Well-Defined Molecular Magnesium Hydride Clusters: Relationship between Size and Hydrogen-Elimination Temperature

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Abstract: A new tetranuclear magnesium hydride cluster, $[{NN-(MgH)_2}_2]$, which was based on a N-N-coupled bis- β -diketiminate ligand (NN²⁻), was obtained from the reaction of [{NN- $(MgnBu)_{2}$ with PhSiH₃. Its crystal structure reveals an almost-tetrahedral arrangement of Mg atoms and two different sets of hydride ions, which give rise to a coupling in the NMR spectrum (J = 8.5 Hz). To shed light on the relationship between the cluster size and H₂ release, the thermal decomposition of $[{NN-(MgH)_2}_2]$ and two closely related systems that were based on similar ligands, that is, an octanuclear magnesium hydride cluster and a dimeric magnesium hydride species, have been investigated in detail. A lowering of the H₂-desorption temperature with

decreasing cluster size is observed, in line with previously reported theoretical predictions on $(MgH_2)_n$ model systems. Deuterium-labeling studies further demonstrate that the released H_2 solely originates from the oxidative coupling of two hydride ligands and not from other hydrogen sources, such as the β -diketiminate ligands. Analysis of the DFT-computed electron density in [{**NN**-(MgH)₂]₂] reveals a counterintuitive interaction between two formally closed-shell H⁻ ligands that are separated by 3.106 Å. This weak interaction could play an important role in H₂ de-

Keywords: cluster compounds • elimination • hydrides • hydrogen storage • magnesium sorption. Although the molecular product after H₂ release could not be characterized experimentally, DFT calculations on the proposed decomposition product, that is, the low-valence tetranuclear Mg(I) cluster $[(NN-Mg_2)_2]$, predict a structure with two almost-parallel, localized Mg-Mg bonds. As in a previously reported β-diketiminate Mg^I dimer, the Mg-Mg bond is not characterized by a bond critical point, but instead displays a local maximum of electron density midway between the atoms, that is, a non-nuclear attractor (NNA). Interestingly, both of the NNAs in $[(NN-Mg_2)_2]$ are connected through a bond path that suggests that there is bonding between all four Mg¹ atoms.

Introduction

Magnesium hydride is receiving widespread attention as a potential hydrogen-storage material.^[1] This compact, light-weight salt-like material is rich in hydrogen (7.7 wt%) and advantageously displays reversible hydrogen-release/uptake: MgH₂ \rightleftharpoons Mg+H₂. However, its drawback is the relatively high temperatures (about 300 °C) that are required for hydrogen release. This requirement is directly related to unfavorable thermodynamics for this formal reductive elimination step (ΔH =74.4(3) kJ mol⁻¹; ΔS =135.1(2) J mol⁻¹K⁻¹).^[2] The high enthalpic contribution to the stability of bulk MgH₂ is primarily due to the enormous lattice energy for the salt-like rutile structure of [Mg²⁺H⁻₂]_∞ (ΔH = 2718 kJ mol⁻¹).^[3]

Recent calculations have shown that thermodynamics and, thus, the desorption temperature can be influenced to some extent by a variation in particle size.^[4,5] Downsizing (MgH₂)_n particles results in a rapid increase in the surface/ volume ratio and in the number of less strongly bound surface hydride ions. This effect starts to become noticeable for (MgH₂)_n clusters with n < 19 (i.e., particles smaller than 1.3 nm) and is dramatically amplified for clusters in the subnanometer range. At the extreme, monomeric linear MgH₂ is calculated to have a negative decomposition enthalpy

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- Supporting information for this article, including details on the crystal structures of [{NN-(MgnBu)₂]₂], [{NN-(MgnBu)(MgH)₂]₂], and [{NN-(MgH)₂]₂], NMR spectra of [{NN-(MgH)₂]₂], PGSE-NMR spectra of [(DIPP-nacnacMgH·THF)₂] and [(DIPP-nacnacCaH·THF)₂], cartesian coordinates and geometrical parameters for the calculated structures of [{NN'-(MgH)₂]₂] and [(NN'-Mg₂)₂], topological parameters for the H…H interaction in [{NN'-(MgH)₂]₂] at different levels of theory, and plots of the interatomic surfaces for the H1 and H2 atoms in [{NN'-(MgH)₂]₂], is available on the WWW under http://dx.doi.org/ 10.1002/chem.201300684.

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 $(\Delta H = -5.5 \text{ kJ mol}^{-1}).^{[4]}$ Although such size effects have been experimentally verified to some extent, $(MgH_2)_n$ clusters in the sub-nanometer range are not easily obtained by using the typical solid-state approaches.^[5] However, a molecular "bottom-up" approach allows for the synthesis of small, well-defined magnesium hydride clusters that could be seen as the smallest possible magnesium hydride particles that are encapsulated by a ligand framework. Owing to their low hydride content, these molecular clusters are impracticable for efficient hydrogen-storage purposes; however, they could serve as well-defined model systems. Their molecular nature allows for their in-depth analysis and precise investigation down to the atomic level.

Recently, dimeric β -diketiminate magnesium hydride complex **1**, [(DIPP-nacnacMgH)₂], has been reported^[6] (DIPP-nacnac⁻ = [(2,6-*i*Pr₂C₆H₃)NC(Me)CHC(Me)N(2,6-

 $iPr_2C_6H_3)$]⁻). As in the previously reported heavier calcium congener,^[7] this complex is stable towards ligand exchange and the formation of the insoluble salt $(MgH_2)_n$, on account of the sterically demanding 2,6-di-isopropylphenyl substituents (DIPP). The thermal release of H_2 could possibly result in formation of the structurally known Mg^I complex 2, [(DIPP-nacnacMg)₂].^[8] However, complex **1** is described as extraordinarily stable (the reported decomposition temperature is 300 °C) and can only be converted into Mg^I complex 2 by reduction with K.^[9] Conversely, pressurizing complex 2 with H_2 does not give hydride complex 1; however, the oxidation of Mg^I with AlH₃ resulted in the formation of complex 1.^[9] It seems that the direct reductive elimination of H₂ requires the combined action of more than two metal atoms. Therefore, we systematically investigated synthetic methods towards multi-metallic magnesium hydride complexes.



We recently introduced a set of bridged bis- β -diketiminate ligands with large DIPP substituents.^[10] A dianionic ligand with a *para*-phenylene bridge (**PARA**²⁻) was previously used in the isolation of a large molecular magnesium hydride cluster, [**PARA**₃Mg₈H₁₀].^[11] This cluster contains a Mg₈H₁₀⁶⁺ core that is encapsulated by three **PARA**²⁻ ligands and releases five equivalents of H₂ at a temperature of only 200 °C. Herein, we report the synthesis, structure, and thermal decomposition of a tetranuclear magnesium hydride cluster that is based on the N–N-coupled bis- β -diketiminate ligand **NN**²⁻. With three clusters of various sizes in hand, we evaluated the thermally initiated elimination of H₂ as a function of cluster size. In addition, we report a first theoretical investigation of possible H⁻···H⁻ interactions in molecu-



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lar magnesium hydride clusters and on the proposed decomposition product, a low-valence $[(Mg^I)_4]$ cluster.

