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Journal

Chemical Communications, 55(22)

ISSN

1359-7345

Authors

Lemmerz, Lara E
Mukherjee, Debabrata
Spaniol, Thomas P
et al.

Publication Date

2019-03-18

DOI

10.1039/c9cc00490d

Peer reviewed



ChemComm

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NNNN-Type Macrocycle**

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-01-2019-000490.R1
Article Type:	Communication

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Cationic magnesium hydride $[MgH]^+$ stabilized by an NNNN-type macrocycle

Received 00th January 20xx,
Accepted 00th January 20xx

Lara Elisa Lemmerz,^a Debabrata Mukherjee,^{a,b} Thomas Paul Spaniol,^a Anthony Wong,^c Gabriel Ménard,^c Laurent Maron^d and Jun Okuda*^a

DOI: 10.1039/x0xx00000x

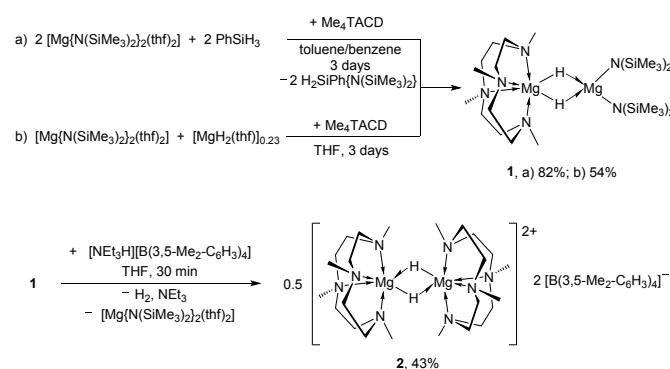
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A magnesium hydride cation $[(L)MgH]^+$ supported by a macrocyclic ligand ($L = Me_4TACD$; 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) has been prepared by partial protonolysis of a mixed amide hydride $[(L)MgH_2Mg(N(SiMe_3)_2)_2]$ and shown to undergo a variety of reactions with unsaturated substrates, including pyridine.

Magnesium dihydride $[MgH_2]_\infty$ has been studied as potential hydrogen storage material for quite some time.¹ A variety of structurally well-characterized molecular magnesium hydrides of diverse nuclearity² has also gained importance as homogeneous catalysts for the hydrofunctionalization of unsaturated substrates.³ In contrast to insoluble $[MgH_2]_\infty$, more soluble albeit structurally ill-defined forms of MgH_2 have been known: a so-called activated form of MgH_2 by Schlesinger et al.⁴ and $[MgH_2(L)_n]$ by Michalczyk.⁵ Simple molecular $[MgH_2]$ or $[MgH]^+$ however remained elusive. σ -Bond metathesis has turned out to be the method of choice to convert magnesium precursors such as alkyls^{3l},⁶ and amides⁷ into molecular magnesium hydrides.² In contrast to its calcium homologs $[CaH]^+$,⁹ σ -bond metathesis of magnesium alkyls and silyls with silanes was not successful so far.^{6m} We have now obtained the dimer of $[MgH]^+$ stabilized by an NNNN-type macrocycle⁸ via partial protonolysis of a mixed amide hydride complex of the type $[Mg(NR_2)H]$.

Colorless crystals of $[(L)Mg(\mu-H)_2Mg(N(SiMe_3)_2)_2]$ (**1**) were isolated in 82% yield by treating magnesium bis(hexamethyl-disilazide) $[Mg\{N(SiMe_3)_2\}_2(thf)_2]$ at room temperature with Me_4TACD ($Me_4TACD = 1,4,7,10$ -tetramethyl-1,4,7,10-tetraazacyclododecane)

dodecane) and $PhSiH_3$ in aromatic hydrocarbons (Scheme 1a). Alternatively, **1** was obtained from a mixture of $[Mg\{N(SiMe_3)_2\}_2(thf)_2]$ and $[MgH_2(thf)_{0.23}]^5$ with Me_4TACD in THF in 54% yield (Scheme 1b).



Scheme 1. Synthesis of $[(Me_4TACD)Mg(\mu-H)_2Mg\{(N(SiMe_3)_2)_2\}]$ (**1**) and of $[(Me_4TACD)_2Mg_2(\mu-H)_2][B(3,5-Me_2-C_6H_3)_4]_2$ (**2**); $Me_4TACD = 1,4,7,10$ -tetramethyl-1,4,7,10-tetraazacyclododecane.

