Magnesium and zinc hydride complexes
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The first chapter provides an overview of the chemistry and properties of magnesium and zinc and in particular their hydride salts and complexes. In addition, it gives a short introduction to magnesium dihydride as a potential hydrogen storage material.
Chapter 1

1.1. Magnesium and zinc in comparison

1.1.1. Magnesium

In the earth’s crust, magnesium is found bound as carbonates, silicates, chlorides, sulfates and different oxides (natural abundance = 2%). The sea water concentration of magnesium averages 1.3 mg/L. Mg is also the most abundant divalent cation in eukaryotic cells with concentrations of free Mg$^{2+}$ ranging from 0.1 to 1 mM.$^1$ Magnesium cations take part in various biological processes, for example, photosynthesis, nerve impulse transmission, muscle contraction and carbon hydrate metabolism.

The best-known example in nature is the green pigment chlorophyll (Figure 1.1a) which allows plants to absorb energy from light. Within this crucial building block for photosynthesis, Mg assures the rigid positions of stacked chlorophyll molecules (Figure 1.1b). The most important enzyme containing magnesium is RuBisCo (Ribulose-1,5-bisphosphate carboxylase oxygenase), the enzyme that catalyzes the formation of hexoses from carbon dioxide and water.$^{2,3}$ Although the catalytic rate is slow and the affinity for atmospheric CO$_2$ is relatively low, it is the most abundant protein in the world.$^3$

![Figure 1.1 a) Chlorophyll a, b) schematic representation of stacked chlorophyll molecules.](image)

The global annual production of magnesium metal amounts to 500 kT and the obtained metal is mainly used for reduction, deoxidization, alloys, organic synthesis and H$_2$- and energy storage. Furthermore it can be utilized for pyrotechnics and flashlights as upon burning Mg produces an intense white light, which is even brighter than sunlight.

Organomagnesium compounds are amongst the best and longest known organometallic compounds. At the beginning they were regarded as curiosities until in 1900 Victor Grignard discovered their synthetic potential when he was working on the optimization of the Barbier reaction (Figure 1.2, B). He found that separately prepared organomagnesium halides (Figure 1.2, A) could be used in the synthesis of secondary and tertiary alcohols from
aldehydes or ketones (Figure 1.2, B) resulting in higher yields than those obtained when using the Barbier procedure, which is a one-pot synthesis.\cite{4} For his discovery and the subsequent development of Grignard reagents, Victor Grignard was awarded the Nobel Prize in Chemistry in 1912.

\[ RX + Mg \xrightarrow{Et_2O} R\cdot Mg\cdot X \quad + \quad O\xrightarrow{H_2O} R'' \quad R = \text{alkyl, aryl} \]

\[ X = \text{Cl, Br, I} \]

**Figure 1.2** Preparation of Grignard reagents (A) and optimized Barbier reaction (B).

The constitution of Grignard reagents in solution has been debated for about 60 years.\cite{5,6} Nowadays it is well-established that the simple representation of Grignard reagents as RMgX is not correct. Instead, Grignard reagents exist as complicated mixtures of various aggregated species, in which the Schlenk equilibrium (Figure 1.3) plays a vital role.\cite{7} The actual structure of the species in solution are dependent on multiple factors like the nature of R and X, the coordinating solvent, the concentration and the temperature.\cite{6,8}

\[ 2 \text{R}\cdot Mg\cdot X \xleftrightarrow{\text{Schlenk}} \text{R}_2\cdot Mg + MgX_2 \quad \text{R = alkyl, aryl} \]

\[ X = \text{Cl, Br, I} \]

**Figure 1.3** Schematic representation of the Schlenk equilibrium.

### 1.1.2. Zinc

The diamagnetic element zinc is found in a relatively low natural abundance (0.007 wt% in the earth crust), however, it has been known for a long time due to the easy isolation from its ores. This facile isolation also makes zinc metal and zinc salts available at low costs.\cite{9}

Zinc is a relatively non-toxic metal and an essential element for humans (daily intake: 22 mg), animals, plants and microorganisms. Primarily; it serves as a cofactor for a large number of enzymatic reactions (40 mg/kg Zn in human beings).\cite{1,10} It is the second most abundant transition metal cation in living organisms after iron.\cite{11} Zinc-binding proteins that perform essential functions in a various living organisms include insulin, metallothionein, DNA topoisomerase, phosphotriesterase,\cite{12} zinc-finger proteins, matrix metalloproteinases, the anthrax toxin lethal factor, human carbonic anhydrase,\cite{13} alcohol dehydrogenase, \(\beta\)-lactamases and copper-zinc dismutase. In those metalloproteins, zinc often functions as a Lewis acid. It can also electrostatically stabilize reactants or intermediates in the active site. In addition, zinc plays a vital role in the healing of wounds.

