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

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Citation

Luo, S. (2017, October 17). *Transition metal compounds with S/N-functionalized NHC ligands: structures, redox properties and electrocatalytic activity*. Retrieved from <https://hdl.handle.net/1887/54936>

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Issue Date: 2017-10-17

CHAPTER 4

Free Pyridyl Groups as Proton Shuttles in Pyridine-Functionalized Ni-NHC Complexes

Two nickel(II) complexes $[\text{Ni}(\mathbf{L1})_2]\text{Br}_2$ and $[\text{Ni}(\mathbf{L2})_2]\text{Br}_2$ ($\mathbf{HL1Cl}$ = 1-benzyl-3-(pyridin-2-ylmethyl)benzimidazolium chloride; $\mathbf{HL2Cl}$ = 1,3-bis(pyridin-2-ylmethyl)benzimidazolium chloride) were synthesized as non-noble metal catalysts for the electrocatalytic hydrogen evolution reaction. Single crystal X-ray crystallography revealed that the nickel metal centers in both compounds are found in a square-planar geometry with like donor atoms of the two bidentate ligands in cis positions. The redox properties of the two compounds were studied using cyclic voltammetry. Electrocatalytic proton reduction experiments using these complexes were performed in DMF with acetic acid as the proton source. Compound $[\text{Ni}(\mathbf{L2})_2]\text{Br}_2$, containing two 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 for the pyridyl group acting as proton relay during the proton reduction process.

4.1 Introduction

Ligands with pendant, non-coordinating Lewis bases have received ample attention from inorganic chemists, because the additional Lewis base might affect the performance of molecular catalysts by providing binding sites for protons.^[1-4] Notably, the introduction of base-functionalized pendant arms in the ligands of molecular catalysts has been quite popular in the electrochemical research area for assisting in proton-coupled electron-transfer processes.^[5-8] For example, Ni-diphosphane complexes bearing pendant amines as proton-binding sites have been shown to exhibit extremely high activity (TOF > 100,000 s⁻¹) in electrocatalytic H₂ evolution.^[9] The molecular design of catalysts using pendant Lewis bases is inspired by the structures of natural enzymes, in which nearby amino acids close to the active site play a role in temporary proton storage.^[8-11] With the aim to investigate the role of the pendant amine group in dihydrogen evolution, DuBois's group compared the electrocatalytic activity of the compound [Co(P^{Ph}₂N^{Ph}₂)(CH₃CN)₃](BF₄)₂ (P^{Ph}₂N^{Ph}₂ = 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane), incorporating pendant amines, with that of the compound [Co(dppp)(CH₃CN)₃](BF₄)₂ (dppp = 1,3-bis(diphenylphosphanyl)propane) without a pendant amine.^[10] Although the two cobalt compounds are equipped with similar diphosphane ligands, the investigations showed that only the former one containing a pendant amine group possesses catalytic activity in proton reduction.

Not only secondary or tertiary amines but also the pyridyl group can realize the function as a proton relay.^[7, 12-14] Recent DFT calculations on a pyridyl-functionalized cobalt diiminedioxime catalyst have been proposed that the non-coordinated pyridyl pendant group may help to reduce the energetic barrier for hydride formation in electrolysis.^[7] Indeed it has been suggested that the pyridyl group may facilitate the reaction of an intermediate metal-hydride with a nearby proton.^[14]

In the research described in this paper, we aimed to explore the role of uncoordinated pyridyl groups in the proton reduction activity of nickel compounds with carbene ligands. N-heterocyclic carbenes (NHCs) are widely recognized as innocent ligands in organometallic chemistry.^[15] In the absence of other redox-active functional groups, the influence of a pendant pyridine arm in electrocatalysis might be more readily understood.

In the design of metal-carbene complexes pyridine-functionalized (benz)imidazole-2-ylidene ligands have received a lot of attention. Coordination compounds of these functionalized carbenes have been reported for a large array of metal centers such as Ag, Hg, Pd, Au, Ni, Ru and Pt.^[16-21] For one and the same ligand, the configuration of the complexes will largely depend on the properties of the metal center. Setting the ligand precursor 1,3-bis(pyridin-2-ylmethyl)benzimidazolium chloride HL2Cl as an example, Pt^{II} and Pd^{II} ions can coordinate with one ligand with both pyridines bound in square-planar geometries;^[16, 21] Ru^{II} ions may bind two ligands without free pyridine arms in an octahedral geometry,^[21] whereas Ag^I and Au^I ions can bind either one^[18] or two ligands^[20]

with both pyridine arms non-coordinated. However, none of these studies report the electrocatalytic properties of the compounds.

Herein, we report the synthesis and characterization of two new nickel complexes of pyridyl-functionalized carbene ligands based on benzimidazole and the study of their electrocatalytic activity in H_2 evolution. By comparing these two related compounds we sought to determine whether the presence of pendant pyridyl groups could enhance H_2 evolution by acting as an intramolecular proton shuttle in electrocatalysis.

