Chapter 2

Magnesium hydride clusters

This chapter contains the detailed study of the decomposition of tetra- and octanuclear magnesium hydride clusters in solution and in the solid state. The decomposition process is analyzed by Töpler pump experiments, DSC and TPD measurements and deuterium labelling studies. The chapter concludes with DFT studies on the electron density of a tetranuclear magnesium hydride cluster and the potential corresponding decomposition product, a low-valent magnesium complex.

Parts of this chapter have been published:


2.1. Introduction

Magnesium dihydride is a promising hydrogen storage material for the future and many efforts have been taken to overcome obstacles for its application like high desorption temperature and slow kinetics. To verify the implications made by theoretical calculations that the size of \((\text{MgH}_2)_n\) cluster influences the desorption temperature\(^{[1]}\), clusters in the sub-nm range are necessary. These are not easily obtained by usual solid-state approaches like ball-milling or incorporation into confined spaces\(^{[2]}\). Therefore, instead of downsizing bulk material, a molecular “bottom-up” approach, using soluble magnesium hydride complexes can be taken. This allows for syntheses of small, well-defined magnesium hydride particles encapsulated by a ligand framework. These are not practicable as actual hydrogen storage materials due to their low hydrogen contents, but they could serve as well-defined model systems. The step from solid state materials towards soluble molecular complexes can also facilitate in-depth analysis and allows for precise investigation down to the atomic level, e.g. by NMR spectroscopy or single-crystal X-ray structure determination. The field of magnesium hydride complexes is still young and only few complexes of this kind have been discovered. To test the influence of cluster size on the hydrogen release temperature, a range of complexes with a differing amount of Mg centers in a comparable environment is needed. These can in turn also provide extensive information on the properties and reactivities of this evolving class of compounds.

The recently reported dimeric \(\beta\)-diketiminate magnesium hydride complex \((\text{DIPP-MgH})_2\) is one of the first examples of a well-defined magnesium hydride complex\(^{[3,4]}\). It can be viewed as a \(\text{Mg}_2\text{H}_2\) cluster and thermally induced hydrogen elimination could result in formation of the structurally characterized Mg(I) complex \((\text{DIPP-MgI})_2\).\(^{[5]}\) However, the hydride complex is described as extraordinarily stable, the reported decomposition temperature being 300 °C\(^{[3,4]}\) and it shows no hydrogen elimination.\(^{[4]}\) It can only be converted into the Mg(I) complex \((\text{DIPP-MgI})_2\) by reduction with potassium metal. Inversely, the low-valent Mg(I) complex \((\text{DIPP-MgI})_2\) can also not be hydrogenated by pressurizing with \(\text{H}_2\), but oxidation with a carbene-\(\text{AlH}_3\) adduct leads to formation of the corresponding hydride complex \((\text{DIPP-MgH})_2\) (Figure 2.1).\(^{[4]}\) Thus; the dimeric magnesium hydride complex \((\text{DIPP-MgH})_2\) behaves significantly different from bulk MgH\(_2\). It seems therefore that more than two metal centers have to be involved in an elimination of hydrogen or different Mg/H ratios that are closer to Mg/H 1/2 are crucial.
Recently, the reaction of a magnesium diamide carbene (IPr) adduct with two equivalents of phenylsilane was reported to yield a hydride-rich magnesium cluster. The structure of the magnesium hydride complex [Mg$_4$H$_6$(IPr)$_2$N(SiMe$_3$)$_2$] (1) comprises a Mg$_4$H$_6$ adamantane-like core with four pseudo tetrahedral Mg centers and six bridging hydride ligands.[6] Unfortunately, there are no reports on the thermal decomposition and potential hydrogen release so far.

A while ago, Harder et al. introduced a set of bridged bis-$eta$-diketiminate ligands with bulky DIPP substituents.[7,8] They could be doubly deprotonated by the reaction with two equivalents of Mg($n$-Bu)$_2$ and subsequently converted into the hydride complex by treatment with phenylsilane (Figure 2.2). X-ray structure determination revealed interesting cluster structures of different sizes and compositions.

The complex with directly connected $\beta$-diketiminate units, [NN-(MgH)$_2$]$_2$ was formed in a stepwise conversion of the two Mg($n$-Bu) functionalities into hydrides by reaction with phenylsilane. The first Mg($n$-Bu) group was significantly more reactive and therefore, after addition of one equivalent of phenylsilane (60 °C, 1 h), an intermediate [NN-(Mg($n$-Bu))(MgH)]$_2$ complex could be isolated and characterized by X-ray diffraction (Figure 2.4b).
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The second Mg(n-Bu) functionality could be converted to a hydride at higher temperature (80 °C) and prolonged reaction times (48 h) and the crystal structure of [NN-(MgH)₂]₂ could also be determined (Figure 2.3).

All three complexes formed dimeric aggregates containing four Mg²⁺ nuclei, but they were arranged in different manners and the bridging mode of the anionic ligands varied. In [NN-(Mg(n-Bu))₂]₂ the Mg atoms are situated more or less in one plane, while each n-Bu⁻ ion is bridging two Mg²⁺ centers, resulting in two four-membered rings (Figure 2.4a). The conversion of two n-Bu⁻ units led to a structure in which the four Mg²⁺ nuclei are situated on the corners of a tetrahedron and the bridging n-Bu⁻ and H⁻ ions form an eight-membered ring instead of two four-membered rings (Figure 2.4a). Full conversion to the hydride resulted in a similar tetrahedral arrangement.

![Figure 2.3](image)

**Figure 2.3** Crystal structure of [NN-(MgH)₂]₂. i-Pr groups and most H atoms have been omitted for clarity.
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Figure 2.4 Crystal structure of \([\text{NN}-(\text{Mg}(\text{n-Bu}))_2]_2\) and \([\text{NN}-(\text{Mg}(\text{n-Bu})(\text{MgH})]_2\); \(i\text{-Pr}\) groups and most H atoms have been omitted for clarity.

The tetranuclear structure of \([\text{NN}-(\text{MgH})_2]_2\) (4) was maintained in solution. This was demonstrated by low temperature \(^1\text{H}\) NMR spectra that displayed two different bridging hydride ligands as triplets. These signals coalesced at 25 °C, probably due to conformational changes or Mg-H bond breaking processes\(^9\).

Replacing the directly bridged \(\text{NN-H}_2\) ligand by the pyridylene-bridged ligand \(\text{PYR-H}_2\) in the magnesium hydride synthesis, led again to a tetrameric structure for \([\text{PYR}-(\text{MgH})_2]_2\) as shown in the X-ray structure (Figure 2.5). In this case the tetrahedron formed by the \(\text{Mg}^{2+}\) nuclei is distorted due to the increased width of the bridging molecule. The structure showed two different hydride positions as well, although these were not observed by \(^1\text{H}\) NMR, probably due to dynamic processes\(^{10}\).
Expanding the bridge further to the para-phenylene bridged PARA-H$_2$ ligand and employing this in an analogous hydride synthesis leads to a new hydride-rich structural motive for PARA-(MgH)$_2$. It can be viewed as a cluster consisting of three equivalents of the expected product PARA-(MgH)$_2$ and two extra equivalents of MgH$_2$. This led to the composition (PARA)$_3$Mg$_6$H$_{10}$ with the Mg$_6$H$_{10}$-core completely protected by three ligand molecules (Figure 2.6).
Figure 2.6 Crystal structure of \((\text{PARA})_3\text{Mg}_8\text{H}_{10}\). DIPP groups and most H atoms have been omitted for clarity.

The cluster structure stayed intact in solution as can be shown by \(^1\text{H}\) NMR spectroscopy. The three different kinds of bridging hydride ligands showed three different signals in a ratio of 3:6:1 with the corresponding coupling pattern. To our best knowledge, this has been the first example of a hydride-hydride coupling in a magnesium hydride compound reported in literature. No coalescence of these signal could be observed up to 100°C.\(^{[11]}\) A detailed description of the aforementioned magnesium hydride clusters including crystal structure data can be found in literature.\(^{[9-11]}\)

2.2. Goal

With a set of various magnesium hydride cluster sizes with a comparable ligand environment at hand, we were intrigued to investigate the thermal decomposition behavior and to evaluate the value of these clusters as molecular model systems for MgH\(_2\) as a hydrogen storage material. The molecular nature of these complexes could allow for in-depth analysis of intermediates and products and precise investigation of decomposition processes down to the atomic level. Further insights into the hydrogen elimination and exchange processes can be gained by replacing the hydride ligands with deuterium isotopes.
Due to low hydrogen content, the here presented molecular hydride clusters are impracticable for efficient hydrogen storage purposes, however, this research could yield an advanced understanding of decomposition processes and products that could turn out to be valuable for the an in-depth understanding of metal-hydride based hydrogen storage materials. This could lead to further development of efficient hydrogen storage materials.

Additionally, as the properties of these well-defined magnesium hydride complexes are vastly unexplored, many interesting features of this class of compounds could be uncovered. Further information on the electronic and structural properties and a comparison to MgH$_2$ could be gained by DFT calculations on magnesium hydride clusters.

2.3. Results and Discussion

2.3.1. Decomposition studies

Stability in solution

In solution, (PARA)$_2$Mg$_8$H$_{10}$ was astoundingly stable against deaggregation or decomposition. A toluene solution heated in a J-Young tube for 2 days at 180 °C showed no signs of decomposition.$^{[11]}$ Additionally, the stability was underscored by the fact, that addition of THF had no influence on the cluster structure. The $^1$H NMR of the cluster in THF-$d_8$ still showed the according coupling pattern for three different hydride positions and only slight changes in the chemical shifts for the hydride ligands. This is in sharp contrast with the usually observed behavior of polar organometallics: addition of polar solvents generally results in solvent coordination and concomitant deaggregation.

Toluene solutions of [NN-(MgH)$_2$]$_2$ were also stable towards hydrogen elimination or other decomposition up to 180 °C for several days. But as described before coalescence of the hydride signals could be observed already at 25 °C. The uncertainty about the cause of the coalescence led us to investigate the behavior of the tetranuclear cluster upon addition of THF. Addition of some drops of THF-$d_8$ to a solution of [NN-(MgH)$_2$]$_2$ in C$_6$D$_6$ resulted in formation of traces of a new compound [NN-(MgH)$_2$]$_2'$. In a pure THF-$d_8$ solution, two thirds of the dissolved compound showed the new set of signals with only a single hydride resonance. One explanation for the coalescence as well as the appearance of a new compound could be a temperature- and solvent-dependent monomer/dimer equilibrium (Figure 2.7)
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Figure 2.7 Monomer/dimer equilibrium including solvent.

An alternative explanation could be found in the structural rearrangement of the cluster itself (Figure 2.8). As the NN-ligands show axial chirality, the cluster in its solid state structure is chiral as well. A chirality change of the ligand is performed through a $90^\circ$ rotation around their N-N axis. Changing the chirality of one of the ligands in the $D_2$-symmetric cluster would give rise to an achiral $S_4$-symmetric structure in which all of the hydride ligands are equal and therefore only a single hydride signal should be observed. A further chirality change would give back a homochiral $D_2$-symmetric cluster. This dynamic process could explain the coalescence of the hydride resonances and coordination of four THF molecules could stabilize the intermediate $S_4$-symmetric cluster and lead to its appearance in the $^1H$ NMR spectrum.

Figure 2.8 Schematic representation and chirality interconversion of [NN-(MgH)$_2$]$_2$. 
As both scenarios would be a possible explanation for the observed behavior, we decided to look deeper into the problem. To gain further information, the ratio of these two compounds ([NN-(MgH)$_2$]$_2$:[NN-(MgH)$_2$]$_2$) in THF-$d_8$ at different temperatures was studied by means of $^1$H NMR (Table 2.1). Starting at 25 °C the solution was cooled down inside the NMR machine and after stabilization of the temperature the amount of [NN-(MgH)$_2$]$_2$ had halved in value. Reheating to 25 °C did not restore the former ratio, instead more of compound [NN-(MgH)$_2$]$_2$ were observed. Further warming to 40 °C, resulted in a slight increase of [NN-(MgH)$_2$]$_2$. Afterwards the NMR solution was heated to reflux outside the NMR spectrometer and the $^1$H NMR spectrum was immediately recorded at 25 °C showing a 50:50 mixture of both compounds (Figure 2.9).

