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Metal complex catalysis in organic electrosynthesis

Yu H Budnikova

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Abstract. Data on the use of electrochemically generated metal complex catalysts in organic synthesis are analysed, systematised and generalised. The considerable potential of organic electrochemistry is shown. Some electrochemical methods provide advantages in the synthesis of compounds where conventional chemical methods fail, are experimentally complicated or have environmental limitations. Particular attention is given to the mechanisms of electrocatalytic reactions. The bibliography includes 333 references.

I. Introduction

The development of environmentally safe and resource-saving chemical and technological processes is one of the strategically important lines of research in science and engineering. Homogeneous catalysis is finding increasing use in organic synthesis because it offers advantages over heterogeneous catalysis, particularly, from the viewpoint of selectivity and efficiency. Actually, complexes of transition metals, such as Ni, Pd or Co in low oxidation states, can react with many functional groups thus catalysing the formation of C – C, C – P, C – Si and other bonds. Electrochemical methods enable one to synthesise many organometallic compounds, study the reactivities of coordination compounds and elucidate possible reaction mechanisms.

In recent years, the use of electrochemically generated catalysts in reactions of organic compounds has assumed great importance both in organic synthesis and in thorough investigations into electron transfer, bond cleavage, substitution, addition and other reactions. The results of these investigations find application in many fields of physical, organic and analytical chemistry. The major breakthrough in the use of electrochemical reactions in industry, particularly, in low-tonnage chemistry, occurred in the past few years. From an industrial standpoint, electrochemical reactions have a number of advantages. Thus the conversion, the rate and, within certain limits, the selectivity of the process can be easily controlled by means of such parameters as the current density and the potential.[1 – 3]

Methods of indirect reduction and oxidation of organic compounds where the formation and regeneration of reactants occurs at an electrode find increasing use in modern organic synthesis. These methods enable one to perform various transformations of organic compounds under conditions of efficient and environmentally safe processes.[4] Presently, the electric energy cost is only an insignificant part of the cost price of the product and it is expected that it will grow more slowly than the price of chemical reagents.[5] Electrochemical processes are environmentally non-polluting and the control over these processes can be easily automated. Electrochemical reactions can provide higher selectivity as compared to conventional chemical transformations with simultaneous reduction of energy consumption and attainment of higher current densities.

Electrochemical metal complex catalysis attracts interest because it enables one to carry out reactions under mild conditions (moderate temperature, ambient pressure) and in a virtually closed system with the use of a minimum amount of the catalyst (mediator), which is cyclically regenerated. It should be noted that mediator processes are not only of practical importance but also offer a unique possibility of studying reaction mechanisms of reduction and oxidation of various substrates by electrochemical methods. For the simple cases, the mathematical approach was elaborated. This approach is based on approximating formulae, which provide a way of determining the rate constants of individual steps of the overall process of formation, consumption and regeneration of the mediator and enable one to obtain information on the energy characteristics of these steps and on the influence of various external factors. For this purpose, the

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dependencies of the current (its catalytic increase as a measure of the rate of the process) and the potential on the conditions of electrolysis are used.

The ever-increasing number of studies are aimed at replacing traditional catalysts based on toxic heavy metals with environmentally safer and cheaper compounds.

The present review surveys the principal results, which were obtained in organic synthesis with the use of electrochemical methods under the conditions of metal complex catalysis in the last 15 years. Some electrochemical reactions related to metal complexes, such as reversible haptotropic shifts, ligand exchange, modelling of molecular switches and modelling of the active sites of metalloenzymes as well as the architecture of electrochemically functionalised fullerenes are beyond the scope of the present review.

II. General principles of metal complex electrocatalysis in organic synthesis and methods of investigation of reaction mechanisms

1. General principles

Reactions involving transition metal complexes can be divided into two classes. One class includes reactions, such as isomerisation, dimerisation or oligomerisation of unsaturated compounds, in which no redox processes occur. In these reactions, the function of the catalyst is to control the kinetics and selectivity of thermodynamically possible processes. In this case, electrochemical methods employing transition metal catalysis are used as an alternative to conventional procedures for generation of some low-valent species that are difficult to access.[6] However, the above-mentioned reactions are not, in essence, electrochemical processes because they require no electricity consumption and, hence, they are not considered in the present review.

The reactions of the second class involve both catalysts (transition metal complexes) and a stoichiometric number of electrons (either from a reducing agent or from an electrochemical source). This class can be subdivided into two groups according to the type of action of the catalyst.

In the first group of reactions, the transition metal complex can serve as a carrier of electrons from their source to the reagent. Generally, these processes proceed by the so-called outer-sphere mechanism without the formation of an intermediate complex of the substrate (**A**) with the catalyst (the redox P/Q pair) and the mediator is regenerated electrochemically.[7–12]

$$P + e \rightleftharpoons Q,$$

$$Q + \mathbf{A} \rightleftharpoons P + \mathbf{B},$$

$$\mathbf{B} \longrightarrow \mathbf{C},$$

where P is a mediator, Q is a catalyst, **A** is a substrate, **B** is a reduction product and **C** is the target product.

The function of the redox catalyst (mediator P) is to transfer an electron from the electrode to the substrate after which the initial product of reduction of the substrate **B** is transformed into the final product **C** in the course of the chemical reaction. In the case of the rapid irreversible conversion of **B** into **C**, the substrate can be reduced under the conditions of homogeneous electron transfer in the direction opposite to the standard potential drop ($E^{\circ}_{P/Q} > E^{\circ}_{A/B}$),[7,8] which substantially extends the possibilities of redox catalysis. The apparent benefit of using redox catalysts is achieved only when these catalysts are stable and can be rapidly regenerated at an electrode in high current yield at potentials which are more positive than the potentials of direct electroreduction of the substrate, or at potentials which are less positive than the potentials of direct electrooxidation of the substrate. In addition, the catalysts must rapidly react with the substrate.

Hence, it is advantageous to use such metal complex catalysis in two cases: (1) if the employment of the homogeneous electron transfer leads to acceleration of the process as a whole, *i.e.*, if the kinetic barrier of the electrochemical process is lowered and the potential approaches the thermodynamical value owing to transfer of the electron to the bulk of the solution and a decrease in the overpotential of the electrochemical reaction; (2) in processes involving substrates whose homogeneous redox reactions proceed more rapidly than heterogeneous reactions for one or another reason.

The second group of faradaic and catalytic reactions includes those proceeding by the inner-sphere mechanism, *i.e.*, processes involving the formation of various intermediate coordination compounds (**PA** or **QA**) in the course of the reaction. This approach was described for the first time 15 years ago and was considered in the reviews.[13–19]

The inner-sphere electron transfer has some advantages over the outer-sphere mechanism for the following reasons.

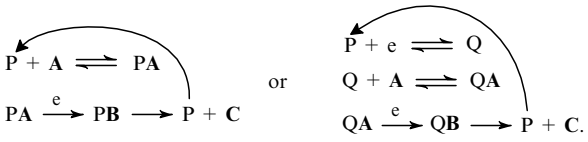
1. Redox processes are independent of the difference between the potentials of the mediator and the substrate and, hence, a large reduction in the overpotential becomes possible.

2. The inner-sphere transfer has a lower activation barrier.

3. Only one electron can be transferred in the outer-sphere process, whereas two or more electrons can be transferred through the inner-sphere mechanism. This is of particular importance in biocatalysis and in activation of small molecules.

In the last decade, attempts have been made to provide theoretical justification for these processes and to extend the range of catalytic reactions. However, many details of the reaction mechanisms remain unclear.

The mechanism of action of metal complex catalysts can be represented by the following scheme



Since transformations of the substrate in the coordination sphere of the metal complex play a decisive role in the catalytic cycle, this type of catalysis is termed coordination electrocatalysis.[13] The electrochemical step of the process and the chemical reaction of the substrate share a common catalyst–substrate complex. The function of the catalyst is to bind and activate the substrate in the coordination sphere of the metal complex with the resulting increase in the reactivity of the substrate in the electron exchange with the electrode. Unlike redox catalysis, coordination electrocatalysis requires that either the mediator P or the catalyst Q be coordinatively unsaturated or their ligands be readily leaving groups, which is necessary for the formation of the intermediate **PA** and **QA** complexes. Different approaches to investigation of mediator processes were first described approximately two decades ago and were covered in the reviews.[7–19]

Abundant data on complex formation and activation of substrates that are kinetically inert in redox reactions are presently available,[14,20] which facilitates the choice of an appropriate metal complex.

For the reactions considered below, electrochemical methods do not necessarily have advantages over conventional chemical methods. However, it should be noted that electrochemical methods make it possible to generate unusual low-valent intermediates, which cannot be prepared with the use of chemical reducing agents. In addition, many reactions require reduction of intermediates of the catalytic cycle, which can be readily accomplished in the electrochemical process by controlling the potential of the working electrode.

In recent years, electrochemical methods were substantially simplified and became cheaper. Many electrochemical reactions are carried out in the direct current mode with the use of constructionally simple current sources. Undivided cells find increasing use because divided cells are less efficient in polar aprotic solvents and require a large amount of a supporting electrolyte. Processes with the use of sacrificial anodes have

considerable promise both for direct and catalytic reactions. In the latter case, the conductivity is enhanced and metal ions generated at an anode can influence the reactivities of chemical intermediates.[21,22]

Data on the electrochemical and chemical behaviour of the simplest transition metal complexes were surveyed in the reviews and papers.[22–33]

2. Methods of investigation of the mechanisms of reactions catalysed by transition metals

Reactions catalysed by transition metals proceed through catalytic cycles involving metal complexes in different oxidation states. Most of the metal complexes are either oxidised or reduced, or both. Consequently, they can be readily detected and characterised by electrochemical methods (voltammetry, amperometry, chronoamperometry, *etc*.). These methods also allow one to estimate the reactivities of metal complexes. Presently, stationary and transient voltammetry are the most readily available methods.

Stationary voltammetry is used for characterising a metal complex which is already present in solution and is characterised by the redox potential and its concentration is determined by the reduction or oxidation current. The reactivity of the complex with respect to the substrate can be examined by monitoring the change in its redox current as a function of time using, for example, the method of rotating disc electrode. If a new electroactive metal complex is formed in the course of the reaction, it can also be detected from its redox peak and its yield in the reaction is determined by the redox current. By this means, both the reagents and the products of the chemical step and its kinetics can be characterised. The stationary state method enables one to obtain kinetic data for chemical reactions whose half-lives $t_{1/2}$ are larger than several tens of seconds.

Transient voltammetry is used for proving the existence of the equilibrium between different complexes by estimating the relative change in the current at the redox peaks of different species as the scan rate is changed. The redox process of one species at the electrode surface leads to a shift of the equilibrium in the diffusion layer. The concentration of the species, which is measured from their redox current, reflects not their true concentration but the dynamic concentration [the CE (chemical–electrochemical) mechanism]. The scan rate fixes the time scale. The equilibrium is more difficult to shift as the time is decreased. In the limit, at very high scan rates, the dynamical equilibrium is frozen though it can be realised within longer periods of time (low scan rates). This method allows one to determine the equilibrium concentrations of different complexes and then their equilibrium constants. In these cases, the thermodynamics and kinetics of the equilibrium can be characterised using staircase transient voltammetry or chronoamperometry (the pulse duration θ) of redox waves of various species. In this case, electrochemical methods are similar to NMR spectroscopy because progressive freezing of the equilibrium as the scan rate is increased (voltammetry) or as the pulse duration θ is decreased (chronoamperometry) is analogous to coalescence in NMR spectroscopy. In the equilibrium reactions, the major species observed in solution are not necessarily reactive because they can be involved in the endergonic equilibrium (which is established with energy absorption). Since conventional methods provide a way of controlling the reaction, efficient reactive species can be identified only in detailed kinetic studies.

Cyclic voltammetry can also be used for generation of stable or short-lived organometallic species through successive electron transfers and chemical reactions in the course of redox processes involving metal complexes. A knowledge of the absolute number of electrons involved in an electrochemical process enables one to determine oxidation states of a cascade of complexes, which can be generated from a particularly stable complex. The kinetics of reactions of electrogenerated species with a particular substrate can be controlled by increasing the scan rate in cyclic voltammetry (or decreasing the pulse duration in chronoamperometry), *i.e*., by reducing the time scale of the chemical reaction. Analysis of the changes in the voltammogram as a function of the scan rate (or the time) makes it possible to obtain the kinetic data for chemical reactions whose half-lives $t_{1/2}$ range from 0.1 s to 10 ns. Hence, intermediate species can be generated and/or identified and their reactivities can be characterised.

However, although electrochemical methods provide a way of studying the kinetics and thermodynamics of reactions, they give no information on the structures of intermediates. Electrochemical methods in combination with NMR spectroscopy allow the elucidation of the characteristic features of the reaction mechanisms and provide detailed structural data. Other spectral methods can also be combined with electrochemical methods to obtain kinetic and structural parameters of the complex reaction system. The efficiency of this approach was demonstrated in many studies on elementary stages, such as oxidative addition, ligand exchange and reductive elimination.

III. Homocoupling of organic halides

1. Homocoupling of organic monohalides

Reductive dimerisation of organic halides is the first known reaction involving both faradaic reduction and catalysis by transition metal complexes. In 1976, Jennings *et al*.[34] reported electrodimerisation of alkyl bromides in DMF by electrolysis between two metal electrodes (Ni, Al or Cu) in the presence of iron or nickel acetylacetonates and triphenylphosphine. Later on, other analogous reactions were carried out, the electrochemical properties of catalyst precursors were studied and the reaction mechanisms were investigated.[35–44] The results published within the last decade are summarised in Table 1. Although dimerisation products can be obtained in high yields, these reactions are of

Table 1. Products of electroreductive coupling catalysed by Ni and Co compounds.

Substrate	Metal–ligand	Solvent	Product	Yield (%)	Ref.
EtBr	Ni–phen	DMF	C_4H_{10}		35
n-$C_6H_{13}Br$	Ni–bipy	DMF or NMP	$C_{12}H_{26}$	85	36
n-$C_5H_{11}Br$	Ni–bipy	DMF or NMP	$C_{10}H_{22}$	89	36
$MeOC_2H_4Br$	Ni–bipy	DMF or NMP	$(MeOC_2H_4)_2$	60	36
$MeO_2CC_5H_{10}Br$	Ni–bipy	DMF or NMP	$MeO_2CC_{10}H_{20}CO_2Me$	65	36
$Cl(CH_2)_4Br$	Ni–bipy	DMF or NMP	$Cl(CH_2)_8Cl$	38	36
$CH_2=CHCH_2Cl$	Co–bipy	H_2O	$(CH_2=CHCH_2)_2$		37
$PhCHCl_2$	Ni–salen	DMF	PhCH(Cl)CH(Cl)Ph + PhCH=CHPh		40
	Co–salen	DMF	$PhCH_2CH_2Ph$ + PhCH=CHPh		41, 42
$X(CH_2)_nCl$ (X = Br, I; n = 2–6)	Ni–salen	DMF	$Cl(CH_2)_{2n}Cl$	80–90	43, 44

Note: phen is 1,10-phenanthroline; bipy is 2,2′-bipyridyl; NMP is *N*-methyl-2-pyrrolidone; salen is the bis(salicylidene)ethylenediamine dianion.

limited synthetic usefulness because most of them can be carried out using either chemical or electrochemical methods in the absence of catalysts.[45]

The synthesis of biaryls from aryl halides attracts great interest because these compounds are of practical use, whereas they are difficult to prepare by chemical methods. First electrosyntheses were carried out in 1980s simultaneously by several research groups[46–49] with the use of $NiCl_2PPh_3$ (1%–20%) as the catalyst precursor in the presence of an excess of PPh_3. Later on, nickel complexes with 2,2′-bipyridyl and bidentate phosphines, *viz*., 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(dialkylphosphino)benzene, were prepared.[50, 51]

The Ni(II) complex with bipy, which can be reduced to the Ni(0) complex, proved to be an efficient catalyst of dimerisation of aryl compounds.[52, 53] In combination with sacrificial anodes, this process can be performed in an undivided cell under very simple experimental conditions in the presence of an excess of bipyridyl.

$$2\,ArX + 2\,e^- \xrightarrow[DMF,\ Mg\ anode]{NiBr_2(bipy)\ (7\%)} Ar{-}Ar + 2\,X^-$$

Ar = Ph, 3-MeC_6H_4, 4-$MeCOC_6H_4$, 2-naphthyl; X = I, Br, Cl.

Interestingly, biaryls were obtained in only slightly lower yields when the reactions were carried out in alcohols, such as methanol or ethanol, instead of DMF with the use of a sacrificial iron or aluminium anode.[54, 55] A nickel complex with either bipy[55] or di(2-bipyridyl)amine can serve as a catalyst. The results obtained in the cited studies evidence the possibility of formation of organonickel intermediates, which are stable in protic solvents and give rise to biaryls. Efficient arylation of activated alkenes was carried out under the same conditions.[55]

The electrosynthesis of biaryls from bromo- or iodoarenes[56] can be carried out in the presence of $PdCl_2(PPh_3)_2$ as the catalyst precursor. Aryl triflate can also serve as the substrate,[57, 58] but the latter process requires higher temperature. These homocoupling reactions catalysed by Ni or Pd complexes can also be performed using conventional chemical methods in the presence of zinc as a reducing agent to obtain biaryls in comparable yields.[58]

$$2ArX + 2\,e^- \xrightarrow[DMF,\ 20\ ^\circ C]{PdCl_2(PPh_3)_2\ (7\%)} \underset{(50\%-98\%)}{Ar{-}Ar} + 2X^-$$

Ar = Ph, 4-$Bu^tC_6H_4$, 4-$MeCOC_6H_4$, 4-$Me_2NC_6H_4$; X = I, Br.

$$2ArOTf + 2\,e^- \xrightarrow[DMF,\ 90\ ^\circ C]{PdCl_2(PPh_3)_2\ (10\%)} \underset{(50\%-70\%)}{Ar{-}Ar} + 2TfO^-$$

Ar = Ph, 4-NCC_6H_4, 4-$CF_3C_6H_4$, 4-ClC_6H_4; Tf = O_2SCF_3.

Catalytic reduction of cyclohexanecarboxylic acid chloride (**A**) in the presence of the electrochemically generated Ni(I)(salen) complex yielded the tetramer, *viz*.,1,2-dicyclohexylethene-1,2-diol dicyclohexanoate (**B**).[59] The first step involves electron transfer from the Ni(I)(salen) complex to acyl chloride to form the acyl radical **C**. The radical anion **E** is generated from diketone **D** either by electroreduction or by the reaction with the Ni(I)(salen) complex. Subsequent reactions of the intermediates **E** and **F** with the initial acid chloride give rise to the reaction product **B**.

$$Ni(II)(salen) + e^- \rightleftharpoons Ni(I)(salen)$$

$$RCOCl + Ni(I)(salen) \longrightarrow \underset{\mathbf{C}}{RC^{\bullet}(=O)} + Ni(II)(salen) + Cl^-$$
(**A**)

$$2\ \underset{\mathbf{C}}{RC^{\bullet}(=O)} \longrightarrow \underset{\mathbf{D}}{RC(=O){-}C(=O)R}$$

$$\underset{\mathbf{D}}{RC(=O){-}C(=O)R} + e^- \rightleftharpoons \underset{\mathbf{E}}{RC^{\bullet}(O^-){-}C(=O)R}$$

$$\underset{\mathbf{D}}{RC(=O){-}C(=O)R} + Ni(I)(salen) \rightleftharpoons \mathbf{E} + Ni(II)(salen)$$

$$\mathbf{E} + RCOCl \xrightarrow[-Cl^-]{} \xrightarrow{e^-} \longrightarrow \underset{\mathbf{F}}{\xrightarrow{RCOCl,\ -Cl^-}} \underset{\mathbf{B}}{}$$

R = cyclo-C_6H_{11}.

However, the function of Ni(I)(salen) is conceivably more complex than the mere role of an outer-sphere electron carrier to form acyl radicals. Heterogeneous reduction of acyl chlorides RCOCl (R = Alk), which also proceeds through acyl radicals, yields aldehydes rather than the tetramers.