Results and Discussion

Synthesis and structures: The magnesium hydride complex $[NN-(MgH)_2]$ was obtained from the reaction of the ligand $NN-H_2$ with nBu_2Mg and the stepwise conversion of the two nBu groups into hydrides by reaction with PhSiH₃ (Scheme 1). It was found that the first MgnBu functionality



Scheme 1. Synthesis of [NN-(MgH)₂].

is considerably more reactive than the second. The first *n*Bu anion could be smoothly transformed into a hydride by reaction with PhSiH₃ in toluene at 60 °C (1 h), however, conversion of the second *n*Bu anion required higher temperatures and prolonged reaction times (80 °C, 48 h). This difference in reactivity allowed for the isolation and characterization of the intermediate [**NN**-(Mg*n*Bu)(MgH)] species, which was obtained as luminescent yellow crystalline blocks in 41 % yield.

The starting complex $[NN-(MgnBu)_2]$, the intermediate complex [NN-(MgnBu)(MgH)], and the final magnesium hydride product $[NN-(MgH)_2]$, which was obtained as yellow pyramid-shaped crystals in 48% yield (the complex was also highly luminescent in the yellow-wavelength range), were all characterized by single-crystal X-ray diffraction. Their structures are shown in Figure 1 and selected bond lengths are summarized in Table 1. All of the com-

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Figure 1. Crystal structures of: a) [{ $NN-(MgnBu)_2$ }, a crystallographic two-fold axis is positioned horizontally in the plane of projection; b) [{NN-(MgnBu)(MgH)}, a crystallographic two-fold axis is positioned vertically in the plane of projection; and c) [{ $NN-(MgH)_2$ }, three perpendicular crystallographic two-fold axes run through the H1 and H1' atoms, through the H2 and H2' atoms, and through the middle of the N-N bond (D_2 symmetry). In all of these structures, the *i*Pr substituents and most H atoms are omitted for clarity.

plexes form dimeric aggregates that contain four Mg^{2+} nuclei, albeit in different arrangements and with differences in the bridging of nBu^- and H^- ions.

 $[NN-(MgnBu)_2]$ forms a dimeric aggregate in which all four Mg²⁺ nuclei are more or less situated in one plane. The nBu^- ions each bridge two Mg²⁺ centers, thereby resulting in two separated four-membered Mg₂nBu₂ rings. The partial conversion of the nBu^- ions into H⁻ ions gives a structure in which the Mg²⁺ nuclei are situated at the corners of a tetra-

Table 1. Selected	distances	[Å]	for	the	crystal	structures	shown	in
Figure 1. ^[a]								

[{ NN -(MgnBu	$ _{2} _{2}$		
Mg1-N1	2.068(2)	Mg2-N3	2.049(2)
Mg1-N2	2.046(2)	Mg2-N4	2.084(2)
Mg1-C35	2.225(3)	Mg2-C39	2.241(3)
Mg-C35'	2.211(3)	Mg2-C39'	2.242(3)
Mg1…Mg1′	2.751(1)	Mg2…Mg2′	2.755(1)
[{NN-(MgnBu	$(MgH)_2$		
Mg1–N1	2.034(1)	Mg2–N3	2.056(1)
Mg1–N2	2.056(1)	Mg2-N4	2.049(1)
Mg1-C35	2.253(2)	Mg2-C35	2.247(2)
Mg1–H1′	1.76(2)	Mg2-H1	1.83(2)
Mg1…Mg1′	3.767(1)	Mg2…Mg2′	3.605(1)
Mg1…Mg2	3.165(1)	Mg2…Mg1′	3.517(1)
$[{NN-(MgH)_2}]$	2		
Mg-N1	2.025(1) [2.055]	Mg…Mg′	3.586(1) [3.555]
Mg-N2	2.010(1) [2.034]	Mg…Mg″	3.030(1) [3.154]
Mg-H1	1.771(12) [1.849]	Mg…Mg‴	3.492(1) [3.580]
Mg-H2	1.845(6) [1.828]	Mg'…Mg''	3.492(1) [3.580]
H1…H1′	4.65(2) [4.713]	Mg'…Mg'''	3.030(1) [3.154]
H2…H2′	2.93(4) [3.106]	Mg"…Mg"'	3.586(1) [3.555]

[a] Theoretical DFT values for $[{NN'-(MgH)_2}_2]$ are given in square brackets.

hedron. Bridging nBu^- and H⁻ ions result in the formation of an eight-membered ring instead of two separated fourmembered rings. Further conversion into $[NN-(MgH)_2]$ affords a dimeric aggregate with a similar tetrahedral assembly of Mg²⁺ nuclei and an eight-membered Mg₄H₄ ring. The transition from a "double dimer" structure into a cyclic structure upon the replacement of nBu^- groups with H⁻ groups is due to the fact that the spherically symmetrical hydride ligand favors a more-linear bridging mode. For example, in [{NN-(MgBu)(MgH)}₂], the Mg-H-Mg and Mg-*n*Bu-Mg angles are 157.5(1)° and 89.4(1)°, respectively.

The structure of $[{NN-(MgH)_2}_2]$ contains a tetrahedron of Mg²⁺ nuclei, in which the Mg...Mg' distances range from 3.030(1) to 3.586(1) Å. The vertices of this tetrahedron are either bridged by the NN^{2-} ligands or by H⁻ groups. This pattern is comparable to a recently reported tetranuclear hydride-rich magnesium cluster,^[12] which crystallized with a similar "adamantane-like" structure; however, the [{NN- $(MgH)_{2}_{2}$ cluster is highly symmetrical (D_{2}) . The asymmetrical ric unit, which represents one-quarter of the tetranuclear aggregate, is repeated by three perpendicular two-fold rotation axes (one through the middle of the N-N bonds, one through the H1 and H1' atoms, and one through the H2 and H2' atoms). The β -diketiminate units in the **NN** ligand are twisted and rotation around the N-N bond is somewhat hindered. Therefore, the NN ligand shows axial chirality that is similar to that in BINOL ligands. The cluster contains two NN ligands of equal axial chirality and, therefore, is homochiral (D_2 symmetry, Scheme 2).

The structure of the tetranuclear cluster $[{\mathbf{NN-(MgH)}_2}_2]$ is maintained in solution. This property is nicely demonstrated by low-temperature ¹H NMR spectroscopy: Two different hydride ligands, H1 and H2, give two triplets at $\delta = 2.85$ and 3.64 ppm at -50 °C, with a coupling of ²J(H,H) = 8.5 Hz (see the Supporting Information). The relatively large difference



Scheme 2. Schematic representation and chirality interconversion for $[{NN-(MgH)_2}_2]$.

between their chemical shifts ($\Delta \delta = 0.79$ ppm) is presumably due to the ASIS effect of the aryl substituents. The highfield signal is assigned to the H1 atom, which is situated between two aryl rings. The chemical shift of the low-field signal ($\delta = 3.64$ ppm) also compares well to the signal for the hydride ligands in [**NN**-(MgnBu)(MgH)], which appears as a singlet at $\delta = 3.59$ ppm. The herein observed magnetic coupling between two hydrides in a magnesium complex is only the second reported example of such an interaction. The coupling constant, ²*J*(H,H)=8.5 Hz, is somewhat larger than those observed in [**PARA**₃Mg₈H₁₀] (4.5 and 5.2 Hz).^[11]

The magnesium hydride complex [{NN-(MgH)₂]₂] is more dynamic than $[\mathbf{PARA}_3Mg_8H_{10}]$ in toluene. Whereas the latter complex shows hydride-hydride coupling at 100°C, signals for the H1 and H2 atoms in [{NN-(MgH)₂]₂] already coalesce at 25 °C ($\Delta G^{\pm} = 56(1)$ kJ mol⁻¹, see the Supporting Information). This result is likely due to conformational changes, rather than Mg-H bond-breaking/making processes. A change in the axial chirality of one of the NN ligands in the D_2 -symmetric cluster would result in the achiral (heterochiral) S_4 -symmetric structure (Scheme 2), in which all of the hydride ligands are equal. A further change in the chirality of the second NN ligand would afford a homochiral D_2 -symmetric cluster that is a mirror image of the original D_2 -symmetric cluster. It should be noted that the positions of the H1 and H2 atoms are exchanged during this process. Therefore, the coalescence of the H1/H2 ¹H NMR resonances can simply be explained as a change in the axial chirality of both ligands through 90° rotations about their N-N axes.

