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

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CHAPTER 1

Introduction

The active sites of hydrogenases are briefly discussed. A brief overview of structural models and functional models of hydrogenases as catalysts for the hydrogen evolution reaction (HER) is provided. Recently reported electrocatalysts for HER are described in more detail. Furthermore, a brief introduction to Metal-NHC (NHC = N-heterocyclic carbene) complexes is provided and related electrochemical research is described. At the end of this Chapter a short overview of the aim and contents of the research described in this thesis is given.

1.1 Hydrogen evolution reaction (HER) and hydrogenases

Hydrogen gas is considered as one of the most attractive clean fuels, which produces only water when it is combusted with pure dioxygen.[1] Nowadays, the largest fraction of dihydrogen gas is produced from fossil fuels by steam reforming and coal gasification; only a small quantity is produced by other renewable methods such as electrolysis of water.[2]

The hydrogen evolution reaction (HER) is a chemical reaction taking place at the cathodic electrode during electrolysis of water. It is one of the most intensively studied reactions, in which with the use of electrical energy two protons are reduced to dihydrogen (Eq. 1).

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Eq. 1}$$

Catalysts for the hydrogen evolution reaction generally can be divided into two categories: heterogeneous catalyst and molecular catalyst.

The most typical heterogeneous catalyst for HER is platinum metal; using platinum as the cathode material, H_2 can be produced efficiently.[3] However the downside is evident: platinum is a scarce noble metal with relatively high price and limited reserves.

In nature, hydrogenases efficiently catalyze the transformation between protons and dihydrogen.[4] The hydrogenases are classified in three groups, the [FeFe], [NiFe] and [Fe] hydrogenases, which are encountered in different microorganisms and differ in the structure of the active site (Figure 1.1 and Figure 1.2).

[FeFe] hydrogenases, which have been found in bacteria and lower eukaryotes, are generally recognized as the fastest and most evolved of the hydrogenases.[5] The active site in the [FeFe] hydrogenase contains a dithiolate-bridged dinuclear ion center (Figure 1.1). The ion center connects with a bridging cysteine thiolate to a [4Fe-4S] cluster, which is important for the electron transfer. The bridging cofactor contains a secondary amine that is involved in proton transfer.

[NiFe]-hydrogenases are commonly found in a wide variety of bacteria, archaea and cyanobacteria, but are not found to be associated with any lower eukaryotes.[6] In the active site of the heterodimeric [NiFe]-hydrogenases, four cysteine thiolates are coordinated to the nickel center, two of which bridge to connect the iron center. Several mechanisms have been proposed for the uptake of dihydrogen by these enzymes but no consensus has been reached yet.[7] The formation of a bridging hydride between the two metal centers during the catalytic cycle is one of the general considerations.

In the active site of both the [FeFe] and the [NiFe] hydrogenases the iron center is bound to carbon monoxide and cyanide. In nature, [FeFe] hydrogenase enzymes catalyze the formation of H_2 from water, with reported rate constants as high as 9000 s^{-1} which is more

active than [NiFe] hydrogenases (700 s^{-1}).[5, 8] However, [NiFe] hydrogenases are less sensitive to inhibition by oxygen and carbon monoxide than [FeFe] hydrogenase.[8]

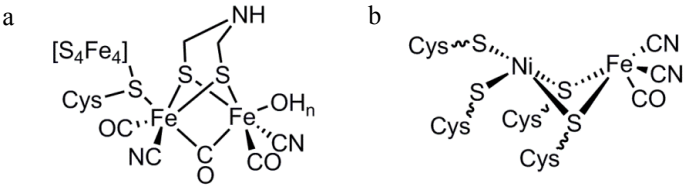

Figure 1.1. Schematic representation of the active site in (a) [FeFe] hydrogenase and (b) [NiFe] hydrogenase.

The [Fe]-hydrogenase, also known as Hmd (hydrogen-forming methylenetetrahydro methanopterin dehydrogenase), is not a redox enzyme and thus does not feature an Fe-S cluster.[5] It only can be observed in some hydrogenotrophic methanogenic archaea. Different from the two other classes of hydrogenase enzymes, it requires the presence of a hydride acceptor/donor substrate to react with or produce H_2.[4] The active site contains an $Fe(CO)_2(SCys)$ fragment bound to a unique guanylylpyridinol/pyridonate ligand through its acyl and pyridyl donor groups (Figure 1.2).

