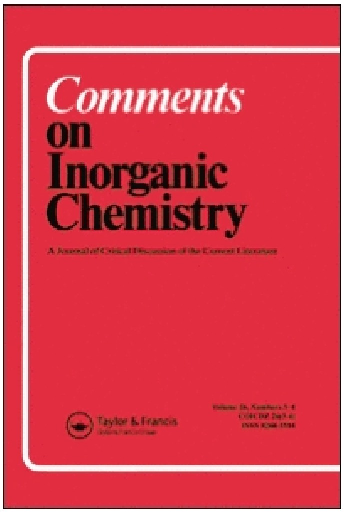

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Electrochemical Synthesis of Metal Complexes and Homogeneous Catalysts

Joseph Grobe[a]
[a] Anorganisch-Chemisches Institut, Universität Münster, Münster, Federal Republic of Germany

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Electrochemical Synthesis of Metal Complexes and Homogeneous Catalysts

JOSEPH GROBE
Anorganisch-Chemisches Institut,
Universität Münster,
D-4400 Münster,
Federal Republic of Germany

This report deals with the development of electrochemical synthetic routes in transition metal coordination chemistry. It was initiated by earlier investigations aimed at a better understanding of the bonding in metal carbonyl derivatives as well as by the results of "metal atom synthesis." Considering metal complexes as matrix-isolated metal ions or atoms, electrochemical reduction of solvates or complexes has been used to promote the exchange of hard for soft ligands and so to prepare metal carbonyls and metal carbonyl derivatives. The electrochemical procedure offers the additional possibility to produce suitable precursors by anodic oxidation of the corresponding metals so that it becomes a real alternative to "metal atom synthesis." Recent developments concern the application of electrochemically generated homogeneous catalysts, if possible, in one-pot procedures.

Key Words: *electrochemical synthesis, transition metal complexes, catalysts*

1. INTRODUCTION

It has always been one of the aims of chemists to prepare a useful or interesting target product at the least possible expense of raw

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materials, energy, and time with the highest possible quality and with a minimum of side products. The problems of the last 15 years concerning costs and supply of energy and natural products as well as increasing ecological consciousness, leading to more restrictive legislation, demonstrate the importance of such efforts above the obvious economic interests.

In this context, electrons as cheap reactants in electrochemical processes as well as catalysts with their classical functions to increase, on the one hand, the rate, efficiency and selectivity and to decrease, on the other hand, the use of energy of a chemical reaction are of particular interest. The combination of both possibilities, i.e., the electrochemical synthesis or regeneration of catalysts and their application to approved or new technical processes, offers considerable improvement of the hitherto available potentials.

Since in the past the intelligent use of optimized catalysts has already led to more economic production, one can expect that progress in research and technique of catalysis will help to solve future tasks. During the past decades, not only the elucidation of important catalytic mechanisms,[1,2] but also the development of simple models allowing the prediction of possible catalytic activities,[3] have been achieved. In the present review, studies are reported on the development and application of electrochemical methods to the synthesis of transition metal complexes and catalysts.

2. ELECTROCHEMICAL SYNTHESIS OF METAL COMPLEXES—AN ALTERNATIVE TO "METAL ATOM SYNTHESIS"?

2.1. Stations on the Route to Electrochemistry

One of the motives to study the electrochemical preparation of transition metal complexes arose from preparative investigations of our research group aimed at elucidating the bonding situation in metal carbonyl derivatives with phosphorus, arsenic, sulfur or selenium donor ligands. The object of our work in this area was the character of the Ⓜ–L bond, Ⓜ being a complex fragment $M(CO)_n$ with a transition metal center of low oxidation state and

L a ligand with a lone pair of electrons for the σ-donor and empty d-orbitals for the π-acceptor bond. These studies were aimed at experimental answers to the question of the existence and measure of M → L (d-d)π backbonding,[4,5] i.e., support for the synergic σ-donor/π-acceptor bonding model. To solve this problem a great number of metal carbonyl derivatives has been prepared by systematic variation of the ligands, and their spectroscopic data have been determined. One of the most important results of these investigations was the surprising versatility of the bonding system with respect to the change of Ⓜ and L as well as their ligands or substituents. This result led us to the optimistic view that further investigations will make possible predictions about the set of ligands a metal center of given oxidation state might select from a broad supply. This possibility obviously will facilitate the search for metals in biological materials as well as the choice of ligands for the selective extraction of metals from waste water and garbage or from deposits not worth mining.

Another motive to develop electrochemical procedures for the synthesis of transition metal complexes came from the results of the so-called "metal atom synthesis."[6-8] The principle of this process is demonstrated in Fig. 1 for the preparation of a complex ML_6.

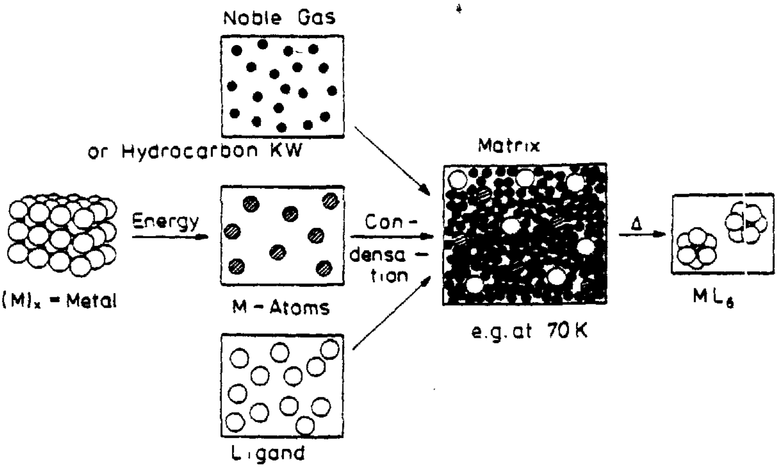


FIGURE 1 Principle of "metal atom synthesis."

Still another stimulation for our project arose from the known success of industrial electrochemical production (electrometallurgy, alkali chloride electrolysis) as well as of electrochemical applications in organic (Kolbe synthesis[9]) and organometallic chemistry (NALCO process for tetraethyl lead[10]). Out of the wealth of literature information,[11,12] only the technically important processes for adipic acid dinitrile[13] and $PbEt_4$[10] are mentioned here.

