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Chemistry of Soluble *β*-Diketiminatoalkaline-Earth Metal Complexes with M−X Bonds (M = Mg, Ca, Sr; X = OH, Halides, H)

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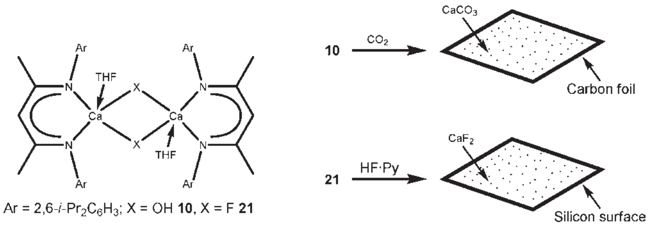
CONSPECTUS



Victor Grignard's Nobel Prize-winning preparation of organomagnesium halides (Grignard reagents) marked the formal beginning of organometallic chemistry with alkaline earth metals. Further development of this invaluable synthetic route, RX + Mg → RMgX, with the heavier alkaline earth metals (Ca and Sr) was hampered by limitations in synthetic methodologies. Moreover, the lack of suitable ligands for stabilizing the reactive target molecules, particularly with the more electropositive Ca and Sr, was another obstacle. The absence in the literature, until just recently, of fundamental alkaline earth metal complexes with M−H, M−F, and M−OH (where M is the Group 2 metal Mg, Ca, or Sr) bonds amenable for organometallic reactions is remarkable.

The progress in isolating various unstable compounds of *p*-block elements with *β*-diketiminate ligands was recently applied to Group 2 chemistry. The monoanionic *β*-diketiminate ligands are versatile tools for addressing synthetic challenges, as amply demonstrated with alkaline earth complexes: the synthesis and structural characterization of soluble *β*-diketiminatocalcium hydroxide, *β*-diketiminatostrontium hydroxide, and *β*-diketiminatocalcium fluoride are just a few examples of our contribution to this area of research. To advance the chemistry beyond synthesis, we have investigated the reactivity and potential for applications of these species, for example, through the demonstration of dip coating surfaces with $CaCO_3$ and CaF_2 with solutions of the calcium hydroxide and calcium fluoride complexes, respectively.

In this Account, we summarize some recent developments in alkaline earth metal complex chemistry, particularly of Mg, Ca, and Sr, through the utilization of *β*-diketiminate ligands. We focus on results generated in our laboratory but give due mention to work from other groups as well. We also highlight the closely related chemistry of the Group 12 element Zn, as well as the important chemistry developed by other groups using the complexes we have reported. Although Mg and Ca are more abundant in living organisms, no other metal has as many biological functions as Zn. Thus Zn, the nontoxic alternative to the heavier Group 12 elements Cd and Hg, occupies a unique position ripe for further exploration.

1. Introduction

Group 2 of the periodic table consists of the alkaline earth metals (beryllium, magnesium, calcium, strontium, barium, and radium) having ns^2 valence shell electronic configuration. Magnesium and calcium are extremely indispensable for every living system, whereas strontium is essential for sea life.[1a] This biological relevance has always been one of the key factors to explore their organometallic chemistry for a comparative understanding.[1,2] The early and remarkable Grignard route (RX + Mg) to organomagnesium halides (RMgX) did not pave the way for the heavier congeners due to the activation problems associated with heavier

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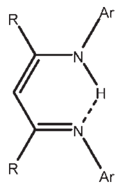
CHART 1. Various *β*-diketimine Ligands **1**−**5**



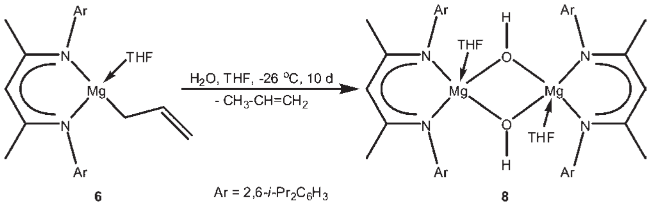
Ar = 2,6-*i*-$Pr_2C_6H_3$; R = Me **1**
Ar = $CH_2CH_2NMe_2$; R = Me **2**
Ar = 2,6-*i*-$Pr_2C_6H_3$; R = CF_3 **3**
Ar = 2,6-*i*-$Pr_2C_6H_3$; R = *t*-Bu **4**
Ar = *t*-Bu; R = Me **5**

metals (Ca or Sr) and high reactivity of RMX (M = Ca or Sr) resulting from the increasing electropositive character of the metals as we descend down Group 2.[1] This leads to Wurtz type coupling (e.g., 2RI + Ca → RR + CaI_2) and ether cleavage (e.g., $RCa(THF)_4I \rightarrow RH + CH_2{=}CH_2 + CH_2CHOCaI$) reactions.[2] The rising electropositive character also makes the Schlenk equilibrium [observed by Schlenk between heteroleptic (RMgX) and homoleptic (R_2Mg and MgX_2) compounds] severe in heavier alkaline earth metal compounds.[1,2] Other periodic trends that play a significant role are the increasing ionic radii and the unsaturation in coordination down the alkaline earth metal series. This leads to oligomerization and eventually decrease in the solubility of the products.[1]

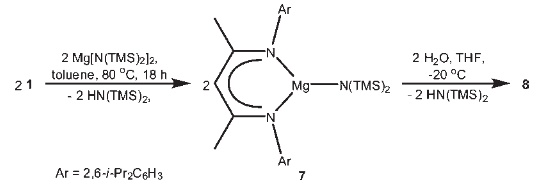
Consistent evolution using various synthetic pathways, ligands, and so forth over several years has taught chemists in recent years the ways of circumventing the encountered problems (vide supra) and to obtain various interesting and stable molecules in recent years which were once assumed to be nonisolable.[1,2] Interest toward the chemistry of nontoxic alkaline earth metals and the synthetic challenges involved attracted us to work in this area, and for that purpose we choose to use the highly versatile monoanionic *β*-diketimine ligands[3] **1** and **2** (Chart 1). Our research has resulted in the preparation of various hydroxide, halide, oxide, and hydride complexes, and this Account will summarize these results with due mention of work carried out by others using *β*-diketimine (**1**, **3**, **4**, **5**, etc.) ligands (Chart 1). Nevertheless, the catalytic applications of *β*-diketiminatoalkaline earth metal complexes will not be discussed in this Account as they are covered extensively in recent reviews.[1a,2b] Also, the aforementioned discussions explicitly reveal that the successful syntheses of most of the *β*-diketiminatoalkaline earth complexes summarized in this Account are achieved only after various unsuccessful attempts, and the details regarding such endeavors will not be presented here.

Zinc, the first Group 12 element, shows ample chemical similarities with lighter alkaline earth metals,[4] and in contrast to its heavier congeners (cadmium and mercury) it is nontoxic. Although magnesium and calcium are much more abundant in living organisms than zinc, it is surprising to note that no other metal has as many functions as zinc. Considering this, this Account will be lopsided at least without a brief foretaste of the corresponding zinc chemistry.

SCHEME 1. Hydrolysis of **6** to Afford *β*-Diketiminatomagnesium Hydroxide **8**



SCHEME 2. Synthesis of *β*-Diketiminatomagnesium Hydroxide **8**



2. Hydrocarbon Soluble Hydroxide Complexes of Magnesium, Calcium, and Strontium

Bochmann and co-workers obtained the first *β*-diketiminatomagnesium hydroxide **8** from a serendipitous hydrolysis of allyl magnesium complex **6** during its recrystallization (Scheme 1).[5]

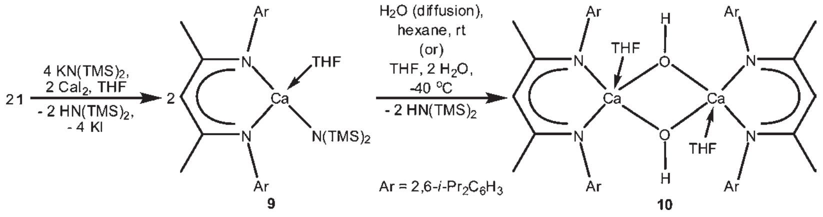
Compound **8** was also obtained through a deliberate synthetic route that involves the hydrolysis of *β*-diketiminatomagnesium amide **7** in tetrahydrofuran (THF) at low temperatures (Scheme 2).[6]

The isolation of **8** encouraged us to explore the possibility of stabilizing the heavier analogues with the same *β*-diketiminate ligand. The premise was apparent with the isolation of *β*-diketiminatocalcium hydroxide **10** by the hydrolysis of *β*-diketiminatocalcium amide **9** (Scheme 3), which was realized in two different routes.[7] The first route consists of very slow diffusion of degassed water into the hexane solution of **9**, thereby achieving its hydrolysis that results in **10**. The other pathway is to carry out the hydrolysis of **9** with one equiv of water at −40 °C. The latter procedure resulted in the better yields of **10**.