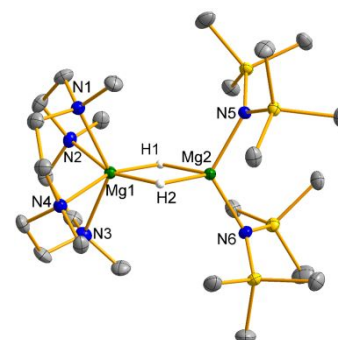


Figure 1. Molecular structure of $[(Me_4TACD)Mg(\mu-H)_2Mg\{(N(SiMe_3)_2)_2\}]$ (**1**). Displacement parameters are shown at the 50% probability level.

The dinuclear structure of **1** with a $[Mg_2(\mu-H)_2]^{2+}$ core ($Mg \cdots Mg$ 2.8847(10) Å) was revealed by X-ray diffraction. In the 1H NMR spectrum of **1** in $THF-d_8$ a characteristic singlet at δ 3.61 ppm was recorded for the Mg-H resonance. This dimer can be

^a Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany

^b Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, West Bengal, India

^c Department of Chemistry and Biochemistry, University of California, Santa Barbara, California, 93106, USA

^d CNRS, INSA, UPS, UMR 5215, LPCNO, Université de Toulouse, 135 avenue de Rangueil, 31077 Toulouse, France

Electronic Supplementary Information (ESI) available: General experimental procedures and analysis/spectroscopic data. See DOI: 10.1039/x0xx00000x

regarded as an adduct of $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with monomeric MgH_2 .^{6j, 7, 10} The mechanism of its formation remains obscure.

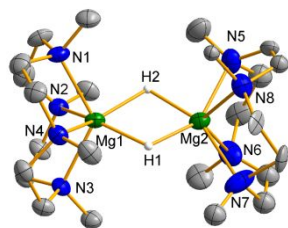
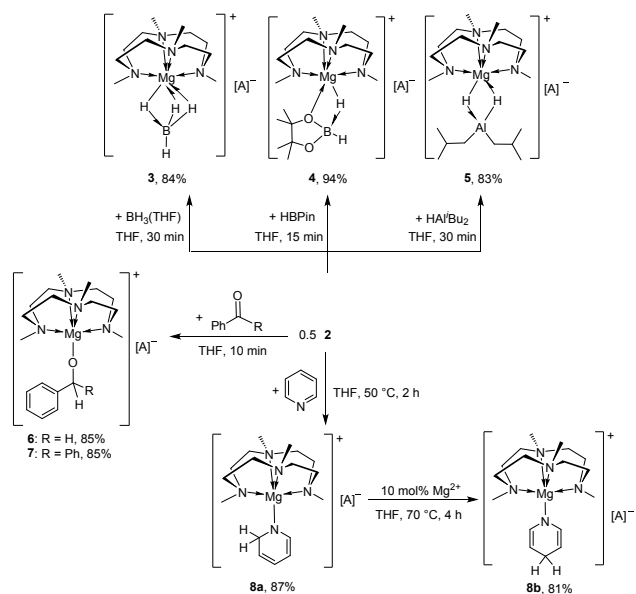


Figure 2. Molecular structure of the molecular cation in $[(\text{Me}_4\text{TACD})_2\text{Mg}_2(\mu\text{-H})_2][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]_2$ (**2**). Displacement parameters are shown at the 50% probability level.

Partial protonolysis of **1** by $[\text{NEt}_3\text{H}][\text{A}]$ ($[\text{A}] = [\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$) in THF afforded the dimeric hydride cation $[(\text{L})\text{MgH}]_2^{2+}$ (**2**) in 43% yield together with the byproducts $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]$, NEt_3 and H_2 (Scheme 1). The hydride is revealed as a singlet at δ 3.38 ppm in the ^1H NMR spectrum in $\text{THF-}d_8$. The deuteride **2-d₂**, prepared analogously using PhSiD_3 ,^{6d} did not scramble with **2** over a period of 3 days, in contrast to the apparently more reactive calcium homolog (complete deuteration within 8 h).⁹ Dideuterium reacted with **2** to give **2-d₂** exclusively after 54 h, again significantly slower than the calcium homolog.

