N2 fixation and dehydrogenation of methanol and formic acid with late transition metal complexes

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Chapter 1

General introduction

1.1 The need for renewable energy

The demand for energy increased with 150% from the 1970’s till now, as a result of economic growth and development.\textsuperscript{[1]} Despite some alternative \textit{renewable energy sources} that are nowadays used, most of this energy is taken from carbon-based fossil fuels. By combustion of these fossil fuels, we release the solar energy that the universe stored in chemical bonds millions of years ago. Unfortunately, this combustion also leads to the unwanted formation of the greenhouse gas carbon dioxide. It is this gas that is the biggest contributor to the damaging changes in our climate.\textsuperscript{[2,3]} Climate change causes negative effects on the environment and on human living conditions (i.e. melting of snow, more extreme weather conditions, spreading of diseases) and should be stopped sooner than later.\textsuperscript{[4,5]} Renewable energy, taken from solar, wind or hydropower, has minimal environmental impact as it does not produce any CO\textsubscript{2}.\textsuperscript{[6,7]} For this reason, the use of renewable energy as an alternative (and eventually as a replacement) to fossil fuels should be stimulated, to prevent any more changes in our climate.

Solar energy is by far the biggest renewable energy source, as the sun is inexhaustible. Fossil fuels were created millions of years ago by the energy of the sun and we can use its energy again. In addition, 1 hour of sunlight can provide us with enough energy for one full year. Therefore, the use of solar energy is a good alternative to fossil fuels. To use solar energy as a potential energy source, two challenges have to be faced. The first challenge is to transfer solar energy into energy that we can use in daily life. The second challenge is to use the solar energy on demand. As the demand for energy and the generation of solar energy are not always simultaneously occurring, it is necessary to be able to store and often also transport this energy. This storage can be done in various ways (see ref: [8]), and one of these ways is to store the energy in chemical bonds. Here, lessons can be learned from nature, as nature is already capable of converting solar energy into chemical energy by means of photosynthesis.

Plants use solar energy captured with their leaves to convert water and carbon dioxide to oxygen and fuel (in the form of sugars).\textsuperscript{[9]} A chemical equivalent of such a light-capturing leaf has been proposed in recent years and is coined the artificial leaf (Figure 1). In such a leaf, water is transformed into a solar fuel, where the energy originates from the sun. The leaf consists of two compartments, the oxidation and the reduction side. At the oxidation site the light-driven water oxidation reaction takes place: releasing oxygen, protons and electrons. The protons move to the reduction side via a proton membrane, while electrons are shuttled to the same place through a wire. On the reduction side a (light-driven) reduction reaction can take place: transforming the protons and electrons into a solar fuel.\textsuperscript{[10]} Water splitting into oxygen and fuel can be accomplished by electrolysis of
water using photovoltaic panels coupled to electrolyzers or by direct solar water splitting using photosensitizers and catalysts in the same solution.

\[
\begin{align*}
H^+ + \text{H}_2\text{O} & \rightarrow \text{O}_2 + H^+ \\
\text{Oxidation} & \quad \text{Reduction}
\end{align*}
\]

The easiest accessible solar fuel is molecular hydrogen, which can be formed directly from the protons and electrons generated in the device (equation 1). Dihydrogen can be used in a fuel cell producing water and energy as only products. Much research is devoted to the design of proton reduction catalysts that are able to drive these reactions, and several catalysts have been reported that display high activity.\textsuperscript{11-17} Challenges in the use of dihydrogen as solar fuel are its low storage capacity: the amount of energy that can be taken per volume is low. In addition, dihydrogen is dangerous as it is an explosive gas, which makes transportation not very safe yet. However, dihydrogen can be used to reduce organic compounds and produce more complex fuels from solar energy in an indirect way (see further).

**Figure 1:** Simplified representation of an artificial leaf.

<table>
<thead>
<tr>
<th>Direct solar to fuel</th>
<th>Indirect solar to fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2)</td>
<td>(\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH})</td>
</tr>
<tr>
<td>(\text{CO}_2 + \text{H}^+ + 2 \text{e}^- \rightarrow \text{HCOOH})</td>
<td>(\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{OH})</td>
</tr>
<tr>
<td>(\text{CO}_2 + \text{H}^+ + 2 \text{e}^- \rightarrow \text{CH}_3\text{OH})</td>
<td>(\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3)</td>
</tr>
<tr>
<td>(\text{N}_2 + \text{H}^+ + 2 \text{e}^- \rightarrow \text{NH}_3)</td>
<td>(\text{CO}_2 \rightarrow \text{HCOOH})</td>
</tr>
<tr>
<td>(\text{CO}_2 \rightarrow \text{CH}_3\text{OH})</td>
<td>(\text{N}_2 \rightarrow \text{NH}_3)</td>
</tr>
</tbody>
</table>

Alternative solar fuels are formic acid or methanol (equation 2 and 3) obtained from the reduction of carbon dioxide. Formic acid and methanol are liquids at room temperature, and thus have a higher energy density per volume than dihydrogen. Both formic acid and methanol can be used directly in a fuel cell or as a substrate for other carbon containing products. \(\text{CO}_2\) can be reduced in a direct way in the solar to fuel device, by reaction with
protons and electrons. Alternatively, a stepwise indirect process can be developed where first dihydrogen is formed, which subsequently can be used to hydrogenate CO\textsubscript{2}. The hydrogenation of carbon dioxide to methanol is already an established process in industry. However, the catalysts that are used are not yet very reactive and suffer from stability issues, which makes that the conversion of syngas to methanol is currently much more profitable.\textsuperscript{[18-20]} The last solar fuel that we will discuss in more detail is ammonia (equation 4), which can be formed by the reduction of dinitrogen. Ammonia has the highest hydrogen density of these three solar fuels and it does not leave a carbon footprint. Besides that, the nitrogen content in air is very high, which makes it an abundant resource. The indirect storage of solar energy by hydrogenation of dinitrogen is already an industrial established process, as the Haber-Bosch process has been developed to generate ammonia from nitrogen as a fertilizer. The reduction of N\textsubscript{2} can also be nature-mimicked by reducing the gas directly with protons and electrons.\textsuperscript{[21,22]} The development of homogeneous catalysts that can directly convert protons and electrons into solar fuels is very challenging and this research is still in its infancy. The next two sections will give an overview of homogeneous catalysts active for the solar fuels methanol (section 1.2) and ammonia (section 1.3).

1.2 Methanol from carbon dioxide

\[
\begin{align*}
\text{CO}_2 & \quad + [\text{H}] \quad \rightarrow \quad \text{HCOOH} \\
& \quad - [\text{H}] \\
\text{HCOOH} & \quad + [\text{H}] \\
& \quad - \text{H}_2\text{O} \\
\text{H}_2\text{O} & \quad + [\text{H}] \\
& \quad + \text{CH}_3\text{OH} \\
\end{align*}
\]

\textbf{Figure 2:} Reversible storage of hydrogen in carbon dioxide.

The reaction of CO\textsubscript{2} with H\textsubscript{2} to methanol is a downhill reaction, but very difficult as a result of the thermodynamic stability and kinetic inertness of the gas. Although much progress has been made in the (reversible) storage of hydrogen (direct and indirect) obtained from solar energy by the reduction of carbon dioxide to formic acid, full reduction to methanol is scarcely observed with homogenous catalysts (Figure 2) (see for two recent reviews refs: [23,24]). The reduction of CO\textsubscript{2} to methanol is to date only possible with a few catalytic systems at low temperatures. The group of Leitner recently found that (Triphos)Ru(TMM) (TMM = trimethylenemethane) (1a) (Figure 3) was able to reduce CO\textsubscript{2} (20 bar) and H\textsubscript{2} (60 bar) at 140 °C in presence of stoichiometric amounts of HNTf\textsubscript{2} with a TON of 442 in 24 hours.\textsuperscript{[25]} 1a has a high stability at high temperatures, which is thought to be one of the reasons that catalysis under these conditions is feasible. The acid is only used for the removal of the TMM ligand, to create a vacant site for carbon dioxide to coordinate. This is supported
by subjecting the acetate complex (the formate complex could not be isolated) (Triphos) Ru($\eta^2$-OAc)(S)NTf$_2$ (1b) to similar reaction conditions, which also resulted in the formation of methanol. Thus, this catalyst is able to reduce CO$_2$ to methanol without the use of an additive, which is to date the only system that is capable hereof.

![Figure 3: The two catalysts that are able to reduce CO$_2$ to methanol without any additives.](image)

The next two examples show different methods that are used to circumvent the difficulties in the CO$_2$ reduction reaction. The first method is the capture of CO$_2$ in an organic molecule, which can subsequently be reduced with a catalyst releasing methanol. This strategy was elegantly described by the group of Milstein in 2011, where they showed the conversion of carbamates, carbonates, urea and formates to methanol with (PNN) RuH(CO)(2a) or (PNP)Ru(H)(CO)(Cl)(2b) (Figure 4) with turnover numbers (TON’s) up to 87 000.$^{[26,27]}$

![Figure 4: Capture of CO$_2$ in organic molecules and subsequent reduction releasing methanol.](image)

The second method is the use of a cooperative system. The group of Sanford designed a system of three catalysts that all promote one of the three following steps: a) CO$_2$ and H$_2$ to formic acid, b) formic acid to formate ester and c) hydrogenation of ester to methanol. Although all steps worked separately, a TON of only 2.5 could be reached when the reaction was performed in one pot.$^{[28]}$ Also the group of Guan used a similar strategy using a (PCP)NiH catalyst that reacts with CO$_2$ to form a nickel formate complex. The addition of excess catecholborane (HBcat) to this nickel formate complex regenerated the (PCP)NiH catalyst and surprisingly the methanol borane adduct CH$_3$OBcat, which can be hydrolysed with water to yield methanol.$^{[24]}$ CH$_3$OBcat could be catalytically formed by reacting the nickel catalyst with 500 equiv. of HBcat under 1 atm of CO$_2$ with a TOF of 495 h$^{-1}$. To date, these catalysts are the best examples
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of homogeneous catalysts that can convert CO₂ into methanol. The future will hopefully bring us more understanding into the homogeneously catalyzed CO₂ reduction reaction.

