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Electrochemical activation of reactions involving organometallic compounds

T V Magdesieva, K P Butin

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Abstract. Data on the electrochemical activation of various reactions involving organometallic compounds are generalised. Primary attention is devoted to the key types of transformation that can be performed using electrochemical electron transfer, namely, redox activation of 16- and 18-electron complexes of transition metals as the first step of a broad range of reactions, electrocatalysis, mediator processes, and electrosynthesis of compounds containing carbon – metal σ-bonds. The bibliography includes 188 references.

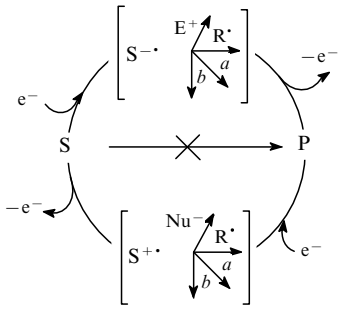
I. Introduction

The problem of increasing the reactivity of compounds arose as soon as chemists became engaged in targeted synthesis. Numerous methods for the increase in the reactivity are currently known, ranging from simple methods (introduction of an appropriate substituent into the molecule) to more complex ones that have become classical (for example, catalysis) and, finally, to the most advanced techniques (in particular, photochemically or electrochemically induced electron transfer). Figure 1 presents classification of the activation processes proposed by Chanon.[1] The diagram axis can be continued without limit because new ways of solving this problem would certainly appear with the progress of science.

Activation through electron transfer is rather effective. In this case, very high process selectivity can be attained because it is possible to specify precisely the potential needed for the generation of a particular active species.

The transformation of a molecule into a reactive radical cation or radical anion (Scheme 1) initiates a wide range of chemical reactions. This is due to the following factors: (1) usually, charged species react with nucleophiles or electrophiles more readily than neutral molecules; (2) the presence of the unpaired electron activates homolytic reaction pathways; (3) further redox processes, disproportionation and so on are also possible.

Scheme 1



S is the substrate, Nu is the nucleophile, E is the electrophile, P is the product; *a* is a redox reaction; *b* is dissociation, *etc*.

Activation of reactions through electron transfer was first employed by Taube [2] and Basolo and Pearson [3–6] for inorganic systems. In organic chemistry, the development of this line of research was triggered by Kornblum's discovery [7,8] of radical nucleophilic substitution ($S_{RN}1$) the mechanism of which has been later studied in detail by Bunnett [9] and Russel.[10,11] Saveant [12] was the first to use electrochemical electron transfer for the activation of organic reactions. Since then, the French electrochemical

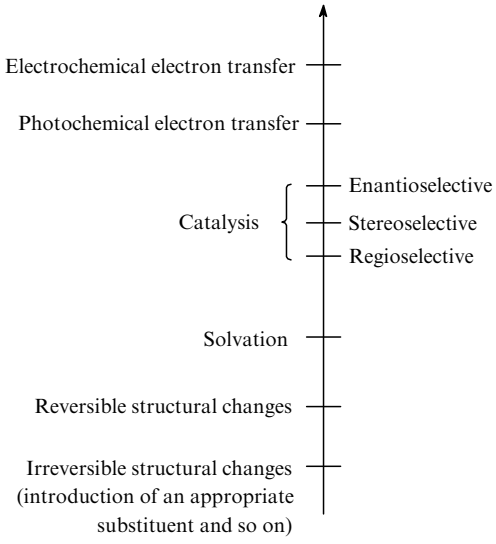


Figure 1. Multilevel diagram of the activation methods of reactions.[1]

T V Magdesieva, K P Butin Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax (7-095) 939 55 46. Tel. (7-095) 939 30 65.
E-mail: tvm@org.chem.msu.ru (T V Magdesieva), butin@org.chem.msu.ru (K P Butin).

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school has held a leading position in the research along this line. A great number of examples in which diverse organic reactions are activated by electrochemical electron transfer have been reported (see, for example, Refs 1, 13).

The intense use of electrochemical electron transfer in reactions involving organometallic compounds started approximately in the early 1980s. Most of the transition metal π-complexes are able to undergo reversible electrochemical redox transitions to give active species with odd numbers of electrons; therefore, electrochemically induced electron transfer can be used efficiently to facilitate ligand exchange, isomerisation, insertion and other reactions.[14–19]

It is of interest to compare the behaviours of mononuclear metal complexes and supramolecular species containing these complexes as structural units.[20] Systems of this type are able to undergo electrochemically induced reversible structural changes, and they can be regarded as prototypes of 'molecular machines.' In this case, the electron transfer involving one structural unit entails changes over the whole supramolecular system (for example, electrically induced charge separation, migration of structural fragments, *etc.*).[20]

A relatively new field in the use of electrochemical electron transfer for changing the reactivity of transition metal complexes is the design of redox-switchable ligands. The introduction into the ligand of ferrocenyl, cobaltocenyl, anthraquinone or other groups prone to reversible redox transitions allows the formation of complexes with switching reactivity.[21] A change in the redox state of the 'switch' induces a change in the electronic properties of the ligand and, hence, the nature of the metal–ligand bond. This promotes various types of reaction, for example, ligand exchange. This approach appears highly promising for the design of 'redox-switchable' catalysts. Chiral metal complexes with 'redox-switchable' ligands can be used in asymmetric synthesis, for the separation of enantiomers, *etc.*[21]

Yet another extensive field of application of the electrochemical electron transfer in reactions involving organometallic compounds is electrochemical generation of labile complexes of transition metals in low oxidation states and involvement of these species in subsequent chemical transformations *in situ*, most often, as catalysts. The combination of catalysis by metal complexes with the electrochemical electron transfer has opened up almost unlimited scope for performing various mediator processes (see, for example, Refs 22–24).

Numerous examples of reactions activated by electrochemical electron transfer have now been reported in the literature. Since it is impossible to embrace them all within a single review, we intended first of all to show what types of transformations can be accomplished by virtue of the electrochemical electron transfer and how the use of electrochemical methods extends the synthetic capacity of a chemist in the field of organometallic chemistry. Primary attention has been devoted to the studies published during the last decade and not covered in earlier reviews.

II. Reactions of odd-electron complexes of transition metals

The transfer from relatively stable 16- and 18-electron configurations to 17- and 19-electron configurations of transition metal complexes can be attained *via* electrochemical oxidation or reduction. The odd-electron complexes thus formed are much more reactive; therefore, they can be involved in reactions that either do not proceed at all or proceed too slowly for complexes with 16- and 18-electron configurations. Research into the chemical transformations of odd-electron complexes has been the subject of numerous studies (see, for example, reviews [15, 18, 22]). If the transformations are classified in terms of the reaction type, the main types are ligand exchange, isomerisation, insertion, extrusion, chelation/dechelation and dimerisation.

1. Ligand exchange

Ligand exchange reactions can be initiated by both oxidation and reduction of mono- or polynuclear metal complexes.

Initiation by oxidation	Initiation by reduction
$\underset{18\,e}{ML} - e^- \rightarrow \underset{17\,e}{ML^{+\bullet}}$	$\underset{18\,e}{ML} + e^- \rightarrow \underset{19\,e}{ML^{-\bullet}}$
$\underset{17\,e}{ML^{+\bullet}} + L' \rightarrow \underset{17\,e}{M(L')^{+\bullet}} + L$	$\underset{19\,e}{ML^{-\bullet}} + L' \rightarrow \underset{19\,e}{M(L')^{-\bullet}} + L$
$\underset{17\,e}{M(L')^{+\bullet}} + \underset{18\,e}{ML} \rightarrow \underset{18\,e}{ML'} + \underset{17\,e}{ML^{+\bullet}}$	$\underset{19\,e}{M(L')^{-\bullet}} + \underset{18\,e}{ML} \rightarrow \underset{18\,e}{ML'} + \underset{19\,e}{ML^{-\bullet}}$

Upon reductive activation, an electron passes to an unoccupied orbital; this is accompanied by weakening of the M–L bond. In essence, a similar reaction takes place during oxidation, because an associative mechanism of ligand exchange including the intermediate formation of a 19-electron complex with an additional ligand has been proven for 17-electron complexes by Kochi and coworkers.[23, 25]

$$[MeCpMn(CO)_2(MeCN)]^+ + PPh_3 \longrightarrow \underset{17\,e}{[MeCpMn(CO)_2(MeCN)(PPh_3)]^+} \longrightarrow \underset{19\,e}{[MeCpMn(CO)_2(PPh_3)]^+} + MeCN \quad (17\,e)$$

Cp = C_5H_5.

A second ligand present in the solution is coordinated to the 17-electron complex to give a 19-electron intermediate (as in the case of reductive activation) in which cleavage of the M–L bond is facilitated.

A large number of examples of electrochemically activated ligand exchange have been described (see, for example, the reviews [15–18, 26] and the monographs [27, 28]). We shall dwell only on some publications that appeared during the last three to four years.

An interesting example of replacement of the arene ligand in binuclear fulvalene (Fv) complexes of iron has been reported.[29] The doubly reduced 38-electron complex readily reacts with CO or with different phosphine ligands.

$$[Fe_2(\mu^2\text{-}\eta^5\text{:}\eta^5\text{-Fv})(C_6H_6)_2](PF_6)_2 \xrightarrow[-2\,PF_6^-]{2\,e^-} Fe_2(\mu^2\text{-}\eta^5\text{:}\eta^5\text{-Fv})(C_6H_6)_2 \longrightarrow \begin{cases} \xrightarrow{PMe_3} Fe_2(\mu^2\text{-}\eta^5\text{:}\eta^5\text{-Fv})(PMe_3)_4 \\ \xrightarrow[-15\ ^\circ C,\ 1\ atm]{CO} Fe_2(\mu^2\text{-}\eta^4\text{:}\eta^4\text{-Fv})(CO)_6 \end{cases}$$

Preparative electrolysis of the fluorenyl complex of cobalt (at a potential of −2.56 V *vs.* Fc/Fc^+, where Fc is ferrocene) in the presence of various phosphine or phosphite ligands also results in ligand exchange.[30]

$$CpCo(PPh_3)(C_{13}H_9) \xrightarrow{e^-} [CpCo(PPh_3)(C_{13}H_9)]^{-\bullet} \xrightarrow[-PPh_3]{P(OMe)_3} \{CpCo[P(OMe)_3](C_{13}H_9)\}^{-\bullet} \xrightarrow[-e^-]{} CpCo[P(OMe)_3](C_{13}H_9).$$

An unusual ligand exchange in the metal coordination sphere accomplished by virtue of a 'redox switch' connected to the reaction centre of the molecule has been reported.[31] The role of the 'redox switch' is played by a ferrocenyl fragment linked by a covalent bond to the arene ligand of the chromiumtricarbonyl complex. Since the ferrocene fragment is oxidised first, the reaction takes place at an anodic overpotential substantially lower than that required for oxidation of the chromiumtricarbonyl group. Thus the partial destruction of the complex is avoided and the process selectivity is increased. Although the

chromium atom has formally an 18-electron configuration, the adjacency of the strong electron acceptor results in easy replacement of the carbonyl group by a phosphorus-containing ligand.

