

A Review on Organometallic M(I)–M(I) Single Bonded Chemistry of Group 2 and 12 Metals

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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. Hg(I)–Hg(I) compounds are known from 14th century. But, the organometallic Cd(I)–Cd(I) and Hg(I)–Hg(I) complexes are reported recently. In 2007, Jones and co-workers were successful in isolating a group 2 metal Mg(I) dimer containing a Mg–Mg single bond. But, till date there is not a single Ca(I) dimer reported. This review article provides some information about such type of complexes and there various applications.

Keywords: Organometallic, metal-metal single bond, Zinc, Cadmium, Mercury, Magnesium

1. Introduction

The study of compounds that contain metal atoms held together by one or more shared electron pairs is one of the most important and attractive chapters of modern inorganic chemistry. Traditionally, interest in compounds with metal–metal bonds has concentrated in complexes on the transition-metal elements, in particular in complexes that contain multiple bonds between metal atoms. In this context, not only single bond there are also reports on metal–metal triple and quadruple-bond¹. For transition-metal elements, two sigma bonds, one pair of π -bonds, and one pair of δ -bonds are possible owing to the availability of s- and d- orbitals. There are also report on quintuple bond in $\text{Cr}_2\text{Ar}'_2$ results from five metal-metal bonding molecular orbitals².

The formation of such compounds in main group elements 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 disfavoured. Even though Hg_2^{2+} could be known since 14th Century, the oxidation state +1 for the lighter element (Zn and Cd) was believed to be accessible to room temperature. Carmona's synthesis of Zn(I) dimer³, the stabilization of the Zn_2^{2+} fragment succeeded with other bulky substituents which allowed the isolation of the homologous Cd(I) and Hg(I) derivatives, too⁴. However, given the unexpected stability of zinc(I) dimers, and the chemical similarities between zinc and the group 2 metals, a number of theoretical studies have predicted that thermally stable compounds of the type RM-MR ($\text{M} = \text{Be}, \text{Mg}, \text{or Ca}$) should be accessible using the correct choice of ligands⁵. Recently, Cameron Jones and co-workers have reported the bulky guanidinate or β -diketiminate coordinated organometallic Mg(I) dimers, $[\text{LMg-MgL}]$ ($\text{L} = [(\text{ArN})_2\text{CN}^i\text{Pr}_2]^-$, priso- or $[(\text{ArNCMe})_2\text{CH}]^-$, nacnac-, $\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_2$ -2,6)⁶. There are also several examples of molecular RMg-MgR derivatives known having bulky R groups for kinetic protection of the reactive Mg-Mg bonds⁷. These dimeric magnesium(I) complexes are surprisingly stable and offer a rich coordination and redox chemistry, acting as selective double one-electron reductants. Like the other alkaline earth-metals (group 2 metals), calcium is present in all its known stable compounds in the +2 oxidation state. The reduction of other metal ions has involved the formation of direct metal-metal bonds.

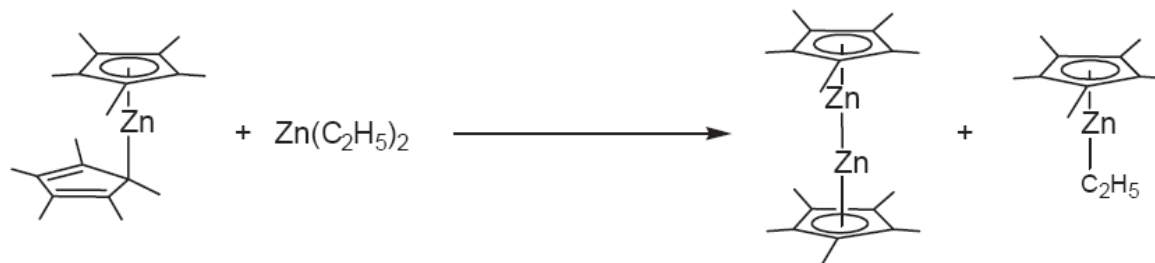
Calculations have shown that Ca-Ca bonds should also be feasible, although the Ca-Ca bond energy (105 kJmol^{-1}) is in the same order of magnitude as the atomization energy of calcium metal (150.6 kJmol^{-1}). Nevertheless, NBO calculation of the HOMO of the optimized linear structure of $[(2,6\text{-Ph}_2\text{C}_6\text{H}_3)\text{Ca-Ca}(\text{C}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]$ clearly shows a large contribution to the electron density between the metal atoms which indicate that the *ortho*-substituents stabilize diaryl dicalcium(I) not only for steric but also for electronic reasons⁸. These studies support the premise that very bulky groups should be able to stabilize Ca-Ca moieties, but bulky groups are necessary in order to sterically shield the reactive metal-metal bond⁹. But till today, there is no report on Ca-Ca dimer.