**Table 2.1** Ratio of compound [NN-(MgH)$_2$]$_2$:[NN-(MgH)$_2$]$_2$' in THF-$d_8$ at different temperatures

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>[NN-(MgH)$_2$]$_2$:[NN-(MgH)$_2$]$_2$'</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>30:70</td>
</tr>
<tr>
<td>- 40</td>
<td>15:85</td>
</tr>
<tr>
<td>25 (after cooling)</td>
<td>35:65</td>
</tr>
<tr>
<td>40</td>
<td>40:60</td>
</tr>
<tr>
<td>25 (after reflux)</td>
<td>50:50</td>
</tr>
</tbody>
</table>

**Figure 2.9** Sections of the $^1$H NMR spectra of [NN-(MgH)$_2$]$_2$ in a) C$_6$D$_6$ and b) THF-$d_8$. 
It can be concluded that the dimeric cluster \([\text{NN-}(\text{MgH})_2]_2\) was favored at higher temperatures whereas the new set of signals represented a species \([\text{NN-}(\text{MgH})_2]_2\)’ that was stabilized at lower temperatures. This could on one hand support temperature-dependent monomer/dimer equilibrium as an entropy gain would favor the dimeric cluster compound at higher temperature (release of coordinating solvent), on the other hand the \(S_4\)-symmetric cluster could be stabilized at lower temperatures. Additional DOSY measurements could not support either hypothesis as no significantly different diffusion coefficients were determined. The diffusion coefficient is dependent on the size of the diffusing particle, thus the size of the compound itself and additional adhering solvent molecules (hydrodynamic radius). Therefore the observation of similar diffusion coefficients could be either due to the hydrodynamic radii of the dimer and the monomer (with coordinating solvent) not being sufficiently different or no monomer/dimer equilibrium taking place.

As even a small amount of monomeric \(\text{NN-}(\text{MgH})_2\) with terminal hydride functions should be more prone to hydride/deuteride exchange with the atmosphere than a closed tetranuclear cluster, a solution of \([\text{NN-}(\text{MgH})_2]_2\) in THF was degassed and subsequently exposed to an atmosphere of deuterium gas. Still no exchange was observed after two days at 25 °C. In addition, \(\text{NN-}(\text{MgH})_2\) was mixed with one equivalent of the deuterated counterpart \(\text{NN-}(\text{MgD})_2\) and THF was added. Also in this case no formation of a mixed complex \([\text{NN-}(\text{MgHD})]_2\) could be observed. These observations suggested the formation of a \(S_4\)-symmetrical cluster, but no final conclusion could be drawn so far.

Additionally, THF had an influence on the stability of the complex in solution. After standing at room temperature for one week, a THF-solution of \(\text{NN-}(\text{MgH})_2\) showed first indications for decomposition by precipitation of metallic magnesium.

A solution of \(\text{PYR-}(\text{MgH})_2\) in benzene was significantly less stable than the other clusters. At temperatures above 100 °C it decomposed into unidentified compounds associated with a color change from yellow to orange. It is likely that an addition of the hydride at the 2, 4- or 6-position of the bridging pyridine takes place which leads to different decomposition products. Such addition reactions are known for MgH₂, they are quantitative already at room temperature, they are characterized by a red coloration and therefore serve as a test for the activity of MgH₂ samples.\(^{[10]}\)
Stability in the solid state

As the behavior in solution often differs from that in the solid state, we decided to investigate the decomposition without solvents. For this purpose the solid material was heated in a stepwise manner inside a thermostated hot-air bath. At around 200 °C a yellow microcrystalline sample of \((\text{PARA})\text{Mg}_8\text{H}_{10}\) (8) slowly started changing its color to a dark reddish brown and the crystals broke visibly due to the release of gasses. Subsequently, it was connected to a high-vacuum line with an attached Töpler pump. Liberated gasses were quantified by pumping them quantitatively into a calibrated burette of the Töpler pump setup (Figure 2.10). During this process condensable solvents and gasses were trapped in liquid N$_2$.

![Töpler-pump setup](image)

To determine the actual release of H$_2$, the gasses were led through an oven heated to 300 °C and filled with CuO. This fully converted released hydrogen to water, which could subsequently be condensed and allowed for discrimination from other possible gasses (N$_2$, O$_2$, CH$_4$) that under these conditions do not react with CuO. These measurements indicated
the release of the expected $4.9 \pm 0.2$ mol equivalents of hydrogen from the (PARA)$\text{Mg}_8\text{H}_{10}$ (8) cluster. For further proof of the $\text{H}_2$ formation, the magnesium hydride complex was decomposed in the closed system of a J-Young NMR tube (see Experimental Section for details) and the released gas was dissolved in THF-$d_8$. A clear singlet $^1\text{H}$ NMR resonance at 4.55 ppm could be observed which is the chemical shift for $\text{H}_2$ in this solvent.

The smaller cluster $[\text{NN}-(\text{MgH})_2]_2$ (4) revealed a similar behavior. Upon stepwise heating to 175 °C, the color changed from bright yellow to red and signs of gas release could be observed. This could be confirmed by gas quantification using the Töpler pump. It has to be mentioned that quantitative gas release was also slow and took up to one hour. After this time, $[\text{NN}-(\text{MgH})_2]_2$ released 2.2 ± 0.1 equivalents of gas which was non-condensable and could be fully converted to condensable water after leading it over CuO at 300°C. Independent NMR studies could confirm the liberation of $\text{H}_2$. Thus, the smaller tetrameric cluster revealed a lower decomposition temperature than the octanuclear magnesium hydride complex, which is according to our expectations.

The second tetranuclear cluster $[\text{PYR}-(\text{MgH})_2]_2$ (7) was subjected to the same procedure. After 30 minutes heating at 130 °C the color changed from yellow-orange to dark red. In this case, gas quantification with the Töpler pump setup showed that only 1.1 ± 0.1 equivalents of gas are released from the complex while two equivalents would be expected theoretically. This gas could be confirmed to be hydrogen by complete oxidation to condensable water. It seemed that this hydride complex splits off two of its hydride ligands to form hydrogen while the remaining two hydrides could easily react with the bridging pyridine ring as described before. Therefore the reactive pyridine function in this ligand explains the differing behavior of this complex.

As this side reaction had been described for this particular complex in solution already, we decided to test the decomposition in solution for the release of hydrogen. Therefore we degassed a toluene solution of $[\text{PYR}-(\text{MgH})_2]_2$ and subsequently heated the solution to 150 °C for one hour. Afterwards the solution was frozen again and attached to the Töpler pump setup. Thereby about 0.8 ± 0.1 equivalents of gas were obtained. These could be proven to be hydrogen by oxidation to condensable water. In this particular case the release of hydrogen also takes place in solution and at lower temperatures than in the solid state.

Finally, the observations, that smaller cluster size indeed leads to a decrease in decomposition temperature, led us to reinvestigate the thermal stability of the smallest dimeric hydride cluster (DIPP-MgH)₂ under similar conditions. For this purpose the solid complex (DIPP-MgH)₂ was heated stepwise in a hot-air bath. At 125 °C a color change from off-white to orange-red could be observed and the compound started to melt slowly.
Bubbles in the melt indicated the release of gases. The gas was quantified like described before and shows $1.0 \pm 0.05$ equivalents of released hydrogen gas. The nature of the liberated gas was proven to be hydrogen by oxidation over CuO and independently by $^1\text{H}$ NMR spectroscopy. Although the amount of data points we obtained are limited, it seems that hydrogen elimination temperatures lower with decreasing cluster size (Table 2.2).

Table 2.2 Summary of decomposition studies.

<table>
<thead>
<tr>
<th>Mg hydride complex</th>
<th>Decomposition temperature [$^\circ\text{C}$]</th>
<th>Released equivalents of $\text{H}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{PARA})_3\text{Mg}<em>8\text{H}</em>{10}$</td>
<td>200</td>
<td>$4.9 \pm 0.2$</td>
</tr>
<tr>
<td>$[\text{NN}-(\text{MgH})_2]_2$</td>
<td>175</td>
<td>$2.2 \pm 0.1$</td>
</tr>
<tr>
<td>$[\text{PYR}-(\text{MgH})_2]_2$</td>
<td>150</td>
<td>$1.1 \pm 0.1$</td>
</tr>
<tr>
<td>$(\text{DIPP}-\text{MgH})_2$</td>
<td>125</td>
<td>$1.0 \pm 0.05$</td>
</tr>
</tbody>
</table>

As Töpler pump gas quantifications necessarily have to be performed by decomposition under high vacuum, we wanted to assure that the observations we made concerning the thermal decomposition were not due to the fact that they were performed under vacuum, we repeated the experiments under a $\text{N}_2$ atmosphere of 1 bar. In this experiment it was not possible to determine the amount of gas released from the complexes, due to high volumes of gas in the reaction flask, but as all decompositions involved an obvious color change, we used this as an indicator for the decomposition process. In all cases the observations at atmospheric pressure matched the observations made under vacuum. Therefore pressure does not seem to have a large impact on the thermodynamics of these processes, still it might have on the kinetics.

**DSC and TPD measurements**

To study the course of the decomposition process as a function of temperature, differential scanning calorimetry (DSC) experiments were carried out. These could provide information on stepwise elimination of hydrogen and yield a more precise desorption temperature. Due to reproducibility issues in preliminary DSC experiments, we decided to collaborate with Petra de Jongh of the Inorganic Chemistry department of the University of Utrecht, which is well-renowned for investigations of MgH$_2$ as a hydrogen storage material. Following samples have been studied with DSC: $(\text{DIPP}-\text{MgH})_2$, $[\text{NN}-(\text{MgH})_2]_2$ and $(\text{PARA})_3\text{Mg}_8\text{H}_{10}$. For quantification of the hydrogen release as a function of temperature, temperature-programmed-desorption (TPD) was used. Therefore the sample was heated with 5 °C/min in an Ar flow and the changes in conductivity of the transport gas were measured. As
hydrogen is more heat conductive than argon it will show positive peaks in the spectrum, whereas organic fragments and molecules give very weak positive or mostly negative peaks as they reduce the conductivity compared to pure Ar.

Reaction or phase transformations were accessed by DSC, measuring heat effects as a function of temperature under different gas atmosphere (Ar or H₂). Measurements were done using a heating rate of 10 °C/min and subsequent cooling. This determines the thermal stability of the samples and gives information about the reversibility of the observed processes. Additionally, the reversibility of the hydrogen elimination was tested by the group of Petra de Jongh using the Sievert’s method. The sample is cycled between vacuum and hydrogen atmosphere and changes in gas pressures are monitored. As the magnesium hydride complexes only incorporate small amounts of hydrogen, these measurements could not be as precise as for actual hydrogen storage materials, but should show major trends for the hydrogen release.

In these experiments (DIPP-MgH)₂ released a majority of its hydrogen (67 %) endothermically just above 200 °. Another endothermic event is recorded in the DSC at around 140 °C, this might be related with small residues of solvent being liberated (Figure 2.11). Neither Sievert’s measurements nor DSC indicated reversibility of the hydrogen elimination. After the measurement, parts of the sample had evaporated and condensed within the heating chamber, they also turned yellow and red.

![TPD spectrum of [DIPP-(MgH)]₂](image)

**Figure 2.11** TPD spectrum of [DIPP-(MgH)]₂.
The tetranuclear cluster [NN-(MgH)\(_2\)]\(_2\) released only a few percent of the expected amount of hydrogen starting above 250 °C, also in this case last traces of incorporated solvent were released around 150 °C. Above 300 °C the complex started decomposing or evaporating and no reversibility of any events could be detected. After the measurements parts of the sample had turned red as observed in the precedent decomposition experiments. Finally, the octanuclear cluster (PARA)\(_3\)Mg\(_8\)H\(_{10}\) was studied, it showed the release of a few percent of its hydrogen at around 225 °C, this event is irreversible. After the measurement the sample had again turned orange-red as observed before.