$$(C_6H_5Fc)Cr(CO)_3 + P(OEt)_3 \xrightarrow[-e^-]{} [(C_6H_5Fc)Cr(CO)_2P(OEt)_3]^+ + CO.$$

The subsequent transfer of an electron from the Cr atom to the Fe atom turns off the 'redox switch'. Upon further displacement of the potential to the anodic region, the 'redox switch' is actuated once more, the Cr atom is activated again, and the reaction gives a purple complex, which was isolated.

$$[(C_6H_5Fc)Cr(CO)_2P(OEt)_3]^+ + P(OEt)_3 \xrightarrow[-e^-]{} \{(C_6H_5Fc)Cr(CO)_2[P(OEt)_3]_2\}^{2+}.$$

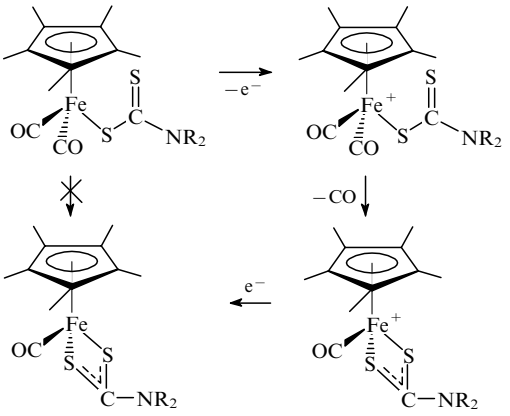
Electrochemical cleavage of the metal–halogen covalent bond with subsequent replacement of the halogen atom by another ligand has been described in detail.[32] Upon single-electron reduction of the rhenium complex with diphenylposphinoethane (dppe) $[ReCl_2(dppe)_2]^+$ [the $Re(d^4) \rightarrow Re(d^5)$ transition], the Re–Cl bond length increases by 0.1 Å; the transfer of one more electron induces cleavage of this bond, and another ligand present in the solution enters the coordination sphere of the metal.

$$[Re(dppe)_2Cl_2]^+ \overset{e^-}{\rightleftharpoons} Re(dppe)_2Cl_2 \overset{e^-}{\rightleftharpoons} [Re(dppe)_2Cl_2]^- \xrightarrow[-Cl^-]{} Re(dppe)_2Cl \xrightarrow{L} Re(dppe)_2Cl(L)$$

L = Bu^tCN.

Oxidation of the central metal atom in the complex results in strengthening of bonds with σ-donor ligands (ammonia, amines, pyridine, *etc.*) and weakening of bonds with π-acceptor ligands (CO, nitriles, cyanides, *etc.*); this stipulates the required type of electrochemical activation (cathodic or anodic) in each particular case.

Actually, chelation/dechelation reactions can also be classified as ligand exchange. Some organic groups, for example, the dithiocarbamate group, act as chelating ligands in the coordination sphere of unsaturated complexes. However, they can also occur in the metal coordination sphere as monodentate ligands. It was shown[33] that the monodentate dithiocarbamate ligand can be readily converted into a chelating ligand upon oxidative activation.

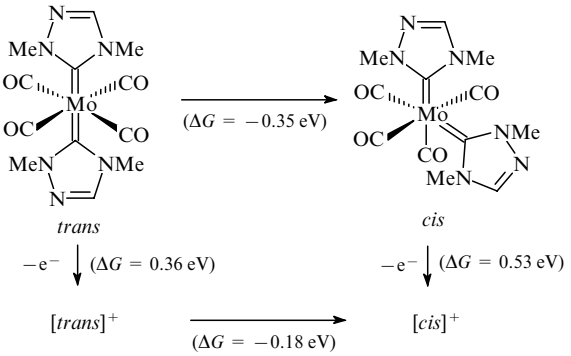


In principle, the inverse problem can also be solved. If it is required to change electrochemically the oxidation state of the central metal atom in a complex but to avoid ligand exchange or coordination of additional ligands, it is expedient to use a so-called cage ligand.[20] For example, oxidation of 1,10-phenanthroline complexes of Cu(I) is irreversible because it is accompanied by a structural rearrangement with coordination of solvent molecules to the copper atom giving rise to an octahedral geometry typical of Cu(II) complexes. If 2,9-dimethyl-1,10-phenanthroline is used as the ligand instead of 1,10-phenanthroline, the oxidation of the Cu(I) complex is completely reversible because the presence of substituents at the α-position relative to nitrogen prevents the coordination of solvent molecules to the metal and, hence, the geometry does not change.[34]

2. Isomerisation

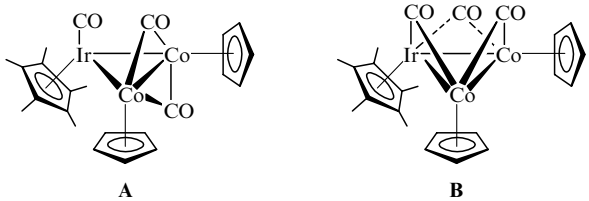
When considering the electrochemically activated isomerisation of transition metal complexes, one can distinguish three main types of transformations encountered most often, namely, *cis–trans* isomerisation, change in the hapto-coordination of aromatic π-ligands to the metal in various sandwich and half-sandwich structures and metal migration in complexes with polydentate aromatic ligands.

The first example of electrochemically activated *cis–trans* isomerisation was described by Rieke *et al.*[35] The reaction follows the scheme



Since then, numerous examples of both cathodically and anodically activated *cis–trans* isomerisations have been reported.[27] In particular, the rate constants for anodic isomerisation of the thiolate isocyanate complexes *cis*-$[M(SC_6H_2Pr^i_3\text{-}2,4,6)_2(NCR)_4]$ (M = Mo, W; R = Me, Bu^t) have been calculated from the data of cyclic voltammetry.[36]

Isomerisation can be accompanied by a change in the type of metal bonding to the ligand: the terminal ligand passes to a bridging position or *vice versa*. For example, the 48-electron cluster $Cp^*IrCp_2Co_2(CO)_3$ ($Cp^* = C_5Me_5$) can exist as two isomers, one containing a terminal and two bridging carbonyl groups (**A**) and one with three bridging CO ligands (**B**), the second isomer being thermodynamically more stable.



The rate of isomerisation depends appreciably on the number of electrons in the cluster [37] and varies in the following sequence: 48 e ≪ 49 e < 47 e (the ratio of the corresponding rate constants is 1 : 104 : 108). Thus, anodic activation is the most efficient.

Anodically activated isomerisation of diene ligands, for example, cyclooctadiene (cod), is known.[38]

$$(C_5Ph_5)Rh(1,3\text{-cod}) \xrightarrow[-e^-]{} [(C_5Ph_5)Rh(1,3\text{-cod})]^+ \longrightarrow [(C_5Ph_5)Rh(1,5\text{-cod})]^+ \xrightarrow{e^-} (C_5Ph_5)Rh(1,5\text{-cod}).$$

The trimetallic carbonyl clusters $M_3(CO)_7(dppm)(tolan)$ (M = Os, Ru; dppm is diphenylposphinomethane; tolan is diphenylacetylene) can also exist as two isomers which differ in the position of the alkyne ligand with respect to the triangle formed by the metal atoms.[39] The interconversion of the two isomers can be performed through electrochemical redox isomerisation because one of them is more stable in the reduced form and the other one, in the oxidised form.

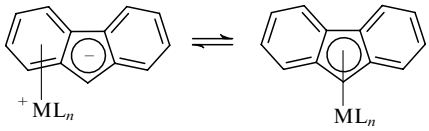
Numerous examples of the change in the type of hapto-coordination of the π-ligand to the metal atom induced by electrochemical electron transfer are known. For example, two-electron oxidation of a trinuclear ruthenium complex induces haptotropic isomerisation giving rise to an unusual μ^3-η^3:η^3-coordination of the benzene ring.[40,41]

$$(Cp^*Ru)_3(\mu\text{-}H)_3(\mu^3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6) \xrightarrow{-2e^-} [(Cp^*Ru)_3(\mu\text{-}H)_3(\mu^3\text{-}\eta^3\text{:}\eta^3\text{-}C_6H_6)]^{2+}.$$

The structure of the resulting complex was confirmed by X-ray diffraction data.

The change in the hapto-coordination upon oxidative or reductive electrochemical activation has also been reported for indenyl, cyclopentadienyl and some other aromatic ligands [41] (see also the review [26] and references therein).

Of special interest are redox-induced reactions of complexes with polydentate ligands having, at least, two possible sites of coordination to the metal. In this case, redox switching of the metal from one coordination site to the other has been observed.[26]



ML_n = FeCp, FeCp*, $Mn(CO)_3$, $Cr(CO)_3^-$.

The ring–ring haptotropic isomerisation of 18-electron fluorenyl complexes with the d^6 metal configuration proceeds very slowly even at high temperatures, and the equilibrium is shifted towards the η^5-isomer. In the case of 19-electron complexes, isomerisation rapidly takes place at −80 °C, the equilibrium being shifted towards the η^6-isomer:

$$(\eta^6\text{-}C_{13}H_9)FeCp \overset{e^-}{\rightleftharpoons} [(\eta^6\text{-}C_{13}H_9)FeCp]^{-\bullet} \rightleftharpoons [(\eta^5\text{-}C_{13}H_9)FeCp]^{-\bullet} \overset{-e^-}{\rightleftharpoons} (\eta^5\text{-}C_{13}H_9)FeCp.$$

Detailed analysis of the mechanism of ring–ring haptotropic tautomerism and a survey of published examples of these processes have been reported.[26]

3. Insertion and extrusion

The electrochemical migrational insertion of a carbonyl group into the Fe–C(sp^3) bond can be used to synthesise the corresponding acyl complexes; this reaction is carried out with either reductive [42] or oxidative [43] activation.

$$CpFe(CO)_2Me \xrightarrow{e^-} [CpFe(CO)_2Me]^{-\bullet} \xrightarrow{PPh_3} [CpFe(CO)(COMe)PPh_3]^{-\bullet} \xrightarrow{-e^-} CpFe(CO)(COMe)PPh_3;$$

$$CpFe(CO)(PPh_3)Me \xrightarrow{-e^-} [CpFe(CO)(PPh_3)Me]^{+\bullet} \xrightarrow{MeCN} [CpFe(CO)(PPh_3)(MeCN)Me]^{+\bullet} \longrightarrow [CpFe(PPh_3)(MeCN)(COMe)]^{+\bullet} \xrightarrow{e^-} CpFe(PPh_3)(MeCN)(COMe).$$

