REVIEWS

Preparative Scope of Organometallic Electrochemistry

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This review begins with a short introduction to preparative aspects of organic electrochemistry. New developments within the field of organometallic chemistry are discussed. Emphasis is put on the syntheses of transition metal-olefin complexes.

Nach einer kurzen Einführung in die organische Elektrochemie aus der Sicht des präparativ orientierten Chemikers werden die neuen Entwicklungen innerhalb der metallorganischen Chemie besprochen. Der Schwerpunkt liegt auf der Behandlung der Synthesen von Übergangsmetall-Olefin-Komplexen.

By definition, organometallic compounds contain at least one bond between a metal and one or more carbon atoms. Typical examples of this compound type are the alkyl- or arylmetals, in which the metal atom and the carbon of the organic rest are joined by a σ-bond, and coordination compounds of metals with unsaturated hydrocarbons, in which the C—C multiple bonds are linked to the metal through their π-electron systems[1].

Electrolysis can often be used successfully for the preparation of organometallic compounds. From the mechanistic viewpoint there are three principally different possibilities.

- The primary generation of organic radicals by reduction of organic compounds, followed by reaction of the radicals with the cathode metal to give organometallic compounds.
- Anodic oxidation of organometallic compounds containing carbanions; firstly, organic radicals are formed by oxidation of the carbanion and these then react with the anode metal. The electrochemical reaction of one alkylmetal compound results in the formation of the alkyl compound of a different metal.
- The reduction of a mixture of a metal compound and an organic ligand results in the formation of a metal-ligand complex. This method has been mainly tested on the 3d transition metals.

1. General Remarks

Electron transitions between the reactant (*E*) and the substrate (*A*) or (*G*) are reductions or oxidations:

$$E + A \longrightarrow E^{\oplus} + A^{\ominus}$$

or

$$E + G \longrightarrow E^{\ominus} + G^{\oplus}$$

A reduction of the substrate signifies an oxidation for the reactant (*E*) when it serves as a reducing agent and vice versa. Electrochemical reactions have the peculiarity that the reduction occurs at a different place than the oxidation.

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[1] See e.g. J. J. Eisch, *The Chemistry of Organometallic Compound*, Macmillan Comp., New York London (1967).

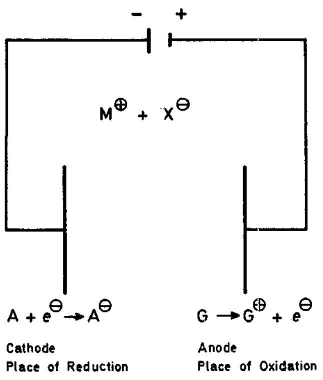


Fig. 1 Schematic representation of the electrochemical change of *A* and *G* in the presence of MX as electrolyte when *A* is more readily reduced than $M^{\oplus}$ and G more readily oxidized than $X^{\ominus}$. *A* and *G* may also be neutral particles, *A* would then accept an electron to give the anion radical $A^{\dot{\ominus}}$ and *G* would loose an electron to give the cation radical $G^{\dot{\oplus}}$. $M^{\oplus}$ and $X^{\ominus}$ are responsible for the electrical conductivity of the solution[2].

It should be possible to use electrochemical reactions for bond formation between metal atoms and carbon atoms of organic groups, or C—C multiple bond systems. For this the organic group must be converted into a reactive form in which it is able to react with the metal or its compounds. This reactivity has been known since the work of Paneth[3] on alkyl radicals, which can also be formed electrochemically by the oxidation of carbanions or by the reduction of alkyl derivatives with electronegative rests.

$$\overset{\delta\oplus}{M}-\overset{\delta\ominus}{R} \xrightarrow[-e^{\ominus}/-M^{\oplus}]{} [R\cdot]$$

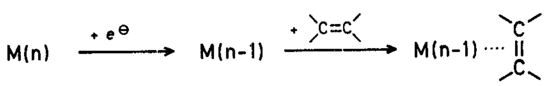
$$\overset{\delta\oplus}{R}-\overset{\delta\ominus}{X} \xrightarrow[-X^{\ominus}]{+e^{\ominus}} [R\cdot]$$

M = metal, R = alkyl group, X = more electronegative group

Further possibilities are the conversion of electron affinitive hydrocarbons into anion radicals by electron acceptance:

$$R-H \xrightarrow{+e^{\ominus}} [R\overset{\cdot}{-}H]^{\ominus}$$

or, by using an electrochemical process, the conversion of the metal into a reactive form in which it can form a complex with C—C multiple bond systems.



$$M(n) \xrightarrow{+e^{\ominus}} M(n-1) \xrightarrow{+\ \rangle C{=}C\langle} M(n-1)\cdots \begin{matrix} \rangle C\langle \\ \| \\ \rangle C\langle \end{matrix}$$

1.1. The Electrochemical Systems

The following factors are decisive for the course of reaction when several oxidizable or reducible substances are present:

- for reductions: the electron affinity. The substance with the largest electron affinity is reduced first:
- for oxidations: the ease with which electrons can be removed from the substance.

In this respect, the characteristic properties of a compound are the reduction and oxidation potentials. These are dependent on the solvent, the concentration, the temperature, and also, by interactions between the metal and the reduced or reducible (resp. oxidized or oxidizable) species, and the electrode materials. The potential range in which electrochemical reactions may be performed is generally limited by electrochemical reactions (oxidation or reduction) of the solvent or the electrolyte.

Because of their resistance to reduction, the following solvents are suitable for electrochemical reductions:

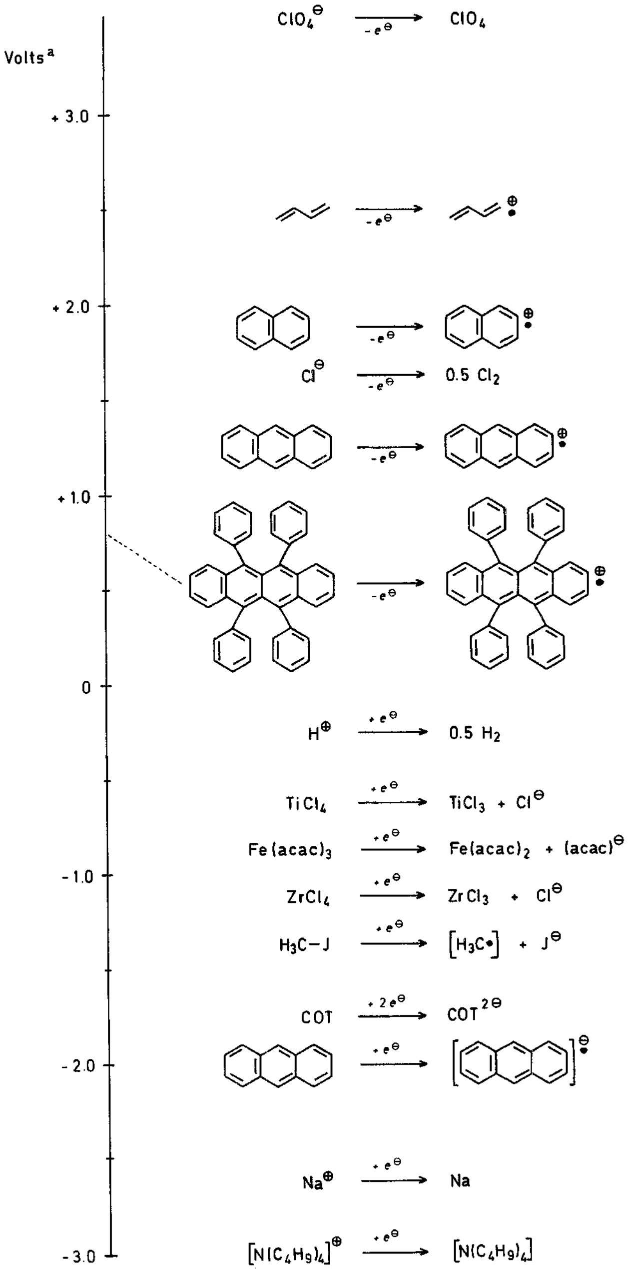


Fig. 2 Diagram of the electrochemically obtainable potential ranges. No compound can undergo cathodic reduction when it is more difficult to reduce than the electrolyte or the solvent; similarly for oxidation.

[a] Volts vs. saturated calomel electrode.

tetrahydrofuran (THF), dimethoxyethane (DME), 2,2′-dimethoxydiethyl ether (diglyme), pyridine, dimethylformamide (DMF), acetonitrile, dimethylsulfoxide (DMSO), propylene carbonate (PC), sulfolane, hexamethylphosphoric triamide (HMPT). The following solvents are suitable for electrochemical oxidations because of their resistance to oxidation: acetic acid, acetonitrile, pyridine, and nitromethane.

Lithium salts may be used as supporting electrolytes for reductions unless mercury electrodes are used (amalgam formation). Tetraalkyl-, and especially, tetrabutylammonium halides are also suitable.

Table 1. Useable Ranges and Dielectric Constants of Solvents Suitable for Electrochemical Reductions

Aprotic Solvent	Liquid State Range	Dielectric Constant	Useable Potential[a] (volts vs. saturated calomel electrode) Cathodic at Pt	at Hg	Anodic at Pt
tetrahydrofuran (THF)	−80 to 66°	7.6	−3.2[b]	−2.95[c]	+1.6[b]
dimethoxyethane (DME)	−58 to 82°	3.5		−2.95[c]	
diglyme	to 159°			−2.95[c]	
pyridine	−42 to 115°	12.3	−2.2	−2.4	+3.3[c]
dimethylformamide	−61 to 153°	38	−2.8[c]	−2.95[c]	
acetonitrile	−45 to 82°	38	−2.7[d]	−2.8[c]	+3.5[f]
dimethylsulfoxide (DMSO)	+18 to 189°	47	−2.3	−2.8[c]	
propylene carbonate (PC)	−49 to 242°	64	−1.9	−2.9[c]	
sulfolane	+28 to 285°	44			
hexamethylphosphoric triamide (HMPT)	+7 to 235°	30	−3.3[b]	−2.95	+1.0[b]

[a] In the presence of the following supporting electrolytes:

[b] $LiClO_4$; [c] $[N(C_2H_5)_4]ClO_4$; [d] $[N(C_4H_9)_4]ClO_4$;

[e] $[N(C_4H_9)_4]Br$; [f] $[N(C_2H_5)_4]BF_4$.

Salts containing the anions perchlorate, tetrafluoroborate, tetraphenylborate are suitable for oxidations. With regard to the potential, the following orders of increasing suitability are valid:
for reductions,

$$Na^{\oplus} < K^{\oplus} < N(C_2H_5)_4^{\oplus} < N(C_4H_9)_4^{\oplus} < Li^{\oplus}$$

and for oxidations,

$$J^{\ominus} < Br^{\ominus} < Cl^{\ominus} < ClO_4^{\ominus} < BF_4^{\ominus} < PF_6^{\ominus}$$

(see Table 2)

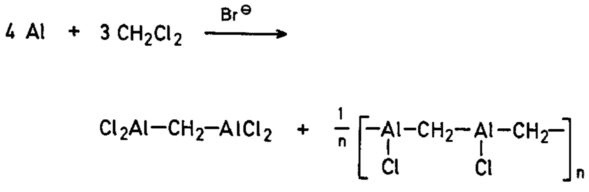
The selection of suitable solvents and electrolytes is dependent on the potential range required for the electrochemical reaction of the substrate. The properties of the desired product must also be considered. Thus, for example, protic solvents or H-acidic electrolytes cannot be used for the synthesis of many organometallic compounds. To summarize, the solvents and electrolytes must

- be sufficiently inert towards starting and end products,
- be more resistant to reduction (or oxidation) than the starting products,
- form systems of sufficient electrical conductivity,
- be so selected that separation of the products is possible after the electrolysis.

1.2. The Electrochemical Reactions

When the total reaction of an electrolysis is considered, electrochemical reactions equivalent to known chemical possibilities may be used for the syntheses of compounds. The preparations of bis-(dichloroaluminium)-methane are described here as an example.

Chemical preparation[4]:



$$4\ Al + 3\ CH_2Cl_2 \xrightarrow{Br^{\ominus}} Cl_2Al{-}CH_2{-}AlCl_2 + \frac{1}{n}\left[{-}\underset{Cl}{Al}{-}CH_2{-}\underset{Cl}{Al}{-}CH_2{-}\right]_n$$

Electrochemical preparation[5]:

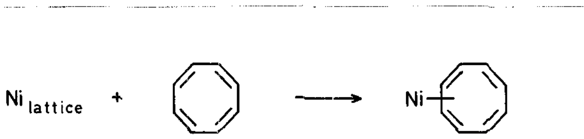
$$\text{Anode:}\quad Cl^{\ominus} + Al \xrightarrow[-e^{\ominus}]{} [Al{-}Cl]$$

$$[AlCl] + \frac{1}{2}CH_2Cl_2 \longrightarrow \frac{1}{2}Cl_2Al{-}CH_2{-}AlCl_2$$

Furthermore, it is sometimes possible to perform a reaction electrochemically which is not possible by direct reaction of the components because of kinetic restraints resulting from high activation energies. Thus, the direct synthesis of cyclooctatetraene-nickel from solid nickel and cyclooctatetraene has not yet been accomplished. The desired total reaction can be realized via electrolysis[6].

