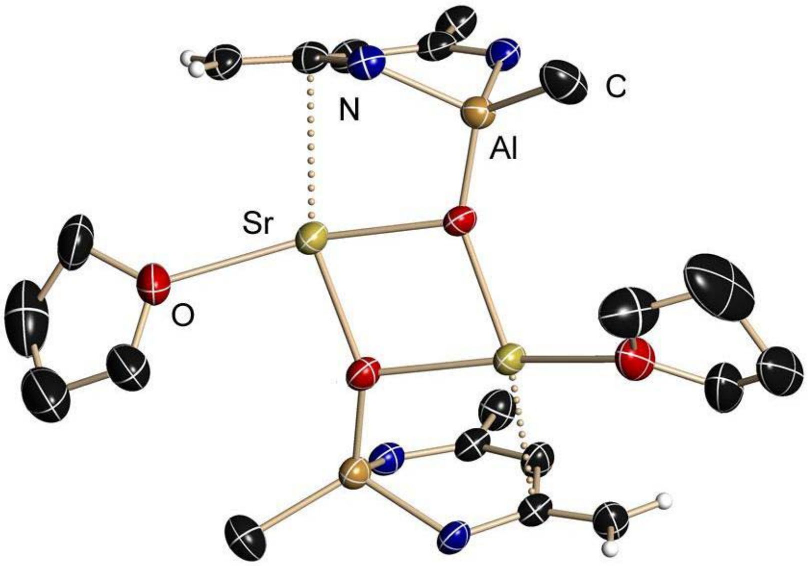
Sarish Sankaranarayana Pillai

β−Diketiminate Ligands as Supports for Alkaline Earth and Aluminum Complexes: Synthesis, Characterization, and Reactivity Studies



Göttingen 2009

β−Diketiminate Ligands as Supports for Alkaline Earth and Aluminum Complexes: Synthesis, Characterization, and Reactivity Studies

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Sarish Sankaranarayana Pillai

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D 7

Referent: Prof. Dr. Dr. h. c. mult. H. W. Roesky

Korreferent: Prof. Dr. Dietmar Stalke

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Dedicated to my parents, brother and sister-in-law

for their love and affection

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Abbreviations

δ	chemical shift
λ	wavelength
μ	bridging
$\tilde{\nu}$	wave number
av	average
C	Celsius
calcd.	calculated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopetadienyl
EI	electron impact ionization
eqv.	equivalents
eV	electron volt
g	grams
h	hours
Hz	Hertz
IR	infrared
J	coupling constant
K	Kelvin
L	ligand
M	metal
m/*z*	mass/charge
Mp	melting point
M^+	molecular ion
Me	methyl
Et	ethyl
*i*Pr	*iso*-propyl
*t*Bu	*tert*-butyl
Ph	phenyl
Ar	aryl
MS	mass spectrometry, mass spectra
NMR	nuclear magnetic resonance
ppm	parts per million

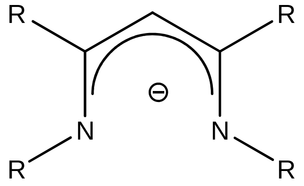
q	quartet
R	organic substituents
s	singlet
d	doublet
t	triplet
sept	septet
m	multiplet
br	broad
THF	tetrahydrofuran

1. Introduction

This section of the thesis gives the background and an overview of the area in several sections before the work is presented.

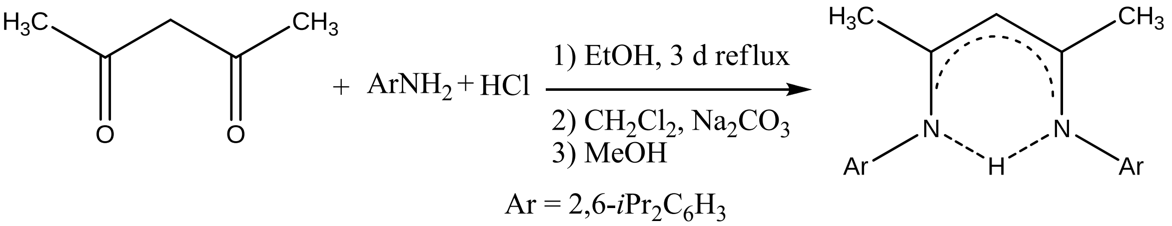
1.1. *β*-Diketiminate Ligands

In recent years, the *β*–diketiminate ligands generally known as "nacnac", or $[\{ArNC(R)\}_2CH]^-$ (where Ar = aryl and R = Me or another organic group) (Figure 1.1) have emerged as popular ligands among other ancillary supports, in view their strong binding to metals, their tunable, steric, and electronic effects, and their diversity in bonding modes.[1-7] The nacnac ligand skeleton is analogous to the "acac" (acetylacetonate) ligand, but the oxygen atoms are replaced with nitrogen-based moieties such as NR (R = alkyl, silyl, Ar) (Scheme 1.1). As a result, steric protection at the metal center is provided by the substituent at the nitrogen donor atom.



Scheme 1.1. Schematic diagram of "nacnac", L

The first complexes of *β*–diketiminate ligands were prepared in the mid to late 1960's as homoleptic complexes of Co, Ni, Cu, and Zn.[8-20] When R is a small moiety such as H, Me and $SiMe_3$, the substance easily forms a dimer and allows higher coordination to the metal center, whereas a bulky aryl group on the nitrogens usually leads to the isolation of monomeric species with low coordination numbers at the metal center. The compound LH can be prepared in good yield by the method of Feldman and coworkers (Scheme 1.2). The direct condensation of 2,4-pentanedione, and 2,6-di-*iso*-propylaniline in the presence of HCl in boiling ethanol afforded the ligand hydrochloride, this upon neutralization with Na_2CO_3 to obtain free LH as colorless crystals.[21]



Scheme 1.2. Synthesis of a sterically encumbered *β*–diketiminate compound LH

To date, various *β*–diketiminate complexes containing main group,[22,23] transition[24-26] and lanthanide elements[27-31] have been synthesized and structurally characterized. For example, the N-aryl substituted ligand **L** (L = CH(CMe2,6-iPr$_2$C$_6$H$_3$N)$_2$) has stabilized the first example of a monomeric aluminum(I) LAl[32] and magnesium(I) compound [LMg]$_2$ with Mg-Mg bonds where aluminum and magnesium are in the +1 oxidation state.[33] Some of them have found application in catalysis[34-38] and also in bioinorganic chemistry as model compounds (e.g. Cu).[39,40] Nevertheless, *β*–diketiminate complexes of the alkaline earth metals especially heavier analogues are few in number and their chemistry is not well established. Therefore, this thesis deals with hydroxides, halides, hydrides, oxide and oxygen bridged hetero-bimetallic complexes of Group 2 stabilized by the *β*–diketiminate ligand and also includes synthesis and reactivities of a C-H activated *β*–diketiminate ligand supported aluminum complex.

1.2. Trimethylsilyl Amides of Group 2

There is a growing interest in the synthesis and characterization of Group 2 amides due to their utility as a precursor for the synthesis of a spectrum of Group 2 compounds[41-47] and also as versatile catalysts in various organic transformations.[38,48,49] *β*–Diketiminate ligand supported calcium amide, LCaN(SiMe$_3$)$_2$(thf) shows good catalytic activity in lactide polymerization,[38] hydroamination,[48] and hydrophosphination.[49] Recently we reported a well-defined calcium hydroxide [LCa(μ-OH)(thf)]$_2$[44] and monofluoride [LCa(μ-F)(thf)]$_2$[45] using LCaN(SiMe$_3$)$_2$(thf)[38] as a precursor. The successful isolation of these complexes prompted us to extend this methodology to strontium. Bis(trimethylsilyl)amides of Group 2 metals also can serve as useful precursors for the preparation of hetero-bimetallic and trimetallic compounds and acetylide complexes.[50] For e.g. the reaction of Mg[N(SiMe$_3$)$_2$]$_2$ with a stoichiometric amount of

LAlOH(Me) in THF/*n*-hexane (1:1 and 1:2) at 0 °C results in the formation of the hetero-bimetallic and trimetallic compounds in high yield.[51]

1.3. Hydroxides of Group 2

The so called water effect in organometallic compounds has resulted in the formation of various interesting hydroxide complexes.[52] The reaction of these hydroxides with suitable metal precursors generally leads to the formation of polymetallic oxides that are emerging as an important class of compounds due to their potential application in catalysis.[53] In addition, the hydroxide complexes can function as model compounds for the insoluble or unstable metal hydroxides $M(OH)_x$. Therefore, we have prepared various p-block hydroxides and have been successful in assembling novel hetero-bimetallic and hetero-polymetallic oxides by utilizing the acidic character of these hydroxide complexes.[51,54-58] For example, the heterodimetallic compound $LAl(Me)(\mu\text{-}O)Zr(Me)Cp_2$ (L = $CH(CMe2,6\text{-}iPr_2C_6H_3N)_2$) has been obtained by the reaction of LAl(Me)OH with Cp_2ZrMe_2 and we have demonstrated that it is a versatile catalyst in ethylene polymerization.[34, 59] Also, the cubic silicon-titanium μ-oxo complex obtained by the reaction of a aminosilanetriol with $Ti(OEt)_4$ showed excellent catalytic activity in the epoxidation of cyclohexene and cyclooctene by *t*-butyl hydroperoxide.[60] In view of this importance, one may think of a possible extension of these principles to Group 2 elements. Nevertheless, two major issues that need to be addressed are the synthesis of stable and soluble Group 2 hydroxides and the basicity of these hydroxides. The preparation of Group 2 hydroxides, mainly those with heavier metals is difficult (due to the large atomic radii and high ionic character of these elements)[61-64] and consequently only few Group 2 hydroxide complexes are reported. Two hydroxide complexes for magnesium[65] and one example for calcium[44] are known. Apart from the magnesium hydroxide complex $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$ (stabilized by tris(1-pyrazolyl)hydroborate ligand ($Tp^{Ar,Me}$); Ar = $p\text{-}tBuC_6H_4$), the other two examples have been obtained by exploiting the unique property of the β−diketiminato ligand L. All these complexes are dimeric in the solid-state and contain coordinated THF molecules except $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$.[65a] The THF molecules can be exchanged with other donors such as benzophenone.[44] Surprisingly, no reactivity study based on these complexes has been reported.

1.4. Halides of Group 2

There is a great deal of interest in the synthesis and characterization of novel group 2 halide complexes of the type RMX (M = an alkaline earth metal) due to their potential applications in synthetic chemistry and material science.[66] In view of these applications, various halide complexes of alkaline earth metals have been synthesized and structurally characterized.[43,45,67-72] Nevertheless, the organometallic halide chemistry with respect to heavier Group 2 elements is still in its infancy. This is due to the percentage of ionic character in the M–X bond increasing from magnesium to strontium and also due to a fast ligand exchange.[61-64] In recent times, a calcium fluoride and a chloride were prepared as stable species by exploiting the unique electronic and steric effect offered by the β−diketiminato ligand L (L = $CH(CMe2,6\text{-}i Pr_2C_6H_3N)_2$).[43,45] Another calcium fluoride was also reported by Hill and co-workers.[73] The synthesis of the well-defined LCaF complex can be used as soluble precursor for the preparation of CaF_2 coatings. These CaF_2 coatings are used as window material for both infrared and ultraviolet wavelengths and exhibit extremely weak birefringence. But the strontium analogues of its lighter congener were missing because of the non availability of a suitable precursor. It is also anticipated that the synthesis of the well-defined halide complexes of strontium enable the investigation of the nature of the Sr-X bond. In accordance with the recent theoretical studies on CpM−MCp (M = alkaline earth metals) of Group 2 elements, [74,75] these β−diketiminate ligand stabilized Group 2 metal halides might also be considered as promising precursor to prepare low valent Group 2 compounds with metal-metal bonds. In recent times, Jones and coworkers reported the first magnesium (I) complex obtained by the reduction of magnesium iodide, $LMgI\cdot Et_2O$ first materialized by Roesky *et al.*[68]

1.5. Hydrides of Group 2

Metal hydrides are important because their complexes are considered as valuable synthons in chemistry[76-84] and also potential targets for hydrogen storage. Metal hydrides can act as catalysts in a number of reactions especially in the case of transition metal complexes.[85] The main group and d-block elements form many metal hydrides especially with β–diketiminate ligands.[86-89] The unique properties of the β–diketiminate ligand provides suitable electronic and steric requirement to materialize a lot of novel complexes including hydrides. Additionally, there is only little molecular information on complexes of Group 2 metals because of predominantly ionic bonding and consequently high lattice energy of the hydrides. A scorpionate ligand stabilized beryllium hydride was reported in 1992.[90] An attempt to prepare β–diketiminate ligand supported magnesium hydride from magnesium iodide with $NaBH_4$ resulted in a hydrogen bridged magnesium complex by Roesky and coworkers.[68] Harder[42] and coworkers decribed the preparation of a well-defined heavier alkaline earth metal, calcium hydride $[LCaH\cdot thf]_2$ and showed its striking reactivity.[91] The extension of lanthanide hydride synthetic methodes to alkaline earth metals helped to materialize this complex by using $PhSiH_3$ as a hydride transfer agent. Recently Jones and coworkers were successful in isolating $[LMgH\cdot thf]_2$.[92] Moreover, Hill and coworkers reported a magnesium hydride cluster compound with N–heterocyclic carbene coordination.[93] Nevertheless, such hydride derivatives are so far not reported as stable species for strontium and barium.

1.6. Acetylides of Heavier Alkaline Earth Metals

The preparation of alkynyl complexes of higher alkaline earth metals is a synthetic challenge due to their higher reactivity and lesser kinetic stability. In the literature only a few examples of bis alkynyl and some mono alkynyl compounds of heavier alkaline earth metals are reported.[41,50] Compounds with metal carbon bonds of heavier alkaline earth metals are also interesting because of their exceptional reactivity and emerging utility.[95-100] Moreover, the exploration of heavier alkaline earth metals gained a momentum nowadays that has striking similarity to lanthanides.[101-104] Recently, Hill and coworkers reported a series of mono alkynyl complexes of calcium,[41] by utilizing the special electronic and steric factors offered by β–diketiminato ligands. It is well known that these ligands can deter the Schlenk type redistribution process, which is more profound in the case of heavier analogues of Group 2. Analogous observations for strontium are so far not possible due to the absence of pure precursor samples.

1.7. Oxides of Heavier Alkaline Earth Metals

Oxides of alkaline earth metals especially calcium oxide are known from ancient times. The heavier alkaline earth metal oxides like calcium oxide commonly known as quick lime and strontium oxide are prepared by heating the corresponding carbonates. Calcination of $CaCO_3$ appears to have been operated in the Stone Age to judge by the remains of kilns that have been found. The Romans achieved a high degree of expertise in its use as a building material. Strontium oxide is mainly important as a source of other strontium salts. These oxides have a broad range of application in material science and technology. For instance, SrO finds application in picture tubes as it can absorb dangerous UV light. Strontium oxide aluminate doped with suitable metals can act a photoluminescent phosphor. CaO and SrO are acting as catalysts for Tishchenko reactions.[105] However these inorganic compounds are insoluble in organic solvents and making them available to organometallic chemistry is a synthetic challenge due to their high lattice energy [CaO (816 kcal/mol) and SrO (769 kcal/mol)]. Therefore, they are not useful as precursors for organometallic compounds and also because of their high melting points (CaO 2707 °C and SrO 2430 °C).[106] A well-defined synthetic strategy is needed to materialize this type of complexes. Organometallic oxides can act as catalysts and can serve as model compounds for the fixation of catalytically active species on an oxide surface to find a structure activity relationship.[107] This would help with the design of good heterogeneous catalysts, which are always preferred by industry. Thus it gains importance in trapping or incorporating molecular inorganic oxides either by an organometallic or organic matrix. These lipophilic complexes can be well studied using characterization techniques available for organometallic complexes.

1.8. Alkaline Earth Metal-Zirconium Oxide Compounds

Zirconates of alkaline earth metals such as $CaZrO_3$, $SrZrO_3$, and $BaZrO_3$ are high melting and insoluble in organic solvents. These inorganic oxides attract much importance in the field of electrical ceramics,[108,109] and refractories.[110] $SrZrO_3$ is used commercially as ceramic dielectric material with high mechanical and chemical stability. In particular, several studies have been reported on the use of calcium zirconate-based systems for monitoring oxygen.[111] Preparation of soluble oxides containing both the alkaline earth and zirconium metal is always a challenge because of the lack of appropriate synthetic strategies. Roesky *et al.* have reported oxide compounds containing magnesium or calcium and zirconium by utilizing zirconium hydroxide and corresponding alkaline earth metal amides.[51] Nevertheless, no example of an oxide compound containing M−O−Zr (M = Sr, Ba) moiety is known. So is it possible to construct soluble heterobimetallic compounds containing strontium? To address this issue, we became interested in developing soluble compounds with the Sr–O–Zr structural motif. Heterobi- and heteropolymetallic compounds find various applications ranging from advanced materials to valuable catalysts. The compounds with different metal centers have often modified the fundamental properties of the individual metal atoms.[112,113]

1.9. Six-Membered N-Heterocyclic Aluminum Compound

Aluminum is the most abundant metal in the earth crust and it finds application in both academics and industry. One of the most attractive things about this metal is its availability and almost no toxicity resulting in its usage even in domestic utensils. Its broad application has been one of the key factors to explore its organometallic chemistry for a comparative understanding and a considerable progress has been made in this area. A breakthrough in organoaluminum chemistry stems from the discovery of the alkene insertion reaction by Ziegler and the low-pressure polymerization of ethene and propene in the presence of organometallic mixed Group 4 and 13 catalysts by Ziegler and Natta. Our group breaks new ground in the organometallic chemistry of aluminum and our contributions include a variety of novel complexes of aluminum especially with β–diketiminate ligands by exploiting unique electronic and steric properties offered by it.[22,23] During our studies we observed the formation of a C–H activated aluminum compound in some reactions involving aluminum complexes supported by β–diketiminate ligands and bases.[114,115] Similar deprotonation reactions at the backbone have been observed for the borane stabilized germylene hydride, for the tautomerization of a iminogermane bearing the β–diketiminato ligand, for a cyclodiazaborane analogue, and for a calcium complex.[116-118,103]

At the same time synthesis and characterization of heterometallic complexes which contain aluminum in general have enormous potential to revive homogeneous catalytic processes. We reported on the development of a new class of heterobimetallic complexes through oxygen bridging. These systems can function as excellent candidates for homogeneous catalysis[34,37,56,57]and this topic was recently reviewed.[119] Our synthetic strategy is based on utilizing various p-block and transition metal hydroxides and has been successful in assembling novel heterobi- and heteropolymetallic oxides by exploiting the acidic nature of the hydroxide complexes (e.g. LAl(OH)Me [34] [L = $CH(CMe2,6\text{-}i Pr_2C_6H_3N)_2$] and $Cp^*{}_2(Me)Zr(OH)$.[56]). The heterobimetallic compound $LAl(Me)(\mu\text{-}O)Zr(Me)Cp_2$ was obtained from the reaction of LAl(OH)Me with Cp_2ZrMe_2 and proved to be an excellent catalyst in ethylene polymerization.[34] The point in question is whether it is possible to assemble aluminum with another metal in the same molecule without an oxygen bridge. To realize this idea a suitable precursor like LAlOH(Me) for oxygen bridged systems is needed to assemble multiple metals in a single molecule.

1.10. Direction of the Thesis Work

The above discussion shows that the organometallic chemistry of heavier alkaline earth metals is still in its infancy. Recent interest in alkaline earth systems is due to their similarity to rare earth[102,-104,120-122] applications in material science and catalysis. So it is interesting to materialize these complexes with different functionality at the metal center and its reactivities towards different reagents. At the same time a C–H activated aluminum complex like its germanium and silicon counterparts as a versatile precursor for various aluminum complexes is not yet known. A direct synthetic method to obtain hetero-bimetallic and -trimetallic methylene bridged complexes is also not known as its oxygen bridged counterparts.

Based on these facts the objective of the present work is as follows:

- to develop a new synthetic strategy for the preparation of β−diketiminate supported strontium hydroxide complexes and study their reactivity.
- to synthesize a monomeric solvent free calcium iodide complex and soluble strontium mono halide complexes.
- to develop a new synthetic strategy for the preparation of β−diketiminate supported heavier alkaline earth metal acetylide complexes.
- to prepare various borohydride complexes with Group 2 metals.
- to develop a synthetic route to obtain soluble strontium oxide
- to use the spectral techniques such as NMR, IR spectroscopy, and X–ray structural analysis methods to characterize the products obtained.

Chapter 2

A Reactivity Change of a Strontium Monohydroxide by Umpolung to an Acid

Group 2 metals except Be react with water and form metal hydroxides by elimination of hydrogen gas. These metal hydroxides exist as $M^{2+}_{(aq)}$ and $OH^{-}_{(aq)}$ ions in aqueous solution. The basic strength increases within this group from Mg to Ba and can be determined by pH measurements. This basic knowledge informs us that the aforementioned Group 2 hydroxide complexes might behave as a base. To shed light into this issue and to find out the exact nature of the OH functionality in these complexes, we prepared a novel strontium hydroxide complex $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (**2**) by the controlled hydrolysis of strontium amide $LSrN(SiMe_3)_2(thf)$ (**1**) and carried out a series of experiments on this hydroxide. Herein, we report the first molecular hydrocarbon soluble strontium mono hydroxide **2** and a heterobimetallic compound $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ (**5**) obtained by the reaction of strontium hydroxide $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (**2**) with $Zr(NMe_2)_4$, where compound **2** behaves as an acid instead of its expected reactivity as a base. Such an umpolung is unprecedented in Group 2 hydroxide chemistry.

2.1. Synthesis of a Strontium Amide

The reaction of LH with two equivalents of $KN(SiMe_3)_2$ in THF was carried out for 5 h. Addition of this reaction mixture to a slurry of SrI_2 in THF at room temperature led to the formation of the strontium amide $LSrN(SiMe_3)_2(thf)$ (**1**) as pale yellow crystals (77.9% yield). Compound **1** is soluble in a number of organic solvents. It has been well characterized by mass spectrometry, NMR spectroscopy (^{1}H, ^{13}C and ^{29}Si), X-ray single crystal structure, and elemental analysis. The ^{1}H and ^{29}Si NMR spectra of compound **1** show a singlet (0.14 ppm) for trimethylsilyl protons and a singlet (–15.95 ppm) for the trimethylsilyl silicon atoms respectively. The molecular ion peak corresponding to **1** was not observed in its EI mass spectrum. Pale yellow crystals of **1** suitable for structural analysis were obtained when a concentrated solution of **1** in *n*-hexane was allowed to stand at room temperature for 12 h.

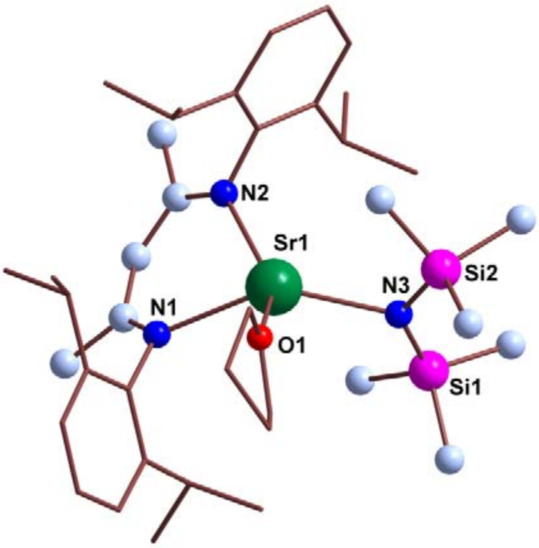


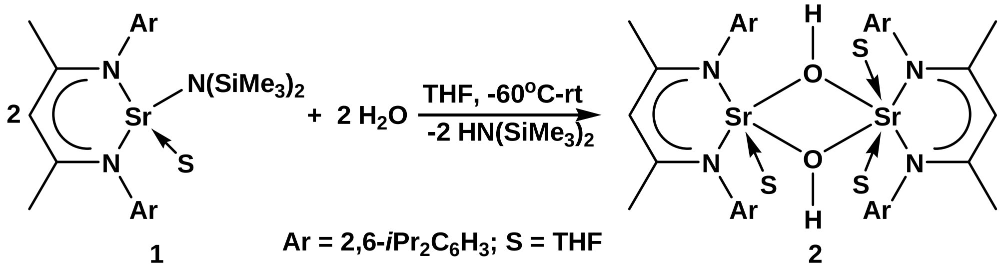
Figure 2.1. Crystal structure of **1**; Selected bond distances (Å) and angles (°): Sr1-N1 2.554(2), Sr1-N2 2.514(2), Sr1-N3 2.446(2), Sr1-O1 2.536(2); N1-Sr1-N2 74.13(7), N1-Sr1-N3 138.55(7), N2-Sr1-N3 118.24(7), N1-Sr1-O1 94.36(7), N2-Sr1-O1 140.77(7), N3-Sr1-O1, 95.43(7). All the hydrogen atoms have been omitted for clarity.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with a molecule of THF coordinated to the metal center. The structure of **1** (Figure 2.1) confirms the presence of a six-membered C_3N_2Sr ring. This ring has an envelope conformation with the strontium atom at a distance of 0.724 Å above the plane of the planar C_3N_2 framework. This can be compared with the magnesium and calcium amides where the respective metals are at a distance of 0.428 and 1.206 Å respectively above the plane of the planar C_3N_2 framework.[123,36] The Sr center is four coordinate with two nitrogen atoms of the β–diketiminate ligand, a nitrogen atom of the amide moiety and an oxygen atom of the THF. The strontium atom has a distorted tetrahedral geometry while that around the nitrogen atom of the amide is trigonal planar.