As discussed above methanol can be used in a methanol fuel cell, thereby releasing energy. Methanol fuel cells are currently mainly based on heterogeneous catalysts, which need high temperatures and pressures and often suffer from CO poisoning (a common side product in the dehydrogenation reaction). In general methanol is first dehydrogenated, and hydrogen is subsequently oxidized to gain energy. For this reason, homogeneous catalysts are explored that can dehydrogenate methanol into dihydrogen, which can then be used in a hydrogen fuel cell. The dehydrogenation of methanol has simultaneously been reported in 2013 by the groups of Grützmacher and Beller (see Figure 5 for an overview of the catalysts and their best performance).

The group of Grützmacher prepared the ruthenium trop₂dad complex \([\text{K(dme)}_2]\) [RuH(trop₂dad)] (trop₂dad = 1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene) (3) and the group of Beller prepared the ruthenium pincer complex RuHCl(CO)(HN(C₂H₄P(i-Pr)₂)₂) (4). The complex of Grützmacher was active in absence of base, dehydrogenating methanol with a TON (10 h) of 540. Beller initially performed the reaction in presence of 8 M KOH leading to a TON (24 d) of 353 400. The high concentration of base was necessary to decompose formic acid with this catalyst. In a subsequent paper this final reaction step was performed by a second catalyst that was capable of the decomposition of formic acid under base free conditions. The use of this bicatalytic mixture led to an initial TON (8 d) of 4286 h⁻¹ for the dehydrogenation of methanol in absence of base. The system of Beller was extended to an iron complex (5) (TON (94 h) = 51 000, no base but LiBF₄ as additive) and a manganese complex (6) (TON (3 h) = 54, in presence of 8 M KOH), which were both shown to be active. The catalyst of Milstein (2) that was earlier shown to catalyze the hydrogenation reaction of trapped CO₂ to methanol, is also an active catalyst in the methanol dehydrogenation reaction, reaching a TON (27 d) of 28 700, in presence of NaOH. Interestingly, these complexes all feature a nitrogen atom next to the metal center, which was proposed to play a role as a proton acceptor. A similar approach was used to form the iridium based complex \([\text{Cp}^*\text{Ir}(\alpha,\alpha',\beta\text{-}

![Figure 5: Several methanol dehydrogenation catalysts and their best performance.](image-url)
through ligand promoted dehydrogenation as the carbonyl group can accept a proton, driving the reaction to a TON (TON) of 10 510 in presence of base (NaOH). The last example is an iridium complex which does not possess a ligand that features a proton acceptor: [(CO) Ir(1,3-dialkyldimidazol-2-ylidene)]+ (8).\cite{37} 8 decomposes methanol to molecular hydrogen with a TON (TON) of 8000 in basic (KOH) media. This catalyst is stable under aerobic conditions, and thus a promising catalyst for the direct application in an artificial leaf, as it doesn’t suffer from oxygen produced on the other side of cell (Figure 1). Several methanol dehydrogenation catalysts have emerged from 2013 onwards. As indicated by experimental work and DFT calculations, the presence of a proton accepting site to the ligand seems to be beneficial for the overall reactivity.

### 1.3 Ammonia from dinitrogen

Ammonia is potentially a very promising solar fuel: dinitrogen is abundant (79 % of the air is N\textsubscript{2} substrate, ammonia (17.8 wt% of hydrogen) has a higher fuel capacity than methanol\cite{38}, it doesn’t contain carbon (so little production of greenhouse gasses) and the infrastructure to synthesize ammonia is already present and thus can be right away used on big scale (we already know how to deal with ammonia synthesis, transport and potential dangers). The purpose of this upcoming section is to give an overview of the approaches used to tackle the challenging problem of N\textsubscript{2} reduction at ambient conditions and of the catalytic systems that are capable of this transformation with the focus on (catalytic) reactions involving iron or cobalt.

#### 1.3.1 Introduction

Dinitrogen has a well-deserved reputation of being one of the most inert molecules. This feature has become the origin of the name of the element with atomic number 7 in many languages. In some it is described as ‘life less’ (as coined by Lavoisier from Greek: αζωω) e.g. azote (French), azoto (Italian), azot (Polish), as it does not support respiration and in some languages as a substance that causes suffocation e.g. Stickstoff (German), Stikstof (Dutch), Dusék (Czech), Kväve (Swedish).\cite{39} Ironically, life as we know it is not possible without this element as all living organisms are based on nitrogen containing molecules (i.e. amino and nucleic acids). However, the biosynthesis of these adducts can only be accomplished once nitrogen is fixed as ammonia.\cite{40} The two most prominent dinitrogen reduction pathways are the industrial Haber-Bosch process\cite{41–44} and the biological reduction by cyanobacteria\cite{45} and each accounts roughly for 50% of the annual ammonia production.\cite{46–48} The industrial process uses N\textsubscript{2} and H\textsubscript{2} that are reacted over a heterogeneous iron or ruthenium catalyst, forming ammonia. The overall process, which includes methane reforming for H\textsubscript{2} production, requires high temperatures and pressures,
and consumes more than 1% of the annual production of world energy.\textsuperscript{[49,50]} Nitrogenases, the metallo-enzymes responsible for ammonia production in the biological process, can perform the reaction at ambient conditions from \( \text{N}_2 \), protons and electrons, and use energy in the form of MgATP.\textsuperscript{[51]} The active site of the most common enzyme is composed of an iron-molybdenum cluster.\textsuperscript{[52]} Other, less common nitrogenases are vanadium-iron, or iron only.\textsuperscript{[53,54]} Inspite of its chemical inertness, \( \text{N}_2 \) can be reduced by nitrogenases already at ambient conditions. This fact triggered much effort in the development of synthetic catalysts capable of ammonia synthesis under mild conditions. Finding systems that would enable reduction of dinitrogen in a manner that is less energy intensive than the Haber-Bosch process could lead to a more sustainable economy. In addition, development of synthetic models of nitrogenase enzymes may provide more fundamental understanding in how this small inert molecule can be transformed into useful nitrogen containing compounds. In recent years, great progress has been made in this field and new catalytic systems for dinitrogen reduction are being reported more and more frequently.

1.3.2 Activation of \( \text{N}_2 \)

For most synthetic (in)organic chemists the inertness of dinitrogen is a very advantageous property since a nitrogen atmosphere prevents presence of oxygen/moisture, thus enabling many advanced chemical transformations. This inertness, however, renders fixation of dinitrogen as one of the more challenging chemical reactions for the reasons described below.

Dinitrogen complexes have been prepared with the majority of transition metals.\textsuperscript{[55,56]} Binding of \( \text{N}_2 \) to a transition metal center involves both \( \sigma \)-donation to the metal and back-donation from the metal to the empty \( \pi^* \) orbital(s). However, \( \text{N}_2 \) is a weak \( \sigma \)-donor and a poor \( \pi \)-acceptor due to a weak overlap of the \( \sigma \) and \( \pi^* \)-orbitals with the metal d-orbitals.\textsuperscript{[57]} Overall, the donation of electron density from the metal to the dinitrogen molecule is the most important interaction.\textsuperscript{[58]} Therefore, \( \text{N}_2 \) will preferentially bind to electron-rich metals with strong capacity of \( \pi \)-backbonding. When choosing a system for activation of \( \text{N}_2 \), one has to take into account the following factors: the energy of d-orbitals of transition metals decreases from left to right of the row and thus the amount of charge-transfer from the metal to the \( \text{N}_2 \) ligand is higher for early, and lower for late transition metals. This means that for example iron forms a stronger bond with dinitrogen than cobalt, and copper dinitrogen complexes are very unusual. The addition of electrons (e.g. reduction of the metal) follows the same trend: lowering the oxidation state will lead to a stronger metal-dinitrogen bond. The use of strongly donating ligands will increase the electron-richness of the metal. Multidentate alkyl phosphines seem to be the privileged ligands in this case, strong binding was also observed for hydride complexes.\textsuperscript{[59,60]} Needless to say, such electron-rich platforms for \( \text{N}_2 \) activation are extremely air sensitive. In addition, dinitrogen coordination is less
favorable to occur with high spin complexes, and therefore the use of weak field sulfide ligands lead to limited success as these ligands generally form high spin complexes.\[^{61}\] This is in big contrast to the nitrogenase, where multiple sulfides per active site are present. The extent of electron transfer to the coordinated N\(_2\) moiety can be probed by measuring the N≡N stretch frequency using infrared or Raman spectroscopy. However, the extent of activation of the triple bond is not a direct measure for performance in N\(_2\) reduction\[^{62}\] since a more electron-rich metal center can also be more prone to side reactions that lead to deactivation of the catalyst. As can be seen from Figure 6 there is no direct correlation between the vibrational frequencies of N\(_2\) bound to the NH\(_3\) forming catalysts and their efficiency. Moreover, many (pre)catalysts that are capable of catalyzing the formation of tris(trimethylsilyl)amine often don’t even feature a bound N\(_2\) ligand. This demonstrates that the activation of the dinitrogen ligand does not predict the overall performance of the complex; it displays if the dinitrogen molecule is bound to the metal center and the electron-richness of the complex.

