

Hydrogen Storage in Magnesium Hydride: The Molecular Approach**

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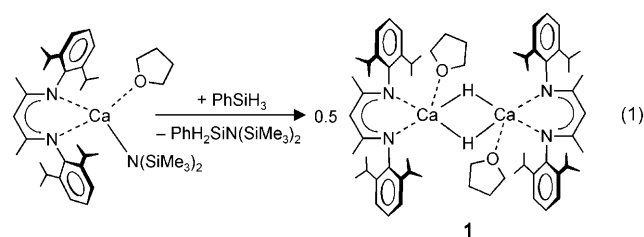
Safe and convenient storage of hydrogen is one of the near-future challenges. For mobile applications there are strict volume and weight limitations, and these limitations have steered investigations in the direction of compact, solid, light-weight main-group hydrides.^[1] Whereas ammonia-borane (NH_3BH_3) is a nontoxic, nonflammable, H_2 -releasing solid with a record hydrogen density of 19.8 wt %, it releases hydrogen in an irreversible process.^[2] Metal hydrides such as MgH_2 are less rich in hydrogen (7.7 wt %) but advantageously display reversible hydrogen release and uptake: $\text{MgH}_2 \rightleftharpoons \text{Mg} + \text{H}_2$.^[3]

Although bulk MgH_2 seems an ideal candidate for reversible hydrogen storage, it is plagued by high thermodynamic stability, which translates into relatively high hydrogen desorption temperatures and slow release and uptake kinetics. The kinetics can be improved drastically by doping the magnesium hydride with transition metals^[4–6] and by ball milling^[7,8] or surface modifications.^[9] The high hydrogen release temperature (over 300 °C), however, is due to unfavorable thermodynamic parameters ($\Delta H = 74.4(3) \text{ kJ mol}^{-1}$; $\Delta S = 135.1(2) \text{ J mol}^{-1} \text{ K}^{-1}$),^[10] which originate from the enormous lattice energy for $[\text{Mg}^{2+}\text{H}^{-}_2]_{\infty}$ ($\Delta H = 2718 \text{ kJ mol}^{-1}$) relative to that of bulk Mg ($\Delta H = 147 \text{ kJ mol}^{-1}$).^[11] Although thermodynamic values are intrinsic to the system, recent theoretical calculations demonstrate that for very small $(\text{MgH}_2)_n$ clusters ($n < 19$), the enthalpy of decomposition sharply reduces with cluster size.^[12] Downsizing the particles has a dramatic effect on the stability of salt-like $(\text{MgH}_2)_n$ but much less on that of the metal clusters Mg_n . For a $\text{Mg}_{18}\text{H}_{18}$ cluster of approximately 0.9 nm diameter a desorption enthalpy of 63 kJ mol^{-1} was calculated,^[12] from which a decomposition temperature of about 200 °C can be estimated. At the extreme limit, molecular MgH_2 is calculated to be unstable even towards decomposition into its elements ($\Delta H = -5.5 \text{ kJ mol}^{-1}$). The sharp decrease of stability for $(\text{MgH}_2)_n$ clusters with $n < 19$ can be understood by the rapid increase in surface/volume ratios: surface atoms have a lower coordination number and are loosely bound. It is of interest to note that only clusters with $n \geq 19$ ($\geq 1.3 \text{ nm}$) have a core with

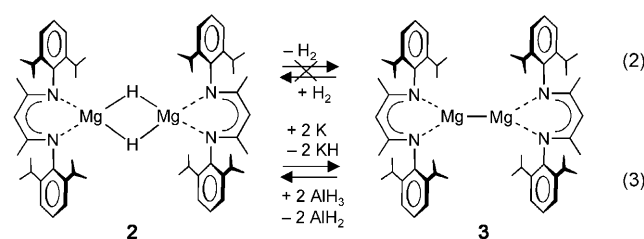
the typical $\alpha\text{-MgH}_2$ rutile geometry (six-coordinate Mg and three-coordinate H). Apparently this is the critical size from which clusters start to show bulk behavior.

