bond and for the oxidation of $[L_nM]^-$ and the quantitative determination of the nucleophilicity of the latter made it possible to establish the fundamental characteristics of the formation of complexes with an M–M bond in the following reactions [216,217]:

$$[L_nM]^- + L_nM'-X \rightarrow L_nM-M'L_n + X^- \quad ;$$
$$[L_nM]^- + L_nM-M'L_n \rightarrow L_nM-ML_n + [L_nM']^- \quad .$$

A linear correlation has also been observed between $E_{1/2}$ for the oxidation of $[L_nM]^-$ and $E_{1/2}$ for the reduction of the hydrides L_nM-H formed when proton donors are added to $[L_nM]^-$. [218]

Electrochemical Reactions Occurring Without the Dissociation of the M–M Bond

(a) Clusters. Clusters containing triangular or polyhedral fragments made up of the metal atoms and the M–M bond are capable of electrochemical oxidation and reduction, the structure of the cluster being retained. The reduction proceeds in a single reversible one-electron stage with formation of paramagnetic radical-anions [60,157]. The stepwise oxidation of $[\pi\text{-}C_5H_5FeCO]_4$ and $[\pi\text{-}C_5H_5FeS]_4$ in acetonitrile at a platinum electrode leads to a series of oxidation states [219,220]. The complex monocations are paramagnetic:

$$[Fe_4]^{2+} \overset{+1.08V}{\rightleftarrows} [Fe_4]^{+} \overset{+0.32V}{\rightleftarrows} [Fe_4]^{0} \overset{-1.30V}{\rightleftarrows} [Fe_4]^{-} \quad .$$

(b) Metal carbonyl complexes with phosphorus- and sulphur-containing bridge ligands. The compounds $[(CO)_4ME(CH_3)_2]_2$ (M = Cr, Mo, or W; E = P or As) and $[Mn(CO)_3SPh]_2$ and $[(CO)_3.ME(CH_3)_2]_2$ (M = Fe or Ru; E = As or P) are reduced to the dianions in a single electrochemically reversible stage [157,179]. The interaction of solutions of the dianions with the initial compounds as a rule leads to the formation of coloured solutions of the radical-anions, which give rise to an ESR signal. A detailed study of $[(CO)_3MP.(CH_3)_2]_2$ (M = Fe or Ru) showed [180] that, on passing from the neutral compound to the radical-anion, the molecular structure is retained, but, on further conversion into the dianion, the molecular geometry is altered. It is assumed [180] that the addition of two electrons to the molecular orbital incorporating the metal orbitals leads to an increase of the charge on the metal and hence to the repulsion of the metal atoms from one another and to an increase of the Fe–Fe distance. This in its turn leads to a decrease of the P–P distance. It has been shown by NMR that, compared with the initial molecule, the frequency of the inversion of the bridge groups in the dianion increases.

The oxidation of the diphosphineiron carbonyl complex $\{[\pi\text{-}C_5H_5Fe(CO)_2]_2Ph_2P(CH_3)_nPPh_2\}$ (n = 2 or 3) also does not lead to the dissociation of the M–M bond [221,222]. The elimination of the first electron proceeds reversibly both electrochemically and chemically and leads to the formation of a cation containing a one-electron M–M bond. The removal of the second electron is electrochemically irreversible and results in the formation of a short-lived dication, which then reacts via the following mechanism:

$$\{[(\pi\text{-}C_5H_5)\,Fe\,(CO)]_2\,Ph_2PCH_2CH_2PPh_2\}^{2+} \longrightarrow$$
$$\xrightarrow{k_1} [(\pi\text{-}C_5H_5)\,Fe\,(CO)_2\,Ph_2PCH_2CH_2PPh_2]^{+} + Fe^{2+}$$
$$\xrightarrow[(Solv\,=\,solvent)]{k_2,\ 2Solv} \{[(\pi\text{-}C_5H_5)\,Fe\,(CO)\,Solv]_2\,Ph_2PCH_2CH_2PPh_2\}^{2+} \quad .$$