4.2 Results and Discussion

4.2.1 Synthesis of the complexes

The ligand precursors 1-benzyl-3-(pyridin-2-ylmethyl)benzimidazolium chloride (**HL1Cl**)^[22] and 1,3-bis(pyridin-2-ylmethyl)benzimidazolium chloride (**HL2Cl**)^[21] were synthesized following literature methods with small modifications, in good yields of 77% and 87%, respectively. The nickel(II) bromide compounds $[Ni(\mathbf{L1})_2]Br_2$ and $[Ni(\mathbf{L2})_2]Br_2$ were obtained as yellow-colored powders from a melt of nickel acetate with these ligand precursors in tetrabutylammonium bromide (TBAB) in vacuum (Figure 4.1). The complexes were characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The absence in the 1H NMR spectra of the characteristic downfield signals for the imidazolium NCHN protons (10 ~10.5 ppm) in both complexes indicates the successful creation of the carbene moieties and their coordination to the nickel(II) center. Whereas the sharp and clear 1H NMR spectrum of $[Ni(\mathbf{L1})_2]Br_2$ is in agreement with a low-spin square-planar nickel ion, the 1H NMR spectrum of $[Ni(\mathbf{L2})_2]Br_2$ showed broad peaks, indicating high-spin five-coordinate or octahedral nickel species (see Section 4.2.2. and Appendix IV Figure AIV.5). The ESI-MS spectra exhibit base peaks corresponding to the $[M - 2Br]^{2+}$ cationic complexes. Crystalline samples of the Ni compounds were dried in vacuo before elemental analysis was performed; however, the analysis results indicated that some amount of lattice water molecules found in the crystal lattice was not totally removed. During synthesis of the complexes the chloride counter ions of the ligands were replaced by the bromide from TBAB.

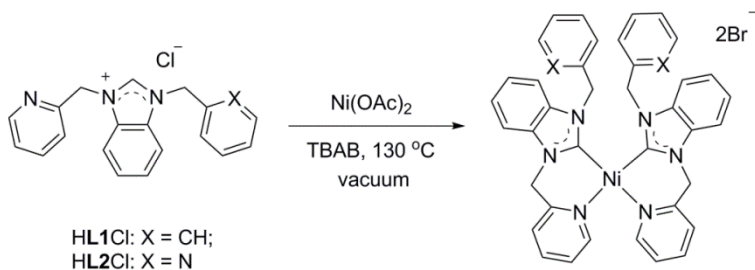


Figure 4.1. Synthesis route of the compounds $[Ni(\mathbf{L1})_2]Br_2$ and $[Ni(\mathbf{L2})_2]Br_2$.

4.2.2 Structural characterization of the complexes

Single crystals of $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ suitable for X-ray structure determination were obtained using the liquid-liquid diffusion method. The crystallographic and refinement data are collected in Appendix IV. Projections of the structures of the cationic nickel centers in $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ are shown in Figure 4.2. Selected bond distances and angles are provided in Table 4.1.

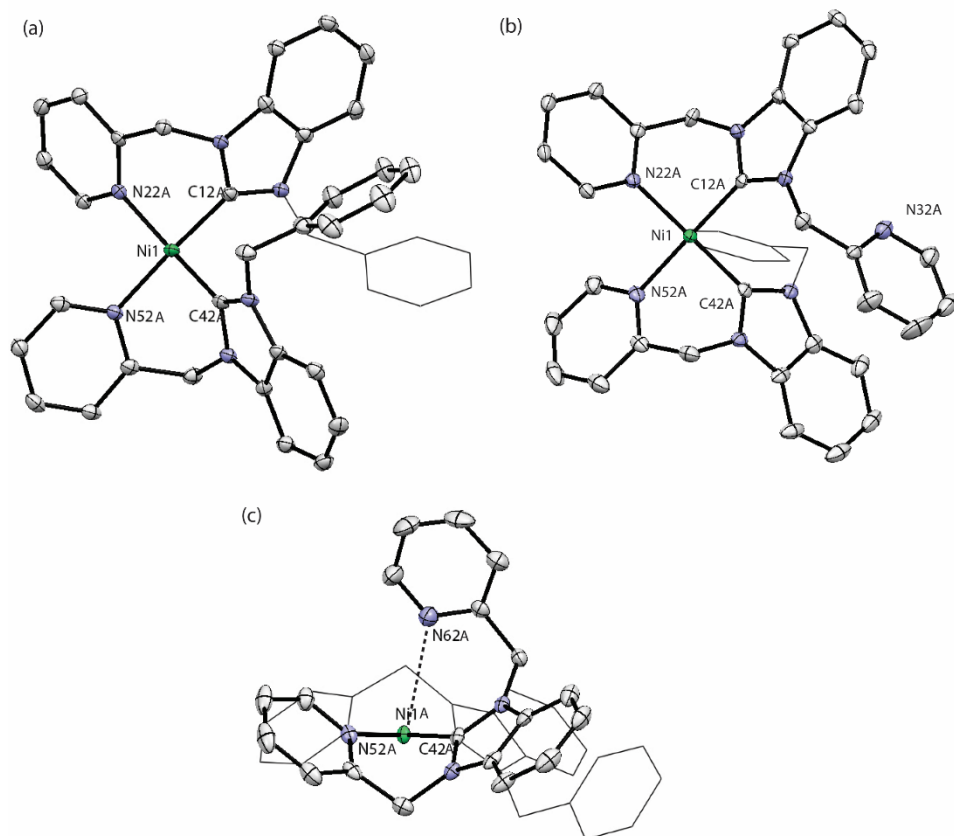


Figure 4.2. Displacement ellipsoid plots of the cationic complexes (a) $[\text{Ni}(\text{L1})_2]\text{Br}_2$, (b) and (c) $[\text{Ni}(\text{L2})_2]\text{Br}_2$ are drawn at 50% probability level with selected atom numbering. For clarity the hydrogen atoms, bromide ions, solvent molecules and the lattice water molecules are omitted and parts of the ligands are displayed in wireframe.