The good compatibility of zinc with the human body, makes it a valuable ingredient for pharmaceuticals and cosmetics. It is used for the treatment of wounds, burns, skin diseases and infections as well as in dandruff shampoos and fungicides. Zinc metal (global annual
production: 6 MT) is mainly applied in the galvanization of iron and steel, for die casting and alloyed with copper as brass. Most of the conventionally used batteries employ zinc as anode metal.[14] Additionally, it is technologically important in ZnO photoluminescent materials and nanoparticles like quantum dots.[15]

Organozinc compounds are known since the preparation of diethylzinc by Edward Frankland in 1849 and were one of the first discovered organometallic compounds.[16] These organometallic reagents were the main tool for the formation of new carbon-carbon bonds until 1900, when Victor Grignard discovered a convenient preparation of organomagnesium compounds.[4] Grignard reagents were found to be a more reactive species and afforded higher yields, while zinc reagents react faster with oxygen and disadvantageously often burn vigorously in air. Therefore, use of organozinc reagents sank into oblivion for decades. However, there were still some common reactions performed with zinc organometallics such as the Reformatsky reaction[17] (Figure 1.4a) or the Simmons-Smith cyclopropanation (Figure 1.4b).[18] Also, some transition-metal catalyzed transformations like Negishi coupling rely heavily on the use of zinc reagents.

![Figure 1.4](image)

**Figure 1.4** a) Reformatsky reaction, b) Simmons-Smith reaction.

In 1943, Hunsdieker et al. reported that, in contrast to Grignard reagents, organozinc reagents bearing long carbon chains with a terminal ester function could be prepared.[19] This functional group tolerance remained largely ignored by synthetic chemists and it took more than 30 years until its high synthetical potential was recognized in transmetalation reactions.[9,20]

With its filled d-shell, zinc represents an interesting borderline case in the periodic table. It can either be considered as a transition metal or a main-group element with considerable analogies to alkaline-earth metals.[21]

### 1.1.3. Direct comparison

Although magnesium and zinc are found in different groups and rows of the periodic table, they show surprisingly similar properties. Due to their electron configuration both metals have one main oxidation state, which is +2 (Table 1.1). When suitable ligand systems are
employed low-valent Mg(I)\textsuperscript{[22,23]} and Zn(I)\textsuperscript{[23,24]} complexes can be stabilized, but these species are scarce. Magnesium and zinc also share various coordination numbers (Table 1.1).

**Table 1.1 Comparison of the properties of magnesium and zinc**

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron configuration</td>
<td>[Ne] 3s\textsuperscript{2}</td>
<td>[Ar] 3d\textsuperscript{10}4s\textsuperscript{2}</td>
</tr>
<tr>
<td>oxidation state</td>
<td>+II, +I (rare)</td>
<td>+II, +I (rare)</td>
</tr>
<tr>
<td>main coordination numbers</td>
<td>6 (octahedral), 4 (tetrahedral, rare)</td>
<td>4 (tetrahedral), 5 (trigonal-bipyramidal, square-pyramidal)</td>
</tr>
</tbody>
</table>

For magnesium the main coordination numbers are 6 with an octahedral coordination sphere (Figure 1.5a) and less common 4 with a tetrahedral coordination. In rare cases, it can adopt all coordination numbers from 1 (for gaseous MgO) up to 10 (for MgCp\textsubscript{2}).\textsuperscript{[25,26]} Zinc prefers coordination number 4 with a tetrahedral environment (Figure 1.5b). However, the prediction of the coordination sphere for zinc is problematic as there are numerous examples for compounds with ambiguous coordination numbers between 4, 5 and 6. For dialkylzinc compounds, a coordination number of 2 is typical.\textsuperscript{[14]}