![Figure 6](image_url)

**Figure 6:** Selected dinitrogen reduction catalysts, their N\(_2\) ligand IR frequencies and the maximum yield of ammonia they provide.

Further aspects to be considered in the design of systems for catalytic reduction of N\(_2\) are factors such as the ease of release of the products; nitrogen containing products bind very strongly to the early transition metals and therefore to date the catalytic N\(_2\) reduction to ammonia has been disclosed only for molybdenum, iron and cobalt. Another factor is the potential poisoning of the catalyst with side products formed during catalysis (e.g. H\(_2\)) or impurities present in the reactants.
1.3.3 Reduction of \( N_2 \) to ammonia

1.3.3.1 Haber-Bosch inspired systems

In the Haber-Bosch process ammonia is formed by reaction of dinitrogen and dihydrogen over an iron catalyst. The reaction proceeds through the stages depicted in Figure 7: dissociative chemisorption of both gasses followed by stepwise formation of \( N-H \) bonds between chemisorbed atoms, and subsequent release of gaseous ammonia. \[65,64\] The homolytic splitting of the \( N_2 \) molecule forming a surface-bound nitride is the rate determining step.\[49,64–68\] The rate of chemisorption is enhanced by the addition of potassium oxide, which alters the electronic properties of the catalyst surface,\[49,67,69\] while a framework of \( Al_2O_3 \) and \( CaO \) stabilizes the catalyst, preventing sintering of the active iron particles.\[46,65,66\] In the quest for processes that can work under lower pressures, ruthenium on graphite (Kellogg Advanced Ammonia Process (KAAP))\[70\] and promoted cobalt\[50,71\] catalysts were developed. Homolytic cleavage of \( N_2 \) is possible at low temperatures and pressures and one can envision that thus formed nitrido species can undergo follow-up reactions similar to the surface nitrides formed during the Haber-Bosch process. The first well defined complex that was able to perform the homolytic splitting of the dinitrogen molecule forming a molybdenum-nitrido complex was reported in 1995\[72\]. Since then, many well defined metal complexes (Ti, Hf, Mo, Nb, Ta, V, Cr, U, Re) were shown to split the \( N_2 \) molecule,\[73–74\] and some of them allowed for further reactions of the thus formed nitrides. \[74,75\] In 2001 an attempt to homolytically cleave the dinitrogen triple bond using iron was made by the Holland group. The dimeric highly reduced \([((\beta\text{-diket}^{\text{Bu}})(\text{K})\text{Fe}(\mu-N_2)\text{Fe}(\text{K})\text{)}\text{(\beta\text{-diket}^{\text{Bu}})}\text{)}\text{]}\text{) (HC(C(Bu)NC_6H_5(\text{Pr})_2)}\text{]}\text{ complex (9) showed extreme weakening of the dinitrogen triple bond } (\nu(N_2) = 1589 \text{ cm}^{-1})\text{ (Figure 8).}\[76\] Quite remarkably, coordination of a potassium cation side-on to the dinitrogen ligand further increases the backbonding of iron into the \( \pi^* \) orbitals of \( N_2 \). This somewhat resembles the operation of the Haber-Bosch process, where promoters as potassium are used to facilitate \( N_2 \) binding to the iron centers.\[66\] Analogous cobalt \( (\nu(N_2) = 1599 \text{ cm}^{-1})\text{ (10) and nickel-adducts} \)
were also reported, however, no further reactivity of these complexes was disclosed.

Figure 8: Dimeric $\beta$-diketiminate $N_2$ complexes of iron (9), cobalt (10) and nickel (11).

Figure 9: Triiron $\beta$-diketiminate $N_2$ complexes that split the dinitrogen bond and subsequent release of ammonia upon addition of hydrogen.
The use of a less sterically demanding $\beta$-diketiminate ligand ($\beta$-diket$^{Me} = \text{MeC}($Me$)\text{C(Me)}(\text{Me})_2$) coordinated to iron allowed for splitting of the N$_2$ triple bond to form the tetrailron dinitrido complex 13 (Figure 9).\[79\] The core of complex 13 consists of two nitrides surrounded by three iron centers and two potassium cations to which a fourth iron center is bound via bridging chloride anions. Addition of HCl to complex 13 resulted in the release of 82% of ammonia. Further studies showed that if the reduction of the parent complex ($\beta$-diket$^{Me}$)(K)Fe($\mu$-Cl)$_2$Fe(K)($\beta$-diket$^{Me}$) (12) is conducted with two equiv. of sodium, the triiron sodium complex (14) is formed, which upon reacting with HCl releases ammonia in 99% yield.\[80\] In the presence of excess reductant (4 equiv.) no cleavage of N$_2$ is observed and triiron complexes with bridging N$_2$ ligands are formed which precludes any catalytic turnover.

The group of Murray used a rigid $\beta$-diketiminate ligand which could template the formation of a triiron complex (15) (Figure 10).\[81\] Upon reduction of the triiron(+I) complex 15 with KC$_8$, homolytic splitting of the N≡N bond occurred, forming complex 16. Surprisingly, the complex incorporates three NH$_x$ fragments, which suggests that (at least one of) the NH fragments is formed via reaction between two triiron complexes. The source of the protons for complex 16 could not be established. Protonation of 16 with hydrochloric acid resulted in the release of 30% of ammonia.

The above examples show that homolytic cleavage of the N≡N bond followed by protonation can yield ammonia already at room temperature and ambient pressure. The difference with the Haber-Bosch reaction is that the hydrogen atoms are introduced in the form of protons and electrons and not as dihydrogen. Although not yet catalytic, this approach demonstrates that it is possible to prepare synthetic models that show a similar mechanism as the Haber-Bosch process. Hopefully, related systems will be explored further in the future to yield some Haber-Bosch inspired catalysts.

\[100\]
1.3.3.2 Nitrogenase inspired systems

The active site of the most common nitrogenase enzyme consists a protein embedded [Mo:7Fe:9S:C]:homocitrate cofactor (FeMo-co)\(^{82–85}\) (Figure 11) which catalyzes the formation of ammonia from dinitrogen, protons and electrons. The electrons are delivered by an [4Fe-4S] cluster\(^{51}\) and although the detailed mechanistic picture remains under debate, it is clear that the reduction takes place at the iron center.\(^{51,86–91}\) The reduction follows a mechanism in which protons are added to the dinitrogen core in an alternate fashion to the terminal and proximal nitrogen atoms (Figure 12).

The overall reaction scheme for nitrogen reduction by nitrogenase (top) is:

\[
N_2 + 8 H^+ + 8 e^- + 16 \text{MgATP} \rightarrow 2 \text{NH}_3 + H_2 + 16 \text{MgADP} + P_i
\]

**Figure 11:** Overall reaction scheme for nitrogen reduction by nitrogenase (top). FeMoco, the active site of the FeMo based nitrogenase (bottom).

**Figure 12:** Two possible pathways of dinitrogen reduction to ammonia: alternating (top) and distal (bottom).
During the reduction, bridging iron-hydrides are formed that reductively eliminate H₂, leaving a reduced vacant iron atom to which N₂ can bind again.\textsuperscript{[92]} The reduction of dinitrogen on transition metal centers can proceed through two (limiting) pathways: alternating and distal (Figure 12). In the alternating pathway, the protons are transferred to the terminal and proximal dinitrogen atoms producing coordinated diazene and hydrazine. The release of the first equivalent of ammonia leads to formation of an amido complex that undergoes subsequent protonation to yield the second equivalent of ammonia. This mechanism has been shown to be operational for FeMo-co\textsuperscript{[5,93]} and for iron-phosphine based\textsuperscript{[94]} model systems. In the distal pathway the protonation occurs initially on the terminal nitrogen atom and after release of ammonia, a nitride complex is formed that after three subsequent protonation and electron transfer steps releases the second equivalent of ammonia.\textsuperscript{[94]} This pathway was shown to operate for molybdenum systems of Schrock and Nishibayashi.\textsuperscript{[95–97]}

Interconversion between the two pathways is also possible as recently shown by Peters and co-workers, who reported that the hydrazide intermediate Fe=N-NH₂⁺ can transform to Fe-NH₂NH₂⁺ through double reduction and protonation (Figure 19).\textsuperscript{[95]} This brings about the possibility of a hybrid pathway in which initial two proton additions occur on a distal pathway while after interconversion, the subsequent steps follow the alternating pathway.