Table 2. Useable Potentials of Electrolytes in Different Solvents (Volts vs. Saturated Calomel Electrode)

Electrolyte	*Cathodic Range* in DMF at Hg	in THF at Hg	in DMSO at Pt	*Anodic Range* in DMSO at Pt
$[N(C_4H_9)_4]Br$		−2.95	−2.4	+1.45
$[N(C_4H_9)_4]ClO_4$	−2.91	−2.94	−2.4	~ +2.1
$[N(C_4H_9)_4]Cl$		−2.88		
$[N(C_4H_9)_4]BF_4$		−2.87		
$[N(C_4H_9)_4]B(C_6H_5)_4$		−2.89		
$[N(C_2H_5)_4]Br$			−2.3	
$[N(CH_3)_4]Cl$			−2.4	+1.52
$LiCl$			−2.68	+1.52
$NaB(C_6H_5)_4$		−1.68		
$NaClO_4$			−2.08	+2.10
$NaBF_4$		−1.7		
$LiClO_4$		−1.95	−2.60	+2.10
$KClO_4$			−2.33	+2.10



The electron acceptence and donation, i.e. reduction and oxidation, in electrolysis reactions take place in spatially separated areas. Thus, by separation of the anode and cathode regions, it is possible to prevent the reduced and oxidized substances from mixing. Reversal of the reaction through diffusion to the opposite electrode is also prevented. Sum reactions which, for thermodynamic reasons, do not proceed in the desired direction under the given temperature and concentration conditions, can be achieved by electrolysis. The concentrations obtained during electrochemical reactions do not correspond to equilibrium concentrations.

The difference in the free enthalpies of the end and starting materials is proportional to the decomposition voltage ε used for the electrolysis:

$$\Delta G = -n \cdot \varepsilon \cdot F \cdot 0.239\ [\text{cal}]$$

n = electrochemical valency
F = Faraday constant

The reaction of aluminium metal with dialkylmercury is a long known method for the preparation of alkylaluminium[7], e.g.,

$$2\,Al + 3\,Hg(C_2H_5)_2 \rightleftharpoons 2\,Al(C_2H_5)_3 + 3\,Hg$$

The free energy of this reaction can be estimated to be about −12 kcal/g-equivalent, by combinations of suitable galvanic elements[8]. Thus the equilibrium lies to the side mercury and trialkylaluminium. Electrolysis of a conducting solution of triethylaluminium results in the formation of diethylmercury at a mercury anode, simultaneously metallic aluminium is deposited at the cathode[9]. Thus, the normal course of a chemical reaction has been reversed by electrolysis. The anode and cathode volumes must be separated by a diaphragm in order to prevent the diethylmercury formed at the anode from reaching the cathode where the normal reaction between aluminium and diethylmercury can occur.

2. Electrolysis

The construction of a current-voltage curve provides a useful, initial survey of the electro-active species in the determined potential range of an electrochemical system containing solvent, electrolyte, substrate, product, and electrodes.

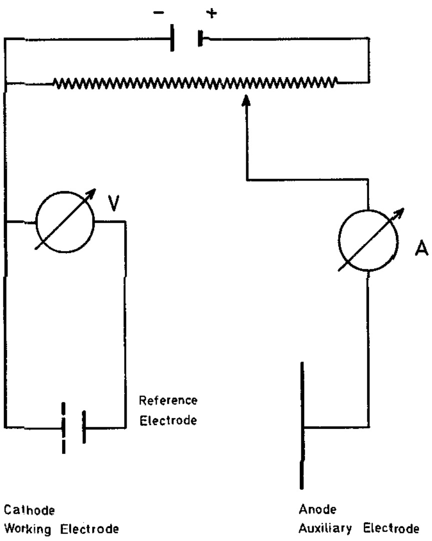


Fig. 3 Schematic diagram of a three-electrode electrolysis for reduction and measurement of a current-voltage curve in negative potential region. The working electrode should have a very small surface, the concentration should then also be low.

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[2] A number of recent review articles and monographs provide a good introduction to the electrochemistry of organic systems. Therein are also further references:
C. K. Mann, K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Dekker, New York (1970).
L. Eberson, H. Schäfer, *Fortschr. Chem. Forschung* **21**, (1971).
J. B. Headridge, *Electrochemical Techniques for Inorganic Chemists*, London-New York: Academic Press (1969).
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B. L. Laube, C. D. Schmulbach, *Progr. Inorg. Chem.* **14**, 65 (1971).
J. Chang, R. F. Large, G. Popp in Weissberger-Rossiter, *Techniques of Chemistry*, Vol. I, *Physical Methods of Chemistry*, Part IIb, Chap. X, 1.
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S. Wawzonek, *Synthesis* **1971**, 285.
R. E. Iversen, *Chemie in unserer Zeit* **5**, 179 (1971).

[3] F. Paneth, W. Lautsch, *J. Chem. Soc.* **1935**, 381.

[4] H. Lehmkuhl, R. Schäfer, *Tetrahedron Lett.* **1966**, 2315.

[5] E. H. Mottus, M. R. Ort, *J. Electrochem. Soc.* **117**, 885 (1970).

[6] H. Lehmkuhl, W. Leuchte, *J. Organometal. Chem.* **23**, C 30 (1970).

The current-voltage curve of a many-component system containing solvent, electrolyte, and substrate consists of several steps. It the transportation rate of the components to the electrodes controls the rate of the electrochemical reaction a plateau of constant current can be reached, when the concentration of the individual components is not too large. The magnitude of the constant limiting current is, among others, a function of the concentration (see Figure 4).

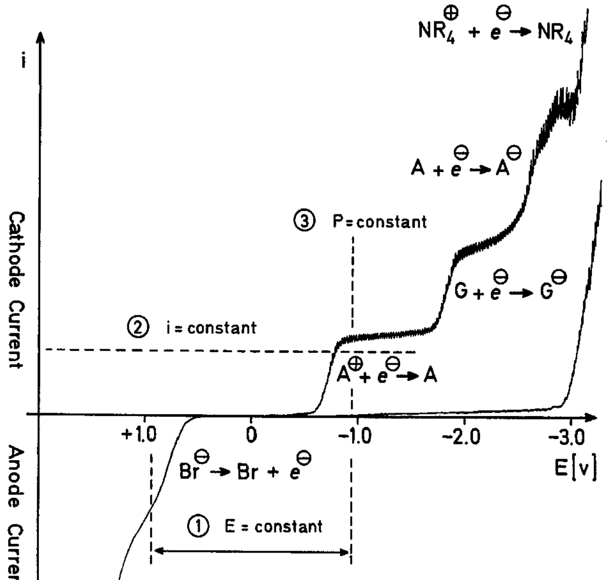


Fig. 4 The current-voltage curve of a many-component system comprised of electrolyte [$N(C_4H_9)_4X$], solvent (THF), and two reducible compounds, $A^{\oplus}$ [iron(III)acetylacetonate] and G [cyclooctatetraene]. At first only $A^{\oplus}$ should be reduced to A [iron(II)acetylacetonate][10]. Anodic depolariser is $Br^{\ominus}$; $X = ClO_4^{\ominus}$. The cathodic region was measured using a dropping mercury electrode, the anodic region using a rotating nickel electrode.

From the course of the polarogram shown in Figure 4 for a many-component system, the following possibilities for carrying out a preparative electrolysis can be seen.

(1) Electrolysis at constant voltage E:

The potential to be chosen is made up of three parts: a cathodic decomposition voltage E_c for $A^{\oplus}$, an anodic decomposition voltage E_A for $Br^{\ominus}$, and the component $i \cdot R$ which is necessary to overcome the resistance of the cell. The necessary terminal potential U is then

$$U = E_c + E_A + i \cdot R.$$

When the $i \cdot R$ component is large, and this is often the case with organic electrolytes, it is difficult to follow these conditions exactly.

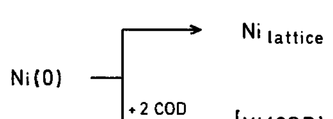
(2) Electrolysis at constant current i:

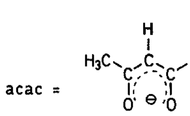
The constant current i must be smaller than the limiting current i_L, controlled by the substance transport. As the magnitude of the limiting current is, among others, dependent on the concentration, the fact that, towards the end of the electrolysis, the limiting current may be smaller than the working current must be considered. Thus a more negative potential will be automatically formed at the cathode and, as a result of this, G as next reducible substance would be electrochemically changed. Therefore the electrolysis cannot be taken to completion with the full current. It is better to reduce the current stepwise towards the end of the reaction. When a metal compound is reduced into a lower, normally unstable oxidation state, the concentration of a ligand which stabilizes the lower oxidation state must be high enough at the electrode during the electrolysis. In order to achieve these conditions a high concentration of the ligand must also be present in the electrolyte. Often, this alone is not sufficient.

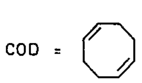
By the synthesis of bis-(cyclooctadiene)-nickel from the reduction of nickel(II)acetylacetonate in the presence of 1,5-cyclooctadiene, the presence of a large concentration of cyclooctadiene in the electrolyte is not sufficient to prevent the formation of metallic nickel at the cathode.

This is, however possible with butadiene, which can be later extracted in part from the electrolyte. After some time, cyclooctadiene alone is now sufficient to capture the nickel(0) formed at the cathode, without the formation of metallic nickel[11].

$$Ni(acac)_2 + 2e^{\ominus} \longrightarrow Ni(0) + 2(acac)^{\ominus}$$







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[7] G. B. Buckton, W. Odling, *Liebigs Ann. Chem.* (Suppl) **4**, 110 (1865/66).

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[9] E. Hüther, Dissertation, Technische Hochschule Aachen (1957).

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[11] W. Leuchte, Dissertation, Universität Bochum (1971).

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[13] T. Sekine, A. Yamura, K. Sugino, *J. Electrochem. Soc.* **112**, 439 (1965).

[14] T. Arai, *Bull. Chem. Soc. Japan* **32**, 184 (1959).

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[16] C. Schall, W. Kirst, *Z. Electrokhem.* **29**, 537 (1923).

Electrolysis by constant current presents no problems when a one or a two electron process is responsible for the step in the current-voltage curve.

Difficulties arise with this method when the steps in the current-voltage curve are formed by two following one electron steps. An example of this from the field of organo-metallic preparative chemistry is seen in the case of cyclooctatetraene (see Figure 5).

Because of the chosen current, of necessity smaller than the limiting current, a potential which lies in the middle part of the step in the current-voltage curve is maintained. The result of this is that, under these conditions, mainly only the first one electron step can take place. In the case of cyclooctatetraene, this is the formation of the anion radical.

