

# The Discovery of New Oxidation States: The Chemistry of Magnesium(I) and Zinc(I)

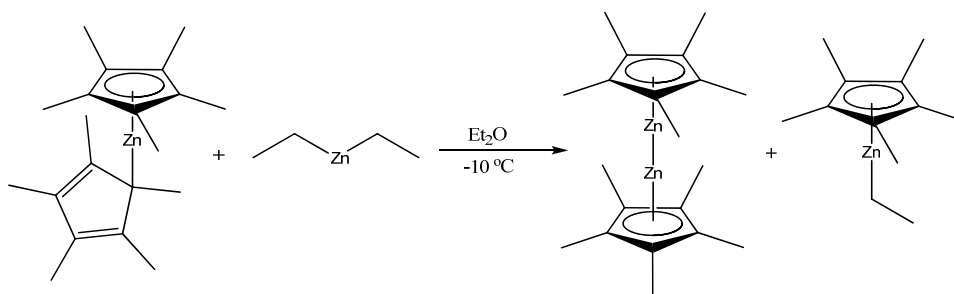
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The stability of an oxidation state is determined by the chemical environment of the metal center. This stability is usually kinetic and can be increased by a proper choice of ligands. For many years zinc(I) and magnesium(I) were considered inaccessible at room temperature, owing to their facile disproportionation to the metallic and +2 oxidation states.<sup>1</sup> The recent syntheses of several  $Zn^I$  and  $Mg^I$  complexes has overturned this idea and has provided important insights into the stereoelectronic factors that stabilize these unusual oxidation states.<sup>2</sup>

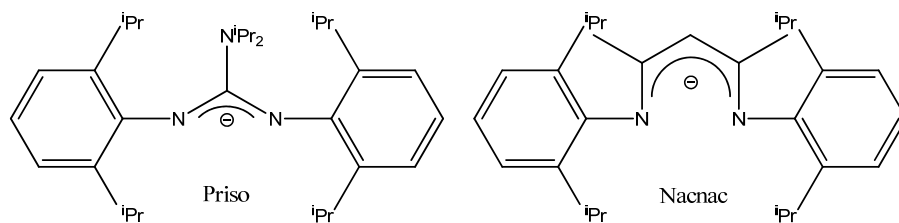
The first  $Zn^I$ - $Zn^I$  complex,  $Cp^*_2Zn_2$ , was synthesized in 2004 by the treatment of  $Cp^*_2Zn$  with diethyl zinc (Scheme 1). This compound was the first metal-metal bonded metallocene that contained no bridging atoms.<sup>3-5</sup> Later, the  $(\eta^5-C_5Me_4Et)_2Zn_2$  analog was added to this class.<sup>4</sup>



**Scheme 1: Synthesis of dcamethyldizincocene<sup>3</sup>**

X-ray diffraction, <sup>1</sup>H-NMR, and MS experiments ruled out the possibility that these complexes were  $Zn^{II}$  compounds of stoichiometry  $Cp^*_2Zn_2H_2$ .<sup>3,4</sup> An additional  $Zn^I$ - $Zn^I$  compound has been synthesized using  $Cp^*_2Zn_2$  as a starting material: the  $Zn_2(Mesnacnac)_2$  complex was synthesized by treatment of  $Cp^*_2Zn_2$  with  $MesnacnacH$ , a mesityl substituted  $\beta$ -ketiminate, in diethyl ether to give a 40% yield.<sup>6</sup> Zinc(I) compounds with other  $\beta$ -ketiminate ligands have also been reported.<sup>6-11</sup> A zinc(I) complex bearing bulky aryl ligands can also be isolated: The addition of sodium to  $Ar^iZn^I$  ( $Ar^i=C_6H_3-2,6-(C_6H_3-2,6-^iPr_2)_2$ ) in diethyl ether afforded the corresponding  $Zn^I$ - $Zn^I$  product, which adopted a linear conformation similar to those of the other zinc compounds detailed above.<sup>12-13</sup>

In 2007, two  $Mg^I$ - $Mg^I$  compounds were reported.<sup>2</sup> As for several of the  $Zn^I$ - $Zn^I$  complexes, sterically bulky chelating ligands (Figure 1) were utilized to stabilize the magnesium(I) oxidation state. Specifically, the reduction of  $(priso)Mg(\mu-I)_2Mg(OEt_2)(priso)$  with potassium in toluene afforded  $Mg_2(priso)_2$ , and the reduction of  $Mg^I(OEt_2)(nacnac)$  with K in toluene afforded the  $Mg_2(nacnac)_2$ .<sup>2</sup>



**Figure 1: Nacnac and priso ligands<sup>2</sup>**

Crystallographic experiments, spectroscopic data, and theoretical calculations strongly support the claim that these products were a  $\text{Mg}^{\text{I}}$  complexes and not  $\text{Mg}^{\text{II}}$  complexed with bridging hydrides. In both of the  $\text{Mg}^{\text{I}}$  dimers the planes of the heterocycles were orthogonal, whereas the heterocycles in the hydride bridged  $\text{Mg}^{\text{II}}$  dimer were coplanar.<sup>2,14</sup> No hydride resonance could be located in the  $^1\text{H-NMR}$  spectrum and the high resolution EI-MS data matched the calculated mass distribution for the hydride-free species. Calculations on a model complex,  $\text{Mg}_2[(\text{Ar}'\text{N})_2\text{C}(\text{NMe}_2)]_2$  ( $\text{Ar}' = 2,6\text{-dimethylphenyl}$ ) at the B3LYP/6-31G\* and BP86/6-31G\* level (with an additional set of diffuse functions on Mg) revealed a mostly Mg-Mg  $\sigma$ -bonding HOMO.<sup>2</sup> These compounds exhibited interesting reaction patterns and have been characterized as “two-center/two electron” reductants: the  $[\text{Mg}(\text{nacnac})]_2$  compound facilitated two electron reductions of cyclooctatetraene and a cyclohexyl substituted carbodiimide.<sup>2,15</sup>

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