2. Homocoupling of organic dihalides

Electroreductive coupling of organic dihalides is one of the approaches to the synthesis of polymers. Polyynes were prepared from diiodoacetylene in the presence of the Ni complex with dppe.[60]

$$n\,IC{\equiv}CI + 2n\,e^- \xrightarrow[DMF]{NiI_2(dppe)\ (5\%)} {-}\!\left(C{\equiv}C\right)_n\!{-} + 2n\,I^-.$$

Electroreductive coupling of aromatic and heteroaromatic dihalides was examined.[61]

The results of studies on reductive electropolymerisation of aryl dihalides are summarised in Table 2.[51, 62–72] Depending on the experimental conditions, polymers either deposit from the bulk of the solution in the course of electrolysis or precipitate as films on the electrode surface. This method is also suitable for preparing copolymers from a mixture of two aryl dihalides. Recently, the mechanism of polymerisation catalysed by the Ni complex with bipy was investigated.[73]

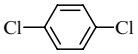
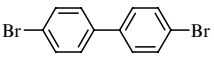
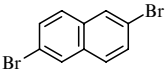
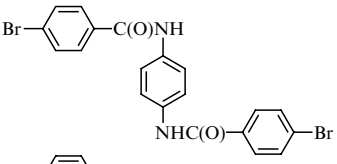
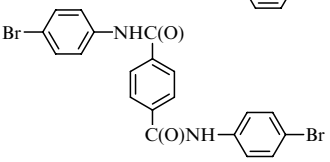
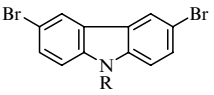
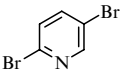
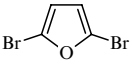
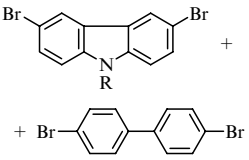
Homogeneous catalytic reduction of α,ω-alkanediyl dihalides under the action of electrochemically generated Ni(I)(salen) complexes was studied. Thus, 1,8-dichlorooctane was prepared from 1-bromo-4-chloro- and 1-chloro-4-iodobutane in a yield of higher than 88%. It was demonstrated that the reaction followed the radical pathway.[73, 74]

Electrochemical reductive coupling of some *gem*-dihalides, in particular, of dimethyl dibromomalonate in the presence of the copper complex with 1,10-phenanthroline and a sacrificial copper anode gave rise to cyclopropanes.[75]

$$\underset{Br}{\overset{Br}{C(CO_2Me)_2}} + \underset{}{\bigcirc\!\!=} \xrightarrow[Cu\ anode]{CuBr_2(phen),\ e^-} \longrightarrow \underset{CO_2Me}{\overset{CO_2Me}{\bigcirc\!\!<}} + 2\,Br^-.$$

Studies by cyclic voltammetry and chronoamperometry showed that reduction of dimethyl dibromomalonate with the Cu(I) complex is a catalytic process, which is kinetically controlled by the rate of concerted electron transfer and cleavage of the carbon–bromine bond. In the presence of styrene, cyclopropane is formed through the addition of $R_2C^{\bullet}Br$ (R = MeO_2C) at the double bond.[75] The radical intermediate is subsequently reduced to the corresponding anion, no transformations into carbene or alkylcopper intermediates being observed. In the reactions with other *gem*-dihalides, the products are formed by the chain mechanism involving addition.

Table 2. Reductive electropolymerisation of aryl dihalides with the use of a nickel catalyst.

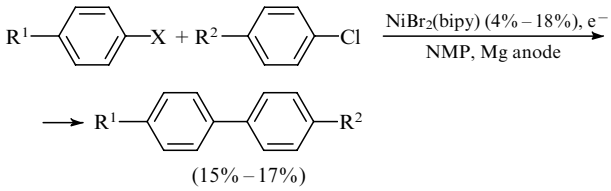
Substrate	Metal–ligand	Solvent	Ref.
	Ni–dppe	DMSO	51
	Ni–dppe	DMA [a]	62
	Ni–PPh_3	MeCN	63
	Ni–bipy	DMA [a]	64
	Ni–bipy	DMA [a]	64
 (R = Alk, aminoalkyldisiloxane)	Ni–bipy	DMA [a]	65–67
	Ni–bipy + PPh_3	MeCN	68, 69
	Ni–bipy	MeCN	70
 (R = Alk, aminoalkyldisiloxane)	Ni–bipy	DMA [a]	71, 72

[a] DMA is *N*,*N*-dimethylacetamide.

IV. Cross-coupling of organic halides

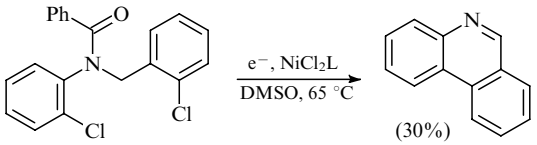
1. Cross-coupling of aryl halides

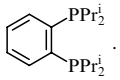
Asymmetrical biaryls, particularly, those containing electron-donating and electron-withdrawing groups in the aromatic nucleus, find use in nonlinear optics. Attempts were made to prepare these compounds, which are difficult to access, from mixtures of two different aryl halides employing electrochemical methods in combination with catalysis by Ni or Pd complexes. The chief drawback of this approach is the low selectivity of the process due to competitive cross- and homocoupling. It was demonstrated [76] that the reactions involving two aryl halides, which possess similar reactivities in the oxidative addition step, afforded three possible products (one asymmetrical and two symmetrical) in a ratio corresponding to statistical distribution (2 : 1 : 1). If the reactivities of the starting aryl halides differ substantially, an asymmetrical product can be obtained in satisfactory yield only upon slow addition of the more reactive aryl halide in the course of electrolysis.[76]



R^1 = MeO, Me_2N, MeS; R^2 = F, CN, CF_3; X = Br, Cl.

Intramolecular cross-coupling catalysed by the Ni complex with 1,2-bis(diisopropylphosphino)benzene was reported.[51]



L = .

In the electrochemical syntheses of asymmetrical biaryls, high selectivity is achieved in two-step processes. The reaction involving a stoichiometric amount of the $PdCl_2(PPh_3)_2$ complex is an example.[56, 77, 78] The Pd(0) complex generated at an electrode first reacted with a molecule of one aryl halide followed by electroreduction of the resulting σ-arylpalladium complex in the presence of another aryl halide to give asymmetrical biaryls in good yields.

$$PdCl_2(PPh_3)_2 \xrightarrow{2\,e^-,\ PPh_3} Pd(0)(PPh_3)_2 \xrightarrow{Ar^1X} Ar^1PdX(PPh_3)_2 \xrightarrow{Ar^2X,\ 2e^-} Ar^1Ar^2 + Pd(0)(PPh_3)_2\,.$$

Yet another two-step synthesis of biaryls was carried out with the use of the catalytic Ni–bipy system. Electroreduction of aryl halides in the presence of Zn^{2+} ions and an excess of bipy with the use of a sacrificial zinc anode afforded not biaryls but arylzinc compounds stable in the reaction medium.[79] The addition of another aryl halide and a catalytic amount of $PdCl_2(PPh_3)_2$ to this reaction mixture gave rise to asymmetrical biaryls in high yields (Table 3).[80]

$$Ar^1X \xrightarrow[DMF,\ Zn\ anode]{e^-,\ Ni(BF_4)_2(bipy)_3\ (7\%)} Ar^1ZnX \xrightarrow[PdCl_2(PPh_3)_2\ (0.5\%-2\%)]{Ar^2X} Ar^1Ar^2$$

This method is also applicable to coupling reactions of aryl halides with allyl chlorides.[79] Functional substituents in aryl halides do not interfere with the reaction.

Table 3. Two-step cross-coupling of aryl halides catalysed first by Ni complexes and then by Pd complexes.[80]

Ar^1X	Ar^2X	Yield (%)
$4\text{-}ClC_6H_4CF_3$	$4\text{-}BrC_6H_4OMe$	83
$4\text{-}ClC_6H_4CF_3$	$4\text{-}BrC_6H_4CN$	83
$4\text{-}BrC_6H_4OMe$	$4\text{-}BrC_6H_4CN$	90
$4\text{-}BrC_6H_4OMe$	$4\text{-}BrC_6H_4NO_2$	84
$4\text{-}ClC_6H_4CO_2Me$	$4\text{-}BrC_6H_4OMe$	84
$4\text{-}BrC_6H_4NMe_2$	$4\text{-}BrC_6H_4NO_2$	84
$4\text{-}BrC_6H_4NMe_2$	$4\text{-}BrC_6H_4CN$	83
$2\text{-}BrC_6H_4OMe$	$2\text{-}BrC_6H_4CN$	55

2. Cross-coupling of aryl halides with activated alkyl halides

The syntheses of pharmaceuticals, agrochemicals and perfumes make use of arylacetic or arylpropionic acids and benzyl ketones as important intermediates. These compounds can be prepared by electrochemical methods. It was shown that esters of α-halocarboxylic acids can react with arylnickel compounds, which are generated electrochemically from aryl halide in a divided cell, to give esters of arylacetic or arylpropionic acids.[81] The chief drawback of this two-step procedure is the use of a large excess of PPh_3, which is necessary for preventing homocoupling.

$$ArX^1 + 2e^- + NiCl_2 \xrightarrow{PPh_3} ArNi(0)X^1(PPh_3) \xrightarrow{X^2CH(R)CO_2Et} ArCH(R)CO_2Et$$

R = H, Me; X^1, X^2 = Cl, Br.

Recently, a more efficient procedure, which combines the use of a sacrificial anode with catalysis by nickel complexes, was developed. To reduce undesirable homocoupling to a minimum, the most reactive substrate, *viz*., activated alkyl halide, was slowly added to the reaction mixture at 60–80 °C. This procedure was applied to cross-coupling of aryl halides with α-chloro esters (Table 4),[82,83] α-chloro ketones (Table 5)[83–85] and allyl and vinyl derivatives (Table 6).[84]

Table 4. Electroreductive cross-coupling of aryl halides with α-chloro esters catalysed by the $NiBr_2$(bipy) complex.[82,83]

$$ArX + ClCH(R)CO_2Me \xrightarrow[DMF,\ Zn\ or\ Al\ anode]{e^-,\ NiBr_2(bipy)\ (5\%-10\%)} ArCH(R)CO_2Me$$

ArX	R	Yield (%)
4-FC_6H_4Br	H	75
4-NCC_6H_4Br	H	60
4-$Me_2NC_6H_4Br$	H	67
4-FC_6H_4Br	Me	65
3-$CF_3C_6H_4Br$	Me	59
4-$CF_3C_6H_4Br$	Me	66
4-CNC_6H_4Br	Me	70
4-$MeOC_6H_4Br$	Me	51
4-$MeOC_6H_4I$	Me	85
2-Bromo-6-methoxynaphthalene	Me	55

This procedure was also successfully used in the asymmetric synthesis of 2-arylpropionic acids.[86] The resulting compounds possess higher biological activities than those of *S*-enantiomers [for example, in the case of 2-(3-phenoxyphenyl)propionic acid (phenoprofen) or 2-(6-methoxy-2-naphthyl)propionic acid (**1a**, R = H) (naproxen)]. However, conventional procedures for the synthesis generally afford racemates. The electrochemical synthesis allows asymmetric arylation of derivatives of α-chloropropionic acid using chiral auxiliary residues bound to the carboxy group. This reaction was used in the synthesis of (*S*)-fluorobiprofen starting from compound **1b**. Compounds **1a**,**b** were prepared in good yields and with a diastereomeric excess (*de*) using one equivalent of α-chloropropionylimide **2**.[86]

Table 5. Electroreductive cross-coupling of aryl halides with α-chloro ketones catalysed by the $NiBr_2$(bipy) complex.[83–85]

$$ArX + ClCH(R^1)COR^2 \xrightarrow[DMF,\ Zn\ or\ Al\ anode]{e^-,\ NiBr_2(bipy)\ (5\%-10\%)} ArCH(R^1)COR^2$$

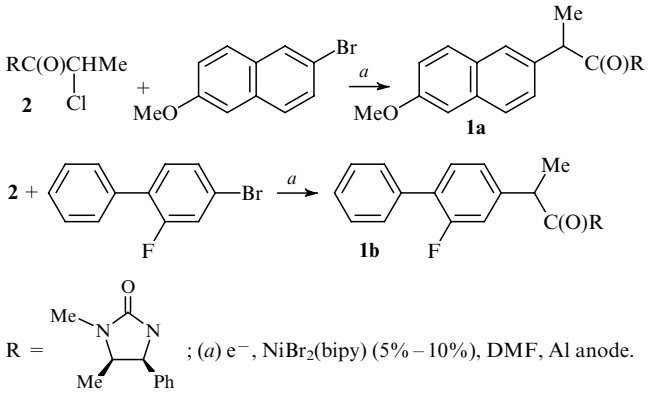
ArX	R^1	R^2	Yield (%)
4-FC_6H_4Br	H	Me	56
4-NCC_6H_4Br	H	Me	80
4-$Me_2NC_6H_4Br$	H	Me	52
4-FC_6H_4Br	H	Me	65
3-$CF_3C_6H_4Br$	H	Ph	52
4-$CF_3C_6H_4Br$	H	Ph	63
4-CNC_6H_4Br	Me	Me	70
4-$MeOC_6H_4Br$	Me	Me	70
4-$MeOC_6H_4I$	Me	Me	53
2-Bromo-6-methoxynaphthalene	Me	Me	45

Table 6. Electroreductive cross-coupling of aryl halides with vinyl or allyl derivatives catalysed by the $NiBr_2$(bipy) complex.[84]

$$ArX + RX \xrightarrow[DMF,\ Zn\ or\ Al\ anode]{e^-,\ NiBr_2(bipy)\ (5\%-10\%)} ArR$$

ArX	RX (the ratio between *Z* and *E* isomers)	Yield of ArR (%) (the ratio between *Z* and *E* isomers)
3-$CF_3C_6H_4Br$	BrCH = CHMe (50 : 50)	66 (20 : 80)
4-NCC_6H_4Br	BrCH = CHMe (50 : 50)	66 (20 : 80)
4-$MeOC_6H_4Br$	BrCH = CHMe (50 : 50)	44 (25 : 75)
3-$CF_3C_6H_4Br$	$AcOCH_2CH=CH_2$	56
4-$CF_3C_6H_4Br$	$AcOCH_2CH=CH_2$	38
4-$MeOC_6H_4Br$	$AcOCH_2CH=CH_2$	52
4-$MeOC_6H_4Br$	AcOCH$_2$CH = CHMe	63 [a]
4-$MeOC_6H_4I$	MeCH(Cl)CH = CH_2	56 [b]

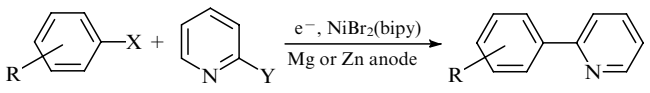
[a] A mixture of ArCH = CHEt and ArCH(Me)CH = CH_2 was obtained in a ratio of 86 : 12. [b] A mixture of ArCH = CHEt and ArCH(Me)CH = CH_2 was obtained in a ratio of 96 : 4.



R = ; (*a*) e^-, $NiBr_2$(bipy) (5% – 10%), DMF, Al anode.

Compound	Yield (%)	*ee*	*de*	Major configuration
1a	62	85	93	*S*
1b	58	82	92	*S*

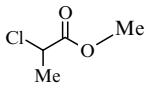
Recently, it has been demonstrated that cross-coupling of some aryl halides with hetaryl halides proceeded in high yields under the action of the Ni(II) complex with bipy.[87–89]



R = H, 4-F, 4-MeO, 4-Me_2N, 4-CN, 4-MeO_2C, 2-MeO; X, Y = Cl, Br.

Products of cross-coupling of aryl halides are listed in Table 7. In the course of electrolysis, the nickel(II) complex was regenerated and its content in the electrolyte is at most 10 mol % with respect to Ar^1X. Organic halides were taken in equivalent ratios. In all cases, the electrosynthesis afforded asymmetrical biaryl as the major product. If aryl halides contain electron-withdrawing substituents in the aromatic nucleus, their cross-coupling reactions proceed in higher yields with the use of a zinc anode. Apparently, this is attributable to higher reactivity of magnesium

Table 7. Products of cross-coupling of organic halides under the action of the electrochemically generated Ni(0)(bipy) complexes. $Q = 2.0-2.5$ e per ArX molecule.

Ar^1X	Ar^2X or RX	Yield (%)	Anode	Ref.
4-$MeOC_6H_4Br$	2-ClC_5H_4N	77	Mg	87
4-$Me_2NC_6H_4Br$	2-ClC_5H_4N	67	Mg	87
PhBr	2-ClC_5H_4N	70	Mg	87, 89
4-FC_6H_4Br	2-ClC_5H_4N	66	Zn	87
4-$MeOC(O)C_6H_4Cl$	2-ClC_5H_4N	33	Mg	87
4-$MeOC(O)C_6H_4Cl$	2-ClC_5H_4N	76	Zn	87
2-$MeOC_6H_4Br$	2-ClC_5H_4N	58	Mg	87
4-CNC_6H_4Br	2-BrC_5H_4N	60	Zn	87
	2-BrC_5H_4N	78	Mg	88
	2-BrC_5H_4N	50	Mg	88
	2-BrC_5H_4N	50	Zn	88
	2-BrC_5H_4N	60	Mg	87
		59	Al	88
		41	Al	88
	MeCH=C(Me)Br	80 [a]	Al	88
PhBr	Me_3SiCl	65	Mg	89

[a] $Z:E = 25:75$.

and its compounds with respect to electron-withdrawing functional groups resulting in transformations of the latter as side reactions. The mechanism of cross coupling was studied in detail and discussed in Ref. 89.

V. Formation of compounds containing the metal–carbon bond

Cathodic alkylation of catalysts upon reduction of alkyl halides is characteristic of various chelate complexes of transition metals, which form rather stable compounds with the alkyl–metal σ-bond (such as cobalamine, phthalocyanine, salen and dithiocarbamate complexes of Co, Fe, Ru, Rh, Ni and Cr).[90,91]

The electrochemistry of vitamin B_{12} and reactions of its reduced form (B_{12s}) with organic halides have been studied extensively.[92–99]

Schrauzer and coworkers[95–97] examined alkylation of vitamin B_{12s}, cobaloximes and other chelate Co(I) complexes [including Co(I)(salen)] with alkyl halides. Generally, these reactions proceed through the S_N2 mechanism including the supernucleophilic derivative of vitamin B_{12}, *viz*., B_{12s}, in which cobalt exists in the Co(I) state. Alkylcobalt intermediates were demonstrated[97] to decompose either photolytically or pyrolytically to form alkyl radicals. Rusling and coworkers[98] studied electrocatalytic reduction of 1,2-dibromoethane and 1,2-dibromobutane under the action of vitamin B_{12s} and found that these vicinal dibromides were transformed into alkenes without the intermediate formation of the alkylcobalt(III) complex. Later on, the catalytic reactions involving B_{12s} were compared with those involving Co(I)(salen)[99] and the rate of reduction of 1,2-dibromocyclohexane was found to depend on the formal potential of the Co(II)–Co(I) pair. In addition, it was demonstrated[100] that reduction of benzyl bromide under the action of Co(I)(salen) gave rise to either benzyl radicals or carbanions depending on the potential at which the intermediate benzylcobalt(III) complex is subjected to electrolysis.

Costa and coworkers[101–103] examined electrochemical reduction of salen complexes of organocobalt(III) and catalytic reactions of organic halides with the electrochemically generated Co(I)(salen) species. Methyl- and ethylcobalt(III)(salen) were electrochemically reduced to Co(I)(salen) and the alkyl radical.[101] It was shown that Co(I)(salen) slowly reacted with *tert*-butyl bromide or chloride to give 2-methylpropene and molecular hydrogen. Apparently, the initially formed unstable intermediate decomposed into Co(II)(salen) and the highly reactive *tert*-butyl radical due to steric hindrances induced by the *tert*-butyl group, no organocobalt(III) derivatives being generated.[103] Peters and coworkers[104] studied these reactions in most detail. Thus, the products of the reaction of Co(II)(salen) with iodoethane were identified and characterised, the reaction scheme was proposed, its kinetic and thermodynamical parameters were measured, the UV spectrum of the EtCo(salen) intermediate was recorded, the electrochemical reduction of this intermediate was characterised and simulation of the mechanism was performed. Preparative electrolysis showed that one electron was consumed per iodoethane molecule. The compositions of the reaction products depend primarily on the solvent. Thus the dimer, *viz*., n-butane, and ethane were obtained as the major products in acetonitrile and DMF, respectively (in all cases, ethylene was present in small amounts). The reaction scheme includes the following steps:

$$Co(II)(salen) + e^- \rightleftharpoons [Co(I)(salen)]^-, \quad (1)$$

$$[Co(I)(salen)]^- + EtI \longrightarrow EtCo(III)(salen) + I^-, \quad (2)$$

$$EtCo(III)(salen) + e^- \longrightarrow [EtCo(II)(salen)]^-, \quad (3)$$

$$[EtCo(II)(salen)]^- \longrightarrow [Co(I)(salen)]^- + Et^\bullet, \quad (4)$$

$$2\,Et^\bullet \longrightarrow C_4H_{10}, \quad (5)$$

$$2\,Et^\bullet \longrightarrow C_2H_6 + C_2H_4, \quad (6)$$

$$Et^\bullet + SolvH \longrightarrow C_2H_6 + Solv^\bullet. \quad (7)$$

SolvH is the solvent.