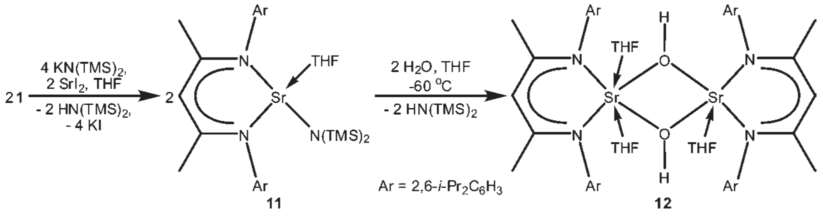
To extend the hydroxide chemistry to strontium, the *β*-diketiminatostrontium amide **11** was prepared by the reaction of **1** with 2 equiv of $KN(TMS)_2$ and 1 equiv of SrI_2 (Scheme 4).[8] Hydrolysis of **11** with one equiv of water at −60 °C resulted in the *β*-diketiminatostrontium hydroxide **12** (Scheme 4).[8]

The presence of M−OH bonds in the hydroxides (**8**, **10**, and **12**) is reflected through the singlet upfield resonances

SCHEME 3. Synthesis of *β*-Diketiminatocalcium Hydroxide **10**



SCHEME 4. Synthesis of *β*-Diketiminatostrontium Hydroxide **12**



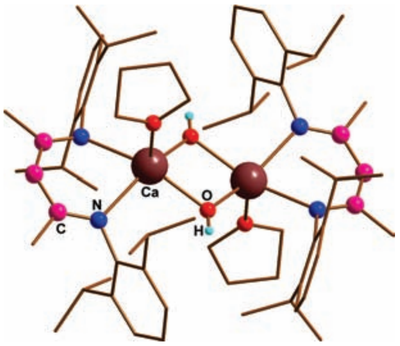
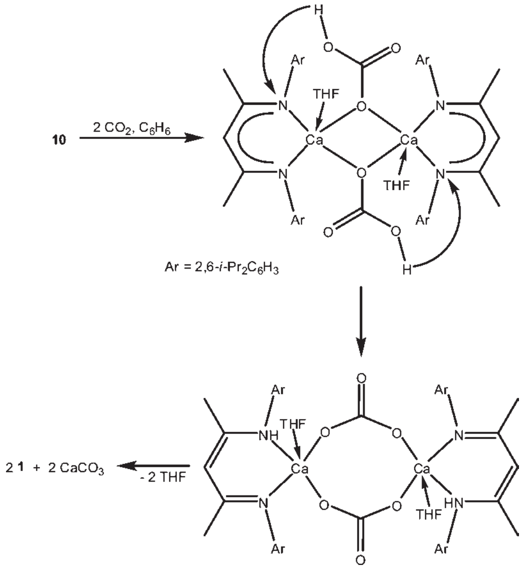


FIGURE 1. Molecular structure of *β*-diketiminatocalcium hydroxide **10**.

(−0.46, −0.78, and −0.72 ppm). In the solid-state, all the hydroxides have nearly planar M_2O_2 [**8** (M = Mg), **10** (M = Ca) (Figure 1), and **12** (M = Sr)] four-membered rings that result from the *μ*-hydroxide bridged dimerization. In hydroxides **8**, **10**, and **12**, one can note the presence of THF coordination on each metal center except on one of the strontium atoms in **12** where two coordinate THF molecules are present. This divergence leads to a difference in coordination geometry around the metal centers in **12**. Thus, when the pentacoordinate metal centers in **8** and **10** have distorted square-pyramidal geometry, the pentacoordinate strontium center in **12** has distorted trigonal-bipyramidal geometry. The average M−OH bond length in **8**, **10**, and **12** is 2.042, 2.225, and 2.402 Å, respectively.

In living systems, the carbonic anhydrase [$(His)_3ZnOH$] scrubs CO_2 to form $(His)_3Zn(HCO_3)$ in a reversible manner and a reaction alike also occurs between $Ca(OH)_2$ and CO_2. Therefore, it is of importance to study the reaction of **10** with CO_2. When a benzene solution of **10** was exposed to CO_2, 2 equiv of **1** and amorphous $CaCO_3$ were obtained through the intermediates shown in Scheme 5.[7] Quite contrary to the discussions (vide supra), this reaction is not reversible owing to the protonation of basic *β*-diketiminate ligand that is swift and irreversible.

SCHEME 5. Reaction of *β*-Diketiminatocalcium Hydroxide **10** with CO_2



This reactivity pattern initiated the possible utility of dip coating. The amorphous $CaCO_3$ that gets precipitated upon exposure of a benzene solution of **10** to CO_2 has been dip coated over metal wire and carbon foil, and the nature of the $CaCO_3$ coating has been proved by scanning electron microscopic (SEM) studies. A umpolung was observed in the reaction of **12** with 2 equiv of $Zr(NMe_2)_4$ where the hydroxide **12** acts as a mild acid (Scheme 6).[8] Heterobimetallic compound **13** was obtained by the elimination of 2 equiv of dimethylamine (Scheme 6).[8] The molecular structure of **13** (Figure 2) shows the presence of a planar Zr_2O_2 four-membered ring with zirconium atoms in pentacoordinate environment. Two tetracoordinate strontium atoms are connected to this ring through its oxygen atoms, leading to a planar $Sr_2Zr_2O_2$ core.

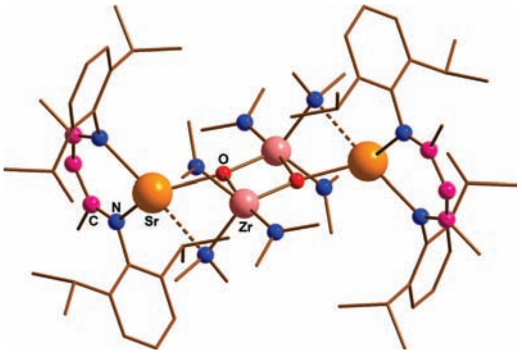
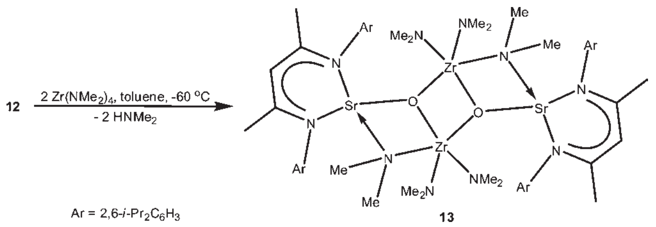


FIGURE 2. Molecular structure of heterobimetallic compound **13**.