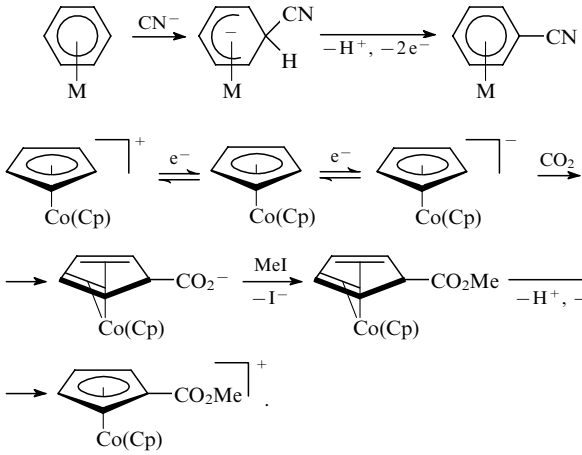
If both anodic and cathodic types of activation are possible, one should prefer the method for which the ratio of the currents of the inverse and forward electrochemical processes (I_{inv}/I_{for}) in the cyclic voltammogram of the product is closer to unity, *i.e.*, a classical electrochemically reversible process should be the method of choice.[15]

The Kochi cathodic activation has provided the possibility of the back reaction, *i.e.*, CO extrusion from formyl metal complexes.[44]

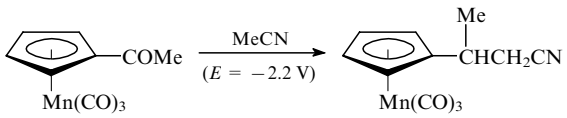
$$[(CO)_5ReRe(CO)_4(CHO)]^- \xrightarrow[-CO\ (E\,=\,-2.1\,V)]{e^-} [(CO)_5ReRe(CO)_4H]^{2-} \xrightarrow{-e^-} [(CO)_5ReRe(CO)_4H]^-.$$

4. Electrochemically activated reactions in the ligand sphere of the metal

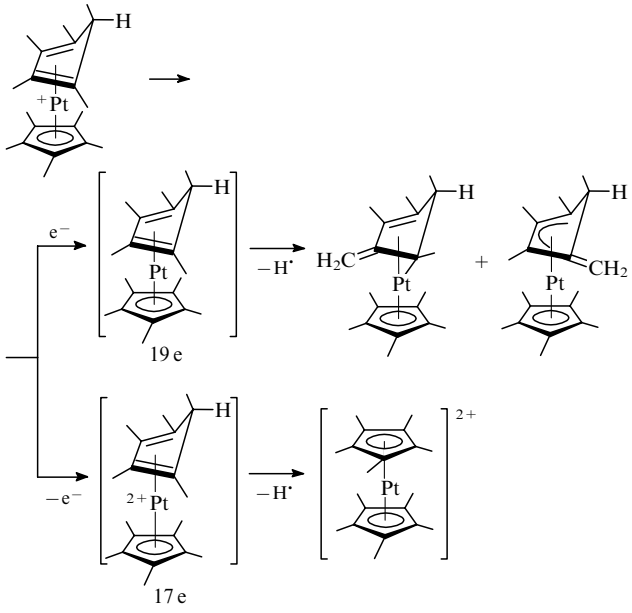
Transition metal complexes tend to undergo reactions accompanied by electrochemical activation of π-bonded ligands, resulting in ligand modification. The activation of C–H bonds followed by substitution in π-coordinated aromatic ligands provides an example.[45]



Examples of reactions of this type can also be found in Walder's monograph.[28] A convenient method for building-up the hydrocarbon side chain during electrochemical reduction of acetyl derivatives of ferrocene, cymanthrene and benzenetricarbonylchromium has been proposed.[46]



Of recent publications devoted to this topic, a study by Gusev *et al.*[47] deserves attention. The researchers identified the main regularities of the redox-induced activation of the C–H bonds in Pd and Pt η^4-pentamethylcyclopentadiene complexes. Single-electron oxidation of these compounds proceeds selectively as homolysis of the C–H bond at the sp^3-hybridised carbon atom of



the Cp ring, while its single-electron reduction results in activation of the C–H bonds of the methyl groups.

Dimerisation of organometallic radicals according to the 'ligand–ligand' type can also be regarded as a reaction in the ligand sphere of the metal. Reductive dimerisation of the $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ cationic complex, resulting in the formation of a new C–C bond, is an example.[48]

$$[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+ \longrightarrow$$

$$\xrightarrow{e^-} 0.5\,[Mn(CO)_3]_2\text{-}\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_6H_6-C_6H_6 \quad (83\%)$$

$$\xrightarrow{2e^-} 0.5\,\{[Mn(CO)_3]_2\text{-}\mu\text{-}\eta^4\text{:}\eta^4\text{-}C_6H_6-C_6H_6\}^{2-} \quad (49\%)$$

Dimerisation giving a new C–C bond in the ligand sphere of a metal was observed in a two-electron reduction of sandwich iridium complexes.[49]

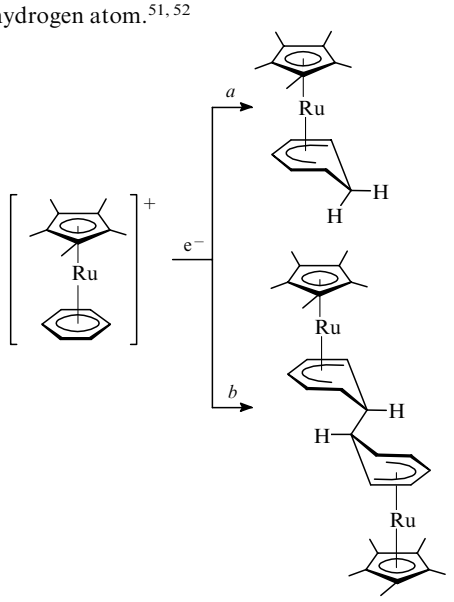
$$2\,[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_5Me_5)]^+ \xrightarrow{2e^-}$$

$$\longrightarrow (\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}\eta^4\text{:}\eta^4\text{-}C_5Me_5\text{—}C_5Me_5)Ir(\eta^5\text{-}C_5Me_5).$$

A similar approach has been used to prepare 'molecular wires' consisting of polyyne chains with ferrocenyl and ruthenocenyl groups at the ends.[50]

In solutions, 19-electron arenecyclopentadienylruthenium radicals either undergo dimerisation involving the six-membered ring (Scheme 2, pathway *b*) or capture a hydrogen atom from the reaction medium (Scheme 2, pathway *a*). It was found that a decrease in the electron-donating capacity of ligands or an increase in the ligand bulk enhances the stability of radicals and dimerisation becomes the preferential process over the addition of a hydrogen atom.[51, 52]

Scheme 2



5. Disproportionation

Disproportionation can also take place with intermediate formation of 19-electron complexes. For example, the $Mn_2(CO)_{10}$ dimeric complex can disproportionate in the presence of highly electron-donating nitrogen-containing tridentate ligands. This reaction is subject to both electrochemical and photochemical initiation[53]

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\,[Mn(CO)_5]^{\bullet},$$

$$[Mn(CO)_5]^{\bullet} + N_3 \longrightarrow [Mn(CO)_3N_3]^{\bullet} + 2\,CO,$$

$$[Mn(CO)_3N_3]^{\bullet} + Mn_2(CO)_{10} \longrightarrow [Mn(CO)_3N_3]^+ + [Mn_2(CO)_{10}]^{-\bullet},$$

$$[Mn_2(CO)_{10}]^{-\bullet} \longrightarrow [Mn(CO)_5]^- + [Mn(CO)_5]^{\bullet}.$$

The overall reaction is as follows:

$$Mn_2(CO)_{10} + N_3 \longrightarrow [Mn(CO)_3N_3]^+ + [Mn(CO)_5]^- + 2\,CO.$$

III. Electrocatalysis: combination of catalysis by metal complexes with electrochemically induced electron transfer

An important application of the electrochemical electron transfer in reactions involving metal complexes and proceeding *via* organometallic intermediates is electrocatalysis. This line of research has been vigorously developing during the last 15 years and combines the advantages of catalysis by metal complexes and activation through electrochemical electron transfer. When the reaction is carried out at an electrode, electron transfer does not require additional oxidants or reducing agents, and the process is highly selective. Modification of the electrode surface by metal complexes (or the addition of complexes as mediators to the solution) provides the possibility of conducting electrochemically activated reaction at a substantially lower overpotential.

The processes that combine catalysis by metal complexes with electrochemical transfer of an electron can be conventionally classified into two types. One type includes so-called mediator processes in which a complex is first reversibly reduced (or oxidised) at an electrode and then it passes the electron to an organic substrate (S) (or withdraws the electron from it in the case of oxidative activation). In this case, the electron transfer usually follows an outer-sphere mechanism, *i.e.*, no bond between the metal complex and the organic substrate is formed. The mediator electron transfer yields an active form of the organic substrate (either reduced or oxidised form), which is then converted into product (P); as this takes place, the mediator (A) is regenerated.

Reduction	Oxidation
$A + e^- \longrightarrow A^{-\bullet}$	$A - e^- \longrightarrow A^{+\bullet}$
$A^{-\bullet} + S \longrightarrow A + S^{-\bullet}$	$A^{+\bullet} + S \longrightarrow A + S^{+\bullet}$
$S^{-\bullet} \longrightarrow P^{-\bullet}$	$S^{+\bullet} \longrightarrow P^{+\bullet}$
$P^{-\bullet} - e^- \longrightarrow P$	$P^{+\bullet} + e^- \longrightarrow P$

In the second type of process, an electron transfer from the catalyst (Cat) to the organic substrate is an inner-sphere process, *i.e.*, it proceeds *via* the formation of an intermediate activated complex, decomposition and subsequent transformations of which afford product P.

Reduction	Oxidation
$Cat + e^- \longrightarrow Cat^{-\bullet}$	$Cat - e^- \longrightarrow Cat^{+\bullet}$
$Cat^{-\bullet} + S \longrightarrow CatS^{-\bullet}$	$Cat^{+\bullet} + S \longrightarrow CatS^{+\bullet}$
$CatS^{-\bullet} \longrightarrow P^{-\bullet} + Cat$	$CatS^{+\bullet} \longrightarrow P^{+\bullet} + Cat$
$P^{-\bullet} - e^- \longrightarrow P$	$P^{+\bullet} + e^- \longrightarrow P$
or	or
$P^{-\bullet} + Cat \longrightarrow P + Cat^{-\bullet}$	$P^{+\bullet} + Cat \longrightarrow P + Cat^{+\bullet}$

An advantage of mediator processes[54] is a decrease in the kinetic barrier to electrochemical reactions; the potential approaches the thermodynamic value. This is valid for processes that include a fast chemical step, $S^{+(-)} \rightarrow P^{+(-)}$. The mediator participating in these reactions should satisfy the following conditions: (1) the ability to undergo reversible oxidation or reduction; (2) $|E_m| \ll |E_s|$ (where E_m and E_s are the potentials of the mediator and substrate, respectively), the optimal potential difference is usually 0.3–0.5 V; (3) structural correspondence between the mediator and the substrate to ensure the electron transfer. The

mediator can occur in the solution or, alternatively, be chemically bound to the electrode (chemically modified electrode).