In contrast to the complexes examined, in neutral compounds with sulphur-containing bridge ligands $[\pi\text{-}C_5H_5.MLSR]_2$ (M = Mn or Mo and L = NO; M = Fe and L = CO) and $[\pi\text{-}C_5H_5MSR]_2$ (M = Co or Ni), there is no M–M bond. However, in the cation formed after reversible one-electron oxidation, the formation of a one-electron M–M bond is postulated [194,223]. The considerable decrease of the M–M distance in the cation (the Fe–Fe distance is 2.93 Å) compared with the neutral compound (3.39 Å) leads to the same conclusion. It is believed that oxidation to the dication can result in a further contraction of the molecule and the formation of a two-electron M–M bond.

2. METAL COMPLEXES WITH A METAL–HALOGEN σ-BOND

Depending on the structure of the complexes, the reduction proceeds in one two-electron or one-electron stage. The irreversible addition of one electron results in the dissociation of the metal–halogen bond and the formation of 17-electron organometallic radicals, the stability of which varies within wide limits [60,173,204,205,209,224]:

$$L_nM-Hal + e \rightarrow [L_nM]^{\cdot} + Hal^- \quad .$$

The gradual transition from one- to two-electron reduction of the M–X bond has been observed in $\pi\text{-}C_5H_5W(CO)_3X$. While the first wave for the iodide is of the one-electron type, the polarograms of the bromide and chloride showed a single two-electron wave [205]:

$$L_nM-Hal + 2e \rightarrow [L_nM]^- + Hal^- \quad .$$

The compounds $(CO)_5M-Hal$ (M = Mn or Re) are reduced via a similar mechanism [158]. The appearance of a two-electron wave in the reduction of the M–Hal bond is associated with the fact that the potential at which there is a possibility of the transfer of the first electron from the electrode is displaced to an increasing extent towards negative values and approaches the reduction potential of the dimers of the symmetrical mercury compounds, which are the products of the stabilisation of the unstable organometallic radicals formed on transfer of the first electron.

The observed sequence based on the decrease in the ease of reduction of the metal–halogen σ bond in both one-electron and two-electron reduction is the opposite of the sequence of the electronegativities of the halogens, which determine the polarity of this bond. The increase of the polarity of the Fe–Hal bond in $\pi\text{-}C_3H_5Fe(CO)_3Hal$ on passing from the iodide to the chloride has been confirmed by Mössbauer spectra [225]. The observed sequence based on the decrease of the ease of reduction of the metal–halogen bond agrees with the sequence based on the variation of the halfwave potentials $E_{1/2}$ for the reduction of the C–Hal bond [226] in alkyl halides. A radical reduction mechanism is postulated in this case and the decrease of the ease of reduction in the sequence C–I > C–Br > C–Cl is explained by the increase of the strength of the C–Hal bond. Presumably, a similar explanation is applicable

also to the reduction of the transition metal–halogen bond. Thus, in contrast to the simplest inorganic halides, the metal–halogen bond in the carbonyl complexes of transition metals is distinctly covalent and exhibits a tendency towards a predominantly homolytic rather than heterolytic dissociation.

The electrochemical oxidation of complexes with a metal–halogen σ bond has been hardly investigated. It is only known that the voltamperometric oxidation of the halogenopentacarbonylmetallate anions $[(CO)_5MHal]^-$ (M = Cr, Mo or W) takes place in two one-electron reversible stages with formation of an uncharged complex and a cation respectively [227].

Electrochemical Behaviour of Cyclopentadienyl Complexes of Titanium and Zirconium Containing Metal–Halogen σ-Bonds

The enhanced interest in the electrochemical reduction of dicyclopentadienyl compounds of titanium is due to the fact that the system incorporating $(\pi\text{-}C_5H_5)_2TiCl_2$ and reducing agents are catalysts of the Ziegler type and are also capable of the active fixation of molecular nitrogen.