In the following, well-characterized molecular compounds of Group 2 and Group 12 elements that contain M-M single bonds will be reviewed.

2. Chemistry of Group 12 M-M single bonded complexes:

2.1. Zn(I) dimers: Dimeric Zn(I) compounds of the general formula $[\text{RZn-ZnR}]$ ($\text{R} =$ monoanionic ligand) are known as stable compounds since Carmona and co-workers synthesized the compound $[\text{Cp}^*\text{Zn-ZnCp}^*]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in 2004 (Scheme 1 and Figure 1)³. Initially, this complex was obtained by the reaction of $[\text{Cp}^*_2\text{Zn}]$ with ZnEt_2 and subsequently, an improved synthesis from $[\text{Cp}^*\text{K}]$, KH and ZnCl_2 was reported¹⁰. These complexes are typically obtained by reduction of zinc(II) precursors complexes with strong reducing agents such as Na, K, KC_8 , and so on or by ligand substitution reactions on $[\text{Cp}^*\text{Zn-ZnCp}^*]$. Notable examples of Zn-Zn bonded complexes include the terphenyl-

stabilized complex $[\text{Ar}'\text{Zn}-\text{ZnAr}']$ ($\text{Ar}' = \text{C}_6\text{H}_3-2,6\text{-Dip}_2$) ($\text{Dip} = \text{C}_4\text{H}_3-2,6\text{-}i\text{Pr}_2$) of dimeric Zn(I) complexes with two-coordinated linear Zn atoms¹¹. The majority of Zn–Zn bonded complexes however feature a range of sterically demanding anionic N,N' -chelating ligands such as the β -diketiminato examples $[\{(\text{Dip}^{\text{nacnac}})\text{Zn}\}_2]$ ($\text{Dip}^{\text{nacnac}} = \text{HC}\{\text{MeCN}(\text{Dip})\}_2$)¹² and $[\{^{\text{Mes}}\text{nacnac}\text{Zn}\}_2]$ ($^{\text{Mes}}\text{nacnac} = \text{HC}\{\text{MeCN}(\text{Mes})\}_2$, $\text{Mes} = \text{C}_6\text{H}_2-2,4,6\text{-Me}_3$)¹³.



Scheme 1: Synthesis of $[\text{Cp}^*\text{Zn}-\text{ZnCp}^*]$ by Carmona *et. al.*³

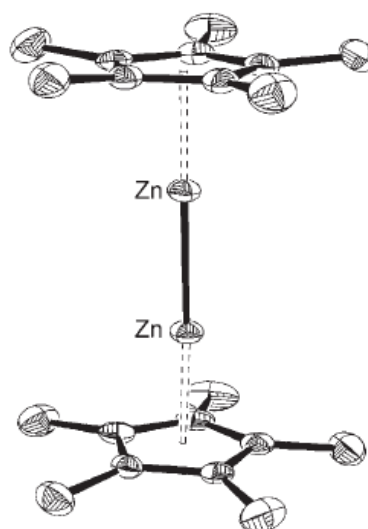
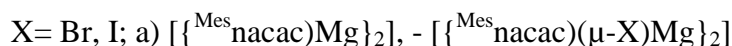
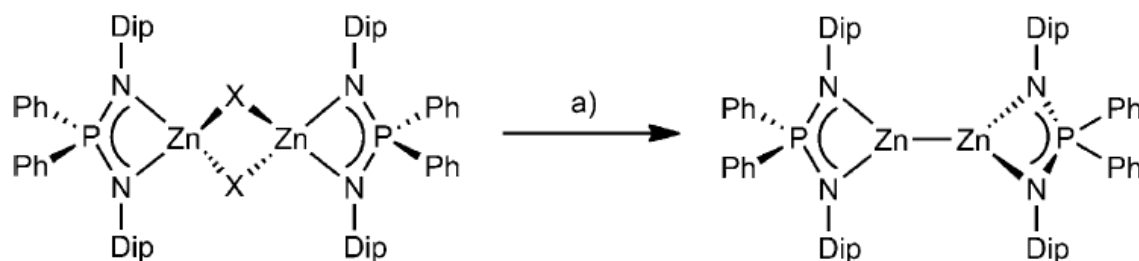