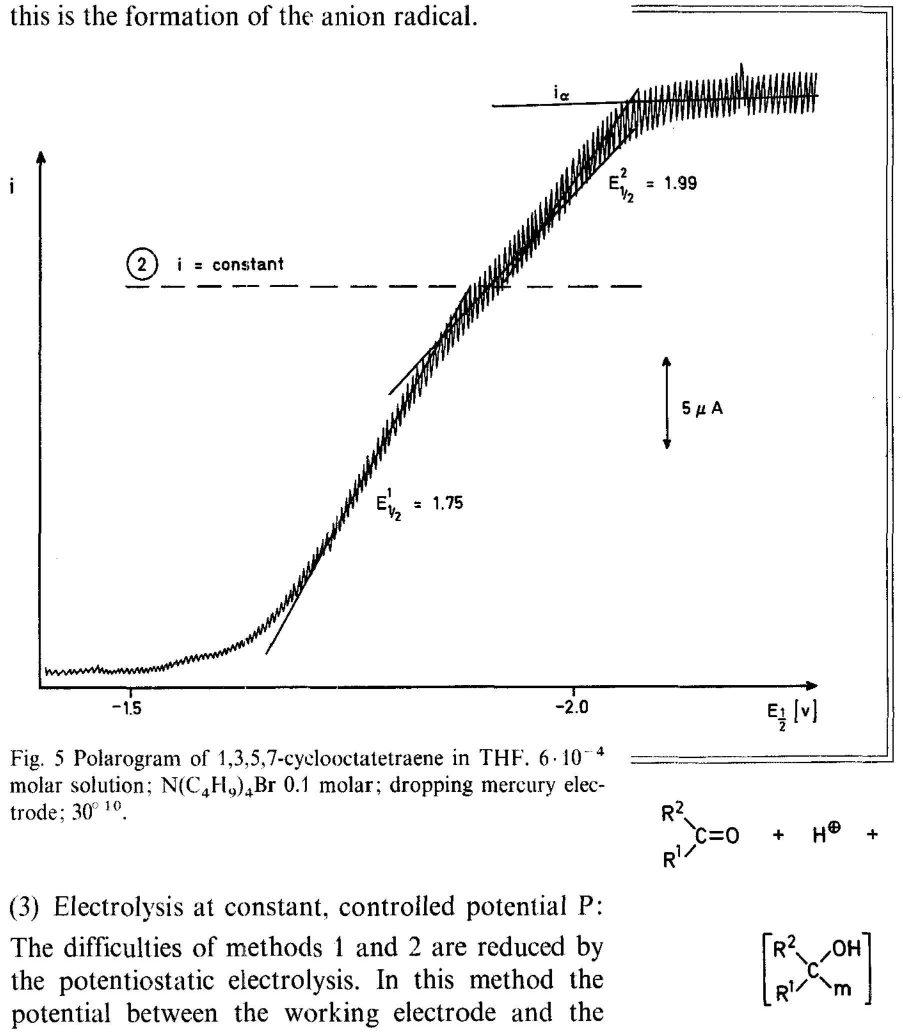


Fig. 5 Polarogram of 1,3,5,7-cyclooctatetraene in THF. $6 \cdot 10^{-4}$ molar solution; $N(C_4H_9)_4Br$ 0.1 molar; dropping mercury electrode; 30° [10].

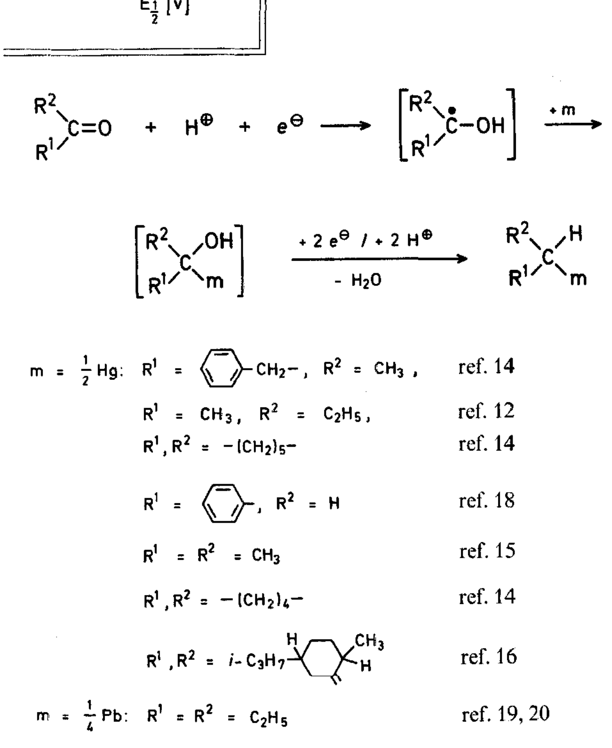
(3) Electrolysis at constant, controlled potential P:

The difficulties of methods 1 and 2 are reduced by the potentiostatic electrolysis. In this method the potential between the working electrode and the reference electrode is continuously controlled to a fixed value; e.g. Figure 4 the cathode potential at -0.9 volt for the reduction of $A^{\oplus}$ to A. As the component which is to be electrochemically changed is used up the current sinks to null without the risk that further components will be electrochemically changed.

3. Electrochemical Synthesis of Organometallic Compounds

3.1. Alkylmetal Compounds by Cathodic Reduction of Organic Compounds

Alkyl radicals can be obtained by cathodic reduction of compounds in which the alkyl rest is positively polarized; e.g. alkyl halides, $R^{\delta+}$—$X^{\delta-}$ and ketones, $RR'C^{\delta+}$=$O^{\delta-}$. When ketones and also some aldehydes are reduced in acid solution at mercury or lead cathodes, the formation of organometallic compounds, which separate as heavy oils from the aqueous solutions, is sometimes observed[12,13].



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[17] L. Holleck, D. Marquarding, *Naturwiss.* **49**, 468 (1962).

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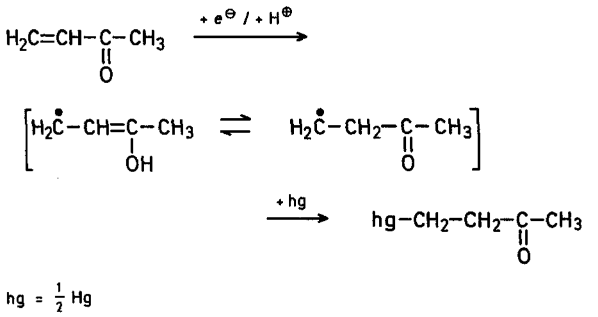
When methyl vinyl ketone is reduced at a mercury cathode at a constant potential (−1.05 volt vs. SCE) and a pH value under 5, the C—C double bond and not the carbonyl group is affected[17].



The reduction of carbonyl compounds is not an important preparative method. By electrolysis of ketones, however, the possibility of the formation of organometallic compounds must be considered.

Di-butyl-2-mercury[12]:

Anode: Water-cooled lead cylinder.
Anolyte: 20% Sulfuric acid in a porous porcelain cup.
Cathode: Mercury in an amount sufficient to give a depth of 1 cm in the glass beaker used as electrolysis vessel.
Catholyte: 30% Sulfuric acid (300 ml).
Starting Material: Methyl ethyl ketone (30 g; 0.24 mol).

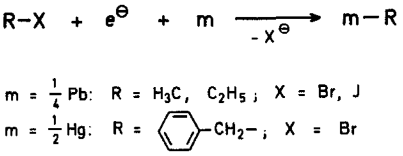
A porous cup is so positioned that its bottom is ~2 cm above the surface of the mercury; the ketone is put into the catholyte. The apparatus is heated at 45–50° and the electrolysis carried out using 7.6–7.8 volt and 25 A/dm² at the cathode surface. Within 2 hr a heavy oil (41.5 g) is formed. When this settles on the cathode the circuit is broken, thus the mixture must be well stirred. The oil is separated off, dried over sodium sulfate and distilled in vacuum below 80° (bath-temperature); yield of dibutyl-2-mercury: 29 g (28%). The yield appears to be independent of acid concentration and current density[12].

Electrolysis of 3-iodopropionitrile in 0.5 *N* sulfuric acid or in aqueous sodium sulfate solution with an anode of tin, lead, or mercury results in the formation of the corresponding organometallic compound[21].

$$J{-}CH_2{-}CH_2{-}CN + e^{\ominus} + m \xrightarrow[-J^{\ominus}]{} m{-}CH_2{-}CH_2{-}CN$$

$$m = \frac{1}{3}Sn,\ \frac{1}{4}Pb,\ \frac{1}{2}Hg$$

The preparation of alkylmetal compounds, especially alkyllead compounds, by the electrochemical reduction of alkyl halides is more important. The method has been known for a long time[22,23], but has only been closely investigated in the past few years.



The electrochemical sum reaction is:

$$R{-}X + m \longrightarrow R{-}m + \frac{1}{2}X_2$$

As well as the formation of unstable di- and trialkyllead compounds, which disproportionate in the electrolyte, sidereactions may also occur.

$$2\,PbR_2 \longrightarrow PbR_4 + Pb$$

At high cathode potentials carbanions are formed on acceptance of two electrons, these are stabilized by abstraction of a proton from the solvent.

$$R{-}X + 2e^{\ominus} \xrightarrow[-X^{\ominus}]{+H^{\oplus}\,(\text{solvent})} R{-}H$$

As the formation of unstable alkyllead compounds is favoured at low potentials and the acceptance of two electrons is favoured at high potentials, optimal yields of tetraalkyllead are obtained using medium potential values (see Table 3)[24].

Table 3. Yields of Tetraethyllead at Varying Cathode Potentials; Conditions: Ethyl Iodide in 1 *M* Sodium Perchlorate Solution in Dimethylformamide.

Potential vs. SCE[a] (volt)	Yield of Tetraethyllead (%)	
	Referred to quantity of electricity	Referred to weight loss of cathode
−1.6	62	51
−1.8	80	70
−2.1	85	70
−2.7	68	60

[a] Saturated calomel electrode.

The cathodic reduction of mixtures of methyl and ethyl iodide result in the formation of mixtures of mixed tetraalkyllead compounds. The compositions of the mixtures are dependent on the cathode potential (see Table 4)[24].

Table 4. Composition of the Mixture of Alkyllead Compounds from the Reduction of Methyl and Ethyl Iodide (1:3) in 0.25 *M* Sodium Perchlorate dissolved in Dimethylformamide. Total Yield is 70–82%.

Potential vs. SCE (volts)	$Pb(CH_3)_4$	$(H_3C)_3Pb{-}C_2H_5$	$(H_3C)_2Pb(C_2H_5)_2$	$H_3C{-}Pb(C_2H_5)_3$
−1.4	3	19	36	21
−1.7	2	13	24	28
−2.1	1	6	19	41

The formation of tetraalkyllead in propylene carbonate is strongly dependent upon the electrolyte[25,26].

$$[N(C_2H_5)_4]^{\oplus} \text{ and } [N(C_4H_9)_4]^{\oplus} > [(C_2H_5)(H_3C)_2S]^{\oplus} \gg\!> (Li^{\oplus},\ Ca^{2\oplus},\ K^{\oplus},\ NH_4^{\oplus} = 0)$$

In acetonitrile/water, methyl bromide is converted quantitatively to tetramethyllead, ethyl bromide to tetraethyllead in 40% yield and hexaethyldiplumbane in 60% yield, isopropyl bromide gives organo-lead compounds in 30% yield, and with *t*-butyl bromide only traces of organometallic compounds are found. In all cases tetraethylammonium bromide was used as electrolyte[27].

From the polarographic half-wave potentials of alkyl bromides at a lead cathode it is possible to derive mechanistic analogues to SN_2 reactions for the alkylmetal compounds. Increasing negative reduction potential and the pseudo-first order rate constants for the hydrolysis in aqueous ethanol produce the same order[28]:

$$H_3C > t\text{-}C_4H_9 > C_2H_5 > i\text{-}C_3H_7$$

In contrast to the bromides, the iodides show no dependence of the half-wave reduction potentials on the alkyl rest with tetraethylammonium iodide as electrolyte. With other electrolytes (tetrapropyl- and tetrabutylammonium iodide) an increasingly more difficult reducibility, depending on the size of the alkyl rest, is observed[28]:

$$H_3C < C_2H_5 < i\text{-}C_3H_7 < t\text{-}C_4H_9$$

These results indicate that a different mechanism in comparison to that for the reduction of the bromides is operative.

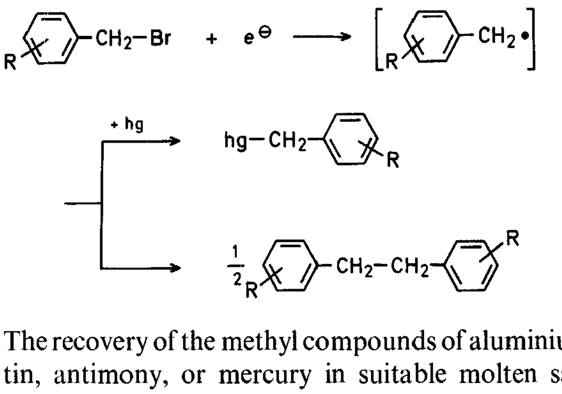
The electrolysis of benzyl bromide or substituted benzyl bromides at a mercury cathode results in the formation of mixtures of the diorganomercury compounds and dimeric hydrocarbons in varying quantities. The proportions of the products are dependent on the type and position of the substituent R, the electrolyte, and the cathode potential[29].

Table 5. Preparation of Dibenzylmercury Compounds; 1*N* Lithium Bromide in Methanol[29].

Cathode potential vs. Ag/AgCl/KCl 0.1 Mol volt	R	Yield (%)
−1.5	4-t-C_4H_9	50
−1.4	H	41
−1.2	4-CH_3	64
−0.94	3,4-di-Cl	39

Bis-(4-methyl-benzyl)-mercury[29]:

The apparatus consists of a diaphragm cell with a mercury cathode and a silver anode. The cathode volume is filled with a solution of 4-methyl-benzyl bromide (1.5 g) in methanol (80 ml). The catholyte and anolyte are also 2*N* in lithium bromide. During the electrolysis a cathode potential of −1.4 volt is maintained, this is 0.2 volt more negative than the polarographic half-wave potential: reference electrode: calomel. After 4–6 hr the current is minimal. The reaction products are separated by chromatography on aluminium oxide. The mercury compound is eluted with pentane/benzene. Yield: 64%; m.p. 113–113.5° after recrystallization from ethanol.