The compound $[\text{Ni}(\text{L1})_2]\text{Br}_2$ crystallizes in the space group $P-1$, whereas the compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ crystallizes in the monoclinic space group Cc . Both compounds crystallized with two independent cationic complexes, four bromide ions and some disordered solvent molecules in the asymmetric unit. The coordination environment of the nickel centers in the two independent molecules is very similar, and for both compounds, the relevant bond distances and angles from only one of the two molecules are provided. The nickel ion in $[\text{Ni}(\text{L1})_2]^{2+}$ is found in a four-coordinate square planar geometry in which two ligands are

bound in a bidentate C, N fashion with the C and N donor atoms in mutual *cis* positions (Figure 4.2a). Although the ligand **L2** potentially is a tridentate ligand, in $[\text{Ni}(\text{L2})_2]^{2+}$ the nickel ion is also found in a square-planar geometry with donor atoms of the two bidentate ligands in *cis* positions (see Figure 4.2b).

The Ni–C bond distances in the two compounds are around *ca.* 1.87 Å whereas the Ni–N bonds are *ca.* 1.94 Å. In comparison with the reported Ru,^[21] Pd,^[16, 17] and Au compounds,^[20] both the Ni–C and Ni–N bond distances are shorter by 0.2 Å, which can be attributed to the smaller ionic radius of the nickel ion. In the compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ the nitrogen atom of one of the pendant pyridyl groups resides in an apical position of the nickel center at a distance of *ca.* 2.98 Å; if this interaction is taken into account the geometry of the nickel ion may be regarded as a distorted square pyramid (Figure 4.2c). This additional binding of the pyridyl group may be the cause of the broad signals observed in the ¹H NMR spectra of this compound, as the nickel center in the five-coordinate (or octahedral in solution) species may be in the high-spin state.

The square-planar geometries of the nickel ions in $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ were evaluated with an equation derived from a report by Yang.^[23, 24] The largest and second-largest L–Ni–L angles in $[\text{Ni}(\text{L1})_2]\text{Br}_2$ are 171.7(1)° and 174.0(1)°, resulting in a τ_4 value of 0.100, indicative of only a very slight distortion of the square-planar geometry. For compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ a τ_4 value of 0.023 is calculated, indicating that the geometry of the central ion (not taking into account the axial coordination of pyridine) is close to the ideal square-planar geometry.

Table 4.1. Selected bond distances (Å) and angles (°) of the compounds $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$.

	$[\text{Ni}(\text{L1})_2]\text{Br}_2$	$[\text{Ni}(\text{L2})_2]\text{Br}_2$
Ni1–C12A	1.880(3)	1.860(4)
Ni1–C42A	1.872(2)	1.863(4)
Ni1–N22A	1.947(2)	1.938(4)
Ni1–N52A	1.953(2)	1.950(4)
Ni1...N62A	/	2.984(4)
N52A–Ni1–N22A	95.10(9)	91.25(15)
N52A–Ni1–C42A	86.47(10)	87.32(17)
C42A–Ni1–C12A	93.12(11)	94.33(18)
C12A–Ni1–N22A	86.15(10)	87.09(17)
N52A–Ni1–C12A	174.00(10)	178.08(18)
C42A–Ni1–N22A	171.71(11)	178.56(17)

Complexes of other metal ions bearing the ligand **L2** have been reported by Adhikary *et al.*^[21] Pt(II) was found to coordinate with one ligand **L2** to form the complex $[\text{Pt}(\text{L2})\text{Cl}]\text{PF}_6$ with the Pt(II) ion in a square-planar geometry, whereas the Ru(II) ion binds two ligands **L2** to form the compound $[\text{Ru}(\text{L2})_2](\text{PF}_6)_2$ with the ruthenium center in an octahedral geometry. A structure has been reported of a nickel compound containing two 1,3-

bis(pyridin-2-ylmethyl)imidazolium ligands, in which similar to $[\text{Ni}(\text{L2})_2]\text{Br}_2$ the ligands are arranged with like donor atoms in *cis* positions.^[17] The nickel ion in this compound is also in a square-planar geometry and one of the pendant pyridyl groups resides in an apical position of the nickel center at a distance of 3.345 Å, significantly larger than the one in $[\text{Ni}(\text{L2})_2]\text{Br}_2$.

4.2.3 Electrochemical properties of the complexes

The redox potentials of the nickel compounds were evaluated using cyclic voltammetry. The electrochemical potentials given in this Chapter are all referred to Ag/AgCl. The cyclic voltammogram (CV) of $[\text{Ni}(\text{L1})_2]\text{Br}_2$ shows two reductive waves, the first of which is reversible at a scan rate of 0.1 V/s (Figure 4.3). The reversible redox process located at $E_{1/2} = -1.00$ V vs. Ag/AgCl is diffusion controlled, as shown by the linear dependence of the peak current on the square root of the scan rate (Figure AIV.1). This redox wave is characterized by a peak-to-peak separation ΔE_p of 80 mV (in our conditions ΔE_p for the $\text{Fc}^{0/+}$ couple was found to be 95 mV), indicating a one-electron transfer. Thus, we assign this first wave to the Ni(II)/Ni(I) redox process. The quasi-reversible reduction event at -1.29 V is tentatively ascribed to a Ni(I)/Ni(0) redox process. The assignment of these two redox waves to nickel-centered reduction events is supported by the fact that the ligand precursor HL1Cl is electrochemically inert in the range of 0 to -1.5 V. Upon increasing scan rate the second reductive wave at -1.29 V gradually becomes reversible, whereas with decreasing scan rates the wave becomes less reversible (see Figure AIV.2). This behavior indicates the occurrence of a dissociative electron transfer (DET) process,^[25] meaning that after the reduction of $[\text{Ni}^{\text{II}}(\text{L1})_2]^{2+}$ to $[\text{Ni}^{\text{I}}(\text{L1})_2]^+$ a stepwise chemical reaction is coupled to the second electron transfer, generating a new product.