Thermal-decomposition studies: The availability of a set of magnesium hydride clusters with similar β -diketiminatebased ligand systems but of different nuclearities enables a study of their thermal decomposition as a function of cluster size. These investigations allow for verification of the calculational result that smaller magnesium hydride clusters show lower enthalpies for the elimination of hydrogen.^[4]

In a previous report, we described the thermal decomposition of the octanuclear magnesium hydride cluster [PAR- $A_3Mg_8H_{10}$].^[11] It was found that a solution of [PAR- $A_3Mg_8H_{10}$] in toluene was surprisingly stable, even when heated at 180°C for 2 days, that is, well above its boiling point, in a J-Young NMR tube. However, heating this solid material on a high-vacuum line with an attached Töpler pump afforded decomposition of the complex at 200 °C, during which process the yellow microcrystalline material became reddish brown. Gas quantification by pumping the gas quantitatively into a calibrated burette of a Töpler pump system indicated the release of the expected 4.9(\pm 0.2) mol equivalents of gas per [**PARA**₃Mg₈H₁₀] aggregate. Moreover, the gas does not condense in liquid N2, but is fully converted into condensable water after leading it over CuO at 300 °C. After leading the gas into deuterated THF, a clear ¹H NMR resonance could be observed at $\delta =$ 4.55 ppm, which is the chemical shift for H_2 in this solvent.^[13]

Complex [{**NN**-(MgH)₂}₂] showed similar behavior: Heating a solution of the complex in toluene in a J-Young tube at 180 °C for 2 days did not show any noticeable decomposition of the complex. However, the stepwise heating of the solid material on a vacuum line afforded a color change from yellow to red at 175 °C and showed signs of gas release. This was confirmed by gas measurements using the Töpler pump. Quantitative gas release was slow and required decomposition times of about 30 min, after which the [{**NN**-(MgH)₂}₂] cluster released $2.2(\pm 0.1)$ mol equivalents of a gas that was non-condensable in liquid nitrogen and was fully converted into condensable water after leading it over CuO at 300 °C. An independent NMR investigation confirmed the formation of H₂.

This observation represents new evidence for the fact that smaller molecular magnesium hydride clusters can release H_2 at substantially lower temperatures than bulk MgH₂ itself (decomposition temperature > 300 °C). In agreement with earlier calculations by de Jong and co-workers,^[4] the smaller magnesium hydride cluster [{NN-(MgH)₂}₂] already released H₂ at 175 °C, that is, significantly lower than the 200 °C that was required for [PARA₃Mg₈H₁₀]. This result led us to reinvestigate the thermal stability of the small dimeric magnesium hydride cluster 1 under similar conditions.

Solid complex **1** was stepwise heated on a high-vacuum line with a Töpler pump. At 125 °C, the light-yellow powder changed into an orange-red melt that released gas by bubbling. Similar to the results described above, gas quantification indicated that $1.0(\pm 0.05)$ mol equivalents of hydrogen gas were released (the nature of the released gas was confirmed by oxidation over hot CuO and independently by ¹H NMR spectroscopy). We noted that compound **1** also started to decompose at 125 °C in a capillary under a N₂ atmosphere. The mismatch with the reported decomposition

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temperature (>300 °C) is likely due to the fact that the decomposition requires a short induction period; thus, fast heating rates during melting-point determination may explain this discrepancy. Although we only have a limited amount of data points, the H₂-elimination temperature seems to decrease with cluster size.

The nature of the product(s) after the thermal decomposition of $[{NN-(MgH)_2}_2]$ is hitherto unknown. Most of the reddish solid residue is soluble in aromatic solvents. ¹H NMR analysis shows the presence of several ligand signals and there is no indication of paramagnetic behavior. We could not characterize any products by crystallization and subsequent structure determination. In addition, the thermal decomposition of complex **1** gave a reddish powder, which, when dissolved in $[D_6]$ benzene, showed several sets of ¹H NMR signals that may include those of complex 2. Although this result could not be unambiguously confirmed, it is tempting to believe that low-valence MgI clusters are formed. First of all, the color change to red may indicate such a formation (the THF adduct of low-valence compound 2 is described as orange-red).^[6a] Secondly, the Mg. Mg distances in complexes 1 and 2 are guite similar. Therefore, a simple elimination of H_2 might generate a tetranuclear Mg^I cluster [(NN-Mg₂)₂] with a comparable tetrahedral arrangement of the metal atoms and, therefore, of similar global shape. However, larger Mg^I clusters are hitherto unknown and it is questionable whether four valence electrons would be sufficient to stabilize the bonding in a Mg₄ tetrahedron (see the DFT calculations below). We could not convert the red residues back into magnesium hydride complexes by pressurizing with H_2 (<100 bar).

Deuterium-labeling studies: Deuterium-labeled species can provide important information regarding the source of hydrogen upon thermal decomposition. In addition, information regarding the dynamics of hydride exchange can be obtained. For this purpose, we synthesized a series of magnesium deuteride clusters by using the original synthetic procedures but substituting PhSiH₃ for PhSiD₃.

 H^- exchange between magnesium hydride clusters: The dimeric hydride complex $1-H_2$ and its deuteride dimer $(1-D_2)$ were dissolved in C₆D₆ and possible H/D exchange between the complexes was monitored by ¹H NMR spectroscopy. After several hours at room temperature, no changes were observed. Whilst performing the same experiments in a mixture of $[D_6]$ benzene/ $[D_8]$ THF (4:1), an exchange of H⁻ and D⁻ ions was observed: A new signal for the H⁻ ligand appeared at slightly higher field. This ¹H NMR signal is assigned to the mixed dimer with bridging H⁻ and D⁻ ligands and showed a characteristic 1:1:1 triplet, owing to H-D coupling $({}^{2}J(H,D) = 4.4 \text{ Hz})$. Although we could not determine the coupling constant between the two identical H⁻ ligands in complex 1-H₂, the observed H–D coupling corresponds to an estimated equivalent H-H coupling constant of 28.6 Hz (based on the gyromagnetic ratios for H and D). This value is substantially larger than the observed hydride-