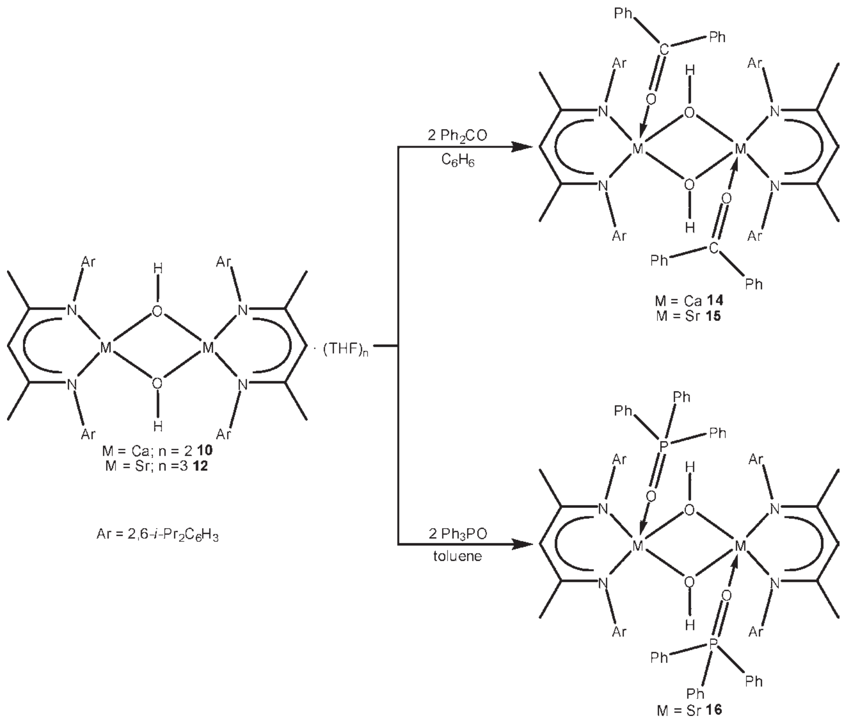
SCHEME 6. Synthesis of Heterobimetallic Compound **13**



The Zr–O bond lengths are 2.1992(13) and 1.9778(13) Å, and the Zr–O–Zr bond angle is 103.67(6)°. Similarly, the Sr–O bond length and Sr–O–Zr bond angle are 2.3423(14) Å and 96.63(5)°, respectively. We further attempted the ligand replacement reaction as one of the possible synthetic tools to accomplish monomeric alkaline earth metal hydroxides. The reaction of hydroxides **10** and **12** in benzene with 2 equiv of benzophenone resulted in the precipitation of hydroxides **14** and **15** with coordinate benzophenone molecules (Scheme 7), respectively.[7,8] Likewise, the addition of two equiv of triphenylphosphine oxide to **12** in toluene resulted in the formation of $Ph_3P{=}O$ coordinate β-diketiminatostrontium hydroxide **16** (Scheme 7).[8] Thus, these reactions resulted only in the displacement of coordinate THF molecules, and the expected monomeric hydroxides were not obtained.

A comparison of the average M–OH bond length of **14**–**16** [**14** (M = Ca), 2.2329(7); **15** (M = Sr), 2.366(3); and **16** (M = Sr), 2.374(2) Å (Figure 3)] with the average M–OH bond length for the corresponding hydroxides with THF coordination (vide supra) reveals that the ligand exchange has resulted in subtle elongation of Ca–OH (in **14**) and

SCHEME 7. Ligand Exchange Reactions of Hydroxides **10** and **12**



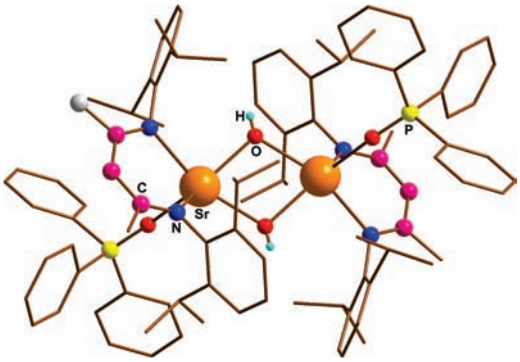
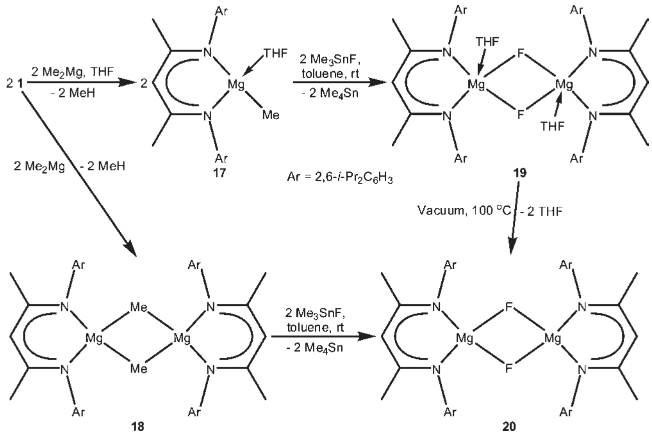
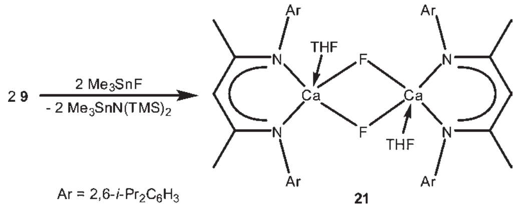


FIGURE 3. Molecular structure of β-diketiminatostrontium hydroxide **16**.

SCHEME 8. Synthesis of β-Diketiminatomagnesium Fluorides **19** and **20**



SCHEME 9. Synthesis of β-Diketiminatocalcium Fluoride **21**

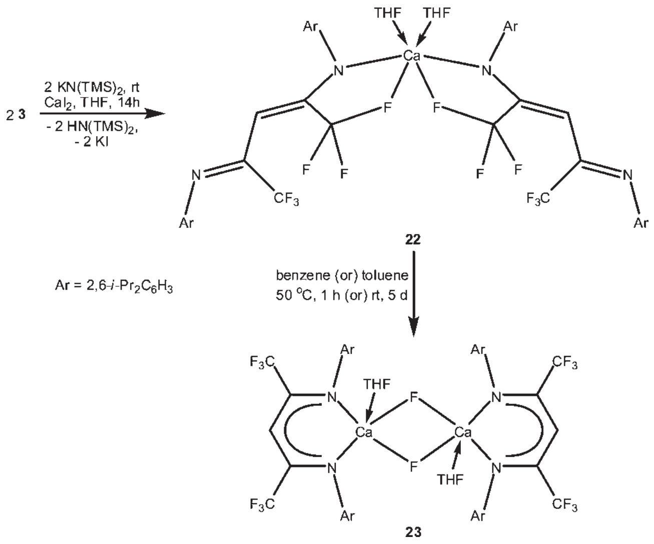


shrinkage of Sr−OH (in **15** and **16**) bonds. The pentacoordinate metal centers in **14** and **15** have distorted square-pyramidal geometry, and distorted trigonal-bipyramidal geometry is seen in the metal centers of **16**.

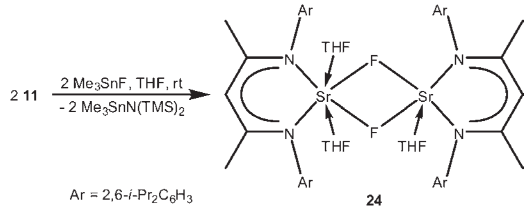
3. Halide Complexes of Magnesium, Calcium, and Strontium

Fluoride Complexes of Magnesium, Calcium, and Strontium. The first structurally characterized β-diketiminatomagnesium fluoride **19** was obtained by reacting the monomeric methylmagnesium complex **17** with Me_3SnF at room temperature for 48 h in toluene (Scheme 8).[9] Tetramethyltin was eliminated in this reaction, and the coordinate THF molecule in **17** was retained in **19**. The coordinate THF molecules in **19** can be eliminated by heating this compound under vacuum to obtain the THF free magnesium fluoride complex **20** (Scheme 8).[9] Alternatively, **20** can also be prepared by the fluorination of the dimeric methylmagnesium complex **18** devoid of THF molecules with Me_3SnF at room temperature for 48 h in toluene (Scheme 8).[9]

SCHEME 10. Thermal Decomposition of **22** in Solution



SCHEME 11. Synthesis of β-Diketiminatostrontium Fluoride **24**



With the successful isolation of β-diketiminatomagnesium fluorides, research was ongoing for a suitable precursor that would afford a stable calcium fluoride complex defiant to ligand exchange reactions. The long-lasting quest came to an end in 2007 with the discovery that compound **9** utilized for the synthesis of β-diketiminatocalcium hydroxide **10** is the suitable candidate. Accordingly, the reaction of **9** with Me_3SnF in THF at room temperature afforded the desired β-diketiminatocalcium fluoride **21** as a dimer (Scheme 9).[10]

It should be apposite to mention here the unstable calcium fluoride complex **23** which was reported after the publication of **21** by Barrett, Hill, and co-workers.[11] It was obtained as a minor product during the decomposition of the homoleptic calcium complex **22** due to its thermal instability in solution (Scheme 10).

