

# APPLICATION OF ELECTROCHEMICAL METHODS IN THE ORGANOMETALLIC CHEMISTRY OF TRANSITION METAL $\pi$ -COMPLEXES

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## ABSTRACT

Polarography on both the dropping mercury and solid electrodes in aprotic solvents, electrolysis at a controlled potential, oscillopolarography, potentiometry, etc., along with non-electrochemical methods (such as e.s.r., nuclear- $\gamma$ -resonance, i.r., n.m.r. spectroscopies) of a great number of organometallic transition metal  $\pi$ -complexes has been covered in detail.

Methods and procedures are considered which may be helpful in the solution of such problems as a localization of electronic changes in a complex which may occur (a) on metal orbitals; (b) on the  $\pi$ -ligand orbitals, and (c) on the anti-bonding orbital of the metal- $\sigma$ -ligand bond. The application of electrochemical methods in the solution of such problems as the relative location of the highest occupied and lowest vacant orbitals for a series of structurally similar  $\pi$ -complexes is discussed. The relation between the reduction potential of the  $L_nM-\sigma-R$  bond and the  $pK_a$  RH has been found;  $pK_a$  values for a number of metallocenes as a C-H-type acid have been determined.

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A little more than fifteen years has passed since the discovery of ferrocene. This short period has been marked by an intensive growth of the chemistry of transition metal  $\pi$ -complexes. Many thousands of new  $\pi$ -complexes have been obtained and their numerous reactions and chemical properties investigated. Many types of complexes have found practical application as homogeneous catalysts, anti-knock additives in fuels, as compounds for preparing metal film coatings in this gaseous phase, and in many other fields.

In the light of this progress our understanding of the metal  $\pi$ -ligand bond is still far from good. In most cases we actually depend on the qualitative bond description of Chatt and Duncanson<sup>1</sup> and the Sidgwick rule<sup>2</sup>. Attempts at a quantum chemical description of the metal  $\pi$ -ligand bond, in spite of their large variety<sup>3</sup>, provide no reliable representation of the molecular electron density distribution. This became most evident when the calculations involving only  $\pi$ -electron approximation were shown<sup>4</sup> to be inadequate for the solution of such problems owing to a considerable  $\sigma$ -contribution. Probably only the non-empirical *ab initio* calculations, which are still not possible for such multi-electron systems<sup>5</sup>, will provide reliable information on the nature of the metal  $\pi$ -ligand bond.

There is observable in recent times a tendency to employ a variety of physicochemical methods for investigating the electronic structures of transition metal  $\pi$ -complexes. Each separate method is limited in its ability to yield and interpret data on the metal  $\pi$ -ligand bond. But a combination of methods may, in our opinion, provide an objective picture of the bond in transition metal  $\pi$ -complexes.

In this paper electrochemical methods will be shown to have application, along with other physicochemical methods, for investigating the electronic structures of transition metal  $\pi$ -complexes. Application of electrochemical methods is based on the very widespread oxidation-reduction reactions of transition metal  $\pi$ -complexes: actually any complex may take part either in oxidation or reduction or in both reactions.

Electrochemical methods are undoubtedly advantageous in giving objective information on the electron density distribution and the relative location of the upper occupied and lower vacant orbitals for a series of structurally similar compounds.

$$\text{Ox.} \xrightleftharpoons[-ne]{+ne} \text{red.}$$

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{\text{Ox.}}}{a_{\text{red.}}} \quad \text{if } a_{\text{Ox.}} = a_{\text{red.}} \\ E = E_0$$

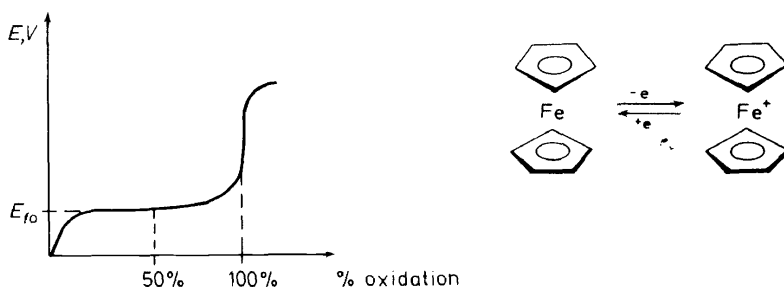


Figure 1

The first quantitative studies on the oxidation-reduction reactions of  $\pi$ -complexes were those of Professor Wilkinson and his colleagues<sup>6</sup>. Subsequently more or less detailed studies of the electrochemical behaviour of complexes were carried out by Tirouflet<sup>7</sup>, Vlček<sup>8</sup>, Furlani<sup>9</sup>, Bublitz and co-workers<sup>10</sup>, Little and co-workers<sup>11</sup>, Valcher and Mastragostino<sup>12</sup>, and Professor Dessy and co-workers<sup>13</sup>.

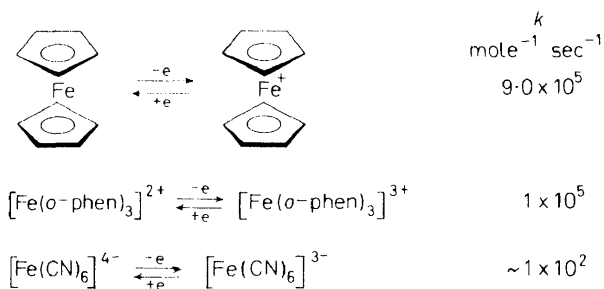
Here we are mainly concerned with the results obtained at the Institute of Organo-element Compounds in Moscow and with the results of other Soviet authors.

Polarography at dropping mercury and rotating platinum electrodes, potentiometry and chronopotentiometry are the techniques most widely

employed in these investigations. Oscillopolarographic methods, electrolysis at controlled potential, and other methods are also used.

These techniques have been described in full in standard textbooks<sup>14</sup>, and there is no need to discuss them in detail here. Certain specific techniques are required with such substances as cobaltocene, for example, which are oxidized exceptionally easily. These have been described in detail by Professor Vlček<sup>15</sup>. It should also be noted that the investigations are usually conducted in aprotic media, such as DMF, CH<sub>3</sub>CN and dimethoxyethane using Bu<sub>4</sub>NClO<sub>4</sub> or Bu<sub>4</sub>NBF<sub>4</sub> as supporting electrolytes. This covers a potential range from +2 to -3 V (using s.c.e. as a reference).

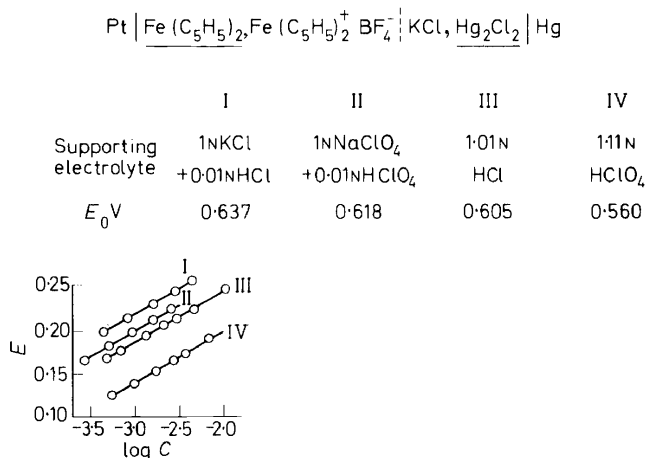
The oxidative potentiometric method played an important part in the development of metallocene chemistry. It should be noted that the limitations of the potentiometric method became evident even in the thirties after the classical work of Michaelis. After the brilliant studies by the Nobel Prize Winner Professor Jaroslav Heyrovsky and other workers, who developed the polarographic method, the potentiometric method practically lost its application as a serious approach in physical organic chemistry. The potentiometric method is based on the Nernst equation and thus requires rather rigid conditions (*Figure 1*): (1) the oxidation-reduction system should be highly reversible, both in the electrochemical as well as in the chemical sense, (2) the equilibrium between oxidized and reduced forms should be established very rapidly, and (3) both the oxidized and reduced forms should be stable during the time of measurement.