Since most of the transition metal carbonyls are produced by "reductive carbonylation," it is not at all surprising that for the essential reduction step electrochemical methods have been applied. Thus, the patent literature of the 1950s describes some electrochemical syntheses of metal carbonyl derivatives.[14] In contrast to the above-mentioned applications, electrochemical carbonylation requires considerably greater expense in apparatus for maintaining the necessary CO pressure. Therefore, the first electrochemical pressure synthesis of the binary metal carbonyl $Cr(CO)_6$ from chromium (III) acetylacetonate[15] was achieved only in 1967. Later, this study was extended to the compounds $V(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$.[16] Significant progress was made by developing a method for the direct generation of metal carbonyls from the metals and carbon monoxide using sacrificial anodes.[17]

2.2. Complexes as Matrix-Isolated Metal Centers

The production of isolated metal atoms and their preservation in a solid matrix caused us to consider complexes as being matrix-isolated metal centers. It has been known for a long time that metal ions in complexes can be reduced or oxidized chemically or electrochemically without changing the type or number of ligands. On the other hand, cyclovoltammetric studies show that the ligand sphere of a complex may be made considerably labile by changing the oxidation state of the metal. Thus, a synthetic method of great variability can be developed, if the redox process is followed by a quick and definite ligand exchange. The analogy of this procedure to "metal atom synthesis" is demonstrated in Fig. 2: A solution contains solvated (i.e., matrix-isolated) metal ions and ligands. Lowering the oxidation state of the metal ions by cathodic reduction weakens the metal–solvent bonds and induces their exchange by nearby ligand molecules. Therefore, the electrochemical proc-

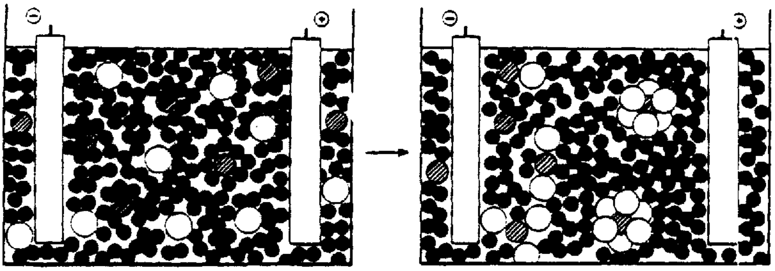


FIGURE 2 Analogy of metal atom and electrochemical synthesis of complexes.

ess given in Eq. (1) can obviously be used as a valuable alternative to "metal atom synthesis."

$$[ML_n^{(m)}]^{m+} \xrightarrow[-L^{(m)},\ +L^{(0)}]{\text{reduction}} [ML_x^{(0)}]^0 \qquad (1)$$

$L^{(m)}$ and $L^{(0)}$ are ligands particularly suited for the oxidation states $m+$ or zero of the metal. For the practical application of this method the following conditions should be fulfilled:

1. The reduction of the metal ion in the complex $[ML_n^{(m)}]^{m+}$ can be performed under control and essentially quantitatively.
2. The adaptation of the "ligand-matrix" to the requirements of the central atom, i.e., the replacement of $L^{(m)}$ by $L^{(0)}$, occurs as a fast reaction.
3. The reverse reaction (at the anode) and metal deposition (at the cathode) can be effectively avoided.

The first presupposition can be best accounted for by electrochemical means, because the reducing power may be adjusted to the special case by variation of the potential. For metal carbonyls and their derivatives this process is a variant of the "reductive carbonylation." The advantages of the electrochemical synthesis as compared with the usual chemical procedures are obvious:

(a) Reduction under mild conditions can be guided by the choice of the electric parameters to proceed in steps, thus allowing the production of definite oxidation states for the exchange of hard by soft ligands.

(b) The single reduction steps, the rate of which is proportional to the amount of current per second, are followed by ligand exchange adapting the coordination sphere successively to the altered electronic properties.

(c) Ligands and reaction conditions (*T*, *p*, current density, electrolyte, solvent) can be varied within wide limits, thus generally allowing an improvement of the syntheses.

2.3. The Principle: "Hard and Hard and Soft and Soft Flock Together"[17]

The particular power of the electrochemical procedure can be explained on the basis of "Pearson's Concept of Acids and Bases," according to which the combinations "hard acid/hard base" and "soft acid/soft base" are most favorable. Figure 3 demonstrates the dramatic change observed for the radius of chromium cations by reducing the oxidation state stepwise from +6 or +3 to zero. Consequently the metal center of a complex becomes larger and

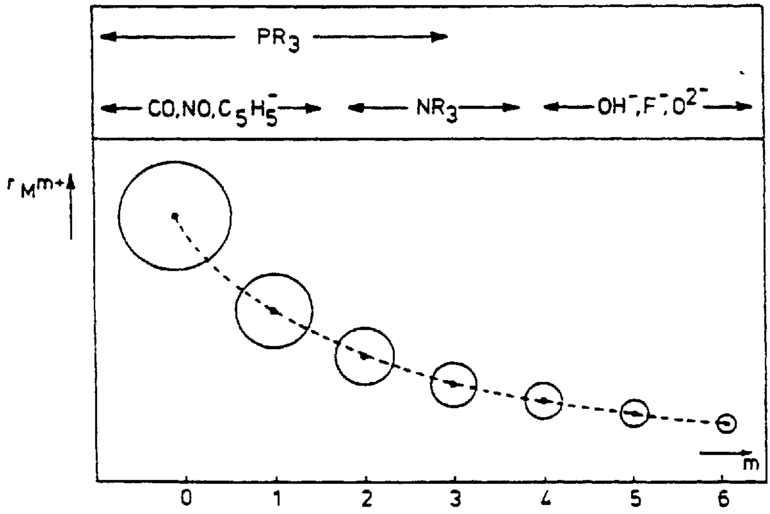


FIGURE 3 Variation of size and softness of M^{m+} ions with *m*.

softer with the stepwise electrochemical reduction, thus enhancing the tendency for exchange of hard ligands or solvent molecules by softer partners. According to thermodynamics one can expect a coordination sphere of maximum stability for each oxidation state, if a variety of ligands is offered.

In Fig. 3 a selection of typical ligands suited for the stabilization of different metal oxidation states is given. Favorable partners for high oxidation numbers are O^{2-}, OH^- and F^-, for low oxidation numbers CO, NO and unsaturated hydrocarbons or aromatic systems, while phosphines are known to be very versatile ligands for oxidation states between +3 and −1. Inert complexes can be made labile by redox reactions, and ligand exchange will follow with the formation of the thermodynamically most stable ligand array.

The possibilities and advantages of the electrochemical synthesis can be described in more detail on the basis of the present MO model of metal–ligand bonding. A systematic view of M/L combinations is shown in Fig. 4 using orbital pictures and giving the prerequisites of both M and L as a function of acidic and/or basic properties.[17,19–21]

In this presentation the effects of substituents R on the ligand atom and of further ligands L′ in the complex fragment have been ignored. In discussing special cases they can be treated in a similar way, thus providing a qualitative but helpful picture for the development of electrochemical synthesis, allowing a selection of the experimental conditions.