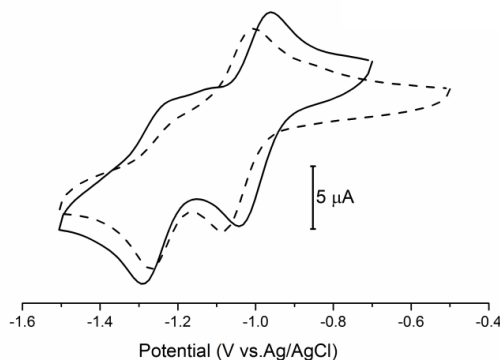


Figure 4.3. CVs of the compounds $[\text{Ni}(\text{L1})_2]\text{Br}_2$ (solid line) and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ (dashed line). Experiments were performed at a complex concentration of 1 mM in DMF with 100 mM TBAP as the supporting electrolyte at scan rate 0.1 V/s, using a glassy carbon working electrode.

Similarly, the CV of compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$, containing two uncoordinated pyridyl groups, shows one reversible redox process at $E_{1/2} = -1.05$ V followed by an irreversible reductive process at -1.27 V (Figure 4.3). The first reversible redox process of $[\text{Ni}(\text{L2})_2]\text{Br}_2$ is at a slightly more negative potential compared to that of $[\text{Ni}(\text{L1})_2]\text{Br}_2$, indicating a slightly

higher electron density at the nickel ion because of the interaction between the nickel center and one of the pendant pyridyl groups in solution. The reversibility of the second reductive wave at $E_{pc2} = -1.29$ V of this tetrapyridyl-functionalized compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ appeared not to depend on the scan rate. Even when the scan rate was increased to 500 mV/s the second reductive process still was quasi-reversible (see Figure AIV.3). The electrochemical data are summarized in Table 4.2.

Table 4.2. Electrochemical data of the nickel compounds.^[a]

	E_{pc1} [V]	E_{pa1} [V]	$E_{1/2}$ [V] (ΔE_p [mV])	E_{pc2} [V]
$[\text{Ni}(\text{L1})_2]\text{Br}_2$	-1.04	-0.96	-1.00 (80)	-1.29
$[\text{Ni}(\text{L2})_2]\text{Br}_2$	-1.09	-1.01	-1.05 (80)	-1.27

[a] Potentials are given vs. the Ag/AgCl electrode. All voltammograms were recorded in DMF. Conditions: scan rate = 0.1 V/s, compound (1 mM), TBAP (0.1 M), using glassy-carbon working electrode.

4.2.4 Electrocatalytic activity for proton reduction in DMF

The two compounds were examined for their activity in the electrocatalytic proton reduction in DMF, using acetic acid (HOAc) as a weak proton source. For each scan the working electrode was freshly polished.

Compared to the CV of acetic acid (10 mM) in DMF, after addition of either the complex $[\text{Ni}(\text{L1})_2]\text{Br}_2$ or $[\text{Ni}(\text{L2})_2]\text{Br}_2$ a relatively large current indicating the reduction of protons was observed at a potential around -2 V vs Ag/AgCl (Figure 4.4). Two small irreversible peaks appear before the electrocatalytic wave, approximately at -1.04 V and -1.17 V for $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and at -1.09 V and -1.20 V for $[\text{Ni}(\text{L2})_2]\text{Br}_2$. These peaks were broad and close to each other making it difficult to identify them separately. Only a broad plateau can be recognized when showing these waves together with the following catalytic wave. A zoom of CVs (ranging from -0.5 V to -1.5 V) is provided in Figure AIV.4.

For both compounds the first small reductive wave occurs at the exact same potential where the metal-centered $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ reduction process was observed (Section 4.2.3 and Figure AIV.4). The second small reductive potential occurs at a more positive potential compared to the ones in the absence of acid, indicating that there is a chemical step before the second electron transfer takes place. The electrocatalysis therefore most likely proceeds via an ECEC mechanism.^[26] The catalytic onset potential for proton reduction in presence of $[\text{Ni}(\text{L2})_2]\text{Br}_2$ (at -1.6 V) occurs at a lower potential than in the presence of $[\text{Ni}(\text{L1})_2]\text{Br}_2$ (at -1.8 V). Furthermore, in the same conditions the compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ shows the larger catalytic current, indicating a higher electrocatalytic activity than that of $[\text{Ni}(\text{L1})_2]\text{Br}_2$ (Figure 4.4).