The inner-sphere electron transfer has a number of advantages over the outer-sphere process.[27]

1. The redox process does not depend on the potential difference between the mediator and the substrate; therefore, a much more pronounced decrease in the overpotential is possible.

2. The inner-sphere transfer is characterised by a lower activation barrier.

3. An outer-sphere process allows the transfer of only one electron, while in the case of the inner-sphere mechanism, transfer of two or more electrons is possible. (This is especially important for bioelectrocatalysis and for activation of small molecules.)

In real processes, the consumption of electricity is determined by the contributions of various competing reactions involving radical cations or radical anions derived from the catalyst. Moreover, apart from the classical cases in which an inner-sphere or outer-sphere mechanism of electron transfer is regarded as proven, there exist a large number of intermediate processes for which it is difficult to draw a conclusion about the nature of the transition state. In the case of metal complexes with an inner-sphere or a similar mechanism of electron transfer, the activated molecule enters the metal coordination sphere, which increases its reactivity.

Numerous examples of electrocatalytic processes involving transition metal complexes are known.[55–61] The greatest number of studies have been devoted to the activation of small molecules and to various reactions of C–C bond formation (homo- and cross-coupling, carboxylation and carbonylation, the addition to multiple bonds).

1. Electrocatalytic reduction of small molecules

A series of reviews and original papers (see, for example, the studies [22, 56–61]) have been devoted to electrocatalytic reduction of nitrogen and its oxides, carbon oxides, and molecules or ions with triple bonds (acetylene, cyanide ion). A common feature of all the above compounds is that they are electrochemically inactive and contain very strong bonds that are fairly difficult to cleave. Therefore, activation of such molecules through introducing them into the metal coordination sphere followed (or preceded) by electrochemical electron transfer is the most promising way of involving these compounds in various chemical transformations. In addition, considerable attention to electrocatalytic processes with participation of metal complexes is inspired by the idea of utilisation of the enormous reserves of N_2, CO_2 and O_2 present in the biosphere as a cheap and readily available feedstock for various chemical transformations.

Since it is impossible to cover the tremendous number of publications devoted to various processes of this type, in this review, we consider only examples of electrocatalytic binding of CO_2. These data, first, provide an idea of the main principles and features of electrocatalytic reactions and, second, they are fairly important from the practical standpoint.

Direct electroreduction of CO_2 at a metallic (for example, mercury) cathode requires a high overpotential: $E_{CO_2/CO_2^{\cdot-}} = -2.21$ V *vs.* a saturated calomel electrode (SCE) in DMF.[62] Other metallic cathodes, for example, copper or gold ones, are able to reduce CO_2 in an aqueous solution at somewhat less cathodic potentials (-1.3 to -1.7 V *vs.* SCE), but these values are also too great for practical application of this process [63, 64] because water is also reduced at these potentials with hydrogen evolution. This could be avoided by using non-aqueous solvents;[65–71] however, such a process is unfavourable due to a high energy expenditure and undesirable reduction of components present in the solution.

A lot of data on the use of transition metal complexes for the electrocatalytic reduction of CO_2 can be found in the literature (see, for example, studies [7, 58, 72, 73]). As a rule, these are complexes with nitrogen-containing macrocyclic ligands such as porphyrins and their analogues, well-known as biocatalysts. Synthetic metal complexes with nitrogen-containing macrocyclic ligands, for example, phthalocyanines (Pc) or 1,4,8,11-tetraazacyclotetradecane (cyclam) derivatives, are often not inferior to enzymes in their catalytic activity.

Metal phthalocyanines [3, 8–11, 15, 74–84] and metal porphyrins,[2, 12, 13, 19, 58, 73, 85–87] Ni(II) complexes with cyclam derivatives,[88–94] bis- and polypyridine complexes of Rh(II),[95] Re(I),[96] Cu(I),[97] Co(II), Fe(II) and Ni(II),[76, 84, 98–101] iron and cobalt complexes with the 4,5-dihydroxybenzene-1,3-disulfonate and 2-hydroxy-1-nitrosonaphthalene-3,6-disulfonate ligands [102, 103] and other complexes can serve as catalysts for CO_2 reduction.

An important advantage of using metal complexes as catalysts for the reduction of CO_2 is the possibility of changing their reactivity by modification of the macrocyclic ligand either by introducing electron-donating or -withdrawing substituents or by replacing the central metal atom.[104] Indeed, a Ni(II) complex with a cyclam analogue, 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane, exhibits a much higher catalytic activity than the unsubstituted Ni(II)(cyclam) complex.[105] Surprisingly, the introduction of σ-acceptor substituents, for example, fluorine, into the nitrogen-containing ring also increases the catalytic activity and the selectivity of CO formation (with respect to hydrogen evolution). The Ni(II) complex with 3,3,10,10-tetrafluorocyclam proved to be the most efficient. Further increase in the number of fluorine atoms at the macrocycle leads to a lower catalytic activity.[106]

The influence of the nature of the central metal atom on the catalytic efficiency of CO_2 electroreduction has been studied. In the case of metal complexes with *meso*-tetraphenylporphyrin, the highest current yield of CO was observed for Co, Fe and Zn complexes, while the catalytic activity of Ni, Cu, Mg and Mn compounds was fairly low.[19]

A wide range of monophthalocyanine complexes of various metals have been tested in the electrocatalytic reduction of CO_2 at a gas-diffusion electrode in an aqueous solution.[3, 15] The electroreduction of carbon dioxide gave CO, HCOOH and CH_4, the ratios and the current yields of which depended appreciably on the properties of the central metal atom in the phthalocyanine complex. With Group VIIIA transition metals such as Co, Ni, Fe and Pd, the reaction usually gives CO as the major product. The electrolysis of CO_2 in the presence of Sn, Pb, In and Al phthalocyanine complexes affords mainly HCOOH, and in the case of Zn phthalocyanine, approximately equal amounts of HCOOH and CO are formed. Under the action of phthalocyanine complexes of Group IIIB and IVB elements, In and Sn, formic acid is produced with the highest selectivity, and in the case of Cu, Ga and Ti, methane is formed, although in a low yield. Metal-free phthalocyanine proved to be almost inefficient in the reduction of CO_2. Thus, coordination of CO_2 to the metal atom in the complex plays an important role. The data on the use of metal phthalocyanines in reactions of CO_2 reduction (see Refs 3 and 15) are listed in Table 1.

It is of interest that the cathodic electrocatalytic activity of cobalt complexes with macrocyclic ligands increases if the Co atom is bound to the axial electron-donating ligand, for example, pyridine or imidazole.[107–109] Thus CO_2 electroreduction in water at a glass-carbon electrode coated by Co tetraphenylporphyrin with the axial pyridine ligand occurs with a high selectivity.[107]

Recently,[110] investigations of diphthalocyanine complexes as catalysts for carbon dioxide electroreduction in protic media have been started. The major reaction products were CO and HCOOH (or methyl formate if electroreduction is carried out in methanol).

It is worthy of note that the formation of a metal–CO_2 complex is postulated as the key step in almost every study devoted to the catalytic fixing of CO_2 by transition metal complexes.[3, 9, 109–114] In most cases, this is supported only by the data of IR or NMR spectroscopy because, first, the lifetime of these intermediates is short and, second, the presence of solvent molecules, also capable of coordination, hampers detailed analysis of the structure of the complex.

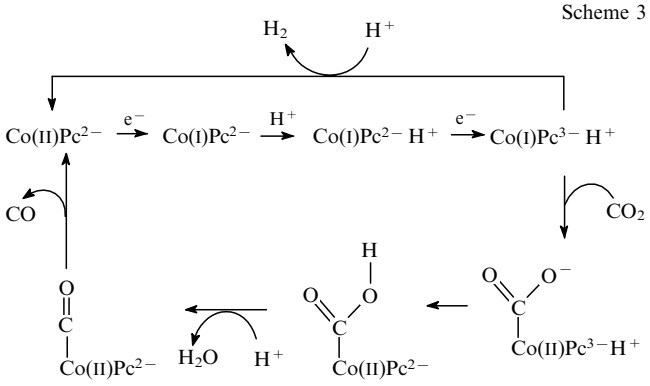
Table 1. Results of cathodic reduction of CO_2 in water in the presence of phthalocyanine complexes of transition metals (PcM).[3,15]

M	E /V (*vs.* SCE)	Current efficiency (%)			
		CO	CH_4	HCOOH	H_2
Ti	−1.98	15.8	28.1	5.0	40.4
In	−1.96	10.0	0.8	26.8	47.7
Zn	−1.94	33.0	0	27.0	40.0
Sn	−1.93	10.0	0	71.0	20.0
Mn	−1.90	7.0	2.0	3.0	88.0
Al	−1.90	6.2	0.2	16.9	69.9
Cd	−1.84	46.0	4.2	4.8	45.5
Ni	−1.75	100.0	1.3	0.4	2.0
Mo	−1.72	0	0	2.0	98.0
Cr	−1.68	5.0	0	5.0	90.2
Pb	−1.64	5.0	0	65.0	30.0
Cu	−1.63	14.0	28.0	3.5	49.2
Pt	−1.59	4.0	0	0	95.6
Pd	−1.50	81.4	0	1.0	9.5
Co	−1.30	98.0	0	0.4	3.0
Fe	−1.21	47.0	0.3	5.0	47.3

A number of calculations for ligand-free complexes MCO_2 (M is an alkali or transition metal) have been carried out (see Ref. 115 and references therein). The first systematic study into the geometry, configurational interactions and electron density distribution for a wide range of MCO_2 complexes (where M is a metal of the 3-rd period: Ca–Mn, Cu, Zn) showed the occurrence of electron transfer from the metal atom to the CO_2 group, the electron density being concentrated on the carbon atom and the M–C bond being nearly ionic. The electron transfer from the metal to CO_2 is accompanied by redistribution of electrons in the internal levels and, in particular, results in a higher electron density on the oxygen atom. Thus, coordination to the metal increased the basicity of the oxygen atoms in the CO_2 group.

Mechanisms for the electrocatalytic reduction of CO_2 have been proposed in a few publications.[79,109] These studies deal with the reduction of CO_2 in an aqueous solution at a graphite electrode coated by PcCo bound to poly-4-vinylpyridine (PVP), the latter acting as a donor axial ligand (Scheme 3).

