



Review

The use of *sacrificial anodes* for the electrochemical synthesis of metallic complexes



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ABSTRACT

In this work, a compilation of electrochemically prepared metallic complexes is presented. All of them were synthesized by using a single step electrolytic process. This procedure is useful in the syntheses of homoleptic and heteroleptic complexes. Perhaps the most important point is the versatility of the proligands which can be used for the syntheses: a variety of functional groups and a number of coordination modes for the different ligands are reported.

However, unpredictable results were also obtained in some cases; these results were successfully interpreted and, many times, they were useful for new syntheses, both by using the results themselves or for the prevention against non desirable products. A summary of these unexpected situations is also presented.

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Abbreviations: acac, acetylacetonato anion; 2-ampy, 2-aminopyridine; bipy, 2,2'-bipyridine; biQ, biquinolyli moieties; dppm, bis(diphenylphosphanyl)methane; dppe, 1,2-bis(diphenylphosphanyl)ethane; DMF, dimethylformamide; DMSO, dimethylsulfoxide; LDA, lithium diisopropylamide; Mes, mesitylene; N-MeABz, 1-methyl-2-aminobenzimidazole; N-Melm, N-methylimidazole; p-TsOH, p-toluenesulfonic acid; phen, 1,10-phenanthroline; py, pyridine; TMEDA, N,N,N',N'-tetramethylethylenediamine.

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1. Introduction

Over the past decades a big effort on the development of new synthetic procedures has been carried out. One of these processes involves the electrolytic oxidation of a metallic anode in an electrochemical cell containing the precursor of the ligand (namely the proligand) in a suitable solvent.

D. G. Tuck and coworkers [1,2] developed this method, not only for coordination complexes but also for organometallic compounds. Several reviews reporting the possibilities of this synthetic procedure have been previously published [3–13].

This review focuses mainly on metal complexes with a variety of ligands which were isolated from an electrolytic cell, with the corresponding metal acting as an anode, and which were crystallographically characterized. Information was retrieved from the Cambridge Structural Database, SciFinder Scholar, and the original articles. Coverage for the period up to the end of 2013 is believed to be exhaustive, and some data published in 2014 were also consulted and included.

The electrochemical synthesis of metallic complexes, with the metal acting as the anode of an electrolytic cell containing a proligand in solution is a very simple technique. This solution is poured in a flask and an electrolyte is added; the most commonly used electrolytes are $(n\text{Bu}_4\text{N})\text{PF}_6$, $(n\text{Bu}_4\text{N})\text{BF}_4$, $(\text{Et}_4\text{N})\text{BF}_4$, $(n\text{Bu}_4\text{N})\text{Br}$, $(\text{Me}_4\text{N})\text{Cl}$ or LiCl . However, even although it is a potentially explosive compound and it should be used in small quantities and with great care, $(\text{Et}_4\text{N})\text{ClO}_4$ was widely used, given the low tendency of the perchlorate anion to bind metallic ions and the solubility of this salt in acetonitrile, the most commonly used solvent for the electrochemical syntheses. This solvent has a high potential ranges, so it is difficult to oxidize. However, some other solvents were used for these synthetic procedures depending on the solubility of the proligands and the electrolyte and its reactivity toward the product and its stability to an applied voltage: DMF, DMSO, CH_2Cl_2 , MeOH. . . or even mixtures of solvents.

The electrochemical syntheses procedures are generally carried out under galvanostatic conditions in undivided electrochemical cells where the electrodes are located in the same compartments or either in a divided cell by a diaphragm to separate the anodic and cathodic compartments. The undivided cells are the most generally used for electrochemical synthesis of the metal complexes; among them, one of the typical simplest cells (Fig. 1a) involves a 100 mL tall-form beaker where the cathode of the cell is a platinum wire and the anode is a sheet of the metal whose complex is searched, which also hangs from another platinum wire. Both electrodes are suspended into the solution phase from a rubber cap. When necessary, a stream of dry nitrogen was passed through the cell in order to achieve oxygen and moisture-free conditions. Direct current was supplied by a purpose-built d.c. power supply. Usually the experiments were carried out at a constant current (usually in the range 5–20 mA) and the voltage (usually 10–20 V) is the required value to achieve such a current; these conditions allowed a smooth dissolution of the metal anodes. The current was maintained for the time previously calculated as a function of the amount of ligand and in accordance with the reaction. In most of the cases, the cells can be summarized as: $\text{Pt}(-)/\text{proligand} + \text{solvent} + \text{electrolyte}/\text{M}(+)$.

