N2 fixation and dehydrogenation of methanol and formic acid with late transition metal complexes
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The transformation to a society based on sustainable energy can be facilitated by new technologies that allow solar energy to fuel conversions. The use of sunlight as the primary energy source is promising as: 1) solar energy will never run out; and 2) 1 hour of sunlight that hits the Earth, contains enough energy currently used by the whole world population in one year. There are several strategies to convert solar energy into a fuel. One is the water splitting reaction, which leads to the formation of oxygen and dihydrogen gas. This gaseous fuel can be used in a fuel cell to release energy on demand. However, the storage of $\text{H}_2$ in gaseous form is problematic for several technical reasons. Alternative (reversible) ways to chemically store solar energy are provided by other reduction reactions, such as those involving the reduction of $\text{CO}_2$ or N$_2$ to form formic acid, methanol (and other C-based fuels) or ammonia. The energy can be released from these fuels either in a fuel cell, or by dehydrogenation of the storage material, yielding dihydrogen that can be applied in a fuel cell to release its energy. Catalytic processes play an essential role in all these transformations and thus the development of new, efficient catalysts that can enable these reactions is important for a successful solar-based fuel economy. This thesis contributes to this challenge in the solar energy to fuel theme by presenting new catalytic systems for the dehydrogenation of C-based fuels based on ruthenium. In addition, the propensity of several ruthenium, iron, cobalt and nickel based complexes for N$_2$-activation is also explored.

Chapter 1 gives an overview of homogeneous catalysts capable of the (reversible) storage of protons and electrons in CO$_2$ and N$_2$. Although many catalysts already exist that can form formic acid from CO$_2$ and hydrogen, catalysts that are able to reduce CO$_2$ to methanol are scarce and no rational for the design of this class of catalysts is yet developed. The reverse reaction, decomposition of methanol to CO$_2$ and H$_2$, is performed already with more success and the presence of a proton-accepting group seems to be beneficial for this reaction. However, also catalysts that do not possess such a proton-accepting group exist, which are similarly active.

The main focus of the Introduction Chapter is on the challenges found in the dinitrogen reduction reaction to ammonia with late, first-row transition metals. In addition, the catalytic reduction of dinitrogen to silylamines is discussed, which is an alternative dinitrogen reduction reaction that operates through a different mechanism but generally has higher activities under less demanding conditions. Two different approaches for the design of catalysts able of dinitrogen reduction to ammonia are discussed: The Haber-Bosch inspired and the Nitrogenase inspired approach. The Haber-Bosch approach is based on initial splitting of the diatomic N$_2$ molecule into two nitrido-type ligands, after which reduction should take place. Systems that are able to split dinitrogen into nitrido complexes are presented, which are shown to subsequently react with protons and
electrons to form stoichiometric amounts of ammonia. Unfortunately, these complexes are not catalytically active yet. The Nitrogenase inspired catalysts operate through simultaneous addition of protons and electrons to the N₂ molecule, either via distal, alternating or (newly proposed) hybrid pathways. The most active catalysts contain an iron metal center coordinated to a tripodal or a pincer ligand. These complexes can reach TONs up to 59 of ammonia respectively and form the basis for the further rational design of new catalysts. The main challenge in the development of an effective system for catalytic ammonia formation is selectivity; preventing the competing proton reduction reaction. This is done by using proton sources with low solubility, which result in low concentration of H⁺ and by using low temperatures (−78 °C), which increases the selectivity of N₂ versus H⁺ reduction reactions. The electronic properties of the ligand and the type of the atom in trans position to the N₂ ligand (to facilitate stabilization of intermediates) are crucial factors as well. With these known factors, newly designed complexes can be developed to further understand the mechanism and improve reactivity.