It was suggested that the solvents have different effects on the relative rates of the last three steps [reactions (5)–(7)]. Dimerisation of ethyl radicals dominated over disproportionation (in acetonitrile, the yield of n-butane was 7.2 times higher than that of ethylene; in DMF, this ratio ranged from 3 to 4). In all cases, the yield of ethane was higher than that of ethylene because hydrogen atoms are readily detached from the solvent under the action of ethyl radicals, the detachment from DMF proceeding more readily than that from MeCN [reaction (7)]. To confirm the proposed mechanism, EtCo(III)(salen), which was prepared by the reaction of electrochemically generated Co(I)(salen) with EtI [reaction (2)], was reduced at a controlled potential. In this process, one electron was demonstrated to be consumed per molecule of the σ-complex with the resulting formation of the green Co(I)(salen) complex and the ethyl radical [reactions (3)–(4)].[104]

Upon reduction of 1,8-diiodooctane under the same conditions,[105] two σ-complexes, *viz*., 8-iodooctylcobalt(III)salen and μ-(1,8-n-octyl)bis[cobalt(III)(salen)], were detected (both by electrochemical methods and UV spectroscopy) as intermediates, their relative amounts being dependent on the substrate : catalyst ratio.

The mechanism proposed in the study[99] was supported by the results of the investigation[106] on catalytic reduction of alkyl halides with the Co(II)(salen) complex at microelectrodes, the reaction scheme being supplemented by two more steps.

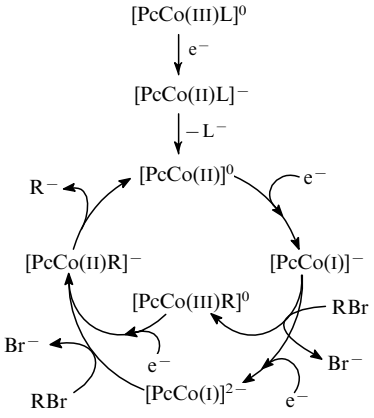
$$[RCo(II)(salen)]^- + RI \longrightarrow R-R + [Co(II)I(salen)]^-,$$

$$[Co(II)I(salen)]^- \longrightarrow Co(II)(salen) + I^-.$$

Electrochemical alkylation of mercury metal with butyl bromide in the presence of bis(dimethylglyoximato)(pyridino)Co(II) [$Co(DH)_2Py_2$] was examined.[107] It was suggested that Co(II) was initially reduced to Co(I). Then the Co(I) complex reacted with BuBr to give $BuCo(III)(DH)_2Py$ under the action of which the alkyl group was transferred to mercury metal.

Cathodic alkylation of the catalyst is typical of various chelate complexes of transition metals, which form rather stable compounds containing the alkyl–metal σ-bond, for example, of cobalamine, phthalocyanine, salen and dithiocarbamate complexes of Co, Fe, Ru, Rh, Ni and Cr.[90] These compounds contain metal atoms, which can exist in three successive oxidation states (for example, +3, +2 and +1 for Co), and possess the external π-system of the ligand favourable for stabilisation of the anionic complex. However, the ability of metal to exist in three oxidation states ($n+1$), n and ($n-1$) and the presence of a chelating ligand are not necessarily sufficient for alkylation of metal complex anions. For example, attempts to subject the Ir dimethylglyoximate complex to either chemical or electrochemical alkylation failed [108] in contrast to the analogous Co and Rh complexes. The potential of formation of the nucleophilic anion interacting with alkyl halides plays a large role in this process. If this potential is more negative than the potential of reduction of the alkylation product, the latter is not formed because of its irreversible reduction accompanied by the cleavage of the metal–alkyl bond. The potential of formation of the metal complex anion and the potential of reduction of the alkylation product depend on the nature of the metal atom, the chelating ligand, the solvent and the σ-bonded organic group.[109] For example, reduction of most metalloporphyrins, which contain an organic group σ-bonded to the metal atom, occurs at more negative potentials than reduction of metalloporphyrins with coordinated ligands. However, some ironporphyrins containing the Fe–Alk bond are reduced more readily than the corresponding complexes with ionic ligands.[110] Studies of the electrochemical properties of a series of Co^{2+} complexes with substituted phthalocyanines in DMF allowed the conclusion that alkylation of electrochemically generated monoanionic complexes in the presence of n-butyl bromide proceeded at the metal atom.[91]

Electrochemical reduction of n-butyl bromide was studied in the presence of the cobalt phthalocyanine complex PcCo(II) (Pc is substituted phthalocyanine) and the catalytic cycle was proposed.[111] This catalytic cycle was called 'chemical catalysis of electrochemical reduction of alkyl halides'.[111]



The above scheme is common to many chelate compounds of transition metals and rare-earth elements. At potentials more cathodic than the potential of reduction of the Co–Alk bond, electrolysis resulted in regeneration of the highly reactive $[PcCo(I)]^-$ anion, which was rapidly alkylated with n-butyl bromide present in the solution and then reduced thus resuming the catalytic cycle.[91]

Metalloenzymes are natural catalysts in which metal ions exhibit different coordination modes. Vitamin-B_{12}-dependent enzymes containing the cobalt atom as the catalytic site catalyse different isomerisation reactions accompanied by skeleton rearrangements.[112–123] New models were proposed [115–123] for enzyme catalysis on the basis of a hydrophobic analogue of vitamin B_{12} in which the peripheral amide groups of natural vitamin B_{12} are replaced by ester groups and this complex was demonstrated to be an efficient catalyst of electrochemical rearrangements of the carbon skeleton of 1-bromopropane derivatives containing two electron-withdrawing groups (COMe, CO_2Et or CN) at position 2.

Among other catalytic processes, the electrochemical transformation of nitrate anions into ammonia was carried out in water under the action of the Co(I) complex with 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene, which was prepared from the corresponding Co(II) complex.[124]

Some theoretical and applied problems of the use of cobalt complexes with ligands, which can stabilise metals in low-valent states, in electrocatalytic dehalogenation, homocoupling and cross-coupling reactions and in functionalisation of white phosphorus were covered in the studies.[125,126] It was shown that electrochemical reduction of organic halides proceeded under the action of either the Co^+(bipy) or $Co^-(bipy)_2^-$ complexes. Intermediates of the catalytic cycle, *viz*., cobalt σ-complexes, were isolated and characterised. It was demonstrated that arylation (alkylation) of white phosphorus occurred under the simultaneous action of electrochemically generated nucleophilic [Co(I)(bipy) or $RCoX_2$(bipy)] and electrophilic (M^{n+}, RX) reagents. Functionalisation of P_4 can follow two pathways, *viz*., P_4 can react with $ArCoX_2$(bipy) or it can be reduced with the Co(I)(bipy) complex to the δ-P_3-cyclotriphosphorus complex of cobalt, which, in turn, reacts with organic halides to form compounds containing the P–C bond.

The Ni σ-complexes are difficult to access and little studied. However, these compounds can be readily synthesised by electrochemical methods under mild conditions. It is known [89] that these complexes are intermediates of electrocatalytic cycles of cross-coupling, functionalisation of alkenes and reactions of aldehydes proceeding in the presence of Ni(0) complexes. In some cases, Ni σ-complexes can be isolated in pure form and they can be considered as model compounds for gaining insight into the mechanisms of organometallic synthesis.[89] Recently,[89] several σ-complexes containing Ni in different oxidation states [for example, RNiX(bipy), R_2NiX(bipy) and R_2Ni(bipy)] and exhibiting different reactivities were found to exist.

VI. Addition of organic halides to unsaturated groups

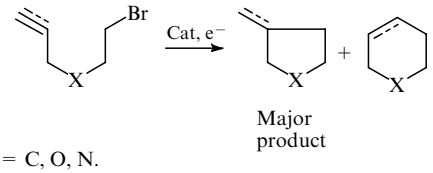
1. Addition at double and triple carbon–carbon bonds

First studies of electroreductive addition of organic halides at double or triple carbon–carbon bonds go back to the 1980s. Two main procedures using various catalysts were developed. In both processes, the key step involves the radical addition to unsaturated hydrocarbons. The first approach, which was considered primarily by Scheffold *et al*.,[127,128] is based on the use of vitamin B_{12} or related cobalt complexes as mediators of indirect electroreduction (in some cases, in combination with photolysis). The second approach, which was proposed by Gosden and Pletcher,[129] is based on the use of nickel complexes with macrocyclic tetradentate ligands, which can stabilise Ni(I) species.

In recent years, various organonickel and organocobalt compounds were studied and their redox properties and reactivities were examined depending on the nature of the ligand coordinated to the metal atom. The reactions described earlier were investigated once again with the aim of optimising the conditions and improving their efficiency. In particular, the reactions using the Ni(cyclam) complexes (cyclam is 1,4,8,11-tetraazacyclotetradecane) were examined and carbanion analogues were generated using the Ni(0) complexes in the presence of Michael acceptors.

a. Reactions with electron-rich double and triple carbon–carbon bonds

Most of reactions with electron-rich double and triple carbon–carbon bonds occur as free-radical cyclisation processes, which are used primarily for the preparation of five-membered rings with the desired stereochemistry.[130]



X = C, O, N.

Electrochemical processes involving cobalt complexes were studied in detail.[127, 131] In recent years, the results of new studies on the application of cobalt complexes other than vitamin B_{12} and nickel complexes with tetradentate macrocyclic ligands were reported. In these reactions, complexes of both types generate radical species.

Direct cyclisation of bromoacetals through cobaloxime(I) complexes was described as early as 1985.[132] The reactions were carried out in a divided cell in the presence of a base (40% aqueous NaOH) and (chloropyridine)cobaloxime(III) (50%) as a catalyst precursor. Later on, it was found [133, 134] that the amount of the catalyst can be reduced to 5% (the number of the catalytic cycles is ~50) and the presence of a base is not needed if the reaction is performed in a divided cell with a zinc anode.

This method was applied [133] to the synthesis of condensed bicyclic derivatives from various ethylene and acetylene compounds in the presence of (chloropyridine)cobaloxime(III) or $Co[C_2(DO)(DOH)_{pn}]$ (see Table 8). Either saturated or unsaturated cyclic products can be obtained depending on the amount of the catalyst used, the cathodic potential and the presence of the hydrogen donor, for example, RSH (see Table 8).[136, 138] Studies of some model reactions showed that the electrochemical method is more selective and efficient than conventional reduction with the use of Zn.[135]

Nickel compounds, for example, the Ni(cyclam) complexes,[129] can also be used for generating radicals in electroreductive processes, including free-radical cyclisation reactions.

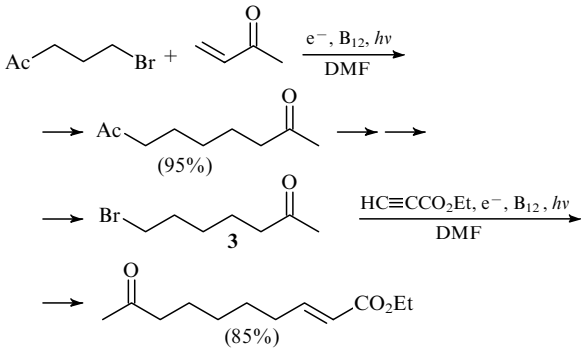
The Ni complexes with cyclam and its analogues and also with Ni(CR) and Ni(tet a) serve as efficient catalysts in DMF in the presence of NH_4ClO_4 as a proton source.[136–138, 141] Electrochemically generated Ni(I) species rapidly react with organic halides to form alkynyl, alkenyl or aryl radicals whose intramolecular addition at double or triple bonds gives rise to cyclopentane derivatives (see Table 8).[136–138] These reactions can also be carried out in an undivided cell with a magnesium anode, as exemplified [139] by the reactions of aryl halides bound to an unsaturated hydrocarbon chain (see Table 8). Nickel complexes with cyclam and other tetradentate donor ligands are catalysts of choice.[139, 142, 143]

The Ni(salen) complex is a good alternative to the Ni(cyclam) complex for generating Ni(I)-containing intermediates. Thus cyclisation of 1-halo-6-phenylpent-5-ynes proceeded much more efficiently than direct electroreduction of the substrate in the presence of 10% of a catalyst (see Table. 8).[140] Electroreductive cyclisation of *N*-alkenyl-2-bromoanilines with the use of the Pd complex with PPh_3 as the catalyst [144] and electrocatalytic dehalogenation of α-haloacetic acids under the action of the reduced form of vitamin B_{12} were reported.[145]

b. Addition to Michael acceptors

Radicals or carbanions and their equivalents, *viz*., organometallic compounds, can be added to Michael acceptors. Free-radical reactions in the presence of nickel or cobalt complexes as catalysts have been studied previously.[127–129]

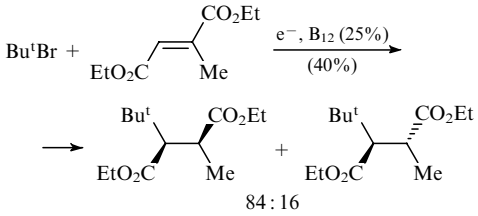
The synthesis of ethyl 8-oxodec-2-enoate, which was isolated from honey queen bees, provides a good example of the potential of the electrochemical approach to the preparation of natural products. This process involves two major electrochemical steps, *viz*., the formation of the C–C bond catalysed by vitamin B_{12} and initiated by visible light and the Michael addition of intermediate **3** at the triple bond.[128]



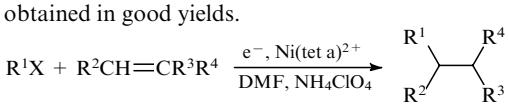
This approach was applied to the synthesis of the pheromone of California red scale,[146] prostaglandin $PGF_{2\alpha}$,[147] the pheromone of house mice [128] and jasmonates.[148] Alkylation and acylation of activated alkenes was used for the preparation of amino acid derivatives (Table 9).[149]



In some cases, protonation of an intermediate radical formed through the addition of alkyl halide to the Michael acceptor proceeds diastereoselectively. This situation is observed upon the addition of Bu^tBr to diethyl mesaconate catalysed by vitamin B_{12}.[150] However, standard reduction with zinc in the presence of vitamin B_{12} proved to be more efficient because the stereoselectivity in the latter case was determined by the addition of amines.

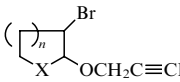
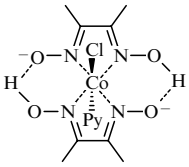
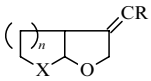
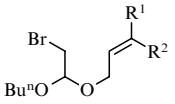
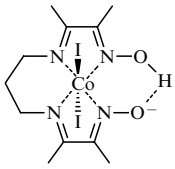
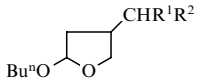
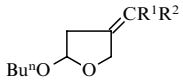
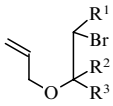
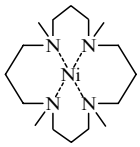
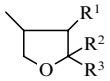
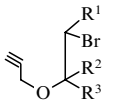
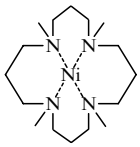
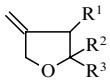
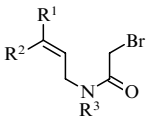
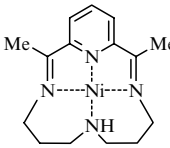
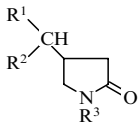
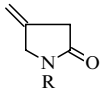
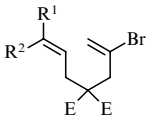
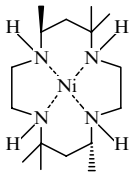
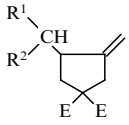
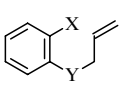
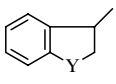
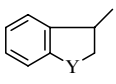
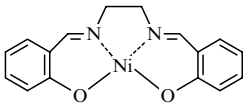


The Ni(cyclam) complexes and related compounds can also be used for alkylation of Michael acceptors. For Ni(tet a) in acetonitrile, the number of catalytic cycles is small.[151] However, this catalyst (2%) in DMF containing NH_4ClO_4 as the proton source shows efficiency in alkylation of unsaturated ethers, ketones or nitriles.[152] In the case of terminal alkenes, the reaction products are obtained in good yields.



R^1X	R^2	R^3	R^4	Yield (%)
BuBr	H	H	CO_2CH_2Ph	53
BuBr	H	H	CO_2H	32
$Ph(CH_2)_3Br$	$(CH_2)_4CO$		H	14
$Ph(CH_2)_3Br$	Me	H	CO_2Me	13
$Ph(CH_2)_3Br$	H	Me	CO_2Me	53
$Ph(CH_2)_3Br$	H	H	CO_2Me	57
$Ph(CH_2)_3Br$	H	H	CN	72
$Ph(CH_2)_3Br$	H	H	COMe	37
$Ph(CH_2)_2CH(Me)Br$	H	H	CO_2Me	60

Table 8. Reductive cyclisation catalysed by Co and Ni complexes.

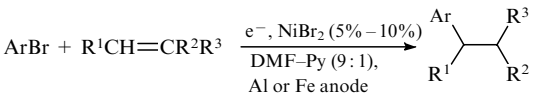
Substrate	Catalyst [short name]	Amount (mol %)	Reaction conditions	Reaction product	Yield (%)	Ref.
 n = 1, 2; X = O, NCO_2Et; R = H, Et, C_5H_{11}, $SiMe_3$	 [(chloropyridine)-cobaloxime(III)]	5	MeOH, 55–60 °C, Zn anode		54–80	133
 R^1 = H, Me, Ph; R^2 = H, Me	 $[CoC_2(DO)(DOH)_{pn}]$	5	MeCN $C_{12}H_{25}SH$		42–96	135
	$CoC_2(DO)(DOH)_{pn}$	40	MeCN		68–97	135
 R^1 = H, R^2 = R^3 = Ph; R^1-R^2 = $(CH_2)_n$, R^3 = H		20	DMF		53–75	136
 R^1 = H: R^2 = R^3 = Ph; R^1-R^2 = $(CH_2)_n$, R^3 = H		20	DMF		85–86	136
 R^1, R^2 = H, Me; R^3 = H, Ts, All, Bn	 [Ni(CR)]	20	DMF or MeCN		11–67	137
 R = H, Ts, All, Bn	Ni(CR)	20	DMF or MeCN		7–33	137
 R^1, R^2 = H, Me; E = CO_2Me	 [Ni(tet a)]	20	DMF		47–81	138
 X = I, Br; Y = O, NH	Ni(tet a)	20	DMF		60–90	136, 138
	Ni(cyclam) [a]	10	DMF, Mg anode		60–90	139
$PhC\equiv C(CH_2)_3CH_2X$ X = Br, I	 [Ni(salen)]	10	DMA		84	140

[a] Hereinafter, cyclam is 1,4,8,11-tetraazacyclotetradecane.