The reason for the throughout higher temperatures and small amounts of hydrogen observed could be the high heating rate applied. Earlier decomposition experiments (2.3.1) have been performed with stepwise heating but a much slower heating. It was also noticed that H\(_2\)-release was in most cases rather slow (60 – 120 min). An initiation period for the hydrogen elimination could explain the somewhat higher decomposition temperatures in the relatively fast DSC measurements. The overall trend that smaller magnesium hydride clusters decompose at lower temperatures, however, is maintained. Fast heating rates could also be an explanation why the decomposition of (DIPP-MgH)\(_2\) at lower temperatures has not been observed by Jones et al. Until now further experiments have not been possible due to technical issues.

**Decomposition products**

The nature of the products after thermal decomposition of the different clusters is hitherto unknown. The main issue with characterization of products from the decomposition of (PARA)\(_3\)Mg\(_8\)H\(_{10}\) (8) is the low solubility of the obtained red powder in aromatic solvents and the small amount that dissolves is mainly undecomposed magnesium hydride cluster mixed with some additional compounds. Until now no product could be isolated from this mixture. To make sure that at least the ligand framework stays intact during the thermal decomposition, we hydrolyzed the decomposition products with water and mainly found the free PARA-H\(_2\) ligand and small amounts of other unidentified products. Therefore we can conclude that the ligand is stable up to the applied temperatures of about 200 °C.

For the other compounds the decomposition products are mainly soluble, but also in these cases, mixtures are obtained. Upon addition of benzene to the decomposition product of [PYR-(MgH)\(_2\)]\(_2\) (7) small gas bubbles could be observed and it resulted in a dark-red solution containing many different species. Therefore some of the products from the thermal decomposition might not be stable in solution. Also in this case no single component could be isolated by crystallization. After the thermal decomposition of [NN-(MgH)\(_2\)]\(_2\) (4), the remains gave a dark red solution upon addition of C\(_6\)D\(_6\). A lot of resonances were found in
the $^1$H NMR spectrum probably belonging to a multitude of compounds, which could not be identified so far. The color change observed for all tested compounds from yellow to red could indicate the formation of Mg(I) compounds (Figure 2.12), as [DIPP-Mg]$^2$·THF 2 has been reported to be orange-red.$^5$

![Figure 2.12 Decomposition of a magnesium hydride cluster.](image)

For identification of the decomposition products of (DIPP-MgH)$_2$ (1) a clear advantage was the existence of spectral data for the corresponding Mg(I) complex (2) that could be consulted for comparison. Still it was not possible to find matching chemical shifts in the mixture, particularly because all signals in the $^1$H NMR spectrum have very broad bases. The only compound that could be isolated from the mixture by crystallization from toluene was a small amount of the hydrolyzed DIPP-H ligand. In addition, 4-dimethylaminopyridine (DMAP) was added to the solution to stabilize a potential low-valent Mg(I) complex and facilitate its crystallization, but no crystals formed from this experiment. However, the DMAP seems to coordinate to a component in the solution as its $^1$H NMR resonances broaden significantly.

To obtain comparable data for the other clusters, we attempted the direct synthesis of the corresponding low-valent Mg(I) complexes along other routes. Our approach was to reduce the corresponding halide compounds using potassium or potassium naphthalide. Therefore we synthesized the chloride, which was known from previous work,$^{12}$ and iodide precursors using the NN-H$_2$ and the PARA-H$_2$ ligand.

The chloride complexes were obtained by reaction of the L-(Mg(n-Bu))$_2$ complexes with trimethylsilylchloride (Me$_3$SiCl). The obtained complex containing the PARA-H$_2$ ligand gave crystals suitable for X-ray diffraction. This complex partly undergoes Schlenk equilibrium and releases one molecule of MgCl$_2$ to give an intriguing new structure (Figure 2.13). This complex was not further taken into account for reductions, as it already lost two reactive functionalities and one Mg center.$^{12}$
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Figure 2.13 Formation of halides.

The NN-(MgCl)\textsubscript{2} complex could not be crystallized, it was characterized solely by NMR spectroscopy. Subsequently, it was reduced using potassium naphthalide, but the product turned out not to be the expected tetranuclear Mg(I) cluster instead the ligand had been split at the N-N bridge and thus reduced (Figure 2.14). The same structural motive only including additional potassium hydride instead of THF molecules could be observed from the reaction of NN-(MgH)\textsubscript{2} with a potassium mirror.\textsuperscript{12} Large scale experiments unfortunately only result in precipitation of Mg metal. Independent experiments were able to show, that the ligand itself cannot be split by potassium or potassium naphthalide, therefore an intermediate Mg(I) compound could be involved in the process which in turn reduces and splits the ligand and is thus oxidized again to Mg(II), resulting in the observed product.

Figure 2.14 Product of the reduction of NN-(MgCl)\textsubscript{2} with K(C\textsubscript{8}H\textsubscript{10}).

As the first characterized Mg(I) compound (DIPP-Mg\textsubscript{2}) was obtained from the reduction of the corresponding iodide precursor, we decided to test these for the synthesis of Mg(I) clusters as well. The according iodides could be synthesized in a one-step reaction of an Mg(n-Bu)-precursor with elemental iodine. This gave the pure iodide complexes in good yields, due to the very low solubility in common solvents they were only characterized by \textsuperscript{1}H NMR spectroscopy. These iodide precursors were subsequently reduced with an excess of potassium in a comparable manner to the reduction reported by Jones\textit{ et al.} for
(DIPP-MgH₂). The reduction of PARA-(Mgl)₂ always showed a color change from orange to yellow and resulted in the formation of an unidentifiable mixture of products showing very broad resonances in the ¹H NMR. No single component could be isolated from the mixture. In the case of NN-(Mgl)₂ the color of the suspension changed slightly during the reaction. Light yellow microcrystals could be isolated, that were not suitable for X-ray diffraction. ¹H NMR shows a single compound that is not identical with the product of the reduction of NN-(MgCl)₂ with potassium naphthalide (Figure 2.14). A further characterization was not successful until now. Further experiments are necessary to determine whether the synthesis of multinuclear Mg(I) clusters is possible and to find the right conditions. This would allow a comparison of their NMR data with those of the products of the decompositions.

2.3.2. Insights into stability and decomposition by deuterium labeling

In order to determine whether the source of hydrogen upon thermal decomposition was solely from the hydride ligands or if the β-diketiminate ligand is involved as well, we have synthesized a series of magnesium deuteride complexes (DIPP-MgD)₂, [NN-(MgD)₂]₂, (PARA)₃Mg₆D₁₀. These deuterated clusters additionally served to investigate the exchange between hydride ligands and the exchange between hydride and atmospheric hydrogen.

Exchange between magnesium hydride complexes in solution

First the exchange between magnesium hydride and magnesium deuteride clusters in solution was studied. The dimeric hydride complex (DIPP-MgH)₂ and the deuterated dimer (DIPP-MgD)₂ were dissolved in C₆D₆ and exchange processes were monitored by ¹H NMR. After several hours at 20 °C no changes in the spectra could be observed. As THF could stabilize an intermediate monomeric complex with a terminal more reactive hydride, the experiment was repeated with a mixture of C₆D₆/THF-d₆(4/1) (Figure 2.15).

![Figure 2.15 Proposed exchange mechanism for H-D exchange between dimeric complexes.](image)

Under these conditions exchange between hydride (H⁻) and deuteride (D⁻) was observed. A new signal in the ¹H NMR at slightly higher field could be assigned to the mixed dimer with bridging H⁻ and D⁻ ions. The 1/1/1 triplet is characteristic for H-D coupling (Figure 2.16).
As the coupling constant between the two identical hydride ligands in (DIPP-MgH)$_2$ cannot be determined directly, the observed H-D coupling constant of $^2J_{H-D} = 4.4$ Hz allowed for estimation of an equivalent H-H coupling constant of $^2J_{H-H} = 28.6$ Hz, based on the gyromagnetic ratios for H and D. This value is substantially larger than the so far observed hydride-hydride coupling constants for $[\text{NN}-(\text{MgH})_2]_2$ ($^2J_{H-H} = 8.5$ Hz) and (PARA)$_3\text{Mg}_8\text{H}_{10}$ ($^2J_{H-H} = 4.5$ Hz and 5.2 Hz) but still far from the theoretical predictions for the germinal H–H coupling in linear MgH$_2$ ($^2J_{H-H} = 50$–80 Hz)$^{[13]}$. Currently it is unclear whether the observed hydride-hydride NMR coupling is taking place through bonds or through space or through a combination of both. We could conclude, however, that there was no correlation of the coupling constant with the Mg–H bond lengths. The average Mg–H bond lengths in (PARA)$_3\text{Mg}_8\text{H}_{10}$ and $\text{NN}-(\text{MgH})_2$ are the same (1.81(2) Å), still the coupling constants differ. The various polymorphs of (DIPP-MgH)$_2$ and its dimeric THF adduct 1·(THF)$_2$ have somewhat longer Mg–H bond lengths of 1.91(5) Å and 1.93(2) Å, respectively.$^{[3,14]}$ Another explanation for the larger coupling constant in 1 is the fact that the hydride ligands in this dimer are integrated in a four-membered ring, whereas inside the larger clusters they are part of more extended eight-membered ring systems. This has a direct influence on the hydride···hydride distance, a smaller ring causes a shorter H···H distance. Bearing in mind that positions of hydrogen atoms in X-ray crystal structures should be treated with care, our group could determine a reasonably accurate value of 2.32(2) Å$^{[14]}$ for the hydride···hydride distance in the THF adduct 1·(THF)$_2$ while a slightly longer distance of 2.44(4) Å was found for another polymorph.$^{[3]}$ Additionally, the H···H distances in two THF-free polymorphs of 1 have been determined as 2.35(8) Å and 2.65(4) Å, this results in an average H···H distance

Figure 2.16 H–D exchange between (DIPP-MgH)$_2$ and (DIPP-MgD)$_2$. 

![Diagram of H–D exchange between (DIPP-MgH)$_2$ and (DIPP-MgD)$_2$.]
of 2.44(4) Å which is significantly shorter than the hydride···hydride distances observed in [NN-(MgH)₂]₂ (2.76(4) Å) and (PARA)₃Mg₈H₁₀ (average value: 2.86(4) Å) and could in turn explain the larger magnetic coupling (Table 2.3). A correlation between hydride···hydride distances and NMR coupling constants give hints that at least a significant part of the coupling mechanism takes place through space. This theory can only be supported by additional data points from measurements of hydride–hydride coupling constants in new complexes.

**Table 2.3** Correlation between the Mg–H bond lengths, H···H distances and magnetic coupling constants.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mg–H bond length [Å] (average)</th>
<th>H···H distance [Å] (average)</th>
<th>NMR coupling constant [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DIPP-MgH)₂</td>
<td>1.92(2)</td>
<td>2.44(4)</td>
<td>28.6</td>
</tr>
<tr>
<td>[NN-(MgH)₂]₂</td>
<td>1.81(2)</td>
<td>2.76(4)</td>
<td>8.5</td>
</tr>
<tr>
<td>(PARA)₃Mg₈H₁₀</td>
<td>1.81(2)</td>
<td>2.86(4)</td>
<td>4.5, 5.2</td>
</tr>
</tbody>
</table>

The larger clusters [NN-(MgH)₂]₂ and (PARA)₃Mg₈H₁₀ did not show signs of exchange also not after addition of THF or prolonged heating to 60 °C. On this basis, H–D exchange could still not be excluded, however, it is safe to say that it was significantly slower than for the dimeric hydride. This is in agreement with the fact that these clusters were more stable towards dissociation in solution. At high temperatures in solution ¹H NMR indicated that both were still present in their solid state form and even in THF (PARA)₃Mg₈H₁₀ still showed the corresponding coupling pattern. This in turn supports the proposed dissociative mechanism for hydride-deuteride exchange between aggregates.