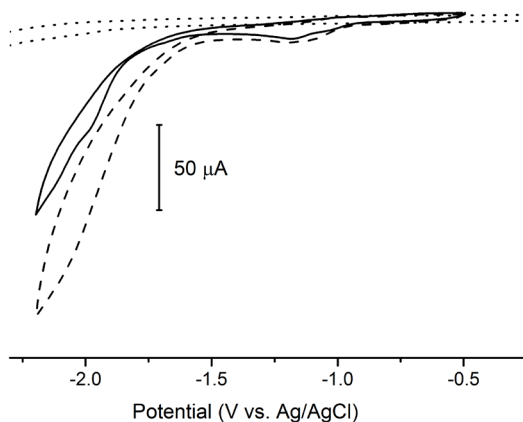


Figure 4.4. CVs of 10 mM acetic acid in presence of 1mM complex $[\text{Ni}(\text{L1})_2]\text{Br}_2$ (solid line), in the presence of 1mM complex $[\text{Ni}(\text{L2})_2]\text{Br}_2$ (dashed line) and in the absence of a complex (dotted line) in DMF containing 0.1 M TBAP as supporting electrolyte at scan rate 0.1V/s, using glassy carbon working electrode.

With the aim to compare the electrocatalytic activity of the two compounds in a more quantitative way, controlled-potential coulometry experiments (CPC) were carried out. The charge consumptions over time of solutions containing just the pure acid or each of the catalysts were also recorded separately as references. The charge accumulation graphs show that over a period of 10 minutes charge consumption is negligible for the solutions containing only acid or only the nickel compounds (Figure 4.5). However, for solutions containing both acid and one of the nickel catalysts continuous charge consumption was recorded. The quantity of dihydrogen gas generated during the CPC experiments can be estimated from the charge consumption of solutions containing both the nickel compound and the acid, after subtraction of the charge consumption of the blanks. The two complexes $[\text{Ni}(\text{L1})_2]\text{Br}_2$ or $[\text{Ni}(\text{L2})_2]\text{Br}_2$ are estimated to produce 3×10^{-4} mmol and 5×10^{-4} mmol H_2 respectively in 10 min in presence of 6×10^{-3} mmol catalyst at a potential of -1.80 V (assuming that all electrons are used in proton reduction). The complex $[\text{Ni}(\text{L2})_2]\text{Br}_2$ equipped with two additional pendant pyridine groups showed almost doubled charge consumption, indicating a higher catalytic activity.

4.2.5 Discussion of the proposed mechanism

Generally, the mechanism of a hydrogen-evolution process based on a metal-containing homogenous catalyst can be divided in three steps. The first step is the reduction of the metal center; if the metal center is equipped with an electron-withdrawing ligand, the metal center is more readily reduced. The second step is the formation of the metal hydride intermediate, which is facilitated by the presence of an electron-donating ligand. The third step is the generation of dihydrogen: the metal-hydride intermediate reacts with another proton and electron to release dihydrogen.^[27] Based on this mechanism, generally a molecular catalyst will work at a small overpotential but with relatively low efficiency (for

electron-withdrawing ligands), or with high efficiency but at a relatively large overpotentials (for electron-donating ligands).

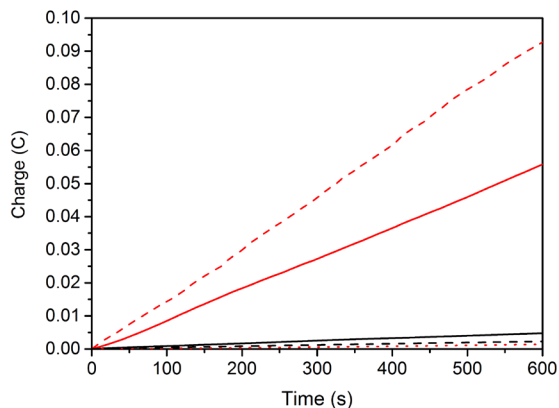


Figure 4.5. Charge vs. time plot over 600 s during CPC at potential of -1.8 V. Black lines: compounds in absence of acid; Red lines: compounds in presence of 50 mM acetic acid (solid = $[\text{Ni}(\text{L1})_2]\text{Br}_2$, dashed = $[\text{Ni}(\text{L2})_2]\text{Br}_2$); Dotted red line: 50 mM acetic acid only.

As discussed in the previous section, in absence of acid, the ligand **L2** is the more electron donating so that the nickel center in $[\text{Ni}(\text{L2})_2]\text{Br}_2$ is reduced at more negative potentials. If the complex $[\text{Ni}(\text{L1})_2]\text{Br}_2$ follows the aforementioned catalytic mechanism, it will show lower catalytic activity but at a smaller overpotential than the pyridine-substituted analogue $[\text{Ni}(\text{L2})_2]\text{Br}_2$. Unexpectedly, the compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ not only shows higher electrocatalytic activity but also a smaller overpotential (Figure 4.4). Thus, the presence of the free pyridyl pendant arms in the compound $[\text{Ni}(\text{L2})_2]\text{Br}_2$ apparently reduces the overpotential for the electrocatalytic proton reduction. The additional pyridyl groups act as an intramolecular proton acceptor and proton shuttle assisting in the generation of dihydrogen.^[7] Based on the assistance of the pyridyl groups for complex $[\text{Ni}(\text{L2})_2]\text{Br}_2$ the catalytic mechanism probably can be described as shown in Figure 4.6. Firstly, in the presence of acid the non-coordinated pyridyl arms are protonated. Then the metal center is reduced to Ni^{I} , followed by the formation of a metal-hydride. Finally the hydride reacts with the proton on the pyridyl arm with the release of dihydrogen.

