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A Review on Subvalent Mg(I)–Mg(I) Single Bonded Chemistry

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ABSTRACT

In recent times, complexes containing metal-metal single bonds are one of the synthetic challenging areas of chemistry. The interest also stems from several perspective including synthetic methodology, structure, reactivity, and theoretical involvement. Compared to group 12, 13 and 14 metals, the alkaline earth metals (group 2) is still its infancy. However, recent years have witnessed major achievements of organo-alkaline earth compounds for catalytic utilization. These include hydroamination, hydrophosphination, hydrosilylation, hydrogenation, and polymerization reactions. After the most important breakthrough of the organometallic low-valent stable Zn(I) –Zn(I) compound by Carmona and co-workers, this field of research gets new direction. In 2007, Jones and co-workers were successful in isolating a group 2 metal Mg(I) dimer containing a Mg–Mg single bond. This review article provides the recent development on this Mg(I) dimeric chemistry reported till today and also will highlight their various reactivities.

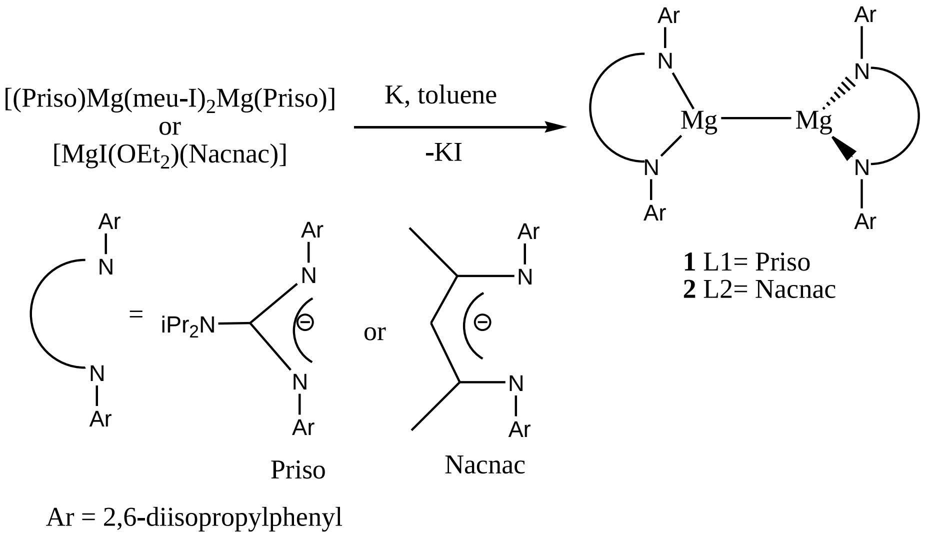
Introduction

Metal-metal bonding as an important dimension of chemistry has attracted much attention in the past two decades. Besides the concept of multiple bonds between transition metals developed by Cotton,[1] several metal-metal bonds involving both p- and d-block metals have been reported in recent years, such as the silicon-silicon triple bond[2] and the chromium-chromium quintuple bond.[3] In 2004, the first stable compound containing a Zn(I)-Zn(I) bond, Cp*Zn-ZnCp*, was synthesized by Carmona and co-workers.[4] Consequently, various researchers have started computation studies about the various possibility to stabilize metal-metal single bonded compounds not only Zn-Zn but also relevant till then unknown Mg-Mg bond. The chemistry of the s-block metals is dominated by the (+1) oxidation state for the Alkali metals and the (+2) oxidation state for the Alkaline Earth metals (group 2). Several theoretical studies have predicted that thermally stable compound of the type LM-ML (where M= Group 2 elements, Be, Mg, Ca) would be possible. But till today, only few Mg(I)-Mg(I) bonded compounds stabilized by various organic ligands have been synthesized and characterized. A number of magnesium(I) compounds, for example, HMg-MgH, have previously been studied under, for example, matrix isolation conditions,[5] and mononuclear compounds, for example, $Mg^I(NC)$, have been detected in circumstellar clouds.[6] Moreover, the formation of synthetically important Grignard reagents, RMgX (where X is a halide), has been proposed to proceed via magnesium(I) compounds of the type RMgMgX.[7] In addition, related cluster compounds, RMg_4X, of undetermined structure have been investigated by using mass spectrometry experiments.[8] 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.