**Early mechanistic studies on N₂ reduction by metal complexes**

As the most common nitrogenase enzyme exists as a cluster of molybdenum and iron atoms,\textsuperscript{[82–85]} the main research on room temperature N₂ reduction was focused on these two metals. The first examples of substoichiometric ammonia formation from dinitrogen were reported in 1964 with molybdenum,\textsuperscript{[98]} and in 1966 with iron.\textsuperscript{[99]} These two systems involved mixing of the “naked” metal salts MoO₄²⁻ or FeCl₃ with reductant, in presence of acid and dinitrogen, but were not investigated mechanistically. Further studies on iron as the active metal for dinitrogen reduction followed roughly 30 years later. Leigh studied a well-defined Fe⁶(dmpe)₂N₂ (17) (dmpe = Me₂P–CH₂CH₂–PMe₂) (υ(N₂)₁₉₇₅ = cm⁻¹) complex (Figure 13) that formed ammonia (20%) and Fe²⁺(dmpe)₂Cl₂ (18) upon addition of HCl.\textsuperscript{[100]} The iron atom is the only electron source for the reduction, so a maximum yield of 33.3 % of ammonia could theoretically be reached if dinitrogen reaction was paired to the oxidation of Fe⁶ to Fe²⁺. The iron(0) dinitrogen complex 17 could be re-formed by reaction with NaBH₄/EtOH to yield a hydrido dihydrogen complex (19),\textsuperscript{[61]} followed by substitution of H₂ with N₂ (20) (υ(N₂) = 2094 cm⁻¹) and reductive deprotonation by base which closed the so-called Leigh cycle. Tyler and co-workers reported that for related systems the reduction step could be performed by using molecular hydrogen in the presence of proton and chloride scavengers instead of NaBH₄. In this way H₂ was used
as a source of electrons for $N_2$ reduction.$^{[101]} \text{}$ Theoretical and experimental mechanistic investigations on the Fe(dmpe)$_2$ and similar iron diphosphine complexes$^{[102-110]}$ showed that an alternating (Figure 12) pathway was operational, similarly to the way the natural system is suggested to proceed.$^{[51,93]} \text{}$ Most importantly, these studies confirmed that a well-defined iron system is able to mediate the formation of ammonia from dinitrogen. A related system in which the dmpe ligand was replaced by the depe ligand (depe = Et$_2$P–CH$_2$CH$_2$–PET$_2$) proved to be active in catalytic reduction of dinitrogen (see further, Figure 27).

**Iron-sulfur systems**

Although the nitrogenase enzyme consists of multiple sulfur atoms in its core, the number of synthetic models that contain sulfur atoms are limited. In fact, sulfides and thiolates are weak-field ligands, that favor formation of high spin complexes which is generally unfavorable for $N_2$ binding.$^{[61]} \text{}$ Some groups prepared mono or dinuclear iron containing sulfide/thiolate complexes, but although these complexes could form ammonia from hydrazine, none of them were shown to bind and subsequently reduce the π-acidic $N_2$ ligand.$^{[111-117]} \text{}$ Sellmann reported various $N_2$ thiolate containing ruthenium complexes, and the hypothetical intermediates ($N_2H_4$, $N_2H_4NH_3$)$^{[116,118]}$ of a dinitrogen reduction cycle. However, this cycle could not be made catalytic.$^{[119]} \text{}$ The Peters group investigated sulfur-containing iron complexes with thioethers. Thioethers have better σ-donating and π-accepting properties than thiolates and sulfides$^{[61]}$ and thus, it was hypothesized that the use of thioether donors may favor dinitrogen binding. Tripodal mono-, bis- and
tris(thioether) ligands with a central silicon donor atom were prepared, from which only the iron complex with the ligand containing one thioether and two electron-donating phosphines coordinated a weakly activated ($\nu(N_2) = 2156$ cm$^{-1}$) dinitrogen ligand (21) (Figure 14). Addition of a hydride resulted in a more activated dinitrogen bond (22) ($\nu(N_2) = 2055$ cm$^{-1}$), and also allowed the bis(thioether) complex to coordinate dinitrogen (23) ($\nu(N_2) = 2060$ cm$^{-1}$). Although these complexes show some resemblance with the nitrogenase active site, they could not be applied in dinitrogen reduction.

Some success was reached with the tripodal diiron sulfide bridged dinitrogen complex (24) ($\nu(N_2) = 2017$ and 1979 cm$^{-1}$) (Figure 15) which not only coordinates dinitrogen, but is also able to reduce it. Stoichiometric amounts of ammonia (1.8 equiv.) are formed upon addition of reductant and acid to 24. The reactivity is attributed to the tripodal structure of the ligand. In the following sections, more successful examples of systems featuring tripodal ligands are shown. Longer reaction times or different reagent concentrations did not lead to higher yields of ammonia; likely the catalyst is unstable under the reaction conditions applied.

Recently the group of Holland reported a high-spin ($S = 1$) iron(0) dinitrogen complex coordinated with a tridentate ligand featuring two thiolato and a carbon-based coordination site (Figure 16). The remarkably low frequency of the N–N bond stretch...
Chapter 1

(\(\nu(\text{N}_2) = 1880 \text{ cm}^{-1}\)) shows that thiolates enable substantial back-donation to the coordinated \(\text{N}_2\) moiety. Complex 25 is a synthetic model with closest resemblance to the nitrogenase site that is able to coordinate to dinitrogen, however no reactivity studies were disclosed.

![Figure 16: Iron dinitrogen complex with a ligand featuring only sulphido and carbon donors.](image)

Synthetic Fe-S clusters\(^{[122,123]}\) that show much resemblance with the nitrogenase active site are known, however these clusters do not bind \(\text{N}_2\).\(^{[92]}\) Interestingly, recently FeMoS-SnS and FeS-SnS clusters embedded in chalcogels were shown to reduce dinitrogen under white light irradiation and in presence of aqueous pyridinium hydrochloride and sodium ascorbate in solutions to ammonia (up to 17 equiv.).\(^{[124,125]}\) Their mechanism has, however, not been investigated.

### 1.3.4 Catalytic ammonia formation

![Figure 17: Selected nitrogen reduction molybdenum catalysts.](image)

The first molecular catalyst that was able to reduce dinitrogen to ammonia (7.6 equiv. per Mo) under ambient conditions was found in 2003 by Yandulov and Schrock (Figure 17).\(^{[97]}\) The catalyst (26) (\(\nu(\text{N}_2) = 1990 \text{ cm}^{-1}\)) contained a molybdenum atom surrounded by a bulky tripodal HIPTN\(_3\)N ligand ((HIPTN\(_3\)N)\(^{2-}\) = ((HIPT)NCH\(_2\)CH\(_2\)N)\(^{2-}\), HIPT =
The ligand was specifically chosen for its large steric bulk, which prevents formation of inactive $\mu$-$\text{N}_2$ dimers. Based on the isolation of most of the intermediates of the catalytic cycle and DFT calculations a distal pathway (Figure 12) was proposed. Molybdenum systems supported with PNP-type ligands described by the group of Nishibayashi were found to have even higher stability which reached up to 63 equiv. of NH$_3$ per metal center. As will be shown below, both tripodal and PNP ligand scaffolds could successfully be used for the development of base metal systems for catalytic ammonia synthesis.

**Tripodal systems**

The activity and stability of iron and cobalt systems supported by tripodal tetradentate ligands was investigated by the group of Peters. These ligands feature three phosphine donors and a coordinating central X-type (Si, C) or Z-type (B) atom. Similarly to the Schrock’s molybdenum system, these complexes feature the ability to accommodate both a $\pi$-acidic $\text{N}_2$ ligand, as well as $\pi$-basic $\text{N}_2$ derived intermediates (e.g. $\text{N}_3^-$, NH$^-$).

Initial investigations were performed on iron complexes featuring a silyl donor atom that allowed isolation of the (SiP$_3$)$_3$FeN$_2$ (29) (SiP$_3$ = (2-Ph$_2$PC$_6$H$_4$)$_3$Si) complex with a moderately activated $\text{N}_2$ moiety ($\upsilon$(N$_2$) = 2041 cm$^{-1}$) (Figure 18). Complex 29 reacts with HBF$_4$ in THF at room temperature to form hydrazine in 17% yield, which could be improved to 47% if the one-electron donor CrCl$_2$ is added. Substitution of the phosphine phenyl groups for the more electron-donating isopropyl groups led to a more activated dinitrogen complex (SiP$_3$i-Pr)$_3$FeN$_2$ (30) ($\upsilon$(N$_2$) = 2003 cm$^{-1}$).

![Figure 18: Reactivity of (SiP$_3$)$_3$FeN$_2$ complexes in reduction of N$_2$.](image-url)
The cobalt analogue (SiP<sub>iPr</sub>)CoN<sub>2</sub> (31) was also prepared, and showed the expected weaker activation of dinitrogen of 2063 cm<sup>-1</sup>[138]. Reaction of complex 30 with HBF<sub>4</sub> in the presence of CrCp<sup>+</sup> led to formation of only 9% of hydrazine. It was proposed that the more reducing nature of 30 caused preferential reduction of protons over dinitrogen reduction, giving rise to lower hydrazine yields.[137] One-electron-reduction of 30 to [(SiP<sub>iPr</sub>)FeN<sub>2</sub>] [Na([12]-c-4)] (32) led to an even stronger charge transfer to the N<sub>2</sub> ligand (ν(N<sub>2</sub>) = 1891 cm<sup>-1</sup>). Interestingly when 32 was subjected to excess KC<sub>8</sub> (50 equiv.) and HBAr<sub>F</sub> (46 equiv.) in diethyl ether at −78 ºC sub-stoichiometric amounts of ammonia (0.7 equiv.) were observed, which was later optimized to give 3.8 ± 0.8 equiv. of ammonia (see below).[139]

Figure 19: Mechanistic investigations on (SiP<sub>iPr</sub>)FeN<sub>2</sub>.