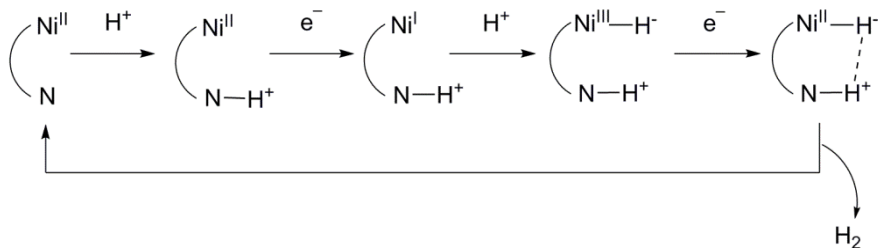


Figure 4.6. Proposed mechanism of the electrocatalytic reduction of protons by $[\text{Ni}(\text{L}2)_2]\text{Br}_2$.

4.3 Conclusion

Two nickel(II) complexes $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ with different ligands were synthesized as non-noble metal molecular catalysts for the hydrogen evolution reaction. The nickel center in both compounds is in a square-planar geometry with two bidentate ligands in *cis* arrangements. The binding of two potentially tridentate ligands in this configuration in the structure of $[\text{Ni}(\text{L2})_2]\text{Br}_2$ results in the presence of two free pyridyl groups. The redox properties of the two complexes were determined using cyclic voltammetry and the electrocatalytic dihydrogen generation with these complexes in DMF was studied using acetic acid as the proton source. Of the two compounds, the complex $[\text{Ni}(\text{L2})_2]\text{Br}_2$ containing two free pyridyl groups exhibited not only the higher activity in electrocatalysis, but also a smaller overpotential for proton reduction. This result indicates that the presence of the free pyridyl groups help to break the anti-correlation between the energy of the reduction and the catalytic activity. The comparison of the catalytic properties of these two related structures (both with redox-innocent carbene backbones) provide convincing experimental evidence of the pyridyl group acting as proton relay during the proton reduction process.

4.4 Experimental

4.4.1 Materials

Commercial chemicals were used without further purification. Acetonitrile and diethyl ether were obtained from a PureSolv MD5 solvent dispenser. Dry methanol and dimethylformamide were prepared by adding molecular sieves into commercial anhydrous solvent. All air-sensitive reactions were performed under argon or dinitrogen gas using standard Schlenk techniques unless mentioned otherwise.

4.4.2 Analytical methods

^1H and ^{13}C spectra were recorded on a Bruker 300 DPX/Bruker 400 AV spectrometer. Mass spectra were obtained using a Finnigan Aqua Mass Spectrometer (MS) with electrospray ionization (ESI). Elemental analyses were performed by the Mikroanalytisches Laboratorium Kolbe, Germany.

Cyclic voltammetry was recorded with an Autolab PGstat10 potentiostat controlled by GPES4 software under argon. A 3 mm diameter glassy carbon electrode was used as working electrode and platinum as the counter electrode. The experimental reference was an Ag/AgCl electrode in the electrolyte solution (TBAP). Cyclic voltammetry was performed in dry DMF with 0.1 M tetrabutylammonium hexafluoridophosphate (TBAP) as the supporting electrolyte under a stream of argon at room temperature. All potentials are given versus Ag/AgCl in this Chapter. Ferrocene was added after each experiment as an internal standard. Under these conditions the $\text{Fc}^{0/+}$ couple was located at $E_{1/2} = 0.510$ V vs.

Ag/AgCl with a ΔE_p of 95 mV. The working electrode surface was polished, ultrasonically cleaned and rinsed before each single CV measurement.

Controlled-potential coulometry (CPC) experiments were carried out with an Autolab PGstat10 potentiostat controlled by GPES4 software under argon. A 3 mm diameter glassy carbon electrode was used as working electrode and platinum as the counter electrode. 1 mM complex and 50 mM acetic acid were added in 6 mL dry degassed DMF with 0.1 M tetrabutylammonium hexafluoridophosphate (TBAP) as the supporting electrolyte under a stream of argon at room temperature. A CPC experiment was run at -1.8 V for 600 s, while the solution was stirred continuously. The blank and reference CPC experiments (only acid or only catalyst added) were performed using the same conditions.

4.4.3 Single crystal X-ray crystallography

All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7^[28, 29] and was refined on F^2 with SHELXL-2014.^[28, 29] Numerical absorption correction based on gaussian integration or analytical numeric absorption correction over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23 or AFIX 43 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms. For $[\text{Ni}(\text{L1})_2]\text{Br}_2$, the H atoms attached to O1W (ordered lattice water molecule) and O2W (only for the major component of the disorder) could be retrieved from difference Fourier maps. Their coordinates were refined freely but the O–H and H...H distances were restrained to be 0.84(1) and 1.33(1) Å, respectively. For $[\text{Ni}(\text{L2})_2]\text{Br}_2$, the O–H and H...H distances were restrained to be 0.84(3) and 1.33(3) using the DFIX instruction. The atoms attached to O4W, O5W, O6W, O7W, O8W and O9W (partially occupied or disordered lattice water molecules) could not be retrieved.