In recent years, several dimeric Mg(I) compounds containing Mg-Mg single bond has been prepared and their chemistry have been developed. These compounds are mostly stabilized by sterically demanding and chelating anionic N-ligands that prevent their disproportionation. Such molecule can be used as a reducing agent for various reduction processes. Focusing on such perspective, the synthesis of stable molecular compound of type LMg-MgL have been going on. In this report, the chemistry of such low valent Mg(I) dimer till date will be highlighted.

Synthesis of stable Mg(I)-Mg(I) low valent compound formation

First such stable Mg(I) dimer compound reported by Green et. al. prepared and characterised in 2007. Reduction of $(Priso)Mg(\mu\text{-}I)_2Mg(OEt_2)(Priso)$ and the known compound, $MgI(OEt_2)(Nacnac)$, with an excess of potassium metal in toluene over 24 hours led to the crystalline magnesium(I) compounds $[Mg(Priso)]_2$, **1** (colorless, yield of 28.5%) and $[Mg(Nacnac)]_2$, **2** (yellow, yield of 56.5%), respectively (Scheme 1).[9] Although both compounds are air- and moisture sensitive, they are thermally stable and fully decompose only at temperatures in excess of 170°C and 300°C, respectively. The X-ray crystal structure shows that both **1** and **2** possess distorted trigonal planar coordination geometries with delocalized ligand backbones. Despite the paucity of Mg-Mg bonds for comparison, the lengths of those interactions in **1** and **2** are similar 285.08(12) and 284.57(8) pm, respectively. 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),[10] η^5-C_5H_5 (280.9 pm),[10] C_6H_3-2,6-Ph_2 (283.8 pm),[11] F (284.1 pm),[12] and Cl (284.6 pm).[12] Figure 1 shows the crystal structure of compound **2**.



Scheme 1: Synthesis of $[Mg(Priso)]_2$, **1** and $[Mg(Nacnac)]_2$, **2**[9a]

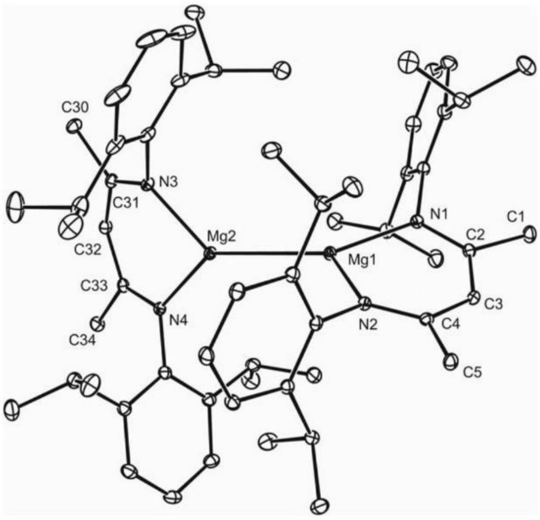
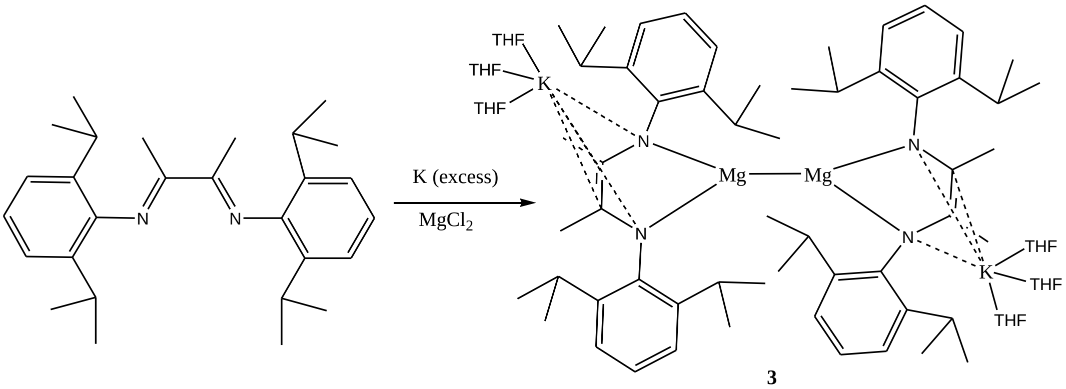


Figure 1: Molecular structure of **2**[9a]