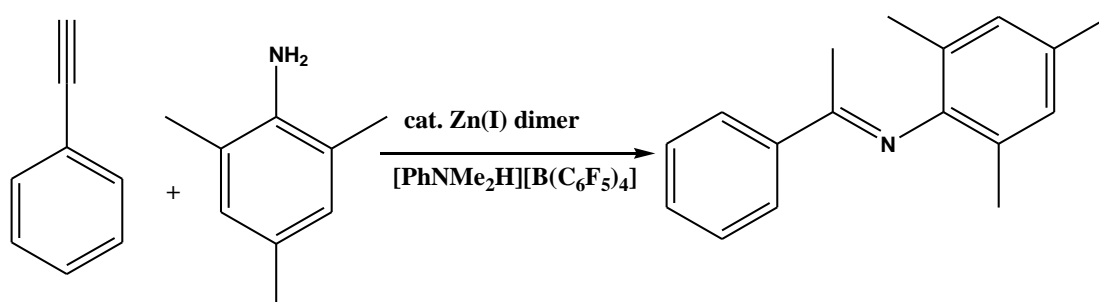
Figure 1: ORTEP view of dizincocene compound $[\text{Cp}^*\text{Zn}-\text{ZnCp}^*]$

The two cyclopentadienyl rings in each molecule (Figure 1) are parallel and separated by a distance of approx. 6.40 Å, which allows adoption of an eclipsed geometry without steric interaction between their Me-substituents. The two Cp* rings are sandwich two directly bonded Zn atoms, thus providing an unprecedented dimetalocene structure. Zn–Zn bonded complex are also reported using sterically demanding diiminophosphinate ligand (Scheme 2)¹⁴.



Scheme 2: Synthesis of Zn–Zn complex of the diiminophosphinate ligand¹⁴.

Very recently, P. W. Roesky and co-workers have reported the inter- and intra-molecular hydroamination reaction with high yield catalyzed by Zn(I) dimer (Scheme 3)¹⁵.



Scheme 3: Intermolecular hydroamination reaction by Zn(I) dimers

2.2. Hg(I) dimers: Apart from the well-known M(II) state common to Group 12 elements, the M(I) state in the form of M_2^{2+} ions is common for mercury and uncommon for zinc and cadmium. This situation is due to the large ionization enthalpy of the Hg atom, which is a consequence of the relativistic stabilization of its 6s atomic orbital. Thus, a strong Hg–Hg bond results when two Hg^+ ions share a pair of 6s electrons¹⁶.

Hg_2Cl_2 have been known since 14th century and the other Hg_2X_2 (dimercury dihalides) were available in the 19th century¹⁷. Organometallic derivative of Hg_2^{2+} ions are uncommon, but recently molecular sigma-bonded silyl derivative, $\text{Hg}_2[\text{Si}(\text{SiMe}_2\text{SiMe}_3)_3]_2$ was prepared (Figure 2)¹⁸. Power and co-workers describe the formation and structural characterization of the dimercury derivative, $\text{Hg}_2\text{Ar}'_2$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$)⁴. This compound could not be obtained by direct arylation of Hg_2I_2 owing to disproportionation to Hg^0 and Hg^{II} , but reduction of $\text{Hg}(\text{Ar}')\text{I}$ with KC_8 provided the desired compound.