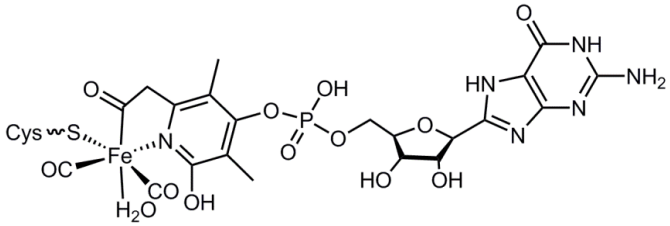

Figure 1.2. Schematic representation of [Fe] hydrogenase active site.[4]

Unfortunately, most of these natural enzymes are extremely air sensitive, restricting their industrial application. However, inspired by the structures of their active sites, chemists are active in the design of molecular electrocatalysts for HER, either by development of structural mimics for the hydrogenase active site or by mimicking the activity of hydrogenases through understanding of their catalytic mechanism. In the next two sections, the structural models as well as functional models for hydrogenases are discussed.

1.2 Structural models for the active sites in hydrogenases

Structural mimics for the active sites of all three classes of hydrogenases have been reported. Compared to the [FeFe] and [NiFe] hydrogenases, relatively few studies have been focused on the design of molecular mimics of the active site in [Fe] hydrogenases.

In the design of structural models for the active site of [FeFe] hydrogenases, the dithiolate ligand bridging the two iron centers is the most important part of the biomimetic

approach.[9] Group of Sun has reported that the nature of this bridge influences the redox properties of the diiron dithiolate model compounds: the use of a rigid and conjugated bridge results in a decrease of the potentials for the $Fe^{I}Fe^{I}$ to $Fe^{I}Fe^{0}$ reduction process.[10] In several cases, an N-heterocyclic carbene (NHC) ligand was used as a ligand for structural mimics, because of its strong σ-donation with negligible π-accepting ability (Figure 1.3a).[11-13] These few NHC-related structural models for [FeFe] hydrogenases indeed present electrocatalytic activities on proton reduction, but the activities are relatively low.

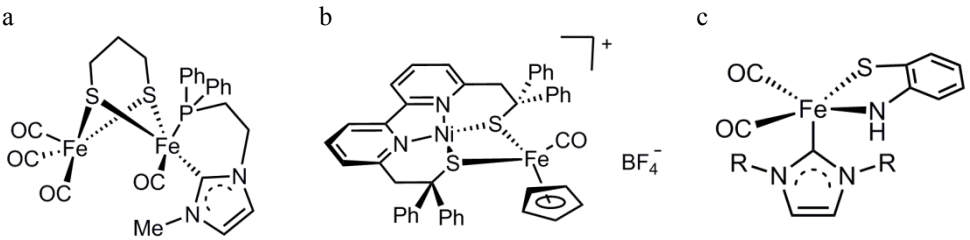

Figure 1.3. Schematic drawing of (a) a NHC-containing structural model for the active site in [FeFe]-hydrogenase;[13] (b) a structural model for the active site in [NiFe] hydrogenase;[14] (c) a NHC-containing structural model for the active site in [Fe] hydrogenase.[15]

As described in Section 1.1 the active site in the [NiFe] hydrogenase comprises a nickel center coordinated to four cysteine thiolates. A general approach to the development of model systems for [NiFe] hydrogenases thus includes tuning of the sulfur-containing ligand with various substituents to directly influence the electron density on the nickel center.[14, 16, 17] Alternatively, inspired by the active site of [FeFe] hydrogenases, an extra functional group on the sulfur bridge can be employeed, which also might affect the efficiency of the molecular catalyst.[18]

Unfortunately, for most of the functional mimics for the active site in [NiFe] hydrogenases it was found that the iron center acted as the catalytic proton reduction center, whereas in the enzyme the iron center does not have a role in catalysis. Recently a new [NiFe] compound was reported in which proton reduction appeared to be nickel centered (Figure 1.3b).[14] Instead of a $[NiS_4]$ coordination sphere, the compound featured an $[NiN_2S_2]$ chromophore.