Although the structure of **23** has been ascertained by single crystal X-ray diffraction studies, its instability in solution precludes the isolation in pure form. The procedure used for the isolation of **21** was further extended for the synthesis of *β*-diketiminatostrontium fluoride **24**.[12] Consequently, the reaction of **11** with Me_3SnF was carried out at room temperature in THF to obtain **24** with the elimination of $Me_3SnN(TMS)_2$ (Scheme 11).

In the ^{19}F NMR spectroscopic studies, the fluorides **19**, **20**, **21** (in C_6D_6), and **24** (in THF-d_8) displayed a sharp singlet resonance at −26, −25, −76, and −59.97 ppm, respectively. From the X-ray structural studies, their dimeric nature and planarity of four-membered M_2F_2 rings [**19** (M = Mg), **20** (M = Mg), **21** (M = Ca) (Figure 4), and **24** (M = Sr)] have been established. The average M−F bond length in **19**, **21**, and **24** is 1.9506, 2.180, and 2.371 Å, respectively. The pentacoordinate magnesium centers of **19** adopt distorted square-pyramidal geometry with the oxygen atom of THF at the apex. Both the calcium atoms and one of the strontium atoms in **21** and **24** display distorted trigonal-bipyramidal environment, respectively.

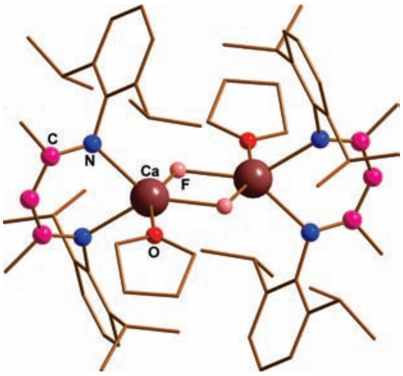
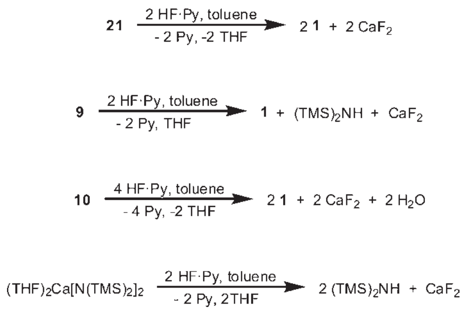


FIGURE 4. Molecular structure of *β*-diketiminatocalcium fluoride **21**.

SCHEME 12. Reaction of *β*-Diketiminatocalcium Fluoride **21** and Other Nonfluoride Complexes {**9**, **10**, and $(THF)_2Ca(N[TMS]_2)_2$} with HF·Py



The utility of CaF_2 in optics encouraged us to behold the undemanding achievability of CaF_2 dip coatings by exploiting the solubility of **21** in common organic solvents.[10] Alternatively dipping the unpolished pure silicon surface in the toluene solution of **21** and HF·Py (Py = pyridine) about 12 times followed by toluene washing and drying at room temperature resulted in a white coating of CaF_2 on the silicon surface (Scheme 12), which was confirmed by SEM and energy-dispersive X-ray (EDX) spectroscopic analyses. Such a simple feat of CaF_2 coatings prompted us to look at the efficacy of other soluble but nonfluorine containing calcium complexes to afford CaF_2 coatings during their reaction with the fluorinating agent HF·Py.[10] For a preliminary study, **9**, **10**, and $(THF)_2Ca(N[TMS]_2)_2$ were employed, and it is amazing to find out that these nonfluoride calcium complexes can also lead to CaF_2 coatings (Scheme 12).

Chloride Complexes of Magnesium, Calcium, and Strontium. Holland and co-workers obtained the monomer-

SCHEME 13. Synthesis of Monomeric *β*-Diketiminatomagnesium Chloride **27**

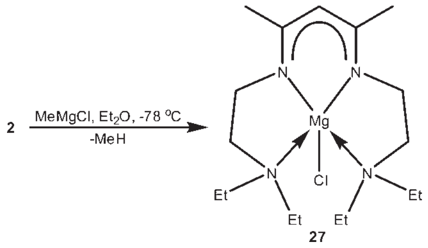
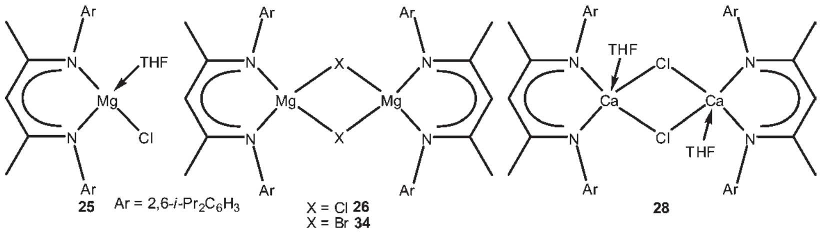
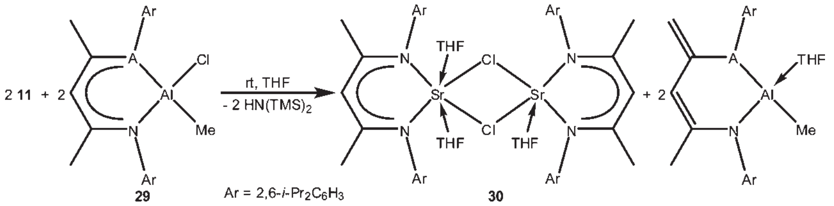


CHART 2. Molecular Structure of Various Alkaline Earth Metal Halide Complexes **25**, **26**, **28**, and **34**



SCHEME 14. Synthesis of *β*-Diketiminatostrontium Chloride **30**



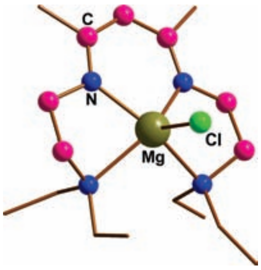


FIGURE 5. Molecular structure of monomeric *β*-diketiminatomagnesium chloride **27**.

ic *β*-diketiminatomagnesium chloride **25** (Chart 2) from the reaction of **1** with MeMgCl in THF.[13]

Gibson's group synthesized the structurally characterized *β*-diketiminatomagnesium chloride dimer **26** without coordinate THF molecules (Chart 2) by performing the aforementioned reaction in toluene (instead of THF) at 0 °C.[14] The preparation of a monomeric magnesium chloride complex devoid of coordinate solvent molecules was accomplished through the *β*-diketimine ligand **2**. Remarkably, the reaction of MeMgCl with **2** in ether afforded the desired *β*-diketiminatomagnesium chloride **27** without ether coordination (Scheme 13).[6]

Harder and Ruspic have prepared the *β*-diketiminatocalcium chloride **28** (Chart 2) by reacting **9** with triethylamine hydrochloride in THF.[15] A different synthetic route resulted in soluble *β*-diketiminatostrontium chloride **30** by the reaction of **11** with *β*-diketiminatoaluminum methyl chloride **29** in THF at room temperature (Scheme 14).[12]

The Mg−Cl bond length in **27** is 2.3605(5) Å, and its pentacoordinate magnesium center has a distorted square-pyramidal geometry (Figure 5). The average M−Cl bond length in the dimeric chlorides **26** (M = Mg), **28** (M = Ca), and **30** (M = Sr), respectively, is 2.4279(10), 2.681(1), and 2.926(1) Å. The penta- and hexacoordinate strontium centers in **30** display distorted trigonal-bipyramidal and octahedral geometries, respectively.