2.4. The Practice of Organometallic Electrolysis

Transfer of the principles given above to the experimental practice demands the development of suitable equipment. In case of gaseous components in the reaction mixture, undivided high pressure cells (electrolytic autoclaves) are used; for experiments at normal pressure, divers glass apparatusses may be applied. The principles of working of the different cells can be deduced from the diagrammatic pictures given in Figs. 5 and 6 without any detailed description. Figure 6 also shows an assortment of electrodes with various forms and connections.[22]

The type and form of the anodes are adjusted to the special aim of the synthesis as far as possible. Suitable cathodes are often made

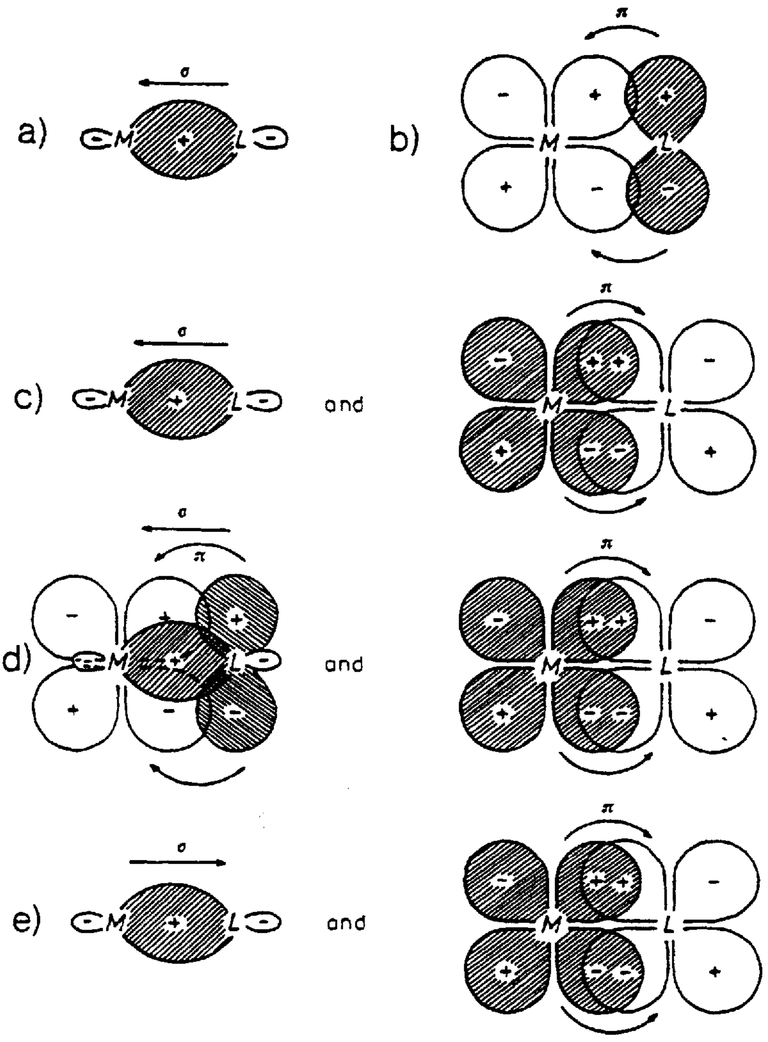


FIGURE 4 The M–L bond as a function of the acidic and basic properties of M and L: MO model (Ref. 17). (a) L: σ-Donor (NR$_3$, NH$_3$); M: σ-Acceptor (hard acid). (a) + (b) L: (σ + π)-donor (H$_2$O, OH$^-$, F$^-$, NR$_2^-$); M: (σ + π)-acceptor, hard (σ + π)-acid. (c) L: σ-donor and π-acceptor (soft σ-base, soft π-acid); M: soft σ-acid, soft π-base. (d) L: (σ + π)-donor and π-acceptor ((σ + π)-base, π-acid; Hal$^-$, PR$_2^-$, SR$^-$); M: (σ + π)-acid and π-base. (e) L: (σ + π)-acceptor (soft acid: BX$_3$, AlX$_3$); M: soft (σ + π)-base (d^8 or d^{10} configuration).

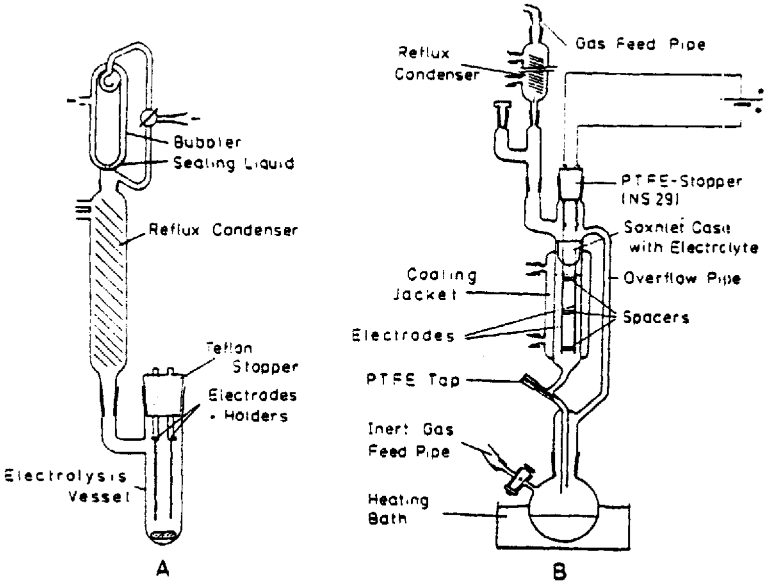


FIGURE 5 (A) Apparatus for preparative electrolysis at normal pressure. (B) Normal pressure electrolytic cell for semi-continuous preparation.

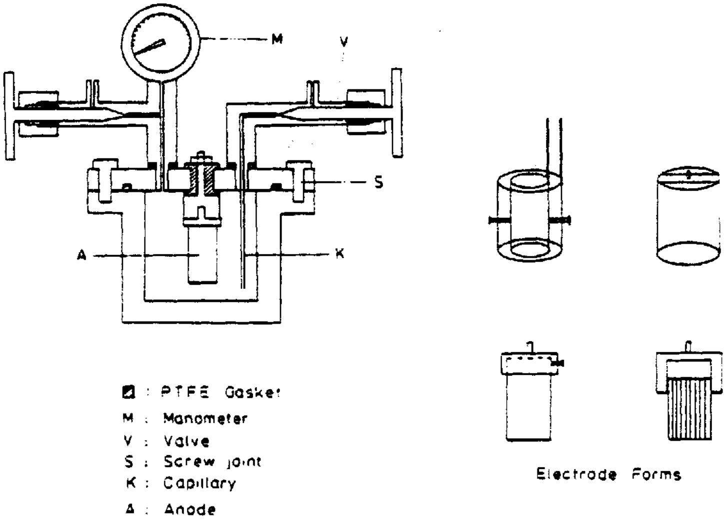


FIGURE 6 High pressure electrolytic cell, electrodes and holding devices.

of aluminum sheets; in most cases, however, the autoclave corpus (V2A or V4A steel) is used as the cathode and thus shielded from the corrosive attack of the electrolyte system. Control of the reaction is possible either by measuring electric parameters (current, voltage), pressure (consumption or evolution of gaseous components) and temperature or by taking off samples for spectroscopic investigations. Special devices (high pressure IR cells) have been developed for the *in situ* detection of high pressure species like metal carbonyl derivatives and active intermediates of a catalytic cycle.