There are many other strategies to design a functional mimic of [NiFe] hydrogenases. For instance, the synthesis of structural and functional models for the [NiFeSe] hydrogenases – a subclass of the [NiFe] hydrogenases containing a selenocysteine bound to the nickel center in the active site. Novel ligands were developed in which selenium was used instead of sulfur.[19, 20] Apart from nickel and iron, other metal ions have been used in the design and synthesis of structural and functional models for the hydrogenases. Ruthenium has been used to replace the iron center, as ruthenium is known to form more stable coordination compounds.[21-25]

The design and synthesis of structural models of the active site in [Fe] hydrogenase have received relatively less attention.[26, 27] Jiang and coworkers used a strongly electron-donating NHC ligand and the dianionic ligand 2-amidothiophenolate bound to an iron center to mimic the [Fe] hydrogenase active site (Figure 1.3c).[15] Two of the models reported by Jiang *et al*. showed reversible protonation and deprotonation properties.

Apart from the attempts of combining the structural features in an enzyme mimic with functional activity of the enzyme, functional models of the hydrogenases are prepared in which the coordination environment of the metal centers in the synthetic molecules is no longer similar with that of the active site in the natural enzyme. Instead, scientists extracted the core essence of the active site structure and design the catalysts with functional groups or metal centers purely to facilitate the catalysis of H_2 evolution. Examples of this approach are described in the next section.

1.3 Bio-inspired molecular electrocatalysts for hydrogen evolution

1.3.1 Nickel bisdiphosphane complexes

Inspired by the structure of the active site in [FeFe] hydrogenases, two of its critical features were used in the rational design of efficient molecular electrocatalysts for proton reduction: the use of first-row transition metals and the incorporation of a pendant amine as a proton relay.[28] New mononuclear compounds were developed containing a square-planar nickel(II) ion coordinated with four phosphane donor atoms in the first coordination sphere, and including several amine groups in the second coordination sphere. With the aim to understand the role of the pendant amine in the active site of [FeFe] hydrogenases both a computational[29] and an experimental study[30] were undertaken. DuBois *et al*. have discussed the role of the amine pendant group in Co-diphosphane electrocatalysts for hydrogen evolution in an experimental way.[30] Comparison of $[Co(P^{Ph}_2N^{Ph}_2)(CH_3CN)_3](BF_4)_2$ ($P^{Ph}_2N^{Ph}_2$ = 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane) comprising a pendant amine, with the compound $[Co(dppp)(CH_3CN)_3](BF_4)_2$ (dppp = 1,3-bis(diphenylphosphanyl)propane) showed that, although the two compounds are equipped with similar diphosphane ligands, only the former one presented proton reduction activity. Similar compounds containing a nickel center were also developed, and these nickel-based bisdiphosphane complexes have been intensively studied for their electrocatlytic activity in the last decade.[31-37] The activity of the nickel-based catalyst was shown to depend on the exact orientation of the pendant amines with respect to each other and the metal center: the formation of undesired endo-exo and exo-exo isomers appeared to be unfavorable for high activity in proton reduction (Figure 1.4).[1] Helm *et al*. developed a new complex $[Ni(P^{Ph}_2N^{Ph})_2](BF_4)_2$ ($P^{Ph}_2N^{Ph}$ = 1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane). The ligand $P^{Ph}_2N^{Ph}$ has only one pendant amine, which precluded the possibility of forming the unfavorable orientation. Turnover frequencies of 33,000 s^{-1} of $[Ni(P^{Ph}_2N^{Ph})_2](BF_4)_2$ as HER catalyst in acetonitrile can be calculated.[38] Unfortunately, the stability of this kind of catalyst is not yet ideal: some of

the catalysts decompose with a loss of activity of approximately 10% within 1 hour in an acidic environment.[35]