Table 9. Alkylation or acylation of activated alkenes catalysed by vitamin B_{12}.[149]

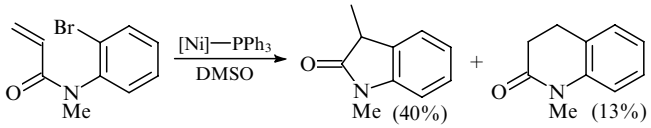
RX	Y	Reaction product	Yield (%)
$Me(CH_2)_3Br$	NHAc	$Me(CH_2)_4CHCO_2Me$ NHAc	70
$Me(CH_2)_3Br$	H	$Me(CH_2)_5CO_2Me$	75
Ac_2O	NHAc	$AcCH_2CHCO_2Me$ NHAc	67
Ac_2O	H	$Ac(CH_2)_2CO_2Me$	70
$MeO_2C(CH_2)_3Br$	NHAc	$MeO_2C(CH_2)_4CHCO_2Me$ NHAc	72

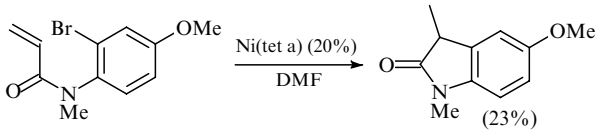
The nucleophilic addition can be performed in the presence of Ni(II) complexes, which are transformed into Ni(0) complexes upon cathodic reduction. The Ni(0)(bipy) complexes rapidly react with alkyl, alkenyl and aryl halides. However, in this case the organonickel intermediate generated through oxidative addition does not give the corresponding addition product in the presence of activated alkenes. In the presence of a Ni complex with a weaker bound ligand (for example, with pyridine, which prevents activated alkene from being coordinated to the metal atom), the regioselective 1,4-addition of aryl groups to activated alkenes was carried out under very mild conditions (60 °C, an undivided cell with a sacrificial aluminium or iron anode). Arylation products were obtained in 20% – 63% yields,[153] which are comparable with those obtained in reactions using arylcopper or cuprates. The reactions performed in methanol or ethanol instead of DMF gave products in only slightly lower yields [the nickel complex with di(2-bipyridyl)amine as the catalyst].[55]

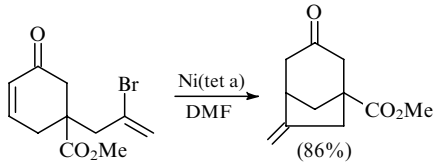


Ar	R^1	R^2	R^3	Yield (%)
Ph	H	H	CO_2Et	63
4-NCC_6H_4	H	H	CO_2 Et	48
2-Naphthyl	H	H	CO_2Et	50
4-$MeOC_6H_4$	CO_2Et	H	CO_2Et	46
4-$MeCOC_6H_4$	CO_2Et	H	CO_2Et	31
2-Naphthyl	H	Me	CO_2Et	27
2-Naphthyl	Me	H	CO_2Et	20
2-Naphthyl	H	H	CN	61
2-Naphthyl	$(CH_2)_4CO$		H	20

Intramolecular nucleophilic addition can follow either the radical or carbanion pathway.[51, 137, 138, 154] Some examples are given below.[51, 137, 138]

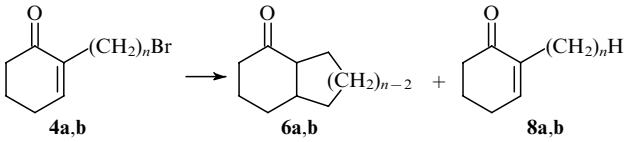






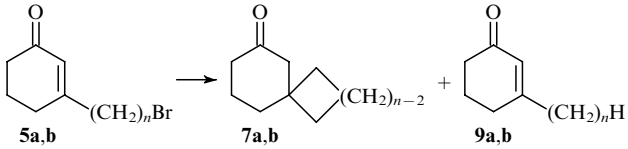
Bicyclic ketones were synthesised in the presence of 5% of vitamin B_{12}.[127]

Some other Co complexes as well as Ni complexes catalysed cyclisation of bromocyclohexenones **4a**,**b** and **5a**,**b** to form bicyclic ketones **6a**,**b** and **7a**,**b**, respectively,[154] but the numbers of catalytic cycles in these cases were rather small. These reactions afforded open-chain compounds **8a**,**b** and **9a**,**b** as by-products. The Ni(cyclam)$(ClO_4)_2$, Ni(CR)$((ClO_4)_2$ and Co(bpp)OAc [bpp = $C_5H_5NC(O)N^-(CH_2)_3N^-C(O)C_5H_5N$] complexes proved to be most efficient as catalysts.[154]



n = 4 (**a**), 5 (**b**).

Catalyst	Substrate	Yields of products (%)			
		6a	**8a**	**6b**	**8b**
Ni(cyclam)$(ClO_4)_2$	**4a**	70	6	–	–
	4b	–	–	33	18
Ni(CR)$(ClO_4)_2$	**4a**	60	1	–	–
	4b	–	–	42	14
Co(bpp)AcO	**4a**	52	5	–	–
	4b	–	–	28	21

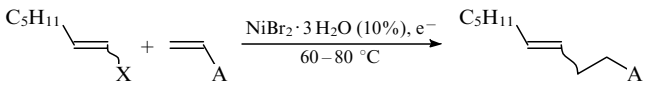


n = 4 (**a**), 5 (**b**).

Catalyst	Substrate	Yields of products (%)			
		7a	**9a**	**7b**	**9b**
Ni(cyclam)$(ClO_4)_2$	**5a**	30	4	–	–
	5b	–	–	65	21
Ni(CR)$(ClO_4)_2$	**5a**	42	4	–	–
	5b	–	–	16	19
Co(bpp)OAc	**5a**	47	11	–	–
	5b	–	–	40	13

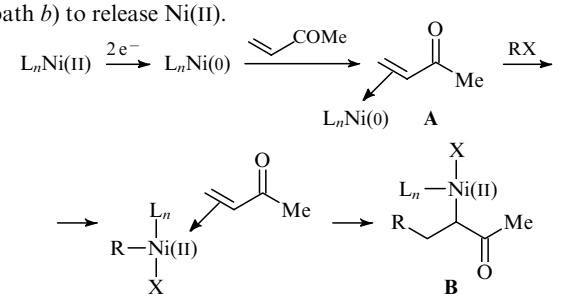
Intramolecular arylation of unsaturated amides gives rise to lactams. These reactions can follow either the radical or carbanion pathway. The carbanion mechanism is realised in the presence of the nickel triphenylphosphine complex to give a mixture of γ- and δ-lactams in a ratio of 3 : 1.[51] The reactions through the radical mechanism [in the presence of the Ni(tet a) complex] proceed selectively to give δ-lactam, although in rather low yield.[137]

The electroreductive addition of (*Z*)- or (*E*)-alkenyl halides to electron-deficient alkenes in the presence of a sacrificial iron anode proceeds in high yields with complete retention of the stereochemistry of the alkenyl fragment. These reactions can be used for functionalisation of isomerically pure (*Z*)- or (*E*)-alkenes.[155]

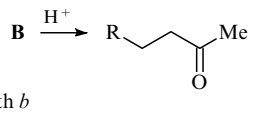


X = Cl, Br, I; A = CO_2Et, COMe, CN.

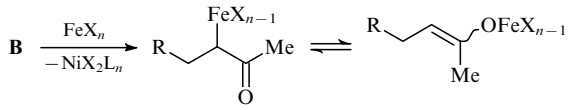
The conditions were optimised using the model reaction of methyl vinyl ketone (A = COMe) with (*Z*)- or (*E*)-1-halohept-1-enes. It was found that high yields (up to 84%) can be achieved in the presence of 1,2-dibromoethane and an iron anode. The process involves preelectrolysis, *viz*., oxidation of an iron anode and reduction of 1,2-dibromoethane, followed by electrolysis of a mixture of alkenyl halide and methyl vinyl ketone. The role of iron ions is not understood. Conceivably, they function as Lewis acids, activate electron-deficient alkenes and facilitate the formation of the C—C bond. The reaction mechanism is not entirely known. Presumably, it involves coordination of electron-deficient alkene by electrochemically generated Ni(0) species. Oxidative addition of vinyl halide to the complex **A** affords the organonickel compound **B**, which is either protonated by residual water (path *a*) to form an addition product or transmetalated with iron ions (path *b*) to release Ni(II).



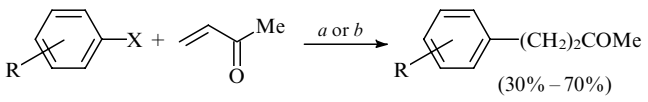
Path *a*



Path *b*



Recently, it was found [156] that cobalt bromide, either in the free form or in the complex with 2,2′-bipyridyl, catalyses the electrochemical addition of aryl halides to activated alkenes in a DMF–pyridine or acetonitrile–pyridine mixture. The reactions proceeded only with the use of a sacrificial iron anode, whereas the addition products were not detected in the reactions performed with other anodes (Zn or Al).



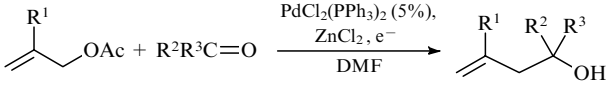
R = 4-CO_2Et, 4-COMe, 4-CF_3, 4-CN, 4-CHO, H, 4-OMe, 2-COMe;
X = Br;
(*a*) DMF–PyH, $CoBr_2$–bipy (1 : 2), Fe anode, Ni cathode, 70 °C;
(*b*) MeCN–PyH, $CoBr_2$, Fe anode, Ni cathode, 60 °C.

2. Addition to carbonyl compounds

Data on electrochemical allylation of carbonyl compounds and the Reformatsky reaction are presently available.

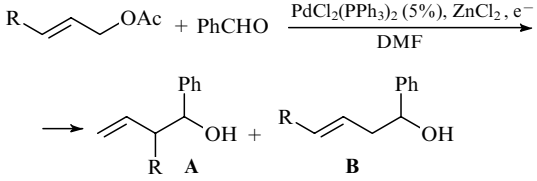
Some carbonyl compounds can be subjected to direct electrochemical allylation; however, coupling reactions catalysed by transition metals are more efficient, particularly, in the case of ketones.

One of procedures involves $PdCl_2(PPh_3)_2$ as the catalyst in the presence of the zinc salt ($ZnCl_2$). This procedure allows one to transform allyl acetates into the corresponding tertiary alcohols in good yields.[157]



R^1	R^2	R^3	Yield (%)
H	Ph	H	77
H	4-$MeOC_6H_4$	H	84
H	4-ClC_6H_4	H	68
H	$(CH_2)_5$		40
Me	Ph	H	62

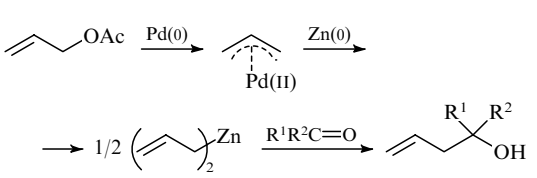
Of two possible isomers, the more branched isomer **A** was obtained as the major reaction product.



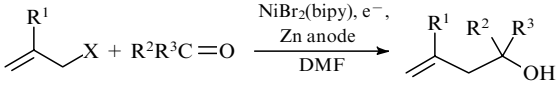
R = Me (56%, **A** : **B** = 91 : 9); Ph (71%, **A** : **B** = 83 : 17).

The reactions with conjugated carbonyl compounds proceed as 1,2-addition.

Exploration into the mechanism of this reaction revealed the key role of $ZnCl_2$,[158] which is most readily reduced to give Zn(0). The latter is capable of reducing the π-allylpalladium intermediate. The reaction products are formed through addition of diallylzinc to carbonyl compounds.



Carbonyl compounds can be allylated with the use of a nickel catalyst.[82, 159, 160]

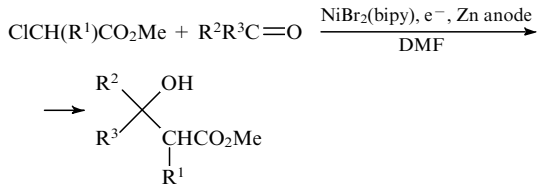


X	R^1	R^2	R^3	Yield (%)
Cl	Me	Ph	H	85
Cl	Me	$Me(CH_2)_5$	H	70
Cl	Me	Ph	Ph	86
Cl	Me	Bu^t	Me	60
Cl	Me	$CH_2=CH$	Me	43
OAc	H	Ph	H	80
OAc	H	$(CH_2)_5$		83

When employing an undivided cell, this reaction proceeds efficiently only in the presence of a sacrificial zinc anode. The reactions of aromatic and aliphatic aldehydes or ketones give rise to the corresponding homoallylic alcohols in good yields. The reactions of branched ketones, such as diisopropyl ketone, afford products in lower yields. In the case of α,β-unsaturated carbonyl compounds, the addition occurs exclusively at the 1,2-position. The Pd–Zn catalytic system is also efficient in these reactions. It was suggested [160, 161] that the process is accompanied by transmetalation of the allylnickel complex, which is formed upon the oxidative addition of allyl halide (acetate) to the Ni(0) complex, with anodically generated Zn(II) species.[160, 161]

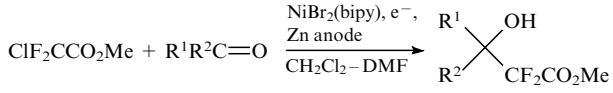
The Reformatsky reaction can also be carried out in an electrochemical mode either directly or with the use of a mediator.

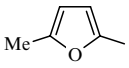
Catalysis by nickel compounds provides an efficient way of transforming the corresponding α-chloro derivatives to β-hydroxy esters or nitriles.[162] These reactions also involve the oxidative addition of cathodically generated Ni(0)(bipy) to a halogen-containing derivative as the first step. In this case, the nature of a sacrificial anode is also of importance although the formation of an organozinc derivative was not unambiguously confirmed.



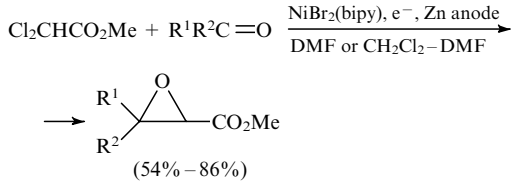
R^1	R^2	R^3	Yield (%)
H	Et	Et	77
H	$(CH_2)_5$		86
H	Ph	Ph	77
Me	Pr^n	Me	64
Me	Ph	H	80
Me	$CH=CH(CH_2)_3$		50

The reaction of carbonyl compounds with methyl chlorodifluoroacetate,[163] which cannot be activated by conventional chemical methods, provides an interesting example demonstrating the possibilities of this procedure. The best results were obtained with the use of a CH_2Cl_2–DMF mixture (9 : 1). The ^{19}F NMR spectroscopic studies demonstrated that the reaction was accompanied by transmetalation.



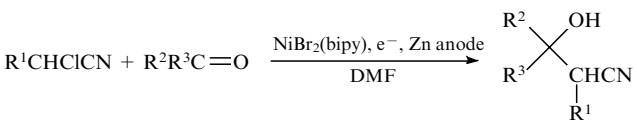
R^1	R^2	Yield (%)
Ph	Me	72
$(CH_2)_5$		63
Ph	H	70
$Me(CH_2)_2$	H	77
	H	45

Under analogous conditions, the reactions of methyl dichloroacetate with acetophenone or cyclohexanone afforded epoxides in high yields.[162]



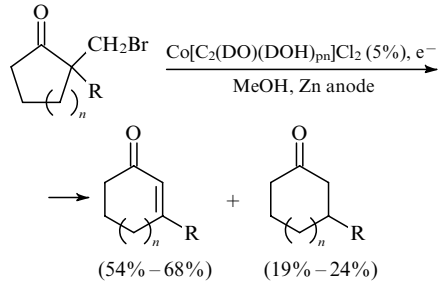
R^1 = Ph, n-C_6H_{13}, Bu^t; R^2 = H, Me, Ph; R^1-R^2 = $(CH_2)_5$.

The reactions of chloroacetonitrile and α-chloropropionitrile with ketones proceeded analogously.[162]



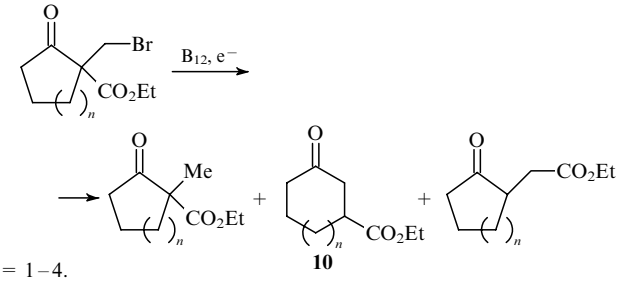
R^1 = H, Me; R^2 = Ph, n-C_6H_{13}, Bu^t; R^3 = H, Me, Ph; R^2-R^3 = $(CH_2)_5$.

The intramolecular addition to the carbonyl group has not been adequately investigated. Only the ring expansion reactions of α-bromomethylcycloalkanones, which were carried out in the presence of $Co[C_2(DO)(DOH)_{pn}]Cl_2$ as the catalyst at 55–60 °C, were reported.[133, 164] It was assumed that the reaction proceeds *via* the radical pathway in accordance with the usual behaviour of alkylcobalt intermediates. The use of a sacrificial zinc anode in combination with a cobalt catalyst leads to an increase in the number of catalytic cycles and improvement in the yield.[133]



R = Bu^n, n-C_6H_{13}, n-$C_{11}H_{23}$; n = 1–4.

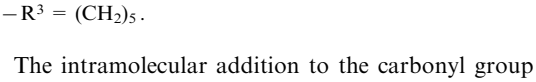
Much attention has been given to the use of catalytic systems based on cobalt complexes in the organic synthesis, particularly, in the ring expansion reactions suitable for the preparation of natural compounds. The traditional electrolytic scheme of the synthesis was proposed. Under electrochemical conditions, Co(II) in heptamethyl cobyrinate perchlorate {[Cob(II)$_7$C$_1$ester]ClO_4}, which is a catalyst simulating vitamin B_{12}, is readily reduced to Co(I) to give highly nucleophilic intermediates. The latter react with alkyl halides to form alkylated complexes containing the Co–C bond. The electrochemical reactions or photolysis of these complexes afford the final products. Torii and coworkers[164] studied the ring expansion reactions of 2-(bromomethyl)cyclopenta(hexa)nones with the use of cobaloxime (MeOH, 60 °C) in the galvanostatic mode under irradiation with visible light. Murakami and coworkers[165] used [Cob(II)$_7$C$_1$ester]ClO_4 as the catalyst of ring expansion reactions in the potentiostatic mode.



n = 1–4.

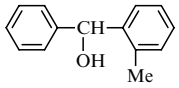
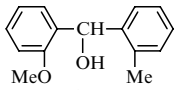
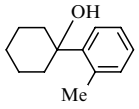
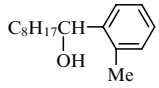
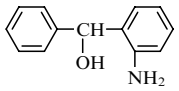
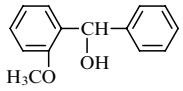
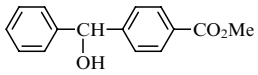
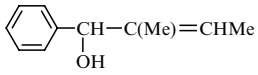
In different electrolytic modes, the ring-expansion product **10** was obtained as the major product (in yields of up to 56%). The course of the reaction was monitored by electronic and ESR spectroscopy, which made it possible to identify intermediates formed at different potentials either in daylight or in the dark. The potentials $\leqslant -1.5$ V (with respect to a saturated calomel electrode) are optimum for electrolysis. The reaction cycle involves electrochemical reduction of the Co(II) complex to supernucleophilic Co(I) species, which react with the substrate to give the corresponding alkylated complex. The latter decomposes upon electrolysis (rather than photochemically) to the final product and the cobalt complex is recycled back to the catalytic cycle as the mediator. The ratio of the reaction products is determined by the strain energy of alicycles. Thus the highest yield of the ring-expansion product was achieved in the transformation of five-membered cyclic ketone to six-membered ketone.[165]

Under particular conditions, electroreductive coupling of organic halides with aldehydes catalysed by the nickel(0) complex with 2,2′-bipyridyl proceeds in good yields (Table 10).[166]



Alcohols can be obtained in high yields with the use of nickel, iron or stainless steel anodes. Aromatic aldehydes bearing the

Table 10. Coupling of organic halides with carbonyl compounds catalysed by the $NiBr_2$(bipy) complex (1 mmol) (see Ref. 166).[a]

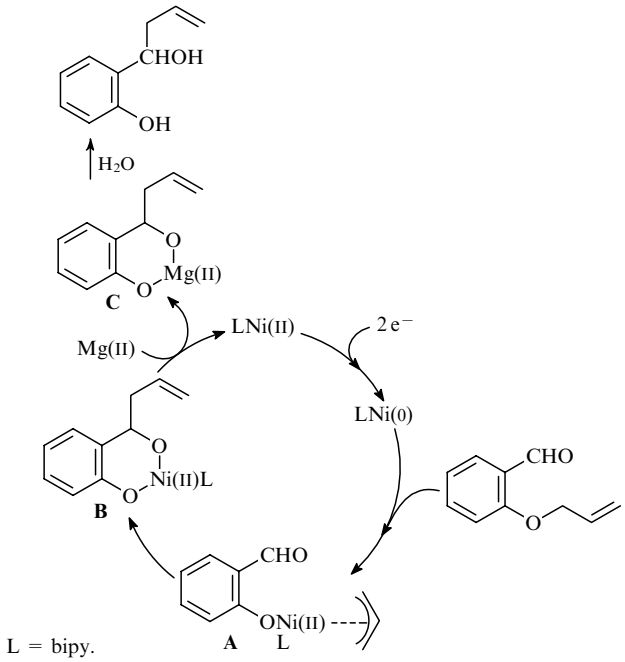
ArX	R^1R^2CO	Reaction product	Anode	Yield (%) (see [b])
2-BrC_6H_4Me	PhCHO		Mg	14 (75)[c]
			Zn	18
			Ni	61
			Fe	63
			inox[d]	80
	2-$MeOC_6H_4CHO$		Ni	60
			inox[d]	71
			Ni	50
	$C_8H_{17}CHO$		inox[d]	58
2-$BrC_6H_4NH_2$	PhCHO		inox[d]	42
2-BrC_6H_4OMe	PhCHO		Ni	85
4-$ClC_6H_4CO_2Me$	PhCHO		inox[d]	50[e]
MeC(Br)=CHMe	PhCHO		inox[d]	52

[a] Reaction conditions: ArX, 15 mmol; R^1R^2CO, 7.5 mmol; Bu_4NBF (10^{-2} mol litre^{-1}) as the supporting electrolyte; I = 0.1 A, a nickel cathode, 20 °C. [b] The yields are given with respect to the carbonyl compound; [c] $NiBr_2$(bipy), 7 mmol; [d] inox is a stainless steel anode; [e] the yield is given with respect to ArCl (ArCl, 7.5 mmol, PhCHO, 30 mmol).

electron-donating groups in the ring, aliphatic aldehydes and cyclohexanone can be involved in these reactions. 2-Bromoaniline and 2-bromoanisole can serve as arylating agents, whereas other isomers cannot perform this function due, apparently, to stability of the arylnickel intermediate ArNi(I)(bipy). The reactions of aryl halides containing substituents at positions 3 and 4 yield predominantly biaryls, whereas the addition at the carbonyl group proceeds to only a small extent. The reaction of benzaldehyde with aryl halide containing the electron-withdrawing methoxycarbonyl group in the ring proceeded in satisfactory yield upon the replacement of Br by Cl. In this case, homocoupling of ArNi(I)(bipy) with ArX was suppressed but a three- to fourfold excess of the aldehyde was required. The fact that aromatic aldehydes containing electron-withdrawing substituents in the ring, which are favourable for π-bonding, virtually do not enter into the reactions (whereas aliphatic aldehydes can be involved in these reactions) is indicative of the predominant σ-character of the bond between the organonickel complex and the carbonyl group of aldehyde.