2.2. Synthesis of a Dimeric Strontium Hydroxide

Controlled hydrolysis of the amide **1** with a stoichiometric amount of degassed water in THF at –60 °C gave the strontium hydroxide $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ **(2)** as colorless solid (55.2% yield) (Scheme 2.1). Colorless crystals suitable for X-ray structural analysis were obtained either by keeping a dilute solution of **2** in THF at -32 °C or by concentrating its THF solution at room temperature.

Compound **2** is freely soluble in common organic solvents such as benzene, toluene, and THF. Compound **2** was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, elemental, and X-ray structural analysis. The complete disappearance of the $SiMe_3$ resonance (0.14 ppm) of **1** clearly indicates the formation of compound **2**. As expected the resonances for the γ-CH (4.74 ppm) and OH (–0.72 ppm) protons appear as singlets in the ^{1}H NMR. The absence of the molecular ion peak in the EI mass spectrum of **2** shows its instability under these conditions. The hydroxide stretching frequency of **2** appears as a sharp absorption band (3677 cm^{-1}) in the IR spectrum and is comparable to those of the inorganic anhydrous strontium dihydroxide (3618 cm^{-1}).[124]



Scheme 2.1: Preparation of the strontium hydroxide complex **2**.

2 crystallizes in the triclinic space group $P\bar{1}$ with two molecules of THF as colorless crystals. The structure of **2** (Figure 2.2) reveals its dimeric nature and shows the presence of two six-membered C_3N_2Sr rings. These six-membered rings are connected to each other by means of two μ-OH groups, which result in the formation of a four-membered Sr_2O_2 ring. The six-membered rings possess envelope conformation and are perpendicular to each other [89.6°]. The four-membered Sr_2O_2 ring is planar and forms an angle of 53.3° and 38.1° with the two six-membered rings.

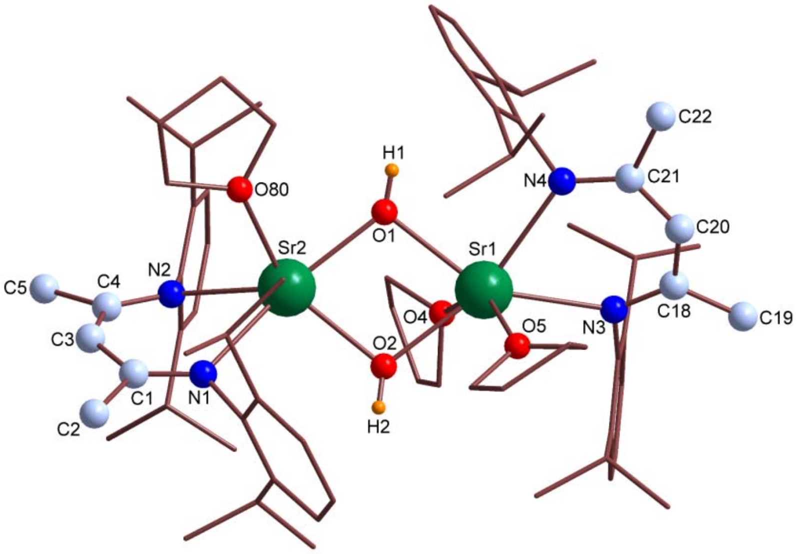


Figure 2.2. Crystal structure of **2**·2THF; Selected bond distances (Å) and angles (°):Sr1-N4 2.658(2), Sr1-O1 2.411(2), Sr1-O2 2.430(2), Sr1-O4 2.642(2), Sr1-O5 2.621(2), Sr2-N1 2.599(3), Sr2-O1 2.384(2), Sr2-O2 2.383(2), Sr2-O80 2.564(2), Sr1···Sr2 3.7811(14); N3-Sr1-N4 70.75(8), O1-Sr1-O2 75.48(7), O1-Sr1-N3 146.21(8),O2-Sr1-N4 150.47(8), N2-Sr2-N1 71.81(8), O1-Sr2-O2 76.86(7), O2-Sr2-N2 128.47(7), O2-Sr2-N1 94.88(8), O1-Sr2-N2 128.16(8). The two non coordinate THF molecules and all the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

Interestingly, the strontium atoms have an environment that differs in the number of coordinated THF molecules. Thus, one of the strontium atoms is penta coordinate and has distorted trigonal bipyramidal geometry with two nitrogen atoms of the β–diketiminate ligand, two oxygen atoms of the two hydroxyl groups, and an oxygen atom of the THF molecule. The other strontium atom has the similar environment but contains one additional THF molecule in its coordination sphere, which makes it hexa coordinate with distorted octahedral geometry. This observation is in contrast to the magnesium and calcium hydroxides ([LMg(μ-OH)(thf)]$_2$ and [LCa(μ-OH)(thf)]$_2$) where the alkaline earth metal centers have the same coordination geometry. As anticipated the Sr–O bond distances in hydroxide **2** (2.402(2)$_{av}$ Å) are longer than the Mg–O (1.988(2) Å) and Ca–O (2.225(6)$_{av}$ Å) distances found in the magnesium[65b] and calcium congeners.[44] The Sr–O–Sr and O–Sr–O bond angles in **2** (103.83(9)$_{av}$°, 76.17(7)$_{av}$°) are comparable with those of Ca–O–Ca (103.49(11)°) and O–Ca–O (76.51(11)°) bond angles present in [LCa(μ-OH)(thf)]$_2$.

2.3. Coordinate Ligand Exchange with Benzophenone and Triphenyl phosphine oxide

We have tried the possibility for preparing a monomeric strontium hydroxide by exploiting the ligand exchange phenomenon observed in alkaline earth metal complexes.[44] Addition of two equivalents of benzophenone and triphenylphosphine oxide at room temperature to $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (**2**) in benzene resulted in precipitation of $[LSr(\mu\text{-}OH)(OCPh_2)]_2$ (**3**) as reddish orange crystals and in toluene led to the formation of $[LSr(\mu\text{-}OH)(OPPh_3)]_2$ (**4**) as yellowish compound (78.3% yield) at room temperature respectively. Compound **4** is soluble in benzene and toluene. Compound **4** shows a singlet (4.89 ppm) for the γ-CH protons and another one for the hydroxyl groups (-0.479 ppm). The ^{31}P NMR spectrum contains only one singlet (29.5 ppm) for the triphenylphosphine oxide. The SrO-H stretching frequency of **3** (3676 cm^{-1}) and **4** (3680 cm^{-1}) matches with that of **2** (3677 cm^{-1}). The molecular ion peak corresponding to **3** and **4** was not observed in the EI mass spectra.

The strontium hydroxide **3** (Figure 2.3) with coordinate benzophenone molecules crystallizes in the triclinic space group $P\bar{1}$ as orange-red diamond shaped crystals containing half of a molecule and half of a molecule of benzene in the asymmetric unit. Similar to the structure of **2** the structure of **3** contains three heterocyclic rings but their orientation differs significantly. The enveloped six-membered C_3N_2Sr rings are exactly parallel to each other caused by the crystallographic inversion center and form an angle of 32.3° with the planar four-membered Sr_2O_2 ring. Both the strontium atoms are penta coordinate (with two nitrogen atoms of the ligand L, two oxygen atoms of the hydroxyl groups, and an oxygen atom of the benzophenone molecule) and adopt a distorted square pyramidal geometry.

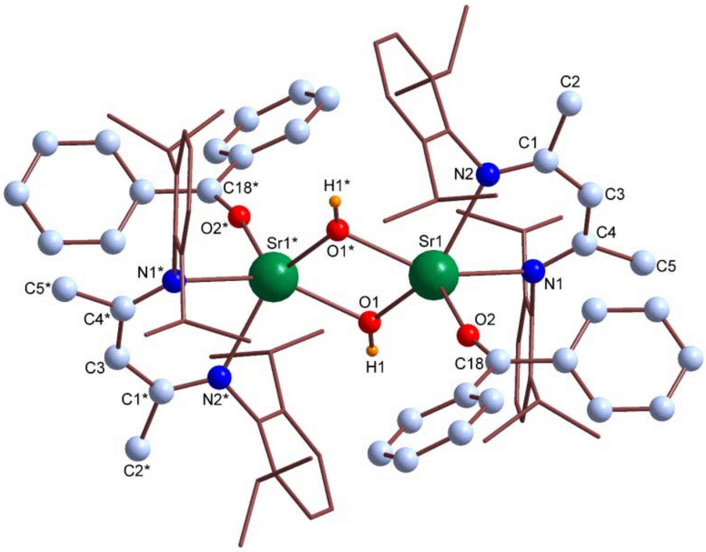


Figure 2.3. Crystal structure of **3**$\cdot C_6H_6$; Selected bond distances (Å) and angles (°): Sr1-N1 2.565(3), Sr1-N2 2.601(4), Sr1-O1 2.351(3), Sr1-O1* 2.381(3), Sr1-O2 2.531(3), Sr1···Sr1* 3.7306(9); N1-Sr1-N2 72.99(11), O1-Sr1-O1* 75.94(13), O1-Sr1-N1 100.94(11), O1*-Sr1-N2 90.63(11), O2-Sr1-N1 99.92(10). The benzene molecule and all the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

Yellow crystals of **4** suitable for structural analysis were obtained when a concentrated solution of **4** in toluene was kept at -5 °C for one day. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with a disordered toluene molecule. The structure of **4** (Figure 2.4) reveals the dimeric nature of **4** and rules out the possibility of a monomeric strontium hydroxide. Both the strontium atoms are penta coordinate with two nitrogen atoms of the *β*–diketiminato ligand, two oxygen atoms of the hydroxyl groups, and an oxygen atom of the triphenylphosphine oxide. In addition, they adopt distorted trigonal bipyramidal geometry with the oxygen atom of a hydroxyl group and a nitrogen atom of the *β*–diketiminato ligand occupying the apical positions. The structure of **4** contains two enveloped C_3N_2Sr six-membered rings and a planar Sr_2O_2 four-membered ring. The six-membered rings are exactly parallel to each other and form an angle of 43.95° with the four-membered ring. This angle shows that the structure of **4** is more twisted than the structure of the strontium hydroxide with coordinated benzophenone molecules where the same angle is 32.3°. The reason might be the more bulky triphenylphosphine oxide ligand than the benzophenone molecule.

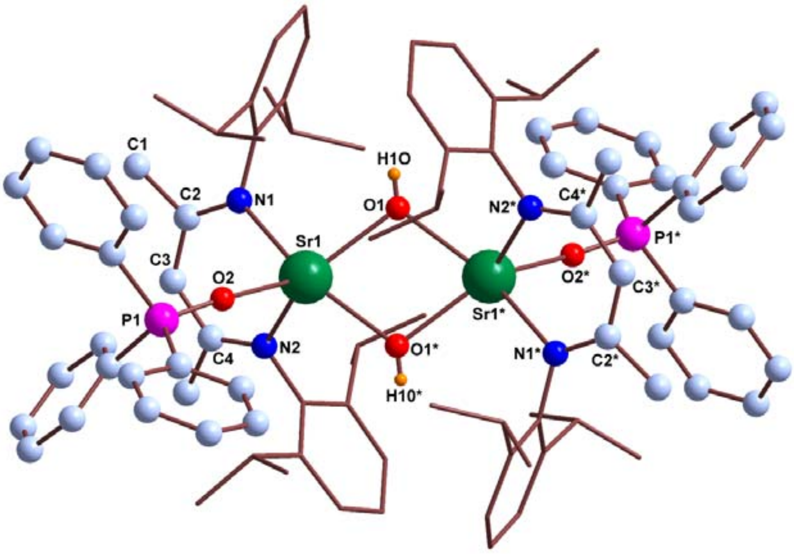
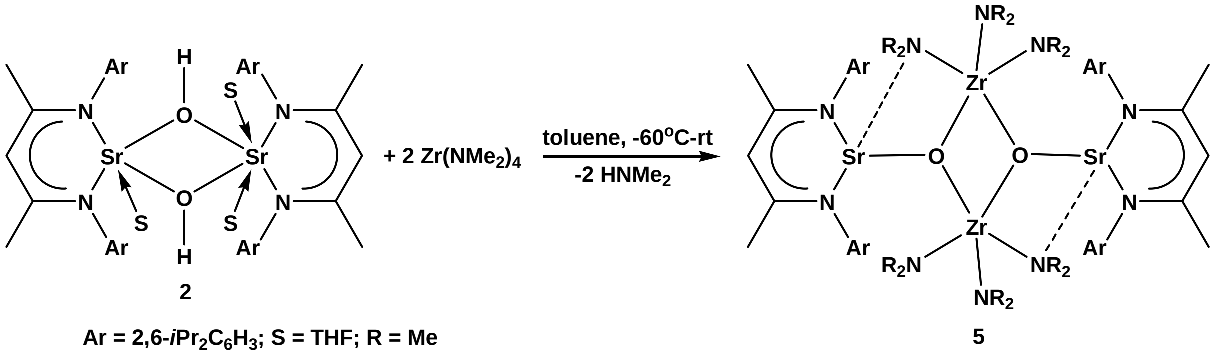


Figure 2.4. Crystal structure of **4**·1/2 toluene+1/2 benzene; Selected bond distances (Å) and angles (°): Sr1-N1 2.623(2), Sr1-N2 2.580(2), Sr1-O1 2.368(2), Sr1-O1* 2.379(2), Sr1-O2 2.538(2), P1-O2 1.496(2), Sr1···Sr1* 3.786(1); N1-Sr1-N2 72.18(6), O1-Sr1-O1* 74.20(8), O1-Sr1-N2 126.18(7), O1*-Sr1-N1 150.18(7), N2-Sr2-N1 72.18(6), O1-Sr1-O2 130.33(7), Sr-O1-Sr*105.80(8). The disordered solvent molecules and all the hydrogen atoms except those of hydroxyl groups have been omitted for clarity.

2.4. Reaction with $Zr[NMe_2]_4$

Reactivity study of the strontium hydroxide complex **2** with non cyclopentadienyl complexes of group 4 metal unveiled its unprecedented mild acidic character. Interestingly, reaction of **2** with two equivalents of $Zr(NMe_2)_4$ in toluene at –60 °C led to the intermolecular elimination of two equivalents of Me_2NH and resulted in the μ–oxo bridged heterobimetallic complex $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ **(5)** as colorless solid (69.1% yield) (Scheme 2.2). The special electronic and steric effect offered by the β–diketiminate ligand may be the reason for the umpolung of the hydroxide group in complex **2**. Although, we anticipate that the facile formation of the Zr–O–Sr bond may be the driving force for the change of the polarity in the hydroxide group of complex **2**.



Scheme 2.2: Preparation of heterobimetallic compound [LSr(μ-O)Zr(NMe$_2$)$_3$]$_2$

Compound **5** is freely soluble in common organic solvents such as benzene and toluene. Compound **5** was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, X–ray structural and elemental analysis. The complete disappearance of the OH resonance and stretching frequency of **2** in the ^{1}H NMR and IR spectrum of **5**, respectively, clearly indicates its formation. The ^{1}H NMR spectrum shows a singlet for the γ-CH (4.72 ppm) and NMe$_2$ (2.62 ppm) protons, respectively. No molecular ion peak was observed in the EI mass spectrum of **5** and only fragment ions are formed. Colorless crystals suitable for X-ray structural analysis were obtained by keeping a concentrated solution of **5** in toluene at –5 °C.

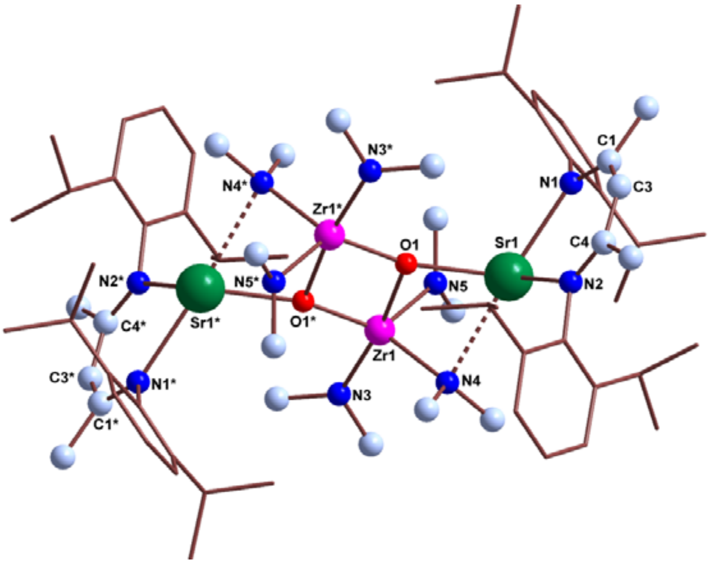


Figure 2.5. Crystal structure of **5**·toluene; Selected bond distances (Å) and angles (°):Sr1-N1 2.5421(17), Sr1-N2 2.5484(16), Sr1-N4 2.7865(17), Sr1-O1 2.3423(14), Zr1-O1 2.1992(13), Zr1-O1* 1.9778(13), Zr1···Zr2 3.2870(4); N1-Sr1-N2 72.17(5), O1-Sr1-N1 115.88(5), O1-Sr1-N2 117.67(5), O1-Sr1-N4 68.11, Zr1-O1-Zr1* 103.67(6), O1-Zr1-O1* 76.33(6), Zr1-O1-Sr1 96.63(5).The toluene molecule and all the hydrogen atoms have been omitted for

clarity. The dashed coordinate bonds represent the weak interactions between the strontium atoms and the –*N*Me$_2$ groups.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ together with a disordered toluene molecule (Figure 2.5). The structure reveals the dimeric nature of **5** and this dimerization results in the formation of a planar four-membered Zr_2O_2 ring. The zirconium atoms are penta coordinate (with three nitrogen atoms of the dimethylamino groups and two oxygen atoms) and adopt a distorted trigonal bipyramidal geometry. Among the three nitrogen atoms of the dimethylamino groups, one nitrogen atom takes up the apical and the other two nitrogen atoms are arranged on equatorial positions. One of the equatorial diaminomethyl nitrogen atoms on each zirconium atom forms a coordinate bond with the strontium atom and consequently two puckered four-membered SrONZr rings are assembled. Interestingly, both the strontium atoms rest almost on the plane of the planar Zr_2O_2 ring and the nitrogen atoms that bridge the zirconium and strontium atoms lie at a distance of 1.51Å above and below the $Sr_2Zr_2O_2$ plane. The strontium atoms are tetra coordinate (with two nitrogen atoms of the *β*–diketiminato ligand, nitrogen atom of one of the dimethylamino groups, and an oxygen atom) and create two six-membered C_3N_2Sr rings due to the bidentate mode of binding offered by the *β*–diketiminato ligands. In contrast to the enveloped C_3N_2Sr rings present in the strontium amide $LSrN(SiMe_3)_2(thf)$ and strontium hydroxide **2**, the C_3N_2Sr rings of **5** are nearly planar. Additionally, the C_3N_2Sr rings of **5** are exactly parallel to each other and are almost perpendicular (89.71°) to the $Sr_2Zr_2O_2$ plane.

2.5. Conclusion

In summary, a novel strontium hydroxide **2** was prepared from strontium amide **1** and water. The reaction of strontium hydroxide **2** with $Zr(NMe_2)_4$ gave the unprecedented heterobimetallic oxide **5** and reveals for the first time the acidic character of an alkaline earth metal hydroxide **2**. The stability and good solubility of **5** has given a route to prepare hitherto unknown strontium oxide complexes. Compound **5** can also act as a precursor for poly metallic complexes in view of its replaceable NMe_2 groups.

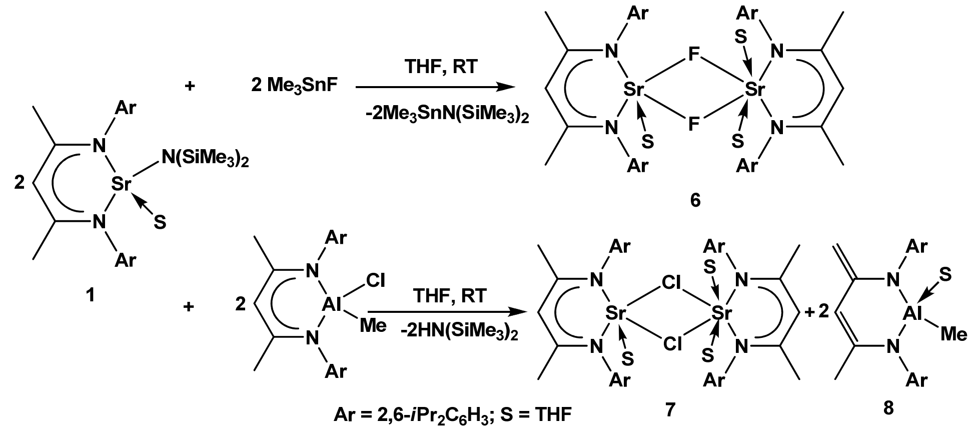
Chapter 3

Synthesis and Characterization of the Calcium and Strontium Halides

The realization of the strontium hydroxide initiated the study of the Sr–OH bond present in these complexes in hydrocarbon solvents.[125] Consequently it is anticipated that the synthesis of well-defined halide complexes of strontium enable the investigation of the Sr-X bond and also the realization of the $[LMg]_2$[33] complex from $LMgI{\cdot}OEt_2$.[68] Therefore, we report the first example of a hydrocarbon soluble molecular strontium mono fluoride $[LSr(thf)(\mu\text{-}F)_2Sr(thf)_2L]$ (**6**) (L = CH(CMe2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$), a mono chloride $[LSr(thf)(\mu\text{-}Cl)_2Sr(thf)_2L]$ (**7**), calcium mono iodide $[LCa(\mu\text{-}I){\cdot}thf]_2$ (**9**), strontium mono iodide $[LSr(\mu\text{-}I){\cdot}thf]_2$ (**10**) and a unique solvent free calcium iodide complex containg CaI_2, [L`CaI($\mu$-ICaI-$\mu$) L`CaI] (**11**) (L=CH{Et$_2$NCH$_2$CH$_2$N(CMe)}$_2$).

3.1. Synthesis of Strontium Fluoride and Chloride

The reaction of $LSrN(SiMe_3)_2(thf)$ (**1**) and Me_3SnF in THF at room temperature for 15 h led to the formation of the strontium fluoride **6** as colorless crystals (Scheme 3.1) while **1** and LAlCl(Me) in THF at room temperature yielded strontium chloride **7** (Scheme 3.1). The formation of **7** proceeds under elimination of $HN(SiMe_3)_2$ and generation of $L^1AlMe(thf)$ (L^1= CH[C(CH$_2$)](CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$) (**8**). Compounds **6** and **7** are soluble in toluene, benzene, and THF respectively. They have been well characterized by EI mass spectrometry, NMR spectroscopy [^{1}H, ^{13}C and ^{19}F (for **2**)], single crystal X-ray diffraction, and elemental analysis.



Scheme 3.1: Preparation of the strontium fluoride **6** and chloride **7** complex.

The ^{1}H and ^{19}F NMR spectra of compound **6** show a singlet (4.51 ppm) for the γ- protons and a singlet (–59.97 ppm) for the fluorine atoms respectively. The γ- protons of **7** resonate at 4.77 ppm.