The κ^4 -coordinated Me_4TACD ligands stabilizes the dinuclear core $[\text{Mg}_2(\mu\text{-H})_2]^{2+}$ with D_{2h} symmetry in **2** (Figure 2). Staggered conformation of the macrocyclic ligands within this magnesium complex was also confirmed by DFT calculation (B3PW91) (ESI, Figure S46), as opposed to the eclipsed conformation within the homologous calcium complex as well as in the related tetrahydride dications of rare earth metals $[(\text{L})_2\text{Ln}_2(\mu\text{-H})_4]^{2+}$ ($\text{Ln} = \text{Y, Lu}$) (ESI, Figure S45).^{9, 11} This difference reflects the significantly shorter intermetallic distance when magnesium is compared with calcium (ca. 30% reduction based on ionic radii for c.n. 6).



Scheme 2. Synthesis of the Lewis acid base adducts $[(\text{Me}_4\text{TACD})\text{Mg}(\mu\text{-H})_3\text{BH}][\text{A}]$ (**3**), $[(\text{Me}_4\text{TACD})\text{Mg}(\mu\text{-H})\text{BPin}][\text{A}]$ (**4**) and $[(\text{Me}_4\text{TACD})\text{Mg}(\text{H}_2\text{Al}^i\text{Bu}_2)][\text{A}]$ (**5**), as well as the

insertion products $[(\text{Me}_4\text{TACD})\text{Mg}\{\text{OCH}(\text{Ph})\text{R}\}][\text{A}]$ (**6**: $\text{R} = \text{H}$; **7**: $\text{R} = \text{Ph}$) and $[(\text{Me}_4\text{TACD})\text{Mg}(1,2\text{-DHP})][\text{A}]$ (**8a**) ($[\text{A}] = [\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$).

Reaction of **2** with the Lewis acids $\text{BH}_3(\text{THF})$, HBPin and $\text{DIBAL}(\text{H})$ gave the mononuclear adducts $[(\text{L})\text{Mg}(\mu\text{-H})_3\text{BH}][\text{A}]$ (**3**), $[(\text{L})\text{Mg}(\mu\text{-H})\text{BPin}][\text{A}]$ (**4**) and $[(\text{L})\text{Mg}(\text{H}_2\text{Al}^i\text{Bu}_2)][\text{A}]$ (**5**) (Scheme 2), indicating the biphilic property of the $[(\text{L})\text{MgH}]^+$ core. Interestingly, each of the product exhibits a distinct type of bridging ligand in the crystal.

X-ray diffraction on a single crystal of **3** revealed a mononuclear structure with a magnesium center coordinated by a κ^4 - Me_4TACD ligand and three μ_2 -bridging hydrides of the BH_4 group in a distorted capped octahedral coordination geometry (Figure 3). The κ^3 -coordinated BH_4 unit agrees with the short $\text{Mg}\cdots\text{B}$ distance of 2.335(5) Å as in other κ^3 -magnesium tetrahydroborates (2.22 - 2.33 Å), whereby κ^2 -coordinated BH_4 groups show longer $\text{Mg}\cdots\text{B}$ distances (2.45 - 2.55 Å).^{12a, 14a, 15} The κ^3 -binding mode of the borate is also confirmed by IR spectroscopy with one band for the stretching vibration $\nu(\text{B-H}_i)$ at 2444 cm^{-1} and two bands for the symmetric and asymmetric stretching vibrations $\nu(\text{B-H}_b)$ at 2291 cm^{-1} and 2214 cm^{-1} .^{12a, 12b}

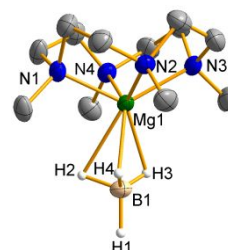


Figure 3. Molecular structure of the molecular cation in $[(\text{Me}_4\text{TACD})\text{Mg}(\mu\text{-H})_3\text{BH}][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**3**). Displacement parameters are shown at the 50% probability level.

The IR spectrum of **4** indicates one terminal and one bridging hydride with two bands for the stretching vibration $\nu(\text{B-H}_i)$ at 2281 cm^{-1} and $\nu(\text{B-H}_b)$ at 2197 cm^{-1} . Asymmetric coordination of pinacolborate follows from a broad ^{11}B NMR signal at δ 1.42 ppm. In the solid state, coordination of the magnesium center by a κ^4 - Me_4TACD ligand, one bridging hydride and one oxygen atom of the pinacolborate leads to distorted octahedral coordination geometry (ESI, Figure S21).

