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Mediated electrolysis of vicinal diols by neocuproine palladium catalysts

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ABSTRACT

Synthetic electrochemistry agrees well with the principles of sustainable chemistry, therefore it is considered as a more environmentally friendly approach than some current synthetic methods. Here, we present a new strategy for the chemoselective oxidation of vicinal diols, viz. the integration of neocuproine palladium catalysts and electrosynthesis. Benzoquinones are used as an effective mediator as the reduced species (hydroquinones) can be easily reoxidized at relative low potentials at an electrode surface. NeocuproinePd(OAc)$_2$ efficiently works as a catalyst in an electrolysis reaction for vicinal diols at room temperature. This is a remarkable observation given the fact that aerobic oxidation reactions of alcohols typically need a more complex catalyst, i.e. [neocuproinePdOAc]$_2$[OTf]$_2$. In this article we describe the optimization of the electrolysis conditions for the neocuproinePd(OAc)$_2$ catalyst to selectively oxidize diols. The suggested approach leads to conversion of alcohols with high yields and provides an interesting alternative to perform oxidation reactions under mild conditions by the aid of electrochemistry.

1. Introduction

Chemoselective oxidation reaction pathways aim to selectively oxidize an alcohol functionality in the presence of other alcohols. The oxidation of vicinal diols to the corresponding α-hydroxyketone functionality is of particular interest as this functionality is present in antitumor antibiotics such as kurasoin A and B [1] and in different natural products such as olivomycin A [2]. The α-hydroxyketone group also plays an important role in the modification of carbohydrates and other reaction schemes in general organic synthesis [3].

Different (non-electrochemical) methods have been proposed to achieve a chemoselective reaction of vicinal diols. The use of peroxotungstophosphates in combination with hydrogen peroxide is reported to give a selective oxidation of different vicinal diols [4]. Also, the stoichiometric use of dioxiranes results in chemoselectivity [5]. Another oxidation pathway consisting of $NaBrO_3$ with $NaHSO_3$ is described in literature to selectively oxidize cyclic vicinal diols to the corresponding hydroxyl ketones [6]. Focusing on catalytic systems using metal catalysts, the combination of $RuCl_3$ with buffered oxone as the stoichiometric oxidant is reported to oxidize different vicinal diols to the corresponding α-hydroxyketones [7]. Other catalysts are organotin compounds in combination with stoichiometric oxidants like Br_2 or N-iodosuccinimide (NIS) [8]. Those organotin catalysts can be also replaced by boronic acids [9], or used in combination with electrochemical oxidized bromo species (Br^+) [8,9].

In general, catalysts for alcohol oxidation can be immobilized on (modified) electrode surfaces, for example a carbon supported platinum electrode modified with bismuth. Using such an electrode glycerol is oxidized to dihydroxyacetone with high selectivity [10]. A second electrochemical approach includes TEMPO as a mediator and a similar selective oxidation of glycerol to dihydroxyacetone can be obtained by reoxidizing TEMPO at the electrode surface. However, only a yield of 25% is reported [11].

Palladium catalysts have been investigated thoroughly for the aerobic non-electrochemical oxidation of alcohols. Catalysts such as Pd carbene catalyst [12] or cationic pyridine based palladium complexes [13] have been reported for selective oxidation reactions with oxygen as stoichiometric oxidant. Another example of a palladium catalyst that can selectively oxidize vicinal diols is the cationic palladium complex using neocuproine as a ligand, developed by Waymouth et al. [14].

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The beneficial use of neocuproine as a ligand for palladium catalysts was first investigated by Sheldon et al. [15], they reasoned that the methyl groups on the 2 and 9 position of the phenanthroline ligand cause steric hindrance and thus prevent the formation of dimeric structures, resulting in a more active catalyst for oxidation reactions. The highest activity for the aerobic oxidation of alcohols was achieved by using the palladium catalyst neocuproinePd(OAc)$_2$ (Scheme 1, structure 1) which has a phenanthroline with two methyl groups substituents at the 2 and 9 position (neocuproine).

Later, this catalyst was used as a basis for the synthesis of a new cationic palladium complex using neocuproine as a ligand [16]. It was reasoned that a cationic palladium complex with non-coordinating counter anions could increase the rate of aerobic alcohol oxidation. The dimeric acetate bridged [neocuproinePdOAc]$_2$[OTf]$_2$ (Scheme 1, structure 2) was synthesized by conproportionation of neocuproinePd(OAc)$_2$ and the ditriflate analogue neocuproinePd(MeCN)$_2$(OTf)$_2$. This catalyst 2 proved to have faster initial rates for the aerobic oxidation of alcohols at room temperature. In comparison, catalyst 1 needs 80 degrees Celsius for an efficient conversion [15].