These insights led to increased research activity on the syntheses of MgH_2 nanoparticles, either by special ball-milling techniques or by incorporation into confined spaces.^[13–17] Thus nanoparticles in the range of 1–10 nm have been reported. Hydrogen elimination studies indeed show a small reduction of ΔH and H_2 desorption temperatures,^[18] but dramatic effects can only be expected for particles smaller than 1 nm.

Production of magnesium hydride particles in the sub-nanometer range would benefit from a molecular “bottom-up” approach. We recently reported a simple synthesis protocol for the first soluble calcium hydride complex **1** by the silane route [Eq. (1)],^[19] and Jones et al. reported the



magnesium analogue **2**, which was obtained by a similar reaction.^[20] Thermally induced hydrogen elimination from **2** could result in formation of the recently introduced Mg^{I} complex **3** [Eq. (2)].^[21] However, the dimeric magnesium



hydride complex **2** is reported to be extraordinarily stable (decomposition temperature: 302–304 °C)^[20] and did not eliminate hydrogen.^[22] Nor can the Mg^{I} complex **3** be hydrogenated to **2** by applying H_2 pressure at various temperatures. However, **2** can be chemically reduced by potassium metal to the Mg^{I} dimer **3**, which can be converted back to **2** by reaction with AlH_3 [Eq. (3)].^[22] Thus the dimeric magnesium hydride cluster behaves differently from bulk MgH_2 . The formation of H_2 from a molecular cluster might

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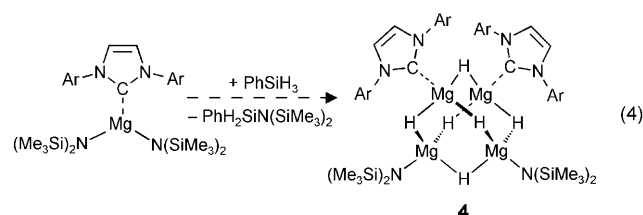
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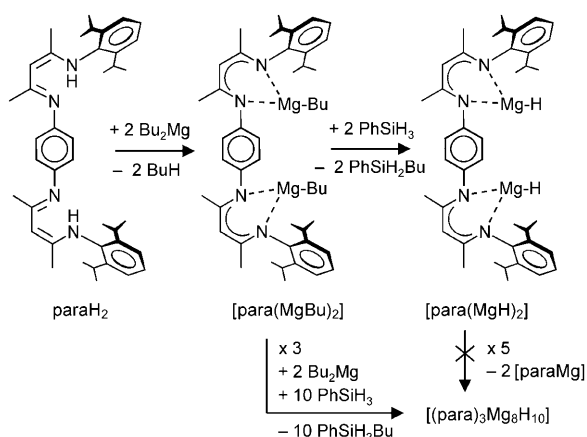
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either need the combined action of more than two magnesium ions or a higher H/Mg ratio.

There is growing evidence for the existence of larger alkaline-earth-metal hydride clusters. Michalczyk reported the synthesis of $[(\text{LB})\text{MgH}_2]_n$ species (LB is a neutral Lewis base).^[23] Harder et al. proposed hydride-rich calcium hydride clusters $[(\text{L}_{>1}\text{CaH}_{<1})_n]$ to be active as hydrosilylation catalysts (L is an anionic ligand).^[24] Conclusive evidence for a hydride-rich magnesium cluster was found by Hill et al., who prepared a tetranuclear magnesium amide hydride cluster (**4**) by the silane route [Eq. (4)].^[25] Herein we present the reproducible synthesis and structure of an octanuclear hydride-rich magnesium cluster that releases H_2 upon heating.



