Transition metal compounds with S/N-functionalized NHC ligands: structures, redox properties and electrocatalytic activity

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CHAPTER 7

Summary, Conclusions &Outlook

7.1 Summary

7.1.1 Introduction

Dihydrogen gas is considered as one of the most attractive clean fuels, which produces only water when it is combusted in pure dioxygen.[1] The hydrogen evolution reaction (HER), the reaction in which protons are reduced into dihydrogen, is one of the most intensively studied reactions. The typical heterogeneous catalyst for HER is platinum; using platinum-based materials as working electrode in electrolytic cells H_2 can be produced efficiently.[2] However the downside is evident: platinum is a noble metal with limited reserves and consequently a relatively high price. In nature, hydrogenases can efficiently catalyze the transformation between protons and dihydrogen.[3] Inspired by the natural enzymes, many structural and functional models of the hydrogenases have been designed by chemists and some of these models have been found to be good electrocatalysts for HER.

N-Heterocyclic carbenes (NHCs) form a class of ligands that generally are regarded as useful ligands comparable with phosphanes for their use in homogeneous catalysts,[4, 5] but the electrocatalytic behavior of transition metal complexes bearing NHC ligands so far have been largely ignored. Nickel compounds with diphosphane ligands have been found to be effective catalysts for HER.[6] The aim of the research described in this thesis is to investigate the electrocatalytic properties of transition metal NHC compounds, in order to make a preliminary estimation on whether this class of complexes has the potential to generate a promising electrocatalyst based on inexpensive transition metals for efficient proton reduction in the near future.

In Chapter 1, the active sites of hydrogenases are briefly discussed, followed by a concise overview of well-studied structural models and functional models of hydrogenases as electrocatalysts for the hydrogen evolution reaction. Furthermore, a brief introduction is provided on transition metal NHC complexes and the electrochemical research reported for these compounds. Subsequently a general mechanism of metal-centered homogenous electrocatalysis for HER is discussed.

7.1.2 Electrocatalytic behavior of nickel complexes bearing thiolate-functionalized NHC ligands

In the design of structural and functional mimics for hydrogenases, a thiolate-bridged dinuclear structure seems to be essential. Therefore thiolate-functionalized carbene ligands were among the first candidates in our study. In Chapter 2, four sulfur-functionalized carbene ligands and their dinuclear nickel-NHC complexes are described. The four ligands differ by the alkyl chain length between the NHC and the thiolate group (two or three carbon atoms) and the second functionality at the NHC being a benzyl or a pyridylmethyl group. The nickel(II) ions are coordinated to the NHC carbon atom and bridged by the pendant thiolate groups. The benzyl-functionalized nickel-carbene compounds [**1**] and [**2**], revealed weak electrocatalytic activity for HER. However, it was found that the pyridyl-

functionalized compounds [**3**]Br_2 and [**4**]Br_2 show higher catalytic activity in HER than their benzyl-containing analogues. Unfortunately, the limited stability of solutions of the complexes [**3**]Br_2 and [**4**]Br_2 in presence of air and the rather low electrocatalytic efficiency of the compounds limit their potential application as proton reduction catalysts. Meanwhile, to generate understanding of the role of the thiolate and pyridine groups in the electrocatalytic cycle still requires further research.

7.1.3 Electrocatalytic behavior of nickel complexes bearing pyridine-functionalized NHC ligands

Based on the conclusion of the research described in Chapter 2, the research focus switched from thiolate-functionalized carbene ligands to pyridine-functionalized carbene ligands. (Chapter 3 to Chapter 5).

In Chapter 3, the synthesis is described of two bis-(benz)imidazolium salts alkylated with pyridyl side arms thus forming potentially tetradentate ligands, which were used as precursors in the synthesis of novel nickel compounds of N-heterocyclic carbenes (Ni-NHC). Four Ni-NHC complexes with different (imidazole-based or benzimidazole-based) carbene ligands and different counter ions (Br^- or PF_6^-) were isolated and characterized by various methods. The nickel ions in these mononuclear complexes are either in square-pyramidal or square-planar geometries. It was found that the use of imidazole-based carbenes results in more negative Ni^{II}/Ni^{I} and Ni^{I}/Ni^{0} redox couples. However, the nickel compounds with imidazole-based ligands revealed much higher activity in the electrocatalytic reduction of protons, as well as better acid tolerance. Furthermore, it was shown that the presence of halide ions results in more negative potentials for the Ni^{II}/Ni^{I} and Ni^{I}/Ni^{0} redox couples, and also leads to larger overpotentials for proton reduction. The imidazole-based complex with PF_6^- counter ions shows the highest catalytic efficiency (i_c/i_p = 50, k_{obs} = 490 s^{-1} at 0.1 V/s) of all complexes investigated for the catalytic proton reduction, using acetic acid in DMF, although the overpotential at which dihydrogen is produced is sizeable.