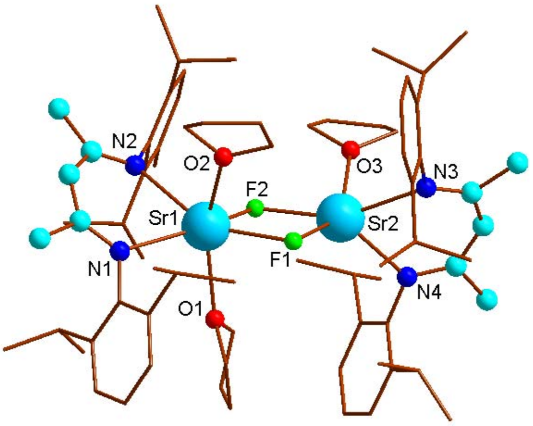


Figure. 3.1 Crystal structure of **6**·1.5C_7H_8; Selected bond distances (Å) and angles (°): Sr(1)–N(1) 2.605(2), Sr(1)–F(1) 2.397(1), Sr(1)–F(2) 2.345(1), Sr(1)–O(1) 2.581(2), Sr(1)–O(2) 2.581(2), Sr(2)–F(1) 2.317(1), Sr(2)–F(2) 2.333(1), Sr(2)–O(3) 2.554(2), Sr(1)–Sr(2) 3.739(1); Sr(1)–F(1)–Sr(2) 104.94(5), Sr(1)–F(2)–Sr(2) 106.09(5), F(1)–Sr(1)–F(2) 73.53(5), F(1)–Sr(2)–F(2) 75.23(5). All the hydrogen atoms and toluene molecules have been omitted for clarity.

The complete disappearance of the $SiMe_3$ resonance (0.14 ppm) of **1** in the ^{1}H NMR spectra of **6** and **7** clearly indicates the elimination of $Me_3SnN(SiMe_3)_2$ and $HN(SiMe_3)_2$ respectively. Compounds **6** and **7** are very sensitive to air and moisture and in non coordinating hydrocarbon solvents both have a tendency slowly to rearrange to form L_2Sr.[126] The molecular ion peak corresponding to **6** and **7** was not observed in the EI mass spectra.

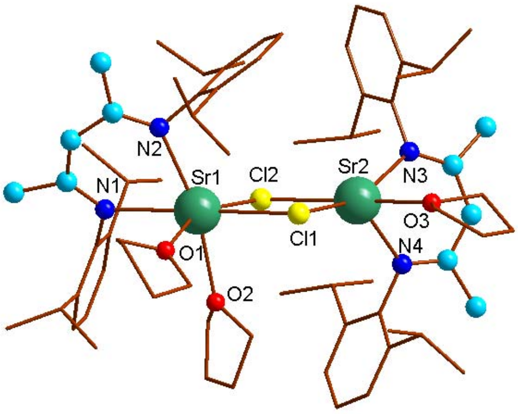


Figure. 3.2 Crystal structure of **7**·$0.5C_7H_8$; Selected bond distances (Å) and angles (°): Sr(1)–N(1) 2.618(3), Sr(1)–Cl(1) 2.954(1), Sr(1)–Cl(2) 2. 898(1), Sr(1)–O(1A) 2.584(7), Sr(1)–O(2) 2.577(2), Sr(2)–Cl(1) 2.890(1), Sr(2)–Cl(2) 2.821(1), Sr(2)–O(3) 2.599(2), Sr(1)–Sr(2) 4.469(1); Sr(1)–Cl(1)–Sr(2) 99.76(3), Sr(1)–Cl(2)–Sr(2) 102.78(3), Cl(1)–Sr(1)– Cl(2) 77.58(2), Cl(1)–Sr(2)– Cl(2) 79.87(3). All the hydrogen atoms and toluene molecule have been omitted for clarity.

Single crystals of **6** and **7** suitable for structural analysis were obtained when a concentrated solution of **6** and **7**, respectively, in a mixture of THF / toluene was stored at –5 °C in a freezer. Compounds **6** and **7** crystallize in the triclinic $P\bar{1}$ and monoclinic $C2/c$ space group respectively. The structures of **6** and **7** (Figures 3.1 and 3.2) reveal the dimeric nature of the complexes and contain two six-membered C_3N_2Sr rings. These six-membered rings are connected to each other by two μ-F or μ-Cl atoms, which result in the formation of a four-membered Sr_2F_2 ring in **6** and a corresponding Sr_2Cl_2 ring in **7**. The six-membered rings are not planar and are almost perpendicular to each other in **6** [81.3°] but exhibit an angle of 55.5° in **7**. The four-membered Sr_2Cl_2 and Sr_2F_2 rings are nearly planar and form angles of 35.84° and 66.48° in compound **6** and of 67.67° and 82.91° in compound **7**, respectively, with the two six-membered rings.

Interestingly, like the strontium hydroxide [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (**2**) the strontium atoms in **6** and **7** have different environments due to the number of coordinate THF molecules. Thus, one of the strontium atoms is penta coordinate and has distorted trigonal bipyramidal geometry with two nitrogen atoms of the β–diketiminate ligand, one oxygen atom of the THF molecule and two fluorine or chlorine atoms. The other strontium atom in **6** and **7** respectively has an additional THF molecule in its coordiantion sphere that results in a hexa coordinate environment. This makes **6** and **7** different from the magnesium and calcium analogues {[LMg(μ-F)(thf)]$_2$[70] and [LCa(μ-X)(thf)]$_2$[43,45] (X = F or Cl)}, where both the alkaline earth metal centers have the same coordination geometry. As expected the average Sr–F (2.348(1)$_{av}$ Å) and Sr–Cl (2.891(1)$_{av}$ Å) bond distances are longer than those of the corresponging calcium [2.180(2)$_{av}$ Å and 2.680(1)$_{av}$ Å] analogues.

3.2. Synthesis of Calcium and Strontium Iodides

The reaction of LH (L = CH(CMe2,6-iPr$_2$C$_6$H$_3$N)$_2$) and one equiv of KN(SiMe$_3$)$_2$ with CaI$_2$ or SrI$_2$ at room temperature led to the formation of the calcium iodide [LCa(μ-I)·thf]$_2$ (**9**) and strontium iodide [LSr(μ-I)·thf]$_2$ (**10**) as colorless compounds in good yields. Compounds **9** and **10** are soluble in organic solvents like benzene, toluene, and THF. **9** and **10** have been well characterized by mass spectrometry, NMR spectroscopy (^{1}H, ^{13}C), X-ray single crystal structure (for **10**), and elemental analysis. The ^{1}H NMR spectra of compounds **9** and **10** show a singlet [4.80 ppm (**9**), 4.84 ppm (**10**)] for γ-protons and another singlet [1.66 ppm (**9**), 1.69 ppm (**10**)] for the ligand backbone methyl protons respectively. The molecular ion peak corresponding to non solvated monomer of **10** (704.3 (100) [M$^+$/2-2THF]) was observed in the EI mass spectrum, while for **9** only fragment ions are observed.

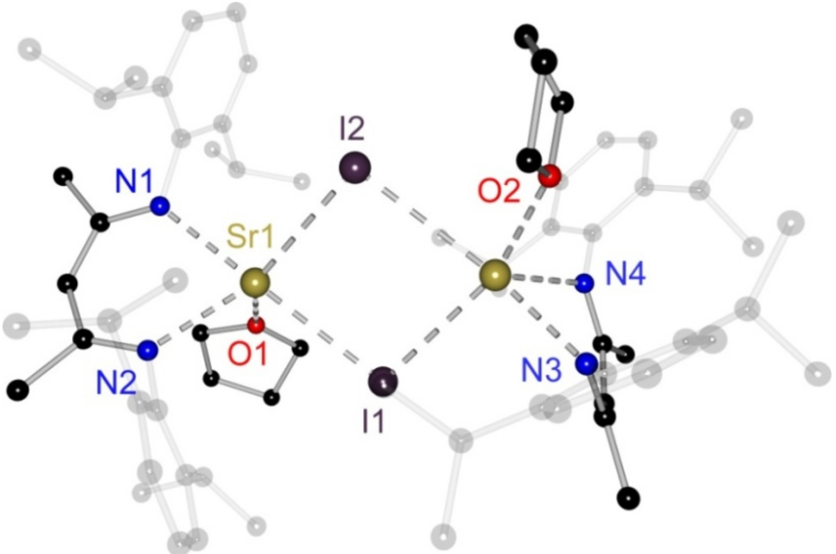


Figure 3.3. Crystal structure of **10**·0.5C$_6$H$_{14}$; Selected bond distances (Å) and angles (°): Sr1-N1 2.5068(15), Sr1-O1 2.5291(13), Sr1-I1 3.2404(4), Sr1-I 3.2481(4), Sr2-N3 2.4768(15), Sr2-O2 2.5118(14), Sr2-I1 3.2284(4), Sr2-I2 3.3100(4), Sr1···Sr2 3.7811(15); N1-Sr1-N2 74.69(5), I1-Sr1-I2 83.892(6), Sr1-I1-Sr2 97.354(6), Sr1-I2-Sr2 95.590(6), N3-Sr2-N4 77.45(5), I1-Sr2-I2 83.099(6). The substituents on the nitrogen atoms are depicted transparent while one non coordinate n-hexane molecule and all hydrogen atoms have been omitted for clarity.

Crystals of **10** suitable for X-ray structural analysis were obtained from a saturated solution of *n*-hexane at room temperature. **10** crystallizes as a dimer in the space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 3.3). The structure reveals the presence of two six-membered C_3N_2Sr rings. These six-membered rings are connected to each other by means of two μ-I atoms, which result in the formation of a four-membered Sr_2I_2 ring. Unlike its chloride and fluoride counter parts.[127] the coordination geometries around both metal atoms of **10** are the same. Thus both the strontium atoms are pentacoordinate and have distorted trigonal bipyramidal geometry with two nitrogen atoms of the β–diketiminate ligand, two bridging iodine atoms, and an oxygen atom of the THF donor molecule. The binding mode of the metal atoms is different when compared with a similar iodide complex $[Sr(\eta^5\text{-}L^{tBu})(\mu\text{-}I)(thf)]_2$ $[L^{tBu} = CH(CMe\textit{t}BuN)_2]$ reported. [72] In the latter each strontium is coordinated to one $\eta^5\text{-}L^{tBu}$ and one THF molecule in addition to two bridging iodine atoms. The Sr–I bond distances (3.257_{av} Å) are in accordance with those reported (3.282_{av} Å).[72] The Sr–I–Sr bond angles in **10** ($96.472(6)_{av}$°) are more acute than those of Sr-Cl-Sr ($101.27°_{av}$) reported in $[LSr(thf)(\mu\text{-}Cl)_2Sr(thf)_2L]$.[127] Unfortunately, up to now we were not able to obtain single crystals of compound **9**.

3.3. A $[I\text{-}Ca\text{-}I\text{-}Ca\text{-}I\text{-}Ca\text{-}I]^{2+}$ Chain Stabilized by Two Chelating β-Diketiminate Ligands

Is it possible to obtain calcium iodide as a solvent free complex? Such a possibility was tried with the ligand L`H (L`=$CH\{Et_2NCH_2CH_2N(CMe)\}_2$).[128]Attempts to obtain a solvent free dimeric calcium compound with 1:1:1 stoichiometry of reactants gives a mixture of products predominately **11**. But by adjusting the stoichiometry, we are able to obtain exclusively compound **11**. The reaction of two equiv L`H and two equiv of $KN(SiMe_3)_2$ with three equiv $CaI_2$ in THF at room temperature led to the formation of a $[I\text{-}Ca\text{-}I\text{-}Ca\text{-}I\text{-}Ca\text{-}I]^{2+}$ chain stabilized by two chelating $\beta$-diketiminate ligands, [L`CaI(μ-ICaI-μ)ICaL`] (**11**) (Scheme 1). Single crystals of compound **11**$\cdot 4C_7H_8$ were obtained by storing a concentrated toluene solution of **11** in a freezer at –32 °C. Crystals were dried under vacuum for 4 hours to remove four toluene molecules. Compound **11** is soluble in organic solvents like benzene, toluene, and THF and it is characterized by NMR spectroscopy (^{1}H, ^{13}C), mass spectrometry, elemental and X-ray single crystal analysis. The ^{1}H NMR spectrum of **11** shows broad resonances at room temperature. Therefore, the ^{1}H NMR experiment was conducted at higher temperature (343 K) to give a better resolution of the resonances. The ^{1}H NMR spectrum shows a singlet (4.57ppm) for the methine

CH protons and and the ^{13}C NMR spectrum exhibits a singlet (96.07 ppm) for the methine CH carbon atoms. No molecular ion peak corresponding to **11** was observed in the EI mass spectrum, while only fragment ions were observed. Furthermore, the structure of **11** was determined by single crystal X-ray diffraction studies.

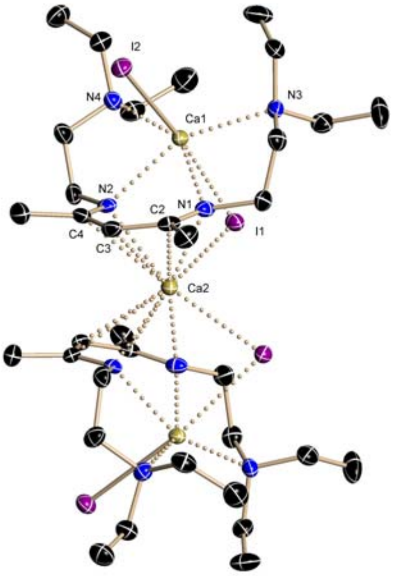


Figure 3.4. Crystal structure of **11**·4C_7H_8; Selected bond distances (Å) and angles (°): Ca(1)–N(1) 2.428(6), Ca(1)–N(2) 2.427(6), Ca(1)–N(3) 2.573(6), Ca(1)–N(4) 2.603(6), Ca(1)–I(1) 3.2109(18), Ca(1)–I(2) 3.1253(17), Ca(2)–I(1) 3.1618(16); N(1)–Ca(1)–N(2) 73.87(19), N(3)–Ca(1)–N(4) 134.70(19), I(1)–Ca(1)–I(2) 173.61(5), Ca(1)–I(1)–Ca(2) 69.72(3). All the hydrogen atoms have been omitted for clarity.

11 crystallizes in the monoclinic space group *P*2/*c* with four molecules of toluene in the asymmetric unit. The core structure reveals that one CaI_2 is connected to two terminal L^{1}CaI units (Figure 1). The coordination geometry around the metal atoms is different for the central calcium unit compared to those of the terminal ones. The core structure reveals that one CaI_2 is connected to two terminal L^{1}CaI units (Figure 3.4). The coordination geometry around the metal atoms is different for the central calcium unit compared to those of the terminal ones. The terminal calcium atoms are coordinate by four nitrogen atoms of L^1 and two iodine atoms exhibiting a pseudo octahedral coordination geometry around the metal atoms and therefore prove that the ligand forms a tetradentate coordination polyhedron. Ca1 exhibits an η^2-coordination mode through the nitrogen atoms of L^1 which is similar to that in calcium fluoride and chloride complexes containing the 2,6-diisopropylphenyl substituted ligand, L. In addition Ca1 is also coordinate to the nitrogen atoms of the two pendant donor side-arms. The Ca1-N bond lengths of the side-arms (2.588_{av} Å) are longer than those of the backbone (2.4275_{av} Å), due to the coordinative and ionic nature involved in different bonding modes. Moreover, the central calcium atom Ca2 is coordinate to two iodine atoms and two η^5- β-diketiminate rings. The calcium–nitrogen bond lengths are 2.540 and 2.510 Å, while the calcium–carbon distances are 2.837 Å C(2), 2.890 Å C(3), and 2.903 Å for C(4). Moreover, the central calcium atom is surrounded by iodine atoms and the ligands. As expected the average Ca–I ($3.166_{av.}$ Å) bond distance is comparable with that of a calcium complex $[Ca(\eta^5\text{-}L^{tBu})(\mu\text{-}I)(thf)]_2$ [L^{tBu} = $CH(CMe\textit{t}BuN)_2$] ($3.144_{av.}$ Å). Interestingly, within the pseudo octahedral coordination of the Ca atoms the I1–Ca1–I2 bond angle of 173.61° is close to linear.

3.4. Conclusion

In conclusion we have shown the facile synthesis of well-defined strontium fluoride **6** and chloride **7** by utilizing strontium amide **1**. β–Diketeminate supported calcium and strontium iodide were prepared from the reaction of LH, $KN(SiMe_3)_2$ with CaI_2 or SrI_2. We were also able to obtain a $[I\text{-}Ca\text{-}I\text{-}Ca\text{-}I\text{-}Ca\text{-}I]^{2+}$ chain stabilized by two chelating β-diketiminate ligands as [L`CaI($\mu$-ICaI-$\mu$)ICaL`] (**11**) from reaction of ligand L^1H ($L^1=CH\{Et_2NCH_2CH_2N(CMe)\}_2$), $KN(SiMe_3)_2$, and calcium diiodide. The stability and good solubility of these compounds have given the possibility to study the nature of M–X bond present in these complexes. These complexes can also serve as good precursors for homometallic compounds with low oxidation state.

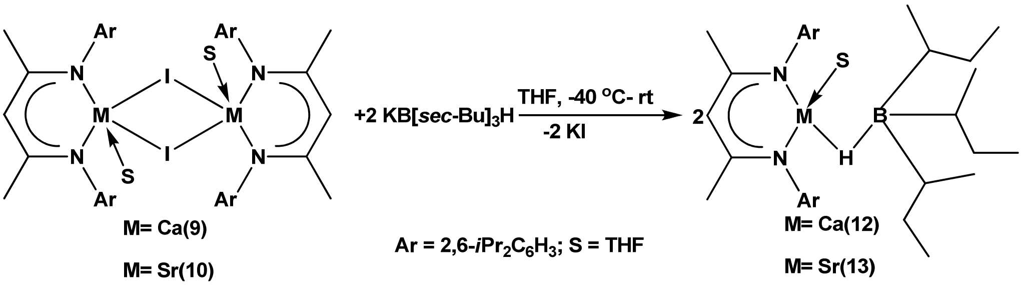
Chapter 4

Synthesis and Characterization of the Calcium and Strontium Borohydrides

The successful preparation of well-defined Group 14 hydride complexes prompted us to try the same method to alkaline earth metals by employing alkaline [R_3BH] complexes.[129] The ion [$R_3BH]^-$ has found extensive use as a hydride source and reducing agent. Moreover, the exploration of heavier alkaline earth metals gained a momentum nowadays that has striking similarity to lanthanides[102,-104,120-122] and that also initiated research in this field. We also assumed that the alkyl borane[132] [$R_3BH]^-$ can stabilize the complex without decomposition or ligand exchange.[61-64] Herein we report the well-defined hydrocarbon soluble alkaline earth metal boron hydride complexes prepared from the corresponding alkaline earth metal iodides and potassium tri*sec*-butylborohydride.

4.1. Reaction of K[*sec*-Bu$_3$BH] with [LCa(μ-I)·thf]$_2$ (9) and [LSr(μ-I)·thf]$_2$ (10) to the Products LCaB(*sec*-Bu)$_3$H·thf (12) and LSrB(*sec*-Bu)$_3$H·thf (13)

K[*sec*-Bu$_3$BH] has proved to be a versatile hydride source for the conversion of Group 14 chlorides to the corresponding hydrides.[129a,b] As shown in Scheme 4.1 potassium tri*sec*-butylborohydride reacts readily with [LCa(μ-I)·thf]$_2$ (**9**) leading to **12** in excellent yield instead of giving the corresponding hydride complex with two μ-H bonds bridging the alkaline earth metals. Monodentate ligation of [$HBR_3]^-$ to the alkaline earth metal center is rare although it contributes to the stability of the hydride complexes. We expected the same type of compound when the β-diketiminate stabilized strontium iodide **10** is used as a precursor. Indeed compound **13** (Scheme 4.1) was formed accordingly with the reaction of **10** with K[*sec*-Bu$_3$BH].



Scheme 4.1: Preparation of β-diketiminate supported calcium **12** and strontium borohydride **13** complexes

Compounds **12** and **13** are yellow solids soluble in toluene, THF, and benzene. Spectroscopic characterization indicates the formation of both compounds **12** and **13**. The ^{1}H and ^{11}B NMR spectra of **12** and **13** show a singlet [4.76 ppm (**12**) and 4.74 ppm (**13**)] for γ-protons and a singlet (–4.4 ppm (**12**) and -4.7 ppm (**13**)) for the boron atoms respectively. The ^{11}B nucleus of **12** resonates in the NMR spectrum downfield when compared with those of other calcium borohydride complexes (–12.0 ppm and–13.3 ppm).[91,130c] The *sec*Bu-methyl groups attached to boron in **12** and **13** are non equivalent and exhibit three doublets and three triplets. The resonance corresponding to the (M-μH-B) hydride appears very broad in the ^{1}H NMR spectrum of both complexes. A ^{11}B-^{1}H correlation clearly indicates the presence of this hydride in the complexes. Molecular ions corresponding to **12** and **13** in the EI mass spectra were not observed and only fragment ions were seen. For the B-H-M unit of **12** and **13**, two absorption bands for **12** (1924 and 1903 cm^{-1}) and a weak absorption band at 1932.06 cm^{-1} for **13** are observed in the IR spectrum. The former are comparable to those of the hydrogen bridged complex [Ca(HBEt$_3$){1,2,4-C$_5$(SiMe$_3$)$_3$H$_2$}(thf)$_2$] (1935 cm^{-1})[130c] and to the K[R$_3$BH] (1904 cm^{-1}). Therefore we assume that in the solid state for **12** two forms of hydrogen bonds might be present. The one that binds more to the alkaline earth metal and the other more to the boron.

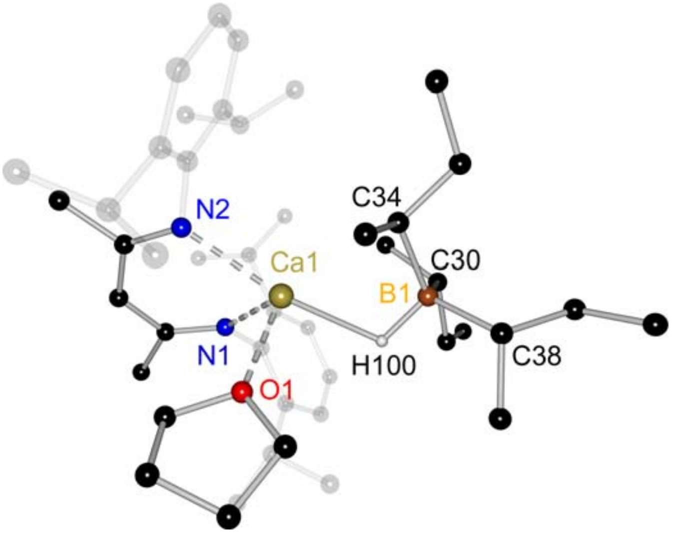


Figure 4.1. Crystal structure of **12**; Selected bond distances (Å) and angles (°): Ca1-N1 2.337(3), Ca1-N2 2.371(3), Ca1-O1 2.337(3), Ca1-B1 2.861(4), Ca1-H100 2.16(3), B1-C30 1.643(6), B-C38 1.655(6), B-C34 1.673(5), B1-H100 1.24(3); N1-Ca1-N2 78.97(9), N1-Ca1-B1 130.00(11), N2-Ca1-B1 143.02(11), O1-Ca1-N2 96.19(9), O1-Ca1-B1 102.03(11), B1-Ca1-H100 23.8(8). The substituents on the nitrogen atoms are depicted transparent and all hydrogen atoms have been omitted for clarity except the hydrogen atom involved in bonding to Ca^{2+}.

