DOI: 10.1002/anie.200705758

Molecular Magnesium(I) Compounds: From Curiosity to Kudos

*Matthias Westerhausen**

Grignard reagents · magnesium · Mg–Mg bonds · reduction · subvalent compounds

Subvalent metal complexes with metal–metal bonds have attracted the interest of many research groups for several decades. The formation of such compounds requires a certain stability of low oxidation states such as +1 for Group 13 and +2 for Group 14. In contrast, intermediate oxidation states for the Group 2 elements and zinc are strongly disfavored. Even though Hg_2^{2+} is well-known, the oxidation state +1 for the lighter congener zinc was believed to be inaccessible at room temperature.

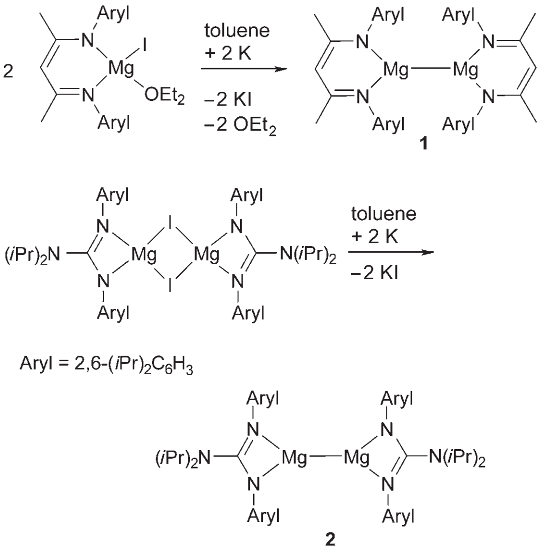
In 2004, the synthesis of [Cp*Zn–ZnCp*] (Cp* = C_5Me_5)[1] by the reaction of [$ZnCp^*_2$] with $ZnEt_2$ attracted tremendous attention.[2] A high-yield synthesis[3] of this zinc(I) compound by the reduction of $ZnCl_2$ with KCp* and KH formed the basis for the development of extensive synthetic chemistry. This preparative success also initiated the research on subvalent alkaline earth metal compounds, especially of magnesium(I) derivatives.[4] The high Mg–Mg bond dissociation energy of 197 kJ mol^{-1} for HMg–MgH[5] was encouraging with respect to the possibility of isolating molecular Mg^I compounds, which is partly a matter of choosing the right ligand. The stabilization of RZn–ZnR was made possible employing R groups bis(2,6-diisopropylphenyl)phenyl[6] and *N,N'*-bis(2,6-diisopropylphenyl)-1,3-diketiminate (Nacnac).[7] The bis(2,6-diisopropylphenyl)phenyl group was also used for the stabilization of the homologous cadmium derivative.[8] Similar exceptional and tuneable steric demands together with the ability to form strong metal–ligand bonds play a dominant role for these spectator ligands.[9]

Theoreticians investigated the reaction of MgX_2 with magnesium atoms according to Equation (1). These reactions are exothermic by 48 and 52 kJ mol^{-1} for X = Cl and F, respectively.[10] The insertion of a magnesium atom into the Grignard reagent MeMgX is also exothermic (23 kJ mol^{-1} (SCF)[11], 28 kJ mol^{-1} (MP2)[12]). Even the insertion of a magnesium atom into MgH_2 yielding HMg–MgH is exothermic by 12 kJ mol^{-1}.[11] However, the atomization energy of magnesium (147 kJ mol^{-1})[10] is much larger than the values observed for these insertion reactions.

$$MgX_2 + Mg \rightarrow X{-}Mg{-}Mg{-}X \qquad (1)$$

The atomization energy has to be invested to profit from the exothermic reaction energies. Thus, magnesium atoms were co-deposited with hydrogen and argon onto a 10 K substrate yielding HMg–MgH together with other molecules, such as MgH_2, MgH, and $Mg(\mu\text{-}H)_2Mg$.[5] Another possibility is the insertion of magnesium atoms into MgX_2 at high temperatures (800 °C) in molten $MgCl_2$.[13] Thereafter, MeMg radicals were also prepared and captured in a 4.3 K neon matrix and investigated spectroscopically[14] and theoretically.[14,15] From these investigations it can be concluded that Mg–Mg bonds are stable, and that the formation of magnesium metal has to be avoided. Employing bulky groups should shield the reactive Mg–Mg unit to prevent metal liberation.