In the ^1H NMR spectrum of **5** the hydrides give rise to a broad resonance at δ 3.04 ppm, as found in other magnesium hydridoaluminates.¹⁷ The stretching vibration $\nu(\text{Al-H})$ in the IR spectrum at 1654 cm^{-1} compares to the band in $[(\text{MesNacnac})\text{Mg}]_2[\text{Al}_6\text{H}_6(\text{Fiso})_2]$ ¹⁹ ($\nu(\text{Al-H})$: 1648 cm^{-1}), suggesting a κ^2 -binding mode. Consistent with the mononuclear structure, the ^{27}Al NMR spectrum shows a broad signal at δ 130.8 ppm ($[(\text{Mg}(\text{AlH}_4)_2(\text{THF})_4]$: δ 110 ppm).¹⁸

Electrophiles such as benzaldehyde and benzophenone inserted into the Mg-H bond to give cationic alkoxides $[(\text{L})\text{Mg}\{\text{OCH}(\text{Ph})\text{R}\}][\text{A}]$ (**6**: $\text{R} = \text{H}$; **7**: $\text{R} = \text{Ph}$) in 85% yield (Scheme 2). The ^1H and ^{13}C signals are similar to those of related magnesium alkoxides.^{3b, 12c, 20} Single crystal structure analysis of **6** confirmed the five-coordinate magnesium center in a distorted square pyramidal coordination geometry (Figure 4, left).

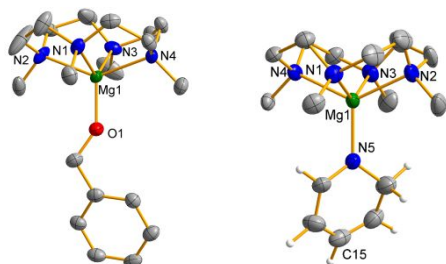


Figure 4. Molecular structure of $[(\text{Me}_4\text{TACD})\text{Mg}(\text{OCH}_2\text{Ph})][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**6**, left) and $[(\text{Me}_4\text{TACD})\text{Mg}(1,2\text{-DHP})][\text{B}(3,5\text{-Me}_2\text{-C}_6\text{H}_3)_4]$ (**8a**, right). Displacement parameters are shown at the 50% probability level. Selected interatomic distances [Å] and angles [°] in **6**: Mg1–O1 1.873(4), Mg1–N1 2.227(4), Mg1–N2 2.214(4), Mg1–N3 2.209(4), Mg1–N4 2.188(4). In **8a**: Mg1–N1 2.247(4), Mg1–N2 2.197(4), Mg1–N3 2.246(4), Mg1–N4 2.198(3), Mg1–N5 2.001(4), Mg1–N5–C15 160.0(2).

At 50 °C, **2** reacted with a stoichiometric amount of pyridine in THF to give the 1,2-dihydropyridyl complex $[(\text{L})\text{Mg}(1,2\text{-DHP})][\text{A}]$ (**8a**) within 2 h, isolated in 87% yield (Scheme 2). In the ^1H NMR spectrum five signals for the 1,2-dihydropyridyl protons at δ 6.45, 5.76, 4.72, 4.21 and 3.46 ppm in a ratio of 1:1:1:1:2 are recorded.^{3d, 6h} X-ray diffraction on a single crystal indicates a five-coordinate magnesium center in square pyramidal coordination geometry and a de-aromatized 1,2-DHP ring (Figure 4, right).

Magnesium 1,2-DHP complexes are known to isomerize to the thermodynamically more stable 1,4-isomer by heating to 60 °C.^{6j, 21} Unexpectedly, **8a** did not convert even after 3 days at 95 °C or in the presence of 30 equiv. of pyridine after 16 h at 95 °C.^{21f} Remarkably, Mg^{2+} catalyzed the quantitative conversion of **8a** in $\text{THF-}d_8$ to $[(\text{L})\text{Mg}(1,4\text{-DHP})][\text{A}]$ (**8b**) at 70 °C within 4 h in the presence of 10 mol% of $[\text{Mg}(\text{thf})_6][\text{A}]_2$ (**9**) (prepared by treating **2** with $[\text{NEt}_3\text{H}][\text{A}]$). The isomerization follows a zero order kinetics in **8a** with $k = (1.64 \pm 0.06) \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. With 20 mol% of **9**, full conversion was reached after 2 h at 70 °C. At this time, we can only speculate that the strong Lewis acid Mg^{2+} accelerates the hydride transfer from the 2- to 4-position in the pyridine ring by accepting the hydride intermittently. Ligand exchange may also play a role.