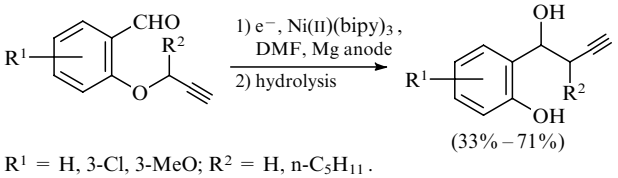
Selective reduction of aryl propargyl ethers to the corresponding phenols in the presence of electrochemically generated nickel complexes proceeds under mild conditions and in good yields. This reaction provides the means of removing the allyl and propargyl protective groups.[167]

The carbonyl group in allyl ether of salicylaldehyde was subjected to electrochemical intramolecular allylation [$NiBr_2$(bipy), Mg anode, −1.2 V with respect to a saturated calomel electrode] using nickel complexes as the catalyst.[168] It is believed that this process involves electrochemically generated Ni(0) complexes as active catalytic species capable of reacting with the allyl fragment of the ether to form the π-allyl nickel complex **A**. The intramolecular transfer of the allyl fragment to the carbonyl group affords intermediate alkoxide, *viz*., nickel(II) phenoxide **B**. Conceivably, the Ni^{2+} ions in this complex can be replaced by the Mg^{2+} ions to give the intermediate **C**, which is accompanied by liberation of the Ni(II) complex and completion of the catalytic cycle. Hydrolysis of the alkoxide **C** gives rise to the final product:



L = bipy.

Later on, it was demonstrated [169] that the propargyl fragment in *o*-(propargyloxy)arenecarbaldehydes was transferred to the carbonyl group under the action of electrochemically generated nickel complexes to produce homopropargyl alcohols.

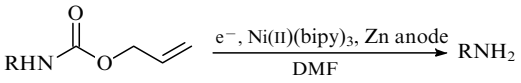


(33% – 71%)

R^1 = H, 3-Cl, 3-MeO; R^2 = H, n-C_5H_{11}.

It was believed that the C–O bond in propargyl ether was initially cleaved followed by the addition of the propargyl fragment to the carbonyl group. The reactions of ring-unsubstituted propargyl ethers afforded allene isomers as by-products.

Electrochemical reductive deprotection of the amino group in allylcarbamates containing several functional substituents in the presence of catalytic amounts of the Ni(II)(bipy)$_3$ complex proceeded selectively to give the corresponding amines in 40% – 99% yields.[170]



R = Ph, 4-$MeO_2CC_6H_4$, 4-NCC_6H_4, 2-$MeCOC_6H_4$, Bn, cyclo-C_6H_{13}, $(MeO)_2CHCH_2$.

The reactions proceed under mild conditions (20 °C) in an undivided cell with a sacrificial zinc anode. The allyl groups in arylcarbamates are selectively removed in 70% – 99% yields. Under these conditions, the ether, ketone, acetal and nitrile groups remain intact.

VII. Electrocatalytic reduction of carbon dioxide

The data on electrocatalytic reduction of nitrogen and its oxides, carbon oxides and small molecules containing triple bonds (acetylene, cyanides) were surveyed in the reviews.[13, 171] All these substrates are electrochemically inactive and contain very strong bonds, which are rather difficult to cleave. Hence, activation of these molecules by inserting them into the coordination sphere of metal followed by (or preceded by) the electrochemical electron transfer is the most promising way for subjecting poorly reactive molecules to various chemical transformations. Besides, electrocatalytic procedures involving metal complexes attract considerable attention because they allow the use of vast biosphere reserves of N_2, CO_2 and O_2 as cheap and accessible starting materials in various chemical processes.

Direct reduction of CO_2 at a metal cathode, for example, at a mercury cathode, requires a high overpotential ($E_{CO_2/CO_2^-\cdot}$ = −2.21 V with respect to a saturated calomel electrode, DMF). Other metal cathodes, for example, copper or gold cathodes, can reduce CO_2 in aqueous solutions at somewhat lower cathodic potentials (from −1.3 to 1.7 V). However, even these values are too high for practical applications because water is reduced at these potentials with hydrogen elimination. In principle, it is possible to use non-aqueous solvents, but these processes require larger energy consumption and are often accompanied by side reactions.

The use of various metal complexes as catalysts has the most promise for selective electroreduction of CO_2. Generally, these processes are carried out using complexes with nitrogen-containing macrocyclic ligands, *viz*., porphyrins and their analogues, which are well known as biocatalysts.[172] Compared to natural catalysts, artificially synthesised metal complexes with nitrogen-containing macrocyclic ligands (for example, with phthalocyanines) possess even more extended π-conjugated chains, whereas their catalytic activity is highly competitive with that of natural analogues. Metal complexes with phthalocyanines,[173–185] Co(II) complexes with porphyrins,[90] Ni(II) complexes with cyclam,[186–191] bis- and polypyridyl complexes of Rh(II),[192] Re(I),[193] Cu(II),[194] Co(II), Fe(II) and Ni(II),[195–199] iron and cobalt complexes with 4,5-dihydroxybenzo-1,3-disulfonate and 2-hydroxy-1-nitrosonaphthalene-3,6-disulfonate [200, 201] ligands proved to be catalysts of CO_2 reduction. Most of the above-mentioned complexes act as efficient catalysts of CO_2 reduction only in non-aqueous media because CO_2 reduction in water is preceded by proton reduction. Only the cobalt complex with phthalocyanine (PcCo)[173, 174, 176–181, 201, 202] and the nickel complex with cyclam [185, 195, 203, 204] proved to be efficient electrocatalysts of CO_2 reduction in water or aqueous acetonitrile, the latter being active only at a mercury cathode at which the overpotential of hydrogen elimination is higher than that at a platinum cathode. It was suggested [186, 187] that higher selectivity of electroreduction of CO_2 compared to that of H_2O observed in these processes is associated with the larger size of the macrocyclic ligand and the presence of the NH groups in Ni(cyclam).

A considerable advantage of metal complexes as catalysts is the possibility of changing their reactivities by modifying the macrocyclic ligand with electron-donating or electron-withdrawing substituents. Thus the nickel(II) complex with a cyclam analogue containing two methyl groups in the macrocycle (3,10-dimethyl-1,3,5,8,10,12-hexaazacyclodecane) exhibits much higher catalytic activity than the nickel(II) complex with unsubstituted cyclam.[205] It should be noted that the insertion of σ-acceptor substituents (for example, of fluorine) into the nitrogen-containing ring also leads to improvement in the catalytic activity and selectivity of CO formation (compared to hydrogen elimination). In these cases, the Ni(II) complex with 3,3,10,10-tetrafluorocyclam proved to be most efficient. The further increase in the number of the fluorine atoms in the macrocycle leads to deterioration of activity.[206]

Metalloporphyrins can also exhibit catalytic activity in reduction of CO_2 to CO in aqueous and non-aqueous media.[207] However, porphyrins are rapidly consumed in the course of electrolysis and the catalysis ceases after a rather small number of catalytic cycles. Catalysts are poisoned due to carboxylation and hydrogenation of porphyrins (see Ref. 208).†

Mechanisms for formation of different products of CO_2 reduction catalysed by metallophthalocyanines have been proposed.[173, 174]

$$CO_2 + PcM \longrightarrow [PcM\cdots CO_2].$$

The formation of carbon monoxide

$$2H^+ + 2e^- + [PcM\cdots CO_2] \longrightarrow H_2O + [PcM\cdots CO],$$

$$[PcM\cdots CO] \longrightarrow CO + PcM.$$

The formation of formic acid

$$H^+ + e^- + [PcM\cdots CO_2] \longrightarrow [PcM\cdots OOCH],$$

$$H^+ + e^- + [PcM\cdots OOCH] \longrightarrow [PcM\cdots HOOCH],$$

$$[PcM\cdots HOOCH] \longrightarrow HCOOH + PcM.$$

The formation of methane

$$2H^+ + 2e^- + [PcM\cdots CO] \longrightarrow H_2O + [PcM\cdots C],$$

$$4H^+ + 4e^- + [PcM\cdots C] \longrightarrow [PcM\cdots CH_4],$$

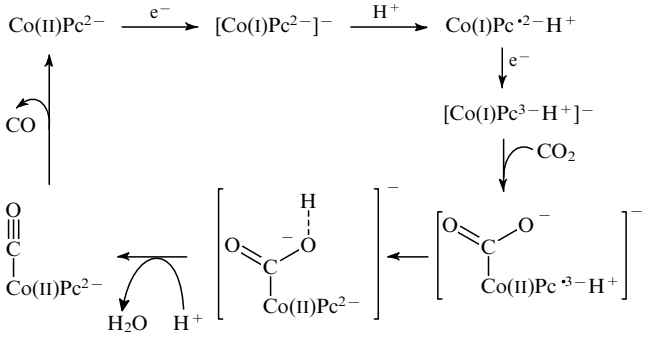
$$[PcM\cdots CH_4] \longrightarrow CH_4 + PcM.$$

† Undesirable cathodic processes can be prevented performing gas-phase reactions of CO_2 with electroactive films at solid electrolytes.[209] In many cases, heterogeneous catalytic reduction of CO_2 was carried out with the use of an active catalyst, for example, metalloporphyrin or metallophthalocyanine, deposited on a solid electrolyte (graphite) and coated with a conducting film (Nafion), which prevents it from passing into solution.[173, 174, 176–181, 210] However, these systems are beyond the scope of the present review.

It should be noted that the formation of the metal$-CO_2$ complex was postulated as the key step in virtually all studies devoted to catalytic binding of CO_2 by transition metal complexes.[211] In most cases, this suggestion was supported only by indirect evidence obtained in IR and NMR spectroscopic studies because, first, the lifetime of these intermediates is short and, second, the presence of the solvent molecules, which are also capable of being coordinated, hinders the detailed analysis of the structure of the complex.

The reaction mechanism was investigated also with the use of semiempirical quantum-chemical calculations. For example, an attempt was made to relate the catalytic activity of phthalocyanines to the energy of the frontier orbitals of the complex.[211] It appeared that the catalytic activity of phthalocyanine complexes correlates with the ability of the metal atom to coordinate an additional ligand, which, in turn, depends on the difference between the energy of the *d* orbitals of the metal atom and the energy of the frontier orbitals of the coordinated ligand.

Electrocatalytic reduction of CO_2 was examined in aqueous solutions at a graphite electrode, which was coated with PcCo bound to poly-4-vinylpyridine as a donor axial ligand.[179, 183, 184] It was demonstrated that the presence of the latter leads to a substantial improvement in the catalytic activity of PcCo due, apparently, to a rise in the electron density on the metal atom. In this catalytic system, the selectivity of CO_2 reduction is much higher than that in the case of pure PcCo in spite of the fact that competitive water reduction persists. This is attributable to an increase in the local concentration of CO_2 in the near-membrane layer through hydrophobic interactions of CO_2 with polyvinylpyridine.[177] The reaction scheme was proposed.[183, 184]



The catalytic process starts only at the second reduction wave of PcCo because the first reduction step is followed by rapid addition of H^+ to the peripheral nitrogen atoms of the phthalocyanine ring and the active species capable of reducing both H^+ and CO_2 to form H_2O and CO, respectively, are generated only at the second wave. However, no direct evidence for the formation of the PcCo$-CO_2$ adduct was obtained.

VIII. Synthesis of carboxylic acids

1. Carboxylation of organic halides

In the early 1980s, it was demonstrated that electroreduction of aryl halides catalysed by nickel complexes with PPh_3 (see Ref. 212) or dppe[213] in the presence of CO_2 affords predominantly arenecarboxylates rather than biaryls. Based on the results of electroanalytical investigation of the [Ni]–dppe system, the catalytic cycle was proposed.[214, 215]

The Pd complex with PPh_3 also catalyses electrocarboxylation of aryl iodides and bromides.[216]

$$RC_6H_4X + CO_2 + 2e^- \xrightarrow[DMF]{PdCl_2(PPh_3)_2\,(7\%),\ PPh_3} \underset{(50\%-90\%)}{RC_6H_4CO_2^-} + X^-$$

R = H, 4-Bu^t, 4-MeO; X = I, Br.

In this reaction, CO_2 was assumed to react as an electrophile with $[ArPd(0)(PPh_3)_2]^-$ generated upon reduction of the aryl-palladium(II) σ-complex.[217] Aryl chlorides react with Pd(0) too slowly to ensure efficient carboxylation. Aryl triflate and aryl bromide possess higher reactivities and, hence, arylcarboxylic acids can be synthesised starting from the corresponding aryl triflate.[57, 58]

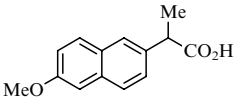
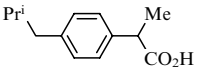
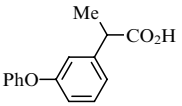
$$ArOTf + CO_2 + 2e^- \xrightarrow[DMF,\ 90\ ^\circ C]{PdCl_2(PPh_3)_2\,(10\%)} \underset{(52\%-95\%)}{ArCO_2^-} + TfO^-$$

Ar = 4-RC_6H_4 (R = Cl, CF_3, CO_2Et, F, Me), 1- or 2-naphthyl.

Nonsteroid anti-inflammatory drugs, *viz.*, α-arylpropionic acids, were prepared from the corresponding benzyl chlorides and CO_2 in the presence of the Ni–dppe or Ni–dppp system [dppp is 1,3-(diphenylphosphino)propane] and cyclooctadiene (COD).[218] There is no need to use a catalyst in these reactions, but it suppresses homocoupling, which becomes the main reaction at high concentrations of benzyl chloride and lower CO_2 pressure.[219]

$$ArCH(Me)Cl + CO_2 \xrightarrow[THF,\ HMPA]{NiCl_2(dppp)\,(10\%),\ COD\,(10\%),\ e^-} ArCH(Me)CO_2H$$

HMPA is hexamethylphosphoramide.

Product	Name	Yield (%)
$PhCH(Me)CO_2H$		89
	naproxen	81
	ibuprofen	80
	phenoprofen	76

There is also no need to use a catalyst in electrocarboxylation of aryl halides or various benzyl compounds in an undivided cell in the presence of a sacrificial aluminium[220] or magnesium[21, 221] anode. Organic halides containing functional groups, which make it impossible to apply direct electrochemical reduction, are subjected to electrocarboxylation using a catalyst simultaneously with a sacrificial anode.

Interest in transition metal complexes with tetraazamacrocyclic ligands as applied to electrocatalysis is associated with the fact that these complexes are similar to natural photosynthetic systems.[222] The mechanism of CO_2 reduction catalysed by tetraazamacrocyclic complexes of Ni(II) and Co(II) was examined by cyclic voltammetry and preparative electrolysis. Reduction affords CO, which then reacts with a Ni(I) complex to form Ni(0) carbonyl compounds, which eventually poison the catalyst.[222]

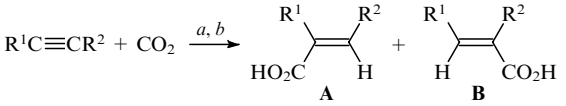
Electrocatalytic reduction of CO_2 under the action of trinuclear nickel cluster radicals was investigated by electrochemical methods and spectroelectrochemistry.[223]

2. Carboxylation of alkenes and alkynes

It is possible to subject unsaturated compounds to direct electrochemical carboxylation.[18, 224] However, this procedure is of limited usefulness because only arylated or activated alkenes can be used as substrates. For alkynes, only a few examples of the successful application of this reaction have been reported.[225–229]

Indirect electrochemical reductive coupling of alkynes with CO_2 gives rise to substituted acrylic acids through hydroxycarboxylation.[60, 225–231] Electrolysis was carried out at 20–80 °C in an undivided cell in DMF containing a catalytic amount of a nickel complex in the presence of a sacrificial magnesium anode at

ambient or slightly elevated (5 atm) CO_2 pressure. Alkynes containing electron-donating groups are more readily subjected to carboxylation at elevated temperatures, whereas carboxylation of alkynes bearing electron-withdrawing groups proceeds more readily at room temperature.



(*a*) $Ni(bipy)_3(BF_4)_2$ (10%), e^-, DMF, Mg anode; (*b*) hydrolysis.

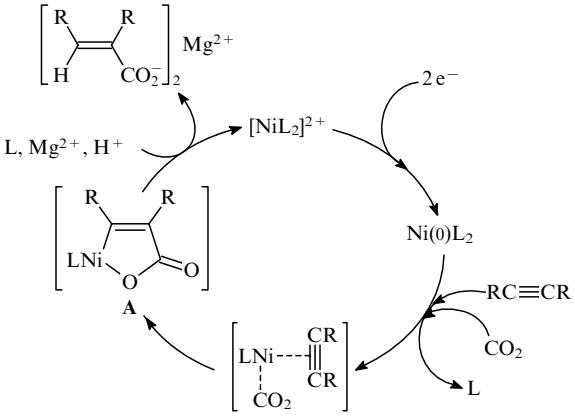
R^1	R^2	Yield (%)	Ratio **A** : **B**
n-C_6H_{13}	H	65	90 : 10
Pr^n	Pr^n	93	
Ph	H	55	71 : 29
Ph	Me	72	38 : 62
Ph	CO_2Et	75 [a]	

[a] The ratio between the di- and monocarboxylation products was 74 : 26.

The reactions proceed predominantly as the *cis*-addition with good regioselectivity (in the case of terminal alkynes, CO_2 reacts at position 2). Monocarboxylation takes place only in the absence of electron-withdrawing groups.

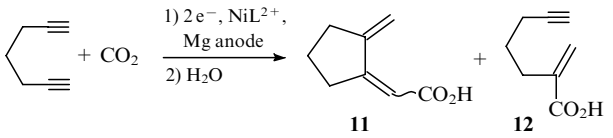
This procedure has advantages over the chemical method devised by Hoberg *et al.*,[232, 233] which, for the most part, required stoichiometric amounts of air-sensitive Ni(0)$(COD)_2$; instead, readily accessible Ni(II) complexes are used in the electrochemical procedure.

In these reactions, the advantages of a sacrificial anode are evident, a magnesium anode being most suitable. Oxidation of the latter gives rise to Mg^{2+} ions, which can be involved in the catalytic cycle to decompose nickelacycle **A** thus liberating Ni for further transformations.