The electrochemical reactions (reduction or oxidation) of substrates are affected by the applied potentials which depend on the variables solvent, concentration, ligands, supporting electrolyte, temperature and electrode material. Most of these influences can be explained by the electrochemical layer model together with the limitations due to the electrochemical stabilities (anodic and cathodic limiting potentials) of the electrolyte components.[12]

In the work described here, as a rule, transition metals have been used as sacrificial electrodes, thus producing one of the reactants during the electrochemical process. Literature information on the oxidation potentials of metals and their dependence on solvents, supporting salts and temperature facilitates the choice of the reaction conditions considerably.[23-25] It is obvious that the broad application of electrochemical methods to the synthesis of transition metal complexes will often demand compromises. The complexity of electrochemical systems might even raise the impression that for any concrete preparation a thorough investigation of all influences is necessary. Practical experience, however, demonstrates that ignorance of the special properties of an electrochemical system will not necessarily hinder application in preparative chemistry.

2.5. Principal Possibilities of Electrochemical Synthesis of Complexes

In contrast to chemical redox reactions, oxidation and reduction in electrolysis occur at different places of the electrolyte system. Reaction partners for the substrates are the electrodes acting either as electron donor (cathode) or acceptor (anode). The two areas—if necessary—can be separated by a diaphragm. In our investigations we generally used undivided cells.

For the electrochemical preparation of transition metal complexes the following procedures can be applied:

A. Electrolysis of solutions of metal salts between inert electrodes implying cathodic reduction of solvated metal ions of high or medium valency and their conversion to complexes with low-valent central atoms by exchange of hard for soft ligands. Suitable substrates are anhydrous salts or complexes, which are soluble in the electrolyte system [Eq. (2)].

$$[\mathrm{M(Solv)}_n]^{m+} \xrightarrow{+(m-1)e^-} [\mathrm{M(Solv)}_n]^+ \xrightarrow[-n\mathrm{Solv}]{+n\mathrm{L}} [\mathrm{ML}_n]^+ \qquad (2)$$

The opposite process at the anode, i.e., the oxidation of a metal ion of medium valency and its stabilization by hard ligands, so far is without any practical significance.

B. The electrochemical dissolution of metal electrodes, i.e., their use as starting material either as sacrificial anode or cathode, is a particularly attractive procedure for the preparation of complexes. On addition of suitable ligands it allows the direct synthesis of complexes with metal centers in medium oxidation states and can also serve to supply substrates for cathodic reduction according to method A [Eq. (3)].

$$\text{Anode: } \mathrm{M}_x \xrightarrow{-me^-} \mathrm{M}^{m+} \xrightarrow{n\mathrm{L}^{(m)}} [\mathrm{ML}_n^{(m)}]^{m+} \qquad (3a)$$

$$\text{Cathode: } [\mathrm{ML}_n^{(m)}]^{m+} \xrightarrow[+x\mathrm{L}^{(0)}]{+me^-} [\mathrm{ML}_x^{(0)}] + n\mathrm{L}^{(m)} \qquad (3b)$$

For the special case of metal carbonyl preparation, this elegant method in its net reaction corresponds to the direct synthesis from metals and CO and is thus analogous to the Mond process[26] or "metal atom synthesis."[6,7] Since the dissolution of the anode is an essential part of the overall process, side reactions at the positive electrode are, as a rule, of little importance.

While the use of sacrificial cathodes is the exception in the electrochemical preparation of complexes, it is of considerable practical value for the synthesis of metal alkyls and related compounds. Equation (4) renders a typical example in general form.

$$\mathrm{RX} \xrightarrow{+e^-} [\mathrm{RX}]^- \longrightarrow \mathrm{R}^\bullet + \mathrm{X}^- \xrightarrow{\mathrm{M}} \mathrm{RM} + \mathrm{X}^- \qquad (4)$$

C. In particular, for the preparation of metal carbonyl derivatives the combination of oxidation or reduction and CO displacement presents a useful route; Eq. (5) renders the possible course of such an "electrochemical substitution."

$$\begin{tikzcd}
{[M(CO)_n]^+} \arrow[d, "+L"', "-CO"] & M(CO)_n \arrow[l, "\text{Ox.}"', "-e^-"] \arrow[r, "\text{Red}", "+e^-"'] & {[M(CO)_n]^-} \arrow[d, "+L"', "-CO"] \\
{[M(CO)_{n-1}L]^+} \arrow[dr, "\text{Red.}", "+e^-"'] & & {[M(CO)_{n-1}L]^-} \arrow[dl, "\text{Ox}"', "-e^-"] \\
& M(CO)_{n-1}L &
\end{tikzcd} \qquad (5)$$

This route goes back to electroanalytical investigations showing that metal carbonyls decompose via CO elimination after electrochemical oxidation or reduction.[27,28] In donor solvents (e.g., THF or CH_3CN) the unsaturated fragments are stabilized by addition of solvent molecules. Such metal carbonyl solvent adducts are valuable precursors for substitution products. The conventional preparation, based on the photochemical elimination of CO, allows only small amounts of substrates and needs long reaction times. Here the electrochemical procedure offers a good alternative as has been demonstrated in a few applications.[29]

In addition to methods A to C described above, combinations of them are possible for the synthesis of complexes. Applications will be demonstrated by a series of examples, partly taken from the literature, but mainly describing results of our own investigations.

2.6. Practice: Examples of Electrochemical Preparations

The presentation of the following examples occurs in two possible ways depending on whether the synthesis is already published or deals with unpublished results. In the first case, the process is described in principle but without details; in the second case, more detailed information will be given.

Example 1: $Cr(CO)_6$ from Chromium(III) Precursors (Method A).

$Cr(acac)_3$ or $Cr(py)_3Cl_3$ are used as starting compounds. Figure 7 presents the conditions under which the product can be obtained in yields of about 80%. The preparation is carried out in an electrolytic autoclave using aluminum as the sacrificial anode. In contrast to most of the chemical carbonylation methods,[30] which as a rule need drastic conditions, the electrochemical synthesis can be performed under relatively mild conditions. For details see Ref. 31.

Example 2: Metal Acetylacetonates from Sacrificial Anodes (Method B).

This synthesis has been chosen as an interesting example for a series of analogous reactions in which both electrode processes take part in product formation. The sacrificial anode supplies the metal cations of medium valency, while the corresponding anions are produced at the cathode by reduction of the acidic proton to give H_2:

$$\begin{array}{r}
\text{Anode: } M \rightarrow M^{n+} + ne^- \\
\text{Cathode: } nHR + ne^- \rightarrow nR^- + n/2\ H_2 \\
\underline{M^{n+} + nR^- \rightarrow MR_n} \\
\text{Overall: } M + nHR \rightarrow MR_n + n/2\ H_2
\end{array}$$

The overall process corresponds to the chemically impossible or unfavorable reaction of the metal with very weak acids HR yielding the salts MR_n and hydrogen. Suitable selection of the solvent often allows precipitation of the product and thereby easy isolation.

Extensive application of this method with alcohols and/or acetylacetone as reaction partners and anodes of iron, cobalt or nickel goes back to Lehmkuhl *et al.*,[32] who also developed a cell for continuous production. This method was later extended to other transition metals by Tuck and co-workers[33] and applied by our group to the preparation of acetylacetonates of chromium, molybdenum, vanadium, titanium and manganese.