With this concept in mind, Green et al.[16] published the synthesis [Eq. (2)] and structural characterization of the first stable molecular Mg^I compounds, yellow **1** and colorless **2**. The thermal stability was surprisingly high, and decomposition was observed at temperatures above 300 °C and 170 °C for **1** and **2**, respectively. Compound **1** could be sublimed intact at 230 °C at 10^{-6} mm Hg, whereas **2** decomposed with deposition of magnesium metal. As expected, these magnesium(I) compounds are air- and moisture sensitive. The Mg–



(2)

---

[*] M. Westerhausen
Institute of Inorganic and Analytical Chemistry
Friedrich-Schiller-Universität Jena
August-Bebel-Str. 2, 07743 Jena (Germany)
Fax: (+49) 3641-948-102
E-mail: m.we@uni-jena.de

Mg bond lengths of **1** and **2** (Figure 1) are 284.57(8) and 285.08(12) pm, respectively.

The possibility that hydrogen atoms bridge the Mg–Mg moiety has to be excluded. Such a structural fragment was already found for calcium in [(Nacnac)Ca(thf)(μ-H)$_2$Ca(thf)(Nacnac)] **3**, which was prepared according to Equation (3).[17] The hydride anions were located during the X-ray structure determination and showed a chemical shift of $\delta = 4.45$ ppm in the ^{1}H NMR spectrum. A central structural Mg_2H_2 fragment for **1** and **2** (giving a Mg^{II} compound) was excluded on the basis of several observations:

1) The molecular structure of **1** (Figure 1) is very similar to the structure of the zinc(I) congener[7] with the MgN_2C_3 heterocycles being nearly orthogonal; in a hydrido complex, these heterocycles should be nearly coplanar to each other and orthogonal to the Mg_2H_2 ring.
2) No significant residual electron density was found between the Mg atoms.
3) No hydride resonances were found in the NMR spectra.
4) Owing to the high thermal stability of these magnesium(I) compounds, the high resolution mass spectra allowed the detection of the molecular ions.

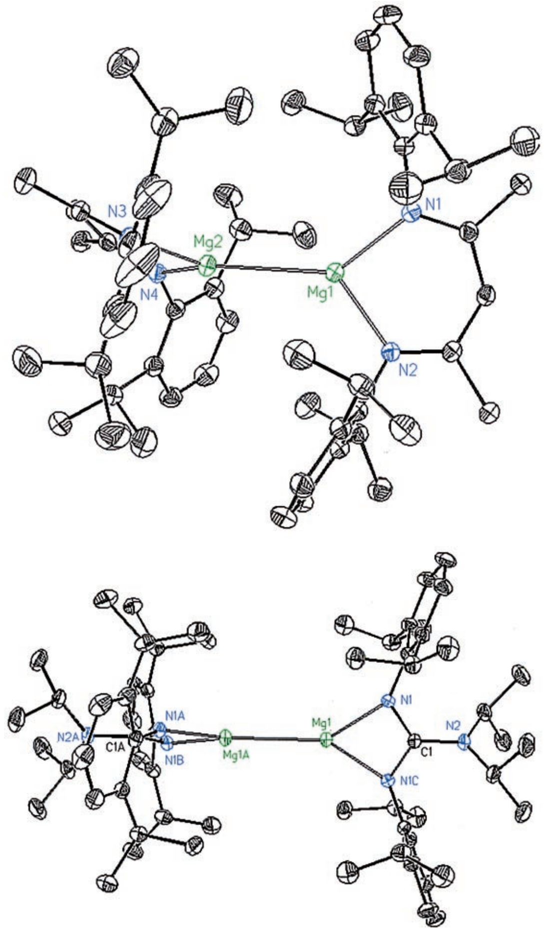
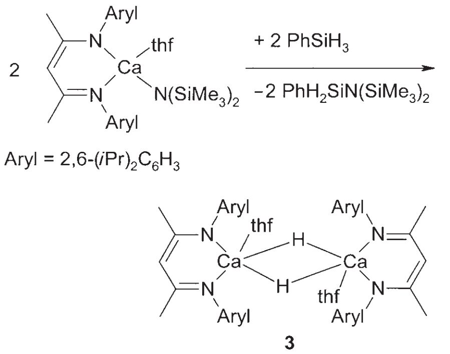