hydride coupling constants in [{NN-(MgH)₂]₂] (8.5 Hz) and $[\mathbf{PARA}_{3}Mg_{8}H_{10}]$ (4.5 and 5.2 Hz), but still remote from theoretical predictions for the value of geminal H-H coupling in linear MgH₂ (55-80 Hz).^[14] At present, it is unclear whether the hydride-hydride NMR coupling is due to through-bond or through-space mechanisms (or a combination). Although the exact positions of the hydride ligands from X-ray diffraction data should be treated with care, it seems likely that there is no correlation between the coupling constant and the Mg-H bond length. The average Mg-H bond lengths in $[PARA_3Mg_8H_{10}]$ and $[{NN-}$ $(MgH)_{2}_{2}$ are both 1.81(2) Å. The various polymorphs of dimeric complex 1 or its dimeric THF adduct, 1.(THF)2, show somewhat (partially significantly) larger Mg-H bond lengths of 1.91(5) Å and 1.93(2) Å, respectively.^[6,15] The larger coupling constant in complex 1 might be explained by the fact that the hydride ligands in the dimer are part of a four-membered ring system, whereas, in the larger aggregates, they are integrated in more-extended ring systems. The smaller ring causes a significantly shorter hydride---hydride distance. We determined a reasonably accurate value of 2.32(2) Å for the H···H distance in the THF adduct 1.(THF)2,^[15] whereas a distance of 2.44(4) Å was found in another polymorph.^[6a] The H···H distances in two polymorphs of THF-free complex 1 are 2.35(8) and 2.65(4).^[6] Therefore, the average H···H distance of 2.44(4) Å is significantly shorter than the H···H distances in $[{NN-(MgH)_2}_2]$ (2.76(4) Å) and $[PARA_3Mg_8H_{10}]$ (average: 2.86(4) Å) and could explain the larger observed magnetic coupling; this correlation between the hydride…hydride distance and its magnetic coupling constant hints that a significant part of the coupling proceeds through space.

This above-described H/D exchange process is highly solvent dependent: No exchange is observed in pure [D₆]benzene, but the addition of [D₈]THF results in complete exchange into a statistical mixture of complexes $1-H_2$ (25%), **1**-H,D (50%), and **1**-D₂ (25%) within 1 h. This notable influence of THF indicates that H/D exchange likely proceeds through a smaller aggregate. Concerning the aggregation state in $[D_6]$ benzene, it should be noted that PGSE NMR measurements show that not only the magnesium hydride [(DIPP-nacnacMgH•THF)₂] but also its calcium analogue, [(DIPP-nacnacCaH·THF)₂], are dimeric in aromatic solvents (see the Supporting Information). The hydrodynamic radii for [(DIPP-nacnacMgH·THF)₂] and [(DIPPnacnacCaH·THF)₂] are both 6.8(1) Å. This result is significantly larger than the hydrodynamic radii for [DIPP-nacnacZnH] (5.2(1) Å)^[16] and [Mes-nacnacZnH] (Mes=mesityl, 5.0(2) Å),^[17] both of which are monomeric in solution. The ratio of the hydrodynamic radii between the magnesium and zinc hydride complexes or the calcium and zinc hydride complexes, 1.3:1, corresponds to a volume ratio of about 2.2:1, thus indicating that the THF adducts of the magnesium and calcium hydride complexes are dimeric in aromatic solvents (at least at room temperature). The observation of H-D magnetic coupling in complex 1-H,D is additional evidence for the dimeric state of the magnesium hydride com-

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plex under exchange conditions. Therefore, THF-stimulated H/D exchange likely proceeds through a short-lived, THF-stabilized, monomeric state.

Interestingly, both larger clusters, that is, $[{NN-(MgH)_2}_2]$ and $[PARA_3Mg_8H_{10}]$, do not show H/D exchange with deuterated clusters (also not after prolonged heating at 60 °C or after THF addition). This result is likely due to their inherent higher stability towards dissociation and underscores the proposed dissociative mechanism for hydride exchange between aggregates.

 H^-/H_2 exchange: The σ -bond metathesis reaction, which is well-established in organolanthanide chemistry,^[18] has recently also been shown to be operative in Group 2 chemistry.^[19,20] A solution of the dimeric calcium deuteride complex [(DIPP-nacnacCaD•THF)₂] in benzene already showed D/H exchange with H₂ (1 bar) at room temperature (90% exchange was observed within 20 min).

Under similar conditions, a solution of magnesium deuteride complex $1-D_2$ in $[D_6]$ benzene did not show any reaction with H_2 (1 bar). However, heating this solution to 60 °C led to partial exchange and the formation of H-D and complex 1-H,D in the reaction mixture, as detected by ¹H NMR spectroscopy. Keeping the sample at this temperature overnight led to 85% exchange. Therefore, magnesium hydride complexes are much less reactive than their corresponding calcium hydrides. The exchange process is not only accelerated by heat but also by the addition of THF. A solution of $1-D_2$ in $[D_6]$ benzene/ $[D_8]$ THF (4:1) already gave slow exchange at room temperature (10% after 1 h, 50% after 5 days). This result was clearly visible by the detection of dissolved H–D and complex 1-H₂ by ¹H NMR spectroscopy (see the Supporting Information). In contrast to the experiment in pure C₆D₆, we could not detect the intermediate mixed complex 1-H,D in the presence of THF. We tentatively explain this result with the mechanism shown in Scheme 3. In THF, dimer $1-D_2$ is in equilibrium with small amounts of monomeric magnesium deuteride species, on which any empty coordination sites are likely filled by THF ligands. These highly reactive monomers exchange D^- for H^- by $\sigma\text{-bond}$ metathesis with H₂. A subsequent recombination of monomers gives dimeric complex 1-H₂. The absence of detectable amounts of complex 1-H,D can be explained by assuming a slow, rate-determining deaggregation step and a considerably faster σ -bond metathesis. In pure C₆D₆, either the σ bond metathesis is much slower or D/H exchange takes place along a route in which the dimer only breaks open (Scheme 3).

Interestingly, neither of the larger magnesium deuteride clusters, [{ $NN-(MgD)_2$ }] and [$PARA_3Mg_8D_{10}$], exchange their deuteride ligands with H₂, even at higher temperatures (60 °C). Partially deuterated clusters might give broad ¹H NMR signals for the remaining H⁻ ligand (due to H/D magnetic coupling) that might not be clearly visible at the start. Therefore, we also investigated the H/D exchange by subjecting [{ $NN-(MgH)_2$ }] to D₂. No exchange was observed (even after heating at 60 °C for several days) and the





Scheme 3. Possible routes for D/H exchange.

¹H NMR spectrum showed the characteristic triplets for magnetic H–H coupling. The inability of these larger clusters to exchange their H⁻ ligand with H₂ might be an indication that smaller monomeric metal hydride complexes—or at least opened clusters—are required for this process. Whereas dimers like complex **1** could be in a dimer/monomer equilibrium, the larger multimetallic/multihydride clusters clearly are not: A solution of [**PARA**₃Mg₈H₁₀] in toluene even shows clear H⁻···H⁻ NMR coupling at 100 °C.^[11] The importance of a monomeric state for hydride/H₂ exchange has also been suggested in [(Cp₂*LnH)₂] complexes (Ln=lanthanide, Cp=cyclopentadienyl).^[21]

Thermal-decomposition studies with deuterium labeling: Within the closed system of a J-Young NMR tube, various magnesium deuterides were thermally decomposed as solids and the gasses were analyzed in THF by ¹H NMR spectroscopy (for technical details, see the Supporting Information). The decomposition of [{**NN**-(MgD)₂}₂] showed no significant quantities of H–D or H₂ (small quantities can be explained by the incomplete labeling of the magnesium compounds: PhSiD₃ with 95% isotopic purity was used). Also, the thermal decomposition of the larger magnesium deuteride cluster [**PARA**₃Mg₈D₁₀] showed no significant formation of H– D. In contrast, clusters that contained 50% hydride and 50% deuteride (which were prepared by using a 1:1 mixture of PhSiD₃ and PhSiH₃) eliminated large quantities of H–D. This result means that hydrogen elimination from $[{NN-(MgH)_2}_2]$ and $[PARA_3Mg_8H_{10}]$ is solely based on the coupling of hydride ligands. The involvement of ligand protons can largely be excluded.