The recovery of the methyl compounds of aluminium, tin, antimony, or mercury in suitable molten salts provides a modification of the preparation of alkylmetal compounds from alkyl halides[30]. The halides of the metals (exclusively chlorides) are allowed to react with methyl chloride in the presence of a halogen accepting metal M^2 (Al, Zn, Mg, Sn, their amalgams, or alkali metals).

$$M^1{-}Cl + H_3C{-}Cl + 2\,M^2 \longrightarrow H_3C{-}M^1 + 2\,M^2{-}Cl$$

The acceptor metal halide in the molten salt is finally electrochemically split into the metal and the halogen.

$$2\,M^2{-}Cl \xrightarrow{\text{electrolysis}} 2\,M^2 + Cl_2$$

Thus, the sum reaction for the whole process is analogous to that shown below in Scheme **A**.

$$M^1{-}Cl + H_3C{-}Cl \longrightarrow H_3C{-}M^1 + Cl_2$$

Scheme A

3.2. Organometallic Compounds by Cathodic Reduction of other Organometallic Compounds

Electrolysis of organometallic compounds themselves gives many reaction possibilities. Only those which are useful for the preparation of organometallic compounds will be discussed in this article. The following scheme (Scheme **B**) was derived by Dessy[31] and modified slightly by the author. R—M is a neutral or ionic organometallic group, X an organic or inorganic rest or a complex forming ligand, and A an electron affinitive hydrocarbon.

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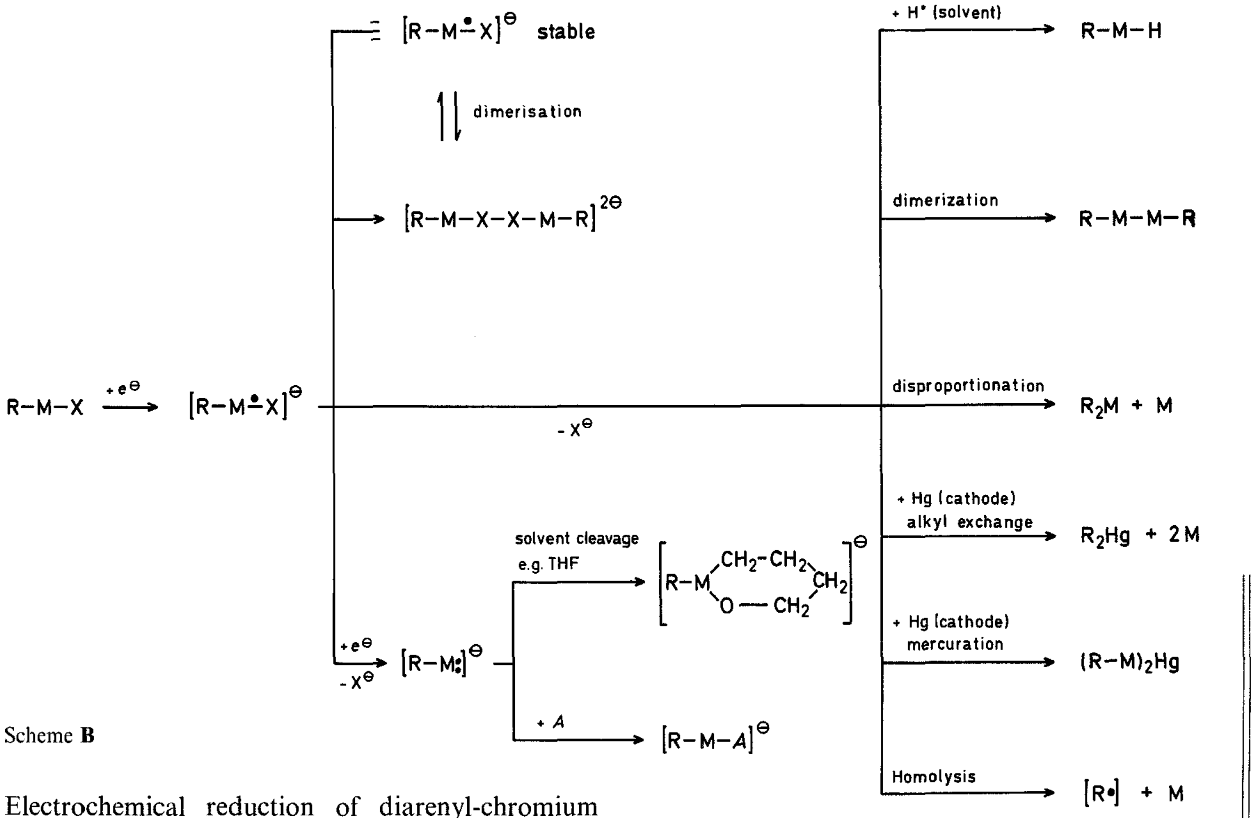
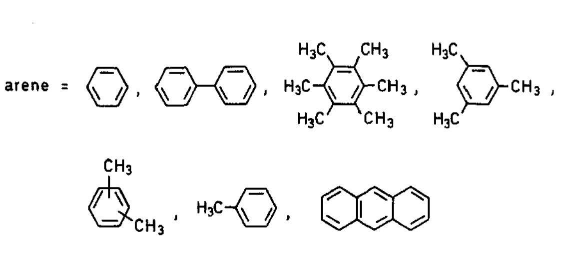
[21] A. P. Tomilov, D. Smirnov, S. L. Varshavskii, *Zhur. obshch. Khim.* **35**, 391 (1965); *C.A.* **63**, 5238 (1965).



Scheme **B**

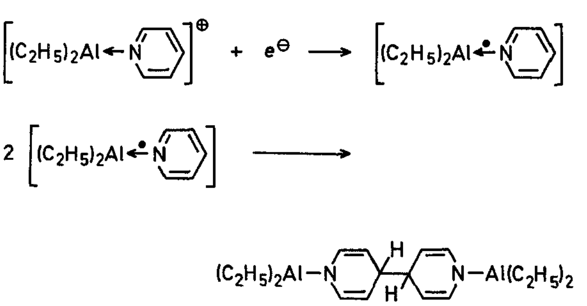
Electrochemical reduction of diarenyl-chromium halides leads to stable diarenyl-chromium(0) compounds[32,33].

$$[(\text{arene})_2\text{Cr}]^{\oplus}\ X^{\ominus} \xrightarrow[-X^{\ominus}]{+e^{\ominus}} [(\text{arene})_2\text{Cr}]$$



X = B$(C_6H_5)_4$, J

Cathodic reduction of the pyridine complex of the diethylaluminium cation [R—M—X $=(C_2H_5)_2$Al—pyr]$^{\oplus}$ gives rise to organo-aluminium radicals which dimerize to tetrahydrodipyridyl derivatives[34]. Ethylberyllium radicals behave similarly[35].



Organometallic radicals can be formed by electron acceptance of organometallic halides and simultaneous splitting off of halide ions. The organometallic radicals may be stabilized in several different ways.

– Hydrogen abstraction from the solvent or the tetraalkylammonium salt electrolyte gives rise to organometallic hydrides[36].

$$(C_6H_5)_{4-n}MCl_n \xrightarrow[-nCl^{\ominus}]{+ne^{\ominus}} [(C_6H_5)_{4-n}M] \xrightarrow{+nH^{\bullet}} (C_6H_5)_{4-n}MH_n$$

M = Si:	n = 1,	$E_{\frac{1}{2}}$ =	−3.1 Volt vs Ag / $AgClO_4$
	n = 2,		−1.9
M = Ge	n = 1,		−2.8
	n = 2,		−2.6

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[22] B. Mead, *U.S. Patent* 1 567 159 (1923), General Motors; *Chem. Zentralbl.* **26** I, 2052 (1926).

[23] H. F. Calingaert, *U.S. Patent* 1 539 297 (1923), General Motors; *Chem. Zentralbl.* **25** II, 761 (1925).

[24] M. Fleischmann, D. Pletcher, C. J. Vance, *J. Electroanalyt. Chem.* **29**, 325 (1971).

[25] R. Galli, *J. Electroanalyt. Chem.* **22**, 75 (1969).

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[29] J. Grimshaw, J. J. Ramsey, *J. Chem. Soc.* [B] **1968**, 60.

[30] W. Sundermeyer, W. Verbeek, *Angew. Chem.* **78**, 107 (1966); *Angew. Chem. Internat. Edit.* **5**, 1 (1966).

[31] T. Psarras, R. E. Dessy, *J. Amer. Chem. Soc.* **88**, 5132 (1966).

[32] C. Furlani, E. O. Fischer, *Z. Elektrokhem.* **61**, 481 (1957).

[33] C. Furlani, *Ricerca Scientifica* **36**, 989 (1966).

[34] H. Lehmkuhl, G. Fuchs, R. Köster, *Tetrahedron Lett.* **1965**, 2511.

- Dimerization of the organometallic radicals results in compounds with a metal-metal bond[37].

$$2\,R_nMX \xrightarrow{+2\,e^{\ominus}} 2\,[R_nM] \longrightarrow R_nM{-}MR_n$$

$M = Pb,\ R = C_2H_5,\ n = 3,\ X = OH$

$M = As,\ R = C_6H_5,\ n = 2,\ X = Br$

$M = Sn,\ R =$ alkyl or aryl, $n = 3,\ X =$ halogen

Hexaethyldiplumbane[38]**:**

Anode: Lead wire, 3–4 cm diameter.
Anolyte: 2N sodium (or potassium) hydroxide (10 ml).
Cathode: Lead sheet formed into a cylinder, surface area 26 cm^2.
Catholyte: 2*N* sodium (or potassium) hydroxide (50 ml).
Starting material: Triethyllead chloride (7 g, 21 mmol).

The electrolysis vessel is a glass cylinder (capacity 100 ml, diameter 6 cm) fitted with an outlet tube with stop-cock at the bottom. The anode is placed in an unglazed clay pot (capacity 15 ml, diameter 1.5 cm). The electrolysis is carried out under an inert atmosphere (nitrogen, argon, or carbon dioxide) using a current of 0.8 amp and 2.5 volt for 2 hr. Dimeric triethyllead separates as a yellow-red oil and is run off from time to time. It is then dried over sodium sulfate and filtered under an inert atmosphere: yield 6.0 g, (97%) referred to the lead compound used, (34%) referred to the quantity of electricity.

- The deposition of metals at the cathode can result from the disproportionation of unstable organometallic radicals[31,39,40,41]. The cathodic deposition of highly pure metals from organometallic electrolytes is of technical importance in the cases of aluminium, gallium and indium[39,42].

$$[AlR_2]^{\oplus} \xrightarrow{+e^{\ominus}} [\bullet AlR_2] \longrightarrow \frac{1}{3}Al + \frac{2}{3}AlR_3$$

- The transference of alkyl rests to mercury has been observed, for example on the reduction of alkyllead compounds[36].

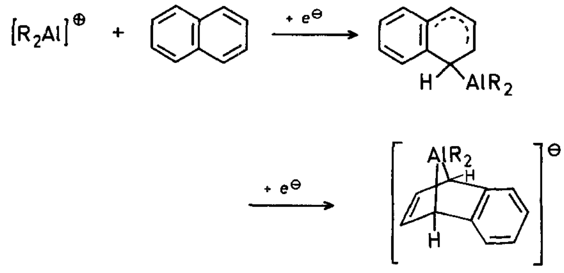
$$(C_6H_5)_2PbX_2 \xrightarrow[-X^{\ominus}]{+e^{\ominus}} (C_6H_5)_2PbX \xrightarrow[-X^{\ominus}]{+e^{\ominus}}$$

$$(C_6H_5)_2Pb \xrightarrow{+Hg} Pb + (C_6H_5)_2Hg$$

- The electrochemical reduction of some transition metal complexes results in the formation of compounds between the organometallic rest and the cathode metal mercury[43].

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]^{\oplus} + e^{\ominus} + hg \longrightarrow hg[(\pi\text{-}C_5H_5)Fe(CO)_2]$$

- The cathodic formation of aluminium, mentioned above, can be avoided when trialkylaluminium is reduced in the presence of an electron affinitive hydrocarbon, e.g. naphthalene, anthracene, styrene, or stilbene, in tetrahydrofuran or another polar solvent with sodium or potassium tetraalkylalanate as electrolyte[44].