**H–D exchange between magnesium hydride cluster and atmospheric H₂**

Apart from exchange of hydride and deuteride between the clusters in solution, exchange between the deuteride in a cluster and molecular H₂ (1 bar) was studied. The required σ-bond metathesis between hydrogen and hydride complexes, well-established in organo-lanthanide chemistry,⁰¹ was recently shown to take place in group 2 chemistry as well.⁰²,⁰³ A benzene solution of the dimeric calcium deuteride (DIPP-CaD·THF)₂ already showed H–D exchange with an atmosphere of H₂ (1 bar) at room temperature. This was a fast process as 90% of the deuteride were exchanged for hydride after 90 minutes.
$^1$H NMR studies on a solution of magnesium deuteride complex $(\text{DIPP-MgD})_2$ in benzene under an atmosphere of 1 bar $\text{H}_2$ do not show any reaction with $\text{H}_2$. Heating of this solution to 60 °C, however, gave partial exchange after several hours and $\text{H-D}$ (Figure 2.17) as well as the mixed hydride-deuteride complex $(\text{DIPP-MgH/D})_2$ was detected in the reaction mixture by $^1$H NMR spectroscopy. The sample was kept at this temperature overnight, leading up to 85% of the deuteride exchanged for hydride. This clearly demonstrated that magnesium hydride complexes are much less susceptible to exchange with $\text{H}_2$ and therefore less reactive when compared to the corresponding calcium hydrides. The exchange process was not only accelerated by heat but could also be facilitated by addition of THF. According to this, a solution of $(\text{DIPP-MgD})_2$ in C$_6$D$_6$/THF (4/1) started to exchange deuteride for hydride slowly already at room temperature. After 1 hour 10% of deuteride was exchanged and after 5 days 50% of the deuteride complex $(\text{DIPP-MgD})_2$ had reacted with $\text{H}_2$ to give $(\text{DIPP-MgH})_2$. The exchange process could be clearly monitored by detection of dissolved $\text{H-D}$ and $(\text{DIPP-MgH})_2$. In contrast to the experiment in pure C$_6$D$_6$ at 60 °C, no intermediate mixed complex $(\text{DIPP-MgH/D})_2$ could be observed in the presence of THF.
A feasible explanation for this unexpected observation is the mechanism shown in Figure 2.18. With THF present in the solution, the dimer (DIPP-MgD)$_2$ could be in equilibrium with small amounts of a monomeric magnesium deuteride species with THF ligands filling empty coordination sites. An according solvent-dependent equilibrium has been suggested for the dimeric (MES-ZnH)$_2$ complex (MES = [2,6-(2,4,6-​​Me$_3$-C$_6$H$_2$)N(Me)C]$_2$CH) based on pulsed-gradient spin echo (PGSE) diffusion measurements that showed that the complex is most likely monomeric in THF-$d_8$.[18] These monomers with terminal hydride ligands are highly reactive and quickly exchange D$^-$ for H$^-$ by σ-bond metathesis with molecular hydrogen. Subsequently, they directly recombine to form dimeric (DIPP-MgH)$_2$. The absence of any detectable amounts of (DIPP-MgH/D)$_2$ can thus be explained by assuming a slow, rate-determining, deaggregation step followed by a considerably faster σ-bond metathesis.

In pure aromatic solvents, the σ-bond metathesis is either significantly slower or the D–H exchange takes place along a different route in which only one Mg-H breaks and no monomers but an open dimer is formed. The resulting terminal deuteride ligand exchanges in a fast σ-bond metathesis with H$_2$ and the new hydride ligand subsequently bridges between the two Mg centers to form the mixed (DIPP-MgH/D)$_2$ dimer (Figure 2.15). The observation that (DIPP-CaD·THF)$_2$ exchanges significantly faster with H$_2$ is certainly due to the fact that calcium complexes are more reactive than magnesium compounds. Due to the larger size of the cation, the ligands are weaker bound, which results in a faster exchange.
Both larger clusters $[\text{NN}-(\text{MgD})_2]_2$ and $(\text{PARA})_3\text{Mg}_8\text{D}_{10}$, however did not exchange their deuteride ligands with $\text{H}_2$ also not at higher temperatures. In none of the cases any dissolved H–D could be detected. As partially deuterated clusters might give broad $^1\text{H}$ NMR resonances for the new hydride ligand due to complex magnetic H–D coupling and therefore could not be clearly visible, we also verified the results by subjecting $[\text{NN}-(\text{MgH})_2]_2$ to D$_2$. No exchange was observed, even after heating to 60 °C for several days. Not even a solution of $[\text{NN}-(\text{MgH})_2]_2$ in pure THF-$d_8$ shows any signs of exchange with D$_2$, after two days under a D$_2$ atmosphere (1 bar) all of the hydrides and the characteristic triplet coupling due to H–H magnetic coupling are still visible in the $^1\text{H}$ NMR spectrum. The inability of the large clusters to exchange their H$^-$ ligand with atmospheric H$_2$ could be a further indication that monomeric metal hydride complexes or at least opened clusters with terminal hydride ligands are needed for such a process. The importance of a monomeric state for hydride/H$_2$ exchange has also been suggested in lanthanide hydride complexes.\cite{16}

**Thermal decomposition of deuterium labeled magnesium hydride clusters**

In order to verify the origin of the released H$_2$ from the magnesium hydride core, the thermal decomposition of deuterium labeled compounds was studied. The absence of H$_2$ or H–D in the released gas could help to exclude the deprotonation of the ligand. Within a special setup (Figure 2.19) of the closed system of a J-Young NMR tube (for detailed description see 2.5.3), various magnesium deuteride complexes have been thermally decomposed as solids and the gasses were analyzed dissolved in THF-$d_8$ by $^1\text{H}$ NMR. Decomposition of $[\text{NN}-(\text{MgD})_2]_2$ showed no significant quantities of H–D or H$_2$, very small resonances for H–D and H$_2$ were explained by incomplete labeling of the magnesium compounds as PhSiD$_3$ of 95% isotopic purity has been used for the synthesis. The thermal decomposition of the largest magnesium deuteride cluster also did not give significant quantities of H–D or H$_2$. For comparison mixed clusters have been synthesized by using a 1/1 mixture of PhSiH$_3$ and PhSiD$_3$ resulting in statistical mixtures of hydrides and deuterides in the magnesium clusters. Upon thermal decomposition, these mixed clusters eliminated large quantities of H–D next to H$_2$ and D$_2$ (not detected by $^1\text{H}$ NMR). It could therefore be concluded that hydrogen elimination in $[\text{NN}-(\text{MgH})_2]_2$ and $(\text{PARA})_3\text{Mg}_8\text{H}_{10}$ is solely based on coupling of the hydride ligands and involvement of any $\beta$-diketiminate ligand protons could be largely excluded.
In addition, the thermal decomposition of solid [NN-(MgH)$_2$]$_2$ and (PARA)$_3$Mg$_6$H$_{10}$ under an atmosphere of D$_2$ (1 bar) was investigated to gain information on the exchange between deuterides and atmospheric hydrogen during the process of decomposition. This could yield first hints on a probable reversibility of the H$_2$/D$_2$ release. As dimeric magnesium hydride complex (DIPP-MgH)$_2$ melted during the decomposition and the melt potentially exchanged with D$_2$ already before decomposition, this experiment would be inconclusive. In the other two cases not only H$_2$ but also significant amounts of H-D were eliminated. This could be due to an exchange of hydride for deuteride prior to the decomposition or a reversibility of the H$_2$ release. As the previous studies have shown that the larger magnesium deuteride clusters in solution are inert towards D−H exchange with H$_2$ (1 bar), we presumed that observed H−D is the product of a reversible H$_2$ elimination. Nevertheless, if we consider the harsh conditions needed for the decomposition (175-200 °C) a partial H−D exchange of the magnesium hydride clusters with D$_2$ prior to decomposition could not be fully excluded.

2.3.3. Theoretical studies[9]

Magnesium hydride clusters

In order to gain more detailed information on the bonding situation in the tetranuclear cluster [NN-(MgH)$_2$]$_2$, we became interested in DFT calculations on this new compound. For this reason a topological analysis of the electron density, $\rho(r)$, using the “atoms in molecules” (AIM) approach, has been carried out by Dr. Peter Sirsch at the University of Tübingen in Germany. The theory of AIM developed by R. F. W. Bader can provide a direct insight into the chemical bonding and thereby reveals information about physical and chemical properties and the nature of atomic interactions.[19] The electron density needed for this kind of studies can either be obtained experimentally from X-ray diffraction studies or theoretically through DFT calculations. In our case the electron density was derived only from DFT calculations in which a high quality split-valence basis set was used that was further augmented with addition polarization and diffuse function: B3-LYP/6-311G(d,p). For the theoretical model system, in order to reduce the computational effort, the DIPP
substituents on each of the ligands have been replaced by methyl groups. In the following, this model system will be denoted as \([\text{NN}'-(\text{MgH})_2]_2\).

Figure 2.20 Optimized geometry for \([\text{NN}'-(\text{MgH})_2]_2\) (B3-LYP/6-311G(d,p)).

In the optimized geometry, the experimental twist angle of 83.4(2)° between the two \(\beta\)-diketiminate units is retained (84.9°) and all other parameters are in good agreement with the experimental counterparts (Table 2.4). It has to be taken account of the fact that hydrogen atom positions in X-ray diffraction studies are always approximate positions.

Table 2.4 Selected distances (Å) for the crystal structure of \([\text{NN}-(\text{MgH})_2]_2\) and theoretical DFT values for \([\text{NN}'-(\text{MgH})_2]_2\) in squared brackets.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Mg–N1})</th>
<th>(\text{H1⋯H1'})</th>
<th>(\text{Mg⋯Mg}'')</th>
<th>(\text{Mg}''\cdots\text{Mg}''')</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg–N1})</td>
<td>2.025(1)</td>
<td>4.65(2)</td>
<td>3.492(1)</td>
<td>3.030(1)</td>
</tr>
<tr>
<td></td>
<td>[2.055]</td>
<td>[4.713]</td>
<td>[3.580]</td>
<td>[3.154]</td>
</tr>
<tr>
<td>(\text{Mg–N2})</td>
<td>2.010(1)</td>
<td>2.93(4)</td>
<td>3.492(1)</td>
<td>3.030(1)</td>
</tr>
<tr>
<td></td>
<td>[2.034]</td>
<td>[3.106]</td>
<td>[3.580]</td>
<td>[3.154]</td>
</tr>
<tr>
<td>(\text{Mg–H1})</td>
<td>1.771(12)</td>
<td>3.586(1)</td>
<td>3.030(1)</td>
<td>3.586(1)</td>
</tr>
<tr>
<td></td>
<td>[1.849]</td>
<td>[3.555]</td>
<td>[3.154]</td>
<td>[3.555]</td>
</tr>
<tr>
<td>(\text{Mg–H2})</td>
<td>1.845(6)</td>
<td>3.030(1)</td>
<td>3.030(1)</td>
<td>3.586(1)</td>
</tr>
<tr>
<td></td>
<td>[1.828]</td>
<td>[3.154]</td>
<td>[3.154]</td>
<td>[3.555]</td>
</tr>
</tbody>
</table>
The topological analysis of the electron density can point out specific features of the studied compound. A bond path is defined as the line between two atoms where the electron density is locally bigger than in any direction from this path and mostly represents an actual bond between these atoms. A bond critical point (BCP) is the point of the minimum electron density along the bond path between two atoms. Additionally, the Laplacian of the electron density $\nabla^2 \rho(r)$ recovers the shell structure of atoms and gives information on open-shell or closed shell interactions.