Bromide Complexes of Magnesium, Calcium, and Strontium. The *β*-diketiminatomagnesium bromide **32** was obtained unexpectedly, although not as a free entity.[16] The reaction of *β*-diketiminatoscandium dibromide **31** with 2 equiv of vinylmagnesium bromide in THF at 0 °C resulted in **32**, where two *β*-diketiminatomagnesium bromide units are sandwiching a coordinating scandium(I) monobromide by offering profuse stabilization through their *β*-diketiminate frameworks in η^5 binding mode (Scheme 15).[16]

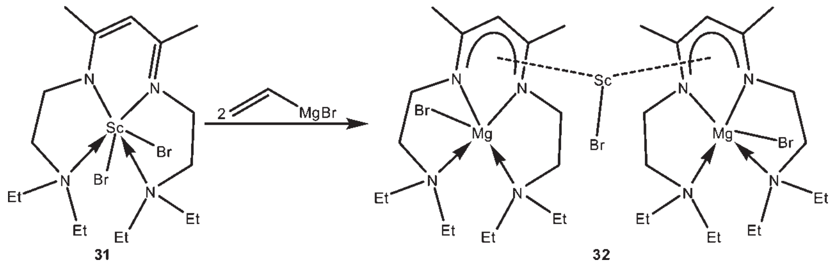
The reaction of compound **32** with alcohol resulted in free *β*-diketiminatomagnesium bromide **33** along with an unidentified scandium compound.[17] Gibson and co-workers reported the magnesium bromide complex **34** (Chart 2) by carrying out the reaction of MeMgBr with **1** at 0 °C in toluene.[14] To the best of our knowledge, well-defined calcium and strontium bromide complexes with *β*-diketiminate ligands are still missing. The pentacoordinate magnesium centers in compounds **32** and **33** (Figure 6) show square-pyramidal geometry, and the Mg−Br bond lengths of 2.534(1) and 2.5526(12) Å, respectively, are almost identical. The dimeric nature of **34** has also been established through single crystal X-ray diffraction studies, and the average Mg−Br bond length is found to be 2.5390(7) Å.

Iodide Complexes of Magnesium, Calcium, and Strontium. The reaction of lithium derivative **35** with MgI_2 in ether at 0 °C led to the isolation of the first structurally characterized *β*-diketiminatomagnesium iodide complex **36** (Scheme 16).[18]

Recently, the iodide **36** has been prepared by Jones and co-workers through a different route that involves the reaction of **1** with MeMgI in ether at −20 °C.[19] Utilizing this methodology, other iodide complexes **37**−**39** (Chart 3) were also reported along with the iodide complex **40** (Chart 3) isolated from the reaction of **4** with *n*-Bu_2Mg in toluene at 100 °C followed by the addition of I_2 at −20 °C.[19]

Winter and co-workers have isolated the calcium (**44**, **45**) and strontium (**46**) iodide complexes where one can see the η^5 binding mode of *β*-diketiminate ligands.[20] The *β*-diketiminatocalcium iodide **44** was obtained from the reaction of **41** with CaI_2 at room temperature (Scheme 17), and the *β*-diketiminatocalcium iodide **45** was realized through an alternate route where **42** and CaI_2 were refluxed in THF for 3 h (Scheme 17). The latter methodology was extended for the synthesis of *β*-diketiminatostrontium iodide **46** (Scheme 17).

SCHEME 15. Synthesis of *β*-Diketiminatomagnesium Bromide **32** with Sandwiched Scandium Monobromide



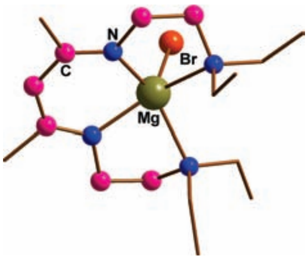


FIGURE 6. Molecular structure of *β*-diketiminatomagnesium bromide **33**.

SCHEME 16. Synthesis of *β*-Diketiminatomagnesium Iodide **36**

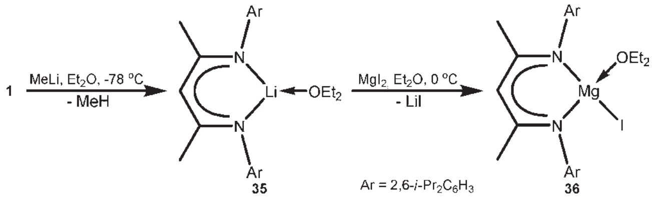
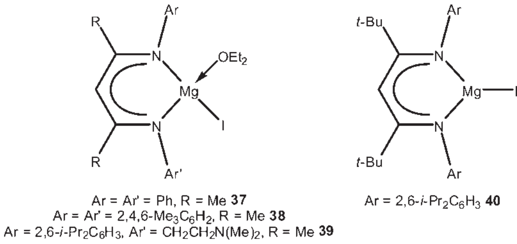
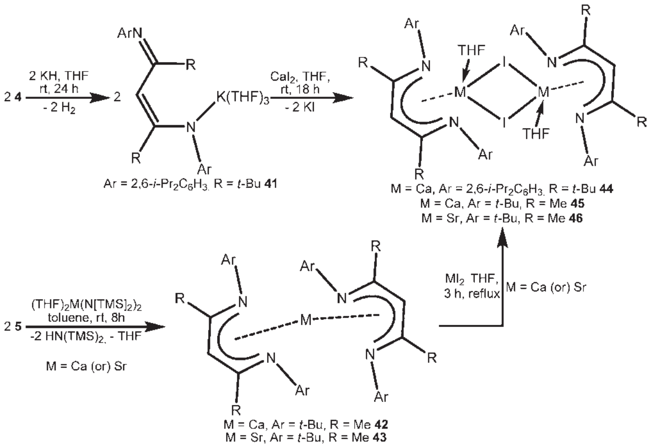


CHART 3. Structure of *β*-Diketiminatomagnesium Iodides **37**–**40**

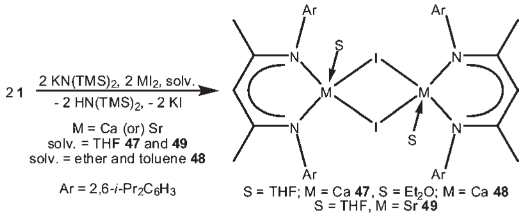


The calcium iodide complex **47** was synthesized by the room temperature reaction of **1** with 1 equiv of KN(TMS)$_2$ and CaI$_2$ in THF (Scheme 18).[21] The *β*-diketiminatostrontium iodide **49** was also obtained from a similar reaction (Scheme 18).[21] Calcium iodide complex **48** that is different from **47** only in terms of coordinate solvent molecules has also been reported by Jones and co-workers.[19] The reaction of CaI$_2$ with the potassium salt of **1** at 20 °C for 48 h afforded **48** (Scheme 18).

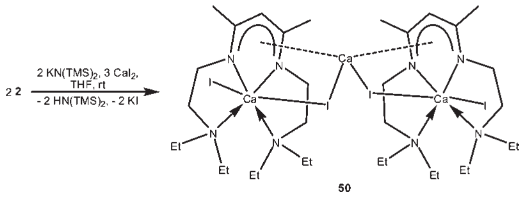
SCHEME 17. Synthesis of Calcium (**44**, **45**) and Strontium (**46**) Iodide Complexes with η^5-*β*-Diketiminate Ligands



SCHEME 18. Synthesis of Calcium (**47**, **48**) and Strontium (**49**) Iodide Complexes



SCHEME 19. Synthesis of Calcium Iodide Complex **50** with a (I–Ca–I–Ca–I–Ca–I)$^{2+}$ Chain



To prepare the solvent free calcium iodide complex, the reaction of **2** was carried out with KN(TMS)$_2$ and CaI$_2$ at room temperature (Scheme 19).[22] Divergent to expectations, two molecules of the formed calcium iodide complex incorporated a CaI$_2$ molecule by providing coordinative interactions through η^5-*β*-diketiminate backbones that

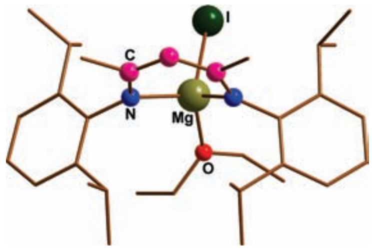


FIGURE 7. Structure of β-diketiminatomagnesium iodide **36**.