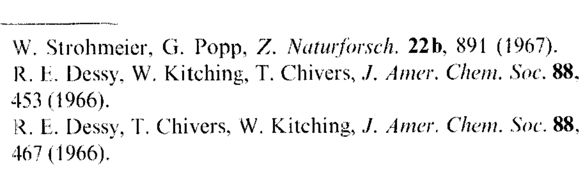
R = H$_3$C, C$_2$H$_5$

Potassium Diethyl-1,4-dihydronapthdiyl-alanate[44]**:**

Anode: Aluminium sheet formed into a cylinder.
Anolyte: 35–40% solution of potassium tetraethylalanate in benzene.
Cathode: Copper sheet formed into a cylinder.
Catholyte: Potassium tetraethylalanate (29 g, 160 mmol), naphthalene (47 g, 365 mmol), and triethylaluminium diethyl etherate 69 g, 365 mmol), in benzene (120 ml).

The electrolysis cell consists of a 500 ml glass flange flask with an aluminium lid. The lid contains fittings for the insulated electrode connections, for the passage of an inert gas, and for an addition funnel. Inside the cylinder formed by the copper cathode is a sleeve of glass-cloth (diameter: ~20 mm) ~8 mm from the copper. The cylindrical aluminium anode is fitted inside this sleeve with a separation of 2 mm. All experiments with organoaluminium compounds must be carried out with strict exclusion of water and oxygen. The electrolysis is performed with a current of 0.12 amp and 20 volt. During the electrolysis a 35% solution of potassium tetraethylalanate is added to the anode space so that the liquid level here remains 1–3 mm higher than that in the cathode space. The product precipitates out from the catholyte after some time as yellow crystals. The catholyte is run off from time to time and the product filtered off. After replenishment with naphthalene, the filtrate may be used again as catholyte; yield: up to 85% referred to the quantity of current.

- The very reactive intermediate products formed in the reduction of aluminium trichloride or alkylaluminium chloride in THF cleave the solvent[45].



R = alkyl, halogen

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[35] W. Strohmeier, G. Popp, *Z. Naturforsch.* **22b**, 891 (1967).

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Aluminium is obtained only in small amounts.

The electrochemical cleavage of metal-metal bonds in hexaphenyldiplumbane and hexaphenyldistannane can be useful preparatively[46].

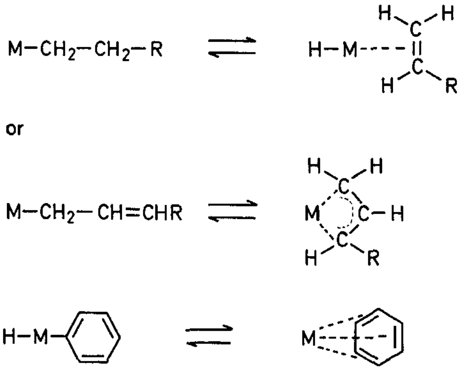
$$R_3M^1{-}M^1R_3 \xrightarrow{+\,2\,e^{\ominus}} 2\,[R_3M^1]^{\ominus}$$

$$[R_3M^1]^{\ominus} + [(\pi{-}C_5H_5)_nM^2(CO)_m]^{\oplus}J^{\ominus} \xrightarrow[-J^{\ominus}]{} R_3M^1{-}M^2(\pi{-}C_5H_5)_n(CO)_m$$

$R = C_6H_5$; M^1 = Sn, Pb; M^2 = Fe; $n = 1$; $m = 2$
Mo; $n = 1$; $m = 3$
Mn; $n = 0$; $m = 4$

3.3. Transition Metal Cycloolefin Complexes by Cathodic Reduction of Olefins

Organometallic compounds of the transition metals are of much technical and preparative interest. Such compounds in which the alkyl or aryl rest is bonded to the transition metal over σ-bonds are often unstable and are mainly of interest as intermediate products. The alkyl or aryl compounds of the transition metals are often in equilibrium with another class of organic transition metal compounds, the coordination complexes, in which the C—C multiple bonds are joined to the metal through the π-electron systems[47].



M = one or more equivalent transition metal

Organic transition metal complexes are important as active catalysts for the conversion of unsaturated organic compounds by:

hydrogenation,
isomerization,
dimerization,
oligomerization,
polymerization,
or hydroformylation.

Others are able to complex hydrogen, nitrogen, or oxygen and so bring these to an active form. This may have special significance in future, e. g. for the chemical conversion of inert nitrogen[48]. Unsaturated hydrocarbons are able to stabilize unusual oxidation states of metals, especially those with oxidation number 0. This can be explained using Pearson's principle[49] of hard and soft acids and bases as follows.

Unsaturated hydrocarbons are soft Lewis bases; soft Lewis acids are suitable partners for complex formation. In the series of transition metal compounds these are the ones with the lower oxidation numbers. Thus the preferred combination soft acid-soft base is obtained. The second alternative is the conversion of the soft base to a hard base by acceptance of one or two electrons. Now the preferred combination hard-hard can be obtained using metal compounds in which the metal has a higher oxidation number, i. e. a hard Lewis acid. Both possibilities for the formation of cycloolefin-metal complexes can be achieved electrochemically.

Previously transition metal complexes with arenes, olefins, or cycloolefins have been prepared either from compounds of the metals in low, mostly 0, oxidation states, i. e. metal carbonyls. The ligand, e. g. carbon monoxide is then replaced by a suitable organic ligand. The second method involves the reduction of a metal compound of higher oxidation state in the presence of the ligand using an electropositive metal (alkali metal, magnesium, aluminium), or hydrides or alkyl-compounds of the alkali metals, magnesium[50], or aluminium[51].

The first synthesis of a metal-olefin complex using an electrochemical method was carried out in 1966. Copper(II) perchlorate was electrolysed between copper electrodes in the presence of 1,5-cyclooctadiene and bis-(1,5-cyclooctadiene)-copper(I) perchlorate was obtained as product[52]. Modifications of this basic method have been used extensively for the synthesis of transition metal cycloolefin complexes. The general principle is the cathodic reduction of mixtures of readily accessible transition metal compounds and suitable olefins[6,53,54,55].

$$M^{\oplus} + \mathrm{Lig} + e^{\ominus} \longrightarrow [M \cdots \mathrm{Lig}]$$

Depending on the magnitudes of the electron affinities of the metal compound and the ligand, either the metal compound or the ligand may be reduced electrochemically first. Thus, the sum reaction may be obtained by combination of one or the other pairs of part reactions, i. e. either

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[44] H. Lehmkuhl, *Chimia* **24**, 182 (1970).

[45] H. Lehmkuhl, S. Kintopf, unpublished results.

[46] R. E. Dessy, P. M. Weissman, *J. Amer. Chem. Soc.* **88**, 5124, 5129 (1966).

[47] see e.g. P. Heimbach, R. Traunmüller, *Chemie der Metall-Olefin-Komplexe*, Verlag Chemie, Weinheim (1970).

[48] see e.g. G. Henrici-Olivé, S. Olivé, *Angew. Chem.* **81**, 679 (1969).

$$M^{\oplus} + e^{\ominus} \longrightarrow M(0)$$
$$M(0) + Lig \longrightarrow [M \cdots Lig]$$

or

$$Lig + e^{\ominus} \longrightarrow Lig^{\ominus}$$
$$Lig^{\ominus} + M^{\oplus} \longrightarrow [M \cdots Lig]$$

The first pair corresponds to the conversion of a hard acid to a soft acid and the formation of a complex of this with a soft base. The second pair corresponds to the formation of a hard base from a soft base; this hard base undergoes a type of neutralization reaction with the hard acid. The formation of the complex can be mainly an equalization of charges. Naturally, both ways lead to the same product when the same metal and the same ligands are involved. Both mechanisms in which charge equalization of the intermediate state leads to stable products can be clearly visualized using the well-known Chatt-Dewar model for metal-olefin complexes[11], see Figure 6.

Table 6. Polarographic Half-Wave Reduction Potentials for Some Metal Compounds[a] in Tetrahydrofuran, Pyridine or Dimethylformamide.

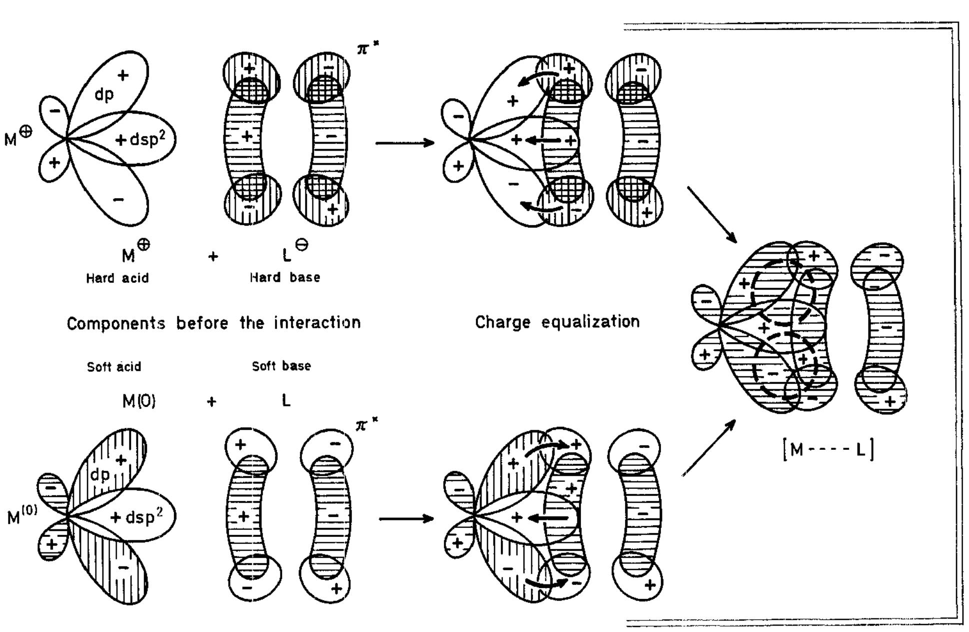
Metal Compound	Half-wave reduction potential (volt vs. SCE) THF[56]	pyridine[56]	DMF
titanium(IV) chloride[b]	1. not measurable		1. −0.73[57]
	2. −1.48		2. −1.58[57]
	3. −2.17		3. −2.33[57]
aluminium(III) chloride	−1.33		
zirconium(IV) chloride	1. −1.36		
	2. −1.86		
	3. −2.13		
hafnium(IV) chloride	1. −1.34		
	2. −2.02		
nickel(II) acetylacetonate	−1.57	−2.17	1. −1.5[56]
			2. −2.04
magnesium(II) bromide[c]	−1.91		
cobalt(II) acetylacetonate	−1.98	−2.03	−1.93
iron(III) acetylacetonate	1. −0.82		
	2. −2.25		

[a] The metal halides were measured with tetraalkylammonium perchlorate as electrolyte; the metal acetylacetonates with tetrabutylammonium bromide.

[b] The waves 1–3 correspond to the following reaction steps[57]:

1: $Ti(IV) + e^{\ominus} \longrightarrow Ti(III)$
2: $Ti(III) + e^{\ominus} \longrightarrow Ti(II)$
3: $Ti(II) + 2e^{\ominus} \longrightarrow Ti(0)$

[c] With consideration of the amalgam formation: −2.3 volt.



The shaded areas represent the occupied orbitals. The free areas show unoccupied levels.

The metal atom has dsp² hybridization.

Fig. 6 Use of the Chatt-Dewar model for olefin-metal complexes from the possible combinations between acid and base: hard↔hard and soft↔soft

A comparative scale for the electron affinities and therefore for the ease of reduction of the metal and the ligand can be obtained from the polarographic half-wave reduction potentials measured under constant conditions. The values for some metal compounds are shown in Table 6 and for some potential ligands in Table 7.

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[51] B. Bogdanović, M. Kröner, G. Wilke, *Liebigs Ann. Chem.* **699**, 1 (1966).

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[56] H. Lehmkuhl, E. Janssen, S. Kintopf, unpublished results.

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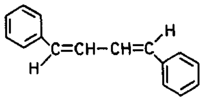
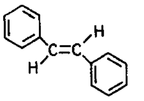
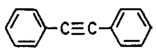
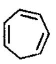
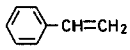
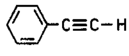
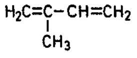
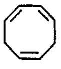
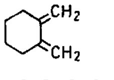
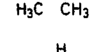
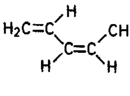
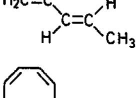
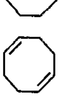
Table 7. Polarographic half-wave reduction potentials for unsaturated hydrocarbons which may be used as ligands for transition metal complexes[56]. (6.10^{-4} *M* solution in THF; dropping mercury electrode; tetrabutylammonium bromide as electrolyte).