The sterically demanding β -diketiminate ligand in the complexes **1–3** has been found most useful in the stabilization of alkaline-earth-metal hydride, hydroxide, fluoride, or cyanide complexes.^[19–20,26] We reasoned that the bridged bis(β -diketiminate) ligands, recently introduced by us,^[27] might stabilize larger magnesium hydride clusters. The ligand with the *para*-phenylene bridge (*para*H₂ in Scheme 1) was doubly



Scheme 1. Synthesis of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$.

deprotonated by reaction with two equivalents of $n\text{Bu}_2\text{Mg}$ and subsequently treated with PhSiH_3 . After cooling, few well-defined colorless crystals could be isolated. X-ray structure determination revealed a hydride-rich product of composition $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ (Figure 1), which can be seen as a cluster consisting of three equivalents of the expected product, $[\text{para}(\text{MgH})_2]$, and two equivalents of MgH_2 . Crystals of the $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ cluster can be obtained in reasonable yields of 46% from a one-pot synthesis using $\text{paraH}_2/n\text{Bu}_2\text{Mg}/\text{PhSiH}_3$ in the correct 3:8:10 stoichiometry.

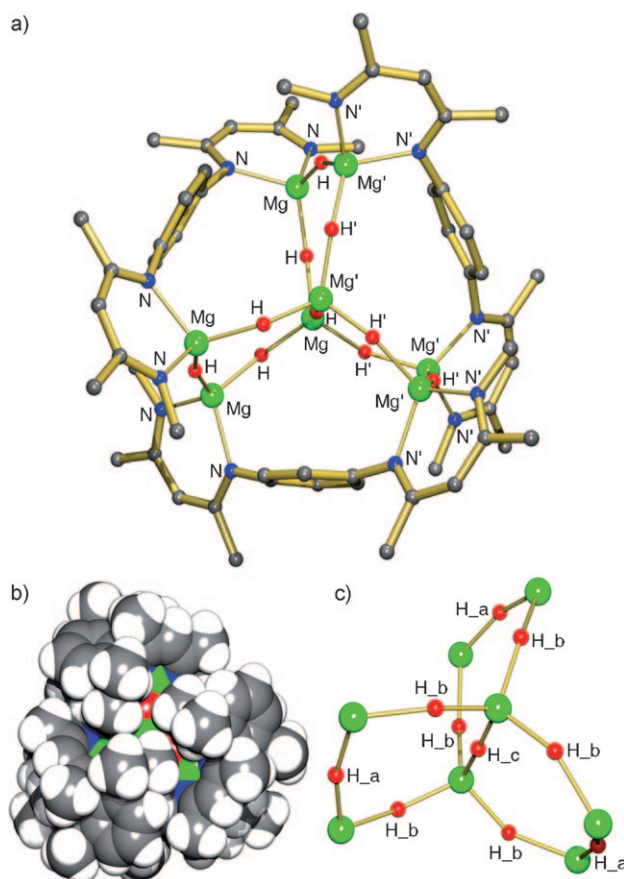


Figure 1. a) Crystal structure of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$; some hydrogen atoms and the aryl substituents have been omitted for clarity. The crystallographic C_2 axis runs vertically through the central and the top hydride ligands. b) Space-filling representation. c) The $\text{Mg}_8\text{H}_{10}^{6+}$ core; H_a , H_b , and H_c represent the three chemically different hydride ligands. Symmetry-related atoms are indicated by apostrophes.

Procedures with a slight excess of *para*H₂, that is, with guaranteed consumption of $n\text{Bu}_2\text{Mg}$, failed to give the product. It is therefore unlikely that the excess of MgH_2 incorporated into the cluster is formed by the Schlenk equilibrium $[\text{para}(\text{MgH})_2] \rightleftharpoons [\text{paraMg}] + \text{MgH}_2$.^[28]

The structure of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ can be described as a $[\text{Mg}_8\text{H}_{10}]^{6+}$ core that is stabilized by three tetradentate *para*^{2−} ligands. The bulky nature of these ligands results in efficient protection of the core, as can be seen in the space-filling representation (Figure 1b). Although the cluster is crystallographically C_2 -symmetric, the propeller-like orientation of the ligands induces near C_3 symmetry and results in overall chirality. The asymmetric unit contains two very similar clusters of opposite helical chirality. The cluster could also be described as an inverse crown ether:^[29] the ring is formed by three connected $[\text{paraMg}_2\text{H}]^+$ units that trap $\text{Mg}_2\text{H}_7^{3-}$ in their center. The Mg–N bond lengths are in the range of 2.026(2)–2.058(2) Å (average over both clusters 2.041 Å). Distances between neighboring Mg nuclei vary from 3.426(1) to 3.619(1) Å. The average Mg⋯Mg' separation of 3.517(1) Å is much longer than that in either the magnesium hydride dimer **2** (2.890(2) Å) or the magnesium(I) dimer **3** (2.8457(8) Å), thus excluding possible incorporation of mag-

nesium(I). Moreover, all hydride atoms could be located in the difference Fourier map and were refined isotropically.