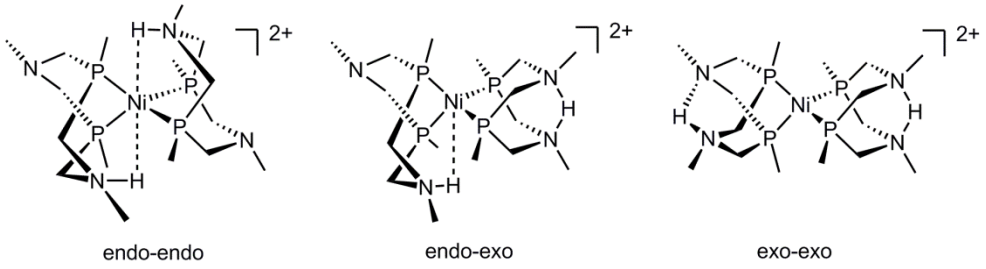

Figure 1.4. Nickel-diphosphane electrocatalysts for proton reduction; different orientations of pendant amines and interactions with protons.[38]

1.3.2 Cobaloxime and cobalt diimine-dioxime complexes

A family of cobalt-based hydrogen evolving catalysts has been reported comprising either two dimethylglyoxime ligands (Figure 1.5a), or a stable tetradentate ligand providing a diimine-dioxime coordination sphere (Figure 1.5b).[39] During the catalytic cycle of proton reduction, the oxime proton from the ligand assists with the proton delivery and is involved in the rate-determining step. The catalytic activity in electrocatalytic proton reduction of the cobalt(III) diimine-dioxime complexes, showing a similar coordination sphere as the cobal(II) dimethylglyoxime compound (also known as cobaloxime) (Figure 1.5), has been studied after that of the cobaloxime.[40-42] It has been suggested that the tetradentate nature of the diimine−dioxime ligand warrants stability of cobal(II) dimethylglyoxime compound against hydrolysis, which is a merit comparing to cobaloxime complexes.[39, 43]

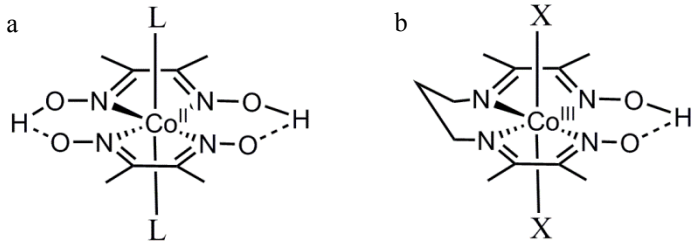

Figure 1.5. General structures of (a) cobalt(II)-dimethylglyoxime compound (cobaloxime compound), L = solvent (H_2O, CH_3CN, DMF) and (b) cobalt(III) diimine-dioxime complex (X = e.g. Br, Cl).[39]

1.3.3 Other molecular catalysts

New classes of molecular catalysts for HER are still being developed and reported over the years (Figure 1.6). Recently, group of Masuda reported a nickel(II) complex with two bidentate phosphanylpyridyl ligand (Figure 1.8a).[44] Catalytic dihydrogen generation was observed even in the absence of proton sources, indicating that the proton transfer is facilitated through the basic site of the amines.

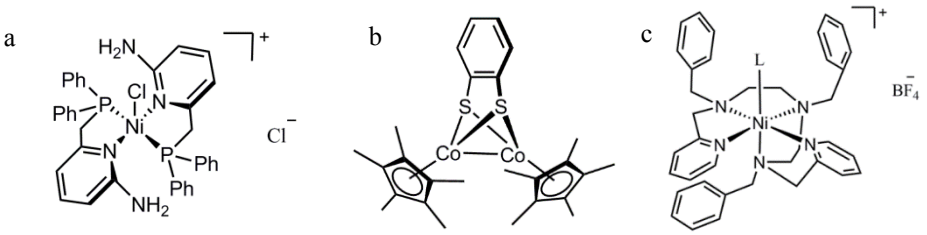

Figure 1.6. Other new classes of molecular catalysts for HER. Schematic drawing of molecular catalysts for proton reduction: a) reported by Tatematsu;[44] b) reported by Tong;[45] c) reported by Zhang.[46]