We also investigated the thermal decomposition of solid $[{\mathbf{NN}-(MgH)_2}_2]$ or $[\mathbf{PARA}_3Mg_8H_{10}]$ under a D₂ atmosphere (1 bar). In both cases, not only H₂ but also significant amounts of H–D could be detected. This result could either be due to H/D exchange prior to the decomposition or to a reversible H₂-elimination process. Because previous studies have shown (see above) that the larger magnesium deuteride clusters are inert towards D/H exchange with H₂, we think that the observed H–D originates from a reversible process. However, considering the harsher conditions that are needed for H₂ elimination (175–200 °C), we do not fully exclude partial H/D exchange of hydride-only clusters with D₂ prior to the elimination step.

DFT calculations and charge-density analysis: To explore the bonding situation in [{NN-(MgH)₂]₂] in more detail, we carried out a topological analysis of its electron density, $\rho(\mathbf{r})$, as derived from DFT calculations, by using the "atoms in molecules" approach.^[22] For our theoretical model system, we replaced the DIPP substituents on each ligand by methyl groups; this model system will be denoted as [{NN'-(MgH)₂]₂]. The experimental twist angle between β diketiminate units, 83.4(2)°, is retained in the optimized geometry (84.9°) and all other parameters are in good agreement with their experimental counterparts, bearing in mind that positions of hydrogen atoms are always approximate in X-ray diffraction studies (for a detailed geometry, see the Supporting Information).

The topological parameters of $\rho(\mathbf{r})$ for selected bonds in $[\{\mathbf{NN'}-(\mathbf{MgH})_2\}_2]$ are listed in Table 2 and selected atomic properties are shown in Table 3. The values for the Mg–H bonds confirm their strongly ionic character:^[23] At the bond critical point (BCP),^[24] $\rho(\mathbf{r})$ is relatively small and $\nabla^2 \rho(\mathbf{r})$, the Laplacian of the electron density, is clearly positive. In addition, the total energy (H_b) at the BCP is close to zero,

Table 2. Selected topological parameters at the BCPs for the theoretical electron densities in $[\{NN'-(MgH)_2\}_2]$ and $[(NN'-Mg_2)_2].^{[a]}$

	$\rho_{\rm b}$ [e Å ⁻³]	$\nabla^2 \rho_{\rm b}$ [e Å ⁻⁵]	ε	H _b [hartree Å ⁻³]	$G/\rho_{\rm b}$ [hartree e^{-1}]	δ
					[nurreee]	
$[{NN'-(MgH)_2}_2]_2$						
Mg-N1	0.327	+7.171	0.10	+0.04	1.43	0.17
Mg-N2	0.348	+7.662	0.10	+0.03	1.45	0.19
N1-N1′	2.014	-7.673	0.02	-1.46	0.46	1.20
Mg-H1	0.249	+3.366	0.03	-0.01	0.98	0.18
Mg-H2	0.247	+3.473	0.01	-0.01	1.01	0.17
H2–H2′	0.047	+0.327	3.43	0.00	0.41	0.05
$[(NN'-Mg_2)_2]$						
Mg-N1	0.320	+6.999	0.11	+0.04	1.42	0.20
Mg-N2	0.329	+7.133	0.10	+0.03	1.42	0.22
N1N1′	1.997	-7.425	0.00	-1.43	0.46	1.20
Mg-NNA	0.195	-0.418	0.07	-0.06	0.15	0.35
NNA1…NNA2	0.046	+0.074	0.13	0.00	0.15	0.03

[a] Values ε and δ are dimensionless.

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14.9

16.9

14.6

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78.3

80.1

30.6

cal electron densities of $[{NN'-(MgH)_2}_2]$ and $[(NN'-Mg_2)_2]$.							
	$q(\Omega) \left[e ight]$	$E(\Omega)$ [hartree]	$Vol(\Omega)$ [Å ³] ^[a]	$Loc(\Omega)^{[b]}$			
[{NN'-($MgH)_2\}_2]$						
Mg	+1.67	-200.103	6.7	96.2			
N1	-0.93	-55.155	14.4	78.5			
N2	-1.23	-55.282	16.6	80.2			
H1	-0.81	-0.719	18.9	81.3			
H2	-0.81	-0.734	17.0	79.2			
[(NN'-1	$Mg_{2})_{2}$						
Mg	+1.25	-200.181	16.7	94.1			

[a] At $\rho(\mathbf{r}) = 0.001$; [b] $Loc(\Omega)$ is dimensionless.

-55.153

-55.272

-0.084

-0.95

-1.24

-0.70

N1

N2

NNA

and a high ratio of G/ρ_b is observed, which represents the kinetic energy per electron. The topological parameters for the Mg–H moieties are comparable to those of their counterparts in solid β -MgH₂, which has recently been investigated in a theoretical study.^[25] However, in this bulk material, the hydride anions are linked to three different Mg atoms, which renders the Mg–H bonds slightly longer and weaker than in the molecular species reported herein.

The atomic charges, $q(\Omega)$, as obtained by integrating the electron density over the respective atomic basins, reveal that 0.81 electrons are transferred from the Mg atoms onto each hydride, thus leaving the Mg atom with a charge of +1.67, that is, close to its oxidation state (Table 3). The additional charge on the hydrides significantly increases their atomic volumes, which are now similar to those of N atoms. For comparison, H atoms that are attached to ligand carbon atoms in [{NN'-(MgH)₂}₂] carry charges of between -0.02 and +0.02 and display atomic volumes of $Vol(\Omega) = 7.0-7.6$ Å³, that is, more than two-times smaller.

The large size and polarizability of the hydridic H atoms in $[{NN'-(MgH)_2}_2]$ allow them to engage in mutual interactions over a relatively long distance. As shown in the contour plot of $\rho(\mathbf{r})$ in Figure 2, there is an accumulation of electron density between two of the hydrides (H2 and H2', 3.106 Å apart) and a corresponding bond path between these atoms can be identified. As expected for such a longrange contact, the topological parameters at the BCP, as shown in Table 2, point to a weak, closed-shell interaction: The value for $\rho(\mathbf{r})$ at the BCP ($\rho_{\rm b}$) is low, albeit somewhat higher than for typical van der Waals interactions,^[26] $\bigtriangledown^2 \rho_b$ is relatively small and positive, and the energy density (H_b) is positive and close to zero. Furthermore, two ring critical points (RCPs)^[27] are close (0.36 Å each) to the H2···H2' BCP, with values of $\rho(RCP)$ that are only slightly smaller $(0.046 \text{ e} \text{\AA}^{-3})$, thus showing that the electron density is relatively flat in this region and that the H…H bond path is potentially unstable.^[28] The topological parameters for this interaction resemble those of homopolar C-H···H-C interactions, for which the term hydrogen-hydrogen bonding has recently been introduced. Although, in this case, the hydrogen atoms only carry negligible or very small (mostly posi-



Figure 2. Contour plot of $\rho(\mathbf{r})$ in the Mg''-H2'-Mg'''-H2 plane of [{**NN**'-(MgH)₂]₂]; selected atoms and bond paths are superimposed. The BCPs and RCPs are represented by green and red circles, respectively. Lines are drawn at 2×10^{-n} , 4×10^{-n} , 8×10^{-n} (n = -3, -2, -1, 0, +1, +2), and 0.0065 au.

tive) charges,^[29] this result might indicate that these interactions represent two sides of the same coin.