![Figure 1.5 Crystal lattices of a) magnesium chloride and b) zinc sulfide; the octahedral and tetrahedral coordination spheres are indicated as black and red polyhedra, respectively.](image)

The higher nuclear charge and the poor electron shielding of the d–orbitals in Zn result in an increased effective nuclear charge. This allows for a remarkable similarity of the ionic radii of Mg\textsuperscript{2+} and Zn\textsuperscript{2+} over a range of coordination numbers (Table 1.2).\textsuperscript{[27]} This results in
formation of several structurally similar compounds like MgS$_2$ and ZnS$_2$ (zinc blende structure, Figure 1.5b) or isomorphous compounds like the vitriols MgSO$_4$·7H$_2$O and ZnSO$_4$·7H$_2$O.[26]

Table 1.2 Ionic radii of Mg$^{2+}$ and Zn$^{2+}$ at different coordination numbers

<table>
<thead>
<tr>
<th>coordination number</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic radius</td>
<td>Mg$^{2+}$</td>
<td>0.57</td>
<td>0.66</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Zn$^{2+}$</td>
<td>0.60</td>
<td>0.68</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Next to the various similarities, there are also numerous differences in the properties of magnesium and zinc. Due to the higher effective nuclear charge of Zn, the outer valence electrons are bound significantly stronger than in Mg. This is represented in the higher electronegativity of Zn (Table 1.3) and the more covalent character of Zn compounds. The covalent character of Zn salts is seen in the lower solubility of oxides and sulfides, compared to their alkaline earth analogues. The increased nuclear charge also renders Zn a more noble metal than the ignoble Mg. This results in a higher ionization potential and more positive standard potential than Mg (Table 1.3).

Zinc forms weaker intermetallic bonds, based on the $s^2$ interactions, which have an influence on the melting and boiling point of the metal. This is also the reason why zinc metal is easy to sublime. In comparison to magnesium, metallic zinc is also significantly denser (Table 1.3).

Table 1.3 Comparison of the properties of magnesium and zinc

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^0$ [V][28]</td>
<td>-2.356</td>
<td>-0.7626</td>
</tr>
<tr>
<td>1st ionization energy</td>
<td>7.642</td>
<td>9.393</td>
</tr>
<tr>
<td>electronegativity</td>
<td>1.31</td>
<td>1.65</td>
</tr>
<tr>
<td>melting point [°C][31]</td>
<td>650</td>
<td>419.53</td>
</tr>
<tr>
<td>boiling point [°C][31]</td>
<td>1090</td>
<td>907</td>
</tr>
<tr>
<td>density [g/cm$^3$][31]</td>
<td>1.74</td>
<td>7.14</td>
</tr>
</tbody>
</table>
1.2. **Metal hydrides**

1.2.1. **Hydrogen**

Hydrogen is a unique group 1 element which for various reasons is sometimes placed in group 17 of the periodic table. With its single valence electron it clearly belongs to the group 1 elements. Hydrogen also forms a stable singly charged cation H^+ like the alkaline metals. Concurrently, hydrogen is a non-metal, its stable elemental form is the diatomic molecule H\(_2\) and it possesses a stable hydride anion H^-. These properties are characteristic for group 17 elements. However, a closer look at the properties reveals that hydrogen turns metallic under increased pressure, H\(_2\) is rather reducing (E\(^0\)(H\(^+\)/H\(_2\)) = 0 V), while halogens X\(_2\) are strongly oxidizing (E\(^0\)(I\(_2\)/I\(^-\)) = +0.54 V – E\(^0\)(F\(_2\)/F\(^-\)) = +2.87 V). In contrast to the very stable halide X\(^-\), the hydride anion is highly reactive (E\(^0\)(H\(_2\)/H\(^-\)) = −2.25 V). In conclusion, these observations classify hydrogen as a group 1 element.