Additionally, a new type of proton reduction catalytsts based on dinuclear cobalt or CoFe complexes have been reported, although the catalytic activity need to be improved (second-ordered rate constant ca. 4.67 $M^{-2} s^{-1}$) (Figure 1.6b).[45] Noteworthy are the transition metal complexes bearing the pyridine-based pentadentate ligand reported by Sun's group. Complexes with different metal centers and different amine-to-pyridine ratios showed significantly different catalytic activities.[46] The fastest catalyst they investigated is a nickel complexes with a 2 to 3 amine-to-pyridine ratios (see Figure 1.6c). The calculated turnover frequency of this catalyst reaches 1650 mol H_2 $(mol\ cat)^{-1}h^{-1}cm^{-2}$ in neutral aqueous solutions, which is more than one-fold higher than that displayed by the analogous cobalt catalysts at the same applied potential.

In comparison with the intensively studied nickel bisdiphosphane and cobaloxime systems, these new types of electrocatalysts still require more investigations to unravel their exact catalytic mechanism and to optimize their structures in order to achieve more efficient electrocatalysis.

1.4 Electrochemical properties of metal-NHC complexes

1.4.1 N-Heterocyclic carbenes

N-Heterocyclic carbenes (NHCs) are cyclic molecules in which the carbene center is found in the α-position of at least one nitrogen atom.[47] Diez-Gonzalez defined N-Heterocyclic carbenes as "cyclic carbenes, bearing at least one R-amino substituent".[48] Nowadays, NHCs are regarded as "broadly catalytically useful ligands comparable with cyclopentadienyls and phosphines", because of their strong σ electron donating properties and redox innocence.[49, 50] In addition, in some cases metal-to-carbene π-back donation further stabilizes the interaction between the metal center and the carbene. Furthermore, NHC ligands are less sensitive to oxidation than alkyl phosphane ligands.[51] The most common subclasses of NHCs are represented in Figure 1.7. The carbene ligands are recognized as an alternative to phosphane ligands in the field of organometallic chemistry and homogeneous catalysis.[52]

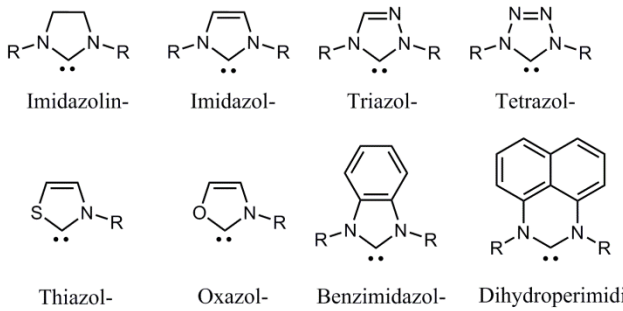

Figure 1.7. Common structures of N-Heterocyclic carbenes. The suffix "ylidene" should be added to obtain the generic name of each NHC subclass.

In some cases binding of the carbene with metal centers may occur through the C4 atom ('abnormal' carbene, Figure 1.8). It is still difficult to achieve selective binding of the NHC through the C4 atom, and a mixture of normal NHC and abnormal NHC complexes is generally obtained.[53, 54] However, methylation of the C2 position of the ligand precursors is a viable method for formation of abnormal NHC complexes.[55]

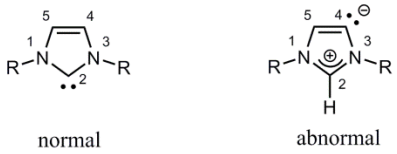

Figure 1.8. Binding sites of normal and abnormal NHC ligands.

1.4.2 N-Heterocyclic carbene complexes and their application

Since Herrmann published an article entitled "Metal Complexes of N-Heterocyclic Carbenes—A New Structural Principle for Catalysts in Homogeneous Catalysis",[56] metal-NHC complexes have received intensive attention in the field of organometallic chemistry and catalysis.[57-60] Various metal-NHC complexes have been synthesized and used as efficient homogenous catalysts for different reactions, such as dehydrogenation,[61, 62], hydrosilylation,[63] C−C coupling reactions,[64-68] hydroamination,[69] and C−H activation.[70] The NHC ligands employed in these homogenous catalysts generally comprise sterically hindered substrates. These bulky auxiliary NHC ligand can help with improving the stability and catalytic performance of the catalysts in homogenous catalytic reactions.[51, 71, 72]