8a and **8b** slowly underwent exchange with pyridine- d_5 at 70 °C through a mixed deuterio/hydropyridyl species **8a-4H- d_5** /**8b-4H- d_5** to give completely deuterated species **8a- d_6** /**8b- d_6** , identified by ^1H and ^2D NMR spectroscopy. The exchange reactions follow pseudo first order kinetics with rate constants for **8a** ($k_1(343 \text{ K}) = (3.89 \pm 0.11) \cdot 10^{-6} \text{ s}^{-1}$, half life time $t_{1/2} = 49.5 \text{ h}$) and **8b** ($k_1(343 \text{ K}) = (1.23 \pm 0.02) \cdot 10^{-5} \text{ s}^{-1}$, half life time $t_{1/2} = 15.7 \text{ h}$). The exchange of **8a** in pyridine- d_5 is slower than the exchange of $[(\text{Me}_3\text{TACD})\text{Mg}(1,4\text{-DHP})]$ ($k_1(343 \text{ K}) = (7.30 \pm 0.13) \cdot 10^{-5} \text{ s}^{-1}$; half life time $t_{1/2} = 2.6 \text{ h}$),²² possibly due to steric constrained in the 1,2-regioisomer.

At 70 °C, 10 mol% of **8a**, **8b** and **9** catalyzed the hydroboration of pyridine using pinacolborane within 45 h (**8a** gave 90% conversion, forming a 1/3 mixture of the 1,2-/1,4-regioisomers; **8b** gave 89% conversion, forming a 1/9 mixture of 1,2-/1,4-isomers; **9** gave only 1,4-isomer at 74% conversion).

In conclusion, we have prepared and characterized the magnesium hydride cation **2** using the cyclen-derived Me_4TACD ligand containing the simple $[\text{MgH}]^+$ unit. While Lewis acids

reacted with **2** to give mononuclear adducts **3-5**, unsaturated substrates such as carbonyls and pyridine smoothly inserted into the Mg–H bond. The mechanism for the remarkable Lewis-acid catalyzed isomerization of the 1,2-DHP complex to its 1,4-regioisomer is currently under study.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft through the International Research Training Group “Selectivity in Chemo- and Biocatalysis” for financial support and Dr. G. Fink for NMR spectroscopic measurements. A. W. acknowledges the National Science Foundation OISE through “IRES: Training Next Generation Researchers in Advanced Magnetic Resonance at Chemistry Interfaces” (#1658652) for financial support.

Notes and references

- (a) B. Bogdanović, A. Ritter and B. Spliethoff, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 223-234; (b) J.-C. Crivello, B. Dam, R. V. Denys, M. Dornheim, D. M. Grant, J. Huot, T. R. Jensen, P. de Jongh, M. Latroche, C. Milanese, D. Milčius, G. S. Walker, C. J. Webb, C. Zlotea and V. A. Yartys, *Appl. Phys. A*, 2016, **122**, 97.
- D. Mukherjee and J. Okuda, *Angew. Chem. Int. Ed.*, 2018, **57**, 1458-1473.
- (a) M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn and C. Weetman, *Organometallics*, 2011, **30**, 5556-5559; (b) M. Arrowsmith, T. J. Hadlington, M. S. Hill and G. Kociok-Köhn, *Chem. Commun.*, 2012, **48**, 4567-4569; (c) M. Arrowsmith, M. S. Hill and G. Kociok-Köhn, *Chem. Eur. J.*, 2013, **19**, 2776-2783; (d) J. Intemann, M. Lutz and S. Harder, *Organometallics*, 2014, **33**, 5722-5729; (e) C. Weetman, M. S. Hill and M. F. Mahon, *Chem. Commun.*, 2015, **51**, 14477-14480; (f) M. D. Anker, M. S. Hill, J. P. Lowe and M. F. Mahon, *Angew. Chem. Int. Ed.*, 2015, **54**, 10009-10011; (g) C. Weetman, M. S. Hill and M. F. Mahon, *Chem. Eur. J.*, 2016, **22**, 7158-7162; (h) C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liprot and M. F. Mahon, *Chem. Sci.*, 2016, **7**, 628-641; (i) C. Weetman, M. S. Hill and M. F. Mahon, *Polyhedron*, 2016, **103**, 115-120; (j) Y. Yang, M. D. Anker, J. Fang, M. F. Mahon, L. Maron, C. Weetman and M. S. Hill, *Chem. Sci.*, 2017, **8**, 3529-3537; (k) M. D. Anker, C. E. Kefalidis, Y. Yang, J. Fang, M. S. Hill, M. F. Mahon and L. Maron, *J. Am. Chem. Soc.*, 2017, **139**, 10036-10054; (l) M. Rauch, S. Ruccolo and G. Parkin, *J. Am. Chem. Soc.*, 2017, **139**, 13264-13267; (m) H. Bauer, M. Alonso, C. Färber, H. Elsen, J. Pahl, A. Causero, G. Ballmann, F. De Proft and S. Harder, *Nature Catalysis*, 2018, **1**, 40-47.
- G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1951, **73**, 4585-4590.
- M. J. Michalczyk, *Organometallics*, 1992, **11**, 2307-2309.
- (a) S. P. Green, C. Jones and A. Stasch, *Angew. Chem. Int. Ed.*, 2008, **47**, 9079-9083; (b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938-955; (c) S. Harder, J. Spielmann, J. Intemann and H. Bandmann, *Angew. Chem. Int. Ed.*, 2011, **50**, 4156-4160; (d) J.