Although iron complexes supported with the tris(phosphino)silyl ligands did not show real catalytic activity, they proved to be good scaffolds for mechanistic investigations. The
iron(II) hydrazine and ammonia complexes with SiP$_\text{Pr}_3$ ligands (33 and 34 respectively) were prepared which supports their possible intermediacy in reduction of N$_2$ (Figure 19). More importantly, one-electron-reduction of complexes 33 or 34 using CrCp$_\text{2}$ in THF under dinitrogen at room temperature resulted in the formation of the iron(I)N$_2$ adduct 30, accompanied by the liberation of NH$_3$ and/or N$_2$H$_4$ which showed the potential to make the system catalytic. The addition of one equivalent of Me$_3$SiCl and Na/Hg to 30 in THF resulted in formation of the stable diazenido complex (SiP$_\text{Pr}_3$)Fe(N$_2$SiMe$_3$) (35), which shows that the terminal nitrogen atom is prone to react with electrophiles.

Stoichiometric reaction of 32 with protons could be studied at low temperatures. Addition of 3 equiv. of HOTf in 2-MeTHF to [(SiP$_\text{Pr}_3$)FeN$_2$]$^-$ (32) at –135 ºC led to formation of the hydrazide complex [(SiP$_\text{Pr}_3$)Fe=NNH$_2$]$^+$ (36), one of the intermediates of ammonia synthesis along the distal pathway (Figure 12). Interestingly, compound 36 reacts with its mono-reduced analog [(SiP$_\text{Pr}_3$)Fe=NNH$_2$] (37) to form [(SiP$_\text{Pr}_3$)FeNH$_2$NH$_2$]$^+$ (38) and the neutral dinitrogen complex 30 through disproportionation of the diazenido ligand. Complex 38 can be viewed as one of the intermediates along the alternating pathway. These results show that N$_2$ bound to iron can be doubly protonated to generate a distal intermediate, and subsequently disproportionate to an alternating intermediate. As such, a hybrid distal/alternating pathway is viable for the iron system.

A breakthrough in catalytic dinitrogen fixation with iron was achieved with the use of the tripodal, neutral Lewis acidic borane (BP$_\text{Pr}_3$ = tris[2-(diisopropylphosphino)-phenyl]borane) scaffold. The use of this borane ligand was expected to stabilize intermediates with multiple iron-nitrogen bonds that would be formed along the distal pathway. The dinitrogen ligand in (BP$_\text{Pr}_3$)FeN$_2$ (39) is rather weakly activated ($\nu$(N$_2$) = 2011 cm$^{-1}$) (Figure 20), however one-electron-reduction with sodium amalgam in the presence of a crown ether results in the formation of [(BP$_\text{Pr}_3$)FeN$_2$][Na([12]-c-4)] complex 40, which not only reveals strong spectroscopic activation of N$_2$ ($\nu$(N$_2$) = 1905 cm$^{-1}$) but also is catalytically active in N$_2$ reduction. Complex 40 catalyzed the formation of 7 equiv. of ammonia when reacted with [H(Et$_2$O)$_2$][BAR$_4^-$] (46 equiv.) and KC$_8$ (50 equiv.) at –78 ºC in Et$_2$O (Figure 19) under 1 atm of N$_2$. The choice of reagents was of crucial importance as the use of other reductants (CoCp$_\text{2}$, CrCp$_\text{2}$, K) or acids (HOTf, LutH[BAR$_4^-$], HCl) decreased the yield to less than 0.6 equiv. of NH$_3$. Even more crucial was the purity of the acid. In an optimized procedure using ~30 times higher loading of KC$_8$ (1600-1800 equiv.) and highly purified HBAr$_4^-$ (1500 equiv.) in diethyl ether at –78 ºC, 59 ± 6 equiv. of NH$_3$ were formed. Under these conditions, the SiP$_\text{Pr}_3$ complex 32 catalyzed formation of 3.8 ± 0.8 equiv. of NH$_3$, and the Cp$_\text{Pr}_3$ complex 46 (Figure 24) 36 ± 7 equiv. of NH$_3$. Electrochemical studies revealed that reduction of N$_2$ is possible already at –2.2 V (vs Fc/Fc$^+$) implying that chemical reductants that are weaker than KC$_8$ can also be used. However, in comparison with sodium amalgam, the use
of KC\textsubscript{8} led to higher yields of NH\textsubscript{3} due to lower rate of the competing background proton reduction. Electrochemical reduction of N\textsubscript{2} could be performed, however only 2.2 equiv. of ammonia per iron atom was produced.

Reactivity studies of the iron BP\textsubscript{i}-Pr\textsubscript{3} complexes shed light on the possible mechanism of the catalytic reaction. Reaction of 40[Na([12]-c-4)] with 10 equiv. of [H(Et\textsubscript{2}O)\textsubscript{2}][BAr\textsubscript{4}F\textsubscript{4}] allowed for characterization of the transient iron-hydrazido complex [(BP\textsubscript{i}-Pr\textsubscript{3})Fe≡N−NH\textsubscript{2}]\textsuperscript{+} (41).\textsuperscript{143} The formation of this species indicates that the two initial protonation steps during the catalytic cycle proceed through a distal pathway.

Isolation of mono- and disilylated intermediates 43 and 44 upon reaction with silylchlorides further supports the distal mechanism in the initial steps of the catalytic reaction (Figure 21).\textsuperscript{144} The mechanism for the catalysis with complex 40 may proceed similarly to the mechanism proposed for the (SiP\textsubscript{i}-Pr\textsubscript{3})FeN\textsubscript{2} complex 32 (Figure 19): the addition of two protons along the distal pathway going to the hybrid pathway after which an intermediate with coordinated hydrazine is formed and subsequent addition proceeds through the alternating pathway (Figure 22). This hypothesis is supported by the isolation of nitrogen fixation intermediates featuring N-NH\textsubscript{2}, N\textsubscript{2}H\textsubscript{4}, NH\textsubscript{3} ligands and the release of ammonia upon reduction of these intermediates.\textsuperscript{145,146} Kinetic studies revealed first order in catalyst concentration and zeroth order in acid concentration. The initial turnover frequency is 1.2 ± 0.1 min\textsuperscript{-1}, which is the highest reported for any synthetic
system. This activity at \(-78\) °C is remarkably high considering the fact that the FeMo nitrogenase from *Klebsiella pneumoniae* exhibits a TOF of approximately 80 min\(^{-1}\) at room temperature.\(^{[146]}\) Further studies revealed no significant decomposition of the catalyst during the course of the reaction and the decreasing efficiency at higher turnover was assigned partly due to the buildup of NH\(_3\) which acts as an inhibitor.

Proton reduction to form H\(_2\) is the main side reaction of nitrogen reduction under acidic conditions, which (apart from the background reaction between protons and KC\(_8\)) is catalyzed by complex 40. The hydrogen evolution stability of 40 is, however, much lower

\begin{equation}
\text{NH}_2^- + \text{H}^+ + 2 \text{e}^- \rightarrow \text{NH}_3 + \text{H}_2
\end{equation}

Figure 21: Stepwise addition of silicon electrophiles to [(BP\(_{i\text{Pr}}^3\))FeN\(_2\)]\(^-\) (40).

Figure 22: Possible mechanisms of reduction of N\(_2\) to NH\(_3\) using [(BP\(_{i\text{Pr}}^3\))FeN\(_2\)]\(^-\) (40) as the catalyst. Characterized intermediates are shown in bold.
than of the silicon analog [(SiPr$_3$)$_2$FeN$_2$]$^-$ 32 which in turn is a worse nitrogen reduction catalyst. Since both dinitrogen and proton reduction are competing reactions that occur simultaneously during the catalytic runs, it seems that increasing the selectivity towards nitrogen reduction is an important goal for improved efficiency of ammonia formation. During catalysis, the buildup of a dihydrido complex (BP$_3$Pr$_3$)(μ-H)Fe(H)(N$_2$) (υ(N$_2$) = 2070 cm$^{-1}$) 42 (Figure 20) was observed with Mössbauer spectroscopy. This hydride complex shows low reactivity towards N$_2$ reduction, but can be converted back to 40 by addition of [H(Et$_2$O)$_2$][BAR$_6$] and KC$_8$. Thus, complex 42 is likely a dormant state that temporarily exits the catalytic cycle, and eventually converts back to the active catalyst 40 in time, releasing H$_2$ (Figure 22).

The cobalt analogue [(BP$_3$Pr$_3$)Co(N$_2$)][Na([12]-c-4)] 45 (υ(N$_2$) = 1978 cm$^{-1}$) was also explored for its catalytic activity towards dinitrogen reduction (Figure 23). The dinitrogen ligand in the cobalt complex is less activated than the iron complex 40 due to the lower π-basicity of Co vs Fe. When 45 was subjected to [H(Et$_2$O)$_2$][BAR$_6$] and KC$_8$ at –78 °C in Et$_2$O, super-stoichiometric amounts of NH$_3$ (2.4 equiv.) were observed. The (SiPr$_3$)$_2$Co and (CP$_3$)$_2$Co analogues were also prepared and investigated, but these did not produce any ammonia.

![Figure 23](image)

The Peters group also investigated tripodal systems with the CP$_3$Co(N$_2$)$_2$[Na([12]-c-4)] 45.