Although metal–hydride bond distances from X-ray data inherently have large uncertainties, some comments should be made. The Mg–H bonds range from 1.72(3) to 1.90(3) Å (average 1.81(3) Å). The smallest and largest Mg–H bond lengths are significantly different, and the 0.18(3) Å difference between these values corresponds well with the 0.193(1) Å difference between the smallest and largest Mg...Mg' distances. The average Mg–H bond length of 1.81(3) Å is shorter than that in **2** (1.96(3) Å) but similar to that in **4** (1.87(2) Å). The broad range of Mg–H contacts can be explained by the three different types of hydride positions. The $\text{Mg}_8\text{H}_{10}^{6+}$ core forms a paddlewheel (Figure 1c) with hydride ligands on the outside (H_a), the spokes (H_b), and the wheel axle (H_c). Ligands H_a and H_b show average Mg–H separations of 1.83(3) and 1.81(3) Å, respectively. The bonds to the central hydride H_c (1.72(3) and 1.74(3) Å) are the shortest reported to date and are close to the theoretically calculated Mg–H distance of 1.718 Å in linear MgH_2 .^[30] They are comparable to the Mg–H distance of 1.75(7) Å in a monomeric magnesium hydride complex with a non-bridging hydride ligand.^[20b] The Mg–H distances in bulk $\alpha\text{-MgH}_2$ with rutile structure is 1.95(2) Å.^[31] Shorter Mg–H distances in $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ can be explained by lower coordination numbers (two for H and four for Mg, cf. three for H and six for Mg in the rutile structure).

$[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ is, despite its large cluster size (MW = 1971), moderately soluble in non-coordinating aromatic solvents. ^1H NMR spectroscopy data in toluene show that the cluster remains intact in solution. The three different kinds of hydride ligands (H_a, H_b, and H_c) show three signals in a 3:6:1 ratio at δ = 2.60, 1.72, and 0.55 ppm, respectively. Although these chemical shifts are upfield from that found for dimeric **2** (δ = 4.03 ppm), the highest value of δ = 2.62 ppm compares well with that found for **4** (δ = 2.52 ppm). The lowest value of δ = 0.56 ppm for the central hydride ligand, that is, the one least disturbed by ligand influences, is close to the reported value for $\beta\text{-MgH}_2$ (δ = 0.9 ppm)^[32] but is considerably upfield from the δ = 3.0–4.6 ppm values for the $\alpha\text{-MgH}_2$ phase.^[5,32]

More convincing evidence for the existence of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ in solution comes from the observation of the expected hydride–hydride coupling patterns, for which the connectivity was established by 2D ^1H , ^1H -COSY experiments (Figure 2). The coupling constants of 4.5 and 5.2 Hz represent, to our knowledge, the first experimental observations of $^2J(\text{H},\text{H})$ in a magnesium hydride. These experimental values strongly disagree with theoretical predictions (55–80 Hz) for the geminal H₂H coupling in linear MgH_2 ,^[33] but they are only slightly lower than the coupling of 7.45 Hz between bridging and terminal hydrides in the somewhat more covalent B_2H_6 .^[34] It is currently unclear whether the hydride–hydride coupling detected by NMR spectroscopy is due to a through-bond or a through-space mechanism. In the crystal structure, the distances between neighboring hydride ligands range from 2.57(4) to 3.06(4) Å (average 2.86(4) Å).