Figure 1. Molecular structures of **1** (top) and **2** (bottom). Thermal ellipsoids are set at 40% probability, and hydrogen atoms are omitted for clarity.



(3)

3

Because of overlap with other bands, the IR and Raman spectra neither allowed the assignment of an Mg–Mg stretching mode nor the observation of Mg–H–Mg stretching absorptions.

The Mg–Mg bonds in **1** and **2** are rather long, being in the range of short nonbonding Mg···Mg contacts of magnesium(II) compounds. Nevertheless, these values agree very well with Mg–Mg distances predicted by quantum chemical methods in RMg–MgR with R being H (288.4 pm[18]), η^5-C_5H_5 (280.9 pm[18]), C_6H_3-2,6-Ph_2 (283.8 pm[19]), F (284.1 pm[10]), and Cl (284.6 pm[10]). Asymmetric species, such as H_3CMg–MgF, have a similar Mg–Mg bond length (288.9 pm) and a bond dissociation energy of 177 kJ mol^{-1}.[12]

The impact of these molecules with extremely stable Mg–Mg bonds[16] on the chemical community will initiate a vastly growing interest in the chemistry of molecular subvalent alkaline earth metal compounds, as was observed after the first report[1] for zinc(I), with derivatization reactions,[6,7,20] expanding the variety of zinc(I) compounds, and theoretical investigations.[18,20,21]. Investigations regarding the reactivity of these spectacular magnesium(I) compounds present future challenges.

Theoreticians as well as synthetic chemists will also expand this concept on the heavier alkaline earth metals. The reaction of calcium with hydrogen in xenon and krypton matrixes at 12 K allowed the identification of HCa–CaH as well as HCa–Ca–CaH along with calcium(II) hydrides.[22] Calcium clusters Ca_n^{2+} are linear up to $n = 4$, whereas larger clusters form three-dimensional cages.[23] $CaCH_3$[24] and CaCp[25] radicals were also prepared from calcium atoms and organometallic precursors; a bond energy of 97 kJ mol^{-1} for Ca–C was calculated for calciummethyl.[26] However, quantum chemical considerations showed that CpBe–BeCp should be much more feasible than CpCa–CaCp.[18] These experiments initiated investigations regarding the importance of d and p orbitals at calcium for the description of Ca–X bonds in species such as $CaCH_3$, $CaNH_2$, CaOH, and CaF.[27] These studies support the premise that very bulky groups should be able to stabilize Ca–Ca moieties,[19] but a competition between σ- and π-based interactions in calciumphenyl complexes could limit the use of phenyl groups as protective units.[28]

---

[1] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136–1138.

[2] G. Parkin, *Science* **2004**, *305*, 1117–1118.

[3] D. del Río, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* **2005**, *117*, 1270–1273; *Angew. Chem. Int. Ed.* **2005**, *44*, 1244–1247.

[4] A. Schnepf, H.-J. Himmel, *Angew. Chem.* **2005**, *117*, 3066–3068; *Angew. Chem. Int. Ed.* **2005**, *44*, 3006–3008.

[5] T. J. Tague, L. Andrews, *J. Phys. Chem.* **1994**, *98*, 8611–8616.