Whilst a bonded radius of 1.553 Å is observed for the H2 and H2' atoms (i.e., the distance between the nuclei and the H···H BCP), the nonbonded radius can also be estimated by tracing the extension of the electron density in the opposite direction, towards the outside of the complex. By taking the 0.001 envelope for $\rho(\mathbf{r})$, nonbonded radii of about 1.7 Å are obtained for the H2 and H2' atoms, which is clearly greater than the accepted van der Waals radius of 1.1 Å for hydrogen.^[30]

These radii suggest that there is significant interference between hydridic hydrogen atoms H2 and H2' and a concomitant redistribution of the electron density in the interatomic region, which results in a stabilizing interaction, as indicated by the H···H bond path. The atomic energies, $E(\Omega)$, confirm that both the H2 and H2' atoms are more stable by 39 kJ mol⁻¹ compared to the non-interacting H1 and H1' atoms. Stabilizing interactions between significantly hydridic H atoms have recently been observed in a DFT study of a range of binary and complex hydrides of light main group metals, in which it was shown that these interactions could occur at a wide range of H···H separations (2.3-3.1 Å).^[25] Although anion---anion bonding interactions might seem contradictory at first, they have been known for some time and are thought to play an important role in the stabilization of crystals.^[31] Hydride…hydride interactions have also been observed in the extended structures of alkali-metal amidoboranes.^[32] Very recently, NMR deuteration studies on the thermal release of H_2 in ammonia borane showed that similar BH···HB interactions are highly relevant.^[33]

The first identification of intramolecular hydride...hydride interactions in the molecular species reported here points to the possibility of a more-ubiquitous bonding feature in compounds that contain hydridic H atoms and also emphasizes their potential role on the reaction coordinate of the dehydrogenation reaction. Moreover, it offers a unique opportunity to directly compare two pairs of hydridic hydrogen atoms in an identical chemical environment, that is, one that engages in H...H interactions (H2, H2') and one that does not (H1, H1').

As mentioned before, the $[{NN'-(MgH)_2}_2]$ cluster displays D_2 symmetry and it is interesting to note that the Mg-H-Mg angles are significantly different for the H1 and H2 atoms: The Mg-H2-Mg angle (153.0°) is clearly larger than the Mg-H1-Mg angle (117.1°); this more-linear arrangement helps to bring the H2 and H2' atoms into closer proximity to one another, in line with their mutual interaction. Whereas the atomic charges on both the H1 and H2 atoms are the same, the values of their atomic volume, $Vol(\Omega)$, differ to some extent (Table 3): H2 is about 10% smaller than H1, which is comparable to the volume changes that are associated with hydrogen-hydrogen bonding.^[29] The value of the electron localization, $Loc(\Omega)$, is also lower for the H2 atom, thus indicating that its electrons exchange slightly more than those of the H1 atom. Finally, the H2 and H2' atoms share a significant interatomic surface (for details, see the Supporting Information) and the weak interaction between these atoms is further reflected in the value of the delocalization index, δ , which typically measures the number of electron pairs that are shared between two atoms, irrespective of existing bond paths.^[34] Table 2 shows that the value for $\delta(H2,H2')$ is small but non-zero, whereas, for atoms H1 and H1', which are separated by 4.713 Å, δ (H1,H1') equals zero.

The differences between the atomic energies of the H1 and H2 atoms are significant (see above); however, there is no direct method to obtain a precise value for the H–H interaction energy from these values, because the formation of a H…H interaction can also raise or lower the atomic energies of other atoms in the compound.^[25a] By using the Espinosa correlation,^[35] which has previously been employed for hydrogen bonds, as well as for other weak interactions,^[35,36] the H…H interaction energy in [{NN'-(MgH)₂}₂] would be about 3.0 kJmol⁻¹, given that this equation also holds true for hydride–hydride interactions. This value is comparable in magnitude to those of very weak hydrogen bonds^[37] and lies within the range of other previously characterized weak interactions, such as intermolecular O…O, N…O, C–H…O, and C–H…H–C interactions.^[36]

DFT calculations are also a perfect tool for studying the possible low-valence residue that remains after H_2 elimination. To evaluate the possible existence of a tetrahedral $[(Mg^1)_4]$ cluster, we simply optimized the DFT geometry of the hydride-free complex $[(NN'-Mg_2)_2]$, by taking the coordinates of $[\{NN'-(MgH)_2\}_2]$ (without the four hydride moieties) as a starting point. The obtained DFT structure is



Figure 3. DFT-optimized geometry of [(**NN'**-Mg₂)₂]; all hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mg–N1 2.063, Mg–N2 2.057, N1–N2 1.430, Mg···Mg′ 4.242, Mg···Mg″ 2.854, Mg···Mg″ 3.776, Mg′···Mg″ 3.776, Mg′···Mg″ 2.854, Mg″···Mg″ 4.242; C1-N1-N1″′-C1″′ 91.05.

shown in Figure 3, along with selected structural parameters. The geometry of $[(NN'-Mg_2)_2]$ is similar to that of its parent compound, albeit with significant changes in the Mg₄ core. Starting from an almost-tetrahedral Mg₄ core, with Mg···Mg distances that ranged from 3.154 to 3.580 Å, the structure optimized towards a minimum in which two of the four Mg···Mg distances were now clearly shorter (2.854 Å), whereas the other two distances were noticeably elongated (4.242 Å). Given a Mg···Mg distance of 3.20 Å in Mg metal,^[38] this suggests the presence of a dimer with two localized Mg–Mg bonds (as in complex **2**), rather than a Mg₄ tetrahedral cluster with delocalized bonding.

This result was confirmed by a topological analysis of the electron density in [(NN'-Mg₂)₂]. Figure 4 shows plots of $\rho(\mathbf{r})$ and $\nabla^2 \rho(\mathbf{r})$ in a contour map that contains two of the Mg atoms that are in closer contact; selected bond paths and critical points are also shown. Clearly, $\rho(r)$ accumulates along the Mg-Mg axis and a bond path can be identified between the atoms. Another striking feature is that the Mg atoms are not directly linked to each other through a bond critical point, but instead are linked through a local maximum of $\rho(\mathbf{r})$ midway between the atoms. Such non-nuclear attractors (NNAs) have been observed before on rare occasions; however, most of these reports were for bulk metals or model metal clusters.^[39] NNAs have also been linked to defects and color F centers in crystals, as well as to solvated electrons.^[40] Very recently, an experimental NNA was reported for the first time in a stable molecular system that was similar to the one reported herein, that is, the aforementioned compound 2, in which two Mg^I atoms were joined together in a dimeric Mg^I species.^[41]

Approximately 0.7 electrons can be allocated to each of the two identical pseudo-atoms in $[(NN'-Mg_2)_2]$, which comprise an NNA along with its corresponding basin (Table 3). The electron density at the position of these NNAs $(0.197 e^{A^{-3}})$ is only marginally higher than at the corresponding Mg-NNA BCPs (0.28 Å away, Table 3), which points to a relatively flat profile of $\rho(\mathbf{r})$ along this axis. The extremely small value for the kinetic energy per electron at the NNAs $(G/\rho(NNA) = 0.03 \text{ hartree } e^{-1})$ is typical for pseudo-atoms and has been interpreted as evidence for the loosely bound and potentially mobile nature of their electron density.^[39b] This is also reflected in the decreased localization of electrons within the boundaries of the pseudoatoms, as expressed by the parameter $Loc(\Omega)$. As shown in Table 3, the majority of electrons on the Mg and N atoms are localized and only exchange to a limited extent, whereas the electrons of the pseudo-atoms are clearly more delocalized.