Interestingly, catalyst 2 allowed the selective oxidization of polyols [14]. More specific, in vicinal diols only the secondary alcohol is oxidized to the corresponding α-hydroxyketone. Also glycerol can be selectively oxidized to the corresponding dihydroxyacetone under mild conditions [17]. In those approaches both oxygen and p-benzoquinone are used as stoichiometric oxidants. Additionally, it was mentioned that catalyst 2 may convert unprotected pyranosyl glucosides to the corresponding ketosaccharides. Here, the catalyst can discriminate between different secondary hydroxyl groups, only the one at the C3 position is oxidized to the ketone by using 2,6-dichlorobenzoquinone as stoichiometric oxidants [18].

The drawback of using oxygen as the stoichiometric oxidant in combination with catalyst 2 is the fact that it may lead to the oxidation of the neocuproine ligand and corresponding losses in reactivity over time [16]. To avoid this, other catalysts have been synthesized. Waymouth et al. reported on a catalyst having a trifluoromethyl substituted phenanthroline ligand instead of neocuproine and studied its oxidation potential of 2-heptanol [19]. The results were not convincing, although the turnover number of this catalyst doubled and no ligand oxidation was observed, the initial rate, however, was 3.7 times lower compared to catalyst 2. Furthermore, the ligand is much more difficult to synthesize. Recently, a deuteration of the methyl substituents in the neocuproine ligand was suggested to obtain a more resistant ligand against oxidation [20].

In this article, an electrocatalytic approach by using catalyst 1 and 2 is suggested. By working in an inert gas atmosphere, the possible degradation of the catalyst by oxygen is prevented. Secondly, the electrochemical recycling avoids the use of a stoichiometric amount (or excess) of the oxidants, making it a more sustainable alternative. In an electrocatalytic oxidation reaction, a mediator gets oxidized at the electrode surface at a low potential followed by the oxidation of the target molecule [21]. Mediators of interest are benzoquinones as it is known that the reduced species (hydroquinones) can be easily reoxidized at relative low potentials [22–26].

The selective oxidation of vicinal diols directly to α-hydroxy ketones is of utmost importance when looking for an atom-economical reaction. For the first time, palladium catalysts with neocuproine ligands are combined with the electrochemical recycling of benzoquinones. A selective electrochemical oxidation of diols under mild conditions and high yield is now presented.

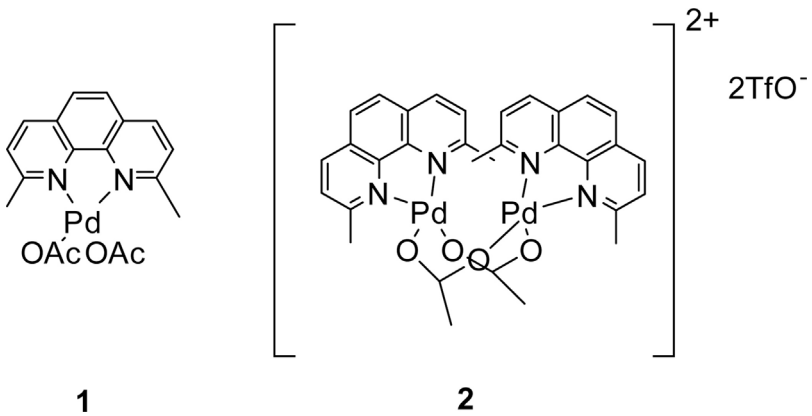
2. Experimental

2.1. Synthesis of neocuproinePd(OAc)$_2$ (catalyst 1)

A solution of neocuproine (5.5 mmol, 1.25 g) in anhydrous CH_2Cl_2 (20 mL) was added to a solution of Pd(OAc)$_2$ (5.0 mmol, 1.12 g) in anhydrous toluene (100 mL) at room temperature under nitrogen. The mixture was stirred overnight and heptane was added to precipitate the complex. A yellow solid was filtered off, washed with acetone and dried under vacuum; yield: 1.78 g (4.0 mmol, 80%).

2.2. Synthesis of neocuproinePd(CH$_3$CN)$_2$(OTf)$_2$

To a slurry of catalyst 1 (0.221 g, 0.511 mmol) in acetonitrile (1.0 mL) was added a solution of triflic acid in acetonitrile (0.33 M, 3.8 mL, 2.5 equiv). The solution was stirred briefly and then precipitated with diethyl ether to give a yellow solid. This solid was isolated by centrifugation, precipitated two more times from acetonitrile using diethyl ether, and dried under vacuum to give a light yellow solid (0.090 g). Additional triflic acid (0.33 M, 1.0 mL) was added to the original supernatant, followed by brief stirring and precipitation with diethyl ether. The resulting yellow solid was subjected to the same workup as described above to give additional product (0.021 g). The pure solids were combined (0.111 g, 0.160 mmol, 31% yield).



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Scheme 1. Two neocuproine palladium catalysts: neocuproinePd(OAc)$_2$ (1) and [neocuproinePdOAc]$_2$[OTf]$_2$ (2).