In the case of the base metals Mn, Fe, Co and Ni the current yields often amount to values over 100%, due to a simultaneous

PRACTICE: Cr Complex $\xrightarrow[+CO]{Red}$ $Cr(CO)_6$

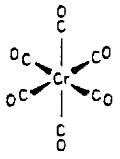
Precursor	Conditions	Product Yield
$Cr(acac)_3$ or $Crpy_3Cl_3$	Solvent: Pyridine Electrolyte: $[Bu_4N]Br$ Ligand $L^{(o)}$: CO (75 bar) $T = 361$ K $U = 5.0$ V $I = 100$ mA $t = 67$ h	 (80%)

FIGURE 7 Electrochemical synthesis of $Cr(CO)_6$ from Cr(III) compounds.

chemical attack of the activated anode by acetylacetone. These syntheses show an interesting dependence on the influence of air on product formation. Whereas in the anaerobic process the oxidation states II and III are formed preferentially, in the presence of oxygen acetylacetonates or oxo-acetylacetonates of higher oxidation states are obtained, e.g., $Fe(acac)_3$, $Mn(acac)_3$, $OM(acac)_2$ (M = Ti, V, Mo).[34]

Compared with conventional preparations of acetylacetonates the electrochemical process offers advantages, because the metals are transformed directly to the products and therefore the synthesis of water-free halides, often used as precursors, can be avoided.

Example 3: Preparation of Anhydrous Metal Halides and Anionic Halide Complexes (Method B).

Anhydrous halides of main group and transition metals are important precursors for the synthesis of

- —organometallic compounds
- —neutral or anionic complexes

They are produced mainly by three different routes:

(a) by dehydration of water containing salts,
(b) by reaction of the elements,
(c) by reaction of metal oxides with HCl or by "reductive" halogenation using carbon and halogens (Oersted Method[35]).

Routes (b) and (c) often need high temperatures and yield halides of high valency. Here the electrochemical synthesis using sacrificial anodes and an inert platinum cathode in acetonitrile or benzene/methanol mixtures has some advantages.[36] The halogens bromine and iodine are added to the electrolyte solution directly, while chlorine is introduced as gas diluted with nitrogen or argon. The metal halide is obtained either solvent-free or as a solvent adduct. The binary halides are accessible by thermal cleavage of the adducts at temperatures between 120 and 350°C. On adding neutral (e.g., dimethylsulfoxide, urea, bipyridine, imidazol) or anionic ligands (halide ions via tetraalkylammonium salts) neutral or anionic complexes can be produced. The latter precipitate as combinations with the large cations from benzene/methanol mixtures. Yields of the possible products (binary halides, neutral or anionic complexes) are in the range 80 to 90%. Details of this method and its mechanism are collected in Ref. 37.

Example 4: Phosphine Derivatives of Chromium Hexacarbonyl (Method B).[31]

In method B the anode serves as electron sink and metal source. Solvated or complexed cations (here Cr^{3+}) after transport to the cathode are reduced and undergo similar substitution steps as in method A. In the present case the electrochemical reaction is carried out with CO and PMe_3 as soft ligands. It occurs under milder conditions than the preparation of $Cr(CO)_6$. Figure 8 describes the formation of *cis*-$Cr(CO)_4(PMe_3)_2$ and $Cr(CO)_5PMe_3$. The conditions specified in Figure 8 show that the degree of substitution can be directed by variation of CO pressure and temper-

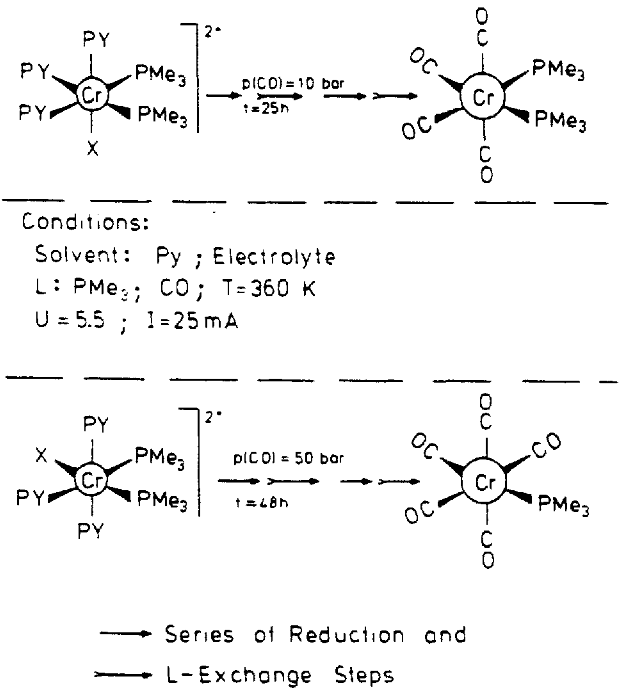


FIGURE 8 Electrochemical preparation of *cis*-$Cr(CO)_4(PMe_3)_2$ and $Cr(CO)_5PMe_3$.

ature. This influence of the external conditions proves the validity of the synthetic principle. Obviously, the phosphine ligands are already coordinated to the Cr^{3+} or Cr^{2+} ions and undergo substitution by the softer ligand CO after replacement of the harder partners Cl^- and Py during the stepwise reduction of the central atoms.

Example 5: Metallocenes and Cyclopentadienyl Metal Carbonyls (Method B).

In spite of the low acidity of cyclopentadiene the electrochemical activation of sacrificial anodes allows a similar procedure for the synthesis of cyclopentadienyl complexes as for the preparation of acetylacetonates:

$$\begin{array}{c}
\text{Anode: } \mathrm{M} \longrightarrow \mathrm{M}^{m+} + me^{-} \\
\text{Cathode: } m\mathrm{HCp} + me^{-} \rightarrow m\mathrm{Cp}^{-} + m/2\ \mathrm{H}_2 \\
\mathrm{M}^{m+} + m\mathrm{Cp}^{-} \rightarrow \mathrm{M(Cp)}_m + m/2\ \mathrm{H}_2 \\
\hline
\text{Overall: } \mathrm{M} + m\mathrm{HCp} \rightarrow \mathrm{M(Cp)}_m + m/2\ \mathrm{H}_2
\end{array}$$

According to this principle either metallocenes or cyclopentadienyl metal complexes, e.g., carbonyl derivatives, can be prepared. Due to the wealth of information on the electrochemical properties of this type of compounds a number of research groups studied their electrolytic synthesis.[38–49] A critical survey shows that the best direct preparation of ferrocene is the electrolysis in dimethylformamide, described by Lehmkuhl *et al.*[11a,41,42] It is a two-step procedure, in which first iron anodes are dissolved in an electrolyte system consisting of sodium bromide and ethanol, yielding scarcely soluble $\mathrm{Fe(OEt)_2}$ and $\mathrm{H_2}$. After separation this product is converted to ferrocene by a purely chemical reaction with monomeric cyclopentadiene in almost quantitative yield.

Some efforts were made[49] to carry out the complete process as a one-pot reaction by choosing a methanol solution of sodium bromide as electrolyte. The electrochemical reaction was performed in an undivided cell of type A (Fig. 5) giving product and current yields of 30%. The analogous synthesis using cobalt or nickel anodes produced $\mathrm{Co(Cp)_2}$ (50%) and $\mathrm{Ni(Cp)_2}$ (21%), respectively.