1.2.2. **Metal hydride salts**

Early transition metals show a strong tendency for hydride formation. This trend decreases in the direction of the late transitions-metals. In general, the metal hydride formation can be divided into three contributing factors. First, energy is needed to convert the crystal structure of the metal into the structure formed by the metal ions in the metal hydride. The second contribution is the loss of cohesive energy when the metal structure is expanded to form the metal hydride. Finally, the only negative contribution is the chemical bonding between hydrogen and the metal in which it is inserted. This is hence favorable to hydride formation.[32]

For zinc, a metal with significantly higher cohesive energy than magnesium, the energy of formation for the hydride is quite positive.[32] However, zinc dihydride has been known for more than 60 years as a metastable compound with an unknown structure.[33,34] ZnH\(_2\) can be isolated as a white, highly oxidizable solid either from the reaction of R\(_2\)Zn (R = Me,[33,35] Et,[36] Ph[37]) and LiAlH\(_4\) or ZnX\(_2\) (X = Cl, Br, I) and MH (M = Li, Na) (Figure 1.6).[38] ZnH\(_2\), obtained from the reaction of alkyl precursors (Figure 1.6a), has been reported to turn black at room temperature within the course of several days and hydrolyzes slowly with water. In contrast, ZnH\(_2\) isolated from the reaction of zinc halides with alkali metal hydrides (Figure 1.6b) remains white for several weeks and hydrolyzes rapidly at room temperature.[38]
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Zinc dihydride starts decomposing at 90 °C (more rapidly at 105 °C) forming zinc and H₂. The thermolabile solid is non-volatile and virtually insoluble in non-polar and almost all polar solvents. It is presumed to be a highly associated, hydrogen-bridged polymer like BeH₂ and MgH₂. The varying stability and different reported X-ray powder patterns, however, suggest that ZnH₂ can adopt various structures.

Magnesium forms a stable hydride MgH₂, which can be synthesized directly from the elements. A relatively unreactive, macrocrystalline form is isolated when the elements Mg and H₂ are reacted at 500 °C and 200 bar, whereas a highly reactive, microcrystalline form (activated MgH₂) can be obtained from the catalytic hydrogenation of magnesium in tetrahydrofuran (THF) at 20 – 60 °C and 1 – 80 bar H₂ pressure (catalyst: anthracene and either TiCl₄, CrCl₃ or FeCl₂).[25]

Magnesium dihydride is a white non-volatile solid that is barely soluble in organic solvents. It shows rutile structure (coordination number H = 3, Mg = 6), very polar bonds and a density (1.45 g/cm³) that is lower than the one of magnesium metal (1.74 g/cm³). MgH₂ reacts violently with water and, depending on the way of preparation, it is either stable in air or self-igniting. At 284 °C activated MgH₂ decomposes and produces hydrogen and pyrophoric magnesium which can be used for hydrogen storage. Furthermore, activated magnesium hydride can be utilized as drying and reducing agent and for the synthesis of soluble MgXH or R₂Mg compounds.[25,39]

1.2.3. Metal hydride complexes

The metal-hydride bond plays a vital role in organometallic chemistry as metal hydrides are able to undergo addition and insertion reactions with a wide variety of unsaturated compounds, resulting in stable species or intermediates with metal-carbon bonds.[40] In addition many catalytic transformations involve hydride insertion as a key step.[41]

The first metal hydride complex was discovered in 1931 by Walter Hieber.[42] When the iron carbonyl hydride complex 1 (Figure 1.7) was first reported, researchers assumed that the hydrogen atoms were not bound to the metal but two of the carbonyl groups were pictured to be aldehydes. The debate, whether it was an actual hydride complex or not, went on until the mid-sixties, when other metal hydride complexes were synthesized and
characterized. In 1938, Otto Roelen discovered the catalytic hydroformylation during an investigation of the origin of oxygenated products occurring in cobalt-catalyzed Fischer-Tropsch reactions. The catalyst was found to be a cobalt carbonyl hydride complex 2 (Figure 1.7). A further important example has been discovered in 1966 by Sir Geoffrey Wilkinson and is known as Wilkinson’s catalyst 3 (Figure 1.7). This rhodium phosphine chloride hydride complex is a highly active homogeneous hydrogenation catalyst for alkenes. Its discovery had widespread significance for organic and inorganic chemists and proved to be valuable for industrial applications. For his work on organometallic compounds, Wilkinson was awarded the Nobel prize in 1973 along with Ernst Otto Fischer.