Table 1: The list of ligands abbreviations of Mg(I)-Mg(I) bonded chemistry

No.	**Ligands formula**
L1	$[(Ar)NC(NR'_2)N(Ar)]^-$ [where Ar = 2,6-diisopropylphenyl and R' is isopropyl (Priso)
L2	$\{[(Ar)NC(Me)]_2CH\}^-$ [where Ar = 2,6-diisopropylphenyl] (Nacnac)
L3	$[(2,6\text{-}i\text{Pr}_2C_6H_3)NC\text{-}(Me)]_2^{2-}$
L4	^{Mes}Nacnac; $\{[(Ar)NC(Me)]_2CH\}^-$ [where Ar = 2,4,6-trimethylphenyl]
L5	^{Dep}Nacnac; $\{[(Ar)NC(Me)]_2CH\}^-$ [where Ar = 2,6-diethylphenyl]
L6	^{Xyl}Nacnac; $\{[(Ar)NC(Me)]_2CH\}^-$ [where Ar = 2,6-dimethylphenyl]
L7	^{tBu}Nacnac; $\{[(Ar)NC(t\text{Bu})]_2CH\}^-$ [where Ar = 2,6-diisopropylphenyl]
L8	$Ph_2P(NDip)_2^-$ where Dip = $2,6\text{-}i\text{Pr}_2C_6H_3$

Compound **3** was readily prepared as pink crystals by reduction of a mixture of ligand L3 and $MgCl_2$ with excess potassium metal (in a 1:1:3 molar ratio) in THF (Scheme 2). It is air- and moisture-sensitive but thermally stable in solution. Upon removal from the mother liquor, the crystals rapidly lose the solvents with a deepening of the color, and they decompose at 115°C. The observed Mg-Mg bond distance in **3** [293.70(18) pm] is slightly longer than those in compounds **1** and **2** but shorter than those in the adducts **9-12** (305.6-319.6 pm).[14]



3

Scheme 2: Synthesis of **3**

A series of binuclear alkaline-earth (including Mg) metallocenes with formula: $M_2(\eta^5\text{-}E_5)_2$ (M = Mg, E = P, As) have been investigated using B3LYP/6-311G* and BP86/6-311G* levels of theory and shows that single M-M bond in $M_2(\eta^5\text{-}As_5)_2$ is weaker in dissociation energy than that in $M_2(\eta^5\text{-}P_5)_2$.[14] Li et. al. also discussed about the nature of the metal-metal bonding by quantum theory of atoms in molecules (QTAIM) analysis by using $(\eta^5\text{-}C_5H_5)_2Mg_2$ model compound and found that that Mg-Mg bond distance is 277.42 pm.[15]

Platts et. al. reported a presence of a non-nuclear local maximum in the electron density of a dimeric Mg(I) molecule using high-resolution X-ray diffraction data coupled with theoretical calculations.[16]
Advanced theoretical calculations suggested that the Mg-Mg interactions of the complexes are best denoted as single σ bonds of predominantly s-type with a Mg-Mg bond dissociation energy (BDE) of ~45 kcal mol^{-1}. The topological analysis using QTAIM on compound **2** shows that the experimental charge density unambiguously locates a bond critical point (bcp) between the atoms, and thus, as expected, a chemical bond exists between the two Mg ions. The value of the Laplacian at the bcp is positive and close to zero.[17]

Bonyhady et. al. reported a series of Mg(I) dimeric compound and its adduct with solvent. Reaction using bulkier precursor $[^{Mes}NacnacMgI(OEt)_2)]$ and reduction with Na yielded (>50%) pale-yellow compound **4** after 5-days (Scheme 3). The compound **4** an also be synthesised by using reduction with K but with less yeild (2-5%).[18] In the similar process two more Mg(I) dimer **5** and **6** was synthesized using ^{Dep}Nacnac (L5) and ^{Xyl}Nacnac (L6) ligand respectively (Table 1).[19]

$$[\mathrm{LMgI(OEt_2)}] \xrightarrow[\text{-NaI}]{\text{Na, PhMe}} [\mathrm{LMgMgL}]$$

$$\begin{aligned} L = L4 &= {}^{Mes}\mathrm{Nacnac},\ \mathbf{4} \\ L5 &= {}^{Dep}\mathrm{Nacnac},\ \mathbf{5} \\ L6 &= {}^{Xyl}\mathrm{Nacnac},\ \mathbf{6} \end{aligned}$$