The magnesium-hydride bond in $[\text{NN}'-(\text{MgH})_2]_2$ shows a strongly ionic character\textsuperscript{[20]} The electron density at the bond critical point in this case is relatively small and the Laplacian of the electron density $\nabla^2 \rho(r)$ clearly positive, which points to a closed-shell, ionic bond.

The topological parameters for the Mg-H moieties in the calculated clusters are comparable to their counterparts in solid $\beta$-MgH$_2$, which have recently been investigated by a theoretical study\textsuperscript{[21]} However, in the bulk material though the hydride anions are linked to three Mg centers and therefore the Mg–H bonds are slightly longer and weaker than in the molecular species.

The atomic charges have been obtained by integrating the electron density over the correspondent atomic basins that represent the atoms. The Mg atoms have transferred 0.81 electrons to the hydride ligands leaving the Mg center with a charge of +1.67 which is close to its formal oxidation state (+2) (Table 2.4). The additional charge of −0.81 on the hydride atoms immensely increases their atomic volumes. The hydrides are as voluminous as the nitrogen atoms on the ligand. For comparison, hydrogen atoms attached to ligand carbon atoms in $[\text{NN}'-(\text{MgH})_2]_2$ are more than two times smaller. They carry charges between −0.02 and +0.02 and display atomic volumes of 7.0–7.6 Å$^3$ (Table 2.5).

Table 2.5 Selected atomic properties derived from the theoretical electron densities of $[\text{NN}'-(\text{MgH})_2]_2$. 

<table>
<thead>
<tr>
<th></th>
<th>Atomic charge $q(\Omega)$ [e]</th>
<th>Atomic energy $E(\Omega)$ [hartree]</th>
<th>Atomic volume $v(\Omega)$ [Å$^3$]</th>
<th>Electron localization $Loc(\Omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>+1.67</td>
<td>−200.103</td>
<td>6.7</td>
<td>96.2</td>
</tr>
<tr>
<td>N1</td>
<td>−0.93</td>
<td>−55.155</td>
<td>14.4</td>
<td>78.5</td>
</tr>
<tr>
<td>N2</td>
<td>−1.23</td>
<td>−55.282</td>
<td>16.6</td>
<td>80.2</td>
</tr>
<tr>
<td>H1</td>
<td>−0.81</td>
<td>−0.719</td>
<td>18.9</td>
<td>81.3</td>
</tr>
<tr>
<td>H2</td>
<td>−0.81</td>
<td>−0.734</td>
<td>17.0</td>
<td>79.2</td>
</tr>
</tbody>
</table>
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The large size and polarizability of the hydrides in $[\text{NN}']\cdot\cdot\cdot(\text{MgH})_2$ allow this species to take part in mutual interactions that range over a relatively long distance. In the contour plot shown in Figure 2.21, an accumulation of electron density between two of the hydrides, H$_2$ and H$_2'$, which are 3.106 Å apart, can be observed and a corresponding bond path can be identified between these atoms. For such long-range contacts a weak, closed-shell interaction is to be expected and indeed the value for the electron density $\rho(r)$ is low, but somewhat higher than for typical van der Waals interactions.[22] Ring critical points (RCP) are minima of the electron density $\rho(r)$ in two dimensions. Two of those RCPs are located in close distance of 0.36 Å each to the BCP between H$_2$ and H$_2'$. Here the values for the electron density are only slightly smaller than at the BCP, which indicates that the electron density in this region is relatively flat and this means that the H···H bond path is potentially unstable (Figure 2.21).[23]

Figure 2.21 Contour plot of $\rho(r)$ in the Mg''−H2'−Mg'''.H2 plane of $[\text{NN}']\cdot\cdot\cdot(\text{MgH})_2$; selected atoms and bond paths are superimposed. BCPs and RCPs are represented by green and red circles, respectively. Lines are drawn at 2x, 4x, 8x10$^{-n}$ au ($n = -3, -2, -1, 0, 1, 2$) and 0.0065 au.

Recently, the term hydrogen-hydrogen bonding has been introduced for homopolar C−H···H−C interactions. The topological parameters for this hydride-hydride interaction are comparable to those of C−H···H−C interactions. In the latter case, the hydrogen atoms carry only very small, mostly positive charges,[24] which is in opposition to the observed high negative charges in the case of the molecular hydride. Still they have one thing in common, they are both counterintuitive bond paths between equally charged atoms.

The distance between the hydride nuclei and the H···H BCP of 1.553 Å is called the bonded radius for H$_2$ and H$_2'$. In turn the nonbonded radius can also be estimated. Therefore the extension of the electron density in the opposite direction, towards the outside of the
complex is traced. When the 0.001 a.u. envelope of the electron density is taken, nonbonded radii of about 1.7 Å can be determined for H2 and H2'; this value is significantly larger than the accepted van der Waals radius for hydrogen of 1.1 Å.[25] These larger radii suggest that there is a substantial interference between the two hydridic hydrogen atoms H2 and H2', which leads to a redistribution of electron density in the region between the atoms. This results in a stabilizing interaction that is indicated by the bond path. A look at the atomic energies $E(\Omega)$ (Table 2.5) confirms the stabilization as H2 and H2' are both more stable by 39 kJ/mol compared to H1 and H1' which show no interaction. Comparable stabilizing interactions between considerably hydridic hydrogen atoms have been reported recently in a DFT study on a range of binary and complex hydrides of light main group metals. These interactions can occur at a wide range of H···H distances between 2.3 and 3.1 Å.[21] Although anion-anion interaction might seem contradictory at first glance, they have been known for some time already and are suggested to play a role in the stabilization of crystals.[26] In addition they have also been observed in the extended structures of alkali-metal amidoboranes.[27] Recent NMR studies on partly deuterated ammonia borane could show that BH···HB interactions are highly relevant for the thermal release of H2.[28]

The intramolecular hydride···hydride interaction described for [NN'-{(MgH)2}]2 is the first identification of this kind of interaction for a molecular species. This suggests that hydride···hydride interactions are a more universal bonding feature in compounds containing hydridic H atoms and also emphasizes their potential role on the thermal dehydrogenation of these species. Moreover the model complex [NN'-(MgH)2]2 offers the unique opportunity to directly compare one interacting and one noninteracting hydride pair in an identical chemical environment (Table 2.6).

Table 2.6 Comparison of calculated values for H1/H1' and H2/H2'.

<table>
<thead>
<tr>
<th></th>
<th>H1/H1'</th>
<th>H2/H2'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance [Å]</td>
<td>4.713</td>
<td>3.106</td>
</tr>
<tr>
<td>Angle Mg-H-Mg [°]</td>
<td>117.1</td>
<td>153.0</td>
</tr>
<tr>
<td>Atomic charge $q(\Omega)$ [hartree]</td>
<td>−0.81</td>
<td>−0.81</td>
</tr>
<tr>
<td>Atomic volume $v(\Omega)$ [Å³]</td>
<td>18.9</td>
<td>17.0</td>
</tr>
<tr>
<td>Electron localization $Loc(\Omega)$</td>
<td>81.3</td>
<td>79.2</td>
</tr>
<tr>
<td>Delocalization index $\delta$</td>
<td>0.00</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The angles Mg-H-Mg are significantly different and the angle for Mg-H2-Mg is clearly larger than the angle for Mg-H1-Mg. This more linear arrangement brings H2 and H2' in closer proximity of each other, which is in agreement with their mutual interaction. The atomic charges $q(\Omega)$ of both hydrides are the same, still the atomic volume $v(\Omega)$ differs slightly. The interacting hydride H2 is about 10% smaller than H1, this number is comparable to volume changes that are associated with hydrogen-hydrogen bonding. The value for the electron localization $\text{Loc}(\Omega)$ is also smaller for H2, indicating that the electrons exchange slightly more in this case than in the case of H1. Next to sharing a significant interatomic surface, the weak interaction between H2 and H2' is further reflected in the delocalization index $\delta$. This value generally reflects the number of electron pairs shared between two atoms, irrespective of existing bond paths. Even if the value for $\delta(\text{H2/H2}')$ is very small, it is different from zero, while the value for H1 and H1', which are much further apart, equals zero.

As mentioned before the differences in atomic energy for H1 and H2 are significant, however, there is no direct way to determine a precise value for the H-H bond energy from these numbers. The formation of a H···H interaction also has influence on the rest of the compound and can raise or lower the atomic energies of other atoms in the compound. The Espinosa correlation has been previously used for estimation of bond strengths for hydrogen bonds as well as for other weak interactions. Employing the Espinosa correlation for $[\text{NN'}-(\text{MgH})_2]_2$ results in an H···H interaction energy of ca. 3.0 kJ/mol, assuming that the equation also holds true for hydride-hydride contacts. This value is comparable to very weak hydrogen bonds and lies within the range of other previously reported weak interactions like intermolecular O···O, N···O, C–H···O, and C–H···H–C contacts.

**Low-valent Mg(I) clusters**

As we could gain a lot of interesting information on the magnesium hydride cluster $[\text{NN'}-(\text{MgH})_2]_2$ by means of DFT calculation, we wanted to use this tool to study the possible low-valent residue that remains after thermal decomposition. First of all, this could give indications whether such a species can exist and secondly, what structure it would have. The major question to be answered is in how far tetracnuclear Mg(I) clusters are existent – or whether four valence electrons are not enough to form six delocalized Mg-Mg bonds in a Mg$_4$ tetrahedron (Figure 2.22a) Additionally, calculation can help in the development of an appropriate synthetical route towards low-valent Mg(I) clusters.
In order to evaluate a potential tetrahedral [Mg(I)]_4 cluster (Figure 2.22a), the DFT geometry of a hydride-free [NN'-Mg₂]₂, using the coordinates of [NN'-(MgH)₂]₂ without the four hydride moieties as a starting point, was optimized. The DFT structure obtained is similar to its parent compound, however with significant changes in the Mg₄-core (Figure 2.23).

The optimization starts from a near tetrahedron of Mg atoms with Mg···Mg distances ranging from 3.154 to 3.580 Å and runs towards a minimum in which two of the four Mg···Mg contacts are clearly shorter (2.854 Å) whereas the other two distances are significantly elongated (4.242 Å) (Table 2.7). Comparing these values to the Mg···Mg distance of 3.20 Å in Mg metal[33] and the bond length of 2.8457(8) Å observed for the Mg(I)-Mg(I) bond in (DIPP-Mg₁₂)[5] suggests the presence of a dimer with two localized Mg-Mg bonds rather than a tetrahedral Mg₄ cluster with delocalized bonds (Figure 2.22b). This means a significant rearrangement in the structure and could already be an explanation why such a complex has not been isolated after the thermal decomposition. For the independent synthesis of a Mg(I) cluster, a precursor with a comparable structural motive, like the [NN-(Mg(n-Bu))₂]₂ could be necessary. It has to be mentioned as well that the reaction enthalpy
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for the formation of a tetranuclear Mg(I) cluster from the corresponding Mg₄H₄ compound is high (ΔE = +222.8 kJ/mol, ΔH = +231.5 kJ/mol). Therefore an alternative route to the thermal decomposition of a magnesium hydride cluster would be favorable for the isolation of a low-valent multinuclear cluster.

Table 2.7 Selected calculated distances [Å] of [NN'-Mg₂]₂.

<table>
<thead>
<tr>
<th></th>
<th>Mg–N1</th>
<th>Mg···Mg'</th>
<th>Mg'···Mg''</th>
<th>Mg''···Mg'''</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–N1</td>
<td>2.063</td>
<td>4.242</td>
<td>3.776</td>
<td></td>
</tr>
<tr>
<td>Mg–N2</td>
<td>2.057</td>
<td>2.854</td>
<td>2.854</td>
<td></td>
</tr>
<tr>
<td>N1–N2</td>
<td>1.430</td>
<td>3.776</td>
<td>4.242</td>
<td></td>
</tr>
</tbody>
</table>

The conclusion based on DFT calculations, that no tetrahedral Mg₄ core is present in the calculated Mg(I) complex, can be confirmed by a topological analysis of the electron density in [NN'·Mg₂]₂. Figure 2.24 shows a detailed section of ρ(r) and −∇²ρ(r) of one of the Mg–Mg bonds. Selected atoms and bond paths are superimposed and BCPs and RCPs represented by green and red circles, respectively. Electron density is clearly accumulated between the Mg–Mg axis and a bond path has been identified between the two atoms.