X-ray quality crystals of **12** and **13** were grown from a mixture of toluene and THF. Both isostructural molecules crystallize in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The boron atoms in **12** and **13** exhibit a distorted tetrahedral coordination environment with bond angles of 104.3(13)° to 114.9(2)º (Figures 4.1 and 4.2). Because of the bulky *sec*-butyl groups, the angles between the hydrogen atom and the carbon atoms are smaller than the ideal tetrahedral angle, whereas the angles between the carbon atoms are larger. As a result of the large metal-boron distance the metal has only small to no steric influence on the geometry around the boron atom. The metal atoms in **12** and **13** display each a distorted trigonal pyramidal environment with the two nitrogen atoms of the ligand and the boron atom at the base and the oxygen atom from the THF at the apex. The space at the base of the pyramid is occupied by the bulky substituents of the nitrogen atoms and the boron atom. The hydride bridge seems to have no influence on the geometry in comparison to the bulky *sec*-butyl and *iso*-propyl groups. In both compounds, the borohydride anion coordinates to the M^{2+} ion through the (M-μH-B) bond. The B-H···Ca^{2+}(2.16(3)) Å contact compares well to those observed in [Ca(HBEt$_3$){(Me$_3$Si)$_3$Cp}(thf)$_2$] of 2.21(4) Å[130c] and [LCa-(H$_2$BC$_8$H$_{14}$) thf)] (2.25(2)) Å.[91] As expected the B-H···Sr^{2+}(2.325(8) Å) bond length is longer compared to its lighter counterpart **12** and is shorter to those in the strontium complex, [(Me$_3$Si)$_2${Me$_2$-(H$_3$B)P}C]$_2$Sr(THF)$_5$ (2.735$_{av}$ Å).[130a]

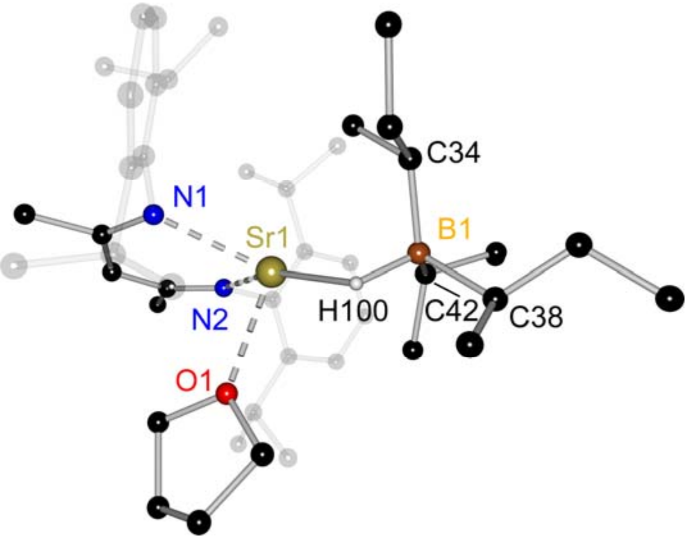


Figure 4.2. Crystal structure of **13**; Selected bond distances (Å) and angles (°): Sr1-N1 2.486(2), Sr1-N2 2.509(2), Sr1-O1 2.501(2), Sr1-B1 3.003(3), Sr1-H100 2.325(8), B1-C34 1.645(4), B-C38 1.661(5), B-C42 1.672(4), B1-

H100 1.246(3); N1-Sr1-N2 73.00(7), N1-Sr1-B1 134.97(8), N2-Sr1-B1 146.01(9), O1-Sr1-N2 94.28(7), O1-Sr1-B1 100.31(8), B1-Sr1-H100 22.8(3). The substituents on the nitrogen atoms are depicted transparent and all hydrogen atoms except the hydrogen atom involved in bonding to Sr^{2+} have been omitted for clarity.

A reaction has been carried out on a NMR scale to check whether the bridging hydride can be released from the compound **13**. LSrB(*sec*-Bu)$_3$H·thf converts LGeCl to LGeH at room temperature and the chemical shift of the product was compared with the reported value.[89]

4.2. Conclusion

In summary, molecular calcium and strontium tri*sec*-butylborohydride complexes were prepared from calcium and strontium iodide and potassium tri*sec*-butylborohydride. In both complexes the anion $[HBR_3]^-$ is linked to the alkaline earth metal through a hydride bridge. This method opens a synthetic pathway for the preparation of borohydride complexes of heavier alkaline earth metals supported by *β*–diketiminate ligands. The bulky *β*–diketiminate ligand and ligation of $[HBR_3]^-$ can be a reason for its good stability. Complexes **12** and **13** are monomeric and can easily liberate its bridging hydride. LGeH is obtained when LSrB[(*sec*-Bu)]$_3$H·thf is reacted with LGeCl to confirm that it can act as a hydride transfer agent.

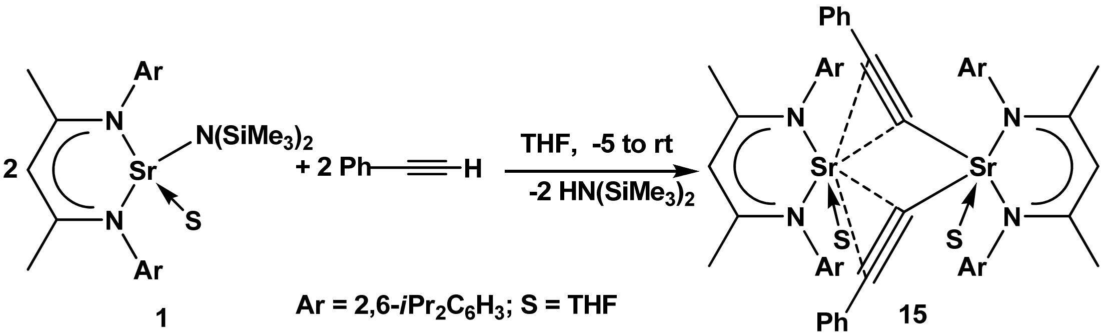
Chapter 5

Synthesis of Acetylide complexes of Heavier Alkaline Earth Metals

The successful isolation of the strontium amide LSrN(SiMe$_3$)$_2$(thf) (**1**) (L = CH(CMe2,6-iPr$_2$C$_6$H$_3$N)$_2$) prompted us to prepare soluble mono alkynyl complexes of strontium. In this chapter we report the synthesis and characterization of a well-defined molecular mono strontium alkynyl [LSr(thf)(μ-C≡CPh)]$_2$ (**15**) prepared from the reaction of PhC≡CH with the strontium amide **1**. The strontium alkynyl complex **15** is compared with its lighter congener [LCa(thf)(μ-C≡CPh)$_2$CaL] (**14**). Both compounds are dimers with an interesting coordination geometry around the metal centers.

5.1. Synthesis of Calcium and Strontium Acetylide Complexes

Compounds **14** and **15** are prepared by the selective protonolysis of the β–diketiminato compounds LCaN(SiMe$_3$)$_2$(thf) and **1** respectively, with PhC≡CH at –5 °C in THF. Unlike its lighter congener, compound **15** retains coordinate THF in hydrocarbon solvents like toluene and n-hexane. Formation of a slight amount of the homoleptic strontium compound L$_2$Sr [126] was observed in toluene, but in n-hexane exclusively the expected **15** was formed. Colorless crystals for X-ray structural analysis were obtained by keeping a solution of **15** in an n-hexane/THF mixture at room temperature and a solution of **14** in a toluene/THF mixture at –5 °C.



Scheme 5.1: Preparation of the β-diketiminate supported strontium monoalkynyl complex.

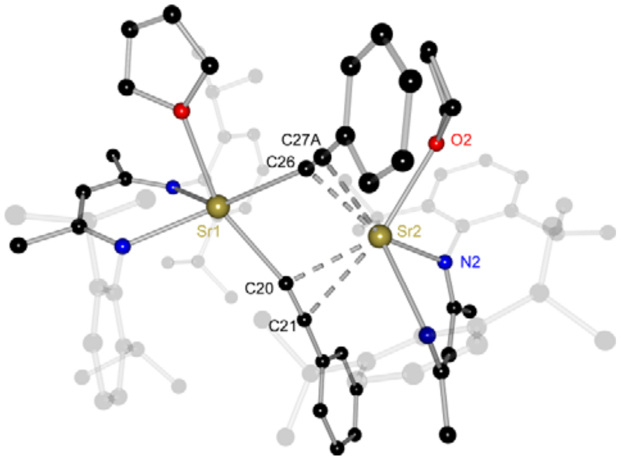


Figure 5.1. Crystal structure of [LSr(thf)(μ-C≡CPh)]$_2$(**15**); Selected bond distances (Å) and angles (°): Sr1–C20 2.694(5), Sr1–C26 2.710(5), Sr1–O1 2.6498(49), Sr2–C20 2.818(4), Sr2–C26 2.678(5), Sr2–C21 3.249(5), Sr2–C27A 3.247(7), Sr2–O2 2.6852(48), C20–C21, 1.215(8), C26–C27A 1.241(9), Sr1···Sr2 4.1300(8); Sr1–C20–C21 163.18(41), Sr1–C26–C27A 136.90(37), Sr1···Sr2–C20 40.35(11), Sr1···Sr2–C26 40.25(10), Sr1···Sr2-C21 62.04(09), Sr1···Sr2-C27A 59.27(11), Sr2–C20–C21 99.47(35), Sr2–C26–C27A 105.44(36). The position of one THF molecule (coordinating via O2) and one alkynyl group (coordinating via C26) are disordered which results in a distortion of the ligand (coordinating via N2); the substituent on the nitrogen atoms is shown in transparent and the second positions of the disordered groups and all hydrogen atoms have been omitted for clarity.

Compound **15** exhibits good solubility in common organic solvents such as benzene, toluene, and THF. It was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, elemental and X-ray structural analysis. The complete disappearance of the SiMe$_3$ resonance at 0.14 ppm present in **1** clearly indicates the loss of the bis(trimethylsilyl)amide group and the formation of **15**. As expected, the resonances for the γ-CH protons display at 4.60 ppm as singlet in the ^{1}H NMR. The C≡C absorption band becomes visible at 2161 cm^{-1} in the IR spectrum. The molecular ion peak corresponding to **15** was not observed and some fragment ions were seen in its EI mass spectrum.

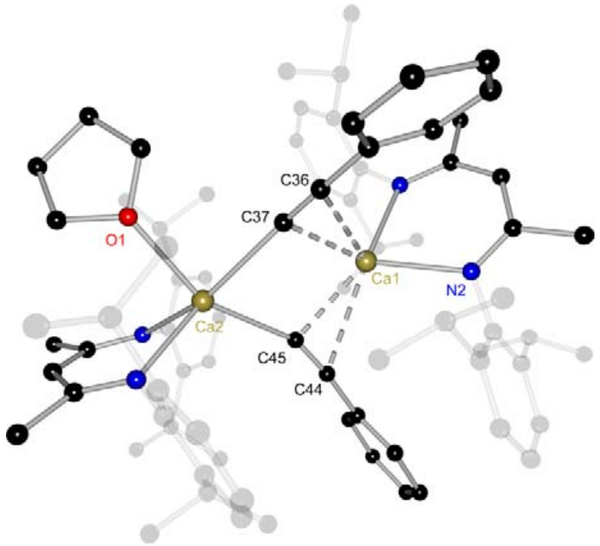


Figure 5.2. Crystal structure of **14**·C_7H_8; Selected bond distances (Å) and angles (°): Ca1···Ca2 3.8294(7), Ca2–C37 2.580(3), Ca2–C45 2.568(3), Ca1–C37 2.532(2), Ca1–C45 2.516(2), Ca1–C36 2.866(2), Ca1–C44 2.995(3), Ca2–O1 2.4383(18), C36–C37 1.210(4), C44–C45 1.221(4); Ca2–C37–C36 162.37(19), Ca2–C45–C44 157.65(20), Ca2···Ca1–C37 41.97(6), Ca2···Ca1–C45 41.65(6), Ca2···Ca1–C36 66.35(5), Ca2···Ca1–C44 64.85(5), Ca1–C37–C36 93.15(17), Ca1–C45–C44 100.77(18). The substituent on the nitrogen atoms is shown in transparent and one uncoordinated toluene molecule and all hydrogen atoms have been omitted for clarity.

Compound **15** crystallizes as a dimer in the orthorhombic space group *Pnma*. Interestingly, the two strontium atoms in **15** show different coordination modes (Figure 5.1). Both strontium atoms are coordinated by two nitrogen atoms of one nacnac ligand, one THF molecule and two terminal sp-hybridized acetylide carbon atoms that μ-bridge the metal atoms via 2e3c bonds. If both metal atoms got the same amount of σ-electron density from the terminal alkynyl carbon atoms C20 and C26 the angles around these atoms should be 120° but the present angles Sr1–C20–C21/Sr2–C20–C21 (163.18°/99.47°) and Sr1–C26–C27A/Sr2–C26–C27A (136.90°/105.44°) clearly indicate that Sr1 gets more σ-electron density whereas Sr2 gets saturated by the additional π-electron density of the alkynyl groups. The angles around C20 and C26 also show that the σ-electron density from C26 is shared more equally between the metal atoms than that from C20. This is also displayed by the Sr-$C_{terminal}$ bond lengths. Whereas the bond lengths of Sr1–C20 (2.694 Å), Sr1–C26 (2.710 Å) and Sr2–C26 (2.678 Å) are in close proximity with those known from the literature.[50] Sr2–C20 (2.818 Å) is much longer, indicating only weak coordination by the σ-electron density from C20. Both metal atoms show distorted trigonal bipyramidal coordination although the geometry around the Sr2-atom is even more distorted.

Compound **14** crystallizes as a dimer in the monoclinic space group $P2_1$ and shows the same overall structural feature as **15** except for the number of coordinated THF molecules (Figure 5.2). Like in **15**, in **14** the two metal atoms exhibit a different coordination mode. The calcium atoms are also coordinated by two nitrogen atoms of one nacnac ligand and bridged by two carbon atoms of the alkynyl groups. In addition, Ca2 is coordinate by one THF molecule resulting in a distorted trigonal bipyramidal geometry whereas Ca1 is also coordinate by the π-electron density of the alkynyl groups. Since the radius of calcium cation is smaller than that of strontium there is not enough space for an additional THF donor molecule, which resulted in a distorted tetrahedral coordination for Ca1.

As anticipated the metal-carbon bond distances in **15** are all longer than those of the calcium congener. The Sr–C–Sr and C–Sr–C bond angles in **15** (98.44°, 80.37°) are comparable to those of the Ca–C–Ca (97.36°) and C–Ca–C (81.96°) bond angles present in **14**. In **15** and **14** the metal-metal distances are too long to be considered as metal-metal interactions.

There are already examples known for dimeric calcium-alkynyl-complexes[41,50] and even examples with a π-coordination of the triple bond of the acetylides,[41] but in contrast to **14** all these complexes show identical coordination geometries for both metal atoms.

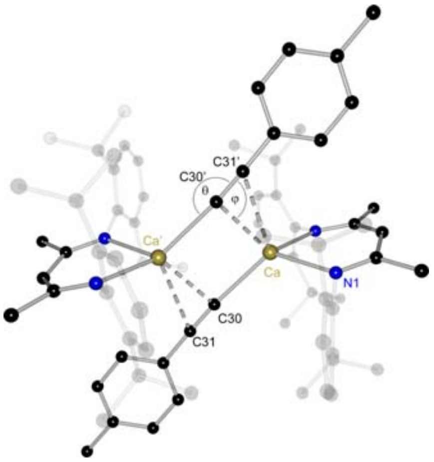


Figure 5.3. Crystal structure of $[LCa(\mu\text{-}C{\equiv}C\ p\text{-tol})_2CaL]$.[41] The substituent on the nitrogen atoms is shown in transparent and all hydrogen atoms have been omitted for clarity.

For **14** the strength of the π-interaction of the alkynyl groups with the metal atoms was studied. This can be documented by looking at the $Ca–C_\alpha–C_\beta$ (θ) and $Ca'–C_\alpha–C_\beta$ (φ) angles (Figure 5.3). The difference between both angles (θ - φ) is an indicator for the strength of the π-interaction; a value of 90° indicates a strong interaction and a value of 0° no interaction.

Hill *et al.*[41] found strong π-interactions (θ - φ = 76.2° and 79.9°) for the complexes with sterically non-demanding alkynyls (phenyl and toluene) and weaker π-interactions (θ - φ = 46.4°) for sterically demanding alkynyls (*tert*-butyl). With an angle of 56.88° and 69.22° the π-interactions in **14** are between those found by Hill *et al.* indicating that a stronger π-interaction was assumed to strengthen the 2e3c bond that bridges both metal atoms. The reason for the distinct smaller angle for one of the two alkynyl groups is the steric demand of the nacnac ligand that does not permit a closer interaction. Beside this, the main difference between the herein discussed structures and the molecules from Hill *et al.* is the additionally coordinated donor base. Due to the additional coordination of the THF molecule the symmetric coordination of the metal atoms is broken and the π-electron density is transferred exclusively to Ca1 leaving Ca2 with the additional electron density from the donor base and a bigger part of the σ-electron density from the terminal carbon atoms. Another structural feature going hand in hand with the THF coordination is the planarity of the central M_2C_2-ring. The examples known from the literature all show a planar Ca_2C_2-ring. In **14** and **15** the four-membered rings are not planar but the $C_{terminal}$-atoms and the associated alkynyl groups are slightly shifted to one side. Both alkynyl groups are bent to the same side leaving the other metal site open for the coordination of one and two THF molecules, respectively.

5.2. Conclusion

In summary we have demonstrated that reaction of strontium amide $LSrN(SiMe_3)_2(thf)$ with PhC≡CH in THF yields the dimeric alkynyl complex $[LSr(thf)(\mu\text{-}C{\equiv}CPh)]_2$ which shows an interesting coordination geometry around the metal center. **15** retains the THF molecules, unlike its lighter congener, even in hydrocarbon solvents. The dimeric alkynyl alkaline earth metal complexes **14** and **15** exhibit unprecedented bis-all-σ- and bis-all-π-coordinated metal atoms in the same molecule.

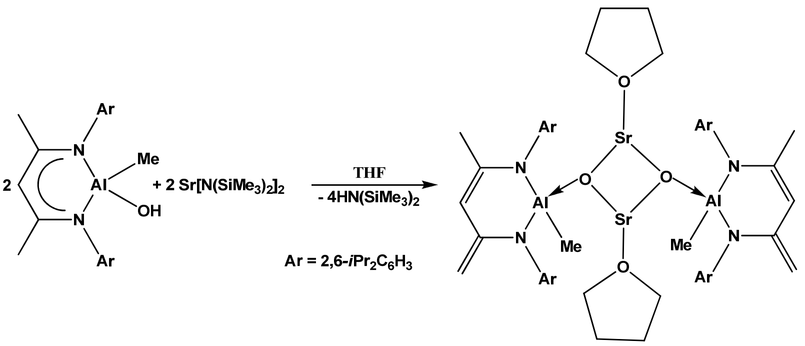
Chapter 6

Stabilization of Strontium Oxide by a Lewis Acid

A suitable way for synthesizing oxide complexes starts from their hydroxide complexes as precursors. The unique property of the β–diketiminate ligand, L [L = CH(CMe-2,6-iPr$_2$C$_6$H$_3$N)$_2$] to stabilize unusual coordination sites has been successfully applied in the syntheses of various hydroxide complexes of main-group metals such as aluminum,[34] gallium [131,132] and germanium.[133] Soluble heavy alkaline earth metal hydroxide complexes of calcium [LCa(μ-OH)(thf)]$_2$ and strontium [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] have been reported. Using the strontium hydroxide [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] as a precursor, we were able to assemble the heterobimetallic oxide [LSr(μ-O)Zr(NMe$_2$)$_3$]$_2$ containing strontium and zirconium.[125] The previously prepared calcium and strontium hydroxides, however, turned out to be useless precursors for the preparation of soluble CaO and SrO compounds. Therefore we reasoned to use LAl(OH)Me [34] as a source for oxygen, because we observed that LAlCl(Me) in the presence of the Lewis base LSrN(SiMe$_3$)$_2$·thf (**1**) is converted to L^{1}Al(Me)·thf (**8**) (L^1= CH[C(CH$_2$)](CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$) under deprotonation of a methyl group of L.[127] Subsequently we reacted LAl(OH)Me with Sr[N(SiMe$_3$)$_2$]$_2$·2thf to yield [L^{1}Al(Me)(μ-OSr·thf)]$_2$ (**16**). Herein, we report the synthesis, characterization and theoretical investigation of the first soluble molecular SrO complex.

6.1. Synthesis of Strontium Oxide 16

[L$_1$Al(Me)(μ-OSr·thf)]$_2$(**16**) was prepared by reaction of LAlMe(OH) and Sr[N(SiMe$_3$)$_2$]$_2$·2 thf in THF at room temperature (Scheme 6.1). L^{1}Al(Me) is formed by deprotonation of LAl(OH)Me with Sr[N(SiMe$_3$)$_2$]$_2$·2thf under formation of HN(SiMe$_3$)$_2$. Simultaneously the oxygen atom of LAl(OH)Me is transferred to the alkaline earth metal forming SrO. L^{1}Al(Me) acts as a Lewis acid and coordinates to the oxygen atoms in **16**. This type of deprotonation is the key step for generating **16**.



16

Scheme 6.1: Preparation of strontium oxide complex.

Compound **16** is a pale greenish yellow solid, soluble in benzene, toluene, and THF. **16** was characterized by NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^{1}H NMR of **16** showed broad signals at room temperature. Therefore, the ^{1}H NMR experiment was conducted at low temperature to give a better resolution of the resonances. The Al–*Me* protons of **16** resonate at –1.06 ppm. Furthermore, the signals at 1.73 ppm and 3.36, and 2.79 ppm can be attributed to the CH_3 group and CH_2 groups of the L^1 backbone. The IR spectrum of **16** shows bands at 1624 cm^{-1}, which can be assigned to the C=C bond. No molecular ion peak was observed in the mass spectrum of compound **16**, but fragment ions were detected.

Compound **16** crystallizes in monoclinic space group *Cc*, with two molecules in the asymmetric unit (Figure 6.1). The structure reveals the dimeric nature of **16** resulting in the formation of almost planar four-membered Sr_2O_2 ring, which is connected to two terminal L^1AlMe units. The strontium atoms are tetracoordinate (with one oxygen atom of THF, one interaction to the ligand backbone and two oxygen atoms of the Al–O group) and both adopt a distorted square planar geometry. The aluminum atoms are also tetracoordinate (with two nitrogen atoms of L^1, the methyl carbon atom, and an oxygen atom) and generate two six–membered C_3N_2Al rings due to the bidentate function of L^1. The coordination polyhedra of the aluminum atoms can best be described as highly distorted tetrahedra. The terminal C–C bond lengths in the ligand backbone [C(1)–C(4) 1.516(7), C(3)–C(5) 1.348(7)] are indicative of a single and double bond, respectively. The bond lengths within L^1 are in the range of those known in literature except for the adjacent N–C bond lengths [N(1)–C(1) 1.354(6) Å, N(2)–C(3) 1.410(6) Å], which differ slightly from each other.[114] The two Sr–O bond lengths in the Sr_2O_2 core are different [on average 2.323, 2.394 Å]. The longer ones are in agreement with those found in $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ (2.402(2)$_{av}$ Å).[125]

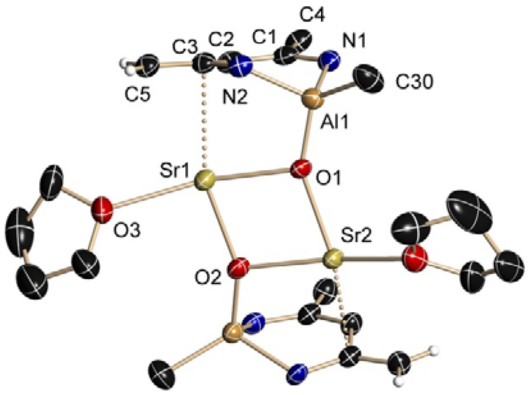


Figure 6.1. Crystal structure of **16**·C_7H_8; anisotropic displacement parameters are shown at a 50% probability level. Selected bond distances (Å) and angles (°) of one half of a formula unit in the asymmetric unit: Al(1)–O(1) 1.729(3), Al(1)-N(1) 1.895(4), Al(1)-N(2) 1.906(4), Sr(1)-O(1) 2.391(3), Sr(1)-O(2) 2.324(3), Sr(1)-O(3) 2.567(3), Sr(1)-C(3) 2.787(4), C(3)–C(5) 1.348(7), O(1)-Sr(1)-O(2) 81.15(11), O(1)–Al(1)–N(2) 105.91(17), N(1)–Al(1)–N(2) 96.96(17), Sr(1)-O(1)-Sr(2) 98.89(12), Sr(1)-O(2)-Sr(3) 98.66(12). Non coordinate THF molecules, substituents on the nitrogen atoms and all hydrogen atoms, except those at C(5) and C(35) have been omitted for clarity.