On the other hand, various metal-NHC complexes with a dangling functionality have been designed and synthesized. The hemilabile systems usually comprise a carbene-metal bond in combination with at least one pyridine,[73] phosphane,[74-76] alcohol,[77] or thioether[69, 78] donor atom that during catalysis may dissociate from the metal center. It has been suggested that metal compounds comprising chelating hemilabile NHC ligand systems may display better catalytic activity in comparison to compounds containing a rigid chelating ligand.[77, 79]

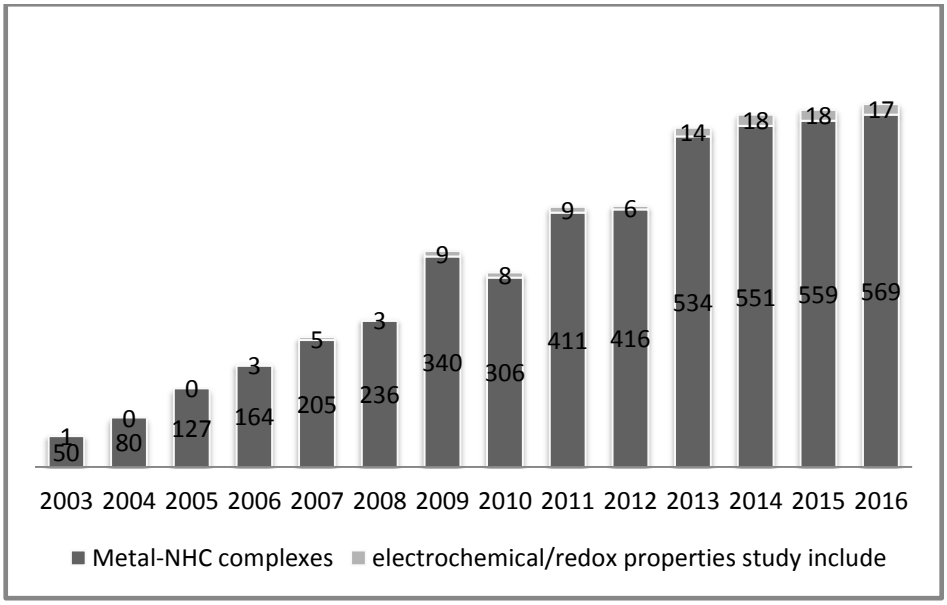

Figure 1.9. Number of publications related to metal-NHC compounds.(until December 2016, using web of science engine)

As carbene ligands are generally regarded as stable auxiliary moieties, research is mainly focused on the synthesis of new metal-NHC compounds and the determination of their catalytic properties. So far, the redox properties of metal-NHC complexes, especially the ones of NHC complexes with functionalized group, have been largely neglected. A search in the Web of Science shows that the electrochemical properties of metal-NHC complexes have been receiving more attention in last four years (Figure 1.9), although such studies still are quite limited in number. Among these studies related to the electrochemical properties of the metal-NHC compounds, reports on metal-NHC compounds as potential electrocatalysts for HER are scarce.[80, 81] Recently reported metal-NHC complexes as catalysts for proton reduction comprise mononuclear cobalt-based compounds with pyridine-functionalized NHC ligands (Figure 1.10).[80, 81]

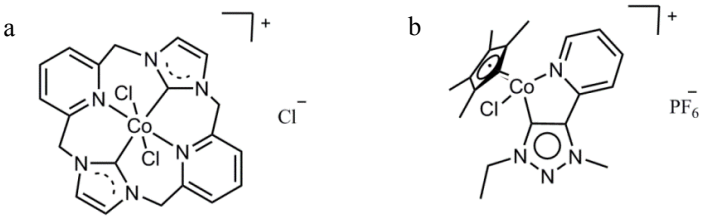

Figure 1.10. Cobalt-NHC complexes that have been studied for their use in HER electrocatalysis from: (a) group of Sakai;[80] (b) group of Sarkar.[81]

1.4.3 Synthesis of metal-NHC complexes

Several methods have been reported for the synthesis of NHC-bearing transition metal complexes. The most accessible synthesis route avoids the use of exotic or unstable reagents and can be handled by 'beginners' in organometallic synthesis.[82] In general, the methods for the preparation of metal-NHC compounds follow a similar recipe: a ligand precursor (azolium salt), metal precursor, and mild base (if necessary) are dissolved in a solvent, and the mixture is stirred with heating if necessary. Such recipes avoid the preparation of the unstable, free carbene.