- Intemann, J. Spielmann, P. Sirsch and S. Harder, *Chem. Eur. J.*, 2013, **19**, 8478-8489; (e) M. Arrowsmith, B. Maitland, G. Kociok-Köhn, A. Stasch, C. Jones and M. S. Hill, *Inorg. Chem.*, 2014, **53**, 10543-10552; (f) D. J. Liptrout, M. S. Hill and M. F. Mahon, *Chem. Eur. J.*, 2014, **20**, 9871-9874; (g) S. Harder, J. Spielmann and J. Intemann, *Dalton Trans.*, 2014, **43**, 14284-14290; (h) H. Xie, X. Hua, B. Liu, C. Wu and D. Cui, *J. Organomet. Chem.*, 2015, **798**, 335-340; (i) D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem. Int. Ed.*, 2015, **54**, 4115-4118; (j) L. Fohlmeister and A. Stasch, *Chem. Eur. J.*, 2016, **22**, 10235-10246; (k) J. Langer, I. Kosygin, R. Puchta, J. Pahl and S. Harder, *Chem. Eur. J.*, 2016, **22**, 17425-17435; (l) J. Langer, B. Maitland, S. Grams, A. Ciucka, J. Pahl, H. Elsen and S. Harder, *Angew. Chem. Int. Ed.*, 2017, **56**, 5021-5025; (m) L. E. Lemmerz, V. Leich, D. Martin, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2017, **56**, 14979-14990.
7. (a) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey and R. B. Rowlings, *Chem. Commun.*, 2002, 376-377; (b) P. C. Andrikopoulos, D. R. Armstrong, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara and R. B. Rowlings, *Eur. J. Inorg. Chem.*, 2003, **2003**, 3354-3362; (c) M. Arrowsmith, M. S. Hill, D. J. MacDougall and M. F. Mahon, *Angew. Chem. Int. Ed.*, 2009, **48**, 4013-4016.
8. J. Coates, D. Hadi and S. Lincoln, *Aust. J. Chem.*, 1982, **35**, 903-909.
9. D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem. Int. Ed.*, 2017, **56**, 12367-12371.
10. E. C. Ashby and A. B. Goel, *Inorg. Chem.*, 1978, **17**, 1862-1866.
11. (a) W. Fegler, A. Venugopal, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem. Int. Ed.*, 2013, **52**, 7976-7980; (b) S. Arndt, M. U. Kramer, W. Fegler, Y. Nakajima, I. Del Rosal, R. Poteau, T. P. Spaniol, L. Maron and J. Okuda, *Organometallics*, 2015, **34**, 3739-3747.
12. (a) M. Bremer, G. Linti, H. Nöth, M. Thomann-Albach and G. E. W. J. Wagner, *Z. Anorg. Allg. Chem.*, 2005, **631**, 683-697; (b) R. A. Collins, J. Unruangsri and P. Mountford, *Dalton Trans.*, 2013, **42**, 759-769; (c) S. Schnitzler, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2016, **55**, 12997-13006.
13. N. Edelstein, *Inorg. Chem.*, 1981, **20**, 297-299.
14. (a) G. Soloveichik, J.-H. Her, P. W. Stephens, Y. Gao, J. Rijssenbeek, M. Andrus and J. C. Zhao, *Inorg. Chem.*, 2008, **47**, 4290-4298; (b) J. Prust, K. Most, I. Müller, E. Alexopoulos, A. Stasch, I. Usón and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2032-2037; (c) G. L. Soloveichik, M. Andrus and E. B. Lobkovsky, *Inorg. Chem.*, 2007, **46**, 3790-3791.
15. (a) H. Nöth, *Z. Naturforsch.*, 1982, **87b**, 1499-1503; (b) M. Bremer, H. Nöth and M. Warchhold, *Eur. J. Inorg. Chem.*, 2003, **2003**, 111-119.