The topology of $\rho(\mathbf{r})$ in the region between the Mg atoms and the NNAs displays the typical features of metall-metall bonding (Table 2): The Laplacian and the total energy, $H(\mathbf{r})$, at the Mg-NNA BCPs are small and negative, which is indicative of weak covalent bonding, whereas the $G/\rho(\mathbf{r})$ ratio is clearly smaller than 1, thus again confirming the shared character of the interaction. As expected for the weak



Figure 4. Contour plots of $\rho(\mathbf{r})$ (top) and the negative Laplacian, $-\nabla^2 \rho(\mathbf{r})$ (bottom), in the Mg'-Mg''-NNA plane of $[(\mathbf{NN'-Mg_2})_2]$; selected atoms and bond paths are superimposed. The BCPs and RCPs are represented by green and red circles, respectively. Lines are drawn at 2×10^{-n} , 4×10^{-n} , 8×10^{-n} au (n=-3, -2, -1, 0, +1, +2), and 0.028 au $(\rho(\mathbf{r})$ only), for the Laplacian with both positive (dashed) and negative values (solid). Solid and dashed lines represent charge concentration and depletion, respectively.

nature of the bonding, the value of $\rho(\text{BCP})$ is relatively small. However, the observed value is more than twice as large as those previously reported for metals (e.g., Be) or small metal clusters, such as Li₄ and Na₄, for which $\rho(\text{BCP})$ typically lies within the range 0.04–0.09 $e^{\text{Å}^{-3}}$ for a metal... NNA interaction.^[39a,b,e] A similar value has only been reported very recently in the above-mentioned experimental study on a dimeric Mg^I molecular species.^[41]

As in this aforementioned study, the pseudo-atoms in $[(NN'-Mg_2)_2]$ are fairly large and comparable in size to the other atoms in this compound (see $Vol(\Omega)$, Table 3). The large region that is claimed by the concentration of charge around the NNA is also noticeable; in Figure 4, this region extends by more than 2.2 Å perpendicular to the Mg-Mg axis. As expected for a Mg^I species, the atomic volume for the Mg atoms is significantly increased compared to that of the Mg^{II} compound $[{NN'-(MgH)_2}_2]$ and is now more than double the size. The lower oxidation state of Mg in [(NN'- Mg_2] is not reflected to the same extent in its atomic charge, which is only decreased by 0.42 electrons. However, it should be taken into account that about 0.35 electrons per Mg atom have been transferred onto an NNA, which gives an effective Mg charge of +0.95 if added to the value given above.

Finally, Figure 5 shows a 3D representation of the negative Laplacian in $[(NN'-Mg_2)_2]$, which also reveals a noteworthy feature: To the best of our knowledge, this is the



Figure 5. 3D-envelope map of the negative Laplacian of $[(NN'-Mg_2)_2]$ for $\bigtriangledown^2 \rho(r) = -0.1 \ e^{A^{-5}}$, superimposed on bond paths and selected gradient paths. The BCPs and RCPs are represented by green and red circles, respectively.

first example for a molecular species in which two NNAs are linked by a bond path. The topological parameters, as listed in Table 2, show that this interaction is clearly weaker than the Mg-NNA interactions; however, these values are

within the same range as those of NNA···NNA interactions that have been reported for some metals and larger metal clusters in theoretical studies.^[39b] It has been proposed that it is this network of linked pseudo-atoms that might be responsible for the delocalized binding and conducting properties in some of these systems.^[39b] In turn, this proposal would suggest that, for [(**NN'**-Mg₂)₂], a description of the bonding solely in terms of a dimer that is linked by two localized Mg–Mg bonds might not be fully adequate; the bonding between the four Mg atoms is also of a delocalized nature, at least to a small extent.

Conclusion

The use of directly coupled β -diketiminate ligands gave rise to the formation of a small tetranuclear magnesium hydride cluster, $[{NN-(MgH)_2}_2]$, in which the Mg atoms are situated at the corners of a tetrahedron. In the cluster, there are two sets of different hydride positions and, in its ¹H NMR spectrum, a coupling constant of J=8.5 Hz is observed, which confirms that the solid-state structure is maintained in solution. The hydride positions exchange through a configurational change in the ligand, rather than through Mg-H bond breaking: Enantiomers of the chiral $(D_2$ -symmetric) cluster exchange through a non-chiral (S_4 -symmetric) intermediate. Also, the NMR coupling constant between the two hydride ligands in [(DIPP-nacnacMgH)₂] (1, J=28.6 Hz) could be determined. Whilst the coupling constant in various molecular magnesium hydride clusters does not seem to correlate to the Mg-H bond lengths, a comparison of the hydride---hydride distances and their NMR coupling constants does show a correlation: Shorter distances relate to larger coupling constants. This correlation could be an argument in favor of a through-space coupling mechanism.

The smaller tetranuclear magnesium hydride cluster $[{NN-(MgH)_2}_2]$ eliminates H₂ at a lower temperature (175 °C) than the larger cluster $[PARA_3Mg_8H_{10}]$ (200 °C). A reinvestigation of hydrogen release in dimeric [(DIPP-nac $nacMgH_{2}$ already shows the loss of one equivalent of H₂ at 120 °C. As predicted by theory, the H₂-elimination temperatures seem to decrease with cluster size. Deuterium-labeling studies show that H₂ elimination is based on the coupling of hydride ligands and is not due to deprotonation of the ligand by the hydride ligands. These studies also show that, as a solution in toluene, hydride exchange between the clusters is either not observed, such as in $[PARA_3Mg_8H_{10}]$ and $[{NN-(MgH)_2}_2]$ (also not at higher temperatures), or is slow, as in [(DIPP-nacnacMgH)₂]. For the latter compound, this process can be accelerated by the addition of the polar solvent THF. Also, H⁻/H₂ exchange is not observed for larger clusters and is slow for [(DIPP-nacnacMgH)₂]; again, the process is accelerated by the addition of THF. The thermal decomposition of $[{NN-(MgH)_2}_2]$ under a D₂ atmosphere gave significant amounts of H-D. This result could be due to the microscopic reversibility of the hydrogen-elimination

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process, although H/D exchange through another route cannot be excluded.

From an analysis of the electron density of a DFT-optimized model system of $[{\mathbf{NN}-(MgH)_2}_2]$, we identified a hydride…hydride interaction between two of the four hydride ions at the cluster core. This interaction can be characterized as a weak closed-shell interaction that is similar in magnitude to other weak interactions that have been reported to date. This first identification of such an interaction within a molecular system highlights a potential role on the reaction coordinate that leads to the release of H₂ and also points to a wider significance of this type of interaction in molecular compounds, outside the solid state.