Scheme 3: Preparation of compound **4-6**

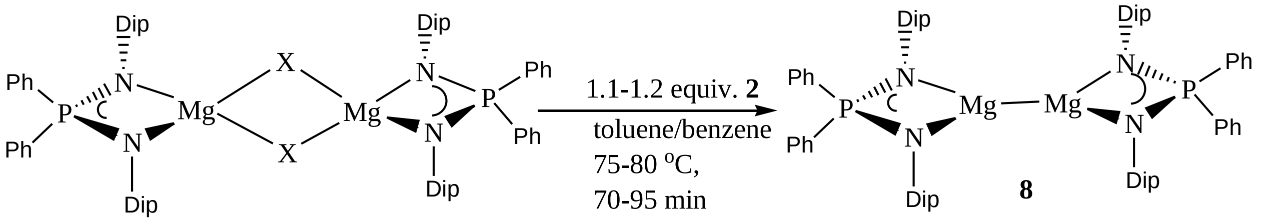
But while the reaction was carried out using much bulkier precursor (L7= ^{tBu}Nacnac) (Table 1) with an excess of potassium in toluene gace orange crystalline compound of compound **7** with good yield (Scheme 4).[18] Both compound **4** and **7** are thermally stable in solid state and also in toluene solution.

$$[\mathrm{L7MgI}] \xrightarrow[\text{-KI}]{\text{K, PhMe}} \underset{\mathbf{7}}{[\mathrm{L7MgMgL7}]}$$

$$L7 = {}^{tBu}\mathrm{NacNac}$$

Scheme 4: Preparation of compound **7**

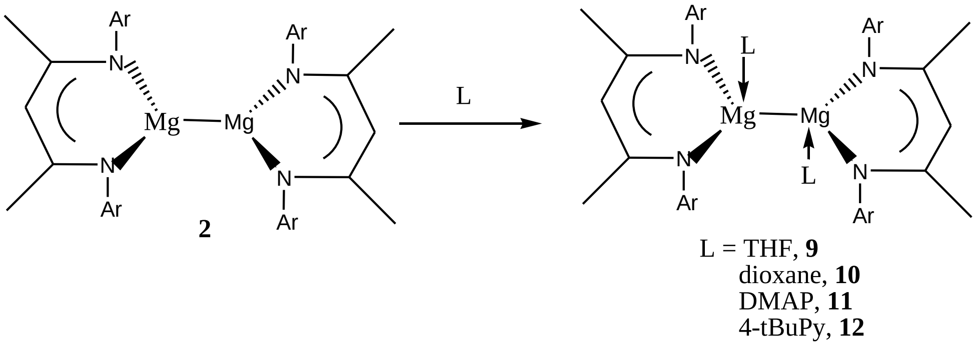
Reacting $[(L8MgX)_2]$ (X= Br, I) with one equivalent of compound **2** in deurated benzene at elevated temperature shows the formation of **8**. Also, the sterically demanding Mg(I) dimer, Suitable crystals were obtained using an excess of **2** followed by recrystallization from cyclohexane (Scheme 5).[20]



Scheme 5: Synthesis of complex **8**

Synthesis of stable adduct formation with Mg(I) dimer

To assess the possibility that **2** could form stable adducts with cyclic ethers, it was dissolved in either neat THF or dioxane to yield red-orange and orange solutions, respectively. When volatiles were removed from these solutions in vacuo, uncoordinated **2** was quantitatively recovered. However, concentration and cooling of the solutions afforded good yields of the crystalline adducts, red-orange **9** and orange **10**. Highly Lewis basic substituted pyridines 4-dimethylaminopyridine (DMAP) and 4-tert-butylpyridine (4-*t*BuPy), which when reacted with **2** in non-coordinating solvents gave good yields of the deep red-brown compounds **11** and **12**, respectively (Scheme 6).[21] Although in compound **9** (Figure 2) the Mg(Nacnac) heterocycles are significantly distorted from planar, the delocalized backbones of both nacnac ligands in each compound are close to planar and effectively parallel to each other. This contrasts to the situation in **2** in which these planes are close to orthogonal.