The formation of the nickelacycle **A**, which was established by cyclic voltammetry, confirms the proposed mechanism. In the absence of Mg^{2+} ions (the reactions were carried out in a divided cell in the presence of ammonium ions), the nickelacycle was not decomposed and the reaction was terminated once the starting nickel compound has been completely consumed. After the addition of $MgBr_2$ to a solution of the nickelacycle prepared electrochemically, Ni(II) was regenerated.[234]

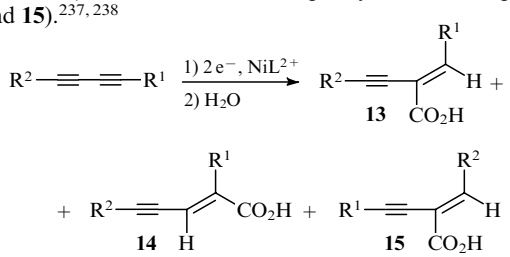
Diacetylenes are used for the construction of polycyclic compounds. Thus bicyclic pyrones were prepared by electrochemical carboxylation in the presence of CO_2 and a stoichiometric amount of a Ni(0) complex.[235] This procedure was also applied to the synthesis of linear and cyclic monocarboxylic acids from nonconjugated diacetylenes.[236, 237] The composition of the reaction products depends on the nature of the ligand. Thus cyclic compounds **11** were prepared with the use of a nickel complex with bipyridyl at normal CO_2 pressure, whereas linear adducts **12** were obtained with the use of pentamethyldiethylenetriamine (PMDTA) as the ligand and elevated CO_2 pressure (5 atm).



L	Yield (%)	Ratio **11** : **12**
bipy	35	59 : 4.5
PMDTA	30	9 : 45

The addition of CO_2 to diacetylenes containing both the terminal and internal triple bonds proceeds predominantly at position 2.

Electrochemical carboxylation of 1,3-diacetylenes in the presence of Ni(PMDTA) as the catalyst proceeded regio- and stereoselectively to give predominantly (*E*)-2-alkylidenealk-3-ynoic acids **13** (sometimes, with an impurity of isomeric products **14** and **15**).[237, 238]

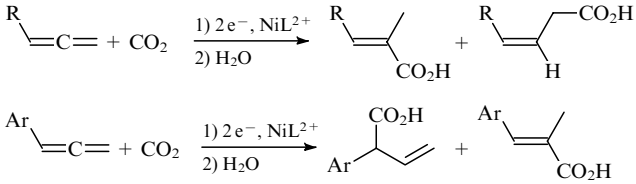


L = PMDTA.

R^1	R^2	Yield (%)		
		13	**14**	**15**
n-C_5H_{11}	n-C_5H_{11}	58	25	–
Ph	Ph	40	0	–
$MeOCH_2$	$MeOCH_2$	60	1	–
Ph	Bu^n	37	16	3
$MeOCH_2$	Ph	50	0	11

In this process, double bonds proved to be less reactive than triple bonds.[239] In nonconjugated as well as in conjugated alkenynes, only the triple bond is carboxylated with regio- and stereoselectivity analogous to those observed for acetylenes.[240]

According to this procedure, monocarboxylic acids were prepared in good yields starting from 1,2-dienes.[241] In the case of alkyl- and cycloalkylallenes, the addition of CO_2 proceeds predominantly at the C(2) atom. In the case of arylallenes, the addition occurs predominantly at the C(3) atom.



R = n-C_8H_{17}, cyclo-C_6H_{11}; Ar = Ph, 4-$MeOC_6H_4$;
L = PMDTA; p_{CO_2} = 5 atm.

Some other examples of homogeneous electrochemical activation of CO_2 were also described among which are the synthesis of lactones by telomerisation of butadiene and CO_2,[242] synthesis of bicyclic lactones using nickel or cobalt complexes,[243] transcarboxylation [244] and insertion of CO_2 into epoxides catalysed by Ni(cyclam)Br_2.[245]

IX. Carbonylation of organic substrates

Carbonylation of organic substrates is still a complicated problem because the presence of CO leads to deactivation of the catalytic system. The reactions of carbon monoxide with transition metals

in low oxidation states afford different metal carbonyls, which exhibit low reactivity with respect to the carbon–halogen bonds because of strong coordination with CO.

Some metal carbonyls can be activated by electrochemical reduction with generation of active anionic species. For example, aldehydes can be synthesised by electrolysis of a stoichiometric mixture of alkyl halides and iron pentacarbonyl.[246, 247]

$$RX + Fe(CO)_5 \xrightarrow[2)\ H^+]{1)\ e^-,\ DMF\ or\ MeCN} RCHO \quad (30\%-70\%)$$

R = n-C_5H_{11}, Et, Bn; X = I, Br.

Carbon dioxide can be used as a CO source. It is well known that complexes of transition metals in low oxidation states catalyse chemical and electrochemical reduction of CO_2 to CO. This approach was applied to the generation of the mixed Ni(0)bipy$(CO)_2$ complex by electrochemical reduction of Ni(bipy)$^{2+}$ in *N*-methylpyrrolidone or DMF in the presence of CO_2.[248, 249] The resulting complex can react with alkyl, benzyl and allyl halides to form symmetrical ketones with regeneration of Ni(bipy)$^{2+}$. The proposed two-step procedure for the synthesis of ketones involves electroreduction and chemical coupling.

It was demonstrated [250] that carbonylation can also be carried out by electrolysis of a solution of organic halide containing a catalytic amount of bipy under an atmosphere of CO in an undivided cell with a stainless steel anode. This process produces symmetrical ketones in good yields.

$$2\,RX + CO + 2\,e^- \xrightarrow[DMF\ or\ MeCN]{FeCl_2\ (5\%),\ bipy\ (5\%),} RCOR + 2\,X^-$$

RX	Yield (%)
BnCl	80
2-$MeC_6H_4CH_2Br$	70
4-$MeC_6H_4CH_2Br$	62
2-$ClC_6H_4CH_2Cl$	75
$MeCH=CHCH_2Cl$	65
$Me(CH_2)_5Br$	62
4-$CF_3C_6H_4Br$	50

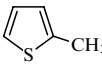
The anodic reactions afford the Ni(II)(bipy) and Fe(II)(bipy) complexes, which are reduced at a cathode to give intermediates catalysing the synthesis of ketones. In these processes, complexes of nickel coordinated both by bipy and CO serve as reactive species. Iron complexes, apparently, exhibit a synergistic effect.

Ketones were successfully prepared by electroreductive coupling of organic halides with CO using the Ni(bipy)$^{2+}$ complex as the catalyst. Either CO entering the solution [250–252] or metal carbonyls [253] serve as a source of carbonyl groups. Electroreduction of CO_2 proceeded under the action not only of Ni(0)(bipy) [248, 249] but also of iron porphyrinates in the presence of anodically generated Mg^{2+} ions.[254]

Ketones can be prepared not only by electrochemical carbonylation of organic halides but also by some other reactions catalysed by nickel complexes. Thus unsymmetrical ketones were obtained by $NiBr_2$(bipy)-catalysed electroreductive coupling of acyl chlorides with alkyl halides.[255] Acid chlorides are transformed into symmetrical ketones in an undivided cell equipped with a nickel or stainless steel anode.

$$2\,RCOCl + 2\,e^- \xrightarrow[stainless\ steel\ anode]{Ni(bipy),\ MeCN} RCOR + 2\,Cl^- + CO \quad (45\%-80\%)$$

R = Bn, Ph, 3-FC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-FC_6H_4,



, 4-BrC_6H_4, 2,4-$F_2C_6H_3$, 1-naphthyl.

It is believed that the first reaction step gives rise to alkynylnickel intermediates through oxidative addition of acid chloride to an electrochemically generated unstable low-valent nickel complex. Regeneration of divalent Ni yields a bisacylnickel complex. Ketone is derived from the bisacylnickel complex by reductive elimination of Ni bound with one CO molecule.[256]

In the presence of the Ni(bipy) complex, arylzinc compounds, which are electrochemically generated from aryl halides and zinc salts, react with $(CF_3CO)_2O$ to give the corresponding aryl trifluoromethyl ketones.[79]

The reactions involving the electroreductive formation of the carbon–heteroatom bond under the conditions of transition metal catalysis are few in number. For example, mention may be made of electrochemical silylation of allyl acetates in the presence of the Pd–PPh_3 system [257] and the electrochemical synthesis of aryl thioethers from thiophenol and aryl halides.[258]

Based on electrochemical activation of salts and complexes of some transition metals, catalytic systems were designed for carbonylation of methanol to form dimethyl carbonate.[259] The reactions are carried out by passing CO through a methanolic suspension or through a solution of a complex under atmospheric pressure at 20 °C in an ion-exchange membrane cell. Metal complexes catalyse oxidative carbonylation of methanol.

$$2\,MeOH + CO + 2\,M^{(n+1)+} \longrightarrow (MeO)_2CO + 2\,H^+ + 2\,M^{n+}.$$

The anodic process leads to regeneration of metal in a higher oxidation state.

$$M^{n+} \longrightarrow M^{(n+1)+} + e^-.$$

The redox pairs, which are active in chemical carbonylation promoted by oxygen, *viz*., Cu(I)/Cu(II), Pd(0)/Pd(II) and Co(II)/Co(III), were tested as catalysts. However, the electrochemical conditions appeared to be milder than those used in conventional chemical reactions. In some cases, the complexes exhibited higher catalytic activity. In these complexes, bipy, salen, acac and PPh_3 were used as ligands. The highest faradaic yields (%) of dimethyl carbonate were achieved with the complexes CuCl(bipy) (84.8), $PdCl_2$(bipy) (64.0), $CoCl_2$ (26.0), $RhCl_3$ (25.0) and $AgBF_4$(bipy) (10.2). The VCl_3, Mn(salen), Mn(acac)$_2$, $ReCl_3$(bipy), Cr(acac)$_3$, $NiCl_2$(bipy) and $RuCl_2(PPh_3)_2$ compounds proved to be either poorly reactive or inactive at all. Only in the presence of the $PdCl_2$(bipy) complex, did more than one redox cycles occur.

It is known that many transition metals catalyse oxidation of CO to CO_2 in water. It is these transition metals that exhibit the highest activity in oxidative carbonylation of alcohols to form dialkyl carbonates. This reaction mechanism involves the formation of methoxycarbonylmetal intermediates (MCO_2Me, where M = Cu, Co or Pd) whose stability and reactivity depends substantially on the structure of the complex and the nature of the ligands.[260, 261] For example, CuCl exhibits activity only at 70 °C, whereas it is active even at 20 °C in the presence of bipy. Electroactivation of CuCl, $PdCl_2$, $PtCl_2$ and $AgBF_4$ occurs only in the presence of bipy. To the contrary, the addition of bipy as well as of acac, salen and PPh_3 to $CoCl_2$, $NiCl_2$ and $AuCl_3$ impairs the efficiency of the process.

X. Electrochemical synthesis of organophosphorus compounds from chlorophosphines or white phosphorus

The development of synthetic approaches to the preparation of compounds containing P–C bonds based on white phosphorus or phosphorus chlorides is of importance in the preparative chemistry of organophosphorus compounds. Considerable attention is given to the synthesis of tertiary phosphines, which are widely used in organometallic and coordination chemistry.

The promising process [262–266] for the preparation of tertiary phosphines is based on electrochemical coupling of mono- or dichlorophosphines with aromatic and heteroaromatic halides catalysed by the nickel complex with bipy in an undivided cell using a sacrificial magnesium or zinc anode (Table 11).

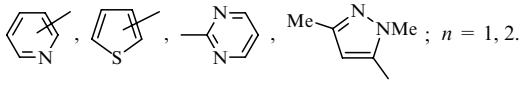
Table 11. Electrochemical coupling of aryl or hetaryl halides and chlorophosphines catalysed by $NiBr_2$(bipy).[262–266]

ArX	Product	Yield (%) [a]	Anode
PhBr	Ph_3P	87	Mg
2-BrC_6H_4Me	$Ph_2PC_6H_4Me$-2	54	Mg
4-BrC_6H_4Me	$Ph_2PC_6H_4Me$-4	56	Mg
4-$MeOC_6H_4Br$	$Ph_2PC_6H_4Me$-4	52	Mg
4-$Me_2NC_6H_4Br$	$Ph_2PC_6H_4NMe_2$-4	70	Mg
4-$EtO_2CC_6H_4Br$	$Ph_2PC_6H_4CO_2Et$-4	63	Zn
3-$EtO_2CC_6H_4Br$	$Ph_2PC_6H_4CO_2Et$-3	66	Zn
2-ClC_5H_4N	$Ph_2PC_5H_4N$-2	80	Mg
3-ClC_5H_4N	$Ph_2PC_5H_4N$-3	63	Mg
2-ClC_4H_3S	$Ph_2PC_4H_3S$-2	65	Mg
2-Cl-6-$MeOC_5H_3N$	Ph_2P(6-MeO-2-C_5H_3N)	66	Mg
2-$ClC_4H_3N_2$	$Ph_2PC_4H_3N_2$-2	50	Mg
3-NCC_6H_4Br	$Ph_2PC_6H_4CN$-3	45	Zn
5-Cl-1,3-$Me_2C_3HN_2$	Ph_2P(5-C_3HN_2-1,3-Me_2)	25	Mg

[a] The preparative yield is given with respect to chlorophosphine.

$$ArX + Ph_nPCl_{3-n} \xrightarrow[\text{Mg or Zn anode}]{e^-,\ NiBr_2(bipy)} Ar_{3-n}Ph_nP$$

Ar =  [R = Me, MeO, Me_2N, CN, CO_2Et, MeC(O)];



; n = 1, 2.

The electrochemical synthesis of tertiary phosphines can be carried out using aryl halides containing either electron-donating or electron-withdrawing substituents in the ring as well as hetaryl halides as substrates. In reactions of aryl halides bearing electron-donating substituents in the ring, a Mg anode must be used, whereas reactions of aryl halides containing electron-withdrawing substituents in the ring must be carried out with the use of a Zn anode. The general scheme of cyclic regeneration of the catalyst was proposed (this scheme is considered below).[262–266]

The problem of the selective opening of the P_4 tetrahedron of white phosphorus and its direct functionalisation assumes increasing importance in connection with a search for new environmentally safe procedures for the synthesis of organophosphorus compounds. Under the action of electrochemically generated catalysts, *viz*., the Ni(0)(bipy) complexes, and organic halides, white phosphorus can be converted into compounds containing the P–C bonds (phosphines and phosphine oxides),[267–269] Ni(II) being cathodically reduced to Ni(0).

$$Ni(II)L_3 + 2e^- \rightleftharpoons Ni(0)L_2 + L$$

L = bipy.

$$M^0 - ne^- \longrightarrow M^{n+}$$

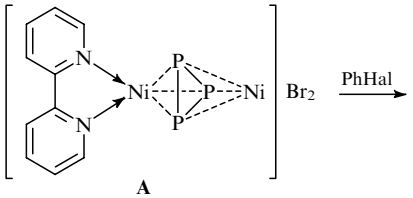
M = Mn, Zn, Al.

$$P_4 + RX \xrightarrow[-X^-]{Ni(0)L_2} \gg P{-}R$$

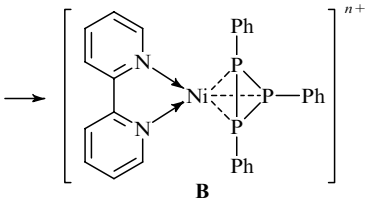
The key step involves the reaction of the organonickel compound $RNi(II)BrL_m$ with white phosphorus according to the following scheme:

$$Ni(0)L_m + RBr \longrightarrow RNi(II)BrL_m \xrightarrow{P_4} \gg P{-}R + Ni(II)L_m.$$

The opening of the P_4 tetrahedron and the cleavage of the remaining P–P bonds under the action of Ni(0) complexes give rise to binuclear complex **A**, which rapidly reacts with organic halides to produce mononuclear complex **B** with the Ph_3P_3 ligand.



A



B

The formation of the P–Ph bond through this path competes with the reaction of the PhNiBr σ-complex with P_4. This procedure made it possible to perform functionalisation of white phosphorus under mild conditions to obtain compounds with the P–C bonds.

For example, the electrochemical method was applied to the preparation of Ph_3P and Ph_3PO in 70% and 59% yields, respectively (DMF, Mg or Zn anode) and to the synthesis of $(n\text{-}C_6H_{13})_3PO$ in 47% yield (MeCN, Al anode).[265–269]

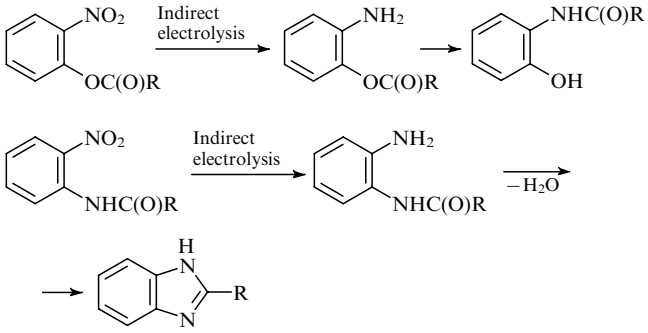
XI. Other examples of electrochemical syntheses catalysed by metal complexes

Nitro compounds were selectively reduced to amino derivatives using the mediator, *viz*., the Cp_2Ti^+ complex, in CH_2Cl_2 in the presence of dilute sulfuric acid.[270] Indirect electrolysis of various nitrobenzene derivatives containing the ester, carbonate or amide group in the *ortho* position was carried out in dichloromethane.

$$6\,Cp_2TiOH^+ + 6e^- + 6H^+ \longrightarrow 6\,Cp_2Ti^+ + 6\,H_2O,$$

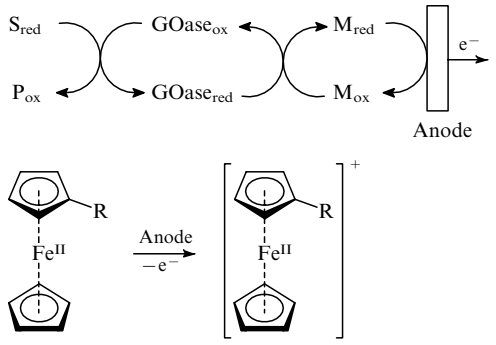
$$6\,Cp_2Ti^+ + ArNO_2 + 4\,H_2O \longrightarrow 6\,Cp_2TiOH^+ + ArNH_2.$$

In the second step, the catalyst is regenerated thus resuming the catalytic cycle. The rearrangements of anilines containing the ester or carbonate group in the *ortho* position into *N*-acylated *o*-aminophenols proceed *in situ*. Upon refluxing in acetic acid, *N*-acylated *o*-phenylenediamines are converted into 2-substituted benzoimidazoles.



In recent years, the principles of indirect anaerobic electrochemical regeneration of galactose oxidase (GOase) were developed.[271] This enzyme oxidises the primary alcohol group of D-galactose to the corresponding aldehyde. The synthetic use of GOase is of interest because it is highly sensitive to the nature of the substrate and can perform selective oxidation of primary hydroxy groups in polyols. Thus xylitol is oxidised to L-xylose. Substituted ferrocenes exhibiting high catalytic activity were used as mediators. The iron(II) and ruthenium(II) complexes with the phenanthroline ligands appeared to be less efficient. For these processes, phosphate buffers with pH 10.8 are the media of choice. Electrochemical regeneration of GOase allows the pre-

vention of the undesirable formation of the enzyme inhibitor (hydrogen peroxide), which is generated under aerobic conditions in reactions involving GOase.



S is a substrate, P is a product, M is a mediator (ferrocene derivative).

XII. Characteristic features and mechanisms of reactions catalysed by nickel and palladium complexes

1. Kinetic regularities

The application of electrochemical methods to generation of complexes of Ni(0) and other metals in low oxidation states makes it possible to use catalytic amounts of complexes generated at an electrode. In addition, electrochemical methods allow one to obtain quantitative estimations of the rates of catalytic reactions and in some cases even to separate the overall process into individual steps and to evaluate the reactivities of intermediates and stability of different forms of metal complexes.

