DOI: 10.1002/anie.201102978

A Record-Breaking Magnesium Hydride Molecular Cluster: Implications for Hydrogen Storage

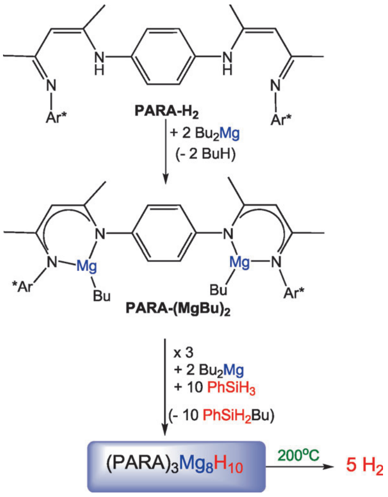
*Eva Hevia and Robert E. Mulvey**

cluster · hydrides · hydrogen storage · magnesium

One of the world's grand challenges in science with regard to energy efficiency is to develop hydrogen storage technologies.[1] Hydrogen storage in this context means the chemical form in which it is carried, for example in a compound, alloy, or nanomaterial. The stimulus is a common consensus amongst scientists that hydrogen, the first element of the periodic table, is the number one contender for the synthetic fuel of the future in mobile applications. Its qualifications are impressive: hydrogen is lightweight, is the most abundant element in the universe and its burning with oxygen produces environmentally friendly water. But the multi-billion dollar challenge to technologists is "how can hydrogen be safely stored in practical volumes and weights within the confines of a mobile vehicle (e.g., a typical car) and in sufficient quantities to run the vehicle for a journey of a decent length before requiring refuelling?" Finding real solutions to this question which would have momentous socioeconomic benefits will, of necessity, require innovative interdisciplinary approaches.

Inorganic chemistry can make major contributions to this field by delivering novel materials with high hydrogen-storage capacity. In attempting to construct such materials, inorganic chemists face the formidable task of finding the correct balance of properties. Among the most important properties, hydrogen storage materials should be safe to transport, be lightweight, be rich in hydrogen, be capable of reversibly releasing/uptaking H_2, and have favorable thermodynamic/kinetic parameters. Some of these properties are intrinsic to low-period main group hydrides. The covalent hydride ammonia–borane ($H_3N{\cdot}BH_3$) boasts an exceedingly high hydrogen density of 19.8 wt.% but unfortunately this innocuous, non-flammable solid releases hydrogen in a non-reversible process.[2] A significantly lower but still acceptable hydrogen density of 7.7 wt.% is found for magnesium hydride (MgH_2) and promisingly it does exhibit reversible release and uptake of hydrogen.[3] However, in its common form, $(MgH_2)_n$ is an ionic solid existing as an infinite ($n=\infty$) lattice comprising Mg^{2+} cations and H^- anions the lattice energy of which is about 20 orders of magnitude larger than that of the bulk metal Mg. As a consequence, common $(MgH_2)_\infty$ is reluctant to release H_2 without the application of high temperature and so the essential H_2 release/H_2 uptake process would be too slow to be of use practically in hydrogen-storage technology. Lowering thermodynamic thresholds and concomitantly speeding up kinetic events may be achievable using alternative molecular forms of $(MgH_2)_n$ (where $n<\infty$) which is why synthetic chemists are exploring new ways of generating them.

Recent elegant work[4] by Harder and co-workers has not only realized the largest magnesium hydride cluster known to date but has shown us a pathway by which other molecular clusters, potentially hydrogen-storage materials, could be formed. Instead of attempting to deaggregate the infinite ionic lattice of preformed $(MgH_2)_\infty$, they have cleverly devised a reaction (Scheme 1) that creates magnesium–hydride bonds starting from an organometallic complex with a pre-organized Mg coordination. There are two key factors behind their approach. Firstly, pre-organisation of the Mg center was accomplished by judicious choice of a supporting anionic donor ligand. Reasoning that a flexible, sterically demanding multidentate hard ligand would be required to kinetically stabilize a good-sized molecular variant of magnesium hydride and prevent it aggregating to its common ionic lattice form, Harder and co-workers turned to the *para*-phenylene bridged bis(β-diketiminate) ligand PARA-H_2 (Scheme 1), which they had introduced successfully in earlier



Scheme 1.