![Figure 1.7 Selection of important transition metal hydride complexes.](image)

Although ZnH$_2$ is a metastable compound for which the structure is still unknown, the choice of suitable ligands allowed for the isolation and characterization of various zinc hydride complexes. The first stable and soluble neutral zinc hydride complex (4) was reported in 1968 by reaction of ZnH$_2$ with N,N,N'-trimethylethylenediamine (Figure 1.8).[45] Within the last 20 years, a range of structural motives with terminal (5)[46] and bridging hydride moieties (6)[47] for zinc hydride complexes has been identified (Figure 1.8). For more examples of zinc hydride complexes see chapter 3.1.

![Figure 1.8 a) First soluble, neutral zinc hydride complex, b) examples for a zinc hydride complex with terminal hydride ligands and c) with bridging hydride ligands.](image)
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In contrast to the wealth of information on transition metal hydride complexes, the area of main-group metal hydride complexes is biased. Whereas the $p$-block metal hydrides are well-documented, only few examples of $s$-block metal hydrides have been reported. A main reason for this imbalance is the relatively small bond energy in these predominantly ionic complexes. Especially for larger metals, this results in a facile ligand exchange and thus formation of ligand-free metal hydride. Additionally, the very high lattice energies for early-main-group metal hydrides gives rise to immediate precipitation of saline $[\text{MH}_x]^-$.

For this reason, most of the few examples of early-main-group metal hydride complexes show the hydride moiety encapsulated in mixed aggregates. The first structurally characterized magnesium hydride complex (7) is an “inverse crown ether” complex, i.e. hydride anions that are encapsulated in a metal containing host ring.\cite{48} To stabilize homometallic, heteroleptic early-main-group hydride complexes, sterically demanding ligands that prevent the formation of homoleptic complexes are necessary. Recently, the dimeric $\beta$-diketiminate magnesium hydride complex ($\text{DIPP-MgH}_2$) has been described.\cite{49} It is the first example of a homometallic magnesium hydride complex with bridging hydride ligands. In a following study, the first magnesium hydride complex with a terminal hydride ligand 8 was structurally characterized. It could be isolated from the addition of 4-dimethylpyridine to the corresponding dimeric magnesium hydride complex ($\text{DIPP-MgH}_2$).

There is also growing evidence for the existence of larger alkaline-earth metal hydride rich $\text{M}_m\text{H}_n$ clusters with $n>m$. Michalczyk et al. reported the synthesis of $[\text{L}_n\text{MgH}_2]_n$ species in which $\text{L}$ represents a neutral ligand.\cite{50} Harder et al. proposed hydride-rich calcium hydride clusters $[\text{L}_1\text{CaH}_{1.1}]_n$ to be active as hydrosilylation catalysts.\cite{51} Conclusive evidence for a hydride-rich magnesium cluster was found by Hill et al. who prepared a tetranuclear magnesium amide-hydride cluster (9).\cite{52}
Further examples for well-defined magnesium hydride clusters have been discovered by Harder et al. and will be presented in detail in chapter 2.1.\textsuperscript{[53]}

\subsection{1.3. Hydrogen storage}

In the last century, the human population has increased by a factor of 6 but energy consumption has risen by a factor of 80.\textsuperscript{[54]} As many sources for fossil fuels are running out in the near future, the search for alternatives is a research field of lively interest. Considering the historical development of energy carriers towards hydrogen-rich fuels (coal, oil, natural gas) and the necessity to reduce carbon dioxide emissions, hydrogen should be the designated energy carrier for the future. Hydrogen is regenerative, environmentally friendly and has the highest heating value per mass of all chemical fuels. A key problem, however, is the volumetric and gravimetric density of hydrogen. This feature is crucial for the storage, particularly for the use as a zero-emission fuel in mobile applications like transportation. Physical storage of hydrogen, as highly pressurized gas or in liquid phase at low temperatures, gives rise to significant security risks, loss of energy (due to the energy needed for pressurization) and large volumes for containers.\textsuperscript{[55]} In addition, physical adsorption onto lightweight nanomaterials like zeolites, carbon nanotubes or activated carbon leads to low storage densities and the need of low temperatures.\textsuperscript{[56]} Alternatively, chemical storage, namely the reversible absorption of hydrogen into another material, can be considered. In this case, metal hydrides of lightweight metals are a promising and safe option, which has been the focus of intensive research.\textsuperscript{[57,58]}