Significant improvement was attained by using a cell of type B (Fig. 5), allowing a semi-continuous process. Current and product yields for $\mathrm{Fe(Cp)_2}$ amount to 50%.

π-cyclopentadienyl metal carbonyls have been prepared using titanium and vanadium anodes, respectively, in pyridine as a solvent at p(CO) = 115 bar (Ti) or 120 bar (V) and $T = 383$ K with $\mathrm{[Bu_4N]Br}$ as the supporting electrolyte and monomeric cyclopentadiene. The high temperature counteracts the dimerization of cyclopentadiene. Since the intended products are unstable at this temperature under normal pressure, a suitable CO pressure is applied to avoid decomposition. The synthetic route is described in Fig. 9. The products $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and $(\pi\text{-}C_5H_5)V(CO)_4$ respectively, have been obtained in about 80% yields via the intermediates $(\pi\text{-}C_5H_5)_nMCl_m$.[22,38]

Example 6: Electrochemical Substitution of $M(CO)_6$ (Method C).

This method like the photochemical substitution can be carried out in two different variants:

- —by electrochemical generation of solvent adducts, e.g., $M(CO)_5(Solv)$, followed by a chemical exchange reaction with more suitable donor ligands,
- —by the "direct electrochemical substitution" of CO by the ligand in question.

Electrochemical reduction of the metal hexacarbonyls in THF or pyridine leads to mixtures of solvent adducts $M(CO)_{6-n}(Solv)_n$ of similar composition as the photochemically produced systems.

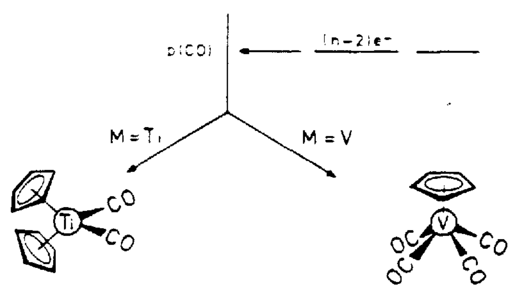


FIGURE 9 Scheme of the preparation of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ and $(\pi\text{-}C_5H_5)V(CO)_4$ by electrolysis.

Whereas by irradiation complete decarbonylation is possible in principle, the electrochemical method, depending on the donor strength of the solvent, only allows substitution of 1 to 3 CO ligands. This result can be explained by the shift of the limiting potential due to the exchange of CO for stronger donor ligands. On adjusting the reduction potential, substitution can be directed within certain limits. In THF the maximum degree of substitution is the replacement of 2, in pyridine of 3 CO groups. While the THF adducts $M(CO)_{6-n}(THF)_n$ ($n = 1, 2$) due to their lability can only be detected by IR spectroscopy, the pyridine complexes may be isolated. Long-time electrolysis in pyridine solution affords fac-$M(CO)_3(py)_3$ as the only product in yields up to 90%. Both types of solvent adducts can be used as precursors for phosphine complexes by replacing the hard for soft ligands.

The "direct electrochemical substitution" is carried out with $M(CO)_6$/THF solutions containing the corresponding ligands. Thus selective preparation of *cis*-$M(CO)_4(PR_3)_2$ complexes in yields of 90% can be effectively accomplished.[29]

Example 7: Metal Alkyl Compounds from Sacrificial Electrodes (Method B).

Alkyl and aryl halides can be converted to divers organometallic compounds using either sacrificial cathodes or a combination of sacrificial anode and inert cathode, such as platinum.

The cathodic formation of such derivatives is due to the attack of organic radicals formed by irreversible electrochemical reduction of RX. Useful synthesis in nonaqueous systems are available for mercury, lead, tin, indium and thallium.

A wider range of application is accessible by combining dissolution of metal anodes with cathodic reduction of organic halides in acetonitrile or benzene/methanol solutions. Product formation corresponds to the oxidative addition of RX to metal atoms and typically occurs with current yields between 1 and 10 F/mol.

Referring to the extensive literature on this subject,[50–52] only the generation of nickel and palladium complexes from the corresponding anodes and RX are briefly mentioned here. With neutral ligands or donor solvents, compounds of the type $RNi(CN)(CH_3CN)_2$, $RNi(CN)(PEt_3)_2$ and $C_6F_5Pd(Br)(PEt_3)_2$ have been obtained.[11b]

Example 8: Electrochemical Preparation of Noble Metal Complexes (Method B, Several Variants).

Dissolution of Platinum[53]

The cathodic dissolution of platinum was described as early as 1965 by a Japanese research group.[54] On electrolysis of methanol/methoxide solutions under a CO pressure of 70 bar, a green solution capable of the catalytic hydroformylation of olefines was obtained. Repeating these experiments, we were able to detect in solution the platinum cluster anions $[Pt_3(CO)_6]_n^{2-}$ first prepared by conventional chemical routes by Chini and co-workers.[55] The compounds with $n = 3$ (red) and $n = 4$ (green) can be isolated by precipitation with tetrabutyl ammonium bromide as the salts $[Bu_4N]_2$-$[Pt_3(CO)_6]_3$ and $[Bu_4N]_2$ $[Pt_3(CO)_6]_4$, respectively. They contain piles of $[Pt_3(CO)_6]$ units, in which three platinum atoms form an equilateral triangle with three bridging and three terminal CO groups.

In a systematic investigation we managed to develop three different courses for the electrochemical dissolution of platinum:[53]

(a) Cathodic dissolution in methanol/methoxide mixtures which very probably occurs by radical attack and leads to reasonable current yields especially at low temperatures ($T \approx 253$ K). The presence of CO is essential for this process.
(b) Anodic dissolution in the presence of halide ions and at high temperatures (~440 K).
(c) Dissolution using an alternating current superimposed by a direct current. thereby avoiding blocking precipitates on the electrode surface.

Procedures (b) and (c) also generate the above-mentioned platinum cluster anions. Current yields depend on temperature, CO pressure, current density and solvent. Attempts to prepare stable carbonyl phosphine complexes of platinum, using the red or green solutions as precursors, proved unsuccessful. However, electrolysis in the presence of CO and PPh_3 affords the mononuclear complex $Pt(CO)(PPh_3)_3$ as the main product. By variation of the CO pressure, mixtures of complexes of the type $Pt(CO)_n(PPh_3)_{4-n}$ can be detected in solution. On releasing the pressure, substitution of CO by PPh_3 takes place, leading to $Pt(CO)(PPh_3)_3$.

Dissolution of Rhodium[53]

The electrochemical dissolution of rhodium has also been successful using the above-mentioned methods. Due to mobile equilibria in solution, the product pattern is very versatile and can be modified by changing the type and concentration of ligands. For example, in methanol/methoxide mixtures the cluster anion $[Rh_4(CO)_{11}COOMe]^-$ is formed, while in the presence of PPh_3 the Vaska-type complex $[Rh(PPh_3)_2(CO)Cl]$ is obtained. A particularly thorough investigation has been carried out using the alternating current process (c). Depending on the supply of ligands and/or reaction gasses, the following known complexes have been generated and partly isolated:

- the VASKA-type complex $Rh(PPh_3)_2(CO)Cl$ in the presence of CO, PPh_3 and Cl^-,
- the anionic species $[Rh(CO)_2Cl_2]^-$ and $[Rh(CO)Cl_5]^{2-}$.