Additional note:

The structure of $[\text{Ni}(\text{L1})_2]\text{Br}_2$ is partly disordered. One phenyl group (C61A-C66A) and one Br^- counter ion are found disordered over two orientations; the occupancy factors of the major components of the disorder refine to 0.59(4) and 0.923(5), respectively. One of the three lattice water molecule (O2W) is disordered over three orientations, and the occupancy factors refine to 0.808(3), 0.109(3) and 0.083(3). The occupancy of the lattice water molecule O3W was refined freely, and its value refines to 0.639(8). The H atoms attached to O3W could not be retrieved. ADDSYM detects a pseudo translation of $\frac{1}{2} \mathbf{a} + \frac{1}{2} \mathbf{c}$. However, the conformations of the two crystallographically independent molecules are different as the orientations of the phenyl groups are significantly different.

The structure of $[\text{Ni}(\text{L2})_2]\text{Br}_2$ is partly disordered. One of the pyridine rings (from molecule A) is found to be disordered over two orientations, and the occupancy factor of the major component of the disorder refines to 0.52(2). In the asymmetric unit, there are five Br^- sites with all occupancies lower than 1. Two sites (Br1 and Br2) are ordered, and their occupancy factors refine to 0.940(2) and 0.942(2), respectively. The remaining counter ions ($\text{Br3}/\text{Br3}'$, $\text{Br4}/\text{Br4}'$ and $\text{Br5}/\text{Br5}'$) are disordered over two orientations. The occupancy factors for Br3 , $\text{Br3}'$, Br4 , $\text{Br4}'$, Br5 and $\text{Br5}'$ refine to 0.853(3), 0.086(3), 0.624(2), 0.0494(15), 0.391(2) and 0.1149(16), respectively. The sum of all occupancies factors for the Br^- counterions was restrained to be 4 using the SUMP instruction. The occupancy factors for $\text{O4W}/\text{O4W}'$ (disordered), $\text{O5W}/\text{O5W}'$ (disordered), O6W , O7W , O8W and O9W refine to 0.434(11)/0.566(11), 0.715(8)/0.285(8), 0.674(15), 0.671(16), 0.429(18) and 0.41(2), respectively.

4.4.4 Ligand and complex synthesis

N-Pyridylmethyl-benzimidazole,^[30] ligand precursors HL1Cl ,^[22] HL2Cl ,^[21] and the complexes $[\text{Ni}(\text{L1})_2]\text{Br}_2$ and $[\text{Ni}(\text{L2})_2]\text{Br}_2$ ^[31] were synthesized following literature methods with small modifications.

$[\text{Ni}(\text{L1})_2]\text{Br}_2$

HL1Cl (0.67 g, 2 mmol), anhydrous $\text{Ni}(\text{OAc})_2$ (0.17 g, 1 mmol) and tetrabutylammonium bromide (1.5 g) were weighed into a 10 mL round-bottomed flask and dried for 4 hours at 80 °C in a Schlenk setup under vacuum. The reaction mixture was stirred for 48 hours at 130 °C under vacuum. The mixture was then cooled to room temperature and triturated with H_2O . The water layer was washed with DCM (3×20 mL) and evaporated to dryness. The remaining solid was dissolved in a mixture of MeCN and methanol and a yellow crystalline solid was obtained using liquid to liquid diffusion method with diethyl ether in 12% yield (90 mg). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.26 – 8.13 (m, 4H), 8.12 – 7.99 (m, 4H), 7.48 (q, J = 8.0, 7.1 Hz, 4H), 7.32 (dt, J = 15.3, 8.0 Hz, 4H), 7.10 – 6.94 (m, 10H), 6.82 (d, J = 15.5 Hz, 2H, *N-CHH-Ph*), 6.47 (d, J = 15.6 Hz, 2H, *N-CHH-Ph*), 5.53 (d, J = 16.4 Hz, 2H, *N-CHH-Py*), 5.05 (d, J = 16.4 Hz, 2H, *N-CHH-Py*). ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) δ 170.32, 154.74, 153.15, 142.04, 141.29, 134.78, 134.05, 133.64, 133.54, 128.33, 127.59, 126.02, 125.06, 124.34, 124.15, 112.16, 111.52, 50.98, 50.54. ESI-MS found (calculated): $[\text{M} - 2\text{Br}]^{2+}$ m/z 328.1 (328.1). $\text{C}_{40}\text{H}_{34}\text{N}_6\text{NiBr}_2 \cdot \text{C}_4\text{H}_{10}\text{O} \cdot 1.5\text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{CN}$: Calcd. H 5.21, C 57.56, N 9.70; Found H 5.45, C 57.68, N 9.90.

$[\text{Ni}(\text{L2})_2]\text{Br}_2$

HL2Cl (0.67 g, 2 mmol), anhydrous $\text{Ni}(\text{OAc})_2$ (0.17 g, 1 mmol) and tetrabutylammonium bromide (1.5 g) were weighed into a 10 mL round-bottomed flask and dried for 4 hours at 80 °C in a Schlenk setup under vacuum. The mixture was stirred for 48 hours at 130 °C under vacuum, after which the mixture was let to cool and triturated with H_2O . The water layer was washed with DCM (3×20 mL), and a brown crystalline solid was obtained from the water solution in 5% yield (40 mg). ^1H NMR gave broad peaks. ^{13}C NMR spectrum was

not recorded. ^1H NMR (300 MHz, DMSO- d_6) δ = 8.53, 8.32, 8.07, 7.57, 7.45, 7.41, 7.31, 7.08, 6.99, 6.43, 5.75, 4.96. MS m/z found (calc): $[\text{M} - 2\text{Br}]^{2+}$ 329.1 (329.1). $\text{C}_{38}\text{H}_{32}\text{N}_8\text{NiBr}_2 \cdot 2.5\text{H}_2\text{O}$: Calcd. H 4.31, C 52.81, N 12.97; Found H 4.80, C 53.08, N 12.99.