The negatively charged iron(0) complex [(CP$_3$)$_2$FeN$_2$][K(Et$_2$O)$_0.5$] (υ(N$_2$) = 1870 cm$^{-1}$) 46[K(Et$_2$O)$_0.5$]) (Figure 24) showed a stronger activation of N$_2$ compared to the silicon complex 31 or the boron complex 40. Reacting complex 46 with KC$_8$ and [H(Et$_2$O)$_2$][BAR$_6$] at –78 °C under conditions optimized for [(BP$_3$Pr$_3$)FeN$_2$]$^-$ (40) in Et$_2$O led to formation of 36 ± 7 equiv. of NH$_3$. Thus, despite stronger activation of N$_2$ triple bond, the efficiency of complex 46 in ammonia production is slightly lower than
for the BP$_3$-Pr$_3$ complex 40 which produced 59 ± 6 equiv. of NH$_3$. To understand the limiting factors of the system, the reaction mixture was analyzed for catalyst decomposition products. The reaction mixture showed formation of the dinitrogen mono hydride complex (CP$_{i}$-Pr$_3$)Fe(H)(N$_2$) (47) ($\nu$(N$_2$) = 2046 cm$^{-1}$) in time reaching 70%. Contrary to the boron dihydrido complex (BP$_{i}$-Pr$_3$)(μ-H)Fe(H)(N$_2$) (42), 47 is inactive towards protons and reductant, and does not regenerate to 46. The initial rate of 46 has not been measured; however, it seems likely that formation of 47 upon protonation can be one of the reasons for the lower overall efficiency of 46 as compared to 42.

Iron and cobalt PNP systems

The most efficient molybdenum systems for reduction of dinitrogen to ammonia are based on PNP and PPP pincer complexes which catalyze the formation of up to 63 equiv. of ammonia (Figure 17). Consequently, the group of Nishibayashi investigated the activity of iron and cobalt dinitrogen complexes supported with anionic PNP ligands. Treatment of the PNP$_{tBu}$FeN$_2$ complex (PNP$_{tBu}$ = 2,5-bis(di-tert-butylphosphinomethyl)pyrrolide) (48) (Figure 25) with KC$_8$ (200 eq), [H(OEt)$_2$]BAR$_4$ (184 eq) in Et$_2$O at –78 ºC under 1 atm of N$_2$ for 1 h, led to formation of 14.3 ± 0.4 equiv. of ammonia, 1.8 ± 0.2 equiv. of hydrazine and 12.3 equiv. of H$_2$. The nature of the solvent and reductant had a large influence on the performance of this system. While in MeO’Bu comparable yields were observed, the use of coordinating THF resulted in formation of 2.9 ± 0.2 equiv. of ammonia and 2.4 ± 0.1 equiv. of hydrazine. No reactivity was observed when toluene was used as solvent. Using CoCp$_{*}$ (Cp$_*$ = C$_5$Me$_5$) instead of KC$_8$ as the reductant decreased the yield by 50%. The low temperature was essential for the reduction of N$_2$ to occur. When the reaction was carried out at room temperature, 5.2 equiv. of H$_2$ were generated and no dinitrogen reduction was observed. This clearly demonstrates that the competing proton reduction reaction is disfavored at low temperatures. The evolution of hydrazine during the catalytic ammonia formation, indicates that iron-hydrazine complex may be involved as a key intermediate during the reaction. Mechanistic studies were performed to shed light on the possible mechanism. Reaction of complex 48 with [H(OEt)$_2$]BAR$_4$.
at room temperature does not lead to protonation of the coordinated N$_2$. Instead, the protonation occurs on the pyrrole ligand backbone forming complex 49. The subsequent addition of reductant to this complex partially recovers 48, but also shows formation of free PNP-H. This decomposition pathway accounts for lower yield of ammonia (2.6 ± 0.2 eq.) when the protonated complex is used as a catalyst. Thus, the formation of 49 is a likely deactivation pathway of the catalyst. DFT studies show that protonation of the dinitrogen ligand in complex 48 is thermodynamically unfavorable, however, for the one-electron reduced [PNP$_{tBu}$Fe$^\text{N}_2$]$^-$ (50) complex, protonation on the terminal nitrogen atom should be kinetically favorable over the protonation of the ligand. Complex 50 is isolable and shows strong activation of the N$_2$ ligand ($\nu$(N$_2$) = 1832 cm$^{-1}$), which renders it a likely intermediate in the catalytic reaction.

The use of the anionic PNP$_{tBu}$ ligand allowed for the first truly catalytic reduction of N$_2$ to ammonia using cobalt.$^{[15]}$ Under identical conditions to the ones applied for the iron complex 48, the cobalt complex PNP$_{tBu}$CoN$_2$ (51) catalyzed the formation of 15.9 ± 0.2 equiv. of ammonia and 1.0 ± 0.4 equiv. of hydrazine. A similar cobalt complex in which the tert-butyl groups of the PNP ligand were substituted with cyclohexyl groups showed slightly lower conversion. The use of THF as a solvent led to a decrease in activity. Also, the choice of reductant was crucial, as the use of metallic potassium instead of KC$_8$ resulted in formation of no ammonia nor hydrazine. Compared to the iron complex 48 the cobalt catalyst 51 seems to be more stable under the catalytic conditions as no protonation of the ligand could be detected. However, the overall performance in N$_2$ reduction is very similar.
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Cyclic aminocarbene iron system

Ung and Peters investigated whether catalytic reduction of N\textsubscript{2} can be performed using iron systems that do not contain phosphine ligands. A two-coordinate iron complex \((\text{CAAC})\text{Fe} (52)\) (CAAC = cyclic(alkyl)(amino)carbene) supported with a CAAC π-accepting ligand reversibly binds N\textsubscript{2} at low temperatures (Figure 26).\textsuperscript{[15]} One-electron-reduction of the transient dinitrogen complex \((\text{CAAC})\text{FeN}_2 (53)\) with KC\textsubscript{8} in the presence of crown ether at −95 °C led to a clean formation of the isolable, negatively charged, moderately activated dinitrogen complex \(\text{[(CAAC)}_2\text{FeN}_2]\text{[K([18]-c-6)]} (54)\) \((\nu(\text{N}_2) = 1850 \text{ cm}^{-1})\). Attempts to perform the reduction of complex 53 at room temperature resulted in decomposition and at −78 °C only traces of 54 were observed, indicating that significant amounts of the N\textsubscript{2}-bound complex 53 are present only at extremely low temperatures. Therefore, catalytic runs were performed at −95 °C. When 52 was reacted with reductant (50 equiv.) and HBAR\textsubscript{4} · 2 Et\textsubscript{2}O (50 equiv.) in Et\textsubscript{2}O, 3.3 ± 1.1 equiv. of ammonia were formed. The use of 54[K([18]-c-6)] at similar conditions led similar ammonia yield (2.6 ± 0.6 equiv.), which suggests that the dinitrogen complex is indeed capable of catalyzing reduction of dinitrogen. Increasing the temperature to −78 °C or higher, led to formation of minor amounts of ammonia (0.9 ± 0.3 equiv. at −78 °C and 0.4 ± 0.2 equiv. at 23 °C) which is in accord with the weak binding of N\textsubscript{2} at higher temperatures. Additionally, the capability of activation of N\textsubscript{2} coordinated to \((\text{CAAC})\text{Fe} center towards addition of nucleophiles was probed by reacting 54 with chlorosilanes forming silyldiazenido iron complexes \((\text{CAAC})\text{FeN}_2\text{SiMe}_3 (55)\) and \((\text{CAAC})\text{FeN}_2\text{SiEt}_3 (56)\) of which the latter could be isolated. The \((\text{CAAC})\text{Fe} complex 52 was also an active catalyst for silylation of dinitrogen (see below).

\[
\begin{align*}
\text{Dipp} & \quad \text{N} \quad \text{Fe} \quad \text{N} \quad \text{Dipp} \\
\text{Dipp} & \quad \text{N} \quad \text{Fe} \quad \text{N} \quad \text{Dipp} \\
\text{K(18-c-6)} & \quad \text{Dipp} \\
\text{NH}_3 & \quad \text{R}_3\text{SiCl}
\end{align*}
\]

\text*Figure 26: Ammonia formation by \((\text{CAAC})\text{Fe} (52)\) and isolation of some reaction intermediates.*
Diphosphine iron system

Recently, the group of Ashley re-investigated the Leigh system (Figure 13), and by careful choice of reductant and proton source they were able to reach catalytic formation of hydrazine using $[\text{Fe}^0\{(\text{depe})_2\text{N}_2\}]$ (depe = $\text{Et}_2\text{P–CH}_2\text{CH}_2–\text{PET}_2$) ($\nu\text{(N}_2\text{)} = 1985\text{ cm}^{-1}$) as the catalyst and (Figure 27). During the reductive protonation of $\text{N}_2$ coordinated to 57, the one-electron oxidized $[\text{Fe}^+\{(\text{depe})_2\text{N}_2\}]$ $^+$ ($\nu\text{(N}_2\text{)} = 2052\text{ cm}^{-1}$) (58) species is formed as a side product. The use of $\text{CoCp}^*\text{2}$ as the reductant allowed for the reduction of complex 58 back to 57 thus making a catalytic turnover possible. When 57 was reacted with $\text{CoCp}^*\text{2}$ (270 equiv.) and $[\text{PhNH}_2\text{OTf}$ (360 equiv.) at $-78\,^\circ\text{C}$ in $\text{Et}_2\text{O}$, 24.5 ± 0.2 equiv. of hydrazine and 24.5 ± 0.2 equiv. of ammonia were formed.