In Chapter 5, the synthesis is described of two pyridyl- and amide-functionalized substituted (benz)imidazolium salts, which were successfully employed as ligand precursors for the syntheses of novel nickel(II) complexes bearing tetradentate NHC ligands. Single crystal X-ray crystallography revealed that the nickel ions in both compounds are in slightly distorted square-planar geometries. Cyclic voltammetry of the two compounds showed irreversible reduction events, indicating that electron transfer is immediately followed by a fast chemical reaction or structural rearrangement. The nickel compounds were shown to be potential electrocatalysts for HER using cyclic voltammetry. The production of dihydrogen gas was confirmed using gas chromatography (GC) monitoring the controlled-potential electrolysis at −1.8 V vs. Ag/AgCl; the faradaic efficiency was determined to be around 85% for both complexes. In the presence of the imidazole-based and benzimidazole-based complexes 185 µL and 105 µL H_2 was generated, respectively, over 2 h electrolysis, corresponding to a mere 1.5 and 0.9 mol H_2 per mol of

catalyst. The imidazole-based compound not only shows higher activity in catalyzing HER, but is also active at a lower overpotential. This indicates that proton delivery between the ligand and the metal center is operative, which breaks the correlation between energy costs and kinetic barriers.

In Chapter 4, the synthesis and characterization is reported of two new nickel complexes of benzimidazole-based carbene ligands containing either one or two pyridyl groups per NHC and the study of their electrocatalytic activity in H_2 evolution. Single crystal X-ray crystallography revealed that the nickel ions in both compounds are in a square-planar geometry with like donor atoms of the two bidentate ligands in *cis* positions. The binding of two potentially tridentate ligands in this configuration in one of the nickel compounds results in the presence of two free pyridyl groups. The redox properties of the two complexes were determined using cyclic voltammetry. Electrocatalytic proton reduction experiments using these complexes were performed in DMF with acetic acid as the proton source. The compound containing two additional free pyridyl groups not only exhibits higher electrocatalytic activity, but also has a smaller overpotential for the reduction of protons. The comparison of these two similar structures provides convincing experimental evidence that the pyridyl group acts as proton relay during the proton reduction process.

7.1.4 Electrocatalytic behavior of cobalt compounds of pyridine-amide-functionalized carbene ligands

Whereas in Chapter 2 – 5 the research was focused on the synthesis and study of the electrocatalytic properties of nickel-NHC complexes, in the research described in Chapter 6, the attention was turned to cobalt-NHC complexes, as cobalt is also known to form active catalysts for HER. The imidazole-based tetradentate ligand described in Chapter 5 and a related tridentate ligand in which one of the pyridyl groups is replaced with a benzyl group were used to synthesise two cobalt-NHC compounds. In contrast to the square-planar geometry observed for the Ni-NHC compound of the tetradentate ligand, the cobalt ions in the Co-NHC complexes are in octahedral geometries by the coordination with two ligands binding in tridentate modes. Both Co(III) complexes display reversible redox couples in organic solution. The electrocatalytic behavior of the two cobalt compounds were investigated in DMF solutions, using acetic acid as proton source. Unfortunately, the Co^{III}/Co^{II} redox potential occurs at very negative potentials compared to that of reported compounds of pyridyl-functionalized carbene ligands.[7] The complex of the tetradentate ligand equipped with an additional pyridyl arm shows a smaller overpotential and higher catalytic activity for proton reduction (the slope of a plot of the k_{obs} vs $[H^+]$ giving an estimated rate constant of 10500 $M^{-1}s^{-1}$). Hydrogen production was confirmed and quantified using gas chromatography (GC) following CPE at −1.8 V vs. Ag/AgCl; in the presence of 1 mM of the benzyl-substituted or pyridine-substituted compound 75 μL and 145 μL H_2 was generated, respectively, over 2 h electrolysis, corresponding to 0.6 and 1.2 mol H_2 per mol of catalyst.