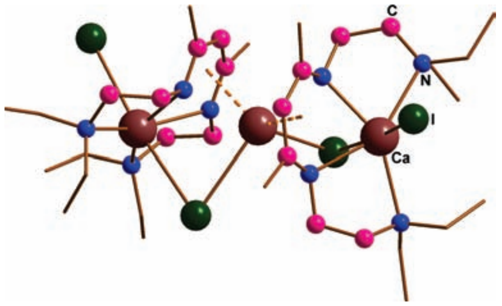
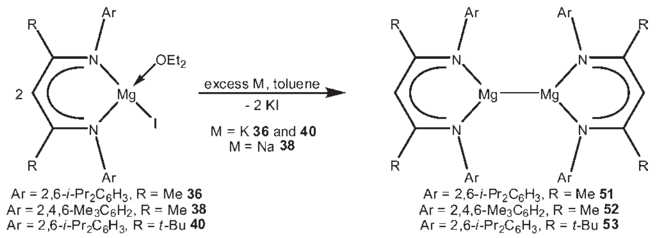


FIGURE 8. Molecular structure of calcium iodide complex **50** with a (I—Ca—I—Ca—I—Ca—I)$^{2+}$ chain.

SCHEME 20. Synthesis of Compounds (**51**—**53**) with Mg(I)—Mg(I) Bond



resulted in **50** with a (I—Ca—I—Ca—I—Ca—I)$^{2+}$ chain.[22] This is almost reminiscent to the situation that prevails in compound **32**.[16]

From X-ray structural studies, it has been shown that the β-diketiminatomagnesium iodide **36** is monomeric and has a magnesium center in a distorted tetrahedral geometry with an anticipated Mg—I bond length of 2.6886(13) Å (Figure 7).

The geometry of the magnesium center in **37** and **38** is reminiscent to that in **36**. Compounds **39** and **40** feature distorted square-pyramidal and trigonal-planar environments around their magnesium centers, respectively. In **37**, **38**, **39**, and **40**, the Mg—I bond lengths are 2.670(1), 2.6915(9), 2.827(1), and 2.597(1) Å, respectively. Complexes **44** and **45** have Ca_2I_2 four-membered rings with μ-I bridges, and the average Ca—I bond length is 3.242(1) and 3.144(1) Å, respectively. Four-membered ring arrangements similar to those present in **44** and **45** can be observed in the structure of **48** that has distorted trigonal-bipyramidal calcium centers with expected Ca—I bond lengths [3.1224(8) and 3.090(1) Å]. The calcium iodide complex **50**, where both the η^2 and η^5 binding modes of β-diketiminate ligand are present, has three calcium atoms with the former and latter binding mode in a 2:1 ratio (Figure 8). The hexacoordinate calcium atoms with η^2-β-diketiminate ligands possess distorted octahedral geometry and contain almost linear I—Ca$\cdots$I$_{Ca}$ fragments (bond angle 173.61°) with shorter I—Ca [3.1253(17) Å] and longer Ca$\cdots$I$_{Ca}$ [3.2109(18) Å] bonds. The other calcium atom interacting with two η^5-β-diketiminate ligands shows a Ca—I bond length of 3.1618(16) Å. In contrast to the β-diketiminatostrontium complexes encountered (*vide supra*), all the strontium centers in **46** and **49** contain the same number of coordinate THF molecules (one on each), which evidently bestows the distorted trigonal-bipyramidal environment to both the pentacoordinate Sr atoms of **49**.

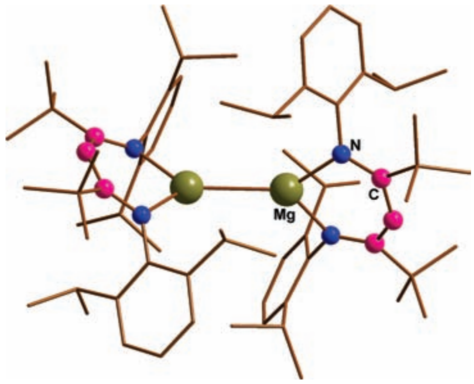


FIGURE 9. Molecular structure of **53**.

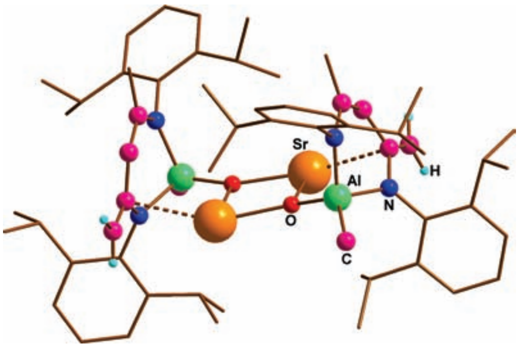
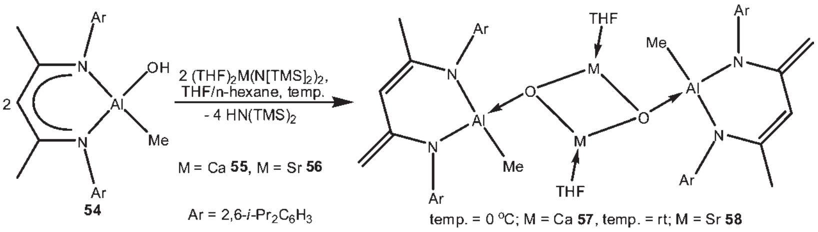


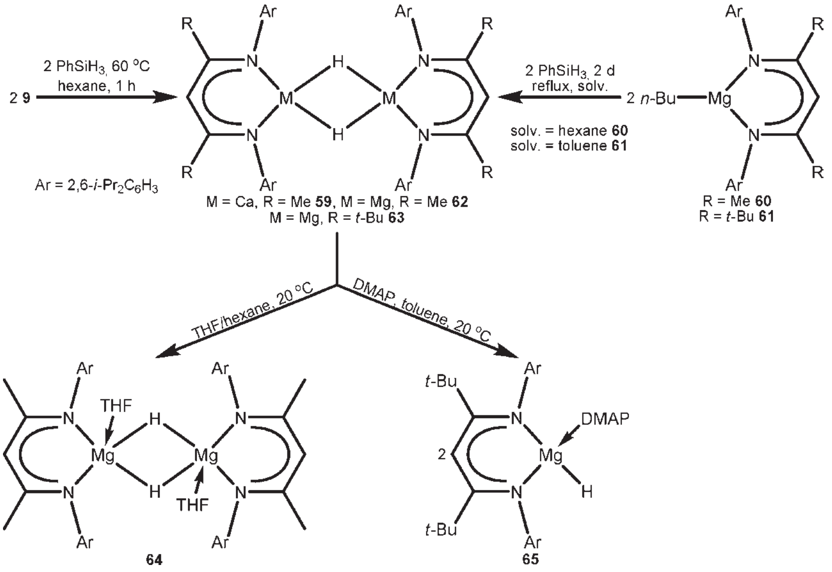
FIGURE 10. Molecular structure of strontium oxide complex **58**.

Another vital utility of β-diketiminatoalkaline-earth metal halides came from the recent work of Jones and co-workers who have utilized **36** as a precursor to obtain one of the first stable Mg_2 compounds with magnesium atoms in +1 oxidation state and a direct Mg—Mg bond.[23] The reduction of **36**

SCHEME 21. Synthesis of Oxide Complexes of Calcium (**57**) and Strontium (**58**)



SCHEME 22. Synthesis of Hydride Complexes of Calcium (**59**) and Magnesium (**62**−**65**)

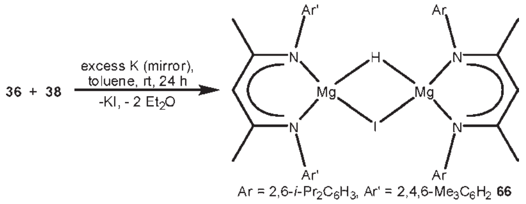


with potassium in toluene at 20 °C for 1 day resulted in **51** (Scheme 20).[23]

The reduction of iodides **38** and **40** under similar conditions (Scheme 20) also led to the formation of **52** and **53**, respectively.[19] The magnesium(I) centers in compounds **51**−**53** are tricoordinate three-coordinate and exhibit distorted trigonal-planar geometry. The Mg−Mg bond length in **51**, **52**, and **53** (Figure 9) is 2.8457(8), 2.808(1), and 2.847(2) Å, respectively.