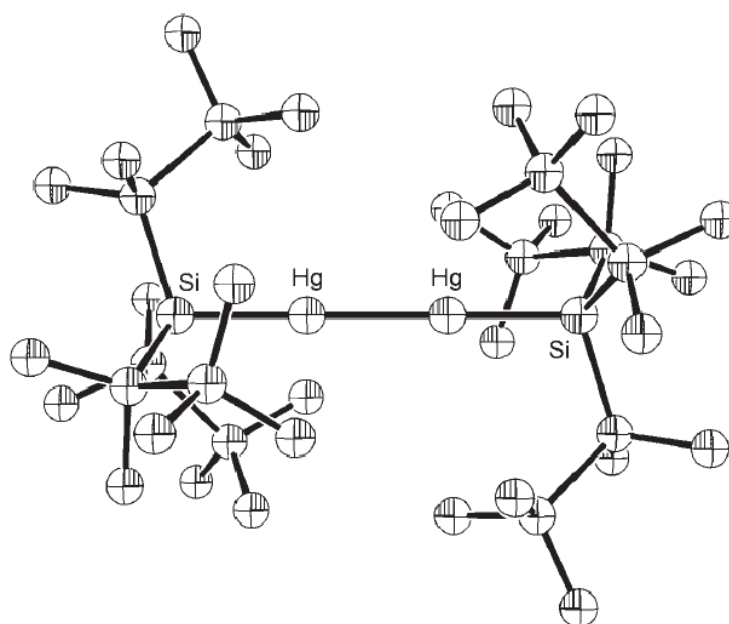


Figure 2: Molecular structure of $\text{Hg}_2[\text{Si}(\text{SiMe}_2\text{SiMe}_3)_3]_2$

2.3. Cd(I) dimers: There are very few reports on stable Cd–Cd bonded compounds till now. Detailed structural information exists only for the ionic species $[\text{Cd}_2][\text{AlCl}_4]_2$ ¹⁹. However, organometallic compound with Cd–Cd bond has been synthesized by treatment of CdCl_2 with $\text{TITP}^{\text{Me}_2}/\text{LiBHEt}_3$ ²⁰. In 2006, P. P. Power and co-workers reported the Cd(I) dimer $[\text{Ar}'\text{Cd}-\text{CdAr}']$ ($\text{Ar}' = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6-^i\text{Pr}_2)_2$) (Figure 3)²¹. Compound was synthesized by addition of 2 equiv of NaH to $\text{Ar}'\text{CdI}$ in THF. The Cd–Cd distance in this compound is reported 2.6257(5) Å.

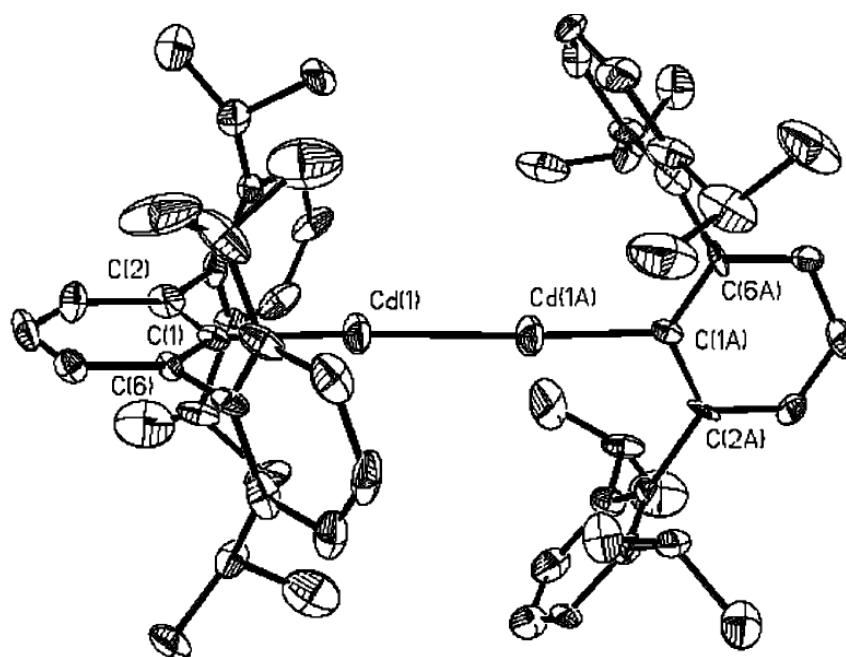
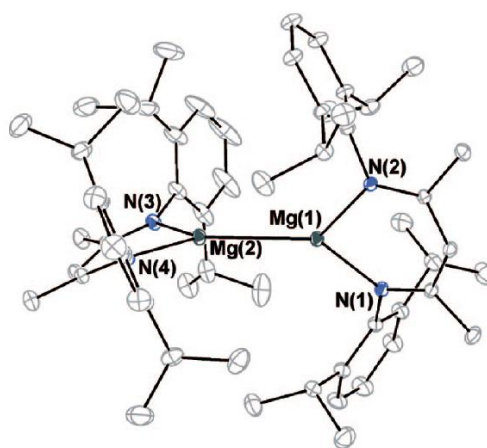