7.2 Conclusions & Outlook

Research related to the electrochemical and electrocatalytic properties of metal-NHC complexes has been largely neglected for several decades, despite the redox-innocent nature of the N-heterocyclic carbene ligands and their successful application in homogeneous catalysis. With the design and development of functionalized carbene ligands, the ligand can take part in the catalytic reaction. In this thesis, our investigations are described of the possibility to use metal-NHC complexes as electrocatalysts for the proton reduction reaction. Criteria for potential electrocatalysts are the ease of preparation, the stability of the compounds in (aqueous) solutions, the overpotential at which proton reduction is catalyzed, the activity of the compounds in terms of dihydrogen production and lifetime.

A number of different nickel(II) complexes and two cobalt(III) compounds of functionalized NHC ligands are reported in this thesis. The mononuclear nickel(II) and cobalt(III) complexes are quite stable in air as well as moist atmospheres, and thus are easy to store and handle. The dimeric thiolate-pyridyl-containing complexes described in Chapter 2 are stable as solids, but are not stable in solutions containing dioxygen. All compounds show activity as potential electrocatalyst for HER, although their performance is far from comparable with the well-studied systems such as the nickel compound with diphosphane ligands[6] and cobaloxime systems.[8] Based on the results described in this thesis a number of conclusions and assumptions can be given.

It was found that generally the nickel compounds of imidazole-based NHC ligands show better catalytic activity for HER than the compounds with benzimidazole-based carbene ligands (Chapter 3 and 5). Thus, in future work, a search for NHC ligands with higher electron density may be recommended for the development of new efficient candidate electrocatalysts for HER. Nevertheless, as the carbene ligand is a strong electron donor, on one hand the use of more electron-donating carbene ligands will aid in the formation of the necessary metal-hydride intermediate, but on the other hand the presence of the electron-donating ligand will make it more difficult to reduce the metal center, resulting in larger overpotentials. Thus the search for a suitable NHC framework may be the first priority for future research.

Additionally, it has been shown that the presence of free pendant pyridine groups can greatly improve catalytic activity of the compounds (Chapter 4 and 6). These pyridine groups may act as proton relay in the catalytic cycle and accelerate proton delivery to the reduced metal center. However, in the synthesis of complexes with pyridine-functionalized carbene ligands, it is challenging to prevent coordination of the pyridine functionality to the metal center. In general, it is relatively difficult to form the metal-carbene bond, which requires relatively harsh experimental conditions. In contrast, the formation of metal-nitrogen bonds is much easier. Thus, if we want to obtain coordination compounds in which a free, non-coordinating pyridine is available as a proton relay, the preference of the metal

center for a certain geometry and the design of the ligands are important. In ligands described in this thesis, the carbene ligands are substituted with the 2-methylpyridyl group. Due to the chelating nature of the resulting ligands, the pyridine functionality readily coordinates with metal center (Chapter 2, 3 and 5). Only in the case that more donor atoms are available than the metal center is willing to accept, the additional pyridine may be left uncoordinated and available for protonation (Chapter 4, 6). Future modifications of this type of electrocatalysts may focus on the use of pyridyl substituents that are connected to the ligand via the 3 or 4 position; by doing so the chelating nature of the ligand is lost, effectively preventing the formation of a metal-nitrogen bond. During the course of the studies described in this thesis attempts have been undertaken to synthesize ligands functionalized with pyridine groups attached via the 3-position, but this appeared to be rather challenging, resulting in alkylation of the pyridine nitrogen atom. New synthesis routes need to be developed in order to create these novel ligands.

In Chapters 2 and 5, the relationship between acid concentration and the magnitude of the catalytic current (i_c/i_p) has been studied. Surprisingly, a linear relationship was observed, indicating that two protons are involved in the rate-determining step of the catalytic reaction using the catalysts described in these chapters. As the nickel compounds described in Chapters 2 and 5 do not have a free pyridine group to accept a proton, it may be postulated that in these catalyst the coordinating pyridyl group dissociates during catalytic turnover. Additional studies are necessary for a better understanding of the catalytic mechanism of these compounds.

Transition metal complexes of N-heterocyclic carbenes have been well studied in the last decades, and a vast amount of creative applications of such complexes as catalysts in various kinds of reactions have been explored. However, research on the electrocatalytic activity of metal-NHC complexes is limited and the results described in this thesis form just a start of a potentially emerging field. Using transition metal compounds of NHC ligands in electrocatalysis of a number of reactions can be attempted in the future, for example CO_2 reduction.[9, 10] The work described in this thesis has provided insight in electrochemistry of transition metal carbene complexes to take upon such new lines of potential application.

7.3 Reference

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