It has been shown that, in an aprotic medium (dimethylformamide, acetonitrile, dimethoxyethane, and tetrahydrofuran), $(\pi\text{-}C_5H_5)_2TiCl_5$ is reduced at the dropping mercury electrode in two stages with subsequent cleavage of the Ti–Cl bonds [60,228,233]. The first wave on the polarogram corresponds to the reversible transfer of a single electron with formation of a titanium(III) compound:

$$(\pi\text{-}C_5H_5)_2TiCl_2 + e \rightleftarrows (\pi\text{-}C_5H_5)_2TiCl + Cl^- \quad .$$

The compound $(\pi\text{-}C_5H_5)_2TiCl$ gives rise to an ESR signal [60, 229]; its subsequent reduction proceeds irreversibly with the apparent formation of titanocene:

$$(\pi\text{-}C_5H_5)_2TiCl + e \rightarrow [(\pi\text{-}C_5H_5)_2Ti]_n + Cl^- \quad .$$

The reduction of $(\pi\text{-}C_5H_5)_2TiX_2$ (X = F, Br, or I) proceeds via analogous mechanisms. The difference between $E_{1/2}$ for the first X = Cl, Br, or I waves is small, while $(\pi\text{-}C_5H_5)_2TiF_2$ is reduced at much more negative potentials [229]. The reduction of $(\pi\text{-}C_5H_5)_2Ti(R)Cl$ [R = CH_3, C_6H_5, C_5F_5, or $OTiCl(C_5H_5\text{-}\pi)$] also begins with the one-electron cleavage of the TiCl bond and the formation of $(\pi\text{-}C_5H_5)_2TiR$. [232] A study [229] has shown that the reduction of $\pi\text{-}C_5H_5TiCl_3$ proceeds in three stages with successive dissociation of Ti–Cl σ-bonds.

In a protic medium, $(\pi\text{-}C_5H_5)_2TiCl_2$ is readily hydrolysed to $(\pi\text{-}C_5H_5)_2TiOH^+$, which is then reduced at the dropping mercury electrode:

$$(\pi\text{-}C_5H_5)_2TiOH^+ + e + H^+ \rightarrow [(\pi\text{-}C_5H_5)_2Ti]^+ + H_2O \quad .$$

The half-wave potentials have also been found for the reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ in other solvents (ethylenediamine [234], morpholine [235], phenylphosphonic dichloride [236], and dimethyl sulphoxide [237]) and for the reduction of $(\pi\text{-}C_5H_5)_2TiBr_2$ in formamide [44].

The reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ in an aprotic medium likewise proceeds in two stages, but has more negative potentials. The product of the addition of the first electron does not give rise to an ESR signal, evidently because of dimerisation and the formation of the M–M bond [60]:

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + e \rightarrow (\pi\text{-}C_5H_5)_2\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Zr}}\!\!-\!\!\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Zr}}(C_5H_5\text{-}\pi)_2 \quad .$$

In an aqueous medium with $NaClO_4$ as the supporting electrolyte, the reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ is not observed, because its reduction potential lies outside the limits of the discharge of the supporting electrolyte [51,55].

Transition Metal Complexes with a Metal–Carbon σ-Bond

Transition metal compounds with a metal–carbon σ-bond are as a rule reduced at more negative potentials than the complexes with metal–halogen and metal–metal σ-bonds. Depending on the structure of the complex, the reduction proceeds via different mechanisms. Octahedral iron, tungsten, manganese, and rhenium complexes are reduced irreversibly at the dropping mercury electrode in an aprotic medium (acetonitrile) in a single two-electron stage with dissociation of the metal–carbon σ-bond [158,205, 238].