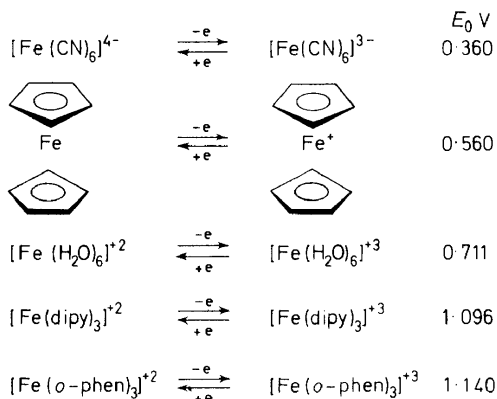
*Figure 2*

The ferrocene-ferricenium cation system has been shown to satisfy all these conditions. Along with high chemical and electrochemical reversibilities it possesses an exceptionally high electron exchange rate between oxidized and reduced forms<sup>16</sup> exceeding that of typical stable iron complexes (*Figure 2*). These peculiarities combined with a complete insolubility of ferrocene in water and aqueous salt solutions were successfully employed by Nikolsky, Zakharyevsky and Pendlin<sup>17</sup> in the preparation of an electrode reversible towards the ferricenium cation. At constant ionic strength, the linear relationship between the electrode potential and  $\log C_{(\text{C}_5\text{H}_5)_2\text{Fe}^+\text{BF}_4^-}$ <sup>5</sup> has been found (*Figure 3*) with an angle coefficient of 59 mV. This allowed an estimate to be made of the standard oxidation-reduction potential of the ferrocene-ferricenium electrode. A comparison of this value with standard oxidation-reduction potentials of typical (formally bivalent) iron complexes shows

that ferrocene is somewhat more readily oxidizable in aqueous media than bivalent iron, and somewhat less readily than the ferrocyanide ion (*Figure 4*). Assuming that the electron changes in the oxidation-reduction process are localized at the metal atom, the ligand should display negligible perturbation on the central metal atom compared, for example, with the iron aquo complexes. Other examples where  $\pi$ -bonded  $C_5H_5$ -ligands behave as the weak field ligands will be discussed below.



*Figure 3.* Dependence of  $E$  on concentration of ferricenium fluoroborate



*Figure 4*

The ferrocene-ferricenium electrode was employed by Nikolsky *et al.* for determination of the activity coefficients of the ferricenium cation complexation<sup>18</sup>. No noticeable complexation between ferricenium and such typical chelating agents of iron as *o*-phen and EDTA was observed. On the other hand, ferricenium gives 1:1 complexes with such anions as  $\text{Cl}^-$ ,  $\text{CNS}^-$  and  $\text{ClO}_4^-$  in aqueous media. In the work of Pendin *et al.*<sup>19</sup> the ferrocene-ferricenium electrode (*Figure 5*) was employed for determination

## APPLICATION OF ELECTROCHEMICAL METHODS

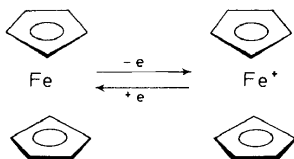
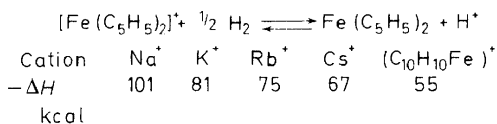


Figure 5

of the free energy, heat and entropy of reaction in an aqueous solution. From the values of  $\Delta G^0_p$ ,  $\Delta H^0_p$ ,  $\Delta S^0_p$  obtained for the reaction, and the known thermodynamic functions of ferrocene, the heat and entropy of ferricenium cation hydration were estimated. A comparison with other values shows that the heat of ferricenium cation hydration is the lowest of the values known for unipositive cations. The energy of ferrocene solvation has been found to be rather small (13 kcal/mole)<sup>20</sup> and is defined in general by the disperse interactions. Both values vary very little from one solvent to another. Determinations showed that the oxidation-reduction potential of the ferrocene-ferricenium cation system does not change from one solvent to another; the heat of equilibrium of an oxidation-reduction is defined by a difference of solvation energies of a neutral molecule and positively charged ion. Thus, the ferrocene-ferricenium electrode satisfies the conditions required by the reference electrodes: large ionic radius, small charge and polarizability, minimum tendency to a specific interaction with a solvent, and minimum solvation energy, hence it can be successfully employed for these purposes. Most other stable closed shell transition metal  $\pi$ -complexes have been found to possess solvating properties similar to those of the ferrocene-ferricenium cation system.

It has been found<sup>21-23</sup> that the introduction of substituents into a five-membered aromatic ring does not alter the unique properties of the ferrocene-ferricenium system: it retains both high reversibility and electron exchange rate. This permitted the formal oxidation-reduction potentials to be determined for a great number of the mono- and hetero-annular disubstituted ferrocenes as well as other ferrocene-containing compounds. The potential has been found to be exceptionally sensitive to a small difference in the electronic effects of substituents (Figure 6): the method can distinguish reliably between the effects of  $\text{CONH}_2$  and  $-\text{CONHCH}_3$ ;  $-\text{COOH}$ ,  $-\text{COOCH}_3$  and  $-\text{COOC}_2\text{H}_5$  groups; this is not usually possible with other methods employed for quantitative estimation of substituent effects.

The theoretical concepts concerning the principle of a linear dependence between the free energy changes and the potentials of reversible and irreversible processes have been derived by Zuman<sup>24</sup> along with the main requirements and limitations applying to such correlations. According to the results described above the ferrocene-ferricenium system should be considered as representing an ideal system for establishing the correlations

between the structure and oxidation potential of the compound. Since there was no *a priori* information as to which set of  $\sigma$  constants will describe the substituent effect on potential values, a systematic correlation analysis was carried out employing sets of  $\sigma$  constants differing by a positive resonance component (Figure 7). The best linear correlation was found with the  $\sigma p^0$  constants of the corresponding substituents both for monosubstituted as

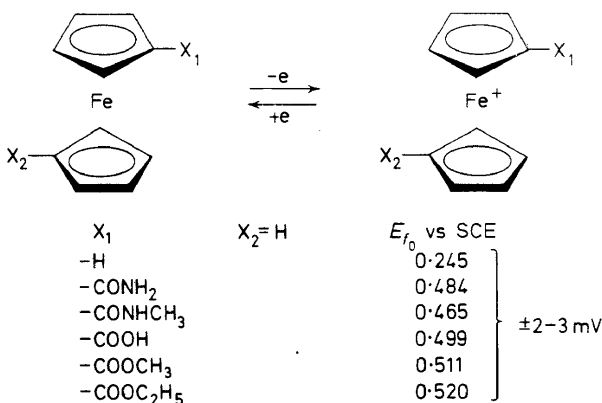


Figure 6

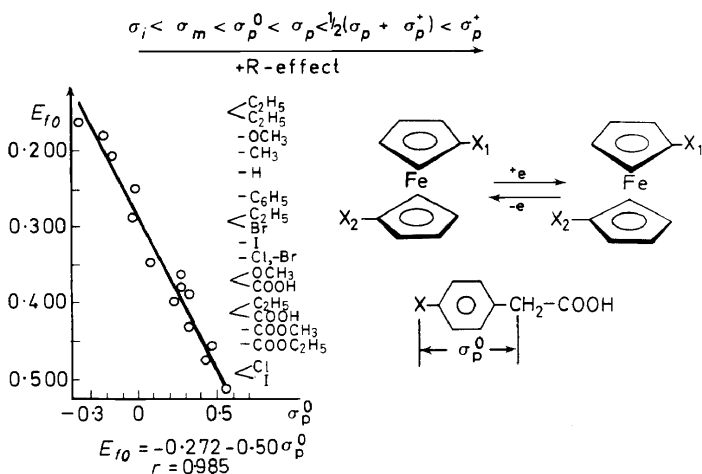


Figure 7

well as for hetero-annular disubstituted ferrocenes. This means that a substituent participates in a conjugation with a five-membered aromatic ring, but of the total polar effect of the substituent an inductive component alone is delivered (in a direction perpendicular to the ring plane) to the metal atom or another ring.

Further investigations showed<sup>25</sup> that this phenomenon first observed in the ferrocene oxidation-reduction reactions is a common occurrence in the

chemistry of transition metal  $\pi$ -complexes, and characterizes a transition metal  $\pi$ -ligand bonding.

When a substituent is separated from the ferrocenyl nucleus by the methylene moiety preventing its conjugation, a good linear dependence is observed between  $E_{f0}$  and the inductive constants of the corresponding substituents in both aliphatic and aromatic series. Employing the dependence observed, a new method was worked out<sup>26</sup> making it possible to determine the inductive parameters of substituents for the majority of other metallocenyl groups and polyatomic substituents. The inductive parameters obtained for the metallocenyl groups investigated give a clear quantitative picture of the other ligand effects along with those of the charge and the nature of the metal on the reactivity of the  $\pi$ -bonded cyclopentadienyl or arene groups (Figure 8). A considerable portion of the known electron deficiency of the

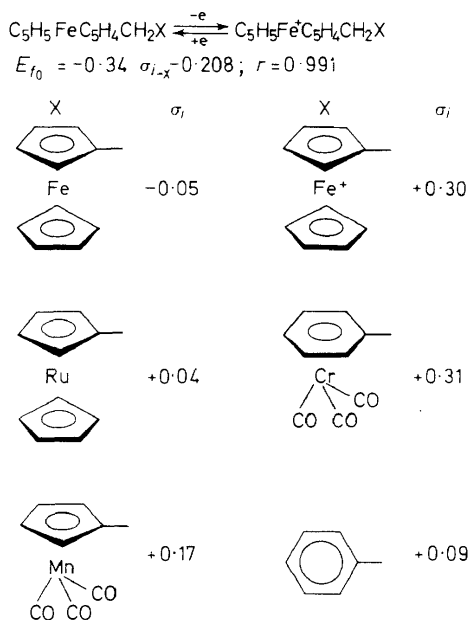


Figure 8

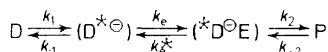
phenyl nucleus in  $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$  has been shown<sup>27</sup> to depend on the high positive inductive aromatic constant. In other words, this deficiency is defined by a considerably increased effective positive charge on the carbon orbitals of the aromatic ring during its coordination with the  $\text{Cr}(\text{CO})_3$  group. In the latter the chromium atom is known to carry a significant effective positive charge<sup>28</sup>.

It should be pointed out that the observed changes in the inductive aromatic constants for a number of  $\pi$ -cyclopentadienyl compounds correlate well with the reactivities of the corresponding metallocenes both in electrophilic as well as in nucleophilic substitution reactions. Thus employing the unique oxidation-reduction properties of the ferrocene-ferricenium cation

system, the  $\pi$ -ligand reactivity differences observed in coordination have been found to relate not to the traditional differences in  $\pi$ -electron densities of rings but to the changes of effective charges on the ring carbon  $\sigma$ -orbitals.

Unfortunately, the possibilities of the potentiometric method are probably exhausted by the ferrocene–ferricenium cation system: several hundred other transition metal  $\pi$ -complexes were investigated but none of them had the properties required for an application of the potentiometric procedure.

The polarographic method allows one to investigate both reversible and irreversible systems. The theoretical concepts of this application of the polarographic method to the study of organic and organometallic reactions were discussed in Perrin's review<sup>29</sup> along with polarogram interpretation and the criteria of wave reversibility. Polarographic behaviour of coordination compounds was considered by Vlček<sup>30</sup>.



D - the depolarizing particle

$D^{\ddagger}$  - the activated particle of depolarizer

E - the electrode surface

P - primary product

$$E = E_{1/2} - \frac{RT}{\alpha nF} \ln \frac{j}{j_d - j}$$

$\alpha$  - transfer coefficient

Figure 9

The process of electron transfer, and the factors governing reversibility or irreversibility of electrochemical reactions<sup>30</sup>, will now be considered in more detail. In the light of the Marcus theory<sup>31</sup> the electron transfer process, when applied to the electrochemical reactions, can be represented as shown in Figure 9. According to the Frank–Condon principle a depolarizing particle participating in the electron exchange with an electrode surface should not undergo configurational changes. Thus, prior to electron transfer, a configuration of the depolarizing particle should already provide the minimum activation energy for this transfer, that is it should be that of an activated depolarizer. Activation occurs under the influence of an electrode field. When the energy of such activation is negligible, that is the depolarizer and products are of the same configuration, the electrochemical reaction should be reversible. However, the larger the difference between configurations of depolarizer and primary product, the larger should be the energy of molecular rearrangement, hence the electrochemical reaction becomes more irreversible. In this respect the physical sense of a transfer coefficient becomes evident as that part of the potential consumed by an electron transfer itself. According to the Vlček review<sup>30</sup>, of a great variety of oxidation–reduction reactions investigated for transition metal  $\pi$ -complexes a choice was made of those having the highest reversibility, uncomplicated by dissociated processes, interaction with solvent and material of electrode, etc.

It is commonly accepted that in a conversion from an activated depolarizer to the primary product of electrode reaction the electron changes occur on



the lowest vacant orbital during the reduction, and on the highest occupied one during oxidation. In the different types of transition metal  $\pi$ -complexes there are usually different relative contributions of the ligand molecular orbitals and metal atomic orbitals into the combined molecular orbital responsible for electron changes in the electrochemical reaction (Figure 10).

$$\phi = c_1\psi_1 + c_2\psi_2$$

$\psi_1$  - the metal orbital  
 $\psi_2$  - the group orbital of the ligand

Figure 10

In this connection it is useful to outline three main regions responsible for electron changes in complexes :

- (1) on the metal orbital
- (2) on the  $\pi$ -bonded ligand orbital
- (3) on the antibonding orbital of the localized metal-ligand  $\sigma$ -bond.

In a number of cases the halfwave potentials of the reversible process were shown to be directly proportional to the energy of the orbital responsible for the electron changes<sup>32</sup>. For irreversible processes no such comparisons are possible, but under certain conditions a correct correlation may nevertheless be obtained between the structure of the depolarizer and the halfwave potentials.

Subsequent discussions will be devoted to the methods usually employed for localizing the electron changes during oxidation-reduction reactions of transition metal  $\pi$ -complexes. These were examined with particular examples.

## LOCALIZATION OF ELECTRON CHANGES ON METAL ATOM

Investigation of a comparatively large number of transition metal  $\pi$ -complexes, and analysis of the published information, led to a conclusion that if the metal in a complex is bound by a delocalized  $\pi$ -bond with the carbocyclic ligands only and has the closed electron shell of the nearest inert gas, then during the oxidation-reduction reactions the electron changes should be localized at the metal atom. The electronic configurations of the oxidized and reduced forms are usually similar in such cases, and the electrode reactions are reversible to some extent. This condition is entirely satisfied with ferrocene, ruthenocene<sup>6a, 10, 33</sup>, osmocene<sup>10</sup>, dibenzene chromium<sup>19</sup> and other sandwiches.

An interesting but more complicated case could be considered when the polarographic method enabled an entire reduction process of arene-iron cyclopentadienyls with metal hydrides<sup>34</sup> to be separated into stages and permitted an investigation of the structural effects on the course of the first reduction stage<sup>35</sup>. Polarograms of arene-iron cyclopentadienyl cations measured in aprotic media show two one-electron diffuse waves, the first being reversible, while the second is irreversible and dependent on the addition of proton donors to the solution. According to the equation the

primary reduction product represents an uncharged formally univalent iron complex (Figure 11). Experiment shows that its oxidation gives one anodic wave with a potential equal to that of the starting complex. Along with other data this is convincing proof of electrochemical reversibility of the reduction process. However, the lifetime of the primary reduction product is probably negligible: it cannot be traced in the chemical reduction of the starting compound with a variety of reducing agents. Under the conditions of polarographic reduction the primary product accepts an electron and a proton at the second stage and is converted into a cyclohexadienyl-cyclopentadienyl iron complex—the same product as in the chemical reduction with metal hydrides.

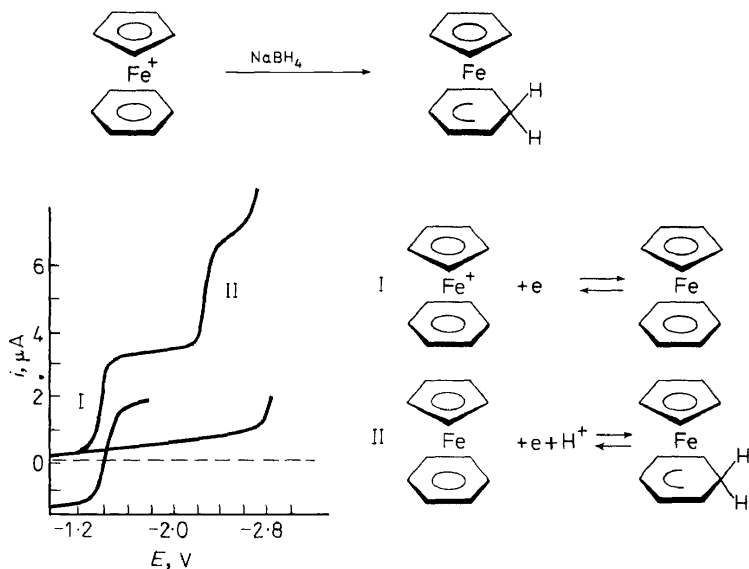


Figure 11

It is known that for electrochemically reversible processes the halfwave potential is a thermodynamic value characterizing the energy of the lowest vacant molecular orbital accepting an electron during the reduction. To set forth a localization of the electron changes in such a case actually means estimating a comparative contribution of the metal atomic orbitals and ligand molecular orbitals into the combined molecular orbitals of the complex where the electron changes occur during reduction. According to Vlček<sup>36</sup> the reduction potential differences of two structurally similar non-coordinated ligands and their complexes may be employed for such a purpose (Figure 12), and the mixing coefficients of the metal atomic orbitals and ligand molecular orbitals can be estimated for the lowest vacant complex molecular orbital. In the case given this value was found to be 0.20, indicating only 20 per cent contribution of the ligand molecular orbital into a molecular orbital of the complex. Hence, during the reduction, the electron changes are localized at the metal atom. This was also confirmed

by the ligand substituent effects on the reduction potentials of the first reversible reduction stage. The latter was found to obey the same mechanism for all the series of compounds, and the substituents caused similar and

$$(E_1 - E_2)_{\text{complex}} = c_2^2 (E_2 - E_1)_{\text{free ligand}}$$

$$c_2^2 = 0.20$$

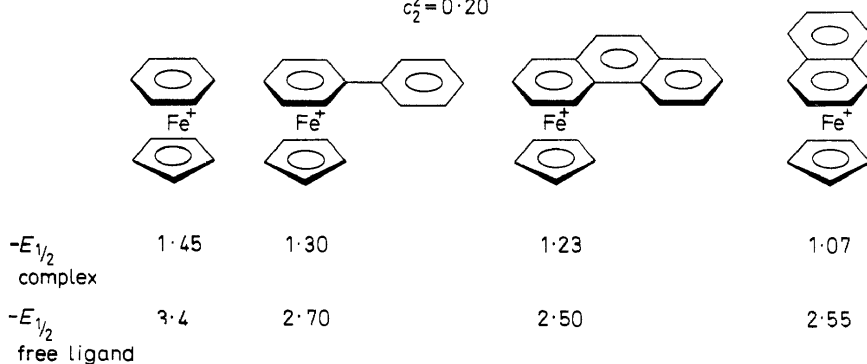


Figure 12

negligible structural changes displaying, however, essentially different effects. Thus, there are present all the criteria necessary to provide an accurate correlation between structures and reduction potentials of the complexes investigated. Furthermore, the range of potential changes from the strongest electron withdrawing to releasing substituents exceeds by several dozen times the mean square error of the experiment. Systematic correlation analysis (Figure 13) with a variety of  $\sigma$ -sets showed that for both arenic and cyclopentadienyl rings the best linear correlation is observed between  $E_{1/2}$  values and  $\sigma^0 p$ -constants of the linear corresponding substituents. Thus it was

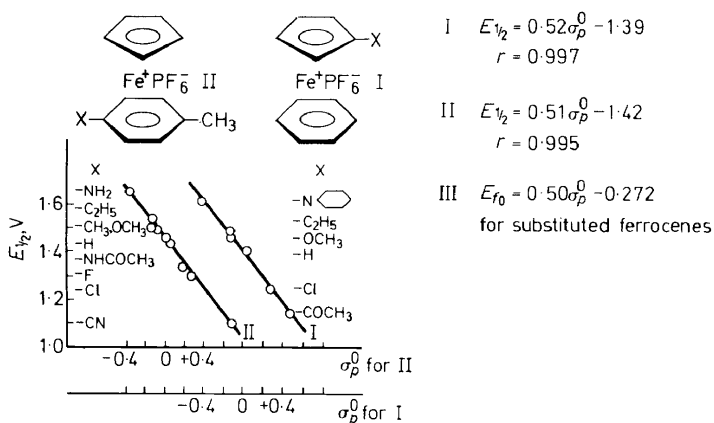


Figure 13

found that there is no difference not only in the nature but also in the magnitudes of the arene and cyclopentadienyl ring substituent effects on the common reaction centre—the iron atom. Moreover, this influence was entirely reminiscent of the substituent effects in the cyclopentadienyl rings on the formal oxidation–reduction potentials of monosubstituted and heteroannular disubstituted ferrocenes<sup>23</sup>. Furthermore, the sensitivity of the reaction centre to the substituent electronic effects is practically the same for all the three series of compounds, which can be readily seen from a comparison of  $\rho$ -values. This means that the character of the substituent effects in the arene–cyclopentadienyl iron complexes is reminiscent of that observed for other transition metal  $\pi$ -complexes (see page 468). It should be pointed out that the linear dependences obtained support the validity of the reaction mechanism suggested and an idea that the electron changes are localized on the metal atom. In conclusion, some characteristic features of the oxidation–reduction reactions where the electron changes occur at the metal atom in transition metal  $\pi$ -complexes should be pointed out: these processes are usually one-electron transfers and highly reversible; they involve rather weak solvent effects, and their wave polarographic characteristics are independent of the addition of a proton donor.

### ELECTRON CHANGES ON $\pi$ -BONDED LIGAND ORBITALS

For the majority of carbocyclic aromatic ligands it is usually impossible for one to observe an oxidation or reduction of ligand in the complex. Indeed the lowest vacant orbital of the cyclopentadienyl aromatic system being of rather high energy, it accepts an electron only at negative potentials which are often beyond the discharge range of the supporting electrolyte. However, by decreasing the energy of the lowest vacant orbital by introducing electron-withdrawing substituents it is possible to obtain reduction waves of the ligands in an area attainable for potential measurements. Some such processes have been studied by Tirouflet<sup>7, 37</sup> and other authors<sup>38</sup> for the reduction of ferrocene, ruthenocene, cyclopentadienyl manganese tricarbonyl and benzene chromium tricarbonyl derivatives. Most of these processes involved proton participation and, being irreversible, could not be used for a true comparison.

The majority of the complex ligand reduction processes in aprotic media were found to be reversible like the reduction of non-coordinated ligands. These results were employed for a quantitative comparison of the coordination effects on the reactivity of  $\pi$ -bonded carbocyclic ligands. Such an approach was probably more correct in respect of other analogous studies<sup>39</sup>. First, in the case given an equilibrium is observed. Hence the different reactivities established are not associated with a transition state character in reactions of coordinated and non-coordinated ligands. Secondly, the processes of one-electron transfer usually have negligible activation energies and proceed very rapidly; one may therefore assume that changes observed in going from a non-coordinated to a coordinated state result from the purely electronic interactions, while there are minimum changes in the steric, solvating and other effects. Thirdly, the reversible reduction potential differences of coordinated and non-coordinated ligands measured under precisely the same conditions (as has been shown repeatedly<sup>32</sup>) may be quite

reliably assumed to be equal to the energy differences between the corresponding lowest ligand orbitals. This allows the results of coordination to be estimated quantitatively.

Consider two limiting cases of charge transfer in the generation of metal  $\pi$ -ligand bonds. It could be suggested that the largest electron shift from ligand to metal may take place in complexes containing the metal-carbonyl moieties since the CO groups are known to behave as strong  $\pi$ -acceptors in the complexes<sup>40</sup>. Polarographic reduction of acetophenone (Figure 14), both coordinated and non-coordinated with the  $\text{Cr}(\text{CO})_3$  group, has been investigated in aprotic media<sup>41</sup>. Both compounds reveal a clear one-electron diffuse wave for reversible reduction into the corresponding anion-radical, and also show the second diffuse wave. Main characteristics of the reduction waves for coordinated and non-coordinated acetophenones are completely identical. In aprotic media, in particular, these waves are equally dependent on the addition of proton donors. The only difference was consistent with a shift of the essential reduction potential to the positive area for the coordinated ligand, indicating a considerable charge transfer from ligand to metal. Assuming that the electron addition occurs on the lowest vacant acetophenone orbital, its energy must be regarded as decreasing by about 0.5 eV after coordination with the  $\text{Cr}(\text{CO})_3$  group. As was shown earlier (page 469), a decrease in the orbital energy occurs owing to an increase in the effective positive charge on the ring carbon  $\sigma$ -orbitals during coordination.

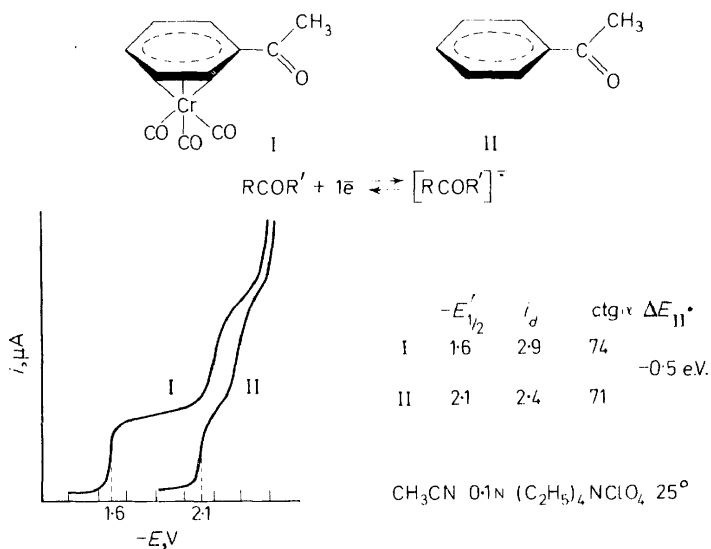


Figure 14

Transition metal quinone complexes are very convenient for investigating the electronic charge transfer from metal to ligand. As shown by Schrauzer<sup>42</sup>, only duroquinone gives stable metallic complexes (Figure 15). All other quinones result in an electron transfer process proceeding to its logical end:

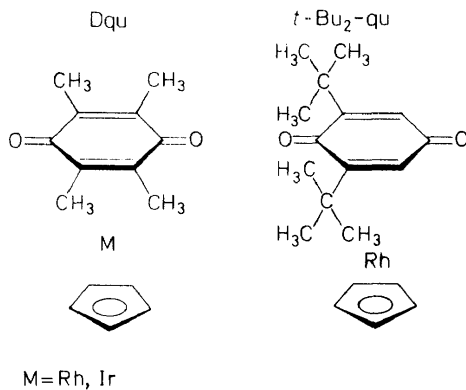


Figure 15

they oxidize metal and produce paramagnetic salts. It may be thus assumed that in the rhodium and iridium complexes of duroquinone there occurs a very marked electron transfer from metal to ligand during coordination. The rhodium and iridium complexes were found to reduce at the dropping mercury electrode. Similar investigations showed that, under the conditions there is no difference between the reduction of coordinated and non-coordinated quinones. Except for the values of the reduction potentials, all other wave characteristics are completely identical. For example, Figure 16

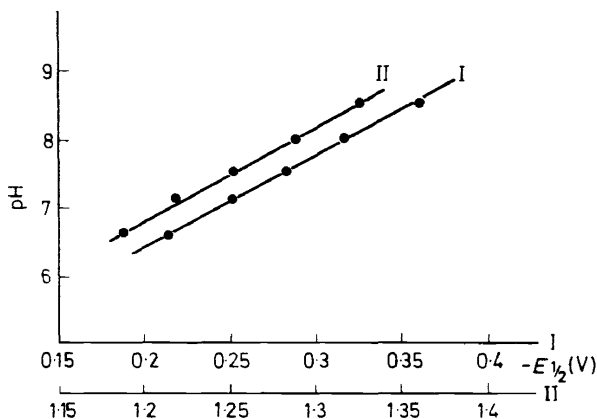


Figure 16. Dependence of  $E_4$  on pH for coordinated II and non-coordinated quinones (phosphate buffer-ethanol, 1:1)


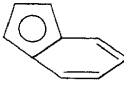
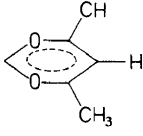
shows practically identical plots for the dependence of  $E_4$  on pH of the medium for coordinated and non-coordinated duroquinones. This led to the conclusion that electron changes are localized in a coordinated ligand. According to the Vlček method<sup>36</sup> mentioned above, estimation of the mixing

coefficient gives the value 0.82, i.e. there is about 80 per cent of the coordinated duroquinone orbital in a molecular orbital responsible for the electron changes (Figure 17). From these experiments the coordination with the M—C<sub>5</sub>H<sub>5</sub> group (M = Rh or Ir) was shown to increase the energy of the lowest vacant quinone orbital by about 1 eV<sup>43</sup>. The donor properties of other ligands combined with the metal undoubtedly considerably influence the charge transfer from ligand to metal. In a series of ligands investigated  $\pi$ -cyclopentadienyl behaves as the strongest electron releaser (Figure 18).

	$Q + 1e \rightleftharpoons Q^+ + H^+ \rightarrow QH^+$	I
	$QH^+ + 1e \rightleftharpoons QH^+ + H^+ \rightarrow QH_2$	II
	$-E_{1/2}^I$	$-E_{1/2}^{II}$
Dqu	0.87	1.39
Dqu Rh C <sub>5</sub> H <sub>5</sub>	1.76	2.03
Dqu Ir C <sub>5</sub> H <sub>5</sub>	1.99	
<i>t</i> -Bu <sub>2</sub> -qu	0.76	1.47
<i>t</i> -Bu <sub>2</sub> -qu RhC <sub>5</sub> H <sub>5</sub>	1.67	1.99

CH<sub>3</sub>CN; 0.1N (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>; vs SCE

Figure 17

D qu Rh L		
L	$-E'_{1/2}$	$-E''_{1/2}$
	√ vs SCE	
	1.76	2.03
	1.36	1.81
	1.2	1.71

CH<sub>3</sub>CN; 0.1 N (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>

Figure 18

Thus the characteristic features of oxidation–reduction reactions involving electron changes on the  $\pi$ -bonded ligand orbitals are a dependence on the protons of the medium and identity of the reduction wave characteristics for coordinated and non-coordinated ligands.

### LOCALIZATION OF ELECTRON CHANGES ON THE ANTIBONDING ORBITALS OF $\sigma$ -BONDS

The discussion above has been concerned with electrochemically reversible processes. In the structural correlations of the irreversible wave potentials,

account should be taken of the additional limitations described by Vlček<sup>36</sup>. Invariance of a transfer coefficient for a series of structurally similar complexes is an obligatory condition for such correlations. Experiment shows that when  $\pi$ -complexes contain localized  $\sigma$ -bonds the reduction involves a  $\sigma$ -bond alone, while the  $\pi$ - and donor-acceptor bonds do not reduce. This can be observed when the metal has either a closed electron shell or some vacant orbitals. A conclusion important for an understanding of the electronic structure of complexes may be drawn from the results available: the  $\sigma$ -antibonding orbital is the lowest vacant one responsible for electron changes during the reduction. Addition of electrons to this orbital causes a cleavage of the  $\sigma$ -bond. The polarographic reduction of the different types of the metal-halogen and metal-carbon  $\sigma$ -bonds can now be discussed in more detail (Figures 19 and 20). Reduction of compounds containing a metal-metal  $\sigma$ -bond was described in detail in the studies of Professor Dessy<sup>44</sup>.

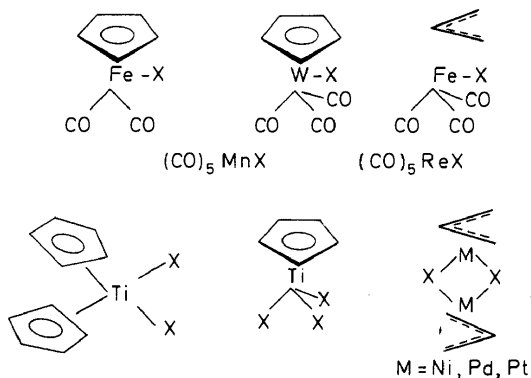


Figure 19

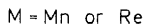
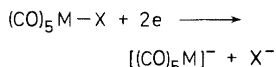
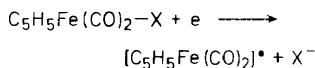


Figure 20

Results of polarographic reduction of compounds containing the metal-halogen  $\sigma$ -bond are shown in Figure 21. These compounds may be separated into two groups: complexes with a closed metal electron shell having the structure of a distorted octahedron, and the complexes in which the number of metal electrons does not attain that of the nearest inert gas.

In complexes of the first type the metal-halogen bonding is covalent without an essential  $\pi$ -contribution. It does not enter into nucleophilic exchange reactions nor dissociate in solution. Depending on the structure



of the complex its reduction involves either a single two-electron stage or a one-electron first stage (Figure 21). The stabilities of organometallic radicals generated at the first stage of the halide reduction usually differ. The radical  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3^{\bullet}$  is stable<sup>45</sup> displaying a signal in an e.s.r. spectrum (Figure 22).

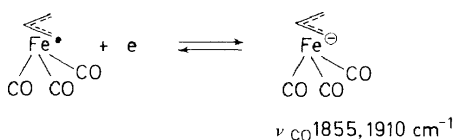
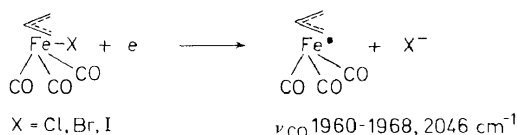


Figure 21

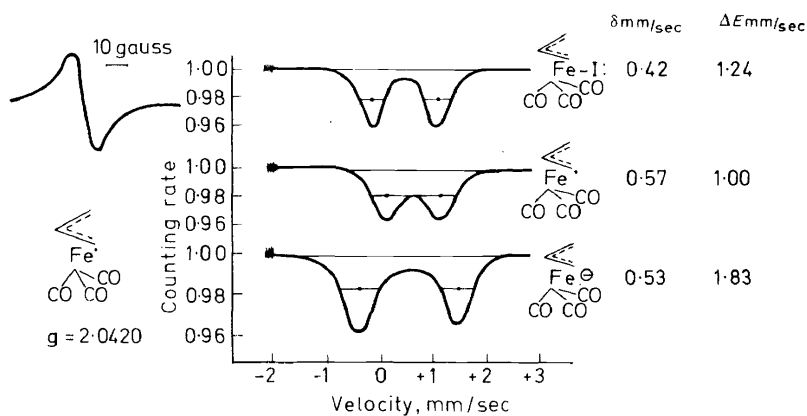


Figure 22

According to Murdoch<sup>46</sup>, this spin should be localized at the metal atom. At the potential of the second wave this radical is reduced reversibly to the anion  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3^-$ . On the contrary, the radicals  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{\bullet}$ <sup>47</sup> and  $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3^{\bullet}$ <sup>48</sup> give no signal in the e.s.r. spectrum. At the limiting current of the first wave potential these radicals react rapidly with the mercury electrode giving rise to symmetrical mercury compounds (Figure 23). There is as yet no explanation for the different stabilities of the radicals.

A characteristic feature of these compounds is the order observed in the reduction of the transition metal-halogen bond (Figure 24). This order resembles that found for the carbon-halogen bond reduction and is opposite to the increase of halogen electronegativities which determine the bond

polarity. Such behaviour may be associated with a homolytic activation of the depolarizer in the field of the electrode, while ease of bond cleavage depends not on polarity but on the stability of the anion being generated.

Quantum mechanical calculations<sup>49</sup> for the  $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  molecule show that the titanium atom has a low substantially vacant orbital. Interpretation of dependence observed for the nucleophilic halogen exchange in

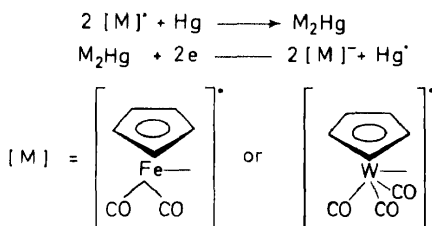


Figure 23

$\text{CH}_3\text{CN}, 0.1 \text{ N } (\text{C}_2\text{H}_5)_4 \text{ N ClO}_4, c=1 \times 10^{-3} \text{ M, SCE}$

	$\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Fe-X}$	$\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe-X}$	$(\text{CO})_5\text{Re-X}$
-X	$-E_{1/2}$	$-E_{1/2}$	$-E_{1/2}$
-Cl	0.44	0.77	1.50
-Br	0.39	0.66	1.46
-I	0.37	0.54	1.24
-X	$-E_{1/2}\text{C}_6\text{H}_5\text{-X}$		Dkcal/mole
-Cl	2.64		80
-Br	2.35		67
-I	1.73		51

Figure 24

$\text{Cp}_2\text{TiX}_2$  assumes that the titanium atom may increase its coordination number by attracting electrons from a nucleophile to this orbital<sup>50</sup>. This is entirely consistent with the substantially different dependence of polarographic behaviour of cyclopentadienyltitanium halides and closed shell metal halides<sup>51</sup>. In all cases the reduction of  $(\pi\text{-C}_5\text{H}_5)_2\text{TiX}_2$  was complicated by hydrolysis, complexation, and specific solvation or mercury dissolving at the anode (Figure 25). In this respect the reduction of cyclopentadienyl titanium halides resembles that of organomercury halides (Figure 26). Detailed study of titanium halides under varied conditions<sup>51</sup> has shown that the essential differences in the reduction mechanisms of  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{CpTiCl}_3$  and  $\text{TiCl}_4$  may only be seen at the last stages of reduction, involving the generation of halogen-free particles. Successive substitution of the chlorines in the  $\text{TiCl}_4$ -molecule introduces no significant change in the

polarographic reduction of the remaining Ti—Cl bonds, neither as regards their readiness to undergo reduction, nor as regards the stability of the intermediates being generated.

Stable transition metal—carbon localized  $\sigma$ -bonds occur in the complexes

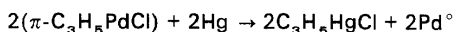
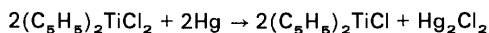


Figure 25

0.1N (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NClO <sub>4</sub> DMF c = 2 × 10 <sup>-3</sup> M		-E <sub>1/2</sub> V	i <sub>d</sub> μA
Cp <sub>2</sub> TiX <sub>2</sub> + e	→ Cp <sub>2</sub> TiX + X <sup>-</sup>	0.63	1.1
Cp <sub>2</sub> TiX + e	→ [Cp <sub>2</sub> Ti] + X <sup>-</sup>	1.94	1.5
CpTiCl <sub>3</sub> + e	→ CpTiCl <sub>2</sub> + Cl <sup>-</sup>	0.87	1.2
CpTiCl <sub>2</sub> + e	→ [CpTiCl] + Cl <sup>-</sup>	1.60	1.4
[CpTiCl] + e	→ [CpTi] + Cl <sup>-</sup>	2.04	1.0
TiCl <sub>4</sub> + e	→ TiCl <sub>3</sub> + Cl <sup>-</sup>	0.73	1.0
TiCl <sub>3</sub> + e	→ TiCl <sub>2</sub> + Cl <sup>-</sup>	1.58	1.2
TiCl <sub>2</sub> + 2e	→ Ti <sup>0</sup> + 2Cl <sup>-</sup>	2.34	2.6

Figure 26

which also contain stabilizing ligands, such as carbonyl, phosphine, cyanide,  $\pi$ -cyclopentadienyl and other groups. A qualitative discussion of bonds in such complexes was given by Chatt and Shaw<sup>52</sup>. It is accepted that both the thermodynamic and the oxidative stabilities of the complexes containing such a  $\sigma$ -bond increase with its *s*-character in going from *sp*<sup>3</sup> to *sp*<sup>2</sup> hybridization of the carbon atom. At the same hybridization these stabilities are enhanced with the electronegativity of a  $\sigma$ -bonded radical. Synthetic methods and properties of compounds containing the metal—carbon  $\sigma$ -bonds are described in ref. 53.

All the compounds investigated containing localized metal—carbon  $\sigma$ -bonding reduce at the dropping mercury electrode via a single irreversible stage. This involves addition of one or two electrons and cleavage of this bond. In the majority of cases the reduction occurs at a more negative potential than that of the metal—metal and metal—halogen bonds (Figure 27). The reaction products usually consist of the stable eighteen-electron metal carbonyl anion and a radical R<sup>•</sup> (at *n* = 1) or carbanion R<sup>-</sup> (at *n* = 2). Irreversibility of the metal—carbon bond cleavage can be explained by a high reactivity of the primary reaction products—radical or carbanion; their

transformations are shown in *Figure 28*. The final organic reaction products may be identified by gas chromatography and other methods.

A study of the effect of substituent in the phenyl ring on the reduction of the compounds  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\sigma\text{-C}_6\text{H}_4\text{Xp}$  supported the suggestion of a homolytic activation of the metal-carbon  $\sigma$ -bond<sup>47</sup> in the field of the electrode (*Figure 29*).

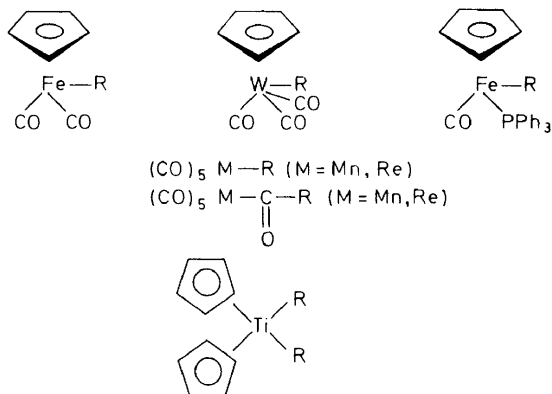


Figure 27

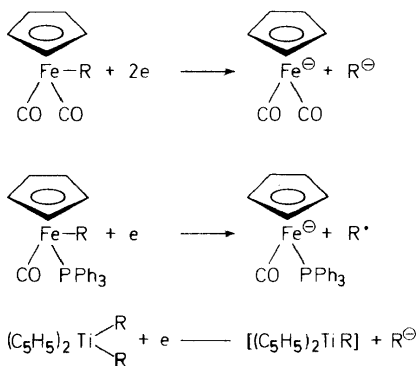


Figure 28

The nature of the radical attached to the metal substantially influences the magnitude of the potential necessary for a cleavage of the metal-carbon bond. The order of radicals indicating the ease of reduction of the metal-carbon bond was shown to be the same for a series of complexes. Thus, the bond polarity is not decisive in determining the potential changes. A homolytic activation of the metal-carbon  $\sigma$ -bond in the field of the electrode takes place in a transition state. Thus, with the same organometallic radical the rate of bond cleavage should depend on the stability of the carbanion being generated. This explains the good linear correlation between halfwave

APPLICATION OF ELECTROCHEMICAL METHODS

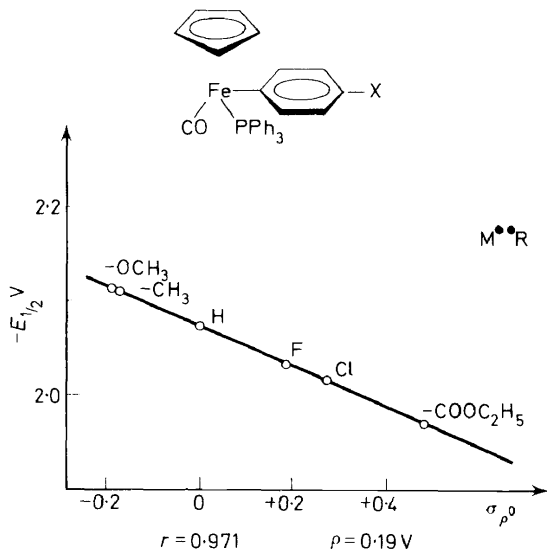


Figure 29

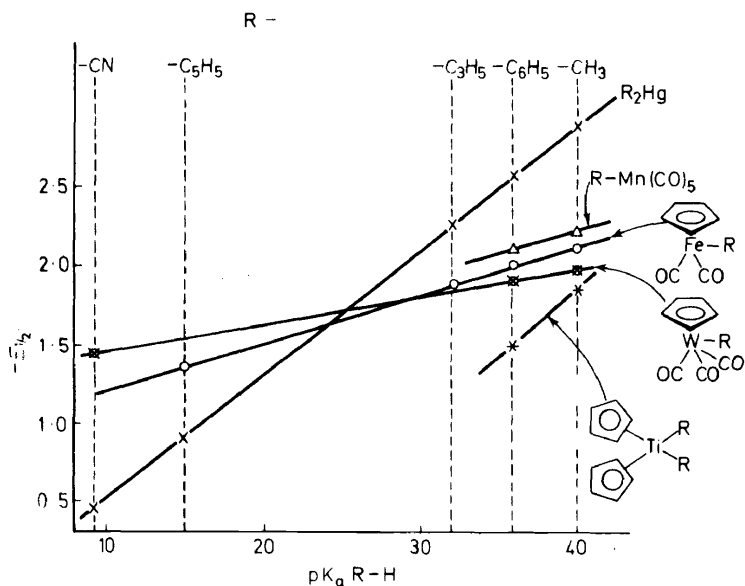


Figure 30

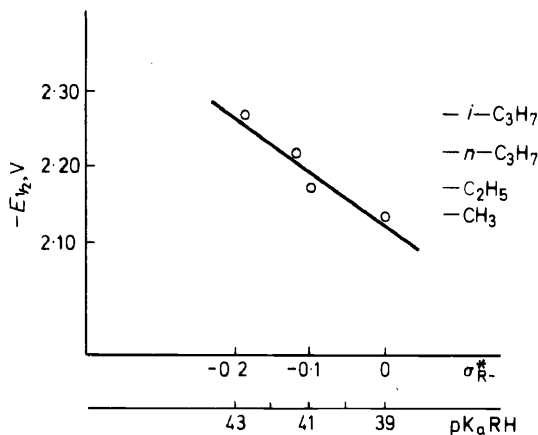
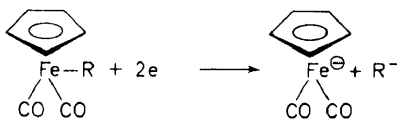
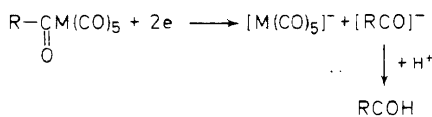


Figure 31

potentials and  $pK_a$ s of R—H, being a measure of the respective carbanion stabilities. Analogous dependences were earlier observed in the polarographic reduction (Figure 30) of symmetrical and unsymmetrical organomercury compounds containing the same radicals<sup>54</sup>. The nature of the organic radical substantially influences the reduction potential (Figure 31) while the nature of a metal-containing particle has only a very small effect on the ease of reduction of a  $\sigma$ -bond in complexes with a closed metal electron shell. It seems surprising since Dessy showed the essentially different nucleophilicities of the metal-containing anions<sup>55</sup>.



M = Mn; Re

R =  $\text{CH}_3$ ;  $\text{C}_6\text{H}_5$ ;  $-\text{C}_6\text{H}_4-\text{Cl}$  *o, m, p*; $-\text{C}_6\text{H}_4-\text{CH}_3$  *o, p*;  $-\text{C}_6\text{H}_4-\text{OCH}_3$  *p*

$-E_{1/2}$ V	$\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$ 2.09	$\text{C}_6\text{H}_5\text{Re}(\text{CO})_5$ 2.01
$-E_{1/2}$ V	$\text{C}_6\text{H}_5\text{C}(\text{O})-\text{Mn}(\text{CO})_5$ 1.75	$\text{C}_6\text{H}_5\text{C}(\text{O})-\text{Re}(\text{CO})_5$ 1.85

Figure 32

Reduction of acyl-manganese and-rhenium carbonyl derivatives was found to involve the same mechanism as that of all the other compounds with a metal-carbon  $\sigma$ -bond. The metalcarbonyl anion and the corresponding aldehyde were revealed in the reaction products (Figure 32). Hence the electron changes in the reduction of these compounds is again localized on the antibonding  $\sigma$ -orbital of the metal-carbon bond leading to its cleavage.

Thus, three principal types of electron change localization can be recognized in the reduction of transition metal  $\pi$ -complexes. The following main procedures are suggested for defining the region of electron changes:

- (1) determination of the primary electrochemical reaction products,
- (2) study of the structures and properties of the primary electrochemical reaction products, in particular their electron density distribution compared with that of the starting compounds,
- (3) comparison of the oxidation-reduction potentials for a series of structurally similar ligands and their complexes (Vlček method),
- (4) study of the ligand substituent effects,
- (5) study of the effects of solvent, pH of medium, the addition of proton donors to aprotic solvents, etc., on the properties of the observed reduction waves.

The empirical dependences of the electron density change in  $\pi$ -complexes, and the electronic properties of a transition metal  $\pi$ -ligand bond thus established may provide, along with other physicochemical data, a basis for quantum chemical calculations and for advancing a quantitative theory of the transition metal  $\pi$ -ligand bond.

### ACKNOWLEDGEMENT

This work was carried out under the leadership of Professor A. N. Nesmeyanov. Dr L. I. Denisovich, Mrs V. S. Khandkarova and S. A. Smirnova participated in these studies.

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