![Figure 2.24](image)

**Figure 2.24** Contour plots of ρ(r) (top) and the negative Laplacian, −∇²ρ(r) (bottom), in the Mg'–Mg'''–NNA plane of [NN'-Mg₂]₂. Lines are drawn at 2x, 4x, 8x10⁻⁷ au (n = −3, −2, −1, 0, 1, 2) and 0.028 au [for ρ(r)], in the case of the Laplacian with both positive (dashed) and negative values (solid); solid and dashed lines represent charge concentration and depletion, respectively.
Additionally, another striking feature is revealed by the contour plot, the Mg atoms are not directly linked to each other through a bond critical point. Instead a local maximum of the electron density is found halfway between the Mg centers. A critical point in the electron density that is a maximum in all directions is called an attractor and paths that trace increasing electron density terminate at such attractors. For typical molecules an attractor is coincident with the position of the atomic nucleus. In rare occasion, maxima that do not correspond with a nucleus have been observed. This phenomenon, called a non-nuclear attractor (NNA), is usually found in bulk metals or model metal clusters.\textsuperscript{[34-36]} They have also been related to defects and color F centers in crystals as well as to solvated electrons.\textsuperscript{[37]}

Recently, the first experimental NNA has been reported for a stable molecular system, the dimeric Mg(I) complex 2.\textsuperscript{[38]} Moreover, very recent theoretical work suggests that NNAs are the main difference between low-valent main group and low-valent transition-metal bimetallocenes: CpM–MCp.\textsuperscript{[39]} The existence of non-nuclear attractors seems to play a vital role in the stabilization of main group atoms in a low oxidation state.

Approximately 0.7 electrons (Table 2.8) can be allocated to each of the two identical pseudo atoms in [NN'-Mg₂]₂, this is slightly less than the value of 0.81 electrons reported for the dimeric Mg(I) complex 2. The electron density at the position of the NNA (0.197 e Å\textsuperscript{3}) is only slightly higher than at the BCP (0.195 e Å\textsuperscript{3}) between the Mg center and the NNA. The BCP is 0.28 Å away from the NNA and the electron density profile is relatively flat along this axis. An extremely small value for the kinetic energy per electron at the NNAs G/ρ(NNA) of 0.03 hartree e\textsuperscript{-1} is observed. This is a typical feature for pseudo atoms and it has been interpreted as evidence for their loosely bound nature and the potential mobile nature of their electron density.\textsuperscript{[35]} This is further reflected in the reduced electron localization of the electrons within the boundaries of the pseudo atom. Whereas the majority of electrons of the Mg and N atoms are localized and only exchange to a certain extent, the electrons of the pseudo atoms are clearly more delocalized (Table 2.8).

Table 2.8 Selected atomic properties derived from the theoretical electron densities of [NN'-Mg₂]₂.

<table>
<thead>
<tr>
<th></th>
<th>Atomic charge q(Ω) [e]</th>
<th>Atomic energy E(Ω) [hartree]</th>
<th>Atomic volume v(Ω) [Å\textsuperscript{3}]</th>
<th>Electron localization Loc(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>+1.25</td>
<td>−200.181</td>
<td>16.7</td>
<td>94.1</td>
</tr>
<tr>
<td>N1</td>
<td>−0.95</td>
<td>−55.153</td>
<td>14.9</td>
<td>78.3</td>
</tr>
<tr>
<td>N2</td>
<td>−1.24</td>
<td>−55.272</td>
<td>16.9</td>
<td>80.1</td>
</tr>
<tr>
<td>NNA</td>
<td>−0.70</td>
<td>−0.084</td>
<td>14.6</td>
<td>30.6</td>
</tr>
</tbody>
</table>
Chapter 2

The topology of the electron density in the region between the Mg atoms and the NNAs shows typical features of metallic bonding. As would be expected for the weak nature of the bonding, the electron density at the bond critical point is relatively small (0.195 e Å$^{-3}$). However, it is more than twice as large as the values that have been previously reported for metals or small metal clusters.$^{[34,35]}$ The value is similar to the one that has been recently reported for the molecular dimeric Mg(I) species $^{2}.$$^{[38]}$ Another similarity to the previous study are the fairly large pseudo atoms in $[[\text{NN}']\text{-Mg}_2]_2$, they are comparable in size to the other atoms in the complex. In general, a larger region is claimed by the charge concentration around the NNA: it extends by more than 2.2 Å perpendicular to the Mg-Mg axis (Figure 2.24). As expected for a low-valent Mg(I) species, the atomic volume of the Mg atoms is significantly increased. Compared to the parent Mg(II) compound $[[\text{NN}']\text{(MgH)}]_2$, it has more than doubled in size. At the same time the lower oxidation state of $[[\text{NN}']\text{-Mg}_2]_2$ is not that strongly reflected in its atomic charge, which is only reduced by 0.42 electrons. However, if the transfer of about 0.35 electrons to the NNA is taken into account, the effective Mg charge adds up to +0.95, which is again close to its expected oxidation state.

Finally, another noteworthy feature of $[[\text{NN}']\text{-Mg}_2]_2$ is revealed by the three-dimensional representation of the negative Laplacian in Figure 2.25. To the best of our knowledge, it displays the first example for a molecular species, in which two NNAs, i.e. two pseudo atoms, are linked by a bond path. The topological parameters identify this interaction as clearly weaker than the Mg-NNA contacts, still they are in the same range as NNA···NNA interactions that have been reported for some metals and larger metal clusters in previous theoretical studies.$^{[35]}$
In this context it was proposed that it is a network of connected pseudo atoms that might be responsible for the delocalized binding and resulting conducting properties in some of these systems.\textsuperscript{[35]} This could in turn mean that the description of the bonding in [NN'-Mg\textsubscript{2}]\textsubscript{2} solely as a dimer linked by two localized Mg-Mg bonds might not be fully adequate. At least to a small extent, the bonding between the four Mg atoms has to be considered as delocalized.

2.4. Conclusions and future perspective

A range of different sized magnesium hydride clusters allowed for the detailed study of their properties and a direct comparison of these. The calculated trend of a decreasing hydrogen elimination temperature upon a decrease in size of the cluster, could be supported by the thermal decomposition of different magnesium hydride clusters with up to 8 Mg atoms. The clusters that have been investigated, released all the hydrogen incorporated in the magnesium hydride core, the only exception is the complex with a pyridinylene bridge in the ligand. In this case one equivalent cannot be released as H\textsubscript{2}, but reacts with the bridging pyridine moiety. The observed thermal hydrogen release is a slow process, therefore long constant heating is required to observe full hydrogen elimination and accordingly adjusted TPD and DSC measurements could gain further information on the decomposition process.

Future isolation of more multinuclear magnesium hydride complexes with an even higher number of Mg atoms and hydride ligand could lead to closing the gap to bulk materials and support the use of soluble magnesium hydride compounds as model systems for hydrogen
storage materials. This requires the design of new ligands to stabilize expanded Mg hydride complexes.

Deuterium-labeling studies confirm that the $\text{H}_2$ release is truly based on the coupling of hydride ligands and not due to a deprotonation of the ligand by hydride ligands. Moreover, these studies could show that, in aromatic solvents and THF, no hydride exchange between hydride and deuteride clusters can be observed for the bigger clusters $[\text{NN}^-\text{(MgH)}]_2$ and $(\text{PARA})_3\text{Mg}_8\text{H}_{10}$. In the case of $(\text{DIPP}-\text{MgH})_2$, hydride exchange with $(\text{DIPP}-\text{MgD})_2$ in benzene was slow but could be accelerated by the addition of THF. A similar observation could be made for the exchange between the clusters and $\text{H}_2$. Whereas the bigger clusters do not show signs of H-D exchange, it is slow for $(\text{DIPP}-\text{MgH})_2$ and can again be accelerated by THF. The thermal decomposition of the tetra- and octanuclear magnesium hydride complexes under an atmosphere of D$_2$ resulted in the detection of significant amounts of H-D. This could be due to microscopic reversibility of the $\text{H}_2$ elimination process but H-D exchange through another route cannot be excluded.

Analysis of the electron density of a DFT-optimized model-system $[\text{NN}^-\text{(MgH)}]_2$ led to the identification of hydride-hydride interactions between two of the four hydride ligands in the cluster core. It is the first identification of such an interaction within a molecular system and can be described as a weak interaction between two formally closed-shell systems (H$^-$: 1s$^2$). It is comparable in magnitude to other weak interactions that have been analyzed to date. Such interactions could be of significant importance for the release of hydrogen and indicate significance also for molecular compounds and not only in the solid state.

An analogous study on the other magnesium hydride complexes could gain further insights into the bonding situation in molecular magnesium hydride compounds and allow for a comparison of different sized clusters. Additionally, DFT calculations could help designing ligands for more expanded magnesium hydride complexes.

The products after the $\text{H}_2$ desorption, potentially low-valent Mg(I) clusters, could not be characterized so far. However, DFT calculations demonstrate that in the potential decomposition product of $[\text{NN}^-\text{(MgH)}]_2$, a low-valent $[\text{NN}^-\text{Mg}]_2$ cluster, the Mg(I) atoms are not situated on the corners of a tetrahedron. Instead, this tetrannuclear compound is best described as a dimer linked by two localized Mg-Mg bonds. Further analysis of the bonding situation revealed another interesting feature; the Mg centers are not directly connected to each other, but linked by two interconnected non-nuclear attractors. This is usually observed for metals and metal clusters and suggests a small degree of electron delocalization between the Mg-Mg bonds.
Implications from DFT calculations nourish the independent synthesis of Mg(I) clusters. As the features identified in the topological analysis of the electron density are comparable to the results obtained for an already isolated Mg(I) compound 2, chances are promising that the isolation of bigger Mg(I) compounds can be achieved.

2.5. Experimental

2.5.1. General

All experiments were carried out in flame-dried glassware under an inert atmosphere using Standard Schlenk-techniques and freshly dried degassed solvents. The following starting materials have been prepared according to literature: PYR·H₂,[7] PARA·H₂,[7] NN·H₂,[8] NN-(Mg(n-Bu))₂,[40] PYR-(Mg(n-Bu))₂,[40] NN-(MgH)₂,[9] NN-(Mg(n-Bu))(MgH),[9] PYR-(MgH)₂[10] and (PARA)₃Mg₈H₁₀.[11] Synthesis of NN-(MgCl)₂ and PARA-(MgCl)₂ and the reduction of the halides were performed according to unpublished results of Dr. Jan Spielmann,[12] the experimental data are therefore listed in this experimental. Mg(n-Bu)₂ solution (1M in heptane) and LiAlH₄ have been obtained commercially and used without further purification. NMR spectra have been recorded on a 400 MHz or 500 MHz NMR spectrometer (specified at individual experiments).

2.5.2. NN-(MgH)₂ in THF

[NN-(MgH)₂]₂ was dissolved in 0.5 mL of THF-d₆ and the ¹H NMR spectra were recorded at 25 °C.

[NN-(MgH)₂]₂

¹H NMR (500 MHz, THF-d₆, 25 °C) δ (ppm) = 0.67 (d, ³J_HH = 6.8 Hz, 6H, i-Pr), 1.00 (d, ³J_HH = 6.8 Hz, 6H, i-Pr), 1.17 (d, ³J_HH = 6.8 Hz, 12H, i-Pr), 1.53 (s, 6H, Me backbone), 1.73 (s, 6H, Me backbone), 2.93 (sept, ³J_HH = 6.8 Hz, 2H, i-Pr), 3.24 (sept, ³J_HH = 6.8 Hz, 2H, i-Pr), 4.41 (s, 2H, H backbone), 6.09-7.02 (m, 6H, Ar-H).