$$\pi\text{-}C_5H_5(CO)_2Fe\text{—}R + 2e \rightarrow [\pi\text{-}C_5H_5(CO)_2Fe]^- + R^- \xrightarrow{H^+} RH \quad .$$

The reaction products are the metal carbonyl anion and the carbanion R^-. The latter is stabilised with formation of RH, evidently on interaction with the solvent or with the traces of water in the solvent¶. The structure of the group R has a significant influence on the values of $E_{1/2}$, displacing them towards more negative potentials with increase of the basicity of R^-. A satisfactory linear correlation is observed between the $E_{1/2}$ for the reduction of the Fe–C bond and the values of pK_a(RH) in the series of compounds $\pi\text{-}C_5H_5(CO)_2FeR$: $E_{1/2} = -0.03\ pK_a - 0.81$ (V); $r = 0.994$†. It has been suggested that the observed correlation be used for the determination of new values of pK_a [151] for C–H acids whose acidity is unknown.

The replacement of one carbonyl group in $\pi\text{-}C_5H_5(CO)_2.FeC_6H_4X$ by a phosphorus-containing ligand L leads to a change in the reduction mechanism [238,240]. In this case, the first stage involves the addition of one electron. Simultaneously with electron transfer, the M–C bond is dissociated. The values of $E_{1/2}$ for the first wave were used to estimate the influence of substituents on the transition state in the electrode reaction [238]. The best linear correlation is observed between $E_{1/2}$ and the values of σ_n^0 for the substituents X ($r = 0.873$; $\rho = +0.19$ V). Consequently, the polar influence of substituents is slight, in good agreement with the hypothesis of the homolytic dissociation of the M–C bond during reduction.

The reduction of the organometallic derivative $(\pi\text{-}C_5H_5)_2.TiR_2$ (R = $CH_2\text{–}C\text{–}CH$, with $B_{10}H_{10}$ attached) proceeds in two irreversible one-electron stages with subsequent dissociation of Ti–C σ-bonds. When R = CH_3 or C_6H_5, a single one-electron wave is observed on the polarogram [241].

The polarographic reduction of $RCOM(CO)_5$—the acyl derivatives of manganese and rhenium carbonyls—has also been investigated [158].

¶ According to Vlček [239], a proton is split off from the solvent in the solvation shell of the depolariser molecule and the R–H bond is formed in the activated complex.

† A similar relation has also been observed in the polarographic reduction of symmetrical organomercury compounds and organomercury salts (see, for example, Denisovich and Gubin [149,150]).

Organometallic Derivatives of Planar Chelate Complexes of Cobalt

The oxidation-reduction reactions of σ-organocobalt derivatives of corrin complexes (natural organometallic compounds related to the vitamin B_{12} series) and of their simpler analogues are of considerable interest. Electrochemical studies have shown that, under certain conditions, the cleavage of the Co–C bond during their reduction or oxidation is preceded by rapid electron transfer. This is also important for the understanding of biochemical processes involving vitamin B_{12}. The availability of a series of model organocobalt chelates makes it possible to determine the role of chelating ligands and of the organic group in the mechanism of the reductive cleavage of the Co–C σ-bond. The polarographic behaviour of the organometallic complexes of cobalt having the general formula $[RCo^{III}(chel)L]$ and $\{RCo^{III}[(do)(doh)pn]L\}^+$, where R is a hydrocarbon group, L a Lewis base (in the simplest case a solvent molecule), and chel and [(do)(doh)pn] are the equatorial chelating dianion and the monoanion respectively‡, has been investigated in greatest detail [242-245]. The reduction of these complexes proceeds with greater difficulty than that of the corresponding chelates without Co–C bonds [244], but much more easily than, for example, the reduction of organomercury compounds with the same groups R. Polarographic cyclic voltamperometric and electrolytic studies at a controlled potential have shown that the reduction at the dropping mercury electrode proceeds in accordance with the following mechanisms:

$$[RCo^{III}(chel)L] \underset{-e}{\overset{+e}{\rightleftarrows}} [RCo^{II}(chel)L]^- \underset{-e}{\overset{+e}{\rightleftarrows}} [RCo^{I}(chel)L]^{2-} ;$$

$$\{RCo^{III}[(do)(doh)ph]L\}^+ \underset{-e}{\overset{+e}{\rightleftarrows}} \{RCo^{II}[(do)(doh)ph]L\}^0 \underset{-e}{\overset{+e}{\rightleftarrows}} \{RCo^{I}[(do)(doh)ph]L\}^- .$$

The above mechanisms show that the reduction is electrochemically reversible and does not therefore require an appreciable activation energy for electron transfer. The values of $E_{1/2}$ for the first reduction stage ($Co^{III} \rightarrow Co^{II}$) of complexes of the same type depend on R. It has been found [243-246] that the values of $E_{1/2}$ vary linearly with the pK_a for the corresponding RH, i.e. the electron affinity of the organometallic chelate depends on the stability of R^-, and the orbital to which the electron is transferred on reduction is therefore the antibonding orbital of the Co–C bond. The electron-donating capacity of the equatorial ligands influences the electron affinity of the complexes investigated [243-246]. The dependence of $E_{1/2}$ on the nature of the equatorial ligand shows that the energy of the antibonding orbital of the Co–C bond increases in the sequence from [(do)(doh)pn] to salen and bae. The stability of the intermediate and final products depends to a large extent on the nature of R. Thus the one-electron reduction of $[C_6H_5Co^{III}(salen)L]$ leads to the formation of a potential carbanion, while the products of the reductive cleavage of $[CH_3Co(salen)L]^-$ are a cobalt(I) complex and $CH_3^{\cdot}$: [246]

$$[C_6H_5Co^{II}(salen)L]^- \xrightarrow{H^+} C_6H_6 + [Co^{II}(salen)L] ;$$

$$[CH_3Co^{II}(salen)L]^- \rightarrow CH_3^{\cdot} + [Co^{I}(salen)L]^- .$$

The differences in the behaviour of these complexes are explained by the changes in the lowest vacant molecular orbital of the complex where the electron is accepted on transition from $[C_6H_5Co(salen)L]$ to $[CH_3Co(salen)L]$, namely in the case of powerful donors (R = CH_3) the lowest free orbital may be a metal orbital of the d_{xy} type.

The ability of organometallic chelates to behave as donors of the methyl group is greatly enhanced on their reduction. Thus $\{CH_3Co^{I}[(do)(doh)pn]L\}^-$ behaves as a methylating agent in relation to the initial compound even under electrolysis conditions:

$$RCo^{I}[(do)(doh)pn]\}^- + \{RCo^{III}[(do)(doh)pn]\}^+ \rightarrow$$
$$\rightarrow \{R_2Co^{III}[(do)(doh)pn]\} + \{Co^{I}[(do)(doh)pn]\} .$$

The reversible one-electron oxidation of cobalt(III) organic chelates in the series [RCo(salen)] and $[RCo(Dh)_2]$ (Dh is the dianion of a 1,2-dioxime) has also been observed at a platinum electrode in acetonitrile with formation of labile cobalt(IV) compounds which readily transfer the σ-linked organic group to nucleophiles [247].

The polarographic behaviour of alkylcobalamins, glucopyranosylcobalamin, and 5′-deoxynucleoside analogues of the cobamide coenzyme in an aqueous medium has been investigated [248]. The great complexity of the polarographic reduction of $RCo(Dh)_2$ compared with organocobalt chelates of other series is also noteworthy [248-250].