Attempts to prepare Ca(I) and Sr(I) compounds by reducing the aforementioned halide complexes of calcium and strontium are elusive to date.

SCHEME 23. Reduction of a 1:1 Mixture of **36** and **38**



4. Soluble Oxide Complexes of Magnesium, Calcium, and Strontium

The alkaline earth metal oxides find various applications, but their insolubility in common organic solvents prevents the study of their interesting properties. Therefore, the preparation of soluble oxide derivatives of alkaline earth metals becomes an elemental target. The equimolar reaction of **54** with **55** and **56** resulted in the soluble oxide complex of calcium **57** and strontium **58**, respectively (Scheme 21).[24] Single crystal X-ray diffraction studies on **57** and **58** reveal the deprotonation experienced by **54** to result in Lewis acidic methylaluminum stabilized by dianionic *β*-diketiminate ligand. The planar four-membered M_2O_2 rings (M = Ca **57**, M = Sr **58**) are the result of dimerization.

Coordination by the ligand backbone makes the metal centers (Figure 10) in these oxides tetracoordinate with distorted square-planar geometry. Excluding the coordinative interactions with THF molecules, the average M-O bond length in **57** (M = Ca) and **58** (M = Sr) is 2.217(2) and 2.358(3) Å, respectively.

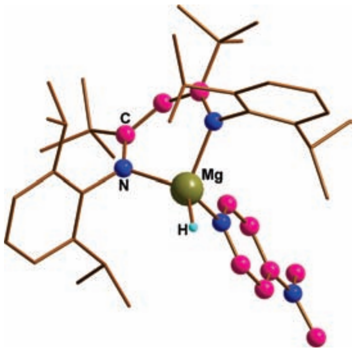


FIGURE 11. Molecular structure of β-diketiminatomagnesium hydride **65**.

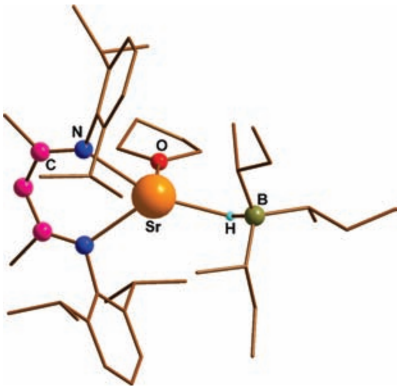


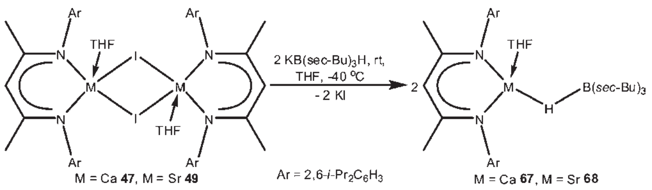
FIGURE 12. Structure of β-diketiminatostrontium borohydride **68**.

5. Hydride Complexes of Magnesium, Calcium, and Strontium

Harder et al. isolated the first definite example of a β-diketiminatocalcium hydride **59**.[25] The reaction of **9** with 2 equiv of $PhSiH_3$ in hexane at 60 °C resulted in **59** (Scheme 22). By applying this methodology to magnesium, Jones and coworkers reported the magnesium hydride complexes **62**[26] and **63**[19] by refluxing a solution of β-diketiminatomagnesium alkyls **60** and **61** with $PhSiH_3$ for 2 days, respectively (Scheme 22). The former reacts with THF to afford **64**[26] with coordinate THF molecules. Interesting is the reaction of the latter (Scheme 22) with DMAP to result in the first monomeric β-diketiminatomagnesium hydride **65**.[19] The same group also reported on β-diketiminatomagnesium hydride–iodide dimer **66** by reducing an equimolar mixture of **36** and **38** with potassium in toluene (Scheme 23).[19]

With these advances, the limelight is on strontium due to the missing example of a stable and soluble strontium hydride complex. Among various attempts to prepare β-diketiminatostrontium hydride, it appeared that it would not be that erroneous to try KB(*sec*-Bu)$_3$H as a hydrogenating agent due to its efficacy in converting germanium(II) monochloride stabilized by the monoanion of **1** to the corresponding germanium(II) hydride complex.[27] The reaction of β-diketiminatostrontium iodide **49** with 2 equiv of KB(*sec*-Bu)$_3$H in THF resulted in β-diketiminatostrontium borohydride **68** and not the desired product (Scheme 24).[21] Repetition of this reaction with β-diketiminatocalcium iodide **47** (Scheme 24) also led to the formation of β-diketiminatocalcium borohydride **67**.[21]

SCHEME 24. Reaction of **47** and **49** with KB(*sec*-Bu)$_3$H



Singlet resonance corresponding to the metal bound hydrogen(s) of the hydride {**59** [4.45 (s)], **62** [4.03 (s)], **63** [3.83], **64** [4.21 (br)], and **65** [4.65] ppm)}, magnesium hydride–iodide dimer [**66** (3.92) ppm], and borohydride {**67** [-0.05 (br)] ppm} complexes can be seen in their ^{1}H NMR spectra. The Ca–H and Mg–H bond lengths average to 2.15(4) and 1.96(3) Å in the hydrides **59** and **62**, respectively. The latter parameter in **63**, **64**, and **65** (Figure 11) is 1.83_{av}, 1.947(19), 1.75(7) Å, respectively.

Tetracoordinate calcium and strontium centers in **67** and **68** comprise a bond length of 2.16(3) and 2.328(8) Å to the hydrogen atom, respectively (Figure 12).

6. β-Diketiminatozinc Complexes

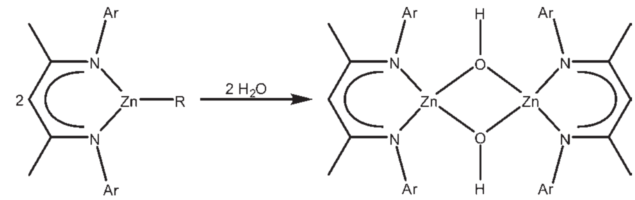
Coates et al. reported β-diketiminatozinc hydroxide **71** as a potential model for zinc enzymes by hydrolyzing β-diketiminatozinc amide **69** in toluene at room temperature (Scheme 25).[28] It was followed by a report by Chisholm et al. on **72** obtained from **70** (Scheme 25).[29]

The ^{1}H NMR spectrum of **71** with a sharp singlet at −0.14 ppm confirms the presence of OH groups. The Zn–O bond lengths (1.98 and 1.97 Å) in **71** are consistent with Mg–O bond lengths in **8**,[5,6] and the environment around the tetracoordinate zinc atoms is distorted tetrahedral.

The first soluble β-diketiminatozinc fluoride **75** was obtained from the reaction of **73** or **74** with Me_3SnF in toluene[30] (Scheme 26), a strategy akin to the preparation of **19**.[9]

The ^{19}F NMR spectrum of **75** shows the expected singlet resonance (−61.6 ppm), and X-ray structural studies corroborate the existence of a planar four-membered Zn_2F_2 ring with a Zn–F bond length (1.975_{av} Å) that is slightly longer than that in **19**. The heavier β-diketiminatozinc halides (**76**–**81**) analogous to those seen with alkaline earth metals (vide

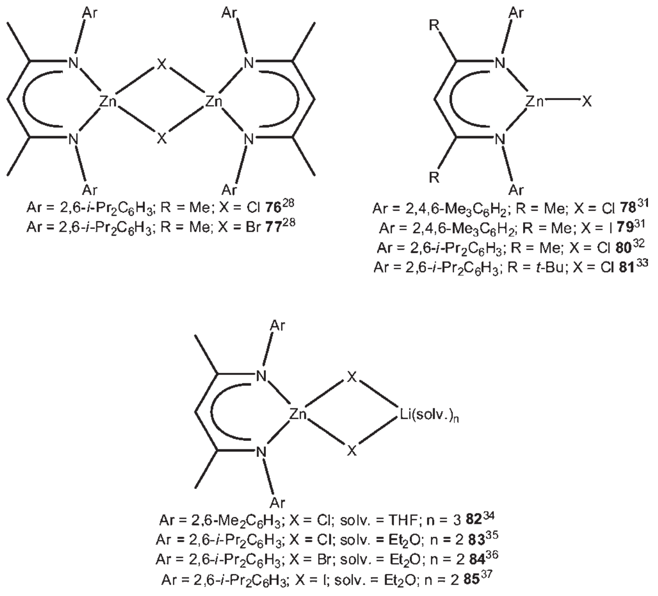
SCHEME 25. Synthesis of *β*-Diketiminatozinc Hydroxides **71** and **72**