As mentioned, this is the simplest electrolytic cell but some other types were used [12]. For example, for the management of extremely air-sensitive compounds the simple cell can be modified according to Schlenck conditions (Fig. 1b) [14] or even with thermostats. . . More sophisticated electrochemical cells were also used; that is the case of electrochemical flow cells [13,15] which were used, in example, for the electrochemical synthesis of organometallic nickel complexes, with a continuous reagent loading (Fig. 1c).

By using this synthetic route the presence of an oxidizing or reducing agent is not required; so, in solution there are no species which could compete with the ligand for the coordination to the metal atom. Moreover, the metallic sheets which are used for this kind of syntheses are pure; when a highly pure metal is not available, it can be deposited on a platinum sheet by an electrolytic procedure in order to be used as an anode for the preparation of the metallic complexes.

The synthetic process can be kinetically controlled; so the product can be generated as slowly as desired merely by controlling the intensity of the current passing through the cell; and it is because of it that, in many cases, monocrystals suitable for X-ray diffraction

could be isolated directly from the cell, without requiring subsequent recrystallization.

Most of the proligands involved in electrochemical synthetic procedures bear weakly acid groups such as $-\text{OH}$, $-\text{NH}$ or $-\text{SH}$ groups, which can be deprotonated along the electrochemical procedure, yield the corresponding anion together with the evolution of hydrogen bubbles. However, some other groups like disulfide or diselenide can be electrochemically reduced; in these cases, hydrogen bubbles are not observed. The electrochemical cleavage of these bonds gives the corresponding thiolato or selenolato species.

Moreover, mercury complexes can also be obtained; in this case, the solution containing the corresponding precursor of the ligand is poured on liquid mercury. A platinum wire is in contact with the liquid metal which acts as an anode.

An example of an electrochemically prepared mercury complex is that obtained by anodic oxidation of the corresponding metal in an acetonitrile solution of 4-trifluoromethyl-6-methylpyrimidine-2-thione (HL1c, Scheme 1). The crystal structure of $[\text{Hg}(\text{L1c})_2]$ [16] shows that the proligand has been deprotonated to yield a thionato species which exhibits a monoanionic monodentate behavior in the complex.

Anodes of many metals have been used for direct electrochemical syntheses; main groups metals, transition metals and even lanthanide group metals as samarium or neodymium [17] or actinide group metals as thorium [18–20] or uranium [21,22]. Moreover, some Au(I) complexes were also electrochemically obtained [23], even though it is a noble metal and its reactivity is expected to be low.

The versatility of this synthetic procedure can also be related with the variety of co-ligands which can be used for the preparation of heteroleptic complexes in a single step. In fact, heteroleptic complexes can be prepared by using an electrochemical procedure in which the metal is the anode of a cell containing the solution of the proligand and an additional neutral co-ligand with donor atoms such as nitrogen or phosphorous. Thus, for example, the electrolysis of an acetonitrile solution of 3-trifluoromethylpyridine-2-thione (HL2b, Scheme 1) and 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) using zinc anodes [24] gave the corresponding mixed complexes $[\text{Zn}(\text{L2b})_2(\text{bipy})]$ and $[\text{Zn}(\text{L2b})_2(\text{phen})]$. The crystal structures of both complexes show that the co-ligand has been incorporated to the metal coordination sphere along the electrochemical process.

The electrochemical template synthesis procedure was also reported as an useful method to obtain metallic complexes [25]. That is the case of the complex $[\text{Co}(\text{L3})_2]$, with HL3 = 1-[(4-methylphenyl)sulfonamido]-2-[(2-pyridylmethylene)amino]-benzene. An acetonitrile solution of the two precursors of the Schiff base, 2-pyridinecarboxaldehyde and *N*-tosyl-1,2-diaminobenzene, was electrolyzed with a cobalt anode; tetramethylammonium perchlorate was used as an electrolyte. This new synthetic procedure was chosen since the synthesis of the proligand by reaction between the two mentioned precursors was not successful, due to unexpected cyclization reactions in solution (*vide infra* in Section 4). In the complex *mer*- $[\text{Co}(\text{L3})_2]$ (Fig. 2, left) the metal center is coordinated by two monoanionic terdentate ligands resulting in the deprotonation of the amide group of the Schiff base along the electrochemical process.

The electrochemical synthesis of the heterobimetallic complex $[\text{Cu}^{\text{I}}\text{Pd}^{\text{II}}(\text{L4})][\text{BF}_4]_3$ was also presented [26]; in this case, two electrolytic processes take place. First of all, a solution of the proligand (a kind of polyamic acids, $\text{H}_n\text{L4}$, with biquinolyl moieties, biQ) in *N*-methylpyridine was electrolyzed in the presence of a Pd anode and a Pt wire as the cathode; the process was stopped after a specified amount of electricity (0.55 F per mol of biQ fragments of the starting polymer) was passed through the solution. Afterwards, the palladium anode was replaced by a copper plate, which was also

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