The resonances for Mg–H were too broad to be clearly assigned.

[NN-(MgH)₂]₂‘

¹H NMR (500 MHz, THF-d₆, 25 °C) δ (ppm) = 0.93 (d, ³J_HH = 6.8Hz, 6H, i-Pr), 1.09 (d, ³J_HH = 6.8Hz, 6H, i-Pr), 1.11 (d, ³J_HH = 6.8 Hz, 6H, i-Pr), 1.13 (d, ³J_HH = 6.8 Hz, 6H, i-Pr), 1.49 (s, 6H, Me backbone), 1.80 (s, 6H, Me backbone), 2.83 (s, 2H, Mg–H), 3.07 (sept, ³J_HH = 6.8 Hz, 2H, i-Pr), 3.13 (sept, ³J_HH = 6.8 Hz, 2H, i-Pr), 4.38 (s, 2H, H backbone), 6.09-7.02 (m, 6H, Ar-H) ppm.
2.5.3. Thermal decomposition of Mg hydride complexes

The compounds (30 - 60 mg, 0.03 - 0.05 mmol) were heated in a teflon-sealed tube by means of a thermostated air-bath and the temperature was monitored by an infra-red thermometer. The eliminated gasses were led through two cold traps cooled with liquid N₂ and were quantified by pumping the gasses quantitatively into a calibrated burette by means of a Töpler pump. The used vacuum line was also equipped with a loop in which a quartz tube filled with CuO pellets and an external electrical oven is integrated. Subsequent circulation of the eliminated gasses over the heated CuO (300 °C) and condensation of the oxidized products in liquid N₂ resulted in removal of the eliminated H₂ in form of H₂O and allowed for distinction between H₂ and additional gasses.

For an additional conformation of the presence of H₂ the compounds were decomposed within a closed J-Young NMR tube. Therefore a special setup has been designed that allows for the separation of the decomposed compounds from the deuterated solvent with glass wool. On account of the high solubility of H₂ in THF, we chose THF-d₈ as the NMR solvent. Because the molecular weight of the clusters is high (885.92 - 1973.63 g/mol) and the hydride contents are accordingly low (0.2% - 0.5%), only small amounts of H₂ are produced. In order to achieve maximum solvation of the H₂ produced, the volume of the NMR tube was reduced by addition of glass pearls (Figure 2.26).

In a typical experiment, in a glove box the THF-d₈ was introduced first into the J-Young tube, followed by a plug of dry glass wool. On top a layer of dry glass pearls was added and

![Figure 2.26 Set-up for thermal decomposition of solid magnesium hydride species.](image)

the magnesium hydride sample was introduced, followed by another layer of glass pearls after which the tube was carefully closed with the Teflon tap. Outside the glove box, the THF was degassed by means of three freeze-pump-thaw cycles, subsequently frozen in N₂ and the tube was carefully evacuated. While the solvent is frozen, the sample was carefully heated with a hot air gun and the temperature was monitored with an infra-red thermometer.

Onset of decomposition is usually gave a color change from yellow to red. After decomposition, the frozen THF was carefully thawed, care has to be taken that it does not...
come into contact with the decomposed product. Partially dissolved gasses were analyzed by $^1$H NMR. H$_2$: 4.55 ppm (singlet) or H-D: 4.50 ppm (triplet, $^1J_{HD} = 43$ Hz).

### 2.5.4. Synthesis of the complexes

#### Synthesis of NN-(MgCl)$_2$[12]

Method a: A solution of [NN-(Mg(n-Bu))$_2$]$_2$ (400 mg, 0.59 mmol) and Me$_3$SiCl (128 mg, 1.18 mmol) in 11 mL of toluene was heated to 60 °C for 18 hours. NN-(MgCl)$_2$ precipitated from this solution as a yellow powder. The product was separated by centrifugation and dried under vacuum. The reaction mixture was concentrated to a volume of approximately 4 mL and slowly cooled to $-27$ °C to yield another small amount of a yellow powder. Combined yield: 223 mg, 0.35 mmol, 60%.

Method b: A solution of [NN-(Mg(n-Bu))$_2$]$_2$ (30 mg, 0.044 mmol) and Et$_3$NHCl (12 mg, 0.088 mmol) in 0.5 mL of benzene did not react. After addition of 0.1 mL of THF-$d_8$ a reaction was observed. After slow cooling of the reaction mixture a yellow powder could be obtained. The product was separated by centrifugation and dried under vacuum. The product was dissolved in THF-$d_8$ but was not pure, therefore method a) is favourable.

NMR data were comparable to those obtained by J. Spielmann:[12]

$^1$H NMR (300 MHz, C$_6$D$_6$/THF-$d_8$: 4/1, 20 °C): δ (ppm) = 1.19 (d, $^3J_{HH} = 6.8$ Hz, 12H, i-Pr), 1.20 (d, $^3J_{HH} = 6.8$ Hz, 6H, i-Pr), 1.37 (d, $^3J_{HH} = 6.8$ Hz, 6H, i-Pr), 1.65 (s, 6H, Me backbone), 2.11 (s, 6H, Me backbone), 3.12 (sept, $^3J_{HH} = 6.8$ Hz, 2H, i-Pr), 3.32 (sept, $^3J_{HH} = 6.8$ Hz, 2H, i-Pr), 4.73 (s, 2H, H backbone), 7.11-7.16 (m, 6H, aryl).

$^{13}$C NMR (75 MHz, C$_6$D$_6$/THF-$d_8$: 4/1, 20 °C): δ (ppm) = 22.2 (Me backbone), 24.5 (Me backbone), 24.6 (i-Pr), 24.7 (i-Pr), 25.8 (i-Pr), 25.9 (i-Pr), 28.7 (i-Pr), 92.4 (backbone), 124.1 (aryl), 124.6 (aryl), 126.0 (aryl), 142.8 (aryl), 143.6 (aryl), 145.6 (aryl), 168.3 (backbone), 168.1 (backbone).

#### Synthesis of PARA$_2$-Mg$_3$Cl$_2$[12]

Method a: A solution of PARA-[Mg(n-Bu)]$_2$ (30 mg, 0.040 mmol) and Me$_3$SiCl (10 mg (0.092 mmol) in 0.6 mL of hexane and 0.1 mL of benzene was heated to 60 °C for 72 hours. The solvent was then evaporated and the residue solved in 0.1 mL of hexane. Standing of this solution at room
temperature afforded yellow crystals of PARA-Mg$_3$Cl$_2$ suitable for X-ray diffraction. The precipitation of MgCl$_2$ was not observed.

In a larger scale experiment PARA-[Mg(n-Bu)$_2$]$_2$-(Mg(n-Bu)$_2$) (verified by $^1$H NMR spectroscopy; prepared from a solution of PARA-H$_2$ with three equivalents of Mg(n-Bu)$_2$ (300 mg, 0.34 mmol) and Me$_3$SiCl (150 mg, 1.38 mmol) in 10 mL of THF was stirred at room temperature for 18 hours. The solvent was removed under vacuum. Hexane was added to the remaining solid which afforded a yellow powder.

Yield: 226 mg, 0.16 mmol, 94%. (Yield calculated for PARA$_2$-Mg$_3$Cl$_2$·(MgCl$_2$) C$_{80}$H$_{104}$Mg$_3$N$_8$·MgCl$_2$ ($M= 1416.77$))

NMR data were comparable to those obtained by J. Spielmann.[12]

$^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ (ppm) = 0.66 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H, i-Pr), 0.86 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.04 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.11 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H, i-Pr), 1.20 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.31 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.33 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.42 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.60 (s, 6H, Me backbone), 1.65 (s, 6H, Me backbone), 1.70 (s, 6H, Me backbone), 1.76 (s, 6H, Me backbone), 2.04 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2H, i-Pr), 3.07 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2H, i-Pr), 3.25 (sept, $^3$J$_{HH}$ = 6.9 Hz, 2H, i-Pr), 3.41 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2H, i-Pr), 4.74 (s, 2H, H backbone), 4.81 (s, 2H, H backbone), 6.35 (d, $^3$J$_{HH}$ = 8.4 Hz, 4H, aryl), 6.65 (d, $^3$J$_{HH}$ = 8.4 Hz, 4H, aryl), 6.98-7.12 (m, 12H, aryl).

$^{13}$C NMR (75 MHz, C$_6$D$_6$, 20 °C): δ (ppm) = 14.4 (i-Pr), 23.1 (i-Pr), 23.3 (i-Pr), 24.2 (i-Pr), 24.4 (i-Pr), 24.5 (i-Pr), 24.6 (i-Pr), 25.0 (i-Pr), 25.0 (i-Pr), 25.1 (i-Pr), 25.5 (i-Pr), 27.7 (i-Pr), 28.1 (Me backbone), 28.4 (Me backbone), 29.5 (Me backbone), 32.0 (Me backbone), 95.9 (backbone), 98.5 (backbone), 123.5 (aryl), 124.1 (aryl), 124.3 (aryl), 124.9 (aryl), 125.2 (aryl), 125.3 (aryl), 126.0 (aryl), 142.5 (aryl), 142.6 (aryl), 144.3 (aryl), 144.6 (aryl), 145.7 (aryl), 146.0 (aryl), 166.2 (backbone), 169.5 (backbone), 169.8 (backbone), 170.4 (backbone).

**Synthesis of NN-(Mgl)$_2$**

NN-H$_2$ (500 mg, 0.98 mmol) was slowly added to a solution of Mg(n-Bu)$_2$ in heptane (1M, 2.0 mL, 2.00 mmol). After the mixture stopped releasing butane, it was stirred at 25 °C for 1 hour. The solvent was removed in vacuum, the light brown solid was dissolved in 10 mL of toluene and 498 mg (1.96 mmol) of elemental iodine were added. After stirring of this mixture at 25 °C for 16 hours, a light yellow solid precipitated from the dark solution. It was separated by centrifugation, dried in vacuum.
Magnesium hydride clusters

Yield: 634 mg (0.77 mmol, 79%):

$^1$H NMR (400 MHz, C$_6$D$_6$/THF-d$_8$: 4/1, 25 °C): $\delta$ (ppm) = 1.15 (d, $^3$J$_{HH}$ = 6.8 Hz, 12H, i-Pr), 1.21 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.35 (d, $^3$J$_{HH}$ = 6.8 Hz, 6H, i-Pr), 1.62 (s, 6H, Me backbone), 2.09 (s, 6H, Me backbone), 3.0 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2H, i-Pr), 3.21 (sept, $^3$J$_{HH}$ = 6.8 Hz, 2H, i-Pr), 4.69 (s, 2H, H backbone), 7.12-7.16 (m, 6H, aryl).

$^{13}$C NMR data could not be obtained due to the low solubility.

**Synthesis of PARA-(MgI)$_2$**

PARA-H$_2$ (500 mg, 0.85 mmol) was slowly added to a solution of Mg(n-Bu)$_2$ in heptane (1M, 1.7 mL, 1.70 mmol). After the mixture stopped releasing butane, it was stirred at 25 °C for 1 hour. The solvent was removed in vacuum, the yellow solid was dissolved in 10 mL of toluene and elemental iodine (431 mg, 1.70 mmol) were added. After stirring of this mixture at 25 °C for 16 hours, the brown coloration from the iodine had disappeared. Half of the solvent was removed and the yellow solution was stored at −30 °C for 2 hours, subsequently a light yellow solid precipitated from the solution. It was separated by centrifugation, dried in vacuum and pure product was isolated.

Yield: 618 mg, 0.69 mmol, 81%.

$^1$H NMR (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ (ppm) = 1.03 (d, $^3$J$_{HH}$ = 6.7 Hz, 24H, i-Pr), 1.54 (s, 6H, Me backbone), 1.68 (s, 6H, Me backbone), 3.18 (sept, $^3$J$_{HH}$ = 6.7 Hz, 4H, i-Pr), 4.79 (s, 2H, H backbone), 6.99-7.13 (m, 8H, aryl), 7.40 (br s, 2H, aryl).