16. D. Mukherjee, A. Ellern and A. D. Sadow, *Chem. Sci.*, 2014, **5**, 959-964.
17. (a) H. Lehmkuhl, K. Mehler, R. Benn, A. Rufi'nska, G. Schroth and C. Krüger, *Chem. Ber.*, 1984, **117**, 389-403; (b) S. J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch and C. Jones, *Angew. Chem. Int. Ed.*, 2017, **56**, 8527-8531; (c) S. Schnitzler, T. P. Spaniol, L. Maron and J. Okuda, *Chem. Eur. J.*, 2015, **21**, 11330-11334; (d) S. Schnitzler, P. Cui, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2017, **46**, 1761-1765; (e) C. Stuhl, M. M. Katzenmayer, C. Maichle-Mössmer and R. Anwender, *Dalton Trans.*, 2018, **47**, 15173-15180.
18. H. Nöth, M. Schmidt and A. Treit, *Chem. Ber.*, 1995, **128**, 999-1006.
19. S. J. Bonyhady, D. Collis, N. Holzmann, A. J. Edwards, R. O. Piltz, G. Frenking, A. Stasch and C. Jones, *Nature Commun.*, 2018, **9**, 3079.
20. (a) K. W. Henderson, J. F. Allan and A. R. Kennedy, *Chem. Commun.*, 1997, 1149-1150; (b) H.-Y. Tang, H.-Y. Chen, J.-H. Huang and C.-C. Lin, *Macromolecules*, 2007, **40**, 8855-8860; (c) M.-Y. Shen, Y.-L. Peng, W.-C. Hung and C.-C. Lin, *Dalton Trans.*, 2009, 9906-9913; (d) W.-C. Hung and C.-C. Lin, *Inorg. Chem.*, 2009, **48**, 728-734; (e) M. S. Hill, D. J. MacDougall, G. Kociok-Köhn, M. F. Mahon and C. Weetman, *Organometallics*, 2015, **34**, 2590-2599; (f) Y. Sun, Y. Cui, J. Xiong, Z. Dai, N. Tang and J. Wu, *Dalton Trans.*, 2015, **44**, 16383-16391; (g) I. E. Nifant'ev, A. V. Shlyakhtin, V. V. Bagrov, M. E. Minyaev, A. V. Churakov, S. G. Karchevsky, K. P. Birin and P. V. Ivchenko, *Dalton Trans.*, 2017, **46**, 12132-12146.
21. (a) A. J. de Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **186**, 173-184; (b) A. J. de Koning, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **186**, 159-172; (c) A. J. de Koning, P. H. M. Budzelaar, B. G. K. van Aarssen, J. Boersma and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1981, **217**, C1-C4; (d) E. C. Ashby and A. B. Goel, *J. Organomet. Chem.*, 1981, **204**, 139-145; (e) M. S. Hill, D. J. MacDougall and M. F. Mahon, *Dalton Trans.*, 2010, **39**, 11129-11131; (f) S. D. Robinson, A. R. Kennedy, J. J. Liggat, R. E. Mulvey, *Chem. Commun.*, 2015, **51**, 5452.
22. L. E. Lemmerz, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2018, **47**, 12553-12561.

Table of Content (TOC)

Cationic Magnesium Hydride $[\text{MgH}]^+$ Stabilized by an NNNN-Type Macrocycle

Lara Elisa Lemmerz, Debabrata Mukherjee, Anthony Wong, Gabriel Ménard, Laurent Maron and Jun Okuda

A magnesium hydride cation $[(\text{L})\text{MgH}]^+$ supported by a macrocyclic ligand (L = Me_4TACD ; 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclo-dodecane) has been shown to react with Lewis acids as well as with unsaturated substrates including pyridine.