In recent years the following three synthesis routes have been the most common: 1) the reaction of nickel acetate with the azolium salt under vacuum with the loss of acetic acid;[64, 65, 78, 83] 2) the reaction of a nickel precursor with the azolium salt in presence of a mild base in an atmosphere of an inert gas;[54, 84-87] 3) via the synthesis of a silver-NHC complex by the deprotonation of the azolium salt with Ag_2O, after which the NHC is transferred from the silver ion to a transition metal.[69, 88]

The compounds reported in Chapters 2, 3, 4 of this Thesis were obtained using the first synthesis method whereas the compounds reported in Chapters 5 and 6 were obtained using the second method.

1.5 General mechanism of electrocatalytic proton reduction with molecular catalysts

The mechanism of the hydrogen evolution reaction based on metal-based homogenous electrocatalysts can be simplified to three basic steps (Figure 1.11). The metal center of the molecular catalyst will be reduced first by an electron (step (A)), which is followed by a proton-transfer (step (B)) leading to the formation of a metal hydride. Finally, with the addition of a second electron and a proton dihydrogen is formed and the catalyst is regenerated (step (C)).

Under this mechanism, an anti-correlation was found between step (A) and step (B). When the metal bears more election-withdrawing ligand, the electron density at the metal center will be lower, which makes the metal center easier to be reduced. However, on the other hand the lower electron density at the metal center will make formation of the metal hydride more difficult. Overall, this means that a lower energy cost in step (A) generally results in a larger kinetic barrier in step (B). This anti-correlation between the reduction potential of the metal center and the kinetics of metal-hydride formation is a major challenge to be overcome in the design of catalyst for HER with both low overpotentials and high catalytic rates.[89]

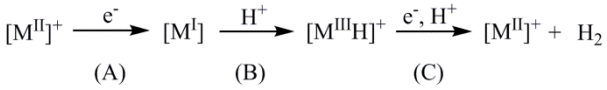

Figure 1.11. Simplified mechanism of the hydrogen evolution reaction. (A): reduction of the metal center; (B): formation of the metal hydride; (C): dihydrogen generation.

The mechanistic pathway shown in Figure 1.11 is only applicable when the metal center of the electrocatalyst takes part in catalytic cycle, and two electron transfer process have been simplified into one-step speed controlled progress.[90, 91]

Inspired by nature, the concept of "proton relay" was introduced in electrocatalytic proton reduction, as discussed in Section 1.3. The proton relay built into molecular catalysts can be an amine,[28, 44] a pyridine[89, 92, 93]. The ligand that is modified with a functional group acting as a proton relay becomes less innocent and takes part in the catalytic cycle (Figure 1.12). First the ligand can be protonated, after which the metal center is reduced. Two different proton transfer pathways may be operative. Either the proton is directly transferred from ligand to the reduced metal center to form a metal hydride, which is followed by the second electron and proton transfer (pathway I in Figure 1.12);[29, 35] or the reduced metal center accepts the second proton and a second electron to form a metal-hydride which then reacts with the proton carried by the ligand to generate dihydrogen (pathway II in Figure 1.12).[93] The intramolecular proton transfer would break the anti-correlation between reduction potential of the metal center and the kinetics of metal-hydride formation. Thus the incorporation of a proton relay is a promising design principle to improve the efficiency of electrocatalysts for proton reduction.