Based on the external morphological traits, three qualitatively different catalytic waves can be distinguished [24, 33, 272–274] in the Ni(II)L_n–Ni(0)L_n system (L = PPh_3 or bipy) (Fig. 1). These are an increase in the current of reduction of the starting Ni(II)L_n complex (see Fig. 1 *a*), the wave corresponding to reduction of the complex involving the substrate as the ligand (see Fig. 1 *b*) and the wave of catalytic reduction of the organometallic compound, which is a product of the reaction of the reduced form of the starting complex with the substrate (see Fig. 1 *c*). In all these cases, the observed pattern can be (with some reservations) considered as a classical pattern and, hence, the increase in the current (the ratio of the catalytic to diffusion current, i_c/i_d) can be used for calculating the rate constant of catalyst regeneration (k_{eff}), which describes the overall process.[33]

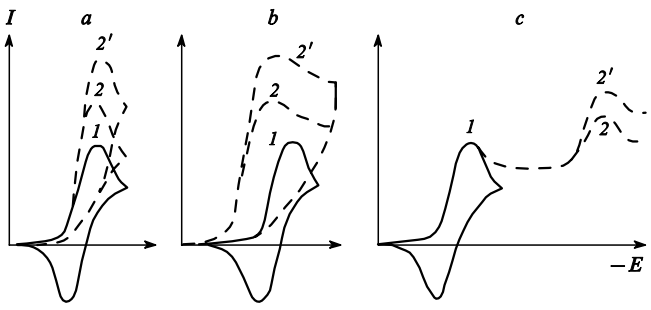


Figure 1. Morphology of catalytic waves in the Ni(II)L_n–Ni(0)L_n system;[24]
(*a*) an increase in the current of reduction of the starting complex; (*b*) the wave corresponding to reduction of the complex with the substrate, (*c*) the wave of catalytic reduction of the organometallic compounds; (*1*) the Ni(II)L complex, (*2*) and (*2′*) the Ni(II)L complex in the presence of increasing amounts of organic halides.

$$\mathrm{Ni(0)(bipy)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ni(0)(bipy)} + \mathrm{bipy},$$

$$\mathrm{Ni(0)(bipy)} + \mathrm{RHal} \xrightarrow{k_2} \text{products},$$

$$k_{eff} = \frac{k_1 k_2}{k_{-1}} \cdot \frac{[\mathrm{RHal}]}{[\mathrm{bipy}]} .$$

The lower the donor number of the solvent, the higher the efficiency of the catalytic process.[33]

The nickel complex with bipy proved to be the most active and versatile catalyst, which exhibits a pronounced catalytic effect in reactions with various substrates containing the C–Hal, P–Cl or Si–Cl bonds.[24, 33]

2. Relationship between electrochemical redox properties of nickel complexes and their reactivities in dehalogenation

The redox potentials of the complexes were used as the starting characteristics for predicting the reactivities and the reaction mechanisms of organometallic compounds.[24, 26, 32, 33, 275] For a series of Ni(II) and Ni(0) complexes, the electrochemical gap $G = E_{ox} - E_{red}$, the electrochemical electronegativity $\chi = (E_{ox} + E_{red})/2$ and the degree of charge transfer $\Delta N = \Delta\chi/\Sigma G$ were estimated experimentally.[24, 26, 32, 33] The G, χ and ΔN parameters can be used for evaluating the reactivities of the complexes in oxidative addition to organic halides.

$$\mathrm{Ni(0)}L_n + \mathrm{RHal} \longrightarrow \mathrm{RNi(II)}L_n\mathrm{Hal}.$$

These parameters are also suitable for estimating interactions between the complex and various ligands and substrates and for obtaining information on the complex-forming properties and donor-acceptor complex–substrate interactions. This is of particular importance in the case of organophosphorus substrates exhibiting both σ-donor and π-acceptor properties in interactions with transition metals. The largest electrochemical gap characterising the degree of 'hardness' of the complex was found for Ni(II)Br_2.[24, 25, 32, 33] For phosphine and phosphite complexes of Ni(II), the G values are much smaller. On the contrary, the electrochemical gap increases and, consequently, the donating ability and polarisability decrease in the series of the Ni(0) complexes with bipy (0.60 V), phen (0.72 V) and Ph_3P (1.04 V). Based on these characteristics, the degrees of charge transfer between the complexes and substrates were calculated on the assumption that the Ni(II) or Ni(0) complex and the substrate act as an electron donor and an electron acceptor, respectively.[24, 25, 32, 33] In the case of Ni(II) complexes, the degrees of charge transfer are small, whereas these values are an order of magnitude higher in the case of Ni(0) complexes. In the latter case, oxidative addition reactions are assumed to proceed. The sign of the degree of charge transfer indicates that the Ni(0) complexes with all substrates exhibit pronounced donor properties ($\Delta N \gg 0$).

The reactivities of nickel complexes in catalytic processes were accounted for based on the data from voltammetric measurements, results of quantum-chemical calculations and estimations of the G, χ and ΔN values.[24, 25, 32, 33] The reactivities of Ni(0) complexes in reduction reactions of organic halides are determined by a number of factors among which are the electrochemical gap G, the degree of charge transfer ΔN, the strength of the Ni–P bond, the electronic and steric effects of the ligands and the occurrence of the subsequent redox processes. In the series of the Ni(0)L, Ni(0)$L^{-\bullet}$, $L^{-\bullet}$ mediators (L = bipy or phen) possessing reducing properties, the energy of stabilisation of the transition state decreases on going from the inner-sphere to outer-sphere reduction processes, which is accompanied by the corresponding decrease in the reaction rate, as compared to the inner-sphere mediator characterised by the same driving force for the process.[30]

In the studies,[26, 276–278] the mechanism of two-electron reduction of the complexes was proposed with consideration for competitive homogeneous redox reactions, the evidence for the

individual steps was cited, and the rate-limiting processes were revealed.

In reduction of the nickel(II) complex with bipy, the transfer of the second electron was the rate-limiting step, $\Delta E^\circ = E_1^\circ - E_2^\circ \approx -60$ to -70 mV (E_1° and E_2° are the standard potentials of transfer of the first and second electrons, respectively), whereas competitive redox reactions did not proceed. In reduction of the nickel(II) complex with phen, the transfer of the first electron was the rate-limiting step and $\Delta E^\circ \approx -30$ to -60 mV; competitive redox reactions were also not observed. Reduction of the Ni(II) complexes with PPh_3 and phosphites $(Pr^iO)_3P$, $PhP(OBu)_2$ and $(PhO)_3P$ as the ligands involves the transfer of the first electron as the rate-limiting step and is accompanied by chemical coproportionation (PPh_3, $\Delta E^\circ \approx 90$ mV) and disproportionation (phosphites, $\Delta E^\circ < 0$) reactions.

Redox disproportionation and coproportionation reactions are typical of phosphine and phosphite complexes of Ni(II) characterised by higher polarisabilities ('softness') due to small electrochemical gaps. Competitive processes lead to a decrease in catalytic activity of these complexes in dehalogenation because the concentration of the active form of the catalyst in the reaction zone falls; the higher the reaction rate the more rapid the decrease. Actually, it was demonstrated that the Ni complex with bipy possesses the highest catalytic activity of all the complexes under study and reduction of this complex is not accompanied by competitive redox reactions. Undoubtedly, this improves the efficiency of the Ni complex with phen; however, the efficiency is lower than that of the complex with bipy and, consequently, other factors must be taken into account. In the series of phosphine and phosphite complexes of nickel, the catalytic activity is determined by the ratio between the rates of the steps giving rise to the final product and those of the competitive reactions.[26]

3. Mechanisms of reactions catalysed by nickel and palladium complexes

Under conditions of homogeneous catalysis by transition metal complexes, the synthesis of organic compounds involves at least one redox process in which one of the reagents is activated.[279,280] In many processes catalysed by metal complexes, oxidative addition plays a key role in the transformation of the organic substrate into a highly reactive intermediate.[280] The mechanisms of these reactions were described in many papers and monographs (see, for example, Refs 280–284).

Functionalisation of organic halides (RX) in the course of oxidative addition to a zero-valent metal complex [M(d^{10})] affords organometallic derivative **A**.

$$M(d^{10}) + RX \longrightarrow \underset{\displaystyle X}{\overset{\displaystyle R}{M(d^{10})}}\ \mathbf{A}$$

Two main mechanisms were proposed for this process. The first mechanism involves both the three-centre addition[285] and S_N2 substitution.[286] The second mechanism describes a multistep process proceeding through the formation of paramagnetic intermediates.[287] Thus the observed selectivity in the reactions of polyhalides[288] indicates that their mechanism is analogous to the well-known nucleophilic aromatic substitution.[289,290] However, the mechanism of the second type must not be ruled out taking into account the formation of paramagnetic nickel(I) complexes and products derived from radical intermediates in reactions of some aryl halides with Ni(0) complexes.

Tsou and Kochi[291] proposed the radical-chain mechanism for the stoichiometric reactions of aryl halides with zero-valent nickel complexes. This mechanism assumes intermediate paramagnetic nickel complexes to account for the formation of diarylnickel(III) species in the catalytic cycle. The authors demonstrated that oxidative addition of aryl halides to (triphenylphosphine)nickel(0) afforded *trans*-arylnickel(II) halide **A**. In addition, the reaction gave rise to paramagnetic nickel(I) halide **B** as a by-product.

$$Ni(0)L_4 + ArX \longrightarrow \underset{\mathbf{A}}{ArNi(II)XL_2} + \underset{\mathbf{B}}{Ni(I)XL_3}$$

L = PEt_3, PPh_3; X = Cl, Br, I.

In this case, the ratio between the products **A** and **B** depends on the nature of the halide ion (increases in the series I < Br < Cl), the nucleophilicity of the substituents and the polarity of the solvent. The general scheme of oxidative addition was reported.

$$Ni(0)L_4 \underset{}{\overset{k_1}{\rightleftharpoons}} Ni(0)L_3 + L$$

$$Ni(0)L_3 + ArX \xrightarrow{k_2} [Ni(I)L_3ArX^{\bullet -}]$$

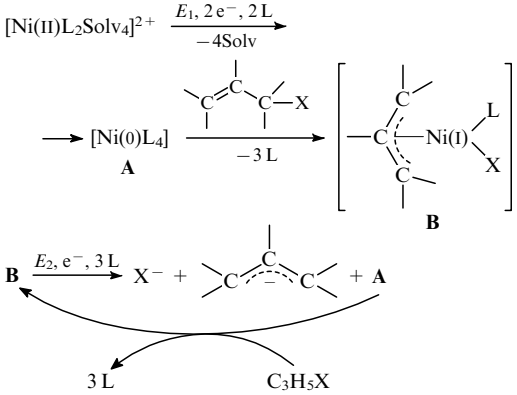
$$[Ni(I)L_3ArX^{\bullet -}] \longrightarrow ArNi(II)XL_2 + L$$

$$[Ni(I)L_3ArX^{\bullet -}] \xrightarrow{\text{diffusion}} Ni(I)L_3 + X^- + Ar^{\bullet}$$

However, the proposed mechanism does not give a precise idea of the sequence of the reaction steps yielding the diarylnickel(III) complex from $ArNi(II)XL_n$ under the conditions of the catalytic cycle, *i.e.*, in the presence of reduced metal.

Amatore and coworkers,[78,215,292–295] Bontempelli and coworkers[296–299] and research teams headed by Perichon[300–302] and Kargin[166,303,304] used electroanalytical methods in combination with the preparative electrosynthesis, which allowed them to reveal the key steps of many electrocatalytic reactions.

One of the first studied processes is catalytic coupling of allyl halides, which proceeds with a very high rate according to the following scheme:[298]



$E_2 < E_1$

L = PPh_3.

In this case, the catalyst, *viz.*, the highly reactive nickel(0) triphenylphosphine complex **A**, is generated *in situ* by electrochemical reduction of the corresponding Ni(II) complex, which is stable and can be prepared by anodic oxidation of nickel in the presence of PPh_3.[48,297–299] The $Ni(0)(PPh_3)_4$ complex (**A**) is involved in oxidative addition with allyl halide resulting in functionalisation of the C–Hal bond to form the allylnickel π-complex **B**. The adduct **B** is reduced at a potential E_2, which is more negative than the potential of reduction of the complex (E_1) but is more positive than the potential of reduction of allyl halide (~ -1.8 V with respect to a saturated calomel electrode). The reduction is accompanied by the cleavage of the Ni–C bond. The subsequent transformation of the allyl fragment affords a coupling product, *viz.*, hexa-1,5-diene. The zero-valent nickel complex is regenerated and the new catalytic cycle starts. The proposed mechanism was experimentally confirmed.

An analogous electrocatalytic cycle was suggested for the synthesis of hexa-1,5-diene from allyl bromide in the presence of nickel complexes with 2,2′-bipyridyl[298] as well as from allyl

chloride under the action of the electrochemically generated cobalt complex with 2,2′-bipyridyl.[305] However, the numbers of the catalytic cycles in these processes were rather low due to rapid decomposition of the catalyst.

Shiavon *et al.*[48] made an attempt to generalise the notions of the reaction mechanisms of organic halides under the conditions of homogenous catalysis by Ni(0) complexes with phosphine ligands. In this case, the efficient electrochemical process occurs through a lowering of the activation energy of RX reduction and cyclic regeneration of the catalyst. At less negative potentials ($|E_{RX}| > |E_{Ni(II)L}|$), a lowering of the activation energy and RX reduction lead to a change in the reaction pathway compared to that observed in non-catalytic conditions because heterogeneous reduction of RX proceeds at substantial overpotentials and high cathodic potentials. As a consequence, the radical generated upon the transfer of the first electron is reduced to the carbanion and the corresponding hydrocarbon RH and does not give coupling products.

In all cases, reduction can proceed *via* a series of simple steps involving electrochemical reduction of the nickel(II) complex to Ni(0), activation of organic halide through its oxidative addition to the Ni(0) complex and reductive elimination with the cleavage of the metal–carbon bond (either thermal decomposition or further cathodic reduction) as the key steps.[48]

$$[Ni(II)L_2(MeCN)_4]^{2+} \xrightarrow[-4MeCN]{2e^-,\,2L} [Ni(0)L_4] \xrightarrow[-2L]{RX} [Ni(II)L_2RX] \xrightarrow{a}$$

A

$$\longrightarrow [Ni(I)L_2RX]^- \xrightarrow[-X^-]{e^-,\,L} [Ni(0)L_3R]^- \xrightarrow[-X^-]{RX} \begin{cases} [Ni(II)L_2R_2] \\ R{-}R + [Ni(0)L_4] \end{cases}$$

$$\mathbf{A} \xrightarrow{b} [Ni(I)L_3X] + R^{\bullet} \longrightarrow R{-}R \text{ and other products}$$

$$\mathbf{A} \xrightarrow{c} \text{alkene} + [Ni(II)L_2HX] \longrightarrow$$

B

$$\longrightarrow \text{alkane} + \text{alkene} + H_2 + Ni(I)L_3X$$

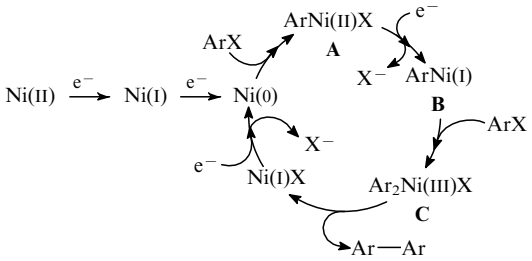
L = PPh_3; X = I, Br, Cl; R = Alk, Ar.

It should be noted that intermediates of the catalytic cycles were neither detected nor isolated.[48]

The path *a* is realised if the σ-organonickel complex **A** is rather stable, as in the case of PhBr and BnCl at low temperature. For the catalytic process involving these halides to occur, the complexes **A** must be reduced. Later on, it was shown[87,301,302,306] that a Ni(0) complex serves as a reducing agent and the catalytic process takes place at $E_{Ni(II)/Ni(0)}$. The path *b* is typical of neopentyl bromide and benzyl iodide at 25 °C, the coupling product being formed *via* dimerisation of the radicals generated upon the homolytic cleavage of the nickel–carbon bond in the complex **A**. The reaction with butyl bromide follows the path *c*. In the latter case, thermal decomposition of an organonickel intermediate occurs through β-elimination involving the nickel hydride complex **B** as an intermediate. For homocoupling to proceed, the reaction must take the path *a*, which is realised at more negative working potentials, the composition of the products being determined by the ratio between the paths *a* and *c*.

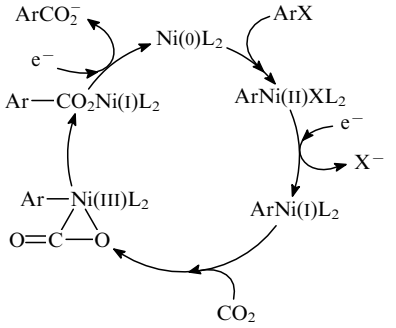
Oxidative addition of organic halide to the Ni(0) complex is the rate-limiting step. An increase in catalytic current allows the comparison of the reaction rates for various halogen-containing derivatives. The reactivity was found to decrease in the series $Bu^nI > Bu^tCH_2I > BnCl > PhBr$ in parallel with the change in dipole moment.

Electroanalytical methods provide information on the reaction mechanisms of coupling of aryl halides. In the general case, a zero-valent nickel or palladium complex is formed at a cathode if PPh_3, dppe or bipy serve as ligands. The first step of the catalytic cycle involves oxidative addition of aryl halide to a Ni(0) or Pd(0) complex giving rise to a σ-arylnickel or σ-arylpalladium intermediate. Coordinatively unsaturated complexes of the Ni(0)(bipy),[272] Ni(0)(dppe)[292] or Pd(0)$(PPh_3)_2$ type[295] proved to be much more reactive than the corresponding coordinatively saturated complexes. The reactivities of the Ni(0) or Pd(0) species depend also on the nature and the concentration of halide ions bound to the starting complex or added to the reaction medium.[218,238] The formation of biphenyl from bromobenzene catalysed by Ni(dppe) was examined in detail[292,293] and the catalytic cycle for this process was proposed. In this catalytic cycle, the σ-arylnickel intermediate **A** is initially reduced to the corresponding Ni(I) complex **B** followed by the transformation into the diarylnickel(III) complex **C**.



The complex **C** is subjected to reductive elimination to form the corresponding product and the Ni(0) complex from which Ni(0) is generated.[292,293] Hence, homocoupling proceeds through intermediate paramagnetic [Ni(I) and Ni(III)] and diamagnetic [Ni(0) and Ni(II)] species. The threshold potential (−2 V with respect to a saturated calomel electrode) was demonstrated to exist, which is necessary for the formation of biphenyl. At a less cathodic potential, the reaction affords the phenylnickel derivative PhNi(II)(dppe)Br, which needs to be reduced for the cyclic process to occur. It should be noted that the scheme proposed based on voltammograms[292,293] lacked experimental support because none of the postulated intermediates was isolated or identified. Equations describing the kinetic characteristics of the assumed sequence of the reactions were derived and the rate constants of different steps were calculated. It is believed that reductive elimination is the rate-limiting step.

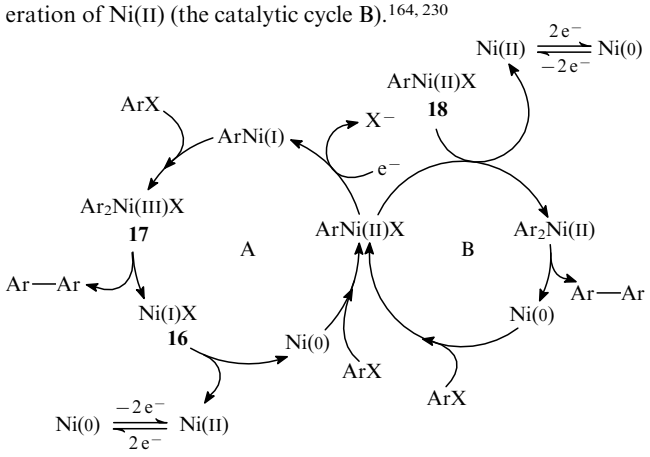
The formation of biphenyl was completely suppressed upon introduction of CO_2 into the reaction system giving rise to a new catalytic cycle to form carboxylation products.