The choice of $\text{Et}_2\text{O}$ as a solvent was crucial as in THF the competing hydrogen evolution reaction between $\text{CoCp}^*\text{2}$ and $[\text{PhNH}_2\text{OTf}$ led to only substoichiometric formation of hydrazine (0.6 equiv) and ammonia (0.4 equiv.). The advantage of using $[\text{PhNH}_2\text{OTf}$ as an acid in $\text{Et}_2\text{O}$ stems from its sparing solubility in $\text{Et}_2\text{O}$ and as a consequence, low proton concentration. The selectivity towards hydrazine is likely caused by solubility factors: the hydrazine salt $[\text{N}_2\text{H}_5\text{OTf}$ is insoluble in diethyl ether and thus removed from the reaction by precipitation. The remaining bottleneck is the low stability of the catalyst which leads to the decomposition under acidic condition which is accompanied with protonation of the depe ligand. This system is remarkable as it is the first system that is selective towards formation of hydrazine over ammonia.

1.3.5 Reduction of $\text{N}_2$ to silylamines

Some reasons of the low performance of molecular catalysts for ammonia synthesis are poisoning of the catalyst with the product, decomposition of the catalyst as a result of impurities in the acid and formation of dihydrogen as the side product. This is not the case...
in catalytic silylation reactions in which silylamines are formed from molecular dinitrogen and halosilanes in the presence of reductant. This reaction generally yields more turnovers in \( \text{N}_2 \) fixation and can be performed at room temperature. Some catalysts that are active in ammonia formation show to have higher reactivity in dinitrogen reduction to silylamines (see further). In this context, the reduction of dinitrogen with halosilanes, can be used to screen the dinitrogen reduction capacity of a new designed complex under more easy accessible reaction conditions.

The ability of transition metals to catalyze the formation of silylamines from dinitrogen was serendipitously discovered by Shiina in 1972 who observed consumption of \( \text{N}_2 \) during reductive silylation of benzene derivatives when using a nichrome wire stirrer. Various transition metal chlorides were investigated on their reactivity among which \( \text{CrCl}_3 \) performed best producing up to 5.4 equiv. of the silylamine. Several other metal chlorides were also active including manganese, iron, cobalt and nickel (Table 1).

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Although single electrophilic addition of halosilanes to a transition metal coordinated \( \text{N}_2 \) molecule is well known\(^{136,157,158}\), there was only one report on catalytic silylation prior to 2011. In 1989 Hidai and co-workers disclosed that a well-defined molybdenum tetraphosphine based dinitrogen complex \( \text{cis}[-\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4] \) \(^{59}\) \((\nu(\text{N}_2) = 1991 \text{ and } 1913 \text{ cm}^{-1})\) (Figure 28) produced up to 24 equiv. of \( \text{N(SiMe}_3)_3 \) upon reacting \( \text{SiMe}_3\text{Cl} \) and sodium with \( \text{N}_2 \) in THF.\(^{159}\) This system has been further improved by the group of Nishibayashi which employed bidentate ferrocenyldiphosphine ligands for stabilization of the molybdenum complex. The complex \( \text{trans}[-\text{Mo}(\text{N}_2)_2(\text{depf})_2] \) \((\text{depf} = 1,10\text{-bis(diethylphosphino)ferrocene}) \) \(^{60}\) \((\nu(\text{N}_2) = 2093 \text{ cm}^{-1})\) catalyzed formation of 90 equiv. of tris(trimethylsilyl)amine in 20 hours. The turnover number could be pushed to 226 equiv. by running the reaction for 200 hours and adding a second batch of reactants halfway, which set the record for catalytic silylation of \( \text{N}_2 \). The very high reactivity of the ferrocenyldiphosphine containing system could in part be caused by ferrocenes, that are also active in nitrogen silylation reactions (vide infra).
Iron

In a subsequent study the group of Nishibayashi showed that simple organoiron complexes are effective pre-catalysts for reduction of N₂ to silylamines (Figure 29). Treatment of Fe(CO)₅ (61) or FeCp₂ (62) with 600 equiv. of trimethylsilyl chloride and sodium in THF under 1 atm. of N₂ for 20 hours at room temperature, yielded 25 and 13 equiv. of N(SiMe₃)₃ respectively. Ferrocenes with trimethylsilyl substituted cyclopentadienyl rings were even more effective and for [{η⁵-C₅H₅(SiMe₃)}₂Fe] (63), the turnover number reached 34. Significant reactivity was also observed for Fe(CO)₅(SiMe₃)₂ (64), Fe(CpSiMe₃)₂ (65) and [FeCp(CO)]₂ (66).

$$\text{N}_2 + \text{Na} + \text{Me}_3\text{SiCl} \rightarrow \text{cat} \rightarrow \text{THF} \rightarrow \text{N(SiMe}_3)_3$$

Figure 28: Selected molybdenum catalysts that are active in the reduction of N₂ to silylamines.

Figure 29: Iron based pre-catalysts for silylation of dinitrogen.
The use of THF as the solvent for 61 was crucial as in benzene, hexane or diethyl ether no desired product was formed, while in 1,2-dimethoxoyethane (2 equiv.) and 1,4-dioxane (0.2 equiv.) the yield was greatly diminished. Also, when lithium was used instead of sodium, the reactivity dropped to only 5 equiv. of N(SiMe₃)₃. An incubation period of approximately 1 hour during which the active catalyst is formed, was observed when the reaction was followed in time. The fact that all pre-catalysts showed similar behavior in terms of activity, regardless of the initial catalyst structure, led to the conclusion that likely the same species is responsible for catalysis. Unfortunately, no dinitrogen containing active species could be observed during catalysis. Based on the mercury test the formation of active Fe-nanoparticles was also disregarded.

In the proposed mechanism (Figure 30), the catalytic cycle starts with the formation of Fe⁺⁺(SiMe₃)₂(THF) (67) which coordinates dinitrogen forming Fe⁺⁺N₂(SiMe₃)₂(THF) (68). The dinitrogen reduction proceeds via a distal pathway (Figure 12) in which the addition of the first three equiv. of trimethylsilyl radicals, which are formed by reduction of Me₃SiCl with sodium, leads to the formation of the first equivalent of N(SiMe₃)₃ and thus cleavage of the N-N bond. This results in the formation of an iron nitrido species which subsequently reacts with trimethylsilyl radicals to release the second equivalent of N(SiMe₃)₃. DFT calculations show the feasibility of such mechanism. This mechanism is substantially different than the proposed mechanisms by Nishibayashi’s molybdenum catalyst[16] and Lu’s Co-Co dimer[117] (see below, Figure 32).

Ung and Peters’ carbene-supported iron complex 52 (Figure 26) was also active in catalyzing silylation of N₂ (Figure 29).[155] When 52 was treated at room temperature with
600 equiv. of Me$_3$SiCl and KC$_8$ 24 ± 2.7 equiv. of (Me$_3$Si)$_3$N were formed. At –78 °C only 7 ± 1.0 equiv. are formed presumably due to a slower generation of trimethylsilyl radical at low temperatures. Nishibayashi’s iron dinitrogen complex 48, which is catalytically active in ammonia formation at –78°C, also revealed catalytic activity reaching formation of 33 equiv. of tris(trimethylsilyl)amine at room temperature.\[153\]

**Cobalt**

Catalytic silylation of N$_2$ using cobalt catalysts was independently reported by groups of Lu and Nishibayashi. Following their discovery that simple organometallic iron complexes catalyze formation of N(SiMe$_3$)$_3$ the group of Nishibayashi evaluated the reactivity of Co$_2$(CO)$_8$ (71) (Figure 31 and 32).\[162\] Initial screening revealed that the use of dimethoxyethyl ether (DME) as solvent led to higher yields compared to THF (36 vs 25 equiv.) while in non-coordinating solvents (diethyl ether, dioxane, benzene and hexane) reduction of N$_2$ did not proceed at all. The hypothesis that the active species is stabilized by bidentate coordination of DME led to the development of the Co$_2$(CO)$_8$ + 2 bpy (bpy = 2,2’-bipyridine) system which produced up to 49 equiv. of NSiMe$_3$ per cobalt atom. Co(CO)$_4$SiMe$_3$ (72), CoH(PPh$_3$)$_3$N$_2$ (73) and CoCp$_2$ (74) were less active (Figure 32).

Similarly, to the iron systems mentioned before (Figure 29), the reaction profile showed an incubation period of one hour, which pointed to a slow formation of the catalytically
active species. The incubation was proposed to involve formation of a tris-trimethylsilyl cobalt(+III) species (\( \text{Co}_{2} \text{CO}_{8} + 2 \text{bpy} \)), however no experimental evidence for the formation of such species under the strongly reducing reaction conditions was provided. DFT calculations showed that this hypothetical species could promote radical addition to \( \text{N}_{2} \) to form tetra(trimethylsilyl)hydrazine cobalt (\( \text{Co}_{2} \text{CO}_{8} \)). Dissociated tetra(trimethylsilyl)hydrazine would undergo further reduction outside of the metal coordination sphere (Figure 31). Carbonyls of other transition metals were also studied: \( \text{Mn}_{2} \text{CO}_{10}, \text{CpMn(CO)}_{3} \), \( \text{Ru}_{3} \text{CO}_{12} \) and \( \text{Mo(CO)}_{6} \) allowed for the formation of 4, 3, 6 and 6 equiv. of silylamine per metal atom respectively while \( \text{NiCp}_{2} \) and \( \text{Ni(cod)}_{2} \) showed no activity.