For a detailed understanding of the electronic structure and bonding properties of **16**, we have performed *ab initio* density functional theory calculations as implemented in the *Gaussian 03* package.[134a]We have adopted a hybrid B3LYP[135-137] exchange and a correlation functional with the LANL2DZ [138-140] basis set. The molecular structure from the X-ray experiment served as starting point for the calculations. Since the hydrogen atom positions from the X-ray structural determination are not comparable to the gas phase, we relaxed all the hydrogen atoms. The calculations for natural atomic orbital (NAO) and natural bond order (NBO) were performed to investigate the charge localization, bonding and hybridization characteristics of the structure under consideration.

We find that although the aluminum atoms of individual rings in **16** are surrounded each by two nitrogen atoms of the bidentate L^1 ligand, one methyl carbon and one oxygen atom in a slightly distorted tetrahedral fashion, the bonding characteristics of Al with those are a mixture of covalent and ionic characters with more contribution from the ionic part. This is evident from the localization of charges on the individual atoms (see reference 134b). The Wiberg bond order analysis also shows a diminished covalency of the bonds (see reference 134b). This can further be argued from the molecular orbital wave functions in Figure 6.2, which show the absence of delocalization over these bonds. However, the Sr_2O_2 rings in between two L^1Al moieties show complete ionic character with approx. +1.9 e charge on each of the cations (see reference 134b). Interestingly, the reduction of the charge on the oxygen atoms (-1.6 instead of -2.0) indicates a charge transfer towards the Al atoms due to their Lewis acidic character.[141-143] The oxygen atoms of the THF molecules reside within the coordination sphere of Sr^{2+} cation solely due to Coulombic attraction. For the same reason, the π-electron cloud of the methylene groups from the ligand backbones also come within the bonding distance of the cation. These arguments are consistent with the NBO analysis as well (see reference 134b). A preference to delocalize electrons over the ligand backbones is observed (Figure 6.2). In fact, the experimental observations of single and double bond characters in the terminal C–C bonds in the ligand backbones are consistent with the Wiberg bond order analysis. Due to the presence of the symmetric ligands on either sides, the highest occupied molecular orbital (HOMO) becomes almost degenerate with the HOMO–1 and so does the lowest unoccupied molecular orbital (LUMO) with the LUMO+1, as can be seen in Figure 6.2.

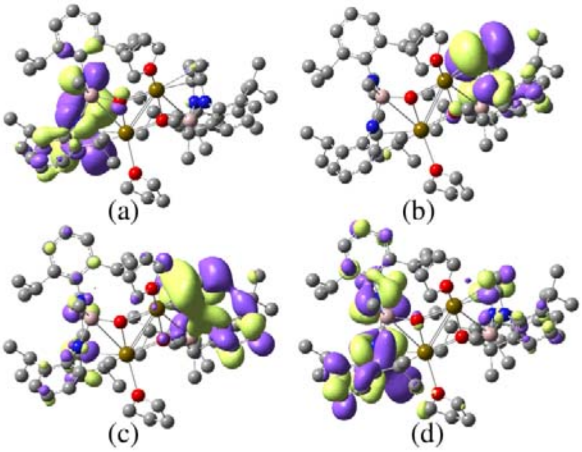


Figure 6.2. (a) HOMO-1, (b) HOMO, (c)LUMO and (d) LUMO+1 pictures of compound **16**. The corresponding energies are -4.47 eV, -4.42 eV, -0.08 eV and -0.05 eV respectively. All hydrogen atoms are omitted for clarity.

6.2. Conclusion

In summary, the reaction of aluminum methyl hydroxide LAl(OH)Me with Sr[N(SiMe$_3$)$_2$]$_2$·2 thf gave the unprecedented heterobimetallic oxide **16** and reveals alkaline earth metal oxide in an organometallic matrix. Formation of the complex is accompanied by deprotonation of one methyl group in the ligand backbone. The stability and good solubility of **16** are requirements for the application of the compound in catalytic reactions due to the recent finding of calcium compounds in hydroamination reactions.[48] Further detailed theoretical calculations suggest that the oxygen atoms of THF molecules and the π-electron cloud of the methylene groups of the ligand backbone come within the coordination sphere of the Sr^{2+} cation to stabilize the Sr_2O_2 cluster in the organic matrix through Coulombic attraction.

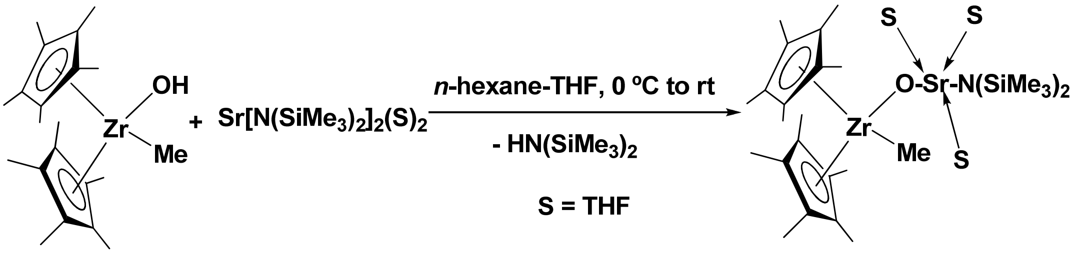
Chapter 7

Synthesis of the Hetero Bimetallic Compound 17 Containing Strontium and Zirconium

In chapter 2, we demonstrated that by using strontium hydroxide and zirconium amide, it is possible to obtain an oxygen brigded bimetallic compound $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ (**5**). But this chapter deals with synthesis of hetero bimetallic compound by the reaction of zirconium hydroxide $Cp^*_2Zr(Me)OH$[56] with the strontium amide, $Sr[N(SiMe_3)_2]_2\cdot 2thf$. Using this synthetic strategy we were able to assemble metal centres in the resulting bimetallic complex. This complex is soluble in hydrocarbon solvents and is well characterized by NMR spectroscopy, mass spectrometry, elemental and X-ray single crystal analysis.

7.1. Synthesis of the Bimetallic Compound $Cp^*_2Zr(Me)\text{-}O\text{-}Sr(thf)_3N(SiMe_3)_2$ (17)

The reaction of $Cp^*_2Zr(Me)OH$[56] with one equiv of $Sr[N(SiMe_3)_2]_2\cdot 2thf$ in *n*-hexane–THF at 0 °C resulted in the formation of the heterobimetallic oxygen bridged complex $Cp^*_2Zr(Me)\text{–}O\text{–}Sr(thf)_3N(SiMe_3)_2$ (**17**). The reaction proceeds under elimination of $HN(SiMe_3)_2$ (Scheme 7.1). Compound **17** can be considered as a promising precursor for the preparation of hetero-trimetallic oxygen bridged systems.



17

Scheme 7.1: Preparation of the heterobimetallic complex **17**.

The ^1H NMR resonances (–0.89 and -0.05 ppm) for **17** correspond to $Zr\text{–}CH_3$ and $Sr\text{–}N(SiMe_3)_2$ respectively. The ^{13}C NMR exhibits three resonances (113.08, 17.16, and 5.36 ppm) for **17** corresponding to Cp* carbon, $Zr\text{–}CH_3$ and $N(SiCH_3)_2$ respectively. No molecular peak was observed in its EI mass spectrum, but some fragment ions were observed.

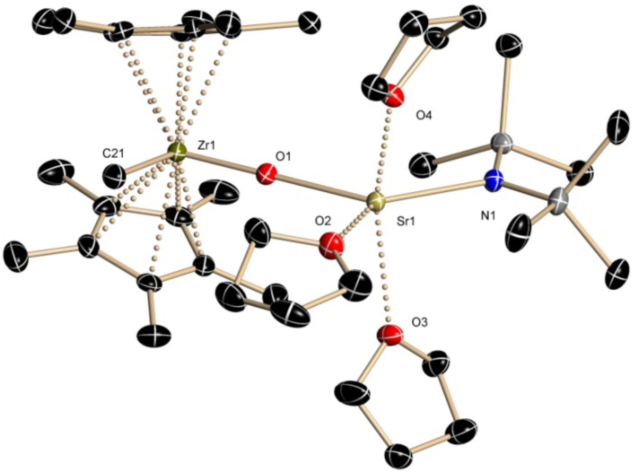


Figure 7.1. Crystal structure of compound [Cp*$_2$(Me)Zr–O–Sr(thf)$_3$N(SiMe$_3$)$_2$] (**17**); Thermal ellipsoids are shown with 50% probability. Selected bond lengths [Å] and bond angles [°]: Sr(1)–O(1) 2.3281(15), Sr(1)–O(2) 2.5467(16), Sr(1)–O(3) 2.5868(15), Sr(1)–O(4) 2.5613(15), Sr(1)–N(1) 2.5039(19), Zr(1)–O(1) 1.8800(15), Zr(1)–C(21) 2.320(2); Sr(1)–O(1)–Zr(1) 178.23(9), O(1)–Sr(1)–N(1) 128.41(6), O(1)–Sr(1)–O(2) 95.81(5), N(1)–Sr(1)–O(2) 135.56(6), O(1)–Sr(1)–O(4) 98.44(5). All hydrogen atoms are omitted for clarity.

Single crystals suitable for X-ray measurement were grown from a solution of **17** in *n*-hexane-THF mixture at –32 °C. Compound **17** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The interesting feature of this compound is the Sr–O–Zr moiety. The X-ray structural analysis of **17** revealed that strontium is bonded through a bridging oxygen atom to a zirconium atom. The strontium atom is surrounded by an oxygen atom, and three THF molecules and a nitrogen atom of the amide group. The geometry around the strontium center is trigonal bipyramidal, whereas the geometry around the zirconium atom is tetrahedral, when the Cp* ring is considered as one coordination site. The Sr–O bond distance (2.3281(15) Å) of Zr-O-Sr core is comparable to those in [LSr(μ-O)Zr(NMe$_2$)$_3$]$_2$ (**5**) (2.3423$_{av}$ Å) and is longer than the Ca–O bond distances found in a similar calcium compound Cp*$_2$Zr(Me)–O–Ca(thf)$_3$N(SiMe$_3$)$_2$ (2.2068(13) Å).[144] Interestingly, the bond angle of Sr–O–Zr is almost linear 178.23° and it is nearly the same like that of Ca–O–Zr in Cp*$_2$Zr(Me)–O–Ca(thf)$_3$N(SiMe$_3$)$_2$ (176.98°).

7.2. Conclusion

Hydrocarbon soluble molecular hetero bimetallic complex containing both strontium and zirconium $Cp^*_2(Me)Zr–O–Sr(thf)_3N(SiMe_3)_2$ was prepared by the reaction of strontium amide, $Sr[N(SiMe_3)_2]_2 \cdot 2thf$ and zirconium hydroxide, $Cp^*_2Zr(Me)OH$. The structural analysis shows that the desired bimetallic compound has been formed in accordance with the synthetic strategy. The preparation of bimetallic complex $Cp^*_2Zr(Me)–O–Sr(thf)_3N(SiMe_3)_2$ is interesting for the preparation of hetero-trimetallic complexes because of the presence of a labile $-N(SiMe_3)_2$ group and can also act as a promising catalysts for hydroamination reactions.

Chapter 8

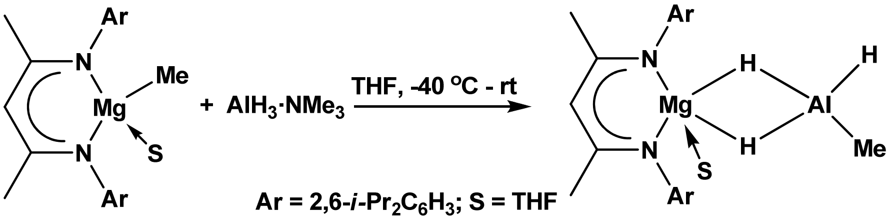
Synthesis of a Butterfly like Magnesium Sulfide [LMg(μ-S_2)MgL]·2thf (19) from Magnesium Aluminum Hydride 18

The role of *β*–diketeminate ligand in obtaining hydride complexes of alkaline earth metals is noteworthy due to its special electronic and steric factors that can deter the usual Schlenk equilibrium commonly found in alkaline earth metals especially in the case of higher analogues. There are a few reports on hydrogen bridged magnesium complexes.[68,92,93] Roesky *et al.* reported a magnesium borohydride complex in 2003.[68] Recently dimeric magnesium hydride and a magnesium hydride cluster compound were reported by C. Jones *et al.* [92] and M. S. Hill *et al.* [93] respectively. These hydrides can find application in catalytic processes and also can serve as hydrogen storage materials. The high hydrogen content of MgH_2 and its complexes resulted in a great interest in these materials for hydrogen storage.

The reactivity of Group 13 and 14 hydrides towards chalcogens is well documented.[129a,145] It is also interesting to know the reactivity of hydrides of Group 2 towards chalcogens because there is little known in this field. Herein, we report the hydrocarbon soluble bimetallic magnesium aluminum hydride complex and a magnesium sulfide by its reaction with elemental sulfur.

8.1. Synthesis of the Bimetallic Magnesium Aluminum Hydride [LMg(μ-H)$_2$AlH(Me)]·thf (18)

The reaction of LMgMe·thf [146] with $AlH_3 \cdot NMe_3$[147-149] leads to the formation of magnesium aluminum complex [LMg(μ-H)$_2$AlH(Me)]·thf (**18**) in good yield (Scheme 8.1). Compound **18** was formed by the insertion of aluminum hydride into the magnesium methyl bond and subsequent formation of hydride bridges between magnesium and aluminum. The driving force for this insertion may be due to the higher coordination preferred by magnesium and the formation of a stable Al-C bond.



18

Scheme 8.1: Preparation of the bimetallic magnesium aluminum hydride complex [LMg(μ-H)$_2$AlH(Me)]·thf

Compound **18** can be considered as an intermediate in the formation of magnesium hydride complex, [LMgH·thf]$_2$. **18** is a white solid, soluble in benzene, toluene, and THF. It was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, elemental and X-ray structural analysis. The protons of the methyl group at Al resonate at –0.68 and –0.69 ppm, and are shifted downfield compared to those in LMgMe·thf (–1.25 ppm) indicative for a migration of the methyl group from magnesium to aluminum. As expected, the resonances for the γ-CH protons display at 4.80 ppm as a singlet in the ^{1}H NMR spectrum. The resonance corresponding to the (Mg(μ-H)$_2$Al) hydride appears broad (3.35 ppm) in the ^{1}H NMR spectrum of **18**. The resonance corresponding to the (Al-H) hydride is silent. The molecular ion peak corresponding to **18** was not observed and some fragment ions were seen in its EI mass spectrum.

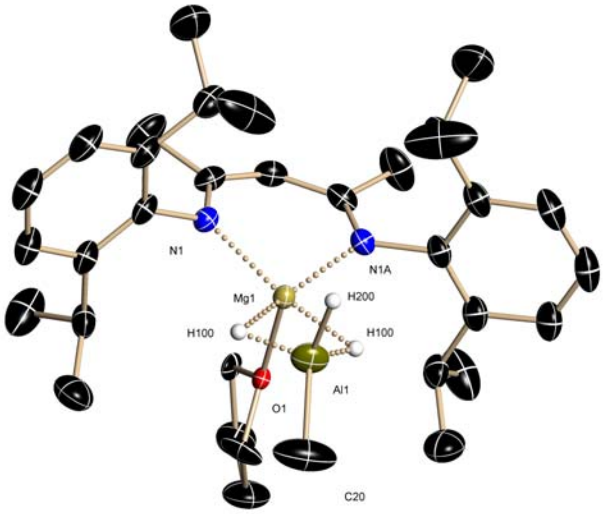
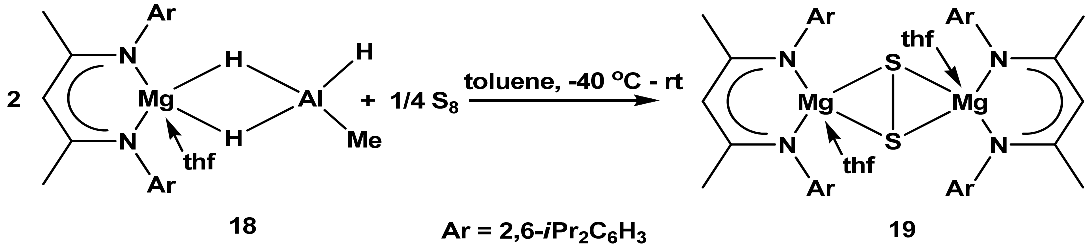


Figure 8.1. Crystal structure of **18**; anisotropic displacement parameters are shown at a 50% probability level. Selected bond lengths [Å] and bond angles [°]: Mg(1)–N(1) 2.045(2), Mg(1)–N(1A) 2.045(2), Mg(1)–O(1) 2.050(2), Mg(1)–H(100) 1.9549(0), Al(1)–H(100) 1.6396(5), Al(1)–H(200) 1.5560(4), Al(1)–C(20) 1.902(5), N(1)–Mg(1)–N(1A) 94.98(12), H(100)–Mg(1)–H(100) 70.10(12), Mg(1)–H(100)–Al(1) 111.92(94), H(100)–Al(1)–H(200) 100.70(8). All hydrogen atoms except those on magnesium and aluminum have been omitted for clarity.

Colorless crystals for X-ray structural analysis were obtained by keeping a toluene solution of compound **18** at –5 °C in a freezer for one day. **18** crystallizes in the orthorhobic space group *Pbcm* with one molecule in the asymmetric unit cell. The structure of **18** (Figure 8.1) confirms the presence of a six-membered C_3N_2Mg ring, and two hydride bridges between magnesium and aluminum centers result in the formation of a four-membered MgH_2Al ring. The Mg center is five coordinate with two nitrogen atoms of the *β*–diketiminate ligand, two hydrogen atoms and an oxygen atom of the THF. The magnesium atom has distorted square pyramidal geometry while that around the aluminum atom is a distorted tetrahedron (with three hydrogen atoms and one carbon atom of methyl group). The average Mg–H (1.9549_{av} Å) bond distance is comparable to that in the magnesium hydride, $[LMgH{\cdot}thf]_2$ ($1.96(3)_{av}$ Å). The bridging Al–H (1.6396_{av} Å) is slightly longer than the terminal Al–H distance (1.5560 Å).

8.2. Reaction of [LMg(*μ*-H)$_2$AlH(Me)]·thf (18) with Elemental Sulfur to [LMg(*μ*-S$_2$)MgL]·2thf (19)

Reaction of **18** with one equiv of sulfur in toluene at –40 °C resulted in the *μ*-S_2 bridged magnesium sulfide complex [LMg(*μ*-S_2)MgL]·2thf **(19)** as yellow solid in very low yield (10 % yield) (Scheme 8.2).



Scheme 8.2: Preparation of *β*-diketiminate supported magnesium sulfide complex **19**

Compound **19** is freely soluble in common hydrocarbon solvents such as benzene and toluene. Compound **19** was characterized by NMR spectroscopy (^{1}H and ^{13}C), EI mass spectrometry, and X-ray structural analysis. The complete disappearance of the Al-*Me* resonance (–0.68, –0.69 ppm) in the ^{1}H NMR spectrum of compound **19** clearly indicates its formation. As expected the resonances for the γ-CH (4.79 ppm) appear as a singlet in the ^{1}H NMR. Moreover the mass spectrum reveals the molecular ion at *m*/*z* 946.68 [M$^+$-2thf] corresponding to the nonsolvated compound.

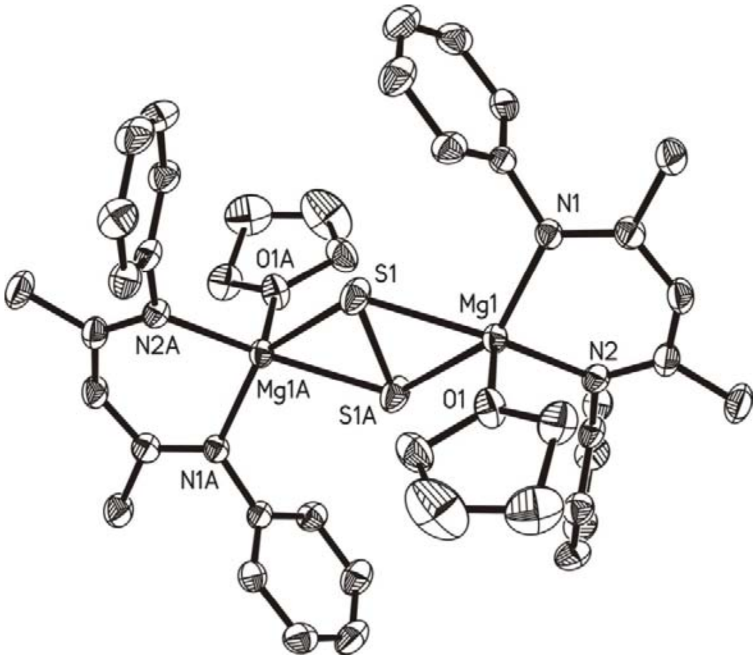


Figure 8.2. Crystal structure of **19**; anisotropic displacement parameters are shown at a 50% probability level. Selected bond lengths [Å] and bond angles [°]: Mg(1)–N(1) 2.064(4), Mg(1)–N(2) 2.073(4), Mg(1)–S(1) 2.450(2), Mg(1A)–S(1) 2.450(2)), Mg(1)–O(1) 2.064(4), S(1)–S(1A) 2.184(3)); N(1)–Mg(1)–N(2) 93.37(17), Mg(1)–S(1)–Mg(1A) 127.45(8), S(1)–Mg(1)–S(1A) 52.55(8). Isopropyl groups on the phenyl rings and all hydrogen atoms have been omitted for clarity.

Single crystals suitable for X-ray structural analysis were obtained by keeping a concentrate solution of **19** in toluene at -32 °C. The magnesium sulfide, [LMg(μ-S$_2$)MgL]·2thf crystallizes in a triclinic space group $P\bar{1}$ as pale yellow crystals. The quality of the crystal is not sufficient enough to get good X-ray data. About 97% of the two Mg are bridged by two sulfur and 3% are bridged by one sulfur (not shown in the Figure 8.2). The structure of **19** (Figure 8.2) reveals the presence of two six-membered C_3N_2Mg rings. These six-membered rings are connected to each other by means of a μ-S_2 group, which results in the formation of two three-membered MgS_2 rings. The magnesium atoms are penta coordinate and have distorted trigonal bipyramidal geometry with two nitrogen atoms of the β–diketiminate ligand, two sulfur atoms, and an oxygen atom of the THF molecule. The average Mg–S bond distances are (2.450(2) Å).

8.3. Conclusion

In summary, we have shown the insertion of aluminum hydride into the Mg-C bond that leads to the formation of the heterobimetallic magnesium aluminum hydride complex **18**, instead of the magnesium hydride complex [LMg(μ-H)·thf]$_2$. The high hydrogen content of **18** and the easy release of hydrogen is an interesting feature of this complex. The stability and good solubility of **18** qualifies this compound for the preparation of the hitherto unknown μ-S_2 bridged magnesium sulfide complex.

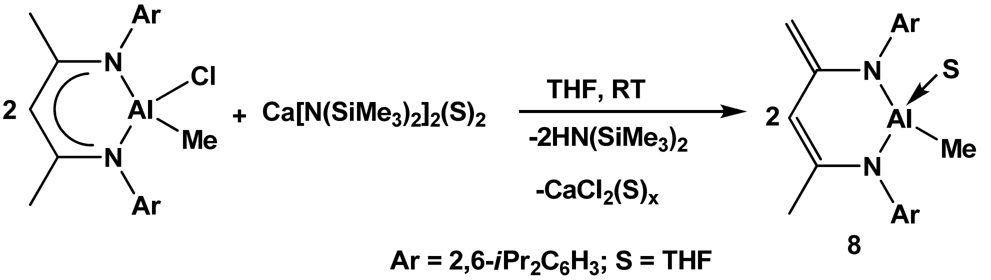
Chapter 9

Synthesis and Reactivity of the Six-membered N-Heterocyclic Aluminum Complex 8

In chapter 3 we described the isolation of a N-heterocyclic aluminum complex during the synthesis of strontium chloride from the reaction of LAlCl(Me) with $LSrN(SiMe_3)_2\cdot$thf. Herein, we discuss about the synthesis and reactivity of aluminum compound $L^1AlMe\cdot$thf (**8**) (L^1= $CH[C(CH_2)](CMe)(2,6\text{-}i Pr_2C_6H_3N)_2$). Complex **8** can serve as a precursor for a variety of aluminum complexes.