Magnesium as a light and highly abundant metal makes magnesium dihydride a promising candidate, combining a high hydrogen capacity of 7.6 wt. \% with low costs.\textsuperscript{[59,60]} Another feature that renders magnesium dihydride an especially interesting hydrogen storage material is the reversibility of the hydrogen desorption (Figure 1.9). This allows for a facile regeneration of the resulting magnesium metal.

\[
\begin{align*}
\text{MgH}_2 & \xrightarrow{300 \ ^\circ \text{C, 1 bar}} \text{Mg}^0 + \text{H}_2 \\
& \xrightarrow{500 \ ^\circ \text{C, 200 bar}} 
\end{align*}
\]

\textbf{Figure 1.9} Reversible hydrogen desorption from magnesium dihydride.
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However, slow desorption kinetics, a high thermodynamic stability and high reactivity towards air and oxygen are main barriers for the direct use of pure MgH$_2$.[61] The high thermodynamic stability is expressed in an unfavorably high desorption temperature of 575 K at 1 bar.[57,62]

Recent research has devoted much effort towards modifying the Mg-based system, mainly aiming at decreasing the desorption temperature and increasing the absorption/desorption rates. The different approaches include alloying magnesium with other elements, high energy or reactive ball milling and surface modification of magnesium metal.[63,64] All methods show drastic improvements of the kinetics up to two orders of magnitude in sorption rates. These improvements can be attributed to surface enlargement and dissolution of other metals into magnesium which disrupts the crystalline structure of magnesium. Furthermore, decrease of diffusion lengths and rupture of the inhibiting and passivating outer oxide layer contribute to the improved desorption kinetics. Nevertheless, upscaling of the ball-milling process is not straightforward and for pure Mg it is limited to grain sizes of 10-50 nm.

Even more important, most of these techniques do not affect the thermodynamics and therefore the desorption temperature, which cannot be lowered below the bulk value of 573 K. Some alloying or doping processes, however, can affect the desorption temperature but they decrease the hydrogen storage capacity at the same time by the additional weight of the alloying or doping metals.[58,65,66] In addition, positive effects are often lost within the first few charging/discharging cycles.[57,60,67] A similar observation was made for γ-MgH$_2$ (α-PbO$_2$ structure), which is less stable than the common β-MgH$_2$ (rutile structure) (Figure 1.11c), but improvement in the desorption temperature is lost after the first dehydrogenation/hydrogenation cycle, upon which solely β-MgH$_2$ is formed. Structurally, β- and γ-MgH$_2$ are closely related, both containing Mg in an octahedral coordination sphere of six hydrides. The octahedra are linked by edge sharing in one direction and by corner sharing in the other two directions. In case of the tetragonal β-MgH$_2$ the chains are linear and run along the fourfold axis of its rutile structure. In γ-MgH$_2$ the chains are zigzag shaped and run along a twofold screw axis of its orthorhombic α-PbO$_2$ structure. The octahedral in γ-MgH$_2$ are strongly distorted. Promising results with lower desorption temperatures have also been reported for thin films of magnesium, often capped with palladium, or for highly amorphous Mg.[65,68]

These experimental results have stimulated theoretical studies on the thermodynamical stability of MgH$_2$ versus Mg and H$_2$ as a function of particle size.[70,71] This idea can be supported by the classical Born-Haber cycle assuming an entirely ionic structure as an approximation (Figure 1.10).[72] The largest contribution is related to the lattice energy of
[MgH$_2$]$_n$\cite{70} is enormous. It is much higher than that for Mg$^0$ and partially the reason for the high stability of MgH$_2$ as a bulk material. Small changes in the lattice enthalpy can have a large impact on the desorption enthalpy. Although the lattice enthalpy is a fixed quantity, it has been calculated that clusters in the nano-regime have much lower lattice enthalpies. This is due to the fact that atoms at the outside of the particle have reduced coordination numbers and due to a decreased coordination number of the atoms, the specific lattice enthalpy decreases upon lowering the number of atoms in a cluster. In addition, distortions of the lattice should result in a shift in lattice enthalpy like it is observed in alloyed magnesium.\cite{63}