A different approach was chosen by the group of Lu who used a well-defined dicobalt complex as the pre-catalyst.\[^{[62]}\] This complex features a dicobalt core supported by a trianionic ligand that features three phosphine donors that bind to the \( \text{Co}^{1} \) centre and three amido and one amine donor that bind to a \( \text{Co}^{II} \) centre (\( \text{Co}^{II} \)) (Figure 32). In the presence of \( \text{N}_{2} \) and 2.2.2. cryptand, the reaction with \( \text{K}_{8} \) results in one-electron-reduction of \( \text{Co}^{1} \) to \( \text{Co}^{0} \) and coordination of \( \text{N}_{2} \) which reveals a rather moderate activation of the \( \text{N} \equiv \text{N} \) bond (\( \text{CoCl}_{2} + 3 \text{PMe}_{3} \)). In the presence of \( \text{Me}_{3} \text{SiCl} \) and potassium graphite in THF complex 80 provides 195 ± 25 turnovers of silylamine formation in 12 hours corresponding to 30% yield in \( \text{Me}_{3} \text{SiCl} \). When additional 2000 equiv. of \( \text{Me}_{3} \text{SiCl} \) and \( \text{K}_{8} \) were added and the reaction was performed for additional 12 hours the TON reached 320 ± 18. The complex remains bimetallic throughout at least the first 10 silyl radical additions.
of the initial rates reveals a pseudo first order kinetics with turnover frequency (TOF) of \(1 \text{ min}^{-1}\). This, together with the lack of an incubation period is consistent with a well-defined homogeneous catalyst. The one-electron reduced anionic complex 81 reveals no significantly different reactivity. The use of KC\(_8\) as a reductant for catalyst 80 proved to be crucial as the use of alkali metals led to a large decrease in product formation which was explained by larger contact area of finely dispersed potassium graphite compared to metallic particles of K, Na or Li. The bimetallic aluminum cobalt complex 82 (\(\nu_{\text{NN}} = 2081 \text{ cm}^{-1}\))\(^{[164]}\) was still active in the dinitrogen reduction reaction, but a much lower conversion of \(30 \pm 9\) equiv. was reached. The proposed mechanism (Figure 33)\(^{[165]}\) for this dicobalt tripodal complex, supported by DFT, is similar to the mechanism calculated for the molybdenum catalyzed formation of trimethylsilylamines.\(^{[159,161]}\)

**Figure 33:** Proposed catalytic cycle for silylation of dinitrogen using the dicobalt complex 80.
Starting from the anionic dinitrogen complex 81 it follows a double (distal) addition at the terminal nitrogen (86 and 87). Dissociation of one of the phosphine arms (88) allows addition on the proximal nitrogen (89). Association of the phosphine arm (80) leads to a release of \([\text{N}_2(\text{SiMe}_3)_3]^–\) which in the presence of Me$_3$SiCl and reductants spontaneously converts to \((\text{Me}_3\text{Si})_3\text{N}\) in a non-catalyzed pathway. Subsequent reduction of 80 and coordination of dinitrogen (81) closes the cycle. The dissociation of the phosphine arm in combination with the bimetallic character is thought to be key for the high turnovers and stability of the catalyst.\[165\] Other cobalt complexes were also found active under these conditions. For instance, in the presence of electron-donating phosphines (83-85) CoCl$_2$ reached a turnover number of up to 94 ± 19. Studies from our group on the silylation of N$_2$ using CoH(PPh$_3$)$_3$N$_2$ (73) as the pre-catalyst in THF showed that the despite having coordinated dinitrogen this complex is not the active catalyst and no direct N-Si bond formation is observed on the cobalt-bound N$_2$. The induction period before any N(SiMe$_3$)$_3$ is formed suggests that the sole presence of activated N$_2$ bound to a metal is not sufficient for its activation and the putative active species has to be first formed by reacting with chlorosilane and a reductant.\[166\]

### 1.3.6 Conclusions

The industrial processes for ammonia production requires the use of very high temperatures and pressures. Natural enzymes, however, can catalyze the formation of ammonia already at room temperature and under atmospheric pressure. This fact has been an inspiration for the development of catalysts that can reduce dinitrogen under similarly mild conditions. In recent years, the understanding of factors that influence the reactivity of the N$_2$ molecule reached a level that allowed for development of the first catalyst systems that use base metals.

The current state-of-the-art iron and cobalt systems reach the performance of the best molybdenum based catalysts yielding 59 and 16 equiv. of ammonia per metal center, respectively at –78 °C. In comparison, the best molybdenum system reaches up to 63 equiv. of ammonia at room temperature. The mechanistic aspects of dinitrogen reduction to form ammonia using iron and cobalt systems are relatively well understood and the possible catalyst deactivation pathways were in most cases investigated. The mechanistic studies performed on the catalytically active iron complexes show that the first two proton additions to the coordinated N$_2$ moiety occur at the distal nitrogen atom to form a hydrazido species, which subsequently undergoes protonation to form hydrazine, which is an intermediate during ammonia synthesis by nitrogenase. This is in stark contrast to the molybdenum systems which operate via a distal pathway via a metal nitrido intermediate. An alternative approach in which the formation of ammonia would start
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with the homolytic splitting of the N\textsubscript{2} molecule has not yet led to a catalytic turnover. Several factors constitute to the current low overall performance of these catalysts. Impurities present in the reagents have detrimental effects on activity and stability; rigorous purification of reactants is necessary. Background reactions between the reductant and protons, results in the formation of sufficient amounts of dihydrogen to slow down or even totally shut off the catalytic ammonia formation reaction. For this reason, reduction of dinitrogen has to be performed at very low temperatures under which the competing proton reduction reaction is retarded. Thus, key to improvement of these catalysts would be preventing the rate of proton reduction. Lastly, product inhibition is another limiting factor.

Even though the exact nature of the catalytically active species is rather poorly understood, much more efficient catalysts are known for the dinitrogen silylation reaction. Cobalt is particularly effective in this transformation and the reaction is believed to proceed via addition of silyl radicals to the metal bound N\textsubscript{2}. As in many cases the structure of the catalyst is not known, rational design of the catalytic system is difficult. Many of the pre-catalysts used, undergo transformations that lead to the formation of active species as evidenced by long induction periods of the catalytic reaction.

Despite increased understanding of the chemistry behind dinitrogen reduction at ambient conditions, much more research is needed before synthetically applicable catalysts are developed. However, especially if these catalysts could be coupled with electrochemical electron sources, they could lead to the development of greener routes towards amines. Overcoming these challenges could lead to the development of homogeneous systems which could be applied in the synthesis of nitrogen-containing compounds.

1.4 Thesis scope and outline

The transformation to a society that runs on sustainable energy can be facilitated by new technologies that allow solar energy to fuel conversions. Catalytic processes play a crucial role in such technology. In this introduction Chapter an overview of homogeneous reduction catalysts is given on some crucial transformations for the storage of solar energy into chemical energy. This research project was funded by the National Research School Combination Catalysis Controlled by Chemical Design (NRSC-C), with aim to design catalysts for (light driven) reduction reactions relevant for the field of solar fuel. This thesis describes the synthesis and characterization of tetradentate Ru, Ni, Co and Fe complexes and their subsequent reactivity in the context of the solar fuel theme. In Chapter 2, the formation of salen-based ruthenium complexes is described. The ruthenium-salen complex takes a carbonylligand from methanol in presence of phosphine,
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which results in the formation of an octahedral \((\text{salalen})\text{Ru(CO)}(\text{P(i-Pr)}_2)_3\) complex. The salen complexes are able to dehydrogenate methanol to dihydrogen and carbonate in basic media. Mechanistic investigations show that the carbonyl ligand can react with KOH forming potassium formate, but that the carbonyl-complex is not the active species during the dehydrogenation reaction, as the carbonyl ligand is not regenerated during catalysis. 

Chapter 3 describes the coordination of a tripodal indolyl-phosphine \((\text{PP}_3)\) ligand to ruthenium\((+II)\) forming an octahedral \(\text{Ru(PP}_3\text{)Cl}_2\) complex. This complex can be stepwise reduced to the corresponding rare \(\text{Ru}^{I}\) and \(\text{Ru}^{0}\)N\(_2\), which in turn can be oxidized back to the stable \(\text{Ru}^{II}\) complex by the addition of organochlorides.

In Chapter 4 the class of ligands is extended to isomers and electronic variations. Coordination to ruthenium shows formation of similar octahedral complexes as in chapter 3. These complexes are subsequently studied for dinitrogen coordination, dinitrogen reduction, and formic acid decomposition.

In the final Chapter, the coordination chemistry of first row transition metals \(\text{Ni}^{II}\), \(\text{Co}^{II}\) and \(\text{Fe}^{II}\) to the same tripodal ligands is reported. These complexes feature a trigonal bipyramidal geometry and possess a non-coordinating counterion. The non-coordinating anion is shown to be either a BF\(_4^-\) or a tetrahalido metalate \((\text{MX}_4^2-)\) anion (obtained from the metal precursor \((\text{MCl}_2)\)). The reduction of these complexes with two electrons shows that the iron complexes can coordinate dinitrogen. The use of ligands with different electronic properties, results in noticeable different activations of the dinitrogen ligand coordinated to the metal atom.

1.5 References

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