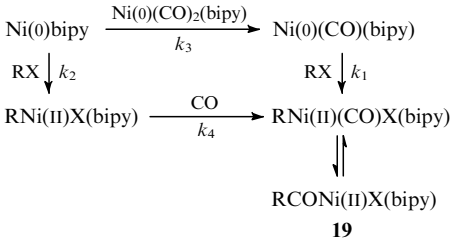
The reaction mechanism was proposed based on the results of an investigation of the reaction products, examination of the voltammetric behaviour of the starting complexes in the presence of the substrate and the behaviour of intermediates and kinetic calculations of individual steps of the process. Since the addition of CO_2 to $ArNi(I)L_2$ ($k = 1-2$ mol^{-1} litre s^{-1}) proceeds approximately 100–200 times faster than the addition of ArX, the formation of biaryls in the presence of stoichiometric amounts of CO_2 is completely eliminated.[215,294,307]

By analogy with the reactions catalysed by Ni(dppe), two hypothetical catalytic cycles involving the formation of a σ-arylnickel intermediate were proposed for the reactions in the presence of the Ni(bipy) complex. In the catalytic cycle A, the Ni(I)X

complex (**16**), which is derived from the Ni(III) complex (**17**) in the reductive elimination step, undergoes disproportionation into Ni(0) and Ni(II) followed by reduction of Ni(II).[305] An alternative mechanism assumes the formation of biaryl in the course of metathesis of σ-arylnickel(II) complex **18** accompanied by regeneration of Ni(II) (the catalytic cycle B).[164, 230]



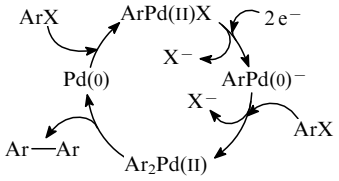
The reactivity of the nickel(0) complex with bipy with respect to carbon monoxide and organic halides under conditions of competitive reactions was examined by electroanalytical methods, which enabled the authors to devise a new procedure for the synthesis of ketones.[251, 252] Reduction of $Ni(bipy)^{2+}$ in the presence of an excess of CO rapidly afforded the inactive $Ni(0)(CO)_2(bipy)$ complex. It was noted that RX remained intact when electrolysis was carried out with bubbling of CO through the reaction mixture, *i.e.*, when the solution was saturated with CO. Organic halides were efficiently converted into ketones when the concentration of CO was limited and the possibility existed of generating a mixture of $Ni(0)(CO)_2(bipy)$ and Ni(0)(bipy). Based on the kinetic data, two alternative pathways for the formation of acylnickel complex **19** were proposed.



The first pathway involves oxidative addition of RX to Ni(0)(CO)(bipy) (the rate constant k_1), whereas the second pathway includes oxidative addition of RX to Ni(0)(bipy) (the rate constant k_2) followed by addition of CO from the mixed complexes $Ni(0)(CO)_2(bipy)$ or Ni(0)(CO)(bipy) or from CO present in the solution (the rate constant k_4). The reactions of highly reactive organic halides (for which $k_2 > k_3$), such as aryl iodides, follow the second pathway. In contrast, benzyl chlorides, aryl bromides and alkyl halides are moderately reactive with respect to Ni(0)(bipy) ($k_2 \ll k_3$) and their reactions follow the first pathway.

The preparative synthesis of ketones was carried out in the presence of catalytic amounts of $Ni(bipy)^{2+}$ (5% with respect to RX).[250] Under these conditions, the constants k_2 and k_3 have similar values and the two pathways for formation of the acylnickel complex **19** compete with each other.[228]

The $Pd-PPh_3$ system is characterised by two-electron reduction of the σ-arylpalladium intermediate [77] analogous to reduction of the corresponding intermediate in the $Ni-PPh_3-ArX$ system studied earlier.[48, 231] In the presence of the $Pd-PPh_3$ system, the biaryl is formed, apparently, through reductive elimination from diarylpalladium(II) followed by regeneration of Pd(0).



Many key steps of the mechanisms of reactions catalysed by Ni(0) complexes were suggested without sufficient substantiation. In some cases,[301] the catalytic waves in voltammograms were incorrectly interpreted and the calculated rates of particular steps were in error.

The reaction mechanism of coupling of organic halides under the action of the electrochemically generated Ni(0)(bipy) complexes was investigated.[303] *o*-Bromotoluene was chosen as a model aryl halide. Its reaction with Ni(0)(bipy) afforded the stable σ-complex 2-$MeC_6H_4Ni(II)Br(bipy)$ (**20**) through oxidative addition.

$$NiBr_2(bipy) + 2\,e^- \longrightarrow Ni(0)(bipy) + 2\,Br^-,$$

$$Ni(0)(bipy) + 2\text{-}MeC_6H_4Br \longrightarrow \underset{\mathbf{20}}{2\text{-}MeC_6H_4Ni(II)Br(bipy)}.$$

Reduction of the complex **20** gave rise to a new complex, *viz.*, $(2\text{-}MeC_6H_4)_2Ni(0)Br(bipy)$ (**21**), which was isolated and characterised. The stability of arylnickel σ-complexes containing the methyl group in the ortho position of the aromatic nucleus is attributed to the steric factors, which hinder the rotation about the Ar—Ni σ-bond and the axial attack of the reagents on the nickel atom.[53, 308] The complex **21** was reversibly reduced to radical-anionic intermediate **22**.

$$\underset{\mathbf{20}}{2\text{-}MeC_6H_4Ni(II)Br(bipy)} \xrightarrow{e^-} 2\text{-}MeC_6H_4Ni(I)(bipy) + Br^-$$

$$\underset{\mathbf{20}}{2\text{-}MeC_6H_4Ni(II)Br(bipy)} \longrightarrow \underset{\mathbf{21}}{(2\text{-}MeC_6H_4)_2Ni(0)Br(bipy)}$$

$$\mathbf{21} \overset{e^-}{\rightleftharpoons} \underset{\mathbf{22}}{[(2\text{-}MeC_6H_4)_2Ni(0)Br(bipy)]^{-\bullet}}$$

As the outer-sphere electron carrier, the complex **22** can reduce 2-bromotoluene to toluene, which was confirmed by chromatography. Slow decomposition of $[(2\text{-}MeC_6H_4)_2.NiBr(0)(bipy)]^{-\bullet}$ (**22**) in solution to form a biphenyl derivative was a competitive reaction. This reductive elimination was induced by electron transfer.

$$\underset{\mathbf{22}}{[(2\text{-}MeC_6H_4)_2Ni(0)Br(bipy)]^{-\bullet}} \longrightarrow (2\text{-}MeC_6H_4)_2 + Ni(0)(bipy) + Br^-.$$

The mechanism of Ni(0)(bipy)-catalysed cross-coupling of aryl and hetaryl halides was investigated taking into account the notion of the mechanism of homocoupling reported earlier.[303] It was demonstrated that a Ni(I) complex serves as the active form in cross-coupling.

$$2\text{-}MeC_6H_4Ni(I)(bipy) + ArX \longrightarrow 2\text{-}MeC_6H_4(Ar)Ni(II)X(bipy) \longrightarrow$$

$$\longrightarrow 2\text{-}MeC_6H_4Ar + Ni(II)X(bipy).$$

A particular complex can either serve as an efficient catalyst of homocoupling of organic halides or be poorly active or even inactive in cross-coupling of two different RX. In the general case, the efficiency of the catalyst depends on the following factors.

1. The possibility of rapid regeneration of the catalyst, *i.e.*, the number of catalytic cycles.

2. The reaction rate of reductive addition of the arylnickel intermediate to aryl halide must be higher than the rates of its competitive decomposition, protonation, *etc.*

3. The reaction rate of reductive elimination of the Ar^1Ar^2NiX complex must be rather high for regeneration of the catalyst (conceivably, promoted by the electron transfer) to be successful.

The electrochemically synthesised stable σ-complex 2-MeC_6H_4Ni(II)Br(bipy) (**20**) proved to be a convenient model for studying the mechanism of formation of tertiary phosphines.[304–306] Thus it was demonstrated that the cross-coupling product containing the P–C bond was generated in the substitution reaction

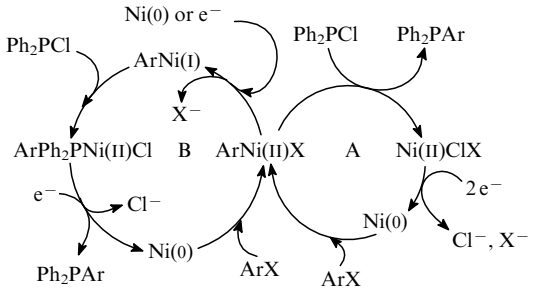
$$(3-n)\,ArNi(II)Br(bipy) + Ph_nPCl_{3-n} \longrightarrow$$
$$\longrightarrow Ar_{3-n}Ph_nP + (3-n)\,NiBr(II)Cl(bipy)$$

$n = 0–3$.

The competitive pathway through nickel phosphides is not realised. Phosphines are generated primarily according to the following sequence of reactions

$$ArNi(II)X + e^- \xrightarrow{bipy} ArNi(I)(bipy) + X^-,$$
$$ArNi(I)(bipy) + Ph_2PCl \longrightarrow ArPh_2PNi(II)Cl(bipy),$$
$$ArPh_2PNi(II)Cl(bipy) \xrightarrow{e^-} [ArPh_2PNi(I)Cl(bipy)]^- \cdot \longrightarrow$$
23
$$\longrightarrow ArPh_2P + Ni(0)(bipy) + Cl^-.$$

Reductive elimination of the (triarylphosphine)nickel complex $ArPh_2PNi(II)Cl(bipy)$ (**23**) affords the target compounds.



X = Cl, Br.

In the initial steps of electrolysis, products are formed through the reactions of the catalytic cycle A, whereas the reactions of the catalytic cycle B become dominant as the catalyst is consumed.

The use of the complex **20** as a model compound made it possible to follow the pathway of formation of secondary alcohols in electroreductive coupling reactions of organic halides with aldehydes catalysed by the nickel complex with 2,2′-bipyridyl.[166] The yield of the product was found to be proportional to the concentration of $NiBr_2$(bipy) in solution. It was suggested that nickel ions were involved in the corresponding nickel alkoxide thus being removed from the catalytic cycle. In addition, it was shown that alcohol was not generated at a potential of Ni(II)/Ni(0) reduction (−1.2 V with respect to a saturated calomel electrode). Cross-coupling proceeded only at more cathodic potentials corresponding to further reduction of the σ-complex 2-MeC_6H_4Ni(II)Br (−1.35 V).

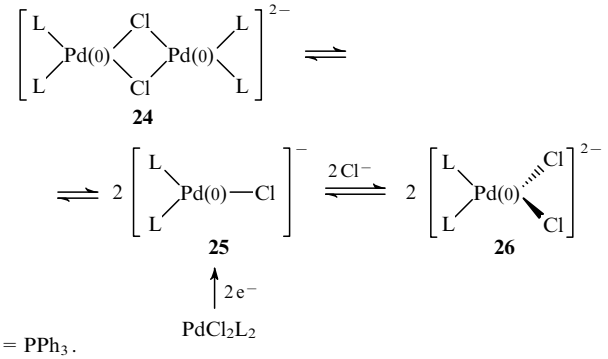
$$2\text{-}MeC_6H_4Ni(II)Br(bipy) \xrightarrow[-Br^-]{e^-} 2\text{-}MeC_6H_4Ni(I)(bipy) \xrightarrow{PhCHO}$$
$$\longrightarrow \underset{\underset{ONi-}{|}}{PhCHC_6H_4Me\text{-}2} + bipy.$$

4. Mechanisms and kinetics of reactions in the presence of palladium catalytic systems

Palladium serves as the most versatile catalyst because of its high efficiency in reactions of aryl halides, vinyl halides (triflates) and allyl derivatives with nucleophiles (cross-coupling, Stille coupling, Suzuki coupling, Heck reaction, Tsuji–Trost reaction) to form the C–C, C–H, C–N, C–O, C–P, C–S and C–C(O)–C bonds.[309] In the presence of an electron source, the reactions of these substrates with electrophiles can give rise to the C–C, C–H and C–CO_2 bonds.[310, 311]

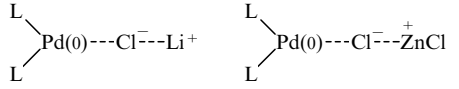
The efficiency of palladium is associated with the fact that zero-valent palladium is capable of activating C–X bonds (X = I,[312, 313] Br,[313] Cl,[313] O[314]) by oxidative addition yielding organopalladium(II) complexes, which are able to react with nucleophiles.[315–318] The nucleophilic reaction affords a new organopalladium(II) complex from which the final product is generated in one or several steps.[309]

The recent data published in the literature (see the review [308] and references cited therein) allowed revision of the commonly accepted mechanisms of palladium-catalysed reactions. It appeared that the reactivity of the low-coordinate 14-electron $Pd(0)L_2$ complex, which serves as an active species initiating the catalytic cycle, depends not only on the nature of the ligand at the Pd atom but also on the precursor of the Pd(0) complex. With the aim of revealing the reasons for this specificity, the structures and reactivities of different Pd(0) complexes prepared by oxidative addition were studied. It was found that the oxidative addition to aryl halides afforded various arylpalladium(II) complexes (neutral, anionic or cationic).[309] For example, the oxidative addition of aryl triflates to $Pd(0)(PPh_3)_4$ gave rise to the cationic $ArPd(II)(PPh_3)_2^+$ complexes, whereas the neutral $ArPd(II)Cl(PPh_3)_2$ complexes were obtained in the presence of chloride ions. These complexes can be related by the dynamical equilibrium. The structures of arylpalladium(II) complexes depend substantially on the structure of the efficient Pd(0) complex involved in the oxidative addition and on the nature of the anions bound to Pd(0). Earlier, it was assumed [295, 309, 312, 313] that two-electron reduction of $PdCl_2(PPh_3)_2$ afforded the $Pd(0)(PPh_3)_2$ complex. However, the ^{31}P NMR spectrum of this complex after its exhaustive electrolysis has three signals [295] belonging to three different anionic complexes (**24**–**26**), which are at dynamical equilibrium.



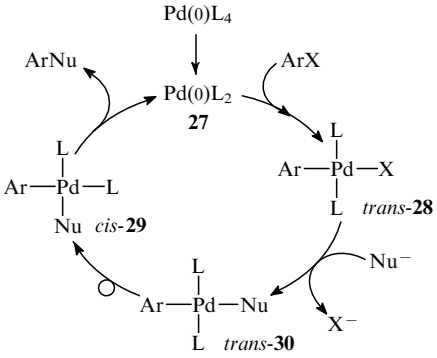
L = PPh_3.

The dimer **24** is the most reactive species. Hence, the $Pd(0)(PPh_3)_2$ complex does not exist in solution. When generated in the presence of halide ions, this complex gives anionic Pd(0) complexes. Oxidative addition proceeds more rapidly in the presence of cations (Li^+ or Zn^{2+}).[309] The reactions of the cations with the chloride anions bound to palladium(0) produce ionic pairs and improve the reactivity of the complex.

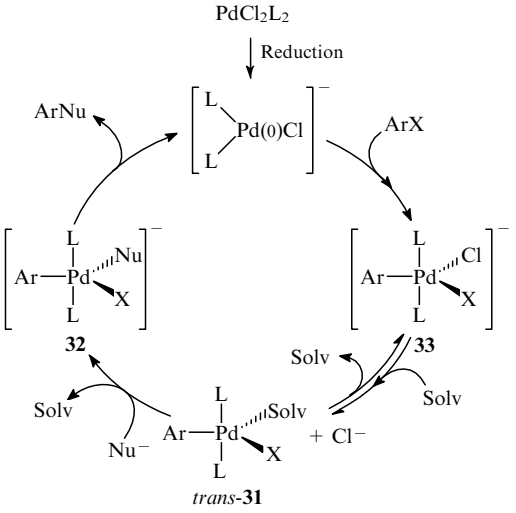


In the reactions with poorly reactive aryl bromides, the oxidative addition of aryl bromide to zero-valent palladium complex **27** is conceivably the rate-limiting step.[315–317] For more reactive aryl halides, transmetalation [the nucleophilic attack on trans-$ArPdXL_2$ (**28**)] was considered as the rate-limiting step.[318, 319] Reductive elimination from *cis*-$ArPdNuL_2$ (**29**) gen-

erated upon the rearrangement of the *trans*-$ArPdNuL_2$ complexes (**30**) can also be the rate-limiting step.[318, 320, 321]



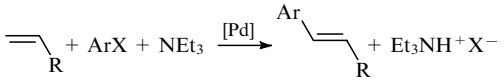
The results of the study [322] provided convincing evidence that reduction of $PdCl_2(PPh_3)_2$ yielded the anionic palladium(0) complex $Pd(0)(PPh_3)_2Cl^-$ and that the oxidative addition afforded the anionic five-coordinate arylpalladium(II) complex $ArPdXCl(PPh_3)_2^-$, which was slowly transformed into *trans*-$ArPdX(PPh_3)_2$.[322] Under these conditions, the Cl^- anion was the best nucleophile and simultaneously the best leaving group. Hence, this rapid equilibrium is the degenerate S_N1 nucleophilic substitution. Based on the above-mentioned results, the new catalytic cycle was suggested.



L = PPh_3.

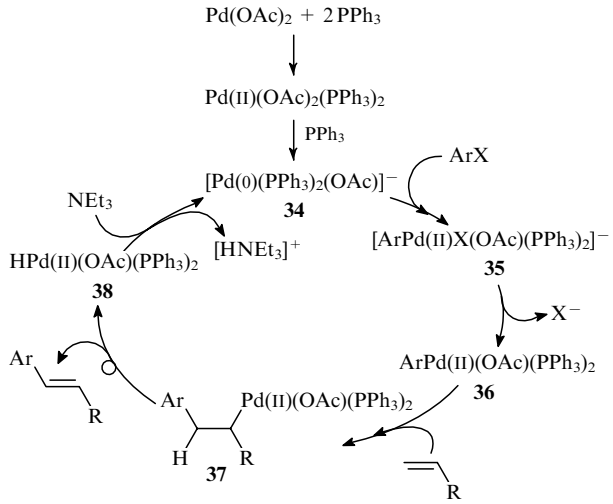
The nucleophile attacks the intermediate five-coordinate neutral arylpalladium(II) complex (**31**) to give the anionic five-coordinate complex $[ArPd(II)XNuL_2]^-$ (**32**) in which the aryl group and the nucleophile are arranged in such a way as to provide rapid reductive elimination. Hence, the *trans*-$ArPdXL_2$ complex (**28**) may be ignored as an intermediate of $PdCl_2(PPh_3)_2$-catalysed cross-coupling. In the absence of nucleophiles, the formation of *trans*-$PhPdI(PPh_3)_2$ was demonstrated to be accelerated by cations [322] because the equilibrium **31** $\rightleftharpoons$ **33** was shifted toward the complex **31**. In the presence of a rather strong nucleophile, the reaction follows the above-described scheme. Evidently, its mechanism can be changed in the catalytic cycle depending on the reaction conditions.

The reaction of alkenes with aryl halides catalysed by palladium complexes was discovered by Heck in 1968 (see the review [323]). In the presence of chiral ligands, enantioselective reactions can be carried out.[323, 324]



[Pd] = $Pd(OAc)_2$ + *n*L.

The Heck reaction is performed in the presence of a base and, generally, in DMF. Of the catalytic systems, which were empirically chosen for the Heck reaction, mixtures of $Pd(OAc)_2$ and phosphines exhibit the highest efficiency. The catalytic cycle proposed for the Heck reaction in the study [309] differs from that postulated earlier [315–317] by the reduction of Pd(II) to Pd(0) under the action of phosphine [325–327] and by the presence of the anionic $Pd(0)(PPh_3)_2(OAc)^-$ complexes (**34**) generated *in situ*. The latter undergo oxidative addition to aryl halides yielding the short-lived five-coordinate arylpalladium (II) complex (**35**). Then the $ArPd(II)(OAc)(PPh_3)_2$ complex (**36**) is subjected to the nucleophilic attack by alkene. Reductive elimination of complex **37** affords the reaction product and hydride complex **38** from which the catalyst **34** is regenerated under the action of triethylamine.



The results of the cited studies provide evidence that the anionic complexes generated from precursors of zero-valent palladium complexes play a key role and account for the empirical data concerning the characteristic features of catalytic palladium systems.[328–333]

XIII. Conclusion

To summarise, many interesting synthetic applications combining electroreduction with transition metal complexes were reported in the last 15 years. Electrochemical equipment and procedures for electrosynthesis become increasingly simple due to which many electrochemical methods compete with conventional chemical methods. Presently, some reactions, which have been previously described as catalytic processes, for example, carboxylation of organic halides or homocoupling of alkyl halides, can be carried out by direct electroreductive coupling in the presence of a sacrificial anode. However, electrochemical transition metal catalysis is often more selective. In recent studies, considerable attention has been given to the synergism between transition metal atoms of the catalyst and metal ions obtained upon dissolution of the anode.

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