Scheme 6: Preparation of Mg(I)-Mg(I) adduct, **9**-**12**

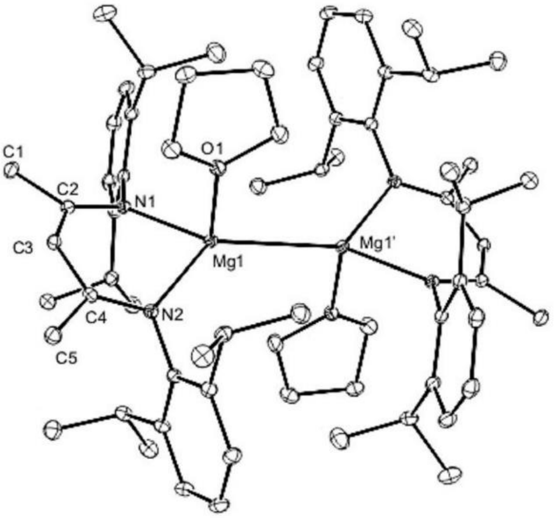
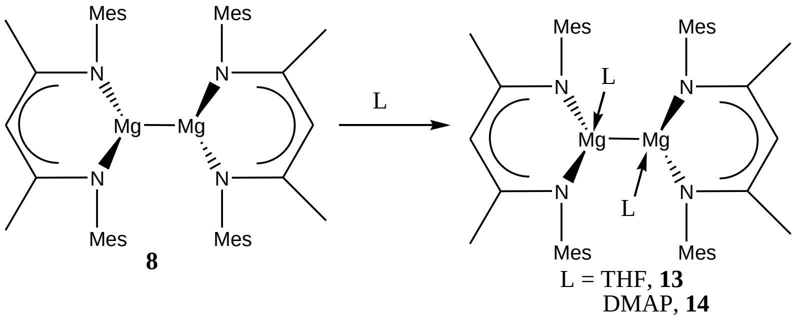


Figure 2: Molecular structure of Mg(I) adduct, **9**[21]

Like compound **2**, dimeric Mg(I) compound **4** with less bulky group also shows adduct formation with THF, (**13)** and DMAP (**14**) with moderate yield (Scheme 7).[18] In contrast, more bolky Mg(I) dimer, **7** does not react when dissolved in THF or in DMAP. Low reactivity of compound **7** possibly due to the sterically well-shielded Mg centers.



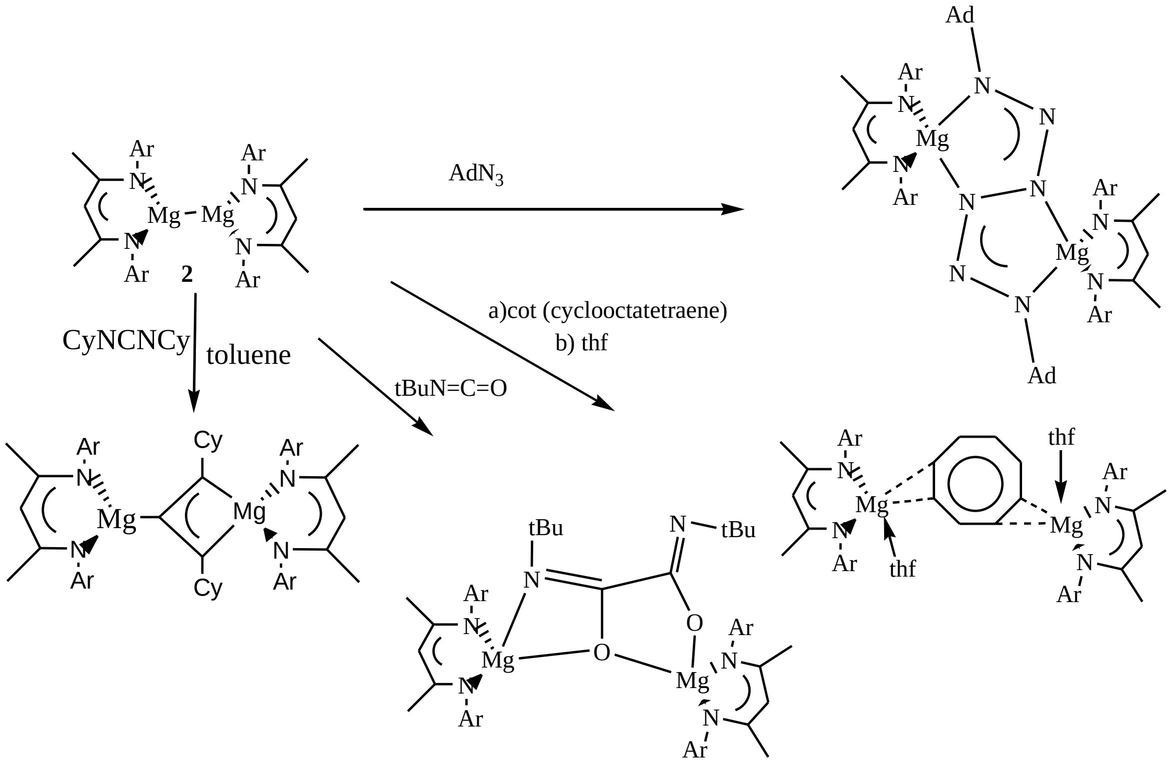
Scheme 7: Adduct formation of **13** and **14**