Varying the experimental conditions, other known rhodium carbonyl derivatives have been detected by high pressure IR spectroscopy in solution, e.g., $[Rh(CO)_n(PPh_3)_{3-n}H]$ ($n = 1$ to 3, depending on p_{CO}), and cluster anions as $[Rh_{12}(CO)_{34}]^{2-}$, $[Rh_{12}(CO)_{30}]^{2-}$ or $[Rh_6(CO)_{15}Cl]^-$. The current yield of dissolution can be increased considerably by raising the temperature from 293 (20%) to 443 K (45%).

The examples presented above demonstrate the usefulness, effectiveness and range of application of the electrochemical method for complex synthesis. In the meantime, similar results have been obtained for a great number of d-block elements as shown in Fig. 10, giving a survey of our investigations.

In the title of the present chapter the question was put forward of whether or not the electrochemical method is an alternative to "metal atom synthesis." The examples presented answer this ques-

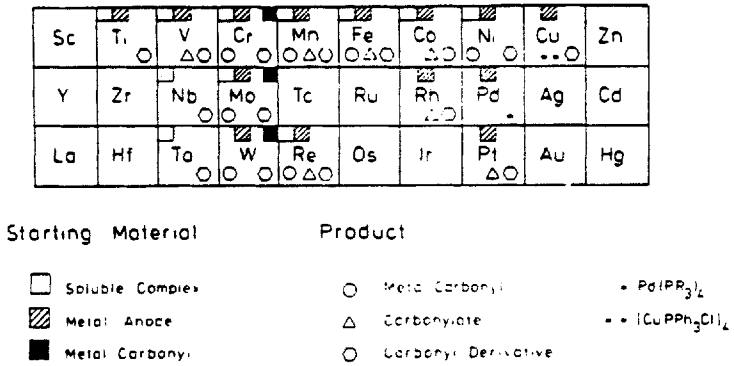


FIGURE 10 Survey of our electrochemical investigations on d-block elements.

tion positively. Advantages and disadvantages of both routes are collected in Table I.

3. CATALYTIC APPLICATIONS OF ELECTROCHEMICAL SYSTEMS

The electrochemical preparation of metal carbonyl derivatives using higher valent compounds or metal electrodes almost necessarily

TABLE I

Comparison of electrochemical and "metal atom synthesis"

Criteria	Electrochemical Synthesis	Metal Atom Synthesis
experimental expenditure	large	very large
convertible quantities	medium	small
reaction time	long	short
yields	good	medium
products	thermodynamically determined	kinetically determined
type of compounds	normal complexes typical coordination numbers high temperature species	unusual compounds varying coordination numbers low temperature species

led us to investigations applying this method to the generation of catalysts. In principle, there are different possibilities for this application.

3.1. Electrochemistry and Catalysis

As a rough consideration there seems to be only a loose relationship between electrochemistry and catalysis. In fact, however, nearly all important electrochemical syntheses involve at least one catalytically active component being essential for the selectivity of the system. The electrodes of an electrolytic cell not only serve as a source or sink of electrons but also function as heterogeneous catalysts. Without electrocatalytic effects and material dependent differences causing over-voltage or selective adsorption, all electrochemical processes should be similar and be exclusively determined by thermodynamics.

Most of the compounds used in homogeneous catalysis only serve as stable precursors for the so-called "active complexes." As a rule, these are labile electronically unsaturated or over-saturated species with a distinct tendency for ligand exchange and are thus able to combine the components of a catalytic reaction in activated form in the coordination sphere of the metal. Formation of the "active complex" often occurs at high temperatures and/or on addition of suitable developing reagents (promoters) and takes up to several hours.

Electron-deficient and excess systems with 16, 17, 19 or 20 electrons can be produced electrochemically under mild conditions. They are typical intermediates of electrochemical processes in spite of the fact that because of their short half-life values they rarely can be detected. However, cyclovoltammetric measurements have shown that radical ions produced by one-electron oxidation or reduction of an 18e-complex in suitable surroundings partly have surprisingly long life-times.[27]

This led us to the idea to generate not only the stable precursors but also the active catalyst by means of electrochemical methods under mild conditions in order to avoid long induction periods. This idea gained support from literature information on the positive influence of UV irradiation on induction periods and efficiencies of catalysts.[56-59]

3.2. Electrochemical Generation of Catalysts

Several combinations of electrochemical synthesis and homogeneous catalysis have to be considered for practical applications:

(a) The catalyst is produced in an electrochemical process preceding the catalytic reaction;
(b) the electrochemical generation of the catalyst is carried out in the reaction mixture under different conditions of temperature and pressure than the catalytic reaction:
(c) catalyst formation and catalytic reaction are performed simultaneously in a one-pot procedure:
(d) the catalyst is regenerated by a continuous or discontinuous electrochemical reaction.

Since the development of electrochemical syntheses is very time-consuming and demands high experimental expenditure, our investigations were first focussed on known processes like the cyclization of acetylene or the hydroformylation of olefines. Several examples are given here to demonstrate applications of electrochemically generated catalysts.

Example 1: Synthesis of 1,5,9-Cyclododecatriene from Butadiene.

Lehmkuhl and co-workers prepared an organometallic catalyst in solution using nickel acetylacetonate as the starting material and tetrabutylammonium bromide in THF as electrolyte. Butadiene was passed into the system during the electrolysis. So the generation of the catalyst was immediately followed by the catalytic cyclization of butadiene, yielding isomers of 1,5,9-cyclododecatriene. The product mixture was similar to that obtained using the corresponding catalyst prepared by chemical reduction.[60]

Example 2: Synthesis of $Ni(PPh_3)_2(CO)_2$ and Catalytic Cyclization of Acetylene (Two-Step Method, According to (b)).[61]

The catalyst is generated in acetonitrile using $[Bu_4N]Br$ as the supporting salt and a nickel anode as the metal source by electrolytic reduction of solvated Ni^{2+} ions in the presence of triphenylphosphine and CO (1 bar). After removing the excess CO by passing a stream of N_2 through the solution, a mixture of N_2

(5 bar) and acetylene (10 bar) is applied to the system under pressure. The development of the catalyst demands temperatures between 373 and 393 K, while the catalytic cyclization already operates at 330 to 345 K to give benzene (60%) and styrene (8%) as the main products.

Example 3: Simultaneous Catalyst Generation and Catalysis with Nickel(II) acetylacetonate (One-Pot Procedure (c)).[61]

An electrolysis autoclave with a nickel anode is charged with $[Bu_4N]BF_4$ in THF as electrolyte and acetylacetone as the ligand source. After degassing the solution by evacuating and ventilating with dry nitrogen, 5 bar of N_2 and 12 bar of acetylene are introduced under pressure. Then the electrolysis is started at 350 K with a constant current of 50 mA. Used acetylene is replaced discontinuously. The overall product yield of 55% consists of 13.5 g cyclooctatetraene and 9.0 g benzene.