9.1. Synthesis of L^1AlMe·thf

$L^1AlMe\cdot$thf (**8**)[127] was obtained by the reaction of $LSrN(SiMe_3)_2\cdot$thf with LAlCl(Me), unfortunately the low yield of **8** hinders its reactivity studies. Therefore a modification of the synthetic procedure was necessary. The reaction of LAlCl(Me) with $Ca[N(SiMe_3)_2]_2\cdot 2$thf [50]at room temperature in THF leads to the aluminum complex $L^1AlMe\cdot$thf (**8**) in good yield (<90%) (Scheme 9.1). The increase in yield of **8** with the new synthetic method opened a door for investigating its reactivity. The driving force for the reaction is the $CaCl_2$ and $HN(SiMe_3)_2$ formation.

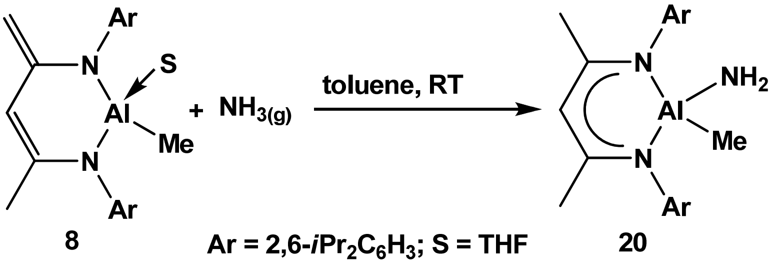


Scheme 9.1: Preparation of **8**.

Compound **8** is soluble in toluene, THF and benzene and melts at 154–156 °C. The Al–*Me* protons of **8** resonate at –0.99 ppm. Furthermore, the resonances at 1.58 ppm, 3.90, and 3.18 ppm can be attributed to the CH_3 group and CH_2 group on the L^1 backbone. So far we are not able to prepare single crystals of compound **8**.

9.2. Fixation of Ammonia with L^1AlMe·thf

Dry ammonia gas was passed through a toluene solution of L[1]AlMe·thf (**8**) at room temperature to generates an aluminum amide with terminal Al–NH_2 group (Scheme 9.2). The previous method for the preparation of aluminumdiamide is based on alumium halides and ammonia using N-heterocyclic carbenes as a halogen acids scavenger.[150]



Scheme 9.2: Preparation of compound **20**

Colorless crystals of **20** were obtained when a solution of LAl(NH_2)Me in a mixture of *n*-pentane- toluene was kept at –5 °C for one day. **20** is soluble in a number of organic solvents. Compound **20** is very sensitive towards traces of moisture and converts easily to LAl(OH)Me.[34] It has been well characterized by mass spectrometry, NMR spectroscopy, and X-ray structural analysis. The ^{1}H NMR spectrum of compound **20** shows a broad singlet (–0.2 ppm) for NH_2 protons and a singlet (–0.91 ppm) for the aluminum methyl protons. The NH_2 protons appear downfield compared to that of the aluminum diamide LAl(NH_2)$_2$ complex (–0.52 ppm).[150] Moreover the molecular ion peak (M^+ = 475.3 (5%)) corresponding to **20** was observed in its EI mass spectrum with low intensity.

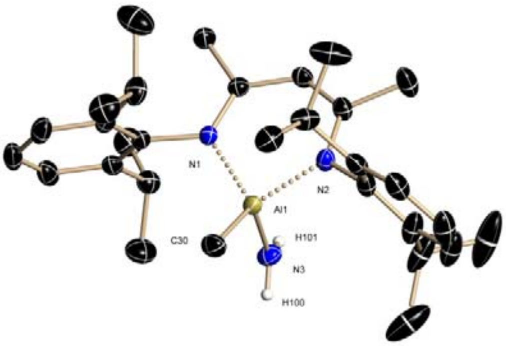
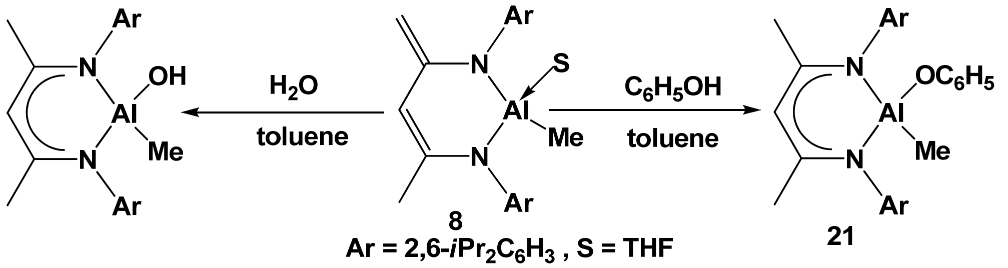


Figure. 9.1. Crystal structure of **20**; Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and bond angles (°): Al(1)-N(1) 1.9092(12), Al(1)-N(2) 1.9086 (13), Al(1)-N(3) 1.7910(14), Al(1)-C(30) 1.9476(16), N(3)-H(100) 0.852(10), N(3)-H(101) 0.848(10); N(1)-Al(1)-N(2) 95.87(5), N(1)-Al(1)-N(3) 107.04(6), N(1)-Al(1)-C(30) 115.26(6). All hydrogen atoms except those on nitrogen have been omitted for clarity.

Compound **20** crystallizes in the monoclinic space group *P*2_1/*c* with one molecule in the asymmetric unit. X-ray crystal structure analysis of compound **20** revealed a monomeric structure as illustrated in Figure 9.1 and the NH_2 group is not involved in any kind of hydrogen bonding. The Al-N bond length (1.7910(14) Å) of Al-NH_2 is comparable with those reported for LAl$(NH_2)_2$ (1.789(2)$_{av}$ Å).[150] The aluminum atom is tetra coordinate (two nitrogen atoms of L, one nitrogen atom of NH_2 group and one carbon atom of methyl group) and the coordination polyhedron around the metal center is distorted tetrahedra.

9.3. Reactions of L^{1}AlMe·thf with O-H Bonded Compounds

We have already discussed the synthesis of LAl(NH_2)Me by cleavage of one N–H bond of ammonia by L^{1}AlMe·thf (**8**). Moreover we report on the synthesis of two different heteroleptic aluminum (III) compounds by the reaction of L^{1}AlMe·thf (**8**) with ROH (R = H, Ph) under cleavage of the O–H bond (Scheme 9.3).

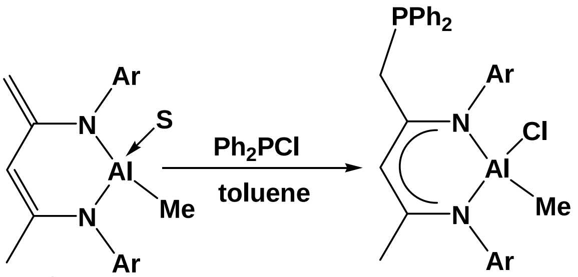


Scheme 9.3: Preparation of compound **21**

Addition of H_2O to a toluene solution of L^{1}AlMe·thf in a 1:1 molar ratio at room temperature resulted in the formation of LAl(OH)Me (Scheme 9.3). This is an alternative route for the preparation of LAl(OH)Me without the use of any N-heterocyclic carbene. We conducted the reaction of L^{1}AlMe·thf with PhOH to obtain compound **21** (Scheme 9.3). **21** is a pale yellow solid, which was soluble in THF, toluene, benzene, and diethyl ether. **21** was characterized by ^{1}H NMR spectroscopy, EI mass spectrometry, and X-ray single-crystal structural analysis. The ^{1}H NMR spectrum exhibits the Al–*Me* and *γ*-CH protons of **21** to resonate at –0.69 and 5.14 ppm respectively. The mass spectrum of **21** reveals the base peak as [M^+-Me] at *m*/*z* 537.5 and the molecular ion [M^+] at *m*/*z* 552.5 in low intensity.

9.4. Synthesis of L^2AlMeCl (22)

From our results we have learnt that the L^1AlMe·thf (**8**) can be utilized for effecting substitution at the α carbon of the ligand back-bone. To introduce the Ph_2P group at this position we have employed Ph_2PCl. A reaction between L^1AlMe·thf (**8**) with Ph_2PCl in toluene at –40 °C yielded L^2AlMeCl (**22**) (L^2= CH[C(CH_2PPh_2)](CMe)(2,6-*i*$Pr_2C_6H_3N)_2$). Compound **22** was characterized by multi nuclear NMR spectroscopy and single crystal X-ray studies (Scheme 9.4).



8 **22**

Ar = 2,6-*i*$Pr_2C_6H_3$,S = THF

Scheme 9.4: Preparation of compound **22**

The ^1H NMR spectrum of **22** contains two non-equivalent CH protons of the methylene bridge (δ 3.20–3.17 and 3.01–2.97 ppm) and one doublet for the γ-CH protons (δ 5.18–5.17 ppm). The methyl protons of Al–*Me* resonate downfield (δ –0.59 ppm) compared to those of **8** (δ –0.99). The ^{31}P NMR spectrum contains only one singlet (–15.18 ppm) for the phosphorus atom. The molecular ion peak corresponding to **22** (M^+ = 678.4 (22%)) was observed in its EI-mass spectrum in relatively moderate intensity.

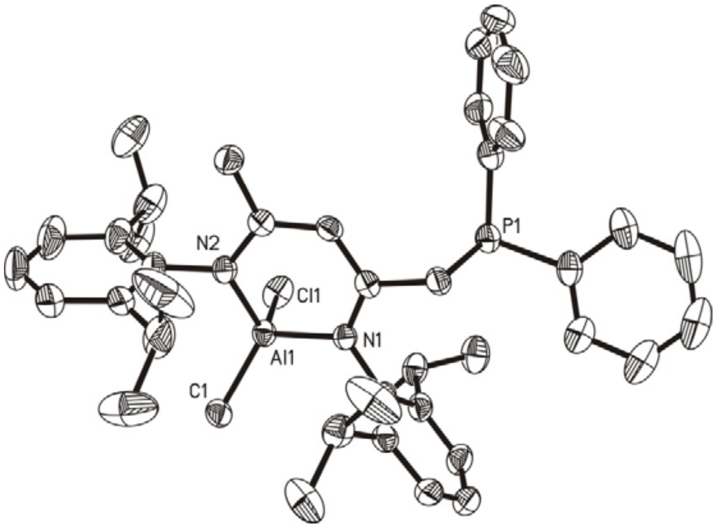
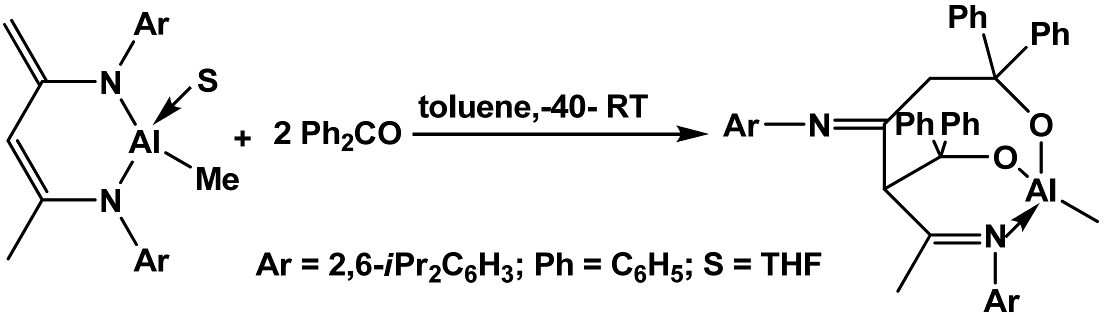


Figure. 9.2. Crystal structure of **22**; Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and bond angles (°): Al(1)-N(1) 1.9019(18), Al(1)-N(2) 1.890 (2), Al(1)-Cl(1) 2.1582(10), Al(1)-C(1) 1.957(2); N(1)-Al(1)-N(2) 98.30(8), N(2)-Al(1)-Cl(1) 106.09(7), N(1)-Al(1)-Cl(1) 108.32(6).All hydrogen atoms are omitted for clarity.

Compound **22** crystallizes in the triclinic space group $P\bar{1}$with one molecule in the asymmetric unit. As shown in Figure 9.2, the *N*,*N'*-chelation mode of the ligand is still intact and forms a six- membered C_3N_2Al ring and the Ph_2P group does not interact with the aluminum center. As compared with the previously reported *β*-diketiminate aluminum complexes,[88] Al–C [1.957(2)] and Al–Cl [2.1582(10)] bond lengths are also typical of such complexes. The aluminum atom is attached to two nitrogen atoms of the ligand, one chlorine atom and one carbon atom of the methyl group showing the coordination geometry around the aluminum center as distorted tetrahedron.

9.5. [4+2] Cycloaddition of L^1AlMe·thf with Benzophenone

Roesky *et al.* reported the synthesis of an aluminum pinacolate LAl[$O_2(CPh_2)_2$] by reduction of $LAlI_2$ in the presence of Ph_2CO.[151] Recently Dries and co-workers were successful in isolating a unusual [4+1] cycloaddition product by the reaction of N-heterocyclic silicon(II) compound with benzophenone.[152] Consequently we describe the reaction of **8** with benzophenone.



8

23

Scheme 9.5. Preparation of compound **23**

The reaction of **8** with two equiv of benzophenone in toluene afforded an eight-membered aluminum complex **23** (Scheme 9.5). The ^{1}H NMR spectrum of **23** shows one singlet (δ 5.87 ppm) for the γ-CH protons. The methyl protons of Al–*Me* resonate downfield (δ –0.31 ppm) compared to those of **8** (δ –0.99). Moreover molecular ion peak corresponding to **23** was observed in its EI-mass spectrum (M^+ = 822.5(100%)).

Compound **23** was obtained as colorless crystalline solid in 68 % yield. **23** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. **23** is monomeric in the solid state and the crystal structure of **23** is shown in Figure 9.3. The compound consists of an eight-membered AlO_2C_5 ring and a six-membered $AlOC_3N$ ring. The aluminum atom is tetra coordinate (with one nitrogen atom of L, the methyl carbon atom, and two oxygen atoms) and shows the anticipated distorted tetrahedral coordination geometry. The aluminum methyl bond length [Al–C 1.946(3) Å] is in the order of those reported for $LAlMe_2$ [Al–C1 1.955(4) Å, Al–C2 1.961(3) Å].[153] The Al–O bond distances (1.7295(2)$_{av}$ Å) are similar to the aluminum complex containing Al–O–C linkages {$LAl[O_2(CPh_2)_2]$ (1.7339$_{av}$ Å) and $LAl[OC(Ph)_2C_2(SiMe_3)_2]$ (1.7273 Å)}.[151]

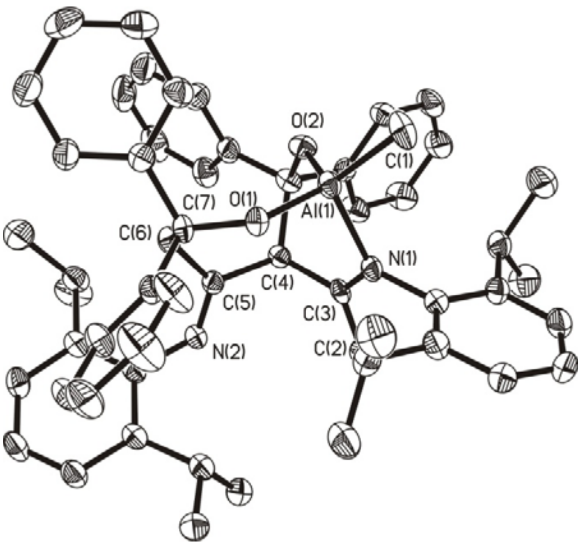
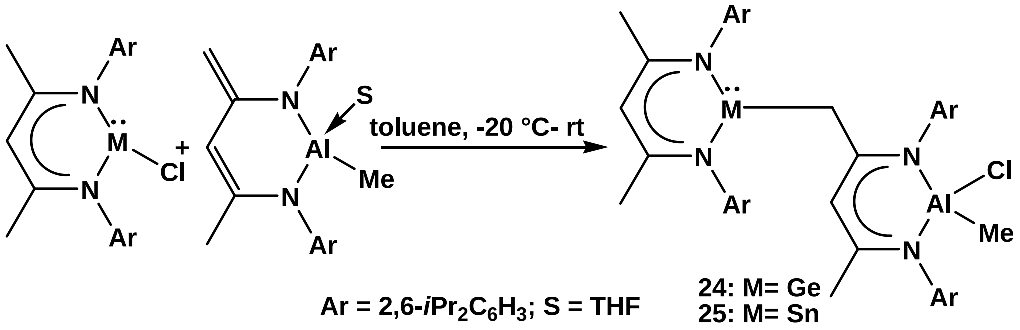


Figure 9.3. Crystal structure of **23**; Thermal elipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Al1–N1 1.988(3), Al1–O1 1.733(2), Al1–O2 1.726(2), Al1–C1 1.946(3); O1–Al1–O2 111.18(10), O1–Al1–C1 117.59(12), O1–Al1–N1 101.61(10). All hydrogen atoms are omitted for clarity reasons.

9.6. Reaction of L^1AlMe·thf with LGeCl and LSnCl

Reaction of LGeCl[154]and LSnCl[154] with **8** at –20 °C yielded the hetereobimetallic compounds **24** and **25** respectively (Scheme 9.6). Crystals for X-ray structural analysis were obtained by storing a solution (*n*-hexane-toluene) of **24** at –32 °C in a freezer and a solution of **25** in *n*-hexane at room temperature, respectively.



Scheme 9.6: Preparation of **24** and **25**

Compounds **24** and **25** show good solubility in common organic solvents such as benzene, toluene, and THF. **24** and **25** were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{27}Al and ^{119}Sn (for **25**)), EI mass spectrometry, elemental and X-ray structural analysis. The ^{1}H NMR spectra of **24** and **25** were recorded at 50 °C to get better resolution of resonances. The spectra contain two non-equivalent CH protons of the methylene bridge (δ 2.39-2.37 and 2.20-2.19 ppm

(**24**) and δ 2.36-2.35 and δ 1.87-1.85 ppm (**25**)) and two singlets for the γ-CH protons of the aluminum part and the germanium or tin moiety (δ 4.65 and 4.17 ppm (**24**) and δ 4.65 and δ 4.01 ppm (**25**)). The methyl protons of Al–*Me* resonate downfield (δ –0.81 ppm (**24**) and δ –0.74 ppm (**25**)) compared to those of **8** (δ –0.99). The ^{27}Al NMR for **24** and **25** was silent, obviously due to the quadrupole moment of the aluminum atom. The ^{119}Sn NMR for **25** (δ 71.54 ppm) is shifted downfield compared to that of LSnCl (δ –224 ppm).[154] The molecular ion peaks corresponding to **24** and **25** were not observed and some fragment ions were seen in its EI- mass spectrum.

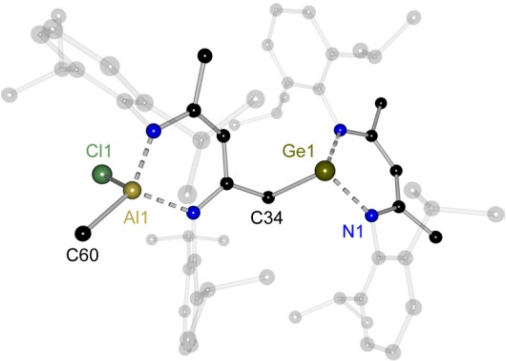


Figure 9.3. Crystal structure of **24**·$(0.2C_7H_8+0.8C_6H_{14})$; the substituents on the nitrogen atoms are shown in transparent. Selected bond lengths [Å] and bond angles [°]: Al(1)–N(3) 1.8685(15), Al(3)–N(4) 1.8997(14), Al(3)–Cl(1) 2.1661(7), Al(3)–C(59) 1.9510(17), Ge(1)–N(1) 2.0350(13), Ge(1)–N(2) 2.0442(13), Ge(1)–C(34) 2.0945(16), C(34)–C(33) 1.484(2), N(3)–Al(3)–N(4) 97.93(6), Cl(1)–Al(1)–C(59) 110.60(6), N(1)–Ge(1)–N(2) 90.66(5), Ge(1)–C(34)–C(33) 107.28(11). Non coordinate *n*-hexane molecules and all hydrogen atoms have been omitted for clarity.

Compounds **24** and **25** crystallize as monomers in the monoclinic space group $P2_1/n$. The structures reveal that the germanium or tin atom is bonded to the aluminum complex by a methylene bridge. The geometry around the germanium as well as the tin is highly distorted tetrahedral (Fig. 9.3 and 9.4). The aluminum atoms are tetracoordinate (with two nitrogen atoms of L^1, the methyl carbon atom, and a chlorine atom) and generate six–membered C_3N_2Al rings. The bond distance Al–Cl [2.1661(7) (**24**) Å] and [2.1603(10) (**25**) Å] is almost the same as in LAlCl(Me).[88] The terminal C–C bond lengths in the ligand backbone of the aluminum part [C(34)–C(33) 1.484(2) Å (**24**) and C(34)–C(33) 1.466(3) Å (**25**)] are indicative of a single bond. The Ge-C (2.0945(16) Å) and Sn–C (2.299(2) Å) bonds are comparable with those reported in the literature for germanium (II) methyl, LGeMe [2.002(4) Å] [117] and tin (II) methyl, LSnMe, [2.253(2) Å][155]complexes.

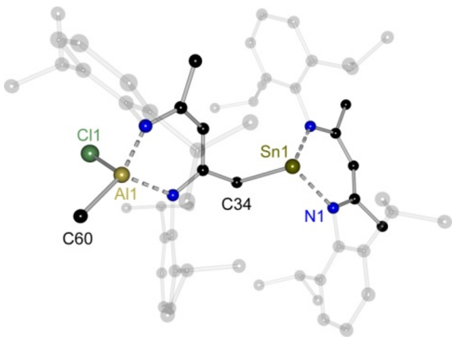
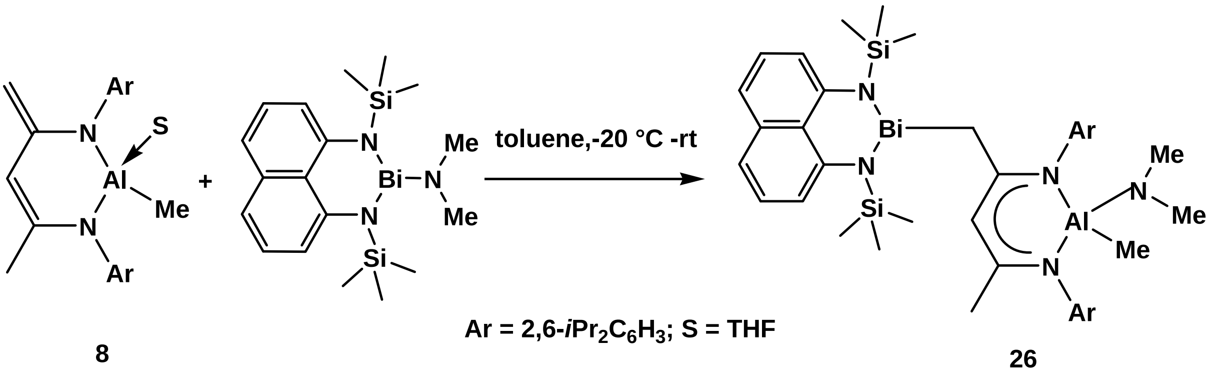


Figure 9.4. Crystal structure of **25**·$1.5C_6H_{14}$; the substituents on the nitrogen atoms are shown in transparent. Selected bond lengths [Å] and bond angles [°]: Al(1)–N(3) 1.897(2), Al(1)–N(4) 1.869(2), Al(1)–Cl(1) 2.1603(10), Al(1)–C(59) 1.954(2), Sn(1)–N(1) 2.223(2), Sn(1)–N(2) 2.227(2), Sn(1)–C(34) 2.299(2), C(34)–C(33) 1.466(3), N(3)–Al(1)–N(4) 97.83(9), Cl(1)–Al(1)–C(59) 110.48(9), N(1)–Sn(1)–N(2) 85.53(7), Sn(1)–C(34)–C(33) 104.16(15). Non coordinate *n*-hexane molecules and all hydrogen atoms have been omitted for clarity.

The results for compounds **24** and **25** clearly show that during the course of the reaction the solvent molecule at the aluminum is displaced and a nucleophilic attack of the chloride occurs under simultaneous formation of the M–CH_2 bond.