\[
\begin{align*}
\Delta H^\text{bond} &= -436 \\
\text{Mg}^{2+}(g) + 2e^- + H_2(g) \\
\Delta H^\text{ion} &= 2205 \\
\text{Mg}(g) + H_2(g) \\
\Delta H^\text{mol} &= -75 = \Delta H^\text{des} \\
\text{Mg}(s) + H_2(g) \\
\Delta H^\text{vap} &= \Delta H^\text{lat}\text{MgH}_2 = 2718 \\
\text{Mg}(g) + H_2(g) \\
\Delta H^\text{affin} &= -146 \\
\text{Mg}^{2+}(g) + 2H^-(g) \\
\Delta H^\text{f}_0 &= -75 = \Delta H^\text{des} \\
\text{MgH}_2(s) \\
\end{align*}
\]

Figure 1.10 Born-Haber cycle for the bulk MgH$_2$ system at standard ambient pressure and temperature (0.1 MPa, 298 K).

The dependency of the desorption enthalpy on the cluster size has been investigated theoretically for up to 56 magnesium atoms by means of \textit{ab initio} and DFT calculations.\cite{70} The results show that MgH$_2$ clusters larger than Mg$_{19}$H$_{38}$ have a rutile-like geometry (Figure 1.11c) and consequently show similar properties to bulk $\beta$-MgH$_2$. Below this limit the clusters begin to be destabilized, which translates into a decrease in desorption energy and thus a lower desorption temperature. As an example, a cluster of 0.9 nm (9 Mg atoms, Figure 1.11b) corresponds to a desorption temperature of 473 K (Figure 1.12).\cite{70}
Recent theoretical work reinvestigated this dependency\cite{71} and similar trends have been confirmed. Interestingly, the extrapolated bulk value for crystalline clusters (76.5 ± 1.5 kJ/mol) is astonishingly close to the experimental value (75.5 kJ/mol), which supports the quality of the theoretical methods used.

In additional theoretical work, crystalline nanoclusters that were the base of the former calculations have been compared to noncrystalline nanoclusters. Contrary to the crystalline nanoclusters, the extrapolated bulk value for noncrystalline material (54 kJ/mol) is considerably smaller and the predicted values drop significantly faster with the cluster size.\cite{73} This result is in agreement with experimental evidence that colloidal MgH\textsubscript{2} nanoparticles are destabilized\cite{74} and that ball-milled MgH\textsubscript{2} can show lower desorption temperatures.\cite{75}

![Diagram](image1.png)

**Figure 1.11** a, b) Selected geometries of (MgH\textsubscript{2})\textsubscript{19}-cluster, c) unit cell of bulk β-MgH\textsubscript{2}.\cite{70}

**Figure 1.12** Calculated desorption energies for crystalline MgH\textsubscript{2} clusters using DFT (B97 functional).
1.4. Outline of this thesis

The aim of the research presented in this thesis is the synthesis of novel magnesium and zinc hydride complexes, the subsequent study of magnesium and zinc hydride clusters and their application in catalysis and as model systems for hydrogen storage materials.

Chapter 2 is dedicated to the detailed study of the decomposition of magnesium hydride clusters by means of Töpler pump experiments, DSC and TPD measurements as well as by deuterium labelling of the complexes. The chapter concludes with DFT studies on the electron density of a tetranuclear magnesium hydride cluster and the potential decomposition product, a low-valent magnesium complex.

Chapter 3 describes the synthesis and characterization of a tetranuclear zinc hydride cluster. The decomposition of this novel zinc complex is investigated and the electron density is analyzed by a DFT study. In addition, the design of new ligands for the development of further magnesium and zinc clusters is presented.

Within the scope of Chapter 4 the reactivity of the novel magnesium hydride clusters is investigated and compared to the reactivity of zinc and calcium hydride complexes. Based on the prior observations a calcium-catalyzed hydrosilylation as well as a magnesium-catalyzed hydroboration can be presented.

Finally, Chapter 5 describes the synthesis and characterization of heterometallic magnesium and zinc complexes. A selection of potential heterobimetallic complexes is subsequently tested for the application in CHO/CO₂ copolymerization and preliminary calculation results on the stability and properties of heterobimetallic magnesium and zinc complexes complete this last chapter.
1.5. References

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Chapter 1

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Introduction