$^{13}$C NMR data could not be obtained due to the low solubility.

**2.5.5. Reduction of halides and hydrides**

Reduction of NN-(MgCl)$_2$ with K(C$_8$H$_{10}$)$^{[12]}$

A solution of NN-(MgCl)$_2$ (30 mg, 0.047 mmol) and K(C$_8$H$_{10}$) (16 mg, 0.096 mmol) in 0.6 mL of THF-d$_8$ was heated to 60 °C for 24 hours. The deep red solution turned orange during this time and precipitation of colourless crystals could be observed (KCl). The precipitate was separated by centrifugation and the reaction mixture was concentrated to a volume of approximately 0.1 mL. Standing of this solution at room temperature afforded colourless crystals of [(DIPP-NCCCN)Mg(THF)]$_2$ suitable for X-ray diffraction.

Reactions in a larger scale to estimate the yield failed.
NMR data were comparable to those obtained by J. Spielmann\cite{12}:

\[ \text{\textsuperscript{1}H NMR (300 MHz, C}_6\text{D}_6, 20 ^\circ\text{C}): \delta (ppm) = 1.30 (d, \text{ }^3 J_{\text{HH}} = 6.9 \text{ Hz, 12H, } i-\text{Pr}), 1.40 (d, \text{ }^3 J_{\text{HH}} = 6.9 \text{ Hz, 12H, } i-\text{Pr}), 1.85 (s, 6H, Me backbone), 3.60 (sept, \text{ }^3 J_{\text{HH}} = 6.9 \text{ Hz, 4H, } i-\text{Pr}), 5.33 (s, 2H, H backbone), 7.27-7.30 (m, 6H, aryl). \]

**Reduction of NN-(MgH)\textsubscript{2} with K-mirror \cite{12}**

A mirror of K (35 mg, 0.90 mmol) was prepared in a J Young NMR tube. A solution of [NN-(MgH)\textsubscript{2}] (30 mg, 0.053 mmol) in 0.6 mL of toluene-\textsubscript{d\text{8}} was added and the reaction mixture heated to 60 °C for 72 hours. The solvent was evaporated and 0.1 mL of hexane were added to the residue. Slow cooling of this solution to −27 °C afforded colourless crystals suitable for X-ray diffraction.

**Reduction of NN-(Mgl)\textsubscript{2} with K**

A suspension of NN-(Mgl)\textsubscript{2} (350 mg, mmol) in 50 mL of toluene was stirred vigorously over a potassium mirror (200 mg, mmol) for 24 h at 25 °C. The generated solids, remaining starting material and the excess of potassium were separated by centrifugation. The resulting yellow solution was concentrated and cooled to −30 °C. After several crystallization attempts only amorphous light yellow powders or microcrystals of the reduction product were obtained. Addition of THF or recrystallization at higher temperatures led to precipitation of Mg metal.

\[ \text{\textsuperscript{1}H NMR (300 MHz, C}_6\text{D}_6, 20 ^\circ\text{C}): \delta (ppm) = 1.15 (d, \text{ }^3 J_{\text{HH}} = 6.7 \text{ Hz, 6H, } i-\text{Pr}), 1.23 (d, \text{ }^3 J_{\text{HH}} = 6. \text{ Hz, 6H, } i-\text{Pr}), 1.25 (d, \text{ }^3 J_{\text{HH}} = 6.8 \text{ Hz, 6H, } i-\text{Pr}), 1.29 (d, \text{ }^3 J_{\text{HH}} = 6.9 \text{ Hz, 6H, } i-\text{Pr}), 1.62 (s, 6H, Me backbone), 1.76 (s, 6H, Me backbone), 3.18 (sept, \text{ }^3 J_{\text{HH}} = 6.8 \text{ Hz, 2H, } i-\text{Pr}), 3.19 (sept, \text{ }^3 J_{\text{HH}} = 6.7 \text{ Hz, 2H, } i-\text{Pr}), 5.17 (s, 2H, H backbone), 7.02-7.14 (m, 6H, aryl). \]

Due to the low solubility no \textsuperscript{13}C NMR data could be obtained.

**2.5.6. Deuterium-labeling studies**

**Synthesis of deuterated phenylsilane**

PhSiD\textsubscript{3} was prepared according to a slightly modified literature procedure\cite{41}. PhSiCl\textsubscript{3} (5.2 mL, 44.4 mmol) was added to a cooled (0 °C) suspension of LiAlD\textsubscript{4} (1.5 g, 35.7 mmol) in diethyl ether. The reaction mixture was diluted with additional 8 mL of diethyl ether and stirred at 45 °C for two hours. The solids were removed by filtration and a majority of solvent was evaporated at 0 °C. The remaining product/solvent mixture was distilled into a liquid N\textsubscript{2} cooled flask to remove left over lithium salt. The residual ether was removed by applying oil
pump vacuum at −30 °C. The product was obtained as a colorless liquid. Yield: 2.5 g, 22.5 mmol, 51%.

1H NMR (400 MHz, C6D6, 25 °C) δ (ppm) = 7.05-7.15 (m, 3H, m-, p-ArH), 7.36-7.42 (m, 2H, o-ArH).

Synthesis of (DIPP-MgD)2

A solution of Mg(n-Bu)2 in heptane (1M, 1.1 mL, 1.1 mmol) was added to a solution of DIPP-H (445 mg, 1.1 mmol) in 5 mL of toluene. After stirring at room temperature for one hour, the solution was heated to 60 °C for an additional hour. The solvent was removed in vacuum. Deuterated phenylsilane was added and the mixture dissolved in hexane. After heating to 60 °C for 48 hours, the solution was concentrated and cooled to −20 °C for crystallization. The product was isolated as colorless crystals.

Yield: 195 mg, 0.44 mmol, 40%.

The 1H NMR signals are largely similar to the reported magnesium hydride complex (DIPP-MgH)2.[4]

1H NMR (C6D6, 400 MHz, 25 °C) δ (ppm) = 0.97 (d, 3JHH = 6.9 Hz, 12H, i-Pr), 1.11 (d, 3JHH = 6.9 Hz, 12H, i-Pr), 1.48 (s, 6H, CH3), 3.05 (sept, 3JHH = 6.9 Hz, 4H, i-Pr), 4.83 (s, 1H, CH), 6.98 – 7.38 (m, 6H, Ar-H).

Synthesis of [NN-(MgD)2]2

A solution of [NN-(Mg(n-Bu))2]2 (400 mg, 0.59 mmol) and PhSiD3 (170 mg, 1.57 mmol) in 10 mL of toluene was heated to 80 °C for 72 hours. The solvent was removed in vacuum and the residue was dissolved in 5 mL of hexane. The solution was cooled to −27 °C for crystallization. The product was isolated as yellow crystals.

Yield: 165 mg, 0.29 mmol; 49%.

The 1H NMR signals are largely similar to the reported magnesium hydride complex [NN-(MgH)2]2.[9]

1H NMR (toluene-d8, 500 MHz, 25 °C) δ (ppm) = 0.76 (d, 3JHH = 6.7 Hz, 6H, i-Pr), 1.18 (d, 3JHH = 6.8 Hz, 6H, i-Pr), 1.31 (m, 12H, i-Pr), 1.57 (s, 6H, CH3), 1.77 (s, 6H, CH3), 3.04 (sept, 3JHH = 6.7 Hz, 2H, i-Pr), 3.31 (sept, 3JHH = 6.8 Hz, 2H, i-Pr), 4.51 (s, 2H, CH), 6.99 – 7.15 (m, 6H, Ar-H).
Synthesis of PARA₃Mg₈D₁₀

PARA-H₂ (500 mg, 0.84 mmol) was added to a solution of Mg(n-Bu)₂ in heptane (1M, 2.4 mL, 2.4 mmol). After the yellow solution was stirred at room temperature for an hour, the solvent was removed in vacuum. 575 mg (5.08 mmol) PhSiD₃ were added and the reaction mixture was dissolved in 4.0 mL of benzene. The yellow suspension was heated to 60 °C for 72 hours without stirring. The product crystallized from the hot solution as yellow crystals.

Yield: 250 mg, 0.13 mmol, 46%

The ¹H NMR signals are largely similar to the reported magnesium hydride complex PARA₃Mg₈H₁₀.[¹¹]

¹H NMR (C₆D₆, 400 MHz, 25 °C) δ (ppm) = 1.29 (d, 3J_HH = 6.7 Hz, 18H, i-Pr), 1.33 (d, 3J_HH = 6.7 Hz, 18H, i-Pr), 1.45 (d, 3J_HH = 6.7 Hz, 18H, i-Pr), 1.63 (d, 3J_HH = 6.7 Hz, 18H, i-Pr), 1.70 (s, 18H, CH₃), 1.95 (s, 18H, CH₃), 3.38 (sept, 3J_HH = 6.7 Hz, 6H, i-Pr), 3.55 (sept, 3J_HH = 6.9 Hz, 4H, i-Pr), 4.77 (s, 6H, CH), 5.81 (br, 6H, Ph-bridge), 6.26 (br, 6H, Ph-bridge), 7.13-7.25 (m, 1H, Ar-H).

Hydride exchange between magnesium hydride clusters

A magnesium hydride complex was mixed with the equivalent amount of a magnesium deuteride complex and dissolved in an appropriate solvent. The exchange between hydride and deuteride was followed by ¹H NMR spectroscopy. In case after prolonged reaction times no exchange was visible, the mixture was heated to 60 °C and monitored by means of ¹H NMR at regular time intervals. For comparison, mixed hydride-deuteride complexes were synthesized separately.

Hydride exchange with H₂ gas

In order to investigate the exchange of deuteride from a magnesium deuteride complex with H₂ gas, a solution of the magnesium deuteride complex in J-Young NMR tube was frozen in liquid N₂ and after three freeze-pump-thaw cycles regassed with 1 bar H₂. Analogous experiments were carried out using magnesium hydride complexes and D₂ gas. The exchange processes were monitored with ¹H NMR spectroscopy.
**Thermal decomposition with deuterium labeling**

In order to check whether the ligand is deprotonated, the deuterated clusters where thermally decomposed in a closed set-up (Figure 2.26). The dissolved gasses were investigated by $^1\text{H}$ NMR.

To check for potential reversibility of the $\text{H}_2$ desorption, the solid magnesium hydride complexes were decomposed thermally in a set-up as described in Figure 2.26, but under an atmosphere of $\text{D}_2$ instead of vacuum. The formation of $\text{H}_2$ and HD was monitored by means of $^1\text{H}$ NMR spectroscopy.

**2.5.7. Computational Details**

DFT calculations were performed with the Gaussian 09 program suite$^{[42]}$ using the B3-LYP density functional,$^{[43]}$ along with the implemented 6-311G(d,p) basis set.$^{[44]}$ This was further supplemented by an additional polarization and a diffuse function for all magnesium and nitrogen atoms, as well as for the hydridic hydrogen atoms at the cluster core. All geometry optimizations were carried out without imposing any symmetry constraints, and the structures obtained were confirmed as true minima by calculating analytical frequencies. Structure optimizations were also carried out using other functionals and basis sets of different size, which gave very similar geometries and electron densities. The H···H interaction, in particular, was invariant to the choice of basis set and level of theory, and was also confirmed by an MP2 calculation at the previously determined B3-LYP geometry. The topology of the electron density was analysed using the software package AIMALL.$^{[45]}$

The atomic energies reported for the hydridic hydrogen atoms in $\left[\text{NN}^\cdot\cdot\cdot(\text{MgH})_2\right]_2$ were estimated by multiplying their atomic kinetic energies by the factor $-(\gamma - 1)$ with $\gamma = -V/T$, as described, e.g., in ref. 24a. The value for the molecular virial ratio $\gamma$ deviated from 2 by $3.8 \times 10^{-3}$ in the optimized system. Plots were generated using AIMALL$^{[45]}$ and CHEMCRAFT.$^{[46]}$
2.6. References


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Magnesium hydride clusters


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