Hydrocarbon		Half-wave reduction potential (volt vs. SCE)
		1. −1.75 2. −1.99
		1. −2.06 2. −2.36
		1. −2.25 2. −2.64
		−2.41
$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$		−2.44
		−2.56
		−2.69
		−2.71
$H_2C{=}CH{-}CH{=}CH_2$		−2.79
 $H_2C{=}C(CH_3){-}CH{=}CH_2$		−2.82
		−2.85
		−2.85
 $H_2C{=}C(CH_3){-}C(CH_3){=}CH_2$		−2.89
		−2.92
		−2.94
	more negative than	−2.95
	more negative than	−2.95

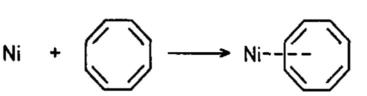
The choice of solvent is limited by the high reactivity of most transition metal compounds towards H-acidic compounds and functional groups. The solvent must be sufficiently polar to assure a good conductivity; it must be difficult to reduce, and must not produce difficulties during the working up of the reaction products and the isolation of the complex compound. Tetrahydrofuran, diglyme, dimethoxyethane, pyridine, and dimethylformamide generally satisfy these conditions. Lithium halides and their mixtures with perchlorates, as well as tetraalkylammonium halides have proved suitable electrolytes.

To date, the cathode metal has been found to have no influence on the course of electrochemical reductions. It could, however, be thought that rest valencies on the metal surface might show an affinity for definite organic groups or force these to a determined orientation on the metal surface. This would cause different structures of the double layer at the phase boundary and thus, among others, result in a different course for the electrochemical reaction.

For the anode material the metal of the desired organometallic product may be chosen. When it is possible to bring this metal into solution by anodic oxidation it may be possible to achieve a sum reaction for the synthesis comprised of the anode metal and the cycloolefin.

$$M_{(anode)} + Lig \xrightarrow{\text{electrolysis}} [M \cdots Lig]$$

This is possible with a nickel anode and cyclooctatetraene in DMF; the weight loss of the anode corresponds to 90% of the current, and the desired complex can be isolated in 85% yield[11].



The dissolution of the nickel anode is not so complete when the electrolysis is carried out in pyridine (65% weight loss) or tetrahydrofuran (28%), see Table 8.

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Table 8. Electrochemical Preparation of Transition Metal-cycloolefin Complexes. (The Preparative Electrolyses were carried out at Constant Current).

Starting Materials		Solvent	Electrolysis Temperature	Anode	Diaphragm	Cycloolefin-metal Complex	Yield (%) (referred to current)	References	
Metal	Olefin							Electro-chem.	Chem.
Ni	COT	DMF	20°	Ni	No	Ni(COT)	86	11	
Ni	COT	pyridine	20°	Ni	No	Ni(COT)	49	11	
Ni	COT	THF	20°	Ni	No	Ni(COT)	17	11	51
$Ni(acac)_2$	COT	THF or pyridine	20°	Al	No	Ni(COT)	80	6	59 60
$Ni(acac)_2$	COD	pyridine	~5°	Al	No	$Ni(COD)_2$	65	6	
$Ni(acac)_2$	CDT	pyridine	−5°	Al	Yes	Ni(CDT)	25	11	
$Co(acac)_2$	COD	pyridine	−10°	Al	Yes	π-cyclooctenyl-Co(COD)	35	54	61
$Co(acac)_2$	COD	pyridine + ethanol	−10°	Al	No	π-cyclooctenyl-Co(COD)	40	11	61
$Co(acac)_2$	COT	THF	−8°	Al	No	π-cyclooctatrienyl-Co(COD)	27	11	62
Fe	COT	THF	−5°	Fe	Yes	$Fe(COT)_2$	14	11	59, 63
$Fe(acac)_3$	COT	THF	−5°	Al	No	$Fe(COT)_2$	33	11	59, 63
$TiCl_4$	COT		40°	Al	No	$Ti(COT)_2$[a]	45	53	51
$(C_5H_5)_2TiCl_2$	COT		0°	Al	No	C_5H_5TiCOT	25	53	64
$TiCl_4$	COT	THF	20°	Al	No	Cl—TiCOT.THF	68	53	59
$TiCl_4$	COT	pyridine	20°	Al	No	Cl—TiCOT.pyridine	77	53	59
$ZrCl_4$	COT	THF	20°	Al	No	$Cl_2ZrCOT.THF$	83	58	65
$ZrCl_4$	COT	THF	20°	Mg	No	$Zr(COT)_2$[b]	37	58	65

[a] Prepared without supporting electrolyte.
[b] Contains $MgCl_2 \cdot THF$ as impurity.
COT = cyclooctatetraene
COD = 1,5-cyclooctadiene
CDT = 1,5,9-cyclododecatriene (all trans)

When the organometallic complex, formed by cathodic reduction, is more readily oxidizable than the metal itself the reaction may be reversed by anodic oxidation of the product. This can be prevented either by using a diaphragm to prevent the product formed at the cathode from reaching the anode, or by using a more electropositive metal for the anode which is then more readily oxidizable than the product. Aluminium and magnesium auxilliary anodes have proved to be suitable.

$$3\,Ni(acac)_2 + 6\,COD + 2\,Al \xrightarrow[-2\,Al(acac)_3]{} 3\,Ni(COD)_2$$

$$3\,Ni(acac)_2 + 3\,CDT + 2\,Al \xrightarrow[-2\,Al(acac)_3]{} 3\,Ni(CDT)$$

$$Fe(acac)_2 + 2\,COT + Al \xrightarrow[-Al(acac)_3]{} Fe(COT)_2$$

acac = acetylacetonate

Nickelcyclooctatetraene[6,11]:

Anode: Aluminium sheet (area 0.1 dm^2) 99.99% purity.
Cathode: Aluminium sheet (area 0.1 dm^2) 99.99% purity.
Electrolyte: Tetrabutylammonium bromide (3.3 g) in pyridine (109 ml).
Starting Materials: Nickelacetylacetonate (10.2 g, 40 mmol) and cyclooctatetraene (19 g, 183 mmol).

The electrodes were placed 30 mm apart; the electrolysis was carried out at 23° using 15 mA/8 volt current conditions; current quantity: 2115 mA—hour; weight loss of Al-anode: 591.8 mg, corresponding to 83.5%. The crystals precipitated from the brown electrolyte were separated from the mother liquor by filtration on a D_3 sinter and washed with cold benzene and finally ether. Yield: 5.1 g, 79.5% referred to current and 95.8% referred to weight loss of the anode.

Starting from tris-(acetylacetonato)-iron, firstly a reduction of iron(III) to iron(II) takes place which is followed by formation of bis-(cyclooctatetraene)-iron, whereby according to the position of the reaction partner in the potential series the cyclooctatetraene is reduced to the dianion and exchanged with the acid rest of the iron(II). Thus the reaction is made up of the following steps (see Figure 4).

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[78] K. Ziegler, W. Eisenbach, *U.S. Patent* 3620954 (1967).

[79] W. Grimme, Dissertation, Technische Hochschule Aachen (1960).

$$\mathrm{Fe(acac)_3} + e^{\ominus} \xrightarrow[-(\mathrm{acac})^{\ominus}]{} \mathrm{Fe(acac)_2}$$

$$\mathrm{COT} + e^{\ominus} \longrightarrow \mathrm{COT}^{\overset{\ominus}{\bullet}}$$

$$\mathrm{COT}^{\overset{\ominus}{\bullet}} + e^{\ominus} \longrightarrow \mathrm{COT}^{2\ominus}$$

$$\mathrm{Fe(acac)_2} + \mathrm{COT}^{2\ominus} \xrightarrow[-2(\mathrm{acac})^{\ominus}]{} \mathrm{Fe(COT)}$$

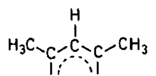
$$\mathrm{Fe(COT)} + \mathrm{COT} \longrightarrow \mathrm{Fe(COT)_2}$$

$$3\,\mathrm{Br}^{\ominus} - 3\,e^{\ominus} \longrightarrow 3\,\mathrm{Br}$$

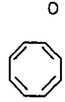
$$3\,\mathrm{Br} + \mathrm{Al} \longrightarrow \mathrm{AlBr_3}$$

$$\mathrm{AlBr_3} + 3\,(\mathrm{acac})^{\ominus} \longrightarrow \mathrm{Al(acac)_3} + 3\,\mathrm{Br}^{\ominus}$$

acac =



COT =



Scheme C

The primary formation of halides at the anode according to the seventh reaction in Scheme **C** has been confirmed by the isolation of nickel bromide-pyridinate in attempts to prepare nickel complexes using a nickel anode in a diaphragm cell[11].

With the same halogen, which comes from the lithium or tetraalkylammonium halide used as electrolyte, the energy of formation of the metal halides, ignoring other energy sizes such as, e.g. the complex formation energy of the metal halide with the solvent, should give an approximate idea of the ease with which the metal anode can be oxidized; the following order was so obtained.

$$\mathrm{mg{-}X} > \mathrm{al{-}X} > \mathrm{fe{-}X} > \mathrm{co{-}X} > \mathrm{ni{-}X}$$

X = Halogen

This corresponds to the observations that anodes of magnesium, aluminium, iron, cobalt, and nickel, in this order, are increasingly less suitable for the preparation of readily oxidizible complexes. In this respect chloride electrolytes are better than bromides as the energies of formation for metal chlorides are higher than those for the corresponding bromides.

Titanium halides, starting from titanium(IV) halide, are reduced electrochemically in several stages[57], see Table 6. On attempts to achieve electrochemical reduction of mixtures of titanium(IV) chloride and cyclooctatetraene in tetrahydrofuran or pyridine using aluminium electrodes the reduction of Ti(IV) to Ti(III) also takes place by chemical reaction without electrolysis. In contrast the tetrachlorides of zirconium and hafnium do not react smoothly with aluminium metal in a one-step reduction[66]. These results agree with the polarographically determined reduction potentials. According to the order of the reduction potentials the following cathodic processes and subsequent chemical reactions should occur with titanium.

Chemical:

$$\mathrm{TiCl_4 \cdot xTHF} + \mathrm{al} \xrightarrow{\mathrm{THF}} \mathrm{TiCl_3 \cdot 3\,THF} + \mathrm{al{-}Cl}$$

Electrochemical

~ −1.5 V:

$$\mathrm{TiCl_3 \cdot 3\,THF} + e^{\ominus} \xrightarrow[-\mathrm{Cl}^{\ominus}]{\mathrm{THF}} \mathrm{TiCl_2}$$

~ −1.75 V:

$$\mathrm{COT} + e^{\ominus} \xrightarrow{\mathrm{THF}} \mathrm{COT}^{\overset{\ominus}{\bullet}}$$

~ −2.0 V:

$$\mathrm{COT}^{\overset{\ominus}{\bullet}} + e^{\ominus} \longrightarrow \mathrm{COT}^{2\ominus}$$

Chemical:

$$\mathrm{COT}^{2\ominus} + \mathrm{TiCl_2} \xrightarrow[-\mathrm{Cl}^{\ominus}]{\mathrm{THF}} \mathrm{Cl{-}Ti \cdot COT \cdot THF}$$

On reduction of mixtures of zirconium(IV) chloride and cyclooctatetraene, the first isolatable reaction product is cyclooctatetraenezirconium dichloride-tetrahydrofuranate.

~ −1.36 V:

$$\mathrm{ZrCl_4 \cdot xTHF} + e^{\ominus} \xrightarrow[-\mathrm{Cl}^{\ominus}]{} \mathrm{ZrCl_3 \cdot 3\,THF}$$

~ −1.75 V:

$$2\,\mathrm{COT} + 2\,e^{\ominus} \longrightarrow 2\,\mathrm{COT}^{\overset{\ominus}{\bullet}}$$

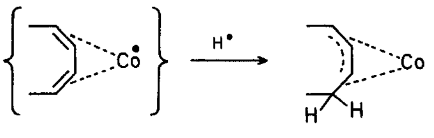
Chemical:

$$2\,\mathrm{COT}^{\overset{\ominus}{\bullet}} \rightleftharpoons \mathrm{COT} + \mathrm{COT}^{2\ominus}$$

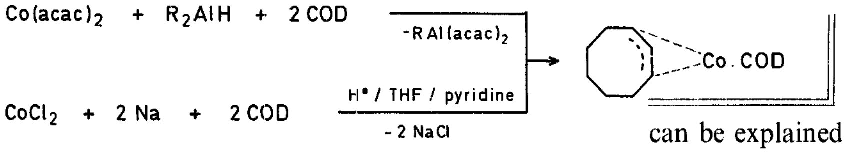
Chemical:

$$\mathrm{ZrCl_3 \cdot 3\,THF} + \mathrm{COT}^{2\ominus} \xrightarrow[-\mathrm{Cl}^{\ominus}]{\mathrm{THF}} \mathrm{Cl_2Zr \cdot COT \cdot THF}$$

In the periodic system cobalt comes between iron and nickel; in the oxidation state (0) the element has an odd number of valence electrons. Therefore its complexes should have radical character; in the case of diolefin complexes these can be stabilized by abstraction of hydrogen from the reaction medium to form π-allylcobalt derivatives.