9.7. Reaction of L^1AlMe·thf with [1,8-$C_{10}H_6(NSiMe_3)_2BiNMe_2$] to 26



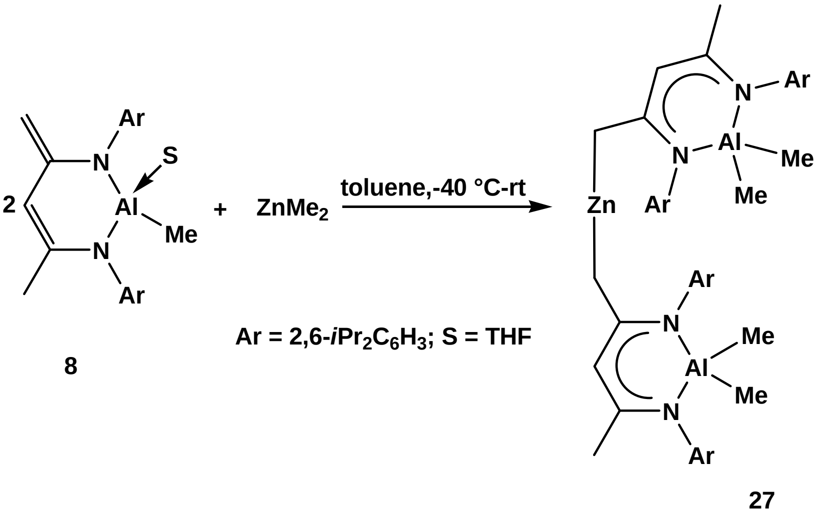
Scheme 9.7: Preparation of **26**

As shown from Scheme 9.7, [1,8-$C_{10}H_6(NSiMe_3)_2BiNMe_2$][156] reacts with L^1AlMe·thf (**8**) under NMe_2 transfer from bismuth to aluminum and formation of a Bi–CH_2 bond. The bimetallic complex **26** is produced in good yield as a red solid. **26** is soluble in toluene, THF, benzene, and diethyl ether. The ^{1}H NMR spectrum of **26** exhibits two different resonances (δ 0.37 and δ 0.20 ppm) for the Si*Me*$_3$ protons and two different resonances for the trimethylsilyl silicon atoms (δ 5.01 and δ 4.99 ppm) in the ^{29}Si NMR. In the ^{1}H NMR spectrum a singlet for the Al–N*Me*$_2$ substituent is observed at δ 2.70 ppm and this is in the same range as that reported for LAlBr(NMe_2) (δ 2.67 ppm).[157] The methyl protons of the Al-*Me* group appeared as singlet (δ –

0.97 ppm) in the spectrum and the resonance shows a down field shift compared to that in **8**. The molecular ion peak (M^+ 1011.5) corresponding to **26** appeared with relative low intensity (5%).

9.8. Reaction of L^{1}AlMe·thf with ZnMe$_2$ to Product 27

Reaction of L^{1}AlMe·thf (**8**) with ZnMe$_2$ at –40 °C in a molar ratio of 2:1 resulted in product **27** in 82 % yield (Scheme 9.7). This reaction is unique and proceeds under breaking of two Zn–CH$_3$ bonds and forming of two new Zn–CH$_2$ bonds. The energy difference between these two processes should be close to zero. Therefore the driving force for the reaction is the formation of the two new Al–CH$_3$ bonds. Single crystals suitable for X-ray structural analysis were obtained by keeping a solution of **27** in *n*-hexane-THF mixture at -5 °C. The crystal structure of **27**·C_4H_8O is shown in Figure. 9.5. Like the other structures, **27**·C_4H_8O is monomeric in the solid state. **27**·C_4H_8O crystallizes in the triclinic space group $P\bar{1}$ and in this structure the aluminum atom shows the anticipated distorted tetrahedral coordination geometry. In **27**·C_4H_8O two aluminum moieties are connected to a zinc atom by methylene bridges resulting in a highly distorted trigonal planar geometry at the zinc atom due to a coordinate THF at the zinc. The zinc carbon bond distances average to 1.978$_{av}$ Å and the aluminum methyl bond lengths [Al–C 1.972$_{av}$ Å, Al–C 1.9675$_{av}$ Å] are comparable to those reported for LAlMe$_2$ [Al–C1 1.955(4) Å, Al–C2 1.961(3) Å].[153]



Scheme 9.8: Preparation of **27**

27 is soluble in a number of aromatic and polar solvents. As expected, the resonances for the γ-CH protons display at 5.09 ppm as singlet in the ^{1}H NMR spectrum. Protons of methylene residue (1.44 ppm) and the aluminum methyl protons (–0.52 ppm) appear as singlets in the ^1H NMR spectrum. No molecular ion peak corresponding to **27** was found in the EI mass spectrum.

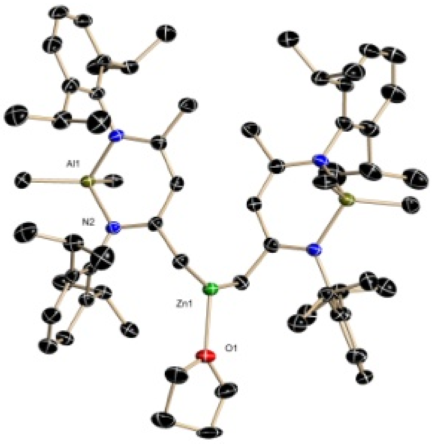


Figure 9.5. Crystal structure of **27**·C_4H_8O; anisotropic displacement parameters are shown at a 50% probability level. Selected bond lengths [Å] and bond angles [°]: Al(1)–N(1) 1.9124(19), Al(1)–N(2) 1.9251(19), Al(1)–C(30) 1.988(2), Al(1)–C(31) 1.958(3), Al(2)–N(3) 1.912(2), Al(2)–N(4) 1.9215(19), Al(2)–C(61) 1.956(3), Al(2)–C(62) 1.977(3), Zn–C(5) 1.978(2), Zn–C(36) 1.978(2), Zn(1)–O(1) 2.1248(16), C(4)–C(5) 1.477(3), C(35)–C(36) 1.482(3), N(1)–Al(1)–N(2) 96.56(8), N(3)–Al(2)–N(4) 96.87(8), C(36)–Zn(1)–C(5) 148.24(10). All hydrogen atoms have been omitted for clarity.

9.9. Conclusion

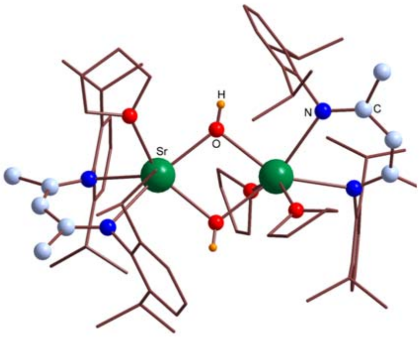
In summary, a N-heterocyclic aluminum complex **8** reacted with ammonia gas at room temperature gives an aluminum amide LAl(NH_2)Me (**20**). The reaction of **8** with phenol and biphenyl phosphine chloride Ph_2PCl showed the complete conversion of **8** and afforded the LAl(OPh)Me and L^2AlMeCl respectively. Interestingly reaction of the N-heterocyclic aluminum complex **8** with benzophenone at –60 °C leads to the isolation of [4+2] cycloaddition product **23**, which consists of an eight-memebered aluminum complex.

We also explored the reactivity of LAlMe.thf with LGeCl, LSnCl, [1,8-$C_{10}H_6(NSiMe_3)_2BiNMe_2$] and $ZnMe_2$. The synthetic method described herein provides a facile and direct route for heterobimetallic and trimetallic compounds in good yields, with strict control of the functionality at the aluminum center. These complexes can find applications in material science and catalysis.

Chapter 10

Summary

In this thesis we have demonstrated the reactivity of the first hydrocarbon soluble molecular strontium hydroxide supported by *β*–diketiminate ligands. A hydrocarbon soluble molecular strontium hydroxide $[LSr(thf)(\mu\text{-}OH)_2Sr(thf)_2L]$ ($L = CH(CMe2,6\text{-}i\text{Pr}_2C_6H_3N)_2$) (**2**) was prepared by the controlled hydrolysis of strontium silylamide with stoichiometric amount of water. The structural analysis shows that the hydroxide is dimeric in the solid state and the coordination geometry around the metal centers is different as it contains an unequal number of coordinated thf molecules, which is in contrast to its calcium and magnesium congeners. Ligand exchange is carried out to check the possibility of obtaining a monomeric species. Interestingly the reaction of **2** with $Zr(NMe_2)_4$ gave a heterobimetallic oxide $[LSr(\mu\text{-}O)Zr(NMe_2)_3]_2$ (**5**). The formation of compound **5** reveals the unprecedented mild acidic character of **2**.



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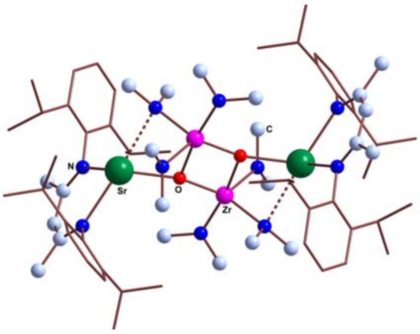
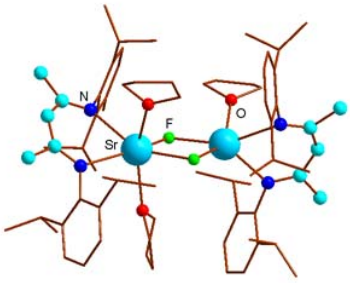


5

A dimeric strontium mono fluoride $[LSr(thf)(\mu\text{-}F)_2Sr(thf)_2L]$ and a corresponding chloride derivative $[LSr(thf)(\mu\text{-}Cl)_2Sr(thf)_2L]$ have been prepared by the reaction of strontium amide $LSrN(SiMe_3)_2(thf)$ with trimethyltinfluoride and $LAlCl(Me)$ respectively. Both compounds can provide an access to study the unexplored chemistry of strontium halides.



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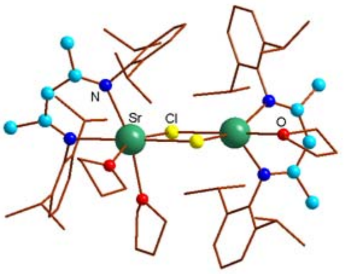
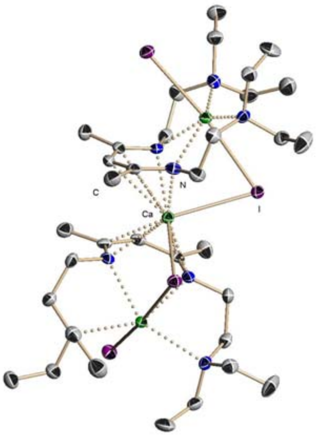


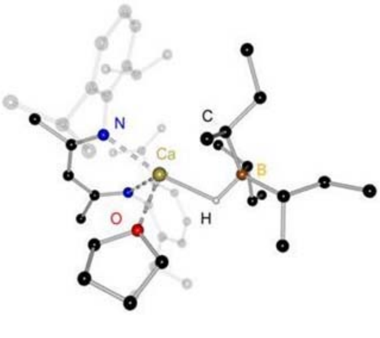
7

We were able to prepare a $[\text{I-Ca-I-Ca-I-Ca-I}]^{2+}$ chain stabilized by two chelating *β*-diketiminate ligands, [L`CaI(*μ*-ICaI-*μ*)ICaL`] (**11**) by the reaction of L′H (L`=CH{$Et_2NCH_2CH_2N(CMe)$}$_2$) with $KN(SiMe_3)_2$ and CaI_2. Compound **11** might be a strong candidate for the preparation of a low valent calcium compound as the ligand itself can provide a high coordination sphere around the metal center.



11

Hydrocarbon soluble molecular calcium and strontium tri*sec*-butylboron hydrides LMB(*sec*-Bu)$_3$H·thf (M= Ca (**12**) and Sr (**13**)) were prepared by reaction of [LCa(*μ*-I)·thf]$_2$ (**9**) and [LSr(*μ*-I)·thf]$_2$ (**10**) with two equiv of potassium tri*sec*-butylborohydride, respectively. The structural analyses show that the alkaline earth boron hydrides are monomeric in the solid state and the coordination geometry around the metal centers is the same in both complexes. Interestingly, the $[R_3BH]^-$ binds to the metal atom through a *μ* H bond.



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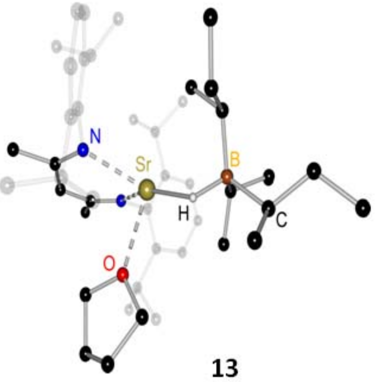
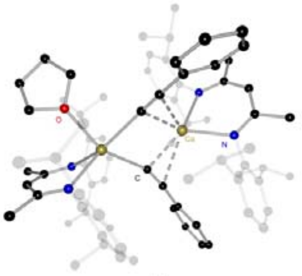


13

The reaction of PhC≡CH with LCaN(SiMe$_3$)$_2$·thf and LSrN(SiMe$_3$)$_2$·thf (**1**) results in the formation of [LCa(thf)(μ-C≡CPh)$_2$CaL] (**14**) and [LSr(thf)(μ-C≡CPh)]$_2$ (**15**) respectively. The X-ray structural analysis of the latter compound exhibits a dimeric arrangement with interesting coordination geometry around the metal centers.



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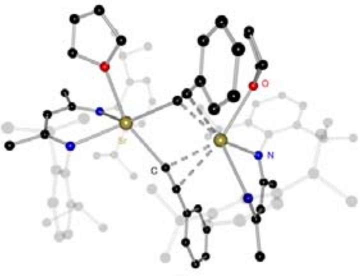
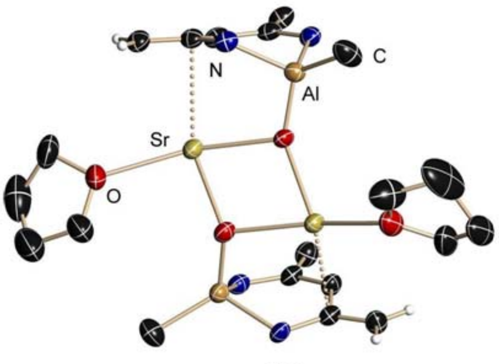


15

The reaction between a β-diketiminate aluminum methyl hydroxide and Sr[N(SiMe$_3$)$_2$]$_2$·2thf results in alkaline earth metal oxide [L^{1}Al(Me)(μ-O)Sr·thf]$_2$ (**16**). This soluble oxide complex is dimeric in the solid state and contains an unprecedented Sr$_2$O$_2$ core. This compound might be useful in material science and catalysis.



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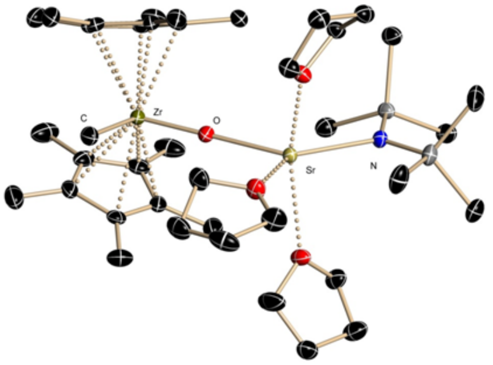
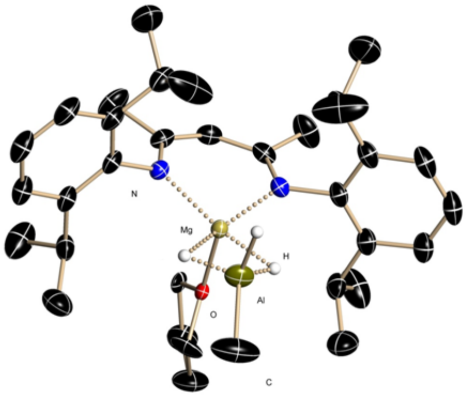
The reaction of $Cp^*_2Zr(Me)OH$ with $Sr[N(SiMe_3)_2]_2 \cdot 2thf$ gave a heterobimetallic compound (**17**) with Zr–O–Sr core. The strontium–zirconium oxide compound has a labile amide group on the strontium atom. It can act as a precursor for hetero-trimetallic compounds and also can find application in hydroamination reactions.



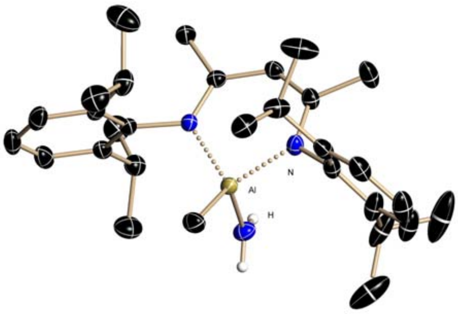
17

Reaction of LMgMe.thf with $AlH_3 \cdot NMe_3$ resulted in a heterobimetallic hydride complex containing aluminum and magnesium (**18**). This compound can be considered as an intermediate in the formation of magnesium hydride.



18

Reactivity of N-heterocyclic aluminium complex $L^1AlMe \cdot thf$ (**8**) towards small molecules and organometallic compounds was studied. It fixes ammonia to form aluminum methyl amide (**20**). It reacts with PPh_2Cl to form the aluminum chloride complex (**22**).



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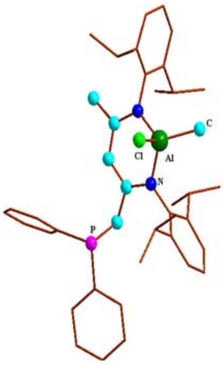

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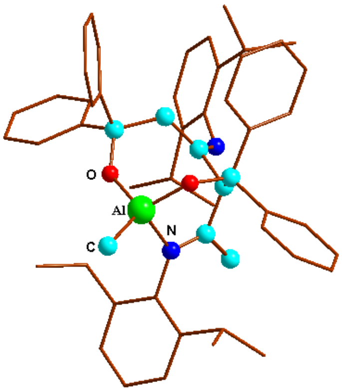
The reactivity of **8** towards benzophenone is unique. It undergoes [4+2] cyclo addition to form an eight-membered aluminum compound, which can find application in polymerization reactions.



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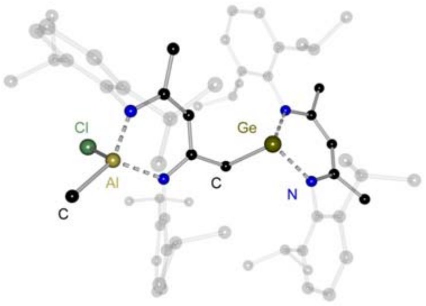
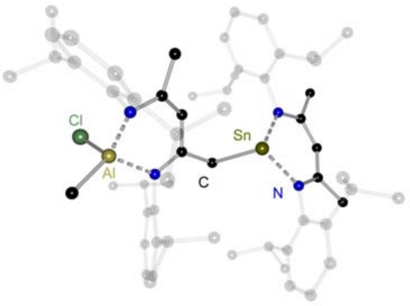
Finally we have prepared hydrocarbon soluble molecular hetero bi- and trimetallic complexes containing aluminum by the reaction of L^{1}AlMe·thf with suitable organometallic complexes such as germanium chloride (LGeCl), tin chloride (LSnCl) [L = CH(CMe2,6-iPr$_2$C$_6$H$_3$N)$_2$], bismuth amide [1,8-C$_{10}$H$_6$(NSiMe$_3$)$_2$BiNMe$_2$] and dimethyl zinc. The structural analysis shows that the desired bi- and trimetallic compounds have been formed in accordance with the synthetic strategy. This synthetic method allows the tuning of the functionality at the aluminum center.



24



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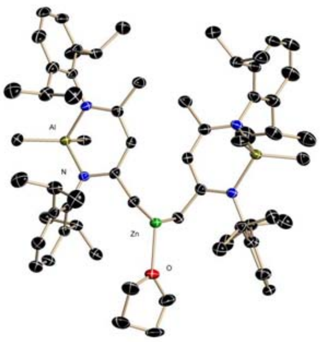

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It is interesting to mention that most of the prepared compounds are stable at room temperature and highly soluble in common organic solvents and therefore favor further functionalization at the metal center, and might be used as catalysts in various organic transformation reactions.

Chapter 11

Experimental Section

11.1. General Procedures

All manipulations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Toluene, *n*-hexane, *n*-pentane, tetrahydrofuran, and diethylether were purified with the M-Braun solvent drying system. Dichloromethane was dried over CaH_2 and distilled prior to use. All glasswares were dried in an oven at 150 °C for at least 24 h, assembled hot and cooled under high vacuum prior to use.

11.2. Physical Measurements

NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 NMR spectrometers. Downfield shifts from the reference are quoted positive; upfield shifts are assigned negative values for the case of external references. Deuterated NMR solvents C_6D_6, C_7D_8, and THF–D_8 were dried by stirring for 2 days over Na/K alloy followed by distillation *in vacuo* and degassed. CD_2Cl_2 was dried stirring with CaH_2 for 6 h followed by filtration. Heteroatom NMR spectra were recorded ^1H decoupled with the exception of ^{11}B. Chemical shifts are reported in ppm with reference to $SiMe_4$ (external) for ^1H and ^{13}C isotopes, $SnMe_4$ (external) for ^{119}Sn nuclei, $CFCl_3$ (external) for ^{19}F nuclei, $BF_3\cdot OEt_2$ (external) for ^{11}B nuclei, 85% H_3PO_4 (external) for ^{31}P nuclei, $SiMe_4$ (external) for ^{29}Si nuclei. **IR spectra** were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range 4000−350 cm^{-1} as nujol mulls between KBr plates. **Mass spectra** were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. **Melting points** were measured in sealed glass tubes on a Büchi B-540 melting point apparatus and are uncorrected. **Elemental analyses** were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

11.3. Starting Materials

SrI_2, CaI_2, $KN(SiMe_3)_2$ (95%), $(Ph)_2CO$, Ph_3PO (98%), $Zr(NMe_2)_4$, $AlCl_2(Me)$ (1 M solution in *n*-hexane), MeLi (1.6 M in Et_2O), MgCl(Me) (3 M solution in THF), $ZnMe_2$ (2 M solution in toluene), $GeCl_2\cdot$dioxane, $SnCl_2$, K[*sec*-Bu_3BH] (1 M solution in THF), PPh_2Cl, and sulfur. All chemicals were purchased from Aldrich and used as received. LH,[21] LGeCl,[154] LSnCl,[154]

$AlH_3 \cdot NMe_3$,[147-149] LAlMe(OH),[34] LAlMe(Cl),[158] $LLi \cdot OEt_2$,[159] $Cp^*{}_2Zr(Me)OH$,[56] and $M[N(SiMe_3)_2]_2 \cdot 2thf$ (M = Ca or Sr) [50]were prepared from known literature procedures.

11.4. Syntheses of Compounds 1-27

11.4.1. Synthesis of $LSrN(SiMe_3)_2 \cdot thf$ (**1**)

LH (2.931 g, 7.00 mmol) and $KN(SiMe_3)_2$ (2.933 g, 14.70 mmol) were dissolved in THF (60 mL) and stirred for 5 h at room temperature. This clear solution was added to a suspension of SrI_2 (2.390 g, 7.00 mmol) in THF (60 mL) at room temperature. It was stirred for another 18 h. After that the solvent was removed and the residue was extracted with *n*-hexane (90 mL) and filtered. Removal of the solvent from the filtrate in vacuum gave compound **1** as pale yellow solid. The solid upon crystallization from *n*-hexane at low temperature gave analytically pure sample of **1**. Yield: (4.02 g, 5.45 mmol, 77.9%); Mp: 116–118 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.14–7.11 (m, 6 H, *m*-, *p*-Ar-*H*), 4.78 (s, 1H, γ-C*H*), 3.31 (m, 4H, O-CH_2-CH_2), 3.18 (sept, 4H, C*H*(CH_3)$_2$), 1.69 (s, 6H, CH_3), 1.33–1.32 (d, 12H, CH(CH_3)$_2$), 125–1.24 (d, 12H, CH(CH_3)$_2$) 1.11 (m, 4H, O-CH_2-CH_2), 0.14 (s, 18H, $SiMe_3$) ppm. ^{13}C {^1H} NMR(125.77 MHz, C_6D_6): δ 164.96, 147.27, 140.95, 124.31, 124.05, 92.49, 68.75, 28.42, 25.52, 25.05, 24.89, 24.51, 5.77 ppm. ^{29}Si NMR (75 MHz, C_6D_6) : δ –15. 95 (s, 2Si, *Si*Me_3). MS (70 eV): *m/z* (%): 505.16 (100) [M^+-$N(SiMe_3)_2$-THF]. Anal. Calcd for $C_{39}H_{67}N_3OSi_2Sr$ (737.76): C 63.49, H 9.15, N 5.70. Found: C 62.4, H 9.20, N 5.61.