Till date, the success had in using the bulky guanidinate, Priso$^-$, and the closely related β-diketiminate, in forming stable magnesium(I) compounds has not been extended to the other group 2 metals. It is, however, only a matter of time before the ranks of stable group 2 metal(I) complexes incorporating these or other ligands will expand. Till today, there is only one reports of the calcium(I) inverse sandwich complex, $[\{(THF)_3Ca\}_2(\mu\text{-}C_6H_3Ph_3\text{-}2,4,6)]$.[22]

Reactivity of Magnesium(I) dimer:

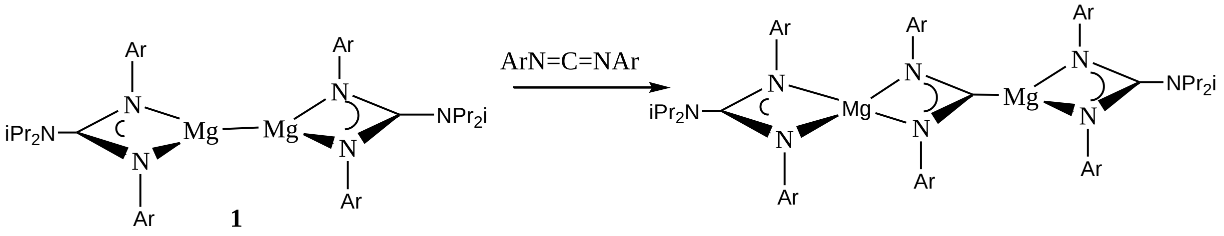
As a reducing agent:

It has been demonstrated in various literature that the magnesium(I) dimer, **2** acts as a facile two-center/two-electron reducing agent towards a variety of N- or O-functionalized unsaturated organic substrates. There are a number of interesting reduction products reported from the reaction of magnesium(I) compounds with unsaturated substrates shows that these compounds may prove useful as selective reducing agents in organic and organometallic synthses.[18,23]
For example, its reactions with CyN=C=NCy (Cy=cyclohexyl), PhN=NPh, AdN3 (Ad=1-adamantyl), or *t*BuN=C=O gave good yields. The mechanism of these reactions is thought to involve coordination of each substrate at the magnesium centers of **2** prior to their reduction (Scheme 8).



Scheme 8: Reactivity of magnesium(I) dimer **2** towards unsaturated substrates

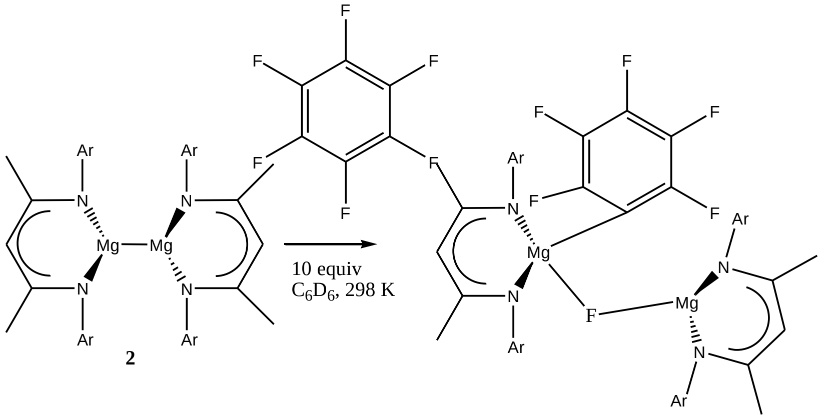
It has also reported that compound **1** can act as a reducing agent with the bulky carbodiimide, ArN=C=Nar (Scheme 9).[23a, 24]



Scheme 9: Reactivity of **1** with unsaturated substratrate

Activation of aromatic C-F bond:

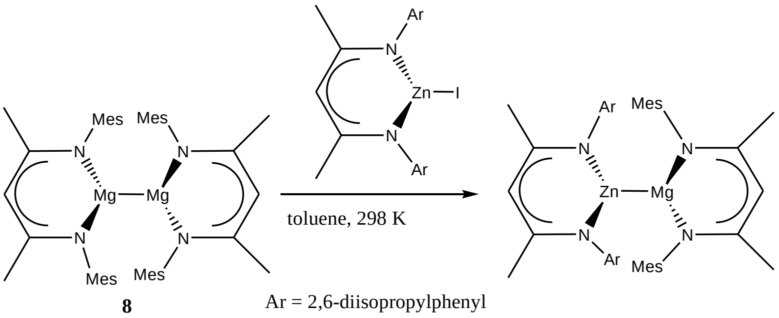
Bakewell et. al. shows that C-F bond activation using low valent Mg(I) dimer, **2** was carried out using fluoroarenes. The reaction results in the formation of a new Mg-C bond and a new Mg-F bond (Scheme 10).[25]



Scheme 10: C-F bond activation of fluoroarenes using Mg-Mg reagents

Metathesis reaction:

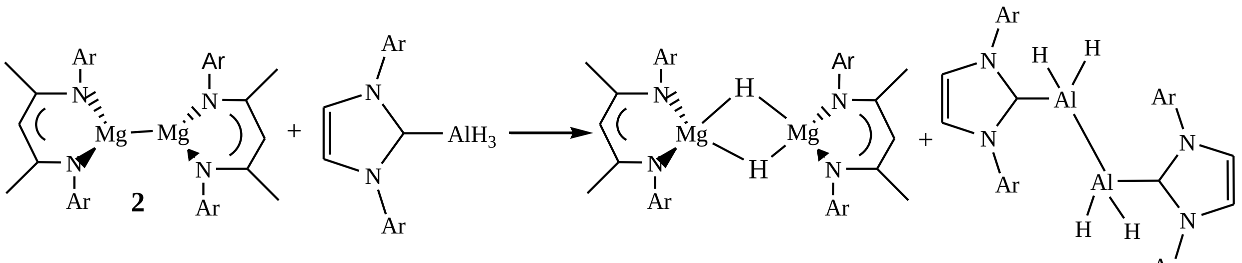
A novel complex containing a new Mg-Zn bond, was synthesized by the stoichiometric reaction of the corresponding zinc iodide with **8** via metathesis reaction (Scheme 11).[25] There are also report on synthesis of Mg-Mn bonded complexes using Mg(I) dimer and Mn-precursor complex.[26a] Mg-Ga bonded compound also reported.[26b]



Scheme 11: preparation of polar Zn-Mg heterobimetallics

Hydrogenation reaction:

The results of a computational study of the reaction of dihydrogen with models of the guanidinato coordinated magnesium(I) dimer, **1**, implied that its hydrogenation, to give [{(Priso)Mg(μ-H)}$_2$], should be exothermic by as much as 25 kcal mol^{-1}.[27] However, in practice, **1** and the related dimers, **2** and **7**, do not react with H_2 under 1 or 5 atm. pressure, and at temperatures of 80°C.[9,18] The lack of reactivity of the magnesium(I) dimers towards dihydrogen under ambient conditions, no doubt reflects a significant kinetic barrier to their hydrogenation, as is known to be the case for the exothermic (ΔH = -17.9 kcal mol^{-1}) hydrogenation of magnesium metal to give MgH_2.[28] The hydrogenation of **2** and **8** was eventually achieved through their reactions with a series of aluminium(III) hydride complexes by formation of neutral aluminium(II) hydride complexes as by product. One of such reaction of compound **2** with aluminium(III) hydride is shown in Scheme 12.[29] Metal-metal bonded compounds with uncommon low oxidation state have been reviewed recently by Cao et. al.[30]



Ar=2,6-diisopropylphenyl

Scheme 12: Hydrogenation of compound **2** using aluminium hydride complex

Conclusion and outlook:

Dimeric magnesium(I) compounds with Mg–Mg single bonds can be stable by using suitable bulky chelating ligands for their kinetic protection from disproportionation into Mg^{II} species and Mg-metal. Several dimeric magnesium(I) complexes have been isolated to date and all those compounds are air- and moisture sensitive, but that can be thermally stable up to 300ºC. These “bottleable” magnesium(I) dimers, especially those stabilised by sterically demanding β-diketiminate ligands, have proven valuable as hydrocarbon soluble, stoichiometric, selective and safe reducing agents in organic and organometallic synthesis, and their reactivity is generally inversely proportional to the steric demand of their ligand sphere. The chemistry of the magnesium(I) dimers has been rapidly expanding in just over a decade and the future promises exciting developments. These compounds will certainly find many more uses as reducing agents and in other chemical applications. The reactivity of Mg(I) dimer towards hydrogenation, methathesis, C-F activation, adduct formation reaction and most important as a reducing agent have already been studied and discussed in this report. Further, the synthesis of stable other subvalent group 2 metal have not been explored till date.