DFT calculations also demonstrate that the possible decomposition product following H_2 desorption, a low-valence $[(NN'-Mg)_4]$ cluster, does not have a structure in which Mg^I atoms are situated at the corners of a tetrahedron. This tetranuclear Mg^I compound is best described as a dimer that is linked through two localized Mg–Mg bonds. However, a closer analysis of the bonding situation revealed a highly interesting topology of the electron density, with two interconnected non-nuclear attractors. This topology has previously been observed in metals and metal clusters and it suggests a small degree of electron delocalization between the two Mg–Mg bonds. We are currently engaged in the isolation and crystallization of multinuclear Mg^I species for experimental studies on such unusual bonding interactions.

Experimental Section

All experiments were carried out under an argon atmosphere by using standard Schlenk techniques and freshly dried degassed solvents. The following starting materials were prepared according to literature procedures: $NN-H_2$ and $[NN-(MgnBu)_2]$.^[10b]

Synthesis of [NN-(MgnBu)(MgH)]: A solution of [NN-(MgnBu)₂] (240 mg, 0.355 mmol) and PhSiH₃ (38 mg, 0.351 mmol) in toluene (8 mL) was heated at 60 °C for 1 h. The resulting solution was concentrated to a volume of 1 mL and slowly cooled to -27 °C, which led to the crystallization of [{NN-(MgBu)(MgH)}2] as large yellow blocks. Yield: 90 mg (0.068 mmol, 41 %); ¹H NMR (300 MHz, [D₆]benzene, 20 °C): $\delta = -0.44$ $(t, {}^{3}J(H,H) = 9.4 \text{ Hz}, 4\text{ H}; n\text{Bu}), 0.14-0.30 \text{ (m, 4H; } n\text{Bu}), 0.48 \text{ (t, }^{3}J-$ (H,H)=7.1 Hz, 6H; nBu), 0.71 (m, 2H; nBu), 1.05 (m, 2H; nBu), 1.18 $(d, {}^{3}J(H,H) = 6.8 \text{ Hz}, 12 \text{ H}; iPr), 1.22 (d, {}^{3}J(H,H) = 6.8 \text{ Hz}, 12 \text{ H}; iPr), 1.31$ $(d, {}^{3}J(H,H) = 6.7 \text{ Hz}, 12 \text{ H}; iPr), 1.49 (d, {}^{3}J(H,H) = 6.8 \text{ Hz}, 12 \text{ H}; iPr), 1.74$ (s, 12H; Me backbone), 1.91 (s, 12H; Me backbone), 3.21-3.31 (m, 8H; iPr), 3.59 (s, 2H; MgH), 4.66 (s, 4H; H backbone), 7.05-7.16 ppm (m, 12H; aryl H); ¹³C NMR (75 MHz, [D₈]THF, 20°C): 6.3 (nBu), 14.0 (nBu), 21.0 (Me backbone), 24.7 (Me backbone), 24.7 (iPr), 24.8 (iPr), 25.3 (iPr), 25.6 (iPr), 28.4 (iPr), 29.5 (nBu), 29.8 (iPr), 30.3 (nBu), 92.5 (backbone), 124.5 (aryl C), 124.9 (aryl C), 125.6 (aryl C), 142,9 (aryl C), 143.2 (aryl C), 146.9 (aryl C), 166.3 (backbone), 167.5 ppm (backbone); elemental analysis (%) calcd for $C_{76}H_{116}Mg_4N_8 \cdot C_6H_6$ ($M_w = 1239.05$): C 73.67, H 9.44; found: C 73.13, H 9.18.

Synthesis of $[NN-(MgH)_2]$: A solution of $[NN-(MgnBu)_2]$ (400 mg, 0.592 mmol) and PhSiH₃ (170 mg, 1.571 mmol) in toluene (10 mL) was heated at 80 °C for 48 h. After the removal of all of the volatile compounds under vacuum, the residue was dissolved in *n*-hexane (5 mL). Slowly cooling this solution to -27 °C gave yellow crystals in the form of tetrahedrons that were strongly yellow luminescent under UV light. Yield: 150 mg (0.133 mmol, 48%); ¹H NMR (300 MHz, [D₆]benzene, 20 °C): $\delta = 0.80$ (d, ³*J*(H,H) = 6.8 Hz, 12H; *i*Pr), 1.16 (d, ³*J*(H,H) = 7.0 Hz,

12 H; *i*Pr), 1.31 (d, ³*J*(H,H) = 7.0 Hz, 12 H; *i*Pr), 1.33 (d, ³*J*(H,H) = 6.8 Hz, 12 H; *i*Pr), 1.61 (s, 12 H; Me backbone), 1.78 (s, 12 H; Me backbone), 2.85 (br s, 2 H; MgH), 3.06 (sept, ³*J*(H,H) = 7.0 Hz, 4 H; *i*Pr), 3.31 (sept, ³*J*-(H,H) = 6.8 Hz, 4 H; *i*Pr), 3.50 (br s, 2 H; MgH), 4.53 (s, 4 H; H backbone), 7.02–7.14 ppm (m, 12 H; aryl H); ¹³C NMR (75 MHz, [D₆]benzene, 20 °C): 20.8 (Me backbone), 23.7 (*i*Pr), 23.8 (*i*Pr), 24.5 (*i*Pr), 24.6 (*i*Pr), 26.3 (Me backbone), 28.6 (*i*Pr), 28.8 (*i*Pr), 91.7 (backbone), 124.1 (aryl C), 125.7 (aryl C), 143.0 (aryl C), 143.0 (aryl C), 144.7 (aryl C), 167.2 (backbone), 168.1 ppm (backbone); elemental analysis (%) calcd for C₆₈H₁₀₀Mg₄N₈ (M_w =1126.83): C 72.48, H 8.95; found: C 73.36, H 8.13; deviations are likely owing to the partial incorporation of *n*-hexane (which appears in the crystal-structure analysis as a severely disordered molecule): elemental analysis (%) calcd for C₆₈H₁₀₀Mg₄N₈·C₆H₁₄ (M_w =1213.01): C 73.27, H 9.47.

Crystal-structure determination: For details on the crystal structures of $[{NN-(MgnBu)_2}_2], [{NN-(MgnBu)(MgH)}_2], and [{NN-(MgH)_2}_2], see the Supporting Information. CCDC-893202 [{NN-(MgH)_2}_2], CCDC-893203 [{NN-(MgnBu)(MgH)}_2, and CCDC-893204 [{NN-(MgnBu)_2}_2] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.$

Computational details: DFT calculations were performed with the Gaussian 09 program suite^[42] by using the B3LYP density functional^[43] and the 6-311G(d,p) basis set.^[44] An additional polarization and a diffuse function were employed for all magnesium and nitrogen atoms, as well as for the hydridic hydrogen atoms at the cluster core. All of the geometry optimizations were performed without imposing any symmetry constraints and the structures were confirmed as true minima by calculating the analytical frequencies. Structure optimizations were also performed by using other functionals and basis sets of different size, which gave very similar geometries and electron densities (for further details, see the Supporting Information). In particular, the H.H interaction was invariant to the choice of basis set and level of theory and it was also confirmed by an MP2 calculation at the previously determined B3LYP geometry. The topology of the electron density was analyzed by using the software package AIMALL.[45] The reported atomic energies for the hydridic hydrogen atoms in [{NN'-(MgH)₂}₂] were estimated by multiplying their atomic kinetic energies by the factor $-(\gamma - 1)$, with $\gamma = -V/T$, as described, for example, in Ref. [29a]. The value of the molecular virial ratio (γ) deviated from 2 by 3.8×10^{-3} in the optimized system. Plots were generated by using AIMALL^[45] and CHEMCRAFT.^[46]

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