Thus, π-cyclooctenylcobaltcyclooctadiene is obtained from the reduction of cobalt(II) compounds using dialkylaluminium hydride[61] or sodium metal[67].



Attempts to prepare this compound electrochemically were at first unsuccessful as a compound was formed by cathodic reduction which was readily oxidized. Also with an aluminium anode the anodic current yield, referred to the weight loss of the anode per Faraday, amounted to only 20%. Polarographic investigations showed that the cobalt wave is increased in the presence of 1,5-cyclooctadiene. This can be explained by the formation of a cobalt-containing anion (A) or (B), which naturally should be readily oxidizable. By addition of a proton donating substance the anion can be converted into a stable compound. In the presence of equi-molar amounts of methanol or ethanol, a quantitative, relative to the current, dissolution of the aluminium anode occurs and π-cyclooctenylcobalt cyclooctadiene, which must be formed by isomerization over multiple Co—H bond cleavage and addition reactions, can be isolated[116].

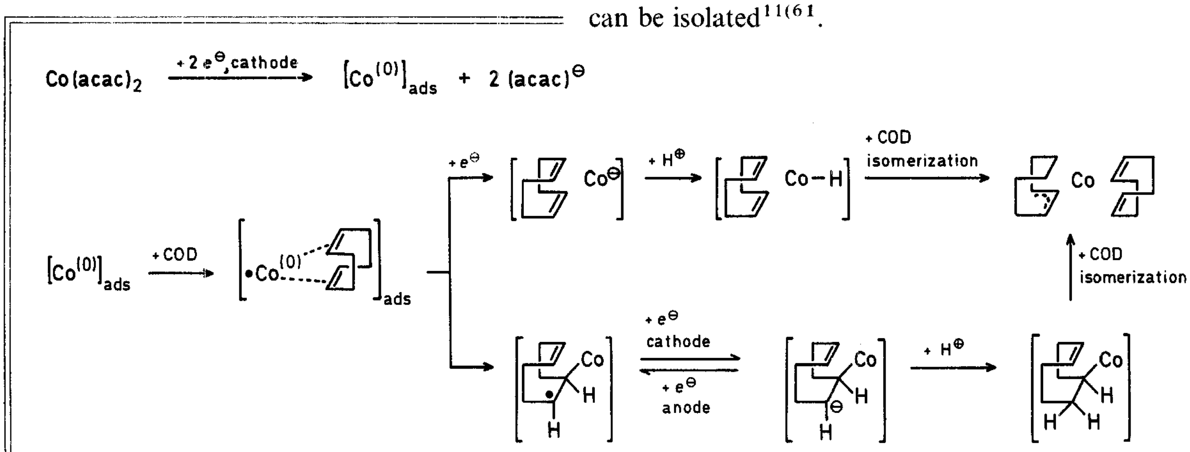
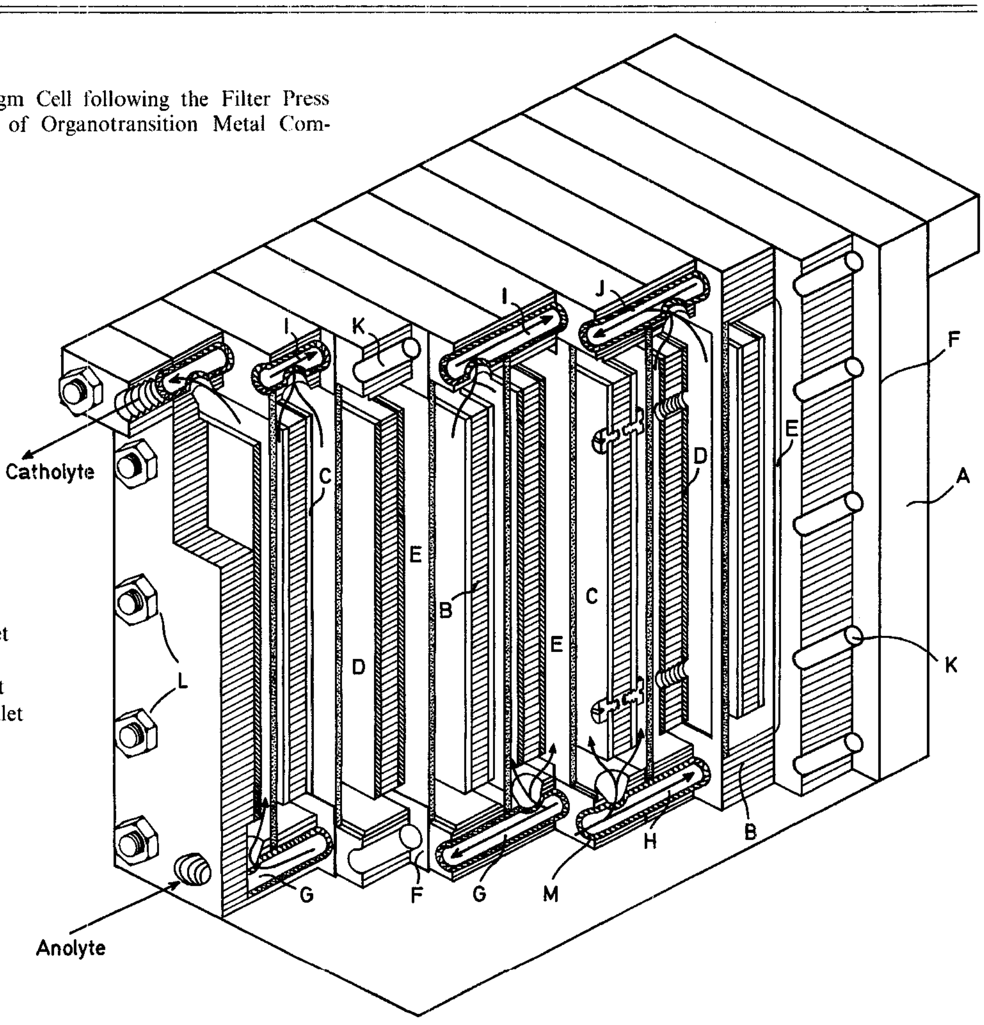


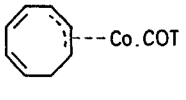
Fig. 7 A Compact Diaphragm Cell following the Filter Press Principle for the Synthesis of Organotransition Metal Complexes[93]



A Endplate (Al)
B Cell unit (Al)
C Co anode
D Al cathode
E Diaphragms
F Seals (Vitron A)
G Passages for catholyte inlet
H Passages for anolyte inlet
I Passages for anolyte outlet
J Passages for catholyte outlet
K Holes for L
L Tension screws
M Insulation tube

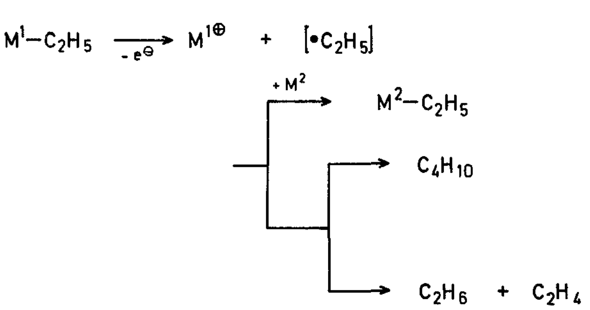
In the absence of alcohol and with separation of the anode and cathode spaces by a diaphragm, cobalt complexes can be also be prepared. The necessary hydrogen is apparently abstracted from the reaction medium. π-Cyclooctatrienylcobaltcyclooctatetraene[11] can be synthesised analogously.

$$\mathrm{Co(acac)_2} + 2\,\mathrm{COT} + 2\,e^{\ominus} \xrightarrow[-\,2\,(\mathrm{acac})^{\ominus}]{+\mathrm{H}^{\bullet}\,/\,\mathrm{THF}}$$



3.4. Electrochemical Metal Exchange in Organometallic Compounds

The anodic oxidation of metal complexes containing carbanions is a widely used method for the preparation of organometallic compounds. The technique is based on observations of Hein[68,69]. Solutions of alkyl compounds of the alkali metals in dialkylzinc or trialkylaluminium, which are relatively good conductors, produce alkyl radicals on anodic oxidation. These radicals dissolve the metal anode in the form of its alkylmetal compound. With metals which do not form stable alkyl compounds, disproportionation or dimerization products of the alkyl radicals are formed[70], e.g.



M^1 = Na, Li, (K), $\frac{1}{3}$Al, $\frac{1}{2}$Mg

M^2 = $\frac{1}{2}$Zn, $\frac{1}{2}$Cd, $\frac{1}{2}$Hg, $\frac{1}{3}$Al, $\frac{1}{3}$Ga, $\frac{1}{3}$Jn, $\frac{1}{4}$Sn, $\frac{1}{4}$Pb, $\frac{1}{3}$Sb, $\frac{1}{3}$Bi.

When the accompanying cathode process is included in the course of the reaction, a metal exchange using electrical energy is obtained. Normally the reaction proceeds in the opposite direction.

$$M^1-C_2H_5 + M^2 \rightleftharpoons M^2-C_2H_5 + M^1$$

Scheme D

These electrochemical syntheses became of technical interest when it became possible to reconvert the metal, deposited at the cathode, which was an aid to the transport of the alkyl radicals, simply to an alkylmetal in the following manner[71]:

$$\mathrm{Al} + 1.5\,\mathrm{H_2} + 3\,\mathrm{C_nH_{2n}} \longrightarrow \mathrm{Al(C_nH_{2n+1})_3}$$

or[72]

$$\mathrm{Na} + 0.5\,\mathrm{H_2} \longrightarrow \mathrm{NaH}$$

$$\mathrm{NaH} + \mathrm{AlR_3} \longrightarrow \mathrm{Na[R_3AlH]}$$

$$\mathrm{Na[R_3AlH]} + \mathrm{C_nH_{2n}} \longrightarrow \mathrm{Na[R_4Al]}$$

or by the corresponding reaction with complexes of sodium hydride with trialkylborane[73].

$$\mathrm{Na[R_3BH]} + \mathrm{C_nH_{2n}} \longrightarrow \mathrm{Na[R_4B]}$$

or

$$\mathrm{Mg} + \mathrm{R{-}Cl} \longrightarrow \mathrm{R{-}Mg{-}Cl}$$

As this development is already 10–15 years old, the results and synthetic possibilities will only be briefly summarized here[74]. The unfavorable equilibrium of the metal exchange process (Scheme **D**) can be influenced by the following electrochemical processes:

- by perturbation of the equilibrium due to amalgam formation of the metal M[75,79];
- by separation of the anode and cathode spaces[76];
- by distilling off the reaction product M^2-R in vacuum[9];
- by rapid reaction of the metal M by addition of alkyl halide with which it reacts more rapidly than with the anodic formed alkyl metal.

From the various possibilities for organoaluminium electrolytes the following variation has proved itself to be optimal. A mercury cathode is employed as this allows the use of a cell without a diaphragm and an anode to cathode separation of only a few millimetres. The cathode is made up of a rotating metal disc, the lower half of which dips into mercury; thus fresh mercury is continuously used and so a perfect vertical mercury electrode is possible[77,78].

The electrolyte consists of a mixture of sodium and potassium tetraethylalanate[79]; the electrochemical reaction is as follows.

$$\mathrm{Na[AlR_4]} + x\,\mathrm{Hg\,(cathode)} + \mathrm{M\,(anode)} \longrightarrow \mathrm{Na(Hg)_x} + \mathrm{AlR_3} + \mathrm{M{-}R}$$

The sodium amalgam formed can be either used as anode in a second electrolysis and so be reconverted to sodium and mercury[80];

$$\mathrm{Na(Hg)_x} \xrightarrow{\mathrm{Na[AlR_4]}\ /\ \mathrm{K[AlR_4]}\text{, electrolysis}} \mathrm{Na} + x\,\mathrm{Hg}$$

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[80] K. Ziegler, H. Dislich, *German Patent* (West, DBP) 1168651 (1962).
K. Ziegler, H. Lehmkuhl, W. Grimme, *German Patent* (West, DBP) 1146258 (1961); *C.A.* **58**, 13458 (1963).

[81] H. Lehmkuhl, *Chem.-Ing.-Tech.* **36**, 612 (1964).

[82] K. Ziegler, W. Eisenbach, unpublished results.