References

1. F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds between Metal Atoms,* 3rd ed.; Springer: New York, 2005.
2. A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science,* 2004, *305*, 1755.
3. T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science,* 2005, *310*, 844.
4. I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science,* 2004, *305*, 1136.
5. X. Wang, L. Andrews, *J. Chem. Phys. A*, 2004, *108*, 11511.
6. S. Petrie, *Aust. J. Chem.,* 2003, *56*, 259.
7. P. G. Jasien, C. E. Dykstra, *J. Am. Chem. Soc.*, 1983, *105*, 2089.
8. L. A. Tjurina, V. V. Smirnov, D. A. Potapov, S. A. Nikolaev, S. E. Esipov, I. P. Beletskaya, *Organometallics*, 2004, *23*, 1349.
9. a) S. P. Green, C. Jones, A. Stasch, *Science*, 2007, *318*, 1754; b) M. Westerhausen, *Angew. Chem.*, 2008, *120*, 2215; *Angew. Chem. Int. Ed.*, 2008, *47*, 2185.
10. A. Velazquez, I. FernJndez, G. Frenking, G. Merino, *Organometallics*, 2007, *26*, 4731.
11. M. Westerhausen, M. GKrtner, R. Fischer, J. Langer, L. Yu, M. Reiher, *Chem. Eur. J.*, 2007, *13*, 6292.
12. P. G. Jasien, C. E. Dykstra, *Chem. Phys. Lett.,* 1984, *106*, 276.
13. Y. Liu, S. Li, X.-J. Yang, P. Yang, B. Wu, *J. Am. Chem. Soc.*, 2009, *131*, 4210.
14. X. Zhang, S. Li, Q-S Li, *Molecular Physics*, 2009, *107(8-12)*, 855.
15. X. Li, S. Huo, Y. Zeng, Z. Sun, S. Zheng, L. Meng, *Organometallics*, 2013, *32*, 1060.
16. J. A. Platts, J. Overgaard, C. Jones, B. B. Iversen, A. Stasch, *J. Phys. Chem. A*, 2011, *115*, 194.
17. J. Overgaard, C. Jones, A. Stasch, B. B. Iversen, *J. Am. Chem. Soc.*, 2009, *131*, 4208.
18. S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.*, 2010, *16*, 938.
19. A. Stasch, C. Jones, *Dalton Trans.*, 2011, *40*, 5659.
20. A. Stasch, *Angew. Chem. Int. Ed.*, 2014, *53*, 10200.
21. S. P. Green, C. Jones, A. Stasch, *Angew. Chem.*, 2008, *120*, 9219; *Angew. Chem., Int. Ed.*, 2008, *47*, 9079.
22. S. Krieck, H. Görls, L. Yu, M. Reiher, M. Westerhausen, *J. Am. Chem. Soc.*, 2009, *131*, 2977.
23. a) S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem. Int. Ed.*, 2009, *48*, 2973; b) A. Stasch, C. Jones, *Dalton Trans.*, 2011, *40*, 5659.
24. C. Jones, *Coordination Chemistry Reviews*, 2010, *254*, 1273.
25. C. Bakewell, B. J. Ward, A. J. P. White, M. R. Crimmin, *Chem. Sci.*, 2018, *9*, 2348.
26. a) J. Hicks, C. E. Hoyer, B. Moubaraki, G. L. Manni, E. Carter, D. M. Murphy, K. S. Murray, L. Gagliardi, C. Jones, *J. Am. Chem. Soc.*, 2014, *136*, 5283; b) O. Bonello, C. Jones, A. Stasch, W. D. Woodul, *Organometallics*, 2010, *29*, 4914.
27. A. Datta, *J. Phys. Chem. C*, 2008, *112*, 18727.
28. B. Bogdanovic, A. Ritter and B. Spliethoff, *Angew. Chem. Int. Ed. Engl.*, 1990, *29*, 223.
29. Y-C. Tsai, *Coordination Chemistry Reviews*, 2012, *256*, 722.
30. C-S. Cao, Y. Shi, H. Xu, B. Zhao, *Coordination Chemistry Reviews*, 2018, *365*, 122.