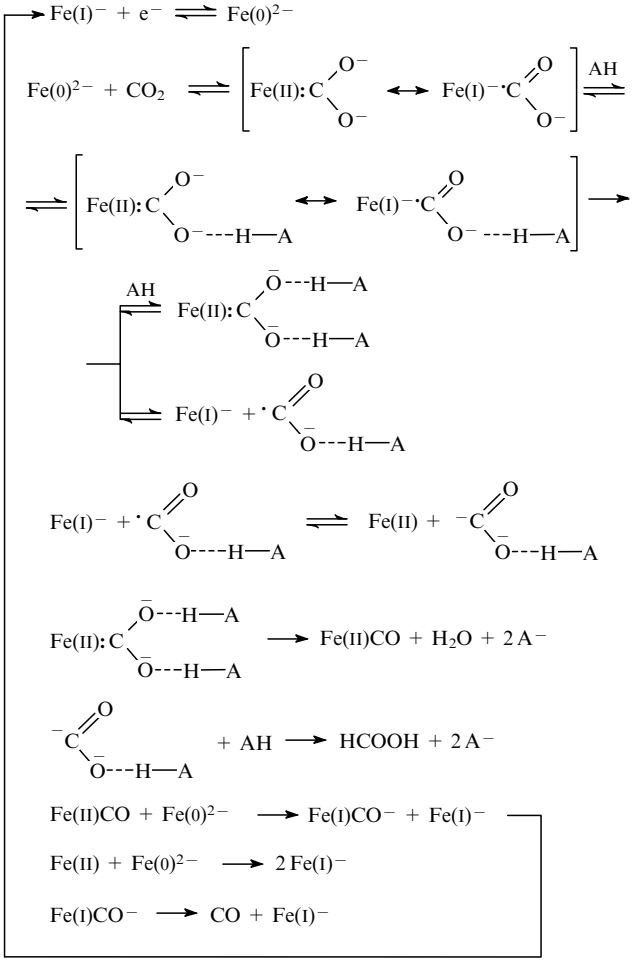
Scheme 3



It can be seen from Scheme 3 that the catalytic process starts only in the second step of PcCo reduction because the first reduction is followed by the fast addition of H^+ to one of the peripheral nitrogens of the phthalocyanine ring, and only the second step gives an active species capable of reducing both H^+ and CO_2 to H_2 and CO, respectively. Nevertheless, researchers[79,83] who studied electrocatalysis by pure PcCo adsorbed on graphite, were unable to observe directly the PcCo–CO_2 adduct.

An interesting sequence of steps taking place during CO_2 reduction catalysed by iron porphyrins has been proposed and confirmed by kinetic data.[112,113] The key step of this process is the formation of the Fe–C bond (Scheme 4, the porphyrin ligands are omitted, AH is a Brønsted acid).

Scheme 4



It has been shown[116] that a rotating ring–disk electrode, in which the disk electrode is represented by graphite coated by cobalt(II) *N*,*N*′,*N*″,*N*‴-tetramethyltetra-3,4-pyridoporphyrazine and protected by a polymeric film (Nafion) and the ring electrode is represented by platinum, can be used for quantitative determination of CO_2 in aqueous solutions (the concentration range is 10^{-4}–3.2×10^{-2} mol litre^{-1}). The method is based on the fact that CO_2 is reduced quantitatively at the disk to give CO (at −1.15 V *vs.* SCE), while the latter is detected on the basis of the typical oxidation peak at the platinum ring (0.4 V *vs.* SCE):

$$[CO]_{ad} + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-.$$

2. Elctroreductive coupling, addition, carboxylation and carbonylation

Electroreductive coupling reactions are extensively used in synthesis. Phosphine, tetraazamacrocyclic and polypyridyl complexes of transition metals (mainly, Ni, Pd and Pt) are used most often as catalysts. Electrochemical electron transfer can play different roles in these reactions — an electron can participate directly in the catalytic cycle, or/and labile complexes of transition metals in low oxidation states can be generated electrochemically and participate in the reaction *in situ*.

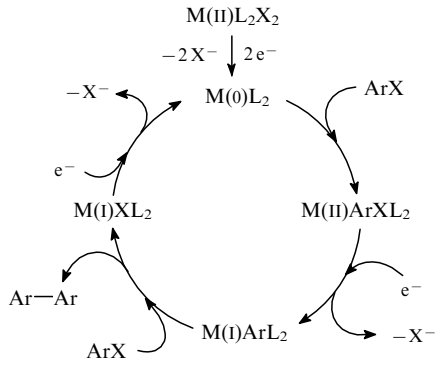
The general scheme of the elctroreductive coupling can be represented in the following way:[27,55,117,118]

$$2\,ArX \xrightarrow{2e^-,\ ML_2Cl_2} Ar{-}Ar + 2\,X^-$$

X = I, Br, Cl, OTf; M = Ni, Pd;

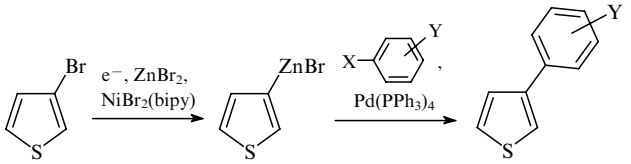
L = PPh_3, dppe, bipyridyl (bipy), *etc.*

The activity of Ni(0) and Pd(0) complexes in coupling reactions of organohalogen compounds was shown [119,120] to depend on a number of factors: the size of the electrochemical gap, the strength of the metal–ligand bond, and electronic and steric effects of the ligands. The first step of the catalytic cycle is the oxidative addition of an organic substrate to a zerovalent metal complex, resulting in the formation of a σ-arylnickel or σ-arylpalladium intermediate.



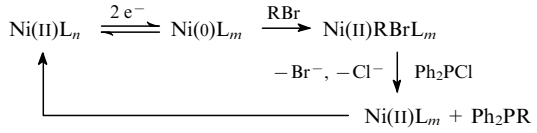
M = Ni, Pd.

Numerous reactions of this type have now been described (see the monograph [27] and the papers [55,118,121,122]). Among these, electrochemical synthesis of substituted 3-phenylthiophenes is noteworthy.[123] The reduction of a mixture of 3-bromothiophene and $ZnBr_2$ in the presence of the bipyridine nickel complex gives rise to 3-thienylzinc bromide, which enters into cross-coupling reactions with various aryl halides (PhI, *p*-NCC_6H_4Br, *o*-$MeOC_6H_4Br$, *p*-$MeOC_6H_4Br$).



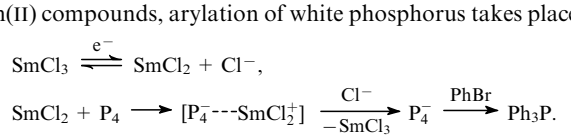
The synthesis of optically active 1,3-dienes containing chiral substituents from alkenylstannanes by electrooxidation and homocoupling with participation of $CuCl_2$ has been reported.[124]

Phosphine and bipyridine Ni complexes serve as the catalysts of the electroreductive coupling of aryl and hetaryl halides with mono- and dichlorophosphines, which allows the synthesis of tertiary phosphines in high yields.[125,126]

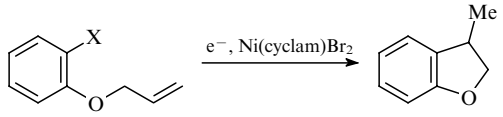


L = PPh_3.

Under the action of electrochemically generated Ni(0) or Sm(II) compounds, arylation of white phosphorus takes place.[127]

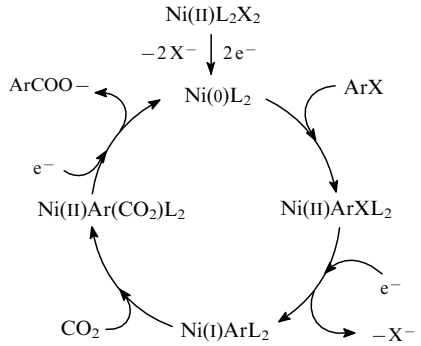


The intramolecular reductive coupling of allyl 2-halophenyl ethers catalysed by the Ni(cyclam)Br_2 complex provides the preparation of 3-methyldihydrobenzofuran in 90% yield.[128]

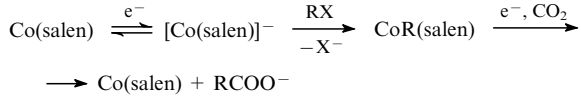


X = Cl, Br, I.

If CO_2 or CO is introduced in the reaction mixture containing an organic halide and the electrochemically generated Ni(0) complex, the reaction gives carboxylic acids or carbonyl compounds, respectively, instead of the homocoupling products.

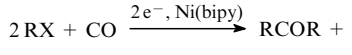


Carbon dioxide adds to Ni(I)ArL_2 approximately twice as fast as ArX; therefore, the side reaction giving biaryls scarcely takes place.[129–133] In the presence of CO_2 and catalytic amounts of electrochemically generated Pd(0) complex, aryl and vinyl triflates are converted into aromatic and α,β-unsaturated carboxylic acids, respectively.[134] Carboxylic acids can also be prepared from allyl and benzyl halides using Co complexes as catalysts.[135]

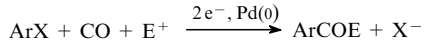


R = $PhCH_2$, Ph(Me)CH, $MeCH=CHCH_2$;
salen is bis(salicylidene)ethylenediamine.

Recently,[136] electrosynthesis of ketones from organic halides and CO catalysed by Ni(0) bipyridine complex was carried out. Study of the process mechanism showed that the reaction involves the intermediate formation of the acyl nickel complex.



The use of electrochemical electron transfer makes it possible to 'invert' the polarity of aroyl halides ArCOX and introduce them into reactions with electrophiles.[137]



The process includes the formation of the PdArX complex and the subsequent CO insertion, resulting in the intermediate PdArCOX complex, which is reduced more readily than the initial aryl halides; after activation by electrochemical electron transfer, this species can react with electrophiles, for example, with H^+.

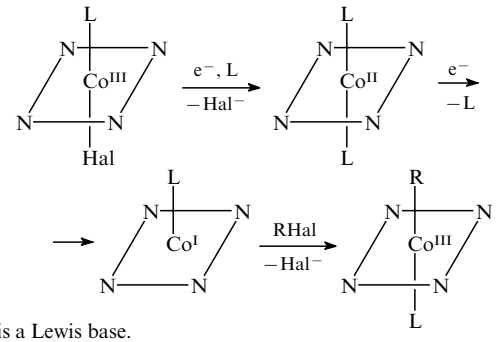
Electrocatalytic arylation of alkenes is documented. Although the process mechanism is not entirely clear, it is assumed that coordinatively unsaturated Ni(0) complexes serve as the basis for the spatial proximity of halobenzenes and alkenes; the subsequent treatment with a base yields arylalkenes.[138]

IV. The formation and cleavage of carbon – metal σ-bonds

Reactions giving carbon – metal σ-bonds are very important from the theoretical and practical standpoints because they allow the synthesis of new organometallic compounds with various useful properties. We shall consider two main types of these reactions, namely, electrochemical alkylation and electrochemical arylation of metal-containing nucleophiles.