Surprisingly, raising the temperature of the toluene solution to 100 °C does not lead to coalescence of hydride

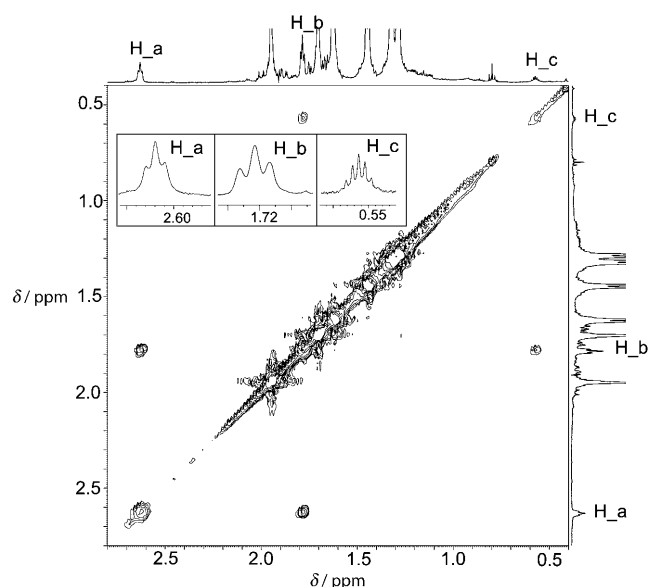
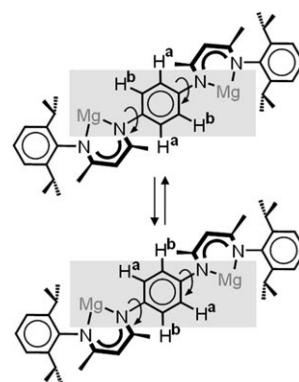


Figure 2. a) Part of the ^1H , ^1H -COSY spectrum of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ (500 MHz, $[\text{D}_8]\text{toluene}$, 25 °C). The insets show the signals for the three types of hydride ligands H_a, H_b, and H_c; $^2J(\text{H}_a, \text{H}_b) = 5.2$ Hz and $^2J(\text{H}_b, \text{H}_c) = 4.5$ Hz.

signals, and even the coupling patterns can still be recognized. This extreme stationary behavior is unusual for main-group hydride complexes, in which bridging hydride ligands are very susceptible to fast exchange even at low temperature (e.g., at –55 °C, complex **4** shows only one broad signal in its ^1H NMR spectrum and thus fast exchange of the different hydride ligands).^[35] The static behavior of the $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ cluster is likely caused by the spiral-like coordination of the three tetradentate para^{2-} ligands that connect to Mg atoms in the top and bottom parts of the Mg_8H_{10} wheel. At 100 °C, the rotation of the aryl rings around the N–C bonds is also blocked (the *i*Pr groups show four doublets and two septets). The only coalescence that can be observed is that of the two inequivalent aromatic bridge H signals. This process ($\Delta G^\ddagger = 64$ kJ mol^{–1}) is due to rotation of the *para*-phenylene bridge (Scheme 2) and not to chirality change of the propeller, which



Scheme 2. Rotation of the *para*-phenylene bridge, which leads to coalescence of the H^a and H^b signals in the ^1H NMR spectrum at elevated temperature.

would involve Mg–N bond breaking and making or internal reorganization of the Mg_8H_{10} core. The high stability of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ is underscored by the fact that the cluster also remains intact in $[\text{D}_8]\text{THF}$ (the ^1H NMR spectra show similar features and only small changes in the chemical shifts for the hydride ligands).

Solutions of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ in toluene are also astoundingly thermally stable. No signs of decomposition were found after heating a toluene solution in a J-Young tube for two days at 180°C. As a solid under high vacuum, however, the compound visibly lost a gas at 200°C. After leading the gas into $[\text{D}_8]\text{THF}$, a clear resonance in the ^1H NMR spectrum could be observed at $\delta = 4.55$ ppm, which is the chemical shift for H_2 . Gas quantification by a Töpler pump setup gave the expected 4.9(2) mol equivalents of a gas that does not condense in liquid N_2 and is fully converted to condensable water by leading it over hot CuO .