Figure 3: Molecular structure of $[\text{Ar}'\text{Cd}-\text{CdAr}']$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$)

3. Chemistry of Group 2 M-M Single Bonded Complexes:

3.1. Mg(I) dimers: Recently, Cameron Jones and co-workers have reported the bulky guanidinate or β -diketiminato coordinated organometallic Mg(I) dimers, $[\text{LMg}-\text{MgL}]$ ($\text{L} = [(\text{ArN})_2\text{CN}^i\text{Pr}_2]^-$, priso- or $[(\text{ArNCMe})_2\text{CH}]^-$ (Figure 4), nacnac-, $\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_2\text{-2,6}$)⁶. These are remarkably thermally stable compounds with Mg–Mg distances of 2.85 Å (approx). Theoretical studies on a model of $[\{\text{Mg}\{[(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\text{N}]_2\text{CNMe}_2\}\}_2]$, showed it to contain a high-s-character, covalently bonded Mg_2^{2+} core, having largely ionic interactions with its guanidinate ligands. Cameron Jones and co-workers were demonstrated a facile insertion of a carbodiimide, CyNCNCy ($\text{Cy} = \text{cyclohexyl}$), into the Mg–Mg bond to give the unusual magnesium magnesioamidinate complex $[(\text{nacnac})\text{Mg}\{\mu\text{-C}(\text{NCy})_2\}\text{Mg}(\text{nacnac})]$ ^{7b}. There are several examples of molecular $\text{RMg}-\text{MgR}$ derivatives known⁷.

Figure 4: Molecular structure of $[\text{RMg}-\text{MgR}]$ ($\text{R} = [(\text{ArNCMe})_2\text{CH}]^-$, $\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_2\text{-2,6}$)

Preparation of M–M bonded compounds via the reduction of “normal oxidation state” precursor complexes using insoluble, and harsh reducing agent (e.g., alkali metals, magnesium, KC_8 etc) can be problematic, and often leads to “over-reduction” of the precursor complex and/or the occurrence of other side reactions. Recently, Mg(I) dimers have been used as reducing agent to prepare a series of group 14 element(I), transition metal element (e.g. Fe(I), Mn(I)) and also Zn(I) dimers²². Synthetic routes to Mg(I) compounds are straightforward and generally high yielding which, in combination with their advantageous physical and chemical properties, make them potentially attractive reducing agents for a variety of synthetic chemists.

3.2. Ca(I) Complexes: The recently reported synthesis of the inverse Ca(I) sandwich complex (Figure 5) shows an alternative for stabilization of Ca(I) derivatives, the only compound till date²³. The central structural fragment consists of a strictly planar 1,3,5-triphenylbenzene anion with two $(\text{thf})_3\text{Ca}$ moieties bound to the arene. To date, however, this

compound is the only example of a stable subvalent organometallic compound of a heavier alkaline earth metal. In the literature, this is the only preparative method reported to achieve the Ca(I) compound but a Ca(I)–Ca(I) bonded complex is still unknown.

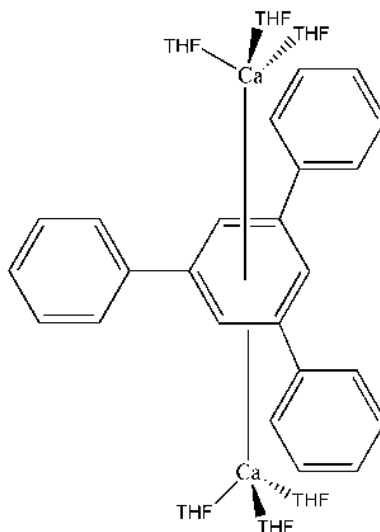


Figure 5: Ca(I) sandwich complex

4. Summary and outlook

The structural characterization of the dizincocene [$\text{Cp}^*\text{Zn}-\text{ZnCp}^*$] has triggered research in this field, which has resulted in remarkable growth of the experimental and theoretical chemistry of Group 12 and 2 compounds with metal-metal bonds. Studies have concentrated on the synthetic, structural, and electronic characteristics of those compounds. Mg(I) dimers are used for mild reduction reaction for synthesis of other M–M bonded chemistry²². Furthermore, the research for related M–M structures of this kind, for example for the lighter Group 2 elements (especially beryllium and calcium), also appears to be an attractive research target.

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