Example 4: Simultaneous Catalyst Synthesis and Catalysis with $HCo(CO)_4$ or $HCo(CO)_3PBu_3$.[62]

The application of the one-pot procedure (c) was tested for the economically important hydroformylation of olefines, for which cobalt or rhodium carbonyl hydrides act as catalytically active components. In preliminary experiments it was ascertained that under the conditions of oxo-synthesis the complexes $HCo(CO)_4$ or $HCo(CO)_3PBu_3$ can be prepared by electrochemical dissolution of cobalt anodes and reductive carbonylation of the metal solvates applying a mixture of H_2 and CO or H_2, CO and PBu_3. The simultaneous electrochemical catalyst production and hydroformylation were carried out with the systems

$$\text{Co anode/CO/H}_2\text{/olefine}$$

and

$$\text{Co anode/PBu}_3\text{/CO/H}_2\text{/olefine}$$

using cyclohexene or 1-hexene as olefines. For the reaction the usual conditions of conventional hydroformylation were applied.[59]

The amount of catalyst is varied by the time of electrolysis at constant current and determined by weight loss of the anode. Referring to the detailed description[62] it should be stated here that the process leads to the same products and similar yields as the conventional method. With $HCo(CO)_4$ 1-hexene reacts to give mainly the isomeric aldehydes *n*-heptanale and 1-methylhexanale, whereas with $HCo(CO)_3PBu_3$ hydroformylation is followed by hydrogenation yielding varying ratios of *n*-heptanale and *n*-heptanol. In long time experiments 90% of the olefines are converted to the alcohols. It is interesting to note that the amount of catalyst for equal conversions is obviously lower than in the conventional process. This can be rationalized by assuming that Co(II) complexes, resulting from disproportionation, can be reactivated more quickly by electrochemical than by chemical reduction with the synthesis gas.

Example 5: Noble Metal Catalysts on the Basis of Platinum and Rhodium.

As shown in Section 2 platinum and rhodium electrodes can be dissolved electrochemically using different procedures and reaction conditions. Ligand supply, electrolyte system, pressure and temperature determine the product pattern, especially in the case of rhodium, where mobile equilibria have been detected in solution. Therefore, an improvement of reaction control enabling the detection of high pressure species under working conditions seemed to be an important task.

IR spectroscopy is particularly suited for the *in situ* control of the formation of metal carbonyl derivatives or carbonylation catalysts, because changes in the number and geometrical arrangement of CO groups, variation of other ligands or of the oxidation state of the central atom are indicated by characteristic alterations of the IR spectrum in the CO valence frequency region.[63]

This fact suggested the development of a high pressure electrolytic cell allowing the registration of IR spectra during a synthetic process. In the literature a number of high pressure cells are described.[64–72] They were used for the investigation of catalytic reactions and are either spectroscopic cells with minimal inner volumes or installed as additional equipment of pressure reactors. In order to overcome the disadvantages of both constructions, we

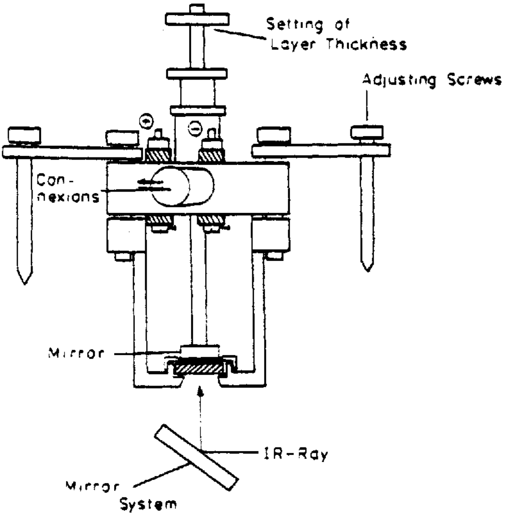


FIGURE 11 Electrolytic high pressure infrared cell for *in situ* spectroscopy.

modified an electrolytic autoclave in such a way that IR control measurements can be performed from time to time using a reflexion unit. Figure 11 gives some details of its construction.[49]

This cell has been tested in a series of practical cases, including the transformation of doubly bridged manganese carbonyl complexes $Mn_2(CO)_8ER_2X$ to singly bridged derivatives $(CO)_5MnER_2Mn(CO)_4X$.[73] A particularly simple example is shown in Fig. 12, demonstrating the existence of a palladium carbonyl compound under CO pressure, which on the attempt to isolate decomposes to give elemental palladium. The new construction has been of great help in the control of several catalytic experiments with rhodium complexes, one of which is briefly described below.

Hydroformylation of 1-Hexene.[53]

Because of the particular importance of the VASKA catalyst for oxo-synthesis we were interested in the catalytic activity of an electrochemically generated system. The simultaneous catalyst formation and catalytic reaction were carried out in methanol solution with 1-hexene as the substrate at a pressure of 13 to 15 bar for the

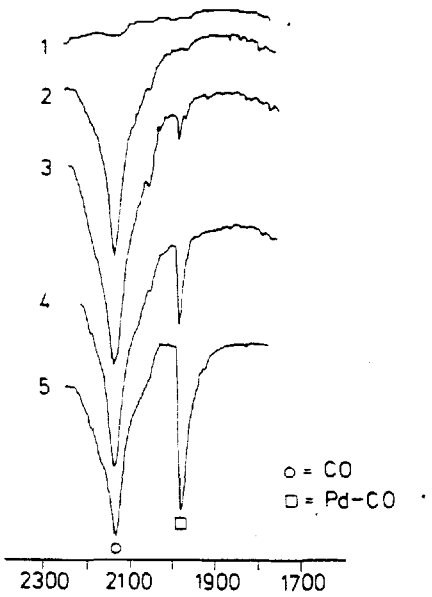


FIGURE 12 Detection of an electrochemically generated PdCO compound.

1:1 mixture of H_2 and CO. An 80% overall yield of a 5:1 mixture of *n*-heptanale and 1-methylhexanale has been obtained in an exothermic reaction with only 3.1 mg of rhodium and 15.1 ml 1-hexene.

This example demonstrates that the one-pot procedure of catalyst generation and catalytic reaction is possible without too many problems. There is no question that this process can be transferred into practice, but certainly needs further careful and fascinating experiments.

OUTLOOK

In this Comment the value of electrochemical methods for the preparation of metal complexes and catalysts has been outlined. Some effort will be required to develop and improve the experimental facilities and practical applications. For future investigations in this interesting area of research, two projects will be of particular significance:

(a) The spectroscopic detection of catalytically active complexes and of as many as possible intermediates of catalytic cycles.
(b) The systematic variation of electrochemical systems to improve the effectiveness and selectivity of the syntheses.

These efforts may one day fulfill the dream of the preparative chemist that a given metal in a given oxidation state will choose a definite coordination sphere of ligands from a large reservoir, and that it will be possible to predict composition and structure of the product.

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