In Chapter 2, the formation of salen-based ruthenium complexes is described, which are studied as catalysts in the methanol dehydrogenation reaction. Finding new catalysts for the release of molecular hydrogen from methanol is of high relevance in the context of the development of sustainable energy carriers. In this Chapter, the synthesis of ruthenium complex Ru(salbinapht)(CO)(P(i-Pr)₃) {salbinapht = 2-[(2′-[[(2-hydroxybenzyl)amino]-[1,1′-binaphthalen]-2-yl]imino)methyl]phenolato} (1) is described, which catalyzes the methanol dehydrogenation reaction in the presence of base and water to yield H₂, formate, and carbonate (Figure 1). Dihydrogen is the only gas detected and a turnover frequency up to 55 h⁻¹ at 82 °C is reached. Complex 1 bears a carbonyl ligand that is derived from methanol, as is demonstrated by labeling experiments. The carbonyl ligand can be treated with OH⁻ to form formate (HCOO⁻) and hydrogen. Labeling studies and characterization of the metal species under the applied reaction conditions revealed that the CO ligand

![Figure 1: Methanol dehydrogenation with catalyst 1.](image-url)
is dissociated from the active species, while the salen-derived ligand is most likely still coordinated. During catalysis, formation of Ru\((\text{CO})_2(H)_{2}(\text{Pi-Pr})_2\) is occasionally observed during catalysis, which is also an active methanol dehydrogenation catalyst.

Chapter 3 describes the use of rigid tetradentate tris(3-methylindole diphenylphosphine) phosphine \((\text{PP}_3)\) ligand to form ruthenium complexes in low oxidation states. In this Chapter, it is shown that the ruthenium (+II) dichlorido \(\text{PP}_3\) complex (2) can be reduced by one-electron to form the ruthenium (+I) adduct (3) as evidenced from EPR spectroscopy and X-ray diffraction analysis. The isolation of this Ru\(^{\text{I}}\)\text{ClPP}_3 complex shows that neutral tripodal ligands can stabilize this metallo-radical ruthenium center. Furthermore, the addition of a second equivalent of reductant, yielded the ruthenium(0)dinitrogen \(\text{PP}_3\) complex, which is of interest for dinitrogen reduction reactions. This complex, however, proved to be inactive in \(\text{N}_2\) reduction to \(\text{NH}_3\) as no ammonia was detected when the ruthenium (+II) dichlorido \(\text{PP}_3\) complex was reacted with \(\text{KClO}_3\) and \([\text{H(OEt}_2]_2)\text{[BAr}_F_4]\) at \(-78\,^\circ\text{C}\) in THF under dinitrogen atmosphere. Radical-type reactivity of the Ru\(^{\text{I}}\)\text{ClPP}_3 and the Ru\(^{\text{II}}\)\text{N}_2\text{PP}_3 complexes was also investigated by reacting these complexes with dichloromethane or attempting the Kharasch addition of chloroform to styrene. No catalytic turnover occurred for any of these reactions, instead, formation of the Ru\(^{\text{II}}\)\text{Cl}_2\text{PP}_3 complex was observed, which is likely a result of a one-electron oxidation of the ruthenium center by the chlorine radical originating from dichloromethane or chloroform.

Figure 2: The formation of ruthenium \(\text{PP}_3\) complex in oxidation states 0, +I and +II.

In Chapter 4, the coordination chemistry of ruthenium complexes coordinated with the tripodal, tetradentate \(\text{PP}_3\) ligands is extended by using ligands with various electronic properties \((L^1 R= \text{phenyl, } p-\text{phenyl–CF}_3 \text{ or } p-\text{phenyl–OMe})\) and the known structural isomer \((L^2 H)\) to investigate the effects of these modifications in catalysis (Figure 3). The synthesis and coordination chemistry of the ruthenium (+II) dichlorido \(\text{PP}_3\) complexes are described, which display octahedral geometries around the metal center. Two rotamers exist for all of these complexes as was evidenced from the obtained crystal structures of
these complexes. Interestingly, where the complexes based on $L_1^H$ are able to flip between these mirror images in solution on the NMR time scale, the complex based on $L_2^H$ retains the two separate mirror images, resulting in a more complicated $^{31}P$-NMR spectrum for the latter complex. All four complexes bind dinitrogen upon two-electron-reduction with KC$_8$. Electronic effects in the N≡N stretch frequency were observed as a result of the ligand modifications. The catalytic reduction of dinitrogen with the ruthenium(+II) complexes in presence of KC$_8$ and SiMe$_3$Cl yielded stoichiometric amounts of the corresponding silylamine. When the reduction reaction was followed in time, an incubation period was observed, which suggests that one and the same active catalyst is performing the reaction in all of the catalytic reactions, regardless of the initial structure. The activity of these complexes in catalytic formic acid dehydrogenation reaction was also evaluated. Activities between TOF = 33 and 124 h$^{-1}$ were reached depending on the ligand used. This finding shows that the modification of the ligand can influence the rate of the formic acid dehydrogenation reaction under the conditions used. Further studies with these complexes should be performed to elucidate the reaction mechanism and stability of the catalysts.