VI. ELECTROCHEMICAL SYNTHESIS OF π-COMPLEXES OF TRANSITION METALS AND OF COMPLEX ORGANOMETALLIC CATALYSTS

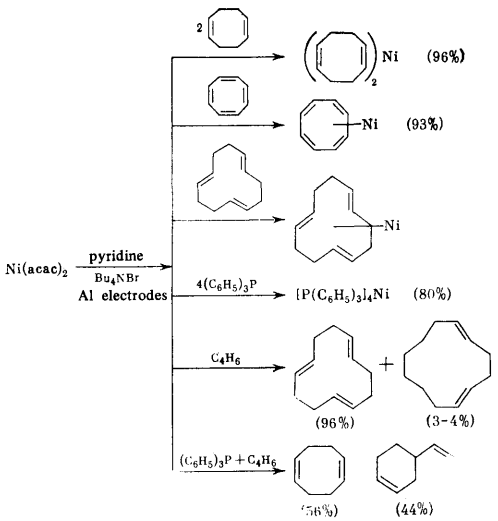
The polarographic study of the behaviour of transition metal π-complexes and of the corresponding non-coordinated ligands at electrodes leads to the possibility of selecting conditions for the electrochemical synthesis of transition metal π-complexes [251,252]. As a rule, the starting compounds for the electrochemical synthesis of transition metal complexes are chelate complexes of the same metals or their salts. Electrolysis is carried out using an organic compound, which subsequently behaves as the π-ligand for the complex to be formed, in the presence of electron-donating molecules [pyridine, DMF, $P(C_6H_5)_3$, etc.] capable of stabilising a low oxidation state of the metal. Thus, transition metal carbonyls have been synthesised from acetylacetonates and carbon monoxide [253, 254]. The electrolysis was carried out at a stainless steel cathode in anhydrous pyridine containing 1–5% Bu_4NBr; the anode was metallic aluminium. The carbon monoxide pressure was varied within wide limits, whereupon the following processes take place at the electrodes:

$$\text{Cathode: } M(acac)_n + XCO + ne \rightarrow M(CO)_x ;$$
$$\text{Anode: } Al \rightarrow Al^{3+} + 3e .$$

The carbonylation of $CrCl_3(Py)_3$ in pyridine at 85 °C and a carbon monoxide pressure of 60 atm leads to the formation of $Cr(CO)_6$ in 85% yield [255]. The reduction of $Fe(acac)_3$ at a mercury cathode in the presence of $P(C_6H_5)_3$ and 1,3-dienes leads to the formation of $FeP(C_6H_5)_3$ (diene)

‡ The following notation has been adopted for various chelating dianions: salen = *NN′*-ethylenebis(7,7′-dimethylsalicylideneaminate); bae = *NN′*-ethylene bis(acetylacetone iminate) [*NN′*-ethylenebis(1-methylethylideaminate)]; saloph = *NN′*-*o*-phenylenebis(salicylideneaminate); [(do)(doh)pn] = monoanion of 1,3-diacetylmonoxime-iminodiacetylmonoximatoiminopropane.

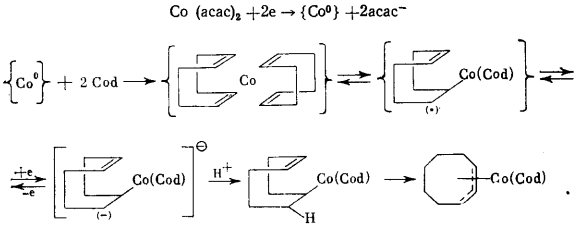
(diene = buta-1,3-diene or isoprene)[256]. Olefin complexes of nickel have also been obtained by a similar procedure[257]:



The last two rows of the above scheme show that the complexes of zero-valent nickel synthesised electrochemically catalyse the oligomerisation of butadiene. The electrochemical preparation of butadiene oligomerisation and polymerisation catalysts containing zero-valent nickel and cobalt has been investigated in greater detail in other studies[258-262]. It has been shown that the conversion of butadiene and the composition of the products formed are influenced by the nature of the initial nickel and cobalt compounds, the nature of the solvent, and the potential at which the electrolysis is carried out. Similarly electrolysis at a platinum electrode of a solution containing $Py_4Ni(ClO_4)_2$ or $NiCl_2$ and butadiene involves the tetramerisation of butadiene[263], but this reaction is not catalytic. The electrochemical synthesis of previously unknown $(Ph_3P)_4Rh(O)$ has also been described[264].