---

[*] Dr. E. Hevia, Prof. R. E. Mulvey
WestCHEM, Department of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street, Glasgow, G1 1XL (UK)
E-mail: r.e.mulvey@strath.ac.uk

work for the preparation of binuclear calcium and zinc complexes used in a study of epoxide/CO_2 copolymerization reactions.[5] Secondly, following deprotonative magnesiation of PARA-H_2 by dibutylmagnesium to form PARA-$(MgBu)_2$, they transformed the Mg–Bu bonds into Mg–H bonds by addition of phenylsilane, $PhSiH_3$. The hydride-carrying aptitude of $PhSiH_3$ had been demonstrated previously by Harder and co-workers,[6] and Jones and co-workers[7] in the respective formation of binuclear calcium and magnesium hydride complexes supported by mono β-diketiminate ligands; while Hill and co-workers[8] exploited it subsequently to build a larger tetranuclear magnesium amide–hydride cluster $[Mg_4H_6(HMDS)_2(NHC)_2]$ (where HMDS is 1,1,1,3,3,3-hexamethyldisilazide and NHC is a N-heterocyclic carbene ligand). Establishing a new record size for a ligand-supported magnesium hydride cluster Harder's compound, $[(PARA)_3Mg_8H_{10}]$ (**1**) displays double this aggregation as it is octanuclear. **1** could be regarded as a co-complex between $(PARA)Mg_2H_2$ and MgH_2 (alternatively formulated as $[(PARA)_3Mg_6H_6{\cdot}2\,MgH_2]$). This extra MgH_2 appears to be an artefact of using excess $MgBu_2$ in the reaction which converts to MgH_2 on contacting the silane. Elucidated by X-ray crystallographic studies, the molecular constitution of **1** shows a $(Mg_8H_{10})^{6+}$ core resembling a paddle-wheel with two-coordinate hydride ligands distributed on the outside, the spokes and the wheel axis, and with four-coordinate Mg atoms also connected to the peripheral-shielding PARA dianions (Figure 1). Harder and co-workers also draw an interesting analogy with inverse crown ether structures – well known in alkali metal magnesiate chemistry[9] – interpreting **1** in this host–guest context as a polycationic host ring made up of three connected $(PARA\text{-}Mg_2H)^+$ units which traps an anionic $(Mg_2H_7)^{3-}$ guest. Significantly the solid-state structure of **1** appears to be retained in [D_8]toluene solution even at elevated temperatures on the evidence of NMR spectroscopic data, specifically the observation of hydride-based ^2J(H,H) couplings in the first recorded example of such for a magnesium hydride composition.

So how do the properties of **1** match up to the requirements of a hydrogen storage material? Promisingly the study proved that all of the hydride content in **1** can be converted to hydrogen gas. Furthermore, this complete hydrogen desorption takes place at the low temperature of 200 °C, a record for a molecular magnesium hydride complex. While **1** could not be used itself for hydrogen storage due to the large organonitrogen ligands needed for its stabilization, it represents an excellent soluble model system with which to study and refine the processes involved in hydrogen storage on a molecular level. This work will undoubtedly stimulate much more activity in this important area and it is likely that even larger magnesium hydride oligomers will be synthesized in the near future.

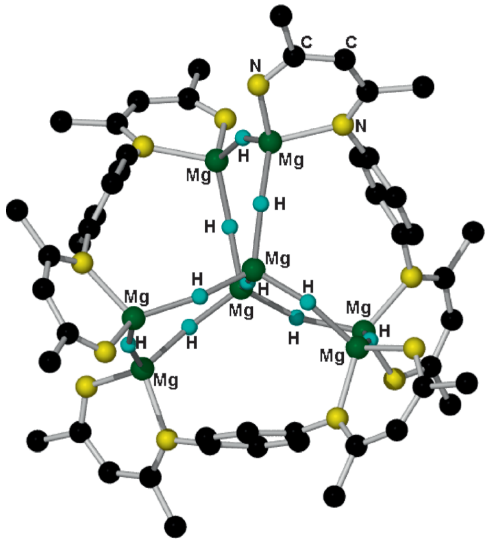


Figure 1. Molecular structure of $(PARA)_3Mg_8H_{10}$ with H atoms (except hydrides) and aryl substituents of the PARA ligands omitted for clarity.

Mixed-metal systems may also come more into focus with the recent reporting[10] by Wang and co-workers that the sodium-magnesium ammonia borane derivative "NaMg$(NH_2BH_3)_3$" can rapidly release about 10 wt. % of hydrogen at 80 °C within two minutes. Exciting times lie ahead in hydrogen storage research.

Received: April 29, 2011

---

[1] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353.
[2] T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116.
[3] C. Wu, H. M. Cheng, *J. Mater. Chem.* **2010**, *20*, 5390.
[4] S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem.* **2011**, *123*, 4242; *Angew. Chem. Int. Ed.* **2011**, *50*, 4156.
[5] D. F. J. Piesik, S. Range, S. Harder, *Organometallics* **2008**, *27*, 6178.
[6] S. Harder, J. Brettar, *Angew. Chem.* **2006**, *118*, 3554; *Angew. Chem. Int. Ed.* **2006**, *45*, 3474.
[7] S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, *120*, 9219; *Angew. Chem. Int. Ed.* **2008**, *47*, 9079.
[8] M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* **2009**, *121*, 4073; *Angew. Chem. Int. Ed.* **2009**, *48*, 4013.
[9] A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts, R. B. Rowlings, *Chem. Commun.* **1999**, 353.
[10] X. Kang, J. Luo, Q. Zhang, P. Wang, *Dalton* **2011**, *40*, 379.