In Chapter 5, the coordination chemistry of first row transition metals Ni$^{II}$, Co$^{II}$ and Fe$^{II}$ to the same tripodal PP$_3$ ligands reported in Chapter 4 is described (Figure 4). Cobalt and iron complexes bearing a tripodal ligand are known to be active catalysts for dinitrogen reduction. The synthesis and coordination chemistry of the metal(+II) precursor to $L_1^H$ is described and the formed complexes display a five-coordinate trigonal bipyramidal geometry around the metal center as evidenced by X-ray diffraction analysis. To
elucidate if these complexes could be catalysts for dinitrogen reduction, coordination of dinitrogen upon two-electron-reduction was investigated. The $M^0-N_2$ complex was only formed with iron as evidenced by infrared spectroscopy. Likely, the 17 (cobalt) or 18 (nickel) VE complexes with the PP$_3$ ligand do not bind a fifth ligand which would lead to an unfavorable 19 and 20 VE configuration respectively. The library of iron complexes was extended using the other PP$_3$ ligands. The reduction of these complexes to form the iron(0) dinitrogen complexes were performed *in-situ*. It can be concluded that the use of ligands with different electronic properties results in noticeable different activations of the dinitrogen ligand that is coordinated to the iron atom. This is similar as found for the ruthenium complexes in Chapter 4. The binding of dinitrogen to these iron complexes indicates that dinitrogen reduction with these catalysts may be feasible.

Figure 4: Coordination of PP$_3$ ligand to cobalt, nickel and iron, and subsequent reduction to the metal(0) complexes, thereby binding dinitrogen only to the iron complex.

The research presented in this thesis contributes to finding solutions to the challenges associated with utilization of solar energy based fuels. The most important contributions towards this goal are the new catalytic systems based on ruthenium for methanol and
formic acid dehydrogenation. Encouraging initial results provide a good starting point for the development of improved catalytic systems. Although these systems do not outperform the current state-of-the-art catalysts known for these reactions, the mechanistic insights obtained can guide improvement of these catalysts in follow-up studies. Future work on these catalysts should focus on the increase of the stability of the ruthenium salen-type complexes under the applied reaction conditions (Chapter 2) and elucidation of the mechanism of formic acid dehydrogenation with tripodal tetraphosphine systems (Chapter 4). New coordination chemistry of the indole-based tetradentate phosphine tripodal ligand with ruthenium and iron e.g. stabilization of uncommon oxidation state (+I) of ruthenium, and the disclosure of ruthenium(0) or iron(0) dinitrogen complexes (Chapter 3, 4 and 5) opens up possibilities for the development of new radical chemistry or activation of \( \text{N}_2 \) molecule. The disclosure of the base metal complexes (Fe, Co, Ni) and understanding of their coordination chemistry with tripodal indolylphosphine ligands opens up possibilities for their future use as sustainable catalysts for e.g. reduction of unsaturated compounds. Since dinitrogen reduction is a quickly evolving field, the future may bring about new insights in optimal reaction conditions required for this challenging transformation. Thus, the reported \( \text{PP}_3 \) dinitrogen complexes of ruthenium and iron remain viable candidates for catalysts capable of dinitrogen reduction to ammonia.