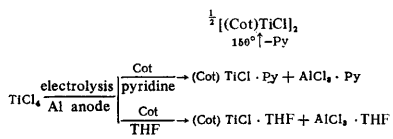
The following mechanism has been proposed for the electrochemical synthesis of cobalt complexes of cyclo-octa-1,5-diene (Cod) at aluminium electrodes[265]:

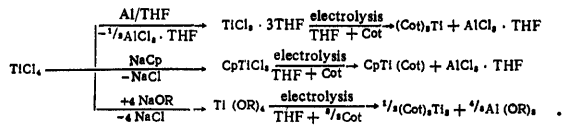
$$Co(acac)_2 + 2e \rightarrow \{Co^0\} + 2acac^-$$



The intermediate biscyclo-octa-1,5-dienecobalt is subsequently reduced to an anionic complex, which reacts with a proton, forming π-cyclo-octenylcyclo-octadienecobalt.

The electrochemical preparation of cobalt complexes of acyclic 1,3-dienes $(\pi\text{-}C_4H_6)Co(\pi\text{-}C_4H_6R)L$, where L = $P(C_6H_5)_3$ or $P(C_4H_9)_3$, by the reduction of $CoCl_2$ at a mercury cathode in the presence of buta-1,3-diene and L has been described[266].





Another approach to the electrochemical synthesis of π-complexes is based on the involvement of the electrode material in the electrode reaction. Ferrocene has been obtained in this way from C_5H_5Tl at an iron anode in 94.6% yield[268]:

$$\text{Anode: } 2C_5H_5Tl + Fe \rightarrow (C_5H_5)_2Fe + 2Tl^+ + 2e \ ;$$

$$\text{Cathode: } 2C_5H_5Tl + 2e \rightarrow 2Tl^0 + 2C_5H_5^- \ .$$

A method for the preparation of cyclopentadienylmanganese carbonyl compounds, based on the anodic dissolution of manganese, has been patented[269,270]. Similarly, in the electrolysis of solutions of indenylsodium and fluorenylsodium in THF or diglyme, the manganese anode dissolves with formation of di-indenylmanganese and difluorenylmanganese[271]. When a current is passed between two copper electrodes in a methanol solution of $Cu(BF_4)_2$ and cyclo-octa-1,5-diene, the copper undergoes anodic dissolution with formation of bis(cyclo-octa-1,5-diene)copper tetrafluoroborate:

$$Cu + n\,(Cod) + BF_4^- \rightarrow Cu\,(Cod)_n\,BF_4 + e \ .$$

At the same time copper(II) is reduced at the cathode to copper(I) and the subsequent reaction of copper(I) with Cod likewise leads to the formation of $Cu(Cod)_nBF_4$:[272]

$$Cu^{2+} + n\,(Cod) + BF_4^- + e \rightarrow Cu\,(Cod)_n\,BF_4 \ .$$

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In conclusion, one should note that, together with the undoubted advances in electrochemical research on transition metal π-complexes, there are a number of branches of this field which have so far been inadequately investigated and whose study is likely to be rewarding: (1) investigation of the mechanisms of electrode processes involving π-complexes; (2) investigation of the properties of the intermediate species and the final products of the electrochemical reactions of π-complexes; (3) the study of the relation between electrochemical data and the chemical and physical properties of π-complexes (acid–base properties, reactivity in relation to electrophiles and nucleophiles, ionisation potentials, electron affinities, quantum-chemical data, etc.); (4) electrochemical synthesis of π-complexes and complex organometallic catalysts.

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