[83] N. V. Kondyrev, *Ber. dtsch. chem. Ges.* **58**, 459 (1925).

or treated with methyl chloride in the presence of trimethylaluminium in 2,2'-dimethoxydiethyl ether to regenerate the electrolyte[81].

$$2\,Na(Hg)_x + H_3C{-}Cl + Al(CH_3)_3 \xrightarrow[-\,NaCl]{diglyme} Na[Al(CH_3)_4]$$

A complex of the trialkylaluminium is often formed in order to ease the separation of the formed alkylmetal from triethylaluminium, as the boiling points are often similar. Either potassium trialkylfluoroalanate[82]

$$AlR_3 + K[R_3Al{-}F] \longrightarrow K[R_3Al{-}F{-}AlR_3]$$

or a sufficiently high boiling ether, e.g. dihexyl ether[82], is suitable for this purpose. From Table 9 it can be seen that the cathodic formed sodium amalgam is predominantly stable relative to the ethyl compounds of magnesium, mercury, aluminium (below 0.7%-wt of Na), tin, lead, antimony, and bismuth; moderately stable relative to those of indium and thallium and unstable relative to those of cadmium, zinc and calcium in the presence of triethylaluminium[79].

Table 9. Yield of Ethylmetal, Weight Loss of Anode, and Yield of Sodium Amalgam in the Electrolysis of $NaAl(C_2H_5)_4$—$KAl(C_2H_5)_4$ (1:1)[79].

Anode Metal	Na in Amalgam (Equiv./100 Faraday)	Dissolution of the anode (Equiv./100 Faraday)	Yield of Ethylmetal (Equiv./100 Faraday)
Mg	85.5	84	65
Ca	11.9	43	0
Zn	1.4	92	0
Cd	0.9	39	0
Hg	96.0	not determined	96
Al	98.5	90	88
In	55	98	46
Tl	23.5	100	15
Sn	97.5	8	0
Pb	99	100	97.5
Sb	97.5	13	0
Bi	98.5	75	56

Tetraethyllead[82]: The cell is shown in Fig.8
Anode: Rotating lead disc (thickness 15 mm)
Cathode: Stirred mercury
Electrolyte: Mixture of potassium tetraethylalanate and potassium triethylfluoroalanate (molar ratio: 10:3; total wt. 300 g)

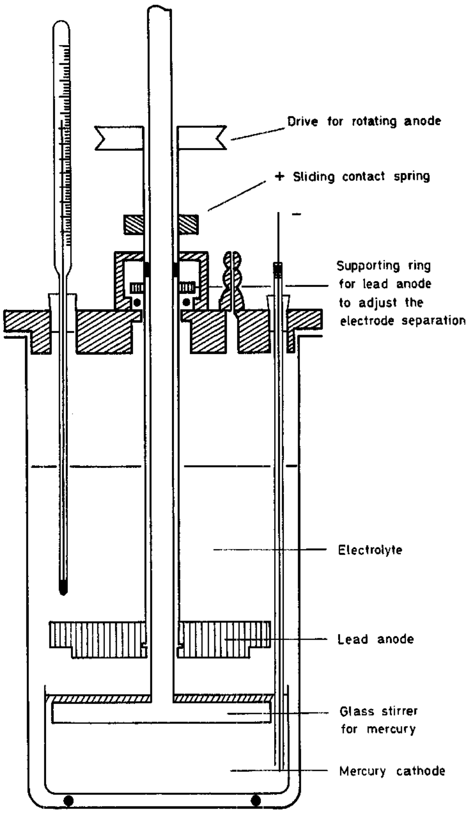

Fig. 8. Cell for preparation of tetraethyllead.

The lead anode is rotated at such a speed that the electrolyte is well-mixed while the mercury is not affected. The separation between the lead anode and the mercury surface is 12 mm. The mercury is stirred by a slow-moving (10 r.p.m.) glass stirrer, the axis of which passes through a hole in the vertical axis of the lead anode.

The electrolysis is carried out at 90–96° using a current of 5 Amp. at 3.8–4.4 Volt (anode current density 18.5 A/dm²).

After the passage of 10 Ampère-hours, the molten electrolyte together with the suspended tetraethyllead is taken out and the vessel rinsed with benzene. In a typical experiment the following results are obtained: potassium as 0.6% potassium amalgam 14.7 g (377 mg-at), (100%); weight loss of anode: 19.0 g (92 mg-at) (98.5%); and by distillation from the electrolyte at 80°/0.001 torr; tetraethyllead, yield 27.0 g (84 mmol) (90%). When the electrolyte is prepared from technical triethylaluminium which generally contains several % butyl groups bonded to aluminium, the lead compound also contains butyl groups. An electrolyte containing 4% butyl groups (referred to total alkyl group content) gives rise to a product containing 17% triethylbutyllead.

Diethylmercury can be prepared analogously. A smaller vessel filled with mercury is placed inside the mercury-filled reaction vessel. A wide, slow-moving glass stirrer is placed above the surface. One mercury mass is the anode and the other the cathode. For the special purpose of the synthesis of diethylmercury a system consisting of two, isolated from each other but mounted on one axis, copper discs which on rotation dip into the separate mercury masses and so are continually moistened with fresh mercury, has proved valuable. The discs serve alternately as mercury anode or mercury cathode. The two cycles of anode and cathode mercury are carried out separately because of the storage compartments[76]. When organoboron complexes are used, the separation of the formed alkylmetal and the trialkylborane is possible due to a sufficient boiling point difference[73]. The trialkylborane formed does not need to be trapped by complex formation.

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Triethylbismuth[73]**:**

A cell similar to that shown on page 394 is used.

Sodium tetramethylboranate (30 g) in water (40 ml) is subjected to electrolysis at 20–25° using 1.8 volt and an anode current density of 3.5 A/dm². After the passage of 120 m Faraday the weight loss of the bismuth anode is 8.2 g (39 mg-at) (98%) and the cathode mercury contains sodium (112 mg-at, 93.5%).

Triethylbismuth and triethylborane can be separated by fractional distillation through a Vigreaux column:

triethylborane: 10.1 g (86%); triethylbismuth: 11.2 g, 34.5 mmol (86%), b.p. 69–70°/10 torr.

Tetraethyllead (91%), tetramethyllead (78%), and diethylmercury (81%) can be obtained analogously.

The electrolysis of alkylmagnesium halides in the dialkyl ethers of diethyleneglycol in the presence of alkyl halides is used for the commercial production, e. g. of tetramethyllead[83, 84].

$$H_3C{-}Mg{-}Cl \;+\; H_3C{-}Cl \;+\; 0.5\,Pb \longrightarrow MgCl_2 \;+\; 0.5\,Pb(CH_3)_4$$

Tetramethyllead[84]**:**

Anode: Lead granules.

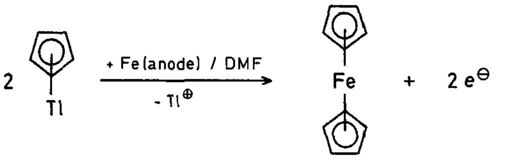
Cathode: Inner surface of steel tube reaction vessel (length 76 cm, Ø5 cm, surface area 5.9 dm², volume 306 ml).

Electrolyte: Methylmagnesium chloride (7.5 mol) and methyl chloride (2.2 mol) in a mixture of benzene, tetrahydrofuran and the polyether $C_6H_{13}OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$ (total volume 3200 g, molar ratio 2:0.77:1).

Flanged fittings for the circulation of the electrolyte are welded to the ends of the reaction tube. The inner surface of the tube (the cathode) is covered with a layer of a fine-meshed polypropylene material as insulation to the lead granules (the anode). During the course of the electrolysis the electrolyte is circulated through a heat exchanger for cooling. The electrolysis is carried out at 40° and 25.5 volts, the average current is 16.6 amperes, falling to 9.5. In the course of the electrolysis methyl chloride (300 g) is passed into the mixture. After 216 ampere-hours, 669 g of lead are dissolved (160% referred to the current).

When a mixture of methyl and ethyl chlorides (0.3 and 0.9 mol per mol of Grignard reagent) is passed into an electrolyte containing methylmagnesium chloride during the electrolysis, mixtures of tetramethyl and tetraethyllead are obtained. It was stated that mixed methylethyllead compounds can also be obtained under these conditions.

The electrolysis of cyclopentadienyl compounds of an alkali metal[85] or thallium[86] is recommended for the preparation of cyclopentadienyl-transition metal complexes.



3.5. Synthesis of Organometallic Catalysts

Organometallic catalyst solutions can be prepared electrochemically without the necessity of isolating defined compounds from the electrolyte. The reactions of unsaturated hydrocarbons using these catalysts generally result in the same products as are obtained using analogous catalysts prepared by chemical reduction[6, 54] (see Table 11).

Preparation of a Catalyst for Butadiene Trimerization[6, 11]**:**

Anode: Aluminium sheet (area 20 cm²).

Cathode: Aluminium sheet (area 20 cm²).

Electrolyte: Tetrabutylammonium bromide (5 g) in THF (100 ml).

Starting Material: Nickel(II) acetylacetonate (12 g, 46.5 mmol).

The electrodes are positioned with a separation of 3 cm and the electrolysis is carried out at 20° using 30 mA and 60 V. Butadiene is passed into the electrolyte during the electrolysis. After passage of 100 mFaradays, all liquid boiling below 60°/0.001 torr is distilled into a cooled receiver flask. Fractionation of the mixture obtained from a typical experiment gives a mixture of the following isomers of 1,5,9-cyclododecatriene; t.t.t. 96.5%, t.t.c. 3.4%, t.c.c. 0.1%; total yield: 21.5 g; b. p. 100–110°/15 torr.

Table 10. Yield of Alkylmetal, Weight Loss of Anode, and Amount of Trialkylborane Recovered from the Electrolysis of $Na[BR_4]$ in Water[73]; Cathode: Mercury

Anode Metal	Alkyl Group	Weight Loss of Anode relative to current (%)	Yield of Alkyl Metal relative to current (%)	Recovered Trialkylborane (%)	Na-Amalgam relative to current (%)
Hg	C_2H_5	~95	81	87	–
Pb	CH_3	100	78	78	–
Pb	C_2H_5	92	91	96	96
Bi	C_2H_5	98	94	86	93
Sb: 7 A/dm²	C_2H_5	34	24	not determined	–
3.5 A/dm²		50	29	not determined	–
0.35 A/dm²		51	51	not determined	–
Sn	C_2H_5	0	0	–	–

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Table 11. Organometallic Catalyst Solutions Prepared by Electrolysis; Co-catalysts and Reaction Products of Unsaturated Hydrocarbons

Starting Materials Metal Compound	Solvent	Ligand	Co-catalyst	Unsaturated Compound	Reaction Product	Reference
$AlCl_3$ $Cl_2Al—OH$	CH_2Cl_2	–	Mn, V, Ti compounds	ethylene	polyethylene	87
$Co(acac)_3$	CH_3OH	butadiene	α,β-unsaturated carbonyl compounds	butadiene	3-methyl-1,4,6-heptatriene, octatriene	88
$Co(acac)_3$	CH_3OH	butadiene	formic acid	butadiene	polybutadiene	88
$Co(acac)_2$ $Co[Al(OR)_4]_2$	THF	butadiene	–	butadiene	3-methyl-1,4,6-heptatriene, octatriene	54
$Ni(acac)_2$	THF/pyridine	butadiene or COD	–	butadiene	1,5,9-cyclododecatriene	6
$Ni(acac)_2$	THF/pyridine	butadiene and triphenylphosphine	–	butadiene	1,5-cyclooctadiene, 4-vinylcyclohexene	6
$NiBr_2$	acetonitrile	alkyne	–	alkynes	polyalkynes	89
$NiCl_2$	CH_3OH C_2H_5OH	triphenylphosphine	–	butadiene	1,3,7-octatriene, alkoxyoctadiene	90, 91
NiJ_2	C_2H_5OH	butadiene	–	butadiene	1,4-polybutadiene	90
$NiBr_2$	C_2H_5OH	butadiene	–	butadiene	dihydrooligomers of butadiene	90

Conclusions

Organometallic electrochemistry is keeping pace with the rapid developments in organic electrochemistry. The application of its methods by preparative chemists is made easier by modern apparative techniques (polarographs, potentiostats). Although organometallic electrochemistry is only at the beginning of its development there is already an abundance of polarographic studies. However, little is known about the nature of the new compounds formed by the donation or acceptance of electrons. In most cases the preparative possibilities arising from these analytical investigations have not been utilised.

Analytical electrochemical methods have already been used for the clarification of structural questions about π-ligand metal complexes. These give an indication of the reaction mechanisms and allow reactivities to be estimated.

Further preparative routes are openned by the electrochemical transference of organometallic groups to organic molecules. This has been accomplished e.g. by anodic oxidation of organomagnesium, -boron, or -sodium compounds in the presence of suitable olefins such as styrene, butadiene, or vinyl ether[92]. The electrochemical conversion of organometallic compounds could only be considered in this article when further organometallic compounds were formed as reaction products.

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