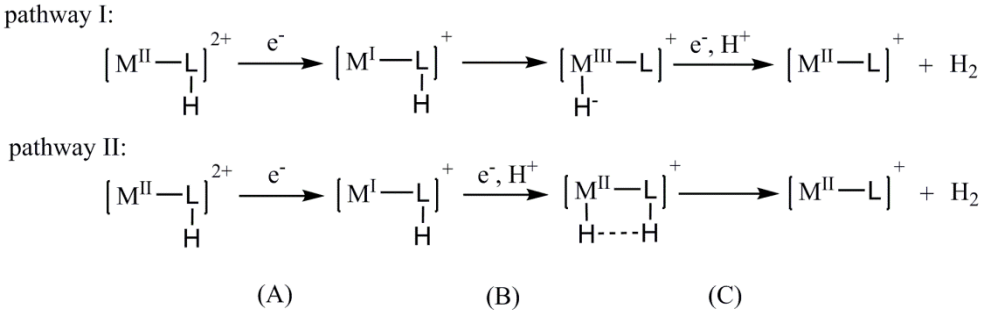

Figure 1.12. Proposed pathways I and II for dihydrogen evolution by a molecular catalyst involving a proton relay. (A): reduction of the metal center; (B): formation of metal hydride; (C): hydrogen generation.

1.6 Aim and outline of this thesis

The research described in this thesis focused on the preparation of S/N functionalized carbene ligands and their transition metal complexes, and the exploration of their application as electrocatalysts for proton reduction. In Chapter 1, an overview is given of

homogenous molecular electrocatalysts that are inspired by natural systems and general mechanisms for the electrocatalytic hydrogen evolution reaction (HER) have been addressed. It was found that the use of transition metal carbene complexes as electrocatalysts for HER is still an unexplored field of research.

In Chapter 2, two sulfur-functionalized carbene ligands and their dinuclear nickel-NHC complexes are described. In addition two carbene ligands functionalized with both a thiolate donor and a pyridyl group and their dinuclear nickel compounds are described. Electrochemical investigations revealed that the nickel-NHC complexes with the additional pyridine proton relays show better electrocatalytic activity in HER.

Four mononuclear nickel compounds with chelating biscarbene ligands comprising pendant pyridyl arms are reported in Chapter 3. The redox properties and catalytic activity in proton reduction of the complexes is influenced by the nature of the NHC carbene group in the chelating ligands as well as the counter ions present in the nickel compounds.

In Chapter 4, the synthesis and characterization is reported of two new mononuclear nickel complexes bearing two pyridine-functionalized carbene ligands. The ligands described in this Chapter are a potentially bidentate NHC ligand with one pyridyl and one benzyl pendant arm, whereas the other ligand is potentially tridentate with two pyridyl pendant arms. Mononuclear nickel compounds are formed bound to two ligands coordinating in a bidentate mode; as a result the nickel compound of the potentially tridentate ligand has two unbound pyridyl groups that can act as a nearby proton binding site for electrocatalysis. This results not only in a higher activity in electrocatalytic proton reduction, but also in a smaller overpotential for proton reduction.

In Chapter 5 the synthesis is described of two new pyridine-amide functionalized (benz)imidazolium salts. Using these (benz)imidazolium salts as ligand precursors two new square-planar nickel-NHC compounds were obtained, whose redox potentials and electrocatalytic behavior are reported. The catalytic activity of the two compounds in HER has been studied in organic solvent using acetic acid as the proton source. Although the nickel compound of the imidazole-based carbene is water soluble, its poor stability in acidic environments restricts further exploration of its application.

With the aim to understand how different metal centers affect the redox behavior and catalytic activity in HER, two cobalt compounds bearing pyridine-amide NHC ligands have been prepared and are reported in Chapter 6. Two different ligands are used in the compounds described in this Chapter: a potentially tridentate NHC ligand with one pyridine-amidate arm and one benzyl pendant arm, whereas the other ligand is potentially tetradentate with two pyridyl pendant arms. The cobalt(III) centers in the obtained compounds are in octahedral geometries bound by two tridentate ligands. Due to the large ligand-field splitting and the coordination geometry, the cobalt ions are reduced only at quite negative potentials. Both of the Co(III) complexes exhibit electrocatalytic activity in

HER, but the compound with the additional free unbound pyridyl groups revealed twice higher catalytic activity compared to the benzyl-substituted analogue.

This thesis is concluded with a general summary and outlook in Chapter 7.

Parts of this thesis have been published (Chapter 3),[94] have been submitted for publication or are in preparation for publication.

1.7 References

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