

## Low-valent magnesium dinuclear complexes and their reactivity

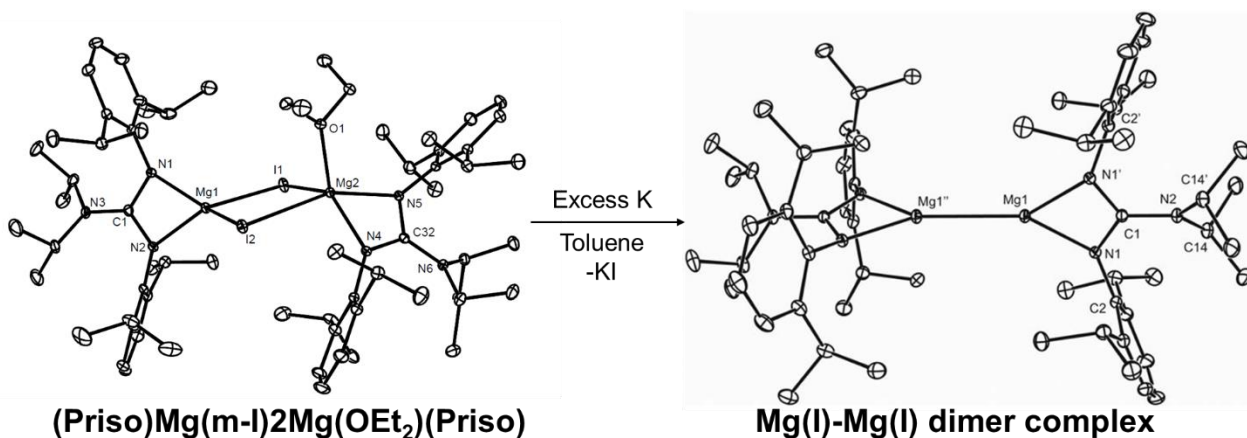
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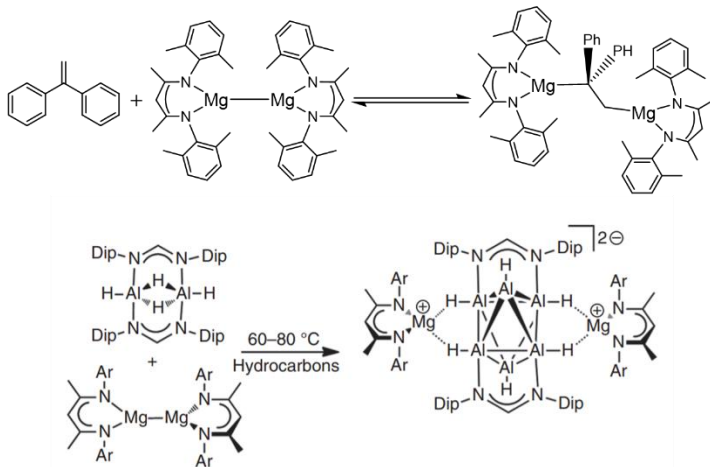
Alkaline earth metals (group 2 metals), such as beryllium, magnesium, and calcium are known as the exclusive formation of the +2 oxidation state. This is because they have low electronegativities and get easily oxidized to form the same electron configuration of noble gas such as He and Ne<sup>1</sup>. Thus, before the Mg(I)-Mg(I) dimer complex was isolated in 2007, the only reported low-valent alkali earth metal complex was calcium hexamine, Ca(NH<sub>3</sub>)<sub>6</sub> which is made in liquid ammonia, but it was not isolated as a crystal, but only analyzed by neutron powder diffraction<sup>2</sup>.

Scientists predicted the possibility of the existence of a low-valent s-block metal dimer complex, based on computational studies and some spectroscopic evidence, but it is a highly undesirable reaction because the reaction is thermodynamically unfavorable and easily undergoes disproportionation between two metal centers. For example, the reaction of Mg atoms with H<sub>2</sub> gas made Mg(I) dimer, HMgMgH, and it was trapped only at an extremely low temperature of 10 K<sup>3</sup>. Also, ClMgMgCl was observed by IR spectroscopy at 10 K in an argon matrix<sup>4</sup>.