Ar = 2,6-Et$_2$C$_6$H$_3$, R = N(TMS)$_2$ **69**
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, R = O*t*-Bu **70**

Ar = 2,6-Et$_2$C$_6$H$_3$ **71**, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$ **72**

CHART 4. Various *β*-Diketiminatozinc Halides **76**−**85**



Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; R = Me; X = Cl **76**[28]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; R = Me; X = Br **77**[28]

Ar = 2,4,6-Me$_3$C$_6$H$_2$; R = Me; X = Cl **78**[31]
Ar = 2,4,6-Me$_3$C$_6$H$_2$; R = Me; X = I **79**[31]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; R = Me; X = Cl **80**[32]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; R = *t*-Bu; X = Cl **81**[33]

Ar = 2,6-Me$_2$C$_6$H$_3$; X = Cl; solv. = THF; n = 3 **82**[34]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; X = Cl; solv. = Et$_2$O; n = 2 **83**[35]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; X = Br; solv. = Et$_2$O; n = 2 **84**[36]
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; X = I; solv. = Et$_2$O; n = 2 **85**[37]

supra) have been isolated and characterized (Chart 4).[28,31−33] Above that, halide complexes (**82**−**85**) with LiCl(solv)$_n$ coordination have also been encountered with zinc (Chart 4).[34−37]

For example, compounds **83**[35] and **85**[37] have been obtained by reacting **35** with ZnCl$_2$ and ZnI$_2$ in ether at low temperature, respectively. Both **83** (X = Cl) and **85** (X = I) (Figure 13) contain a ZnX$_2$Li four-membered ring with an average Zn-X bond length of 2.3001 and 2.6395 Å, respectively.

Carmona and co-workers isolated the first zinc compound Cp*ZnZnCp* (Cp* = C$_5$Me$_5$) with a direct Zn(I)−Zn(I) bond from the reaction of Cp*$_2$Zn with Et$_2$Zn.[38] This marked a major breakthrough in organometallic chemistry but also initiated huge interest that was evidenced by the synthesis of more than half a dozen of complexes with the Zn$_2^{2+}$ moiety and other similar compounds such as **51**−**53** with the Mg$_2^{2+}$ core. The first *β*-diketiminatozinc(I) compound **86** was isolated by Robinson and co-workers when **85** was reduced with potassium (Scheme 27).[39] The bond length between the tricoordinate Zn centers in **86** is 2.3586(7) Å.

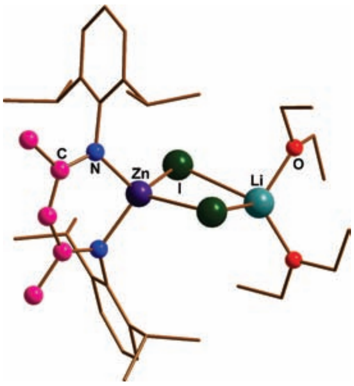
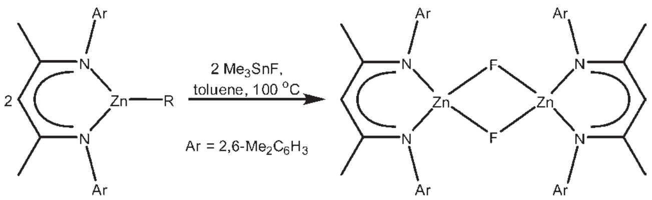


FIGURE 13. Molecular structure of *β*-diketiminatozinc iodide **85**.

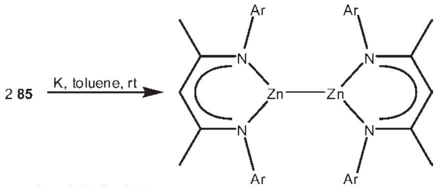
SCHEME 26. Synthesis of *β*-Diketiminatozinc Fluoride **75**



R = Me **73**, R = Et **74**

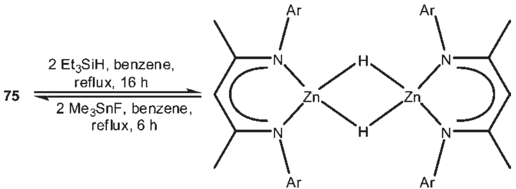
75

SCHEME 27. Synthesis of *β*-Diketiminatozinc(I) Complex **86**



86

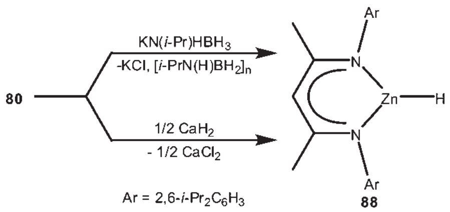
SCHEME 28. Synthesis of *β*-Diketiminatozinc Hydride **87**



87

The first *β*-diketiminatozinc hydride **87** was obtained by refluxing **75** with Et$_3$SiH in benzene (Scheme 28).[30] Heating **87** under reflux with Me$_3$SnF converts it back to **75** (Scheme 28).[30] Interestingly, Harder's group isolated its monomeric version **88** from the reaction of **80** with KN(*i*-Pr)HBH$_3$ originally anticipated to yield *β*-diketiminatozinc amidoborane (Scheme 29).[40] It can also be obtained by reacting **80** with CaH$_2$ (Scheme 29).[40]

SCHEME 29. Synthesis of Monomeric β-Diketiminatozinc Hydride **88**



Both the hydrides (**87** and **88**) display a singlet resonance for the hydride proton(s) in their ^{1}H NMR spectra (4.59 and 4.39 ppm, respectively). The zinc center(s) in **87** and **88** exhibit a Zn−H bond length of 1.766 and 1.46(2) Å, respectively.

7. Summary and Future Prospects

In general, the β-diketiminatometal amides upon controlled hydrolysis have afforded metal hydroxide complexes. Compounds **10** and **12** not only represent the first hydroxide complexes of calcium and strontium but also signify a foremost advancement in *s*-block organometallic chemistry. While more examples are required to make the hydroxide chemistry richer, the isolation of monomeric hydroxides using appropriate ligands will also be a rewarding exercise. Even if we have shown the initial reactivity such as the interesting strontium monohydroxide umpolung in the reaction of **12** with Zr(NMe$_2$)$_4$, further work is required to fully understand their chemistry.

Among various halide complexes of alkaline earth metals, the fluoride complexes **21** and **24** stand as the first example of soluble monofluoride of calcium and strontium. The issues of monomerization and isolation of more examples are yet to be addressed, and the synthesized fluorides remain completely open for reactivity studies. The feasibility to coat CaCO$_3$ and CaF$_2$ in an energy efficient manner using the solutions of **10** and **21** is a remarkable innovation and can be contemplated as a potential method in industries dealing with dip coating. Establishment of such utility is currently underway in our laboratories. Equally important is the finding that, apart from **21**, other soluble nonfluorine containing calcium complexes can also lead to CaF$_2$ coatings.

The hitherto unknown soluble alkaline earth metal oxide complexes were isolated for the first time with calcium and strontium, and the preparation of the missing magnesium oxide complex may require an alternate synthetic route. The reactivity studies on the former and isolation of the latter are the next expected developments. Furthermore, the recent isolation of stable hydride complexes of magnesium, calcium, and zinc makes strontium devoid of such complexes. We are sure that the continuing efforts will lead to its isolation as stable species in the years to come.

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Herbert W. Roesky was born in 1935 in Laukischken. He is presently working as an emeritus professor at the Institute of Inorganic Chemistry, Göttingen University, Germany. He has various research activities in the areas of inorganic chemistry and material sciences.

FOOTNOTES

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