4.5 Acknowledgements

S. Luo gratefully acknowledges a grant from the Chinese Scholarship Council (no. 201306410011). We thank Mr. J.M.M. van Brussel for ESI-MS measurements.

4.6 References

- [1] V.G. Organo, A.S. Filatov, J.S. Quartararo, Z.M. Friedman, E.V. Rybak-Akimova, *Inorg. Chem.* 2009, 48, 8456-8468.
- [2] P. Zhang, M. Wang, Y. Yang, D. Zheng, K. Han, L. Sun, *Chem. Commun.* 2014, 50, 14153-14156.
- [3] E.I. Musina, V.V. Khrizanforova, I.D. Strel'nik, M.I. Valitov, Y.S. Spiridonova, D.B. Krivolapov, I.A. Litvinov, M.K. Kadirov, P. Lonnecke, E. Hey-Hawkins, Y.H. Budnikova, A.A. Karasik, O.G. Sinyashin, *Chem. -Eur. J.* 2014, 20, 3169-3182.
- [4] J. Berding, T.F. van Dijkman, M. Lutz, A.L. Spek, E. Bouwman, *Dalton Trans.* 2009, 6948-6955.
- [5] R. Tatematsu, T. Inomata, T. Ozawa, H. Masuda, *Angew. Chem. Int. Ed.* 2016, 55, 5247-5250.
- [6] A. Kochem, M. O'Hagan, E.S. Wiedner, M. van Gastel, *Chem. -Eur. J.* 2015, 21, 10338-10347.
- [7] P.F. Huo, C. Uyeda, J.D. Goodpaster, J.C. Peters, T.F. Miller, *ACS Catalysis* 2016, 6, 6114-6123.
- [8] D.L. DuBois, R.M. Bullock, *Eur. J. Inorg. Chem.* 2011, 1017-1027.
- [9] M.L. Helm, M.P. Stewart, R.M. Bullock, M.R. DuBois, D.L. DuBois, *Science* 2011, 333, 863-866.
- [10] G.M. Jacobsen, J.Y. Yang, B. Twamley, A.D. Wilson, R.M. Bullock, M.R. DuBois, D.L. DuBois, *Energy Environ. Sci.* 2008, 1, 167-174.
- [11] P.D. Tran, J. Barber, *Phys. Chem. Chem. Phys.* 2012, 14, 13772-13784.
- [12] D.J. Martin, B.D. McCarthy, C.L. Donley, J.L. Dempsey, *Chem. Commun.* 2015, 51, 5290-5293.
- [13] N. Queyriaux, R.T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.* 2015, 304-305, 3-19.
- [14] J. Wang, C. Li, Q. Zhou, W. Wang, Y. Hou, B. Zhang, X. Wang, *Catal. Sci. Technol.* 2016, 6, 8482-8489.
- [15] J.-N. Luy, S.A. Hauser, A.B. Chaplin, R. Tonner, *Organometallics* 2015, 34, 5099-5112.
- [16] Q.-X. Liu, H.-L. Li, X.-J. Zhao, S.-S. Ge, M.-C. Shi, G. Shen, Y. Zang, X.-G. Wang, *Inorg. Chim. Acta* 2011, 376, 437-445.
- [17] C. Chen, H. Qiu, W. Chen, *J. Organomet. Chem.* 2012, 696, 4166-4172.
- [18] X. Zhang, S. Gu, Q. Xia, W. Chen, *J. Organomet. Chem.* 2009, 694, 2359-2367.
- [19] L.B. Munro, V.J. Catalano, *Eur. J. Inorg. Chem.* 2014, 4994-5007.
- [20] K. Chen, M.M. Nenzel, T.M. Brown, V.J. Catalano, *Inorg. Chem.* 2015, 54, 6900-6909.

- [21] S. Das Adhikary, T. Samanta, G. Roymahapatra, F. Loiseau, D. Jouvenot, S. Giri, P.K. Chattaraj, J. Dinda, *New J. Chem.* 2010, 34, 1974-1980.
- [22] J. Liu, M. Liu, Y. Yue, M. Yao, K. Zhuo, *Chin. J. Chem.* 2012, 30, 644-650.
- [23] M.H. Reineke, M.D. Sampson, A.L. Rheingold, C.P. Kubiak, *Inorg. Chem.* 2015, 54, 3211-3217.
- [24] L. Yang, D.R. Powell, R.P. Houser, *Dalton Trans.* 2007, 955-964.
- [25] G. Armendariz-Vidales, C. Frontana, *Phys. Chem. Chem. Phys.* 2015, 17, 29299-29304.
- [26] C. Costentin, J.-M. Saveant, *Chemelectrochem* 2014, 1, 1226-1236.
- [27] M.T.M. Koper, E. Bouwman, *Angew. Chem. Int. Ed.* 2010, 49, 3723-3725.
- [28] G.M. Sheldrick, *Acta Cryst. A* 2008, 64, 112-122.
- [29] G.M. Sheldrick, *Acta Cryst. C* 2015, 71, 3-8.
- [30] J. Dinda, S.D. Adhikary, S.K. Seth, A. Mahapatra, *New J. Chem.* 2013, 37, 431-438.
- [31] J. Berding, M. Lutz, A.L. Spek, E. Bouwman, *Organometallics* 2009, 28, 1845-1854.