This is the first observation of complete H^- to H_2 conversion in a magnesium hydride complex. The decomposition temperature of 200°C corresponds well with de Jong's predictions for a Mg_8H_{18} cluster (see above)^[12] and is the lowest H_2 desorption temperature reported to date for magnesium hydride. The stabilizing effect of the tetradentate para^{2-} ligand and the color change from light yellow to red suggest conversion into the mixed-valence cluster $[(\text{para})_3\text{Mg}_8]$ (Mg^{I} compounds such as **2** are orange-red).^[20] The red residue is for the most part soluble in aromatic solvents, and no metal particles were detected visually. Analysis by ^1H NMR spectroscopy shows only traces of $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ and mainly one new set of signals for the para^{2-} ligand. This finding offers a positive perspective for the possible characterization of well-defined decomposition products, in which we have not succeeded to date.

In summary, we have shown that bridged bis(β -diketiminate) ligands are well suited for the stabilization of larger multinuclear magnesium hydride complexes. The $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ cluster is extraordinarily rigid and shows, even at 100°C, no exchange of bridging hydride ligands on the time scale of NMR spectroscopy. This stability allowed for measurement of the first $^2J(\text{H},\text{H})$ values in a magnesium hydride material. The $[(\text{para})_3\text{Mg}_8\text{H}_{10}]$ cluster is currently the largest known magnesium hydride cluster. In contrast to the dimeric magnesium hydride complex **2**, it releases its H_2 completely at 200°C. The large ligands used in the stabilization of these clusters make these systems less relevant for practical hydrogen storage. As soluble model systems, however, they could contribute to detailed studies of the processes involved on a molecular level. We will soon report on our current activities, which include the synthesis of a range of magnesium hydride clusters (partially with newly designed ligand sets), more accurate measurements on the H_2 desorption process (including its possible reversibility), and further attempts to isolate large low-valent Mg clusters.