[6] Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 5939–5942; *Angew. Chem. Int. Ed.* **2006**, *45*, 5807–5810.

[7] Y. Wang, B, Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, *127*, 11944–11945.

[8] Z. Zhu, R. C. Fischer, J. C. Fettinger, E. Rivard, M. Brynda, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 15068–15069.

[9] L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3065.

[10] P. G. Jasien, C. E. Dykstra, *Chem. Phys. Lett.* **1984**, *106*, 276–279.

[11] P. G. Jasien, C. E. Dykstra, *J. Am. Chem. Soc.* **1985**, *107*, 1891–1895.

[12] A. V. Nemukhin, I. A. Topol, F. Weinhold, *Inorg. Chem.* **1995**, *34*, 2980–2983.

[13] M. Krumpelt, J. Fischer, I. Johnson, *J. Phys. Chem.* **1968**, *72*, 506–511.

[14] A. J. McKinley, E. Karakyriakos, *J. Phys. Chem. A* **2000**, *104*, 8872–8881.

[15] A. F. Jalbout, *Chem. Phys. Lett.* **2001**, *340*, 571–580.

[16] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757.

[17] S. Harder, J. Brettar, *Angew. Chem.* **2006**, *118*, 3554–3558; *Angew. Chem. Int. Ed.* **2006**, *45*, 3474–3478. See also: J. Spielmann, S. Harder, *Chem. Eur. J.* **2007**, *13*, 8928–8938.

[18] A. Velazquez, I. Fernández, G. Frenking, G. Merino, *Organometallics* **2007**, *26*, 4731–4736.

[19] M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu, M. Reiher, *Chem. Eur. J.* **2007**, *13*, 6292–6306.

[20] a) D. del Río, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* **2005**, *117*, 1270–1273; *Angew. Chem. Int. Ed.* **2005**, *44*, 1244–1247; b) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* **2007**, *129*, 693–703 (erratum: A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Río, R. A. Andersen, *J. Am. Chem. Soc.* **2007**, *129*, 14100).

[21] a) H. S. Kang, *J. Phys. Chem. A* **2005**, *109*, 4342–4351; b) Z.-Z. Xie, W.-H. Fang, *Chem. Phys. Lett.* **2005**, *404*, 212–216; c) Z.-Z. Liu, W. Q. Tian, J.-K. Feng, G. Zhang, W.-Q. Li, Y.-H. Cui, C.-C. Sun, *Eur. J. Inorg. Chem.* **2006**, 2808–2818; d) Z.-Z. Liu, W. Q. Tian, J.-K. Feng, G. Zhang, W.-Q. Li, *THEOCHEM* **2006**, *758*, 127–138; e) M. R. Philpott, Y. Kawazoe, *THEOCHEM* **2006**, *776*, 113–123; f) M. R. Philpott, Y. Kawazoe, *Chem. Phys.* **2006**, *327*, 283–290; g) M. R. Philpott, Y. Kawazoe, *Chem. Phys.* **2007**, *333*, 201–207; h) K. K. Pandey, *J. Organomet. Chem.* **2007**, *692*, 1058–1063.

[22] Z. L. Xiao, R. H. Hauge, *High Temp. Sci.* **1991**, *31*, 59–77.

[23] E. Blaisten-Barojas, C.-H. Chien, M. R. Pederson, J. W. Mirick, *Chem. Phys. Lett.* **2004**, *395*, 109–113.

[24] C. R. Brazier, P. F. Bernath, *J. Chem. Phys.* **1987**, *86*, 5918–5922.

[25] A. M. Ellis, E. S. J. Robles, T. A. Miller, *J. Chem. Phys.* **1991**, *94*, 1752–1758.

[26] A. El Hammadi, M. El Mouhtadi, H. Cardy, A. Dargelos, *THEOCHEM* **2003**, *624*, 1–11.

[27] J. V. Ortiz, *J. Chem. Phys.* **1990**, *92*, 6728–6731.

[28] S. Petrie, *Int. J. Mass Spectrom.* **2003**, *227*, 33–46.