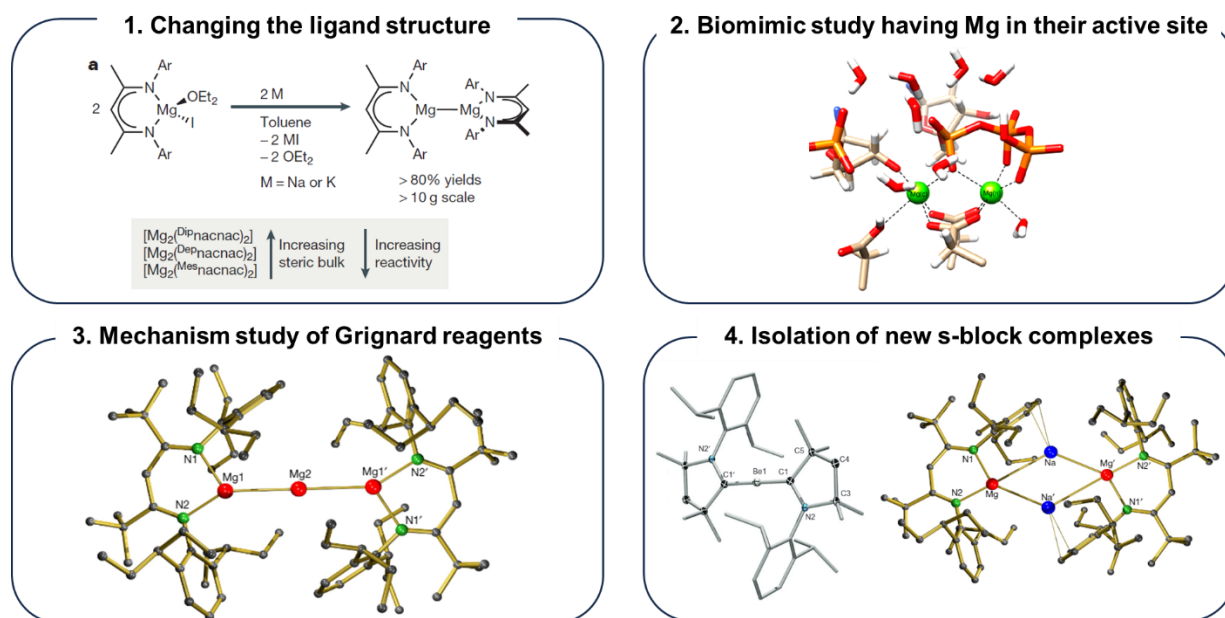
**Figure 1.** First isolated Mg(I)-Mg(I) complex. Adapted from Ref. 5.

To isolate thermodynamically unstable metal complex, the Stasch group tried to kinetically stabilize the reactive metal center by using super bulky ligands such as guanidinate, or  $\beta$ -diketiminates. Gratifyingly, they could get the first isolated magnesium dinuclear complex having the +1 oxidation state<sup>5</sup> (Figure 1). In this study, they found that the low-valent Mg(I) dinuclear complex could be a powerful reducing agent as the complex reacted with carbodiimide CyNCNCy (Cy is cyclohexyl).



**Figure 2.** Examples of the reactivity of low-valent Mg complex as a reducing agent<sup>7,8</sup>.

Following studies of the low-valent Mg(I) dimer complex are expanding the area of reducing agent<sup>6</sup>. Even though there are many traditional reductants such as  $\text{KC}_8$ , metallocene,  $\text{SmI}_2$ , and alkali metals (Na or K), but these have some drawbacks such as low solubility, over reduction, byproducts, and safety problems. The low-valent s-block complexes could be an alternative option because it is soluble in a hydrocarbon solvent such as toluene, can proceed stoichiometric reaction. Also, it could be easily separated after the reaction as precipitation, and it is safer than alkali metals. With these advantages, many promising results as a reductant were reported both in organic and inorganic synthesis recently<sup>7,8</sup> (Figure 2).



**Figure 3.** Promising research area with the low-valent Mg complex.

There are many promising research areas with low-valent Mg complexes (Figure 3). 1) With the systematic ligand structure changes could adjust the reducing ability. As the bulkiness of the ligand changes, the reactivity of the complex will be controllable. This is quite different from selecting a conventional reductant<sup>6</sup>. 2) The mechanism study of Mg-containing enzymes such as DNA polymerase  $\beta$  and arginase can be available<sup>9</sup>. 3) Mechanism of Grignard reagent formation is still unknown but there is some evidence that the formation proceeded with low-valent Mg<sup>10</sup>. 4) The development of a new low-valent group 2 metal complex is also possible. For instance, there are many complexes that are not isolated yet such as Mg(I) mononuclear complex, Ca(I) mononuclear complex. Overall, the development of the low-valent Mg complex will shed light on many unexplored areas<sup>1</sup>.

## References

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