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- [1] L. Schlappbach, A. Züttel, *Nature* **2001**, 414, 353–358.
- [2] For recent reviews, see: a) T. B. Marder, *Angew. Chem.* **2007**, 119, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, 46, 8116–8118; b) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; c) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, 12, 8634–8648; d) A. Karkambar, C. Aardahl, T. Autrey, *Mater. Matters* **2007**, 2, 6–10; e) N. C. Smythe, J. C. Gordon, *Eur. J. Inorg. Chem.* **2010**, 509–521.
- [3] a) M. Dornheim, S. Doppiu, G. Barkhordarian, U. Boesenberg, T. Klassen, O. Gutfleisch, R. Bormann, *Scr. Mater.* **2007**, 56, 841–846; b) K.-F. Aguey-Zinsou, J.-R. Ares-Fernández, *Energy Environ. Sci.* **2010**, 3, 526–543; c) I. P. Jain, C. Lal, A. Jain, *Int. J. Hydrogen Energy* **2010**, 35, 5133–5144; d) C. Wu, H.-M. Cheng, *J. Mater. Chem.* **2010**, 20, 5390–5400.
- [4] B. Bogdanović, B. Spliethoff, *Int. J. Hydrogen Energy* **1987**, 12, 863–873.
- [5] P. C. M. M. Magusin, W. P. Kalisvaart, P. H. L. Notten, R. A. van Santen, *Chem. Phys. Lett.* **2008**, 456, 55–58.
- [6] P. Larsson, C. M. Araújo, J. A. Larsson, P. Jena, R. Ahuja, *Proc. Natl. Acad. Sci. USA* **2008**, 105, 8227–8231.
- [7] J. Huot, G. Liang, R. Schulz, *J. Alloys Compd.* **2003**, 353, L12L15.
- [8] W. Oelerich, T. Klassen, R. Bormann, *J. Alloys Compd.* **2001**, 315, 237–242.
- [9] X. L. Wang, S. Suda, *J. Alloys Compd.* **1995**, 231, 380–386.
- [10] J. F. Stampfer, Jr., C. E. Holley, Jr., J. F. Suttle, *J. Am. Chem. Soc.* **1960**, 82, 3504–3508.
- [11] C. M. Stander, R. A. Pacey, *J. Phys. Chem. Solids* **1978**, 39, 829–832.
- [12] R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2005**, 127, 16675–16680.
- [13] P. E. de Jongh, R. W. P. Wagemans, T. T. M. Eggenhuisen, B. S. Dauvillier, P. B. Radstake, J. D. Meeldijk, J. W. Geus, K. P. de Jong, *Chem. Mater.* **2007**, 19, 6052–6057.
- [14] L. Haas, A. Gedanken, *Chem. Commun.* **2008**, 1795–1797.
- [15] S. Zhang, A. F. Gross, S. L. Van Atta, L. Maribel, P. Liu, C. C. Ahn, J. J. Vajo, C. M. Jensen, *Nanotechnology* **2009**, 20, 204027.
- [16] M. Paskevicius, D. A. Sheppard, C. E. Buckley, *J. Am. Chem. Soc.* **2010**, 132, 5077–5083.
- [17] Z. Zhao-Karger, J. Hu, A. Roth, D. Wang, C. Kübel, W. Lohstroh, M. Fichtner, *Chem. Commun.* **2010**, 46, 8353–8355.
- [18] Lowering of the decomposition temperature is somewhat less than expected: the concomitant decrease in ΔS partially counteracts the lower ΔH value, see Refs. [16, 17].
- [19] S. Harder, J. Brettar, *Angew. Chem.* **2006**, 118, 3554–3558; *Angew. Chem. Int. Ed.* **2006**, 45, 3474–3478.
- [20] a) S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, 120, 9219–9223; *Angew. Chem. Int. Ed.* **2008**, 47, 9079–9083; b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, 16, 938–955.
- [21] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, 318, 1754–1757.
- [22] S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* **2010**, 2, 865–869.
- [23] M. J. Michalczyk, *Organometallics* **1992**, 11, 2307.
- [24] a) F. Buch, J. Brettar, S. Harder, *Angew. Chem.* **2006**, 118, 2807–2811; *Angew. Chem. Int. Ed.* **2006**, 45, 2741–2745; b) S. Harder, *Chem. Rev.* **2010**, 110, 3852–3876.
- [25] M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2009**, 121, 4073–4076; *Angew. Chem. Int. Ed.* **2009**, 48, 4013–4016.
- [26] a) C. Ruspici, S. Nembenna, A. Hofmeister, J. Magull, S. Harder, H. W. Roesky, *J. Am. Chem. Soc.* **2006**, 128, 15000–15004; b) S. Nembenna, H. W. Roesky, S. Nagendran, A. Hofmeister, J. Magull, P.-J. Wilbrandt, M. Hahn, *Angew. Chem.* **2007**, 119, 2564–2566; *Angew. Chem. Int. Ed.* **2007**, 46, 2512–2514; c) C. Ruspici, S. Harder, *Inorg. Chem.* **2007**, 46, 10427–10433.

- [27] D. F.-J. Piesik, S. Range, S. Harder, *Organometallics* **2008**, 27, 6178–6187; b) D. F.-J. Piesik, R. Stadler, S. Range, S. Harder, *Eur. J. Inorg. Chem.* **2009**, 3569–3576.
 - [28] [paraMg] could not be detected in the NMR spectrum of the reaction mixture.
 - [29] a) R. E. Mulvey, *Chem. Commun.* **2001**, 1049–1056; b) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* **2002**, 376–377.
 - [30] J. A. Pople, B. T. Luke, M. J. Frisch, J. S. Binkley, *J. Chem. Phys.* **1985**, 83, 2198–2203.
 - [31] W. H. Zachariasen, C. E. Holley, Jr., J. F. Stamper, Jr., *Acta Crystallogr.* **1963**, 16, 352–353.
 - [32] S. Hayashi, *J. Alloys Compd.* **1997**, 248, 66–69.
 - [33] I. Alkorta, P. F. Provasi, G. A. Aucar, J. Elguero, *Magn. Reson. Chem.* **2008**, 46, 356–361.
 - [34] T. C. Farrar, G. R. Quating, *Inorg. Chem.* **1985**, 24, 1941–1945.
 - [35] S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, 101, 3305–3365.
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