11.4.2. Synthesis of [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (**2**)

Distilled and degassed water (24 µL, 1.36 mmol) was added to a solution of $LSrN(SiMe_3)_2(thf)$ (1.00 g, 1.36 mmol) in THF (50 mL) at –60 °C. Then it was taken to room temperature and stirred for 1 h. Filtration followed by removal of the solvent in vacuum to give compound **2** as off-white solid. It was washed with a small amount of *n*-hexane and crystallized from THF at –32 °C to exhibit compound **2** as colorless crystals. Yield: (0.47 g, 0.37 mmol, 55.2%); Mp: 172-176 °C. ^1H NMR (300.132 MHz, C_6D_6): δ 7.15–7.06 (m, 12H, *m*-, *p*-Ar-*H*); 4.74 (s, 2H, γ-C*H*) 3.44 (m, 12H, O-CH_2-CH_2), 3.19 (sept, 8H, C*H*(CH_3)$_2$), 1.72 (s, 12H, CH_3), 1.40 (m, 12H, O-CH_2-CH_2), 1.25–1.22 (d, 24H, CH(CH_3)$_2$), 1.09–1.07 (d, 24H, CH(CH_3)$_2$), –0.72 (s, 2H, Sr-O*H*). ^{13}C NMR (75.48 MHz, C_6D_6): δ 163.48, 147.81, 141.46, 123.48, 123.34, 93.15, 68. 25, 28.00, 25.55, 25.15, 24.50, 24.36. IR (nujol): $\tilde{\nu}$ 3677, 3053, 1917, 1624, 1549, 1510, 1429, 1408, 1379, 1314, 1254, 1225, 1166, 1100, 1042, 1018, 924, 890, 828, 783, 758, 724, 668, 618, 523, 437, 348 cm^{-1}. MS (70 eV): *m/z* (%): 403 (100) [L$^+$-Me]. Anal. Calcd for $C_{70}H_{108}N_4O_5Sr_2$, (M =1260.87): C 66.68, H 8.63, N 4.44. Found: C 65.23, H 8.57, N 4.53.

11.4.3. Synthesis of [LSr(μ-OH)(OCPh$_2$)]$_2$ (**3**)

A solution of benzophenone (0.072 g, 0.397 mmol) in benzene (2 mL) was added to a colorless solution of compound **2** (0.25g, 0.198 mmol) in benzene at room temperature (6 mL). Compound **3** was formed instantaneously and separated out of the solution as orange red crystals. Yield: (0.15 g, 0.109 mmol, 55.2 %); Mp: 147–149 °C (dec.). IR (Nujol): $\tilde{\nu}$ 3676, 3059, 2278, 1667, 1641, 1626, 1596, 1576, 1551, 1508, 1465, 1364, 1321, 1286, 1255, 1227, 1175, 1167, 1099, 1078, 1056, 1018, 999, 946, 937, 925, 852, 827, 806, 793, 784, 769, 757, 729, 706, 640, 622, 532, 504, 434, 412, 352 cm^{-1}. MS (70 eV): *m/z* (%): 403(100) [L$^+$-Me]. Anal. Calcd for $C_{84}H_{104}N_4O_4Sr_2$ (M = 1408.99): C 71.60, H 7.44, N 3.98. Found: C 71.63, H 7.49, N 3.79.

11.4.4. Synthesis of [LSr(μ-OH)(OPPh$_3$)]$_2$ (**4**)

[LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (0.35 g, 0.28 mmol) and Ph$_3$PO (0.156 g, 0.56 mmol) were dissolved in toluene (15 mL) and stirred for 0.5 h at room temperature. Removal of the solvent from the filtrate in vacuum gave compound **4** as yellow solid. The solid upon crystallization from toluene at –5 °C gave analytically pure sample of **4**. Yield: (0.348 g, 0.217 mmol, 78.3%); Mp: 189–191 °C. ^{1}H NMR (300.132 MHz, C_6D_6): δ 7.69–7.66 (m, 30H, Ar-*H*), 7.13–7.01 (m, 12H, *m-*, *p*-Ar-*H*), 4.89 (s, 2H, γ-C*H)*, 3.31 (sept, 8H, C*H*(CH$_3$)$_2$), 1.79 (s, 12H, C*H*$_3$), 1.09–1.07 (d, 24H, CH(C*H*$_3$)$_2$), 0.98–0.97 (d, 24H, CH(C*H*$_3$)$_2$), –0.479 (s, 2H, Sr-O*H*). ^{13}C NMR (75.48 MHz, C_6D_6): δ 163.26, 149.45, 141.00, 132.87, 132.79, 132.13, 132.03, 125.64, 123.23 ,122.89, 92.63, 27.77, 25.64, 25.08, 24.39. ^{31}P NMR (75 MHz, C_6D_6) : δ 29.5 (s, 2P, O*P*Ph$_3$); IR (nujol): $\tilde{\nu}$ 3680, 3049, 1965, 1909, 1683, 1624, 1591,1548, 1507, 1380, 1362, 1338, 1313, 1275, 1253, 1225, 1174, 1118, 1100, 1072, 1053, 1028, 1015, 998, 935, 923, 857, 827,807, 794, 785, 751, 727, 693, 619, 598, 537, 512, 465, 436, 346 cm^{-1}. MS (70 eV): *m/z* (%): 403 (100) [L$^+$-Me]. Anal. Calcd for $C_{94}H_{114}N_4O_4P_2Sr_2$ (1601.12): C 70.51, H, 7.18, N 3.50. Found: C 70.92, H 7.42, N 3.26.

11.4.5. Synthesis of [LSr(μ-O)Zr(NMe$_2$)$_3$]$_2$ (**5**)

A toluene solution of [LSr(thf)(μ-OH)$_2$Sr(thf)$_2$L] (**2**) (0.5 g, 0.397 mmol) was added drop by drop to a solution of Zr(NMe$_2$)$_4$ (0.212 g, 0.793 mmol) in toluene at –60 °C using a cannula. After the addition was complete the solution was brought to room temperature and stirred for one day. Then the solvent was removed *in vacuo* to get the crude sample of **5**. Colorless crystals were obtained when a toluene solution of **5** was kept at –5 °C for 3 days. Yield: (0.408 g, 0.274 mmol, 69.1%); Mp: 252–254 °C. ^{1}H NMR (500.132 MHz, C$_6$D$_6$): δ 7.14–7.09 (m, 12H, Ar-*H*), 4.72 (s, 2H, γ-C*H*), 3.24 (sept, 8H, C*H*(CH$_3$)$_2$), 2.62 (s, 36H, N(C*H*$_3$)$_2$), 1.69 (s, 12H, C*H*$_3$), 1.34–1.33 (d, 24H, CH(C*H*$_3$)$_2$), 1.25–1.23 (d, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75.48 MHz, C$_6$D$_6$): δ 165.12, 147.56, 141.32, 124.34, 123.98, 91.77, 43. 22, 28.64, 25.25, 24.93, 24.45. MS (70 eV): *m/z* (%): 505.2 (15) (M$^+$-OZr[NMe$_2$]$_3$), 403 (100) [L$^+$-Me]. Anal. Calcd for C$_{70}$H$_{108}$N$_{10}$O$_2$Sr$_2$Zr$_2$ (M =1489.44): C 56.45, H 7.99. Found: C 56.52, H 7.59.

11.4.6. Synthesis of [LSr(thf)(μ-F)$_2$Sr(thf)$_2$L] (**6**)

A solution of LSrN(SiMe$_3$)$_2$(thf) (**1**) (2.213 g, 3.00 mmol) in THF (25 mL) was added to a slurry of Me$_3$SnF (0.548 g, 3.00 mmol) in THF (40 mL) at room temperature and stirred for 16 h. The solvent was removed in vacuum and the residue was dissolved in a mixture of THF-toluene, concentrated and stored for crystallization at –5 °C in a freezer for 2 days. Compound **6** was obtained as colorless crystals. Yield: (0.526 g, 0.416 mmol, 27.7%); Mp: 169–170 °C. ^{1}H NMR (500 MHz, THF-*d*$_8$): δ 6.97–6.86 (m, 12H, *m-, p*-Ar-*H*); 4.51 (s, 2H, γ-C*H)*, 3.08 (sept, 8H, C*H*(CH$_3$)$_2$), 1.49 (s, 12H, C*H*$_3$), 1.09–1.08 (d, 24H, CH(C*H*$_3$)$_2$), 1.06–1.05 (d, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (125.77 MHz, THF-*d*$_8$): δ 163.99, 149.47, 142.14, 123.73, 123.50, 93.35, 28.34, 25.38, 24.83, 24.73 ppm. ^{19}F NMR (188.3 MHz, THF-*d*$_8$): δ –59. 97 ppm (s, 2F, Sr*F*). MS (70 eV): *m*/*z* (%): 403.2 (100) [L$^+$-Me]. Anal. Calcd for C$_{70}$H$_{106}$F$_2$N$_4$O$_3$Sr$_2$ (1264.85): C 66.5, H 8.5, N 4.4. Found: C 65.6, H 8.4, N 4.5.

11.4.7. Synthesis of [LSr(thf)(μ-Cl)$_2$Sr(thf)$_2$L] (**7**)

A solution of LAlCl(Me) (1.485 g, 3 mmol) in THF (25 mL) was added to a clear solution of LSrN(SiMe$_3$)$_2$(thf) **1** (2.213 g, 3 mmol) in THF (40 mL) at room temperature under stirring and after the completion of addition the stirring was continued for one day. All volatiles were removed in vacuum and the residue was dissolved in THF-toluene mixture. The solution was concentrated and stored for crystallization at –5 °C in a freezer. Compound **7** was obtained as pale yellow crystals. Yield: (0.974 g, 0.751 mmol, 49.59%); Mp: 155–157 °C. ^{1}H NMR (500.13 MHz, C_6D_6): *δ* 7.13–7.10 (m, 12 H, *m-, p*-Ar-*H*), 4.77 (s, 2H, *γ*-C*H*), 3.53 (m, 12H, O-CH_2-CH_2), 3.26 (sept, 8H, C*H*(CH_3)$_2$), 1.67 (s, 12H, CH_3), 1.33 (m, 12H, O-CH_2-CH_2), 1.25–1.24 (d, 48H, CH(CH_3)$_2$). ^{13}C {^{1}H} NMR(125.77 MHz, C_6D_6): *δ* 164.33, 147.36, 141.95, 124.02, 123.73, 93.88, 68.72, 28.15, 25.40, 25.37, 24.71 ppm. MS (70 eV): *m*/*z* (%): 403 (100) [L$^+$-Me]. Anal. Calcd for $C_{70}H_{106}Cl_2N_4O_3Sr_2$, (1297.76): C 64.8, H 8.2, N 4.3. Found: C 64.3, H 8.2, N 4.2

10.4.8. Synthesis of L^{1}AlMe·thf (**8**)

Method A: A solution of LAlCl(Me) (1.485 g, 3 mmol) in THF (25 mL) was added to a clear solution of LSrN(SiMe$_3$)$_2$(thf) (**1**) (2.213 g, 3 mmol) in THF (40 mL) at room temperature under stirring and after the completion of addition the stirring was continued for one day. All volatiles were removed in vacuum and the residue was dissolved in THF-toluene mixture. The solution was concentrated and stored for crystallization at –5 °C in a freezer. After the separation of compound **7** as crystals, the solvent was removed and the residue was dissolved in toluene/*n*-pentane mixture, filtered, dried and washed with minimum amount of *n*-pentane. Again dried in vacuum to yield compound **8** as pale yellow solid.

Method B. A THF solution (15 mL) of Ca[N(SiMe$_3$)$_2$]$_2$.2thf (1.515 g, 3.0 mmol) was added to a THF(20 mL) solution of LAlCl(Me) (2.971 g, 6.0 mmol) using a cannula at room temperature. The reaction mixture was stirred for 4.5 h and formation of a precipitate of $CaCl_2$ is an indication of the formation of **8**. All volatiles were removed under vacuum and the residue was extracted with toluene. All volatiles were again removed under vacuum to get the compound **8** as pale yellow solid. Yield: (2.983 g, 5.62 mmol, <90%); Mp: 154–156 °C. ^{1}H NMR (500.131 MHz, C_6D_6): *δ* 7.28–7.26, 7.19–7.18, 7.09–7.08 (m, 6 H, *m-, p*-Ar-*H*), 5.38 (s, 1H, *γ*-C*H*), 4.05 (sept, 1H, C*H*(CH_3)$_2$), 3.91 (sept, 1H, C*H*(CH_3)$_2$), 3.90 (s, 1H, NCCH_2), 3.84 (m, 2H, O-CH_2-CH_2), 3.77 (m, 2H, O-CH_2-CH_2), 3.33 (sept, 1H, C*H*(CH_3)$_2$), 3.21 (sept, 1H, C*H*(CH_3)$_2$), 3.18 (s, 1H, NCCH_2), 1.59–1.58 (d, 3H, CH(CH_3)$_2$), 1.58 (s, 3H, CH_3), 1.52–1.50 (d, 3H, CH(CH_3)$_2$), 1.44–1.41 (3d (merged together), 9H, CH(CH_3)$_2$), 1.20 (m, 4H, O-CH_2-CH_2), 1.18–1.16 (d, 3H, CH(CH_3)$_2$), 1.07–1.06 (d, 3H, CH(CH_3)$_2$), 1.00–0.99 (d, 3H, CH(CH_3)$_2$), –0.99 (s, 3H, Al*Me*).

$^{13}C\{^1H\}$ NMR(125.77 MHz, C_6D_6): δ 155.21, 148.66, 147.59, 147.01, 145.47, 145.46, 143.14, 143.01, 125.71, 125.51, 124.67, 124.45, 123.74, 123.14, 104.88, 81.30, 72.48, 29.03, 28.55, 27.69, 27.15, 26.53, 26.09, 26.06, 25.75, 25.30, 25.10, 24.65, 24.63, 24.37, 23.34, –15.13 ppm. EI-MS (70 eV): *m/z* (%): 461.3 (100) [M^++H-thf], 460.3(36) [M^+-thf]. Anal. Calcd for $C_{34}H_{51}AlN_2O$, (530.76): C 76.94, H 9.69, N 5.3. Found: C 74.64, H 9.25, N 5.06.

11.4.9. Synthesis of [LCa(μ-I)·thf]$_2$] (**9**)

LH (3.349 g, 8.00 mmol) and $KN(SiMe_3)_2$ (1.676 g, 8.40 mmol) were dissolved in THF (60 mL) and stirred for 5 h at room temperature. The clear solution was added to a suspension of CaI_2 (2.351 g, 8 mmol) in THF (60 mL) at room temperature and stirred for another 12 h. The solvent was removed from the solution in vacuum and the residue was extracted with toluene (90 mL). Removal of the solvent from the filtrate in vacuum gave compound **9** as off-white solid. Yield: (3.82 g, 2.91 mmol, 72.8%); Mp: 360–368 °C (decomp). ^1H NMR (500.13 MHz, C_6D_6): δ 7.17–7.10 (m, 12 H, *m*-, *p*-Ar-*H*), 4.80 (s, 2 H, γ-C*H*), 3.65 (m, 8 H, O-CH_2-CH$_2$), 3.22 (sept, 8H, C*H*(CH$_3$)$_2$), 1.66 (s, 12 H, CH_3), 1.36 (d, 24 H, CH(CH_3)$_2$), 1.32 (m, 8H, O-CH$_2$-CH_2), 1.23 (d, 24 H, CH(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ 165.9, 147.1, 141.8, 124.59, 123.8, 94.8, 69.5, 28.5, 25.6, 25.3, 24.8, 24.5 ppm. MS (70 eV): *m/z* (%): 704.3 (100) [L^+-Me]. Anal. Calcd for $C_{66}H_{98}Ca_2I_2N_4O_2$ (1313.47): C, 60.35; H, 7.52; N, 4.27. Found: C, 60.08; H, 7.92; N, 4.31. Anal. Calcd for $C_{66}H_{98}Ca_2I_2N_4O_2$ (1313.47): C 60.35, H 7.52, N 4.27. Found: C 60.08, H 7.92, N, 4.31.

11.4.10. Synthesis of [LSr(μ-I)·thf]$_2$ (**10**)

Compound **10** was prepared by the same method as compound **9** with LH (3.349 g, 8.00 mmol), $KN(SiMe_3)_2$ (1.676 g, 8.40 mmol) and SrI_2 (2.731 g, 8.00 mmol). The solid upon crystallization from a saturated solution of *n*-hexane at –5 °C gave analytically pure sample of **10**. Yield: (4.247 g, 3.02 mmol, 75.4 %); Mp: 188–190 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.20–7.15 (m, 12 H, *m*-, *p*-Ar-*H*), 4.84 (s, 2 H, γ-C*H*), 3.56 (m, 8 H, O-CH_2-CH$_2$), 3.29 (sept, 8 H, C*H*(CH$_3$)$_2$), 1.69 (s, 12 H, CH_3), 1.36 (d, 24 H, CH(CH_3)$_2$), 1.25 (d, 24 H, CH(CH_3)$_2$) 1.19 (m, 8 H, O-CH$_2$-CH_2) ppm. $^{13}C\{^1H\}$NMR (125.77 MHz, C_6D_6): δ 164.6, 146.6, 141.6, 124.4, 124.0, 94.0, 69.5, 28.4, 26.2, 25.0, 24.7, 24.6 ppm. MS (70 eV): *m/z* (%): 704.3 (100) [M^+/2-2THF]. Anal. Calcd for $C_{66}H_{98}I_2N_4O_2Sr_2$ (1408.56): C 56.28, H 7.01, N 3.98. Found: C 56.48, H 7.29, N 3.66.

11.4.11. Synthesis of L\`CaI(*μ*-ICaI-*μ)*ICaL\` (**11**)

L\`H (1.482 g, 5.00 mmol) (L=CH{$Et_2NCH_2CH_2N(CMe)\}_2$) and $KN(SiMe_3)_2$ (1.047 g, 5.25 mmol) were dissolved in THF (60 mL) and stirred for 5 h at room temperature. The clear solution was added to a suspension of CaI_2 (2.783 g, 10.00 mmol) in THF (60 mL) at room temperature and stirred for another 12 h. All volatiles were removed in vacuum and the residue was extracted with toluene (90 mL). The solution was concentrated and stored in a freezer at –5 °C to get analytically pure sample of **11**. Yield: (2.183 g, 1.791 mmol, 71.67 %); Mp: 269–272 °C (decomp). ^1H NMR (300 MHz, C_6D_8, 343 K): ^1H NMR (300 MHz, C_7D_8, 343 K): δ 4.57 (s, 2H, C*H*), 3.58, 3.31−3.26, 3.05−2.03, 2.5 (br, 32H, CH_2CH_2N, CH_3CH_2N and CH_2CH_2N), 1.88 (s, 12H, CH_3), 0.82 (t, 24H, CH_2CH_3) ppm. ^{13}C {^1H} NMR (75.47 MHz, C_6D_6): δ 174.26, 96.07, 54.00, 47.43, 46.98, 44.35, 23.19, 8.86 ppm. EI-MS: *m*/*z* (%) 296.3 (100) [L\`H]$^+$. Anal. Calcd for $C_{34}H_{70}Ca_3I_4N_8$ (1218.83): C 33.50, H 5.79, N 9.19. Found: C 33.83, H 5.90, N 9.16.

11.4.12. Synthesis of LCaB(*sec*-Bu)$_3$H·thf (**12**)

A solution of compound **9** (1.31g, 1 mmol) in THF (25 mL) was cooled to –40 °C and 2 equiv of potassium tri*sec*-butylborohydride (1 M solution in THF) (2.00 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. From the solution all volatiles were removed in vacuum and the residue was extracted with toluene (30 mL). Single crystals of **12** were obtained from a solution of toluene-THF mixture (1:0.25) stored at –32 °C in a freezer. Yield: (1.09 g, 1.53 mmol, 76.8%); Mp:175–177 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.14 (m, 6H, *m*-, *p*-Ar-H), 4.76 (s, 1H, *γ*-C*H*), 3.84 (m, 4H, O-CH_2-CH_2), 3.10 (br, sept, 4H, $CH(CH_3)_2$), 1.72–1.06, 1.66–1.34, 1.67–0.73) (m, 6H, B-CH(CH_2-CH_3)(CH_3)), 1.62 (s, 6H, CH_3), 1.34 (m, (4H, O-CH_2-CH_2), 1.33 (d, 12H, CH(CH_3)$_2$), 1.17 (d, 12H, CH(CH_3)$_2$), 1.08 (t, 3H, B-CH(CH_2-CH_3)(CH_3)), 1.05 (d, 3H, B-CH(CH_2-CH_3)(CH_3)), 0.92 (t, 3H, B-CH(CH_2-CH_3)(CH_3)), 0.83 (t, 3H, B-CH(CH_2-CH_3)(CH_3)), 0.76 (d, 3H, B-CH(CH_2-CH_3)(CH_3)), 0.73 (d, 3H, B-CH(CH_2-CH_3)(CH_3)), 0.41 (m, 1H, B-C*H*(CH_2-CH_3)(CH_3)), 0.07 (m br, 2H, B-C*H*(CH_2-CH_3)(CH_3)), –0.05 (br, 1H, Ca-H-B) ppm. $^{13}C\{^1H\}$NMR(125.77 MHz, C_6D_6): δ 166.6, 146.6, 141.6, 125.2, 124.3, 94.6, 70.3, 31.1, 30.1, 29.7, 28.6, 25.2, 25.1, 25.0, 25.0, 24.9, 24.7, 20.5, 20.2, 19.9, 15.4, 14.9, 14.7 ppm (B-C is not visible). ^{11}B NMR (128.38 MHz, C_7D_8) : δ –4.4 ppm (d, $^1J_{BH}$ = 50 Hz B, BR). IR (Nujol, cm^{-1}) : $\tilde{\nu}$ 2649, 2601, 1924, 1903, 1771, 1696, 1625, 1540, 1514, 1458, 1377, 1313, 1262, 1225, 1167, 1098, 1054, 1018, 926, 871, 834, 788, 759, 747, 694, 668, 622, 597. MS (70 eV): *m/z* (%): 403.3 (100) [L^+-Me]. Anal. Calcd for $C_{45}H_{77}BCaN_2O$ (712.99): C 75.80, H 10.89, N 3.93. Found: C 73.41, H 10.86; N 4.01. (The low value for carbon probably due to the high air-sensitivity of the compound and/or partial loss of coordinate thf molecule).

11.4.13. Synthesis of LSrB(*sec*-Bu)$_3$H·thf (**13**)

Compound **13** was prepared by the same method as described for compound 1**2** with [LSr(μ-I)·thf]$_2$ (1.409 g, 1.00 mmol) and potassium tri*sec*-butylborohydride (1 M solution in THF) (2.00 mmol). Analytically pure compound **13** was obtained when a solution of **13** in toluene-THF (1:0.25) was stored at –5 °C in a freezer. Yield: (1.15 g, 1.51 mmol, 75.7%); Mp: 195 °C. ^{1}H NMR (500.13 MHz, C_7D_8): δ 7.11–7.06 (m, 6H, *m*-, *p*-Ar-H), 4.74 (s, 1H, γ-C*H*), 3.80 (m, 4H, O-C*H*$_2$-CH$_2$), 3.09 (br sept, 4H, C*H*(CH$_3$)$_2$), 1.69–1.53 (m, 3H, B-CH(C*H*$_2$-CH$_3$)(CH$_3$), 1.65 (s, 6H, C*H*$_3$), 1.40 (m, 4H, O-CH$_2$-C*H*$_2$), 1.29 (br d, 12H, CH(C*H*$_3$)$_2$), 1.23 (m, 1H, B-CH(C*H*$_2$-CH$_3$)(CH$_3$), 1.18 (d, 12H, CH(C*H*$_3$)$_2$), 1.02 (t, 3H, B-CH(CH$_2$-C*H*$_3$)(CH$_3$)), 1.02 (m, 1H, B-CH(C*H*$_2$-CH$_3$)(CH$_3$), 0.93 (d, 3H, B-CH(CH$_2$-CH$_3$)(C*H*$_3$)), 0.92 (t, 3H, B-CH(CH$_2$-C*H*$_3$)(CH$_3$)), 0.89 (d, 3H, B-CH(CH$_2$-CH$_3$)(C*H*$_3$