1. Electrochemical alkylation

The methods used most widely for the introduction of alkyl groups are based on S_N2 reactions of various organic compounds with metal-containing nucleopiles. The latter can be synthesised conveniently by an electrochemical procedure using reductive activation, which yields metal complexes in low oxidation states. This method was used to prepare the alkyl derivatives of Co,[139] Fe [140] and Rh porphyrins [141, 142] as well as complexes with other nitrogen-containing macrocyclic ligands, in particular, dimethylglyoximate [143] and phthalocyanine.[144]



L is a Lewis base.

A comparative study of alkylation of electrochemically generated nucleophilic Co, Rh, Ir, Ni and Pd complexes with various nitrogen- and sulfur-containing ligands on treatment with butyl bromide was carried out.[143] Electrochemically activated reactions with transfer of the methyl group from dimethylglyoximate complexes of methylcobalt onto Au(I) [145] and Ni(I) [146] complexes and onto mercury [147] and germanium salts[148] are also known.

2. Electrochemical arylation and vinylation

Using the approach described above, only alkyl fragments can be introduced into the metal coordination sphere. The introduction of aryl and vinyl substituents requires not only electrochemical activation of a metal-containing nucleophile but also an additional activation of the C(sp^2)–Hal bond ($S_{RN}1$ reactions). Theoretical investigation into the electrochemically activated $S_{RN}1$ type reactions was started by Saveant's group.[12, 149–157] The stabilities of the radical anions formed initially, the relative rates of each step of the $S_{RN}1$ process, the most important competing reactions and the types of chain termination have been studied. A number of procedures for preparative electrosynthesis of various organic compounds underlain by $S_{RN}1$ processes have been developed.[153, 158–160]

However, until recently, the authors of only two studies [161, 162] have described examples of electrochemically activated $S_{RN}1$ reactions involving organometallic compounds, namely, the synthesis of aryl and vinyl derivatives of iron porphyrin [161] and the reactions of the $[CpM(CO)_3]^-$ anions (M = Mo, W) with iodonitrobenzene.[162]

Apparently, this is due to the fact that the double electrochemical activation of both reagents requires that a specified potential be strictly maintained during the reaction. This creates some difficulties for practical implementation of these processes because the reaction product can be subsequently destroyed (compounds containing a carbon–metal σ-bond are usually oxidised and reduced irreversibly with cleavage of this bond). If the product is reduced at more cathodic potentials than the reaction begins (the activation potential of the initial reactants), the product destruction at the electrode can be avoided.[161] Systematic investigations of electrochemically activated arylation in which the reaction product is irreversibly reduced at potentials less cathodic than the activation potential of the reactants have been started [163–167] in relation to electrochemical arylation and vinylation of anionic iron, molybdenum and tungsten carbonyl complexes.

The general scheme of the reaction is as follows:

$$RHal + 0.5\,[CpM(CO)_n]_2 \xrightarrow{e^-} MR(CO)_nCp + Hal^-$$

M = Fe, Mo, W.

Electrochemical electron transfer activates the organic halide by transforming it into a reactive radical and leads to generation of metal-containing nucleophiles as a result of cleavage of the M–M bond in the dimer. The active species that arise react with each other *in situ* to give a σ-organometallic compound.

Activation of the first reactant

$$RHal \xrightarrow{e^-} RHal^{-\cdot} \longrightarrow R^{\cdot} + Hal^-.$$

Activation of the second reactant

$$0.5\,[CpM(CO)_n]_2 \xrightarrow{e^-} [CpM(CO)_n]^-$$

M = Fe, n = 2; M = Mo, W, n = 3.

The formation of the σ-organometallic compound

$$R^{\cdot} + [CpM(CO)_n]^- \longrightarrow [MR(CO)_nCp]^{-\cdot},$$

$$[MR(CO)_nCp]^{-\cdot} \xrightarrow[-e^-]{} MR(CO)_nCp.$$

These reactions have been carried out for both aryl halides (p-XC_6H_4Hal: X = H, Me, Cl, I, COMe, CN, NO_2; Hal = I, Br; C_6F_5X: X = H, F, Cl, Br; C_5F_5N) and vinyl halides (Z-, E-PhCH=CXHal: X = H, Ph; Hal = I, Br; Z-, E-PhCF=CFHal, Z-, E-Bu^{t}CF=CFHal: Hal = F, Cl, Br).

Direct electrochemical activation of this reaction is possible only for those aryl halides that are reduced more readily than the reaction product, a cyclopentadienyldicarbonyliron derivative. This is due to the fact that electrochemical reduction of σ-organometallic compounds of this type is irreversible and is accompanied by C–M bond cleavage. For any other compound, the product resulting from electrochemical activation decomposes immediately at the electrode. It can be seen from Fig. 2 that the region of

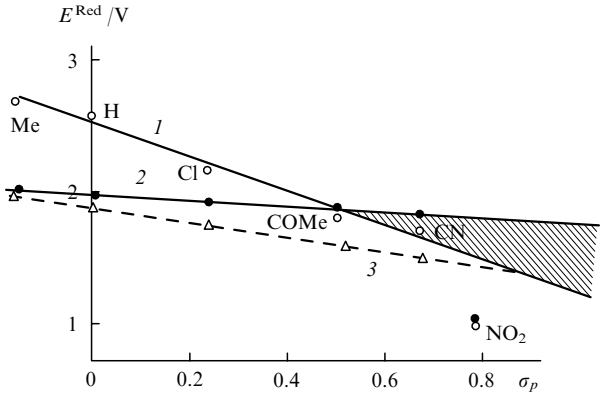


Figure 2. Reduction potentials (E^{Red}) (Pt cathode) of aryl iodides p-IC_6H_4X (*1*) and the products p-$CpFe(CO)_2C_6H_4X$ (*2*) *vs.* Hammett σ_p-constants of substituents. Reduction potentials of initial aryl iodides at a Hg electrode (*3*). The region of possible electrochemical activation of the reaction is hatched.[163]

possible electrochemical activation of the reaction is rather narrow. It can be extended by decreasing the potential of the onset of the reaction, *i.e.,* the potential at which active species are generated.

Three approaches have been proposed to solve this problem. One approach includes fast potential cycling toward a less cathodic region and back; thus, at least some of the product formed at the electrode has time to diffuse into the solution.[164]

According to the second approach,[163] the electrode material is replaced (Hg is used instead of Pt); this allows a significant decrease in the potential at which the reaction starts because this facilitates the reduction of aryl and vinyl halides (see Fig. 2, dashed line). In this case, direct electrochemical activation can be used for iodobenzene, *p*-bromobenzonitrile and other aryl halides (see Fig. 2), the reduction of which at mercury falls into the required potential range, while electrochemical activation of these compounds at platinum is impossible. For vinyl halides studied by Magdesieva *et al.,*[163] except for β-iodostyrene, the mere replacement of the electrode material does not suffice for electrochemical activation of the nucleophilic vinyl substitution because σ-vinyl derivatives of η^5-cyclopentadienyldicarbonyliron are reduced more readily than the initial substrate even at mercury.

The third approach [165] implies the use of homogeneous redox catalysis in which a decrease (in magnitude) in the potential of the reaction onset is attained by adding an appropriate reversible $A/A^{-\bullet}$ redox pair, which acts as a mediator† by carrying an electron from the electrode to the aryl or vinyl halide.

$$[CpFe(CO)_2]_2 + 2e^- \xrightarrow{\text{electrode}} 2\,[CpFe(CO)_2]^-,$$

$$A + e^- \overset{\text{electrode}}{\rightleftharpoons} A^{-\bullet},$$

$$A^{-\bullet} + RX \overset{\text{solution}}{\rightleftharpoons} (RX)^{-\bullet} + A,$$

$$(RX)^{-\bullet} \xrightarrow{\text{solution}} R^{\bullet} + X^-,$$

$$R^{\bullet} + [CpFe(CO)_2]^- \xrightarrow{\text{solution}} [FeR(CO)_2Cp]^{-\bullet},$$

$$[FeR(CO)_2Cp]^{-\bullet} + RX \overset{\text{solution}}{\rightleftharpoons} FeR(CO)_2Cp + RX^{-\bullet},$$

$$[FeR(CO)_2Cp]^{-\bullet} + A \overset{\text{solution}}{\rightleftharpoons} FeR(CO)_2Cp + A^{-\bullet}$$

R is aryl, vinyl.

Owing to the homogeneous redox catalysis, these reactions can be carried out for such substrates for which the replacement of electrode material alone does not result in a positive value of

$$\Delta E = E^{\text{Red}}_{\text{RHal}} - E^{\text{Red}}_{\text{FeR(CO)}_2\text{Cp}}$$

(for example, *p*-iodotoluene, bromostyrenes and *Z*-bromostilbene). In addition, by using this approach, one can increase the yield of nucleophilic substitution products for substrates that formally fall into the region of possible reaction activation upon the replacement of the electrode material but still have too small ΔE values, for example, for iodobenzene (Table 2).

Thus, Magdesieva *et al.*[165] were the first to show experimentally that the use of homogeneous redox catalysis allows the electrochemically activated reactions of organometallic compounds to be performed under conditions where the products are redox-unstable upon direct electrochemical activation. This implies selection of a mediator whose activities with respect to the reactant and the product are appreciably different. This has markedly extended the scope of applicability of electrochemical activation, first of all, for the synthesis of σ-organometallic compounds.

† Study of a wide range of conceivable mediators showed that phthalonitrile is the compound of choice for this reaction.[165]

Table 2. Yields of products of direct and mediator preparative electrolysis [a] of aryl and vinyl halides in the presence of $[CpFe(CO)_2]_2$.[163–165]

Substrate	Potential of electrolysis /V	Product	Preparative yield (%)
p-MeC_6H_4I	−1.95	*p*-MeC_6H_4Fp [b]	0–1
p-MeC_6H_4I	cycling from −1.95 to −1.55	*p*-MeC_6H_4Fp	2–3
p-MeC_6H_4I in the presence of *o*-NCC_6H_4CN [c]	−1.80	*p*-MeC_6H_4Fp	43.0
PhI	−1.90	C_6H_5Fp	5.0
PhI	cycling from −1.90 to −1.55	C_6H_5Fp	15.0
PhI in the presence of *o*-NCC_6H_4CN [c]	−1.75	C_6H_5Fp	45.0
PhCH=CHI	−1.55	PhCH=CHFp	12.5
PhCH=CHI	cycling from −1.90 to −1.55	PhCH=CHFp	19.0
PhCH=CHI in the presence of *o*-NCC_6H_4CN [c]	−1.75	PhCH=CHFp	28.0

[a] Electrolysis conditions: Hg, $Bu^n_4NBF_4$ (0.25 mol litre^{-1}), MeCN, $Ag^+/AgCl/KCl$, 20 °C. [b] Fp = $CpFe(CO)_2$. [c] The phthalodinitrile concentration is 5×10^{-4} mol litre^{-1}.

This approach has permitted the preparative synthesis of about twenty aryl and vinyl derivatives of $CpFe(CO)_2$ containing the C(sp^2)—metal σ-bond, particularly high product yields being attained when using homogeneous redox catalysis.

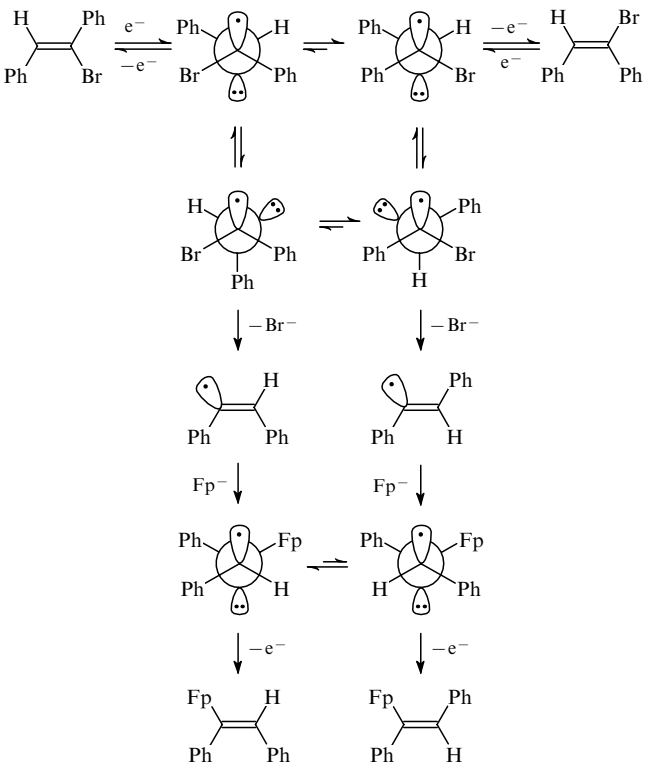
Study of the stereochemistry of the reaction products (Table 3) showed that, irrespective of the configuration of the initial vinyl halide, the product with the *trans*-arrangement of the organometallic group and the organic group always predominates. This is due to the fact that generation of the radical anion is accompanied by isomerisation to give the most stable configuration (Scheme 5).

Table 3. Results of preparative electrolysis [a] of vinyl halides RCF=CFX in the presence of the $[CpFe(CO)_2]_2$ binuclear complex.[167]

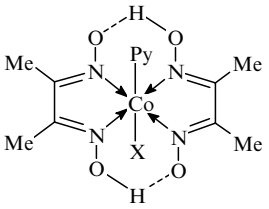
R	X	Substrate configuration	Nucleophilic substitution product	Product configuration	Preparative yield (%)
$(CF_3)_3C$	F		$(CF_3)_3CCF=CFFp$	*Z*	40
				E	traces
$(CF_3)_3C$	Cl	*Z*	$(CF_3)_3CCF=CFFp$	*Z*	15
				E	traces
$(CF_3)_3C$	Br	*Z*	$(CF_3)_3CCF=CFFp$	*Z*	14
				E	traces
Ph	F		PhCF=CFFp	*Z*	42
				E	5
Ph	Cl	*Z*	PhCF=CFFp	*Z*	32
				E	3
Ph	Cl	*E*	PhCF=CFFp	*Z*	10
				E	5

[a] Electrolysis conditions: Hg, $Bu^n_4NBF_4$ (0.25 mol litre^{-1}), MeCN, $Ag^+/AgCl/KCl$, 20 °C.

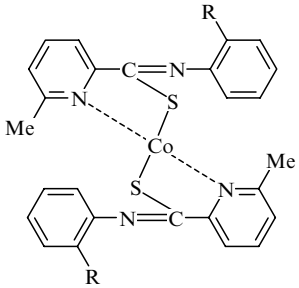
Scheme 5



Using electrochemical activation, it is possible to arylate [168] Co(II) and Co(III) complexes with chelating ligands containing nitrogen and sulfur atoms, for example:



X = Py, Hal.



R = Me, OMe.

The essence of the 'iodonium method' proposed in one study [168] is to use diphenyliodonium salts including those containing various substituents in the benzene ring as arylating agents.

$$Ph_2I^+ \xrightarrow{e^-} Ph^{\bullet} + PhI,$$

$$Ph^{\bullet} + Co(II)(Chel)_2 \longrightarrow Co(III)Ph(Chel)_2$$

Chel is a chelating ligand.

Not only Co(II) complexes but also Co(III) complexes, which are normally more stable and more readily available, can be introduced in the arylation. However, in this case, electrochemical activation of both reactants is needed.

$$Ph_2IBF_4 \xrightarrow{e^-} Ph^{\bullet} + PhI + BF_4^-,$$

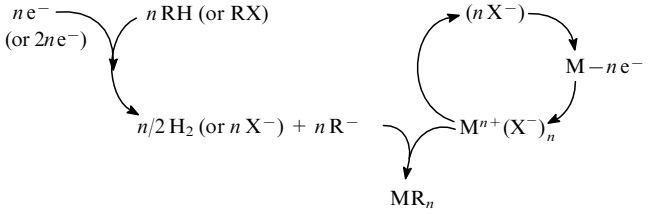
$$Co(III)(Chel)_2 \xrightarrow{e^-} Co(II)(Chel)_2,$$

$$Ph^{\bullet} + Co(II)(Chel)_2 \longrightarrow Co(III)Ph(Chel)_2.$$

It is noteworthy that the use of diphenyliodonium salts as arylating agents has obvious advantages over halobenzenes used traditionally in $S_{RN}1$ reactions, because the former provide generation of phenyl radicals upon electrochemical activation at much lower cathodic overpotentials.

3. Electrosynthesis with sacrificial electrodes

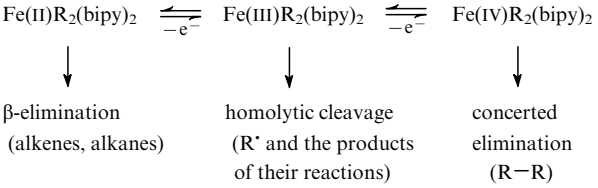
Yet another widely used electrochemical approach to the synthesis of organometallic compounds is the use of sacrificial (this is the name for soluble) anodes. In an undivided cell, metal dissolution takes place at the anode and the organic substrate is reduced at the cathode to give anions which should be stable enough to avoid side reactions with the solvent.[28, 169–171]



Examples of syntheses with anodes made of Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, Cu, Al, Pb, Sn and various ligands are documented.[172–175]

Kharisov *et al.*[176] have compared the traditional chemical and electrochemical methods for the synthesis of transition metal complexes with nitrogen-containing ligands. An advantage ensured by the use of sacrificial anodes is the possibility of preparing Cu, Ni, Co, Pd, Zn and Cd complexes in one step in high yields.

Electrochemical cleavage of the carbon–metal σ-bond gives in most cases organic radicals the further transformations of which are determined [177] by the applied potential and the solution composition.



V. Electrochemically activated reactions involving 'electron sponges'

When considering electrochemical activation of reactions involving organometallic compounds, two types of processes can be distinguished:

(1) electrochemical activation of various types of bonds (C–Hal, C–M, M–Hal, M–M, *etc.*), resulting in their cleavage to give highly reactive species (cations, anions, radicals);

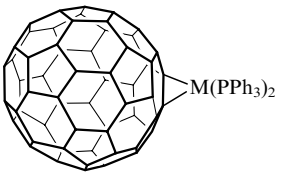
(2) activation through transfer of one or several electrons accompanied by the change in the electronic structure and, hence, properties of the molecule, but involving no bond cleavage.

In the reactions considered above, activation of the former type takes place. Now we shall give some examples of the latter type of processes.

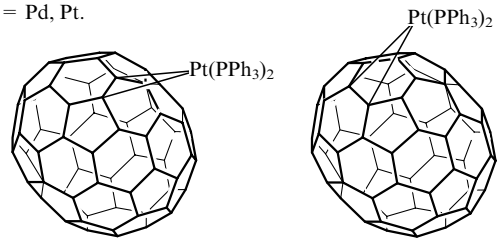
Systems capable of reversible stepwise addition or release of several (three or more) electrons are referred to as 'electron sponges'. The transfer of an electron onto such systems results in activation of the whole molecule and in the change in its properties (for example, catalytic, spectroscopic and other properties) but does not induce cleavage of any bond. A fairly large number of such systems have been reported;[178, 179] however, here we restrict ourselves to consideration of two of them, namely, phthalocyanine complexes and fullerene derivatives, for which electrochemically activated reactions involving organometallic compounds are known.

1. Electrosynthesis of exohedral metal complexes of C_{60} and C_{70}

A unique feature of fullerenes and their derivatives is the capability of reversible stepwise addition of up to six electrons, which makes them fairly promising participants of redox processes. Recently,[180, 181] we proposed an electrochemical method for the synthesis of exohedral complexes of C_{60} and C_{70}, namely, $C_{60}ML_2$ [M = Pd, Pt; $L_2 = (Ph_3P)_2$, bis(diphenylposphino)ferrocene (dppf) or diphenylposphinocymanthrene] and $C_{70}Pt(PPh_3)_2$ (a mixture of two isomers) from simple and stable inorganic salts (MCl_2) or complexes of platinum group metals (ML_2Cl_2).



M = Pd, Pt.



Reactive complexes of zerovalent metals sensitive to atmospheric oxygen can be generated *in situ* using electrochemically generated C_{60}^{2-} or C_{70}^{2-} dianions as reducing agents. In this case, fullerene plays a dual role acting simultaneously as an electron transporter (mediator) and as one of structure-forming reagents.

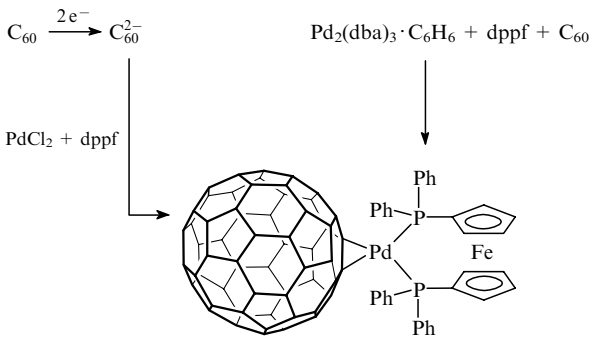
$$C_{60} \overset{2e^-}{\rightleftharpoons} C_{60}^{2-},$$

$$C_{60}^{2-} + ML_2Cl_2 \longrightarrow C_{60} + ML_2 + 2Cl^-,$$

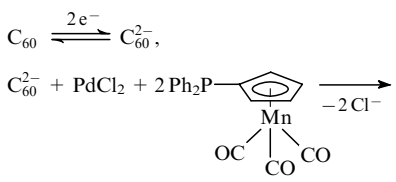
$$C_{60} + ML_2 \longrightarrow C_{60}ML_2.$$

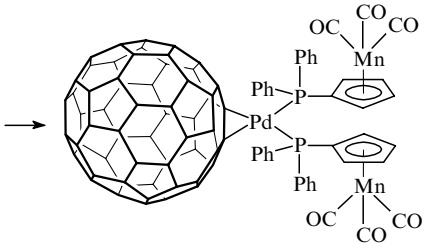
An advantage of this method is the possibility of preparing a pure monometal complex containing no polymetallated fullerenes. This is related to the fact that the electron transfer is followed by the fast reaction of C_{60} with the ML_2 compound formed *in situ*, which is formed in an exactly equimolar amount.

This approach has also been used to prepare new exohedral heteropolymetallic complexes of [60]fullerene containing Pd, Fe and Mn atoms.[182, 183]



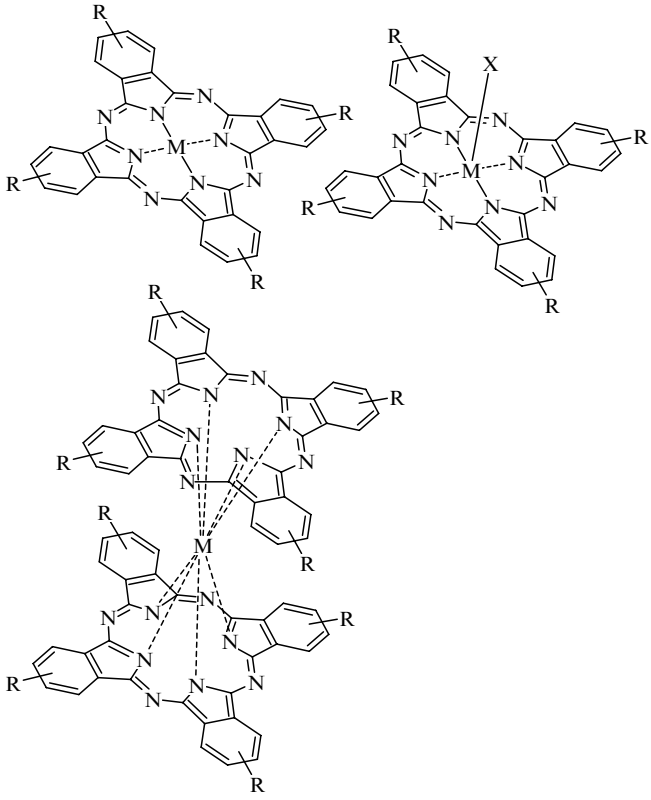
dba is dibenzylideneacetone;





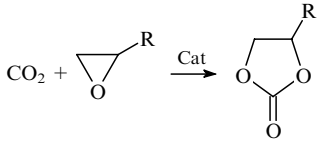
2. Electrochemically activated reactions of phthalocyanines

Typical examples of 'electron sponges' are mono- and diphthalocyanine metal complexes.



Recently, it has been found[184] that some diphthalocyanine complexes are able to undergo eight reversible and quasi-reversible redox transitions in the anodic and cathodic regions. Owing to this feature, they are rather promising participants of various redox processes, in particular, electrocatalytic ones. In Section III.1, we presented examples of electrocatalytic reduction of CO_2 by various complexes with macrocyclic nitrogen-containing ligands, including phthalocyanine complexes. Now we consider one more example of an electrochemically activated reaction of phthalocyanines in which the electrochemical transfer of an electron is used for catalyst activation.

The binding of CO_2 by epoxides resulting in the formation of alkylene carbonates is known[185] to be catalysed by metal phthalocyanines. However, this reaction proceeds under rigorous conditions, *i.e.*, in an autoclave at high pressure and temperature. With electrochemically reduced forms of metal phthalocyanines used as catalysts, this reaction was found[74] to proceed at 20 °C and under atmospheric pressure, in conformity with the scheme

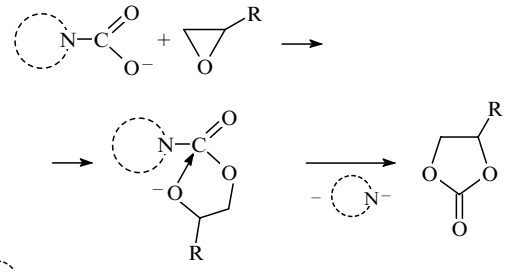


R = Me, CH_2Cl.

The electrochemical activation of the catalyst and the subsequent nucleophilic attack occur in the following way:

$$PcM \overset{e^-}{\rightleftharpoons} (PcM)^{-\bullet},$$

$$(PcM)^{-\bullet} + CO_2 \rightleftharpoons (PcM \cdot CO_2)^{-\bullet},$$



N = PcM.

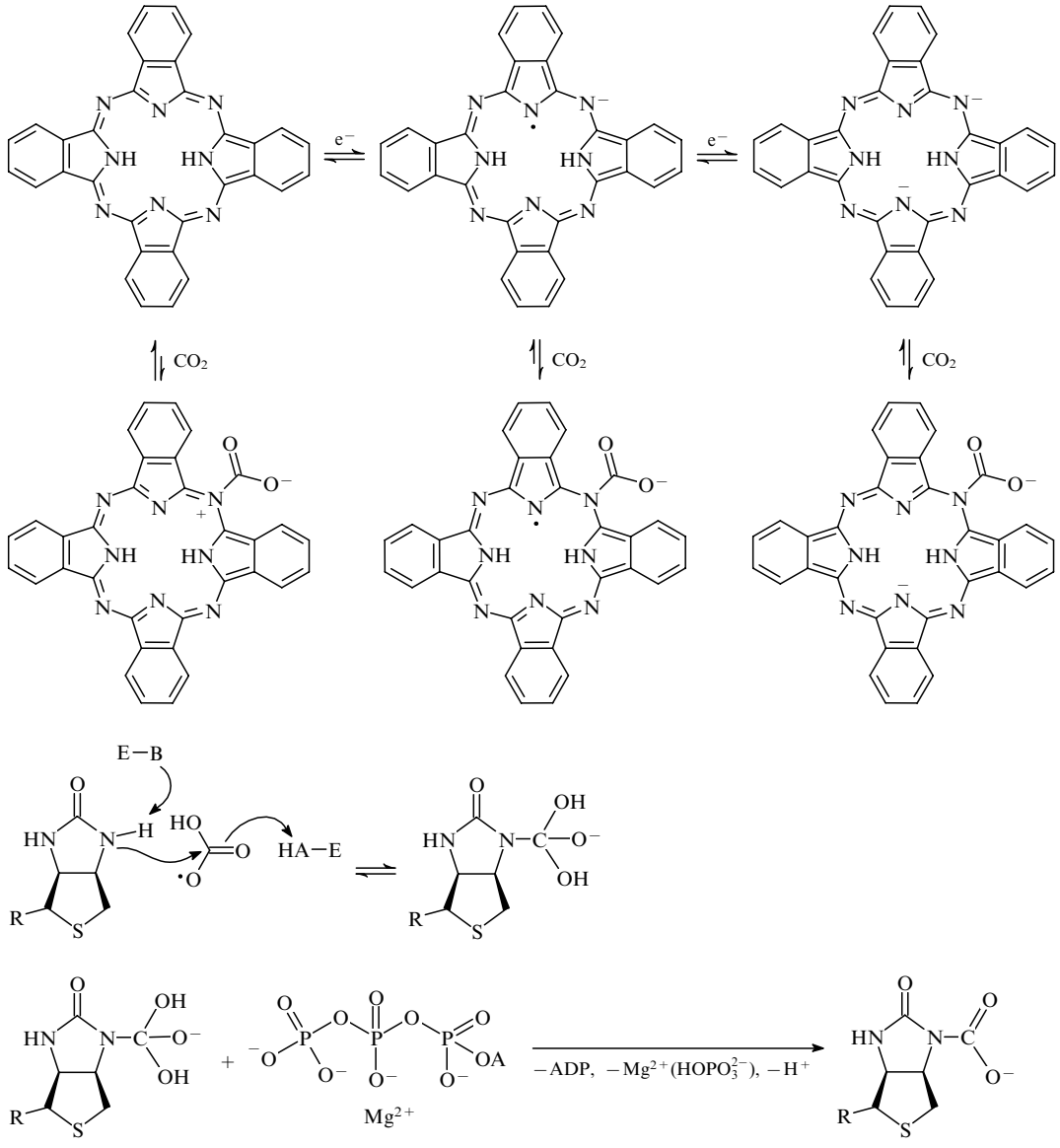
Thus, electrochemically reduced forms of metal phthalocyanines exhibit much higher catalytic activities than neutral forms. Both mono- and diphthalocyanine complexes can be used as catalysts in this reaction; however, the latter offer an advantage, namely, in this case, the electrochemically activated binding of CO_2 can be carried out at a low cathodic polarisation (the potentials of the first redox transition of Pc_2M range from $+0.01$ to -0.65 V *vs.* Ag/AgCl/KCl).[74, 104, 186]

A study of the influence of the catalyst immobilisation mode on the efficiency of the catalytic process showed that the highest efficiency is observed in the case of amino-substituted mono- and diphthalocyanine complexes (NH_2PcM and NH_2Pc_2M, respectively) electropolymerised on smooth electrodes. Turnover numbers as high as $10^4 - 10^5$ have been achieved for these catalysts, which is close to the efficiency of natural enzymes.[187]

Monomer	^{NH_2}PcCu	^{NH_2}PcCo	^{NH_2}PcPd	$^{NH_2}Pc_2$Lu	$^{NH_2}Pc_2$Er
Catalyst turnover number in 75 min	2.65×10^5	4.7×10^3	1.05×10^3	1.4×10^4	7.0×10^3

It is of interest that carboxy-containing adducts formed under the action of phthalocyanine complexes and biotin (the co-enzyme which binds CO_2 and transports it to organic molecules *in vivo*) are structurally similar: in both cases, they contain a fragment similar to carbamic acid (Scheme 6).

Scheme 6



ADP is adenosine diphosphate, A is adenosine; R = $(CH_2)_4COOH$.

The above data indicate that the simulation of functioning of the active sites of enzymes operating by the proton transfer mechanism by processes occurring by a redox mechanism is possible but only at the level 'the same intermediate (in this particular case, the resonance-stabilised planar N anion) — the same product,'[188]

* * *

The information presented here demonstrates that, although numerous studies on electrochemically activated reactions involving organometallic compounds have been performed, the list of types of these reactions is quite limited. The vast majority of publications are devoted to transformations in the coordination sphere of transition metal complexes and electrocatalysis. Therefore, development of new electrochemical approaches to the synthesis of organometallic compounds and conduction of reactions involving them remains to be quite a topical task. In this review, we attempted to demonstrate the extensive potential of organic electrochemistry and thus facilitate implementation of electrochemical methods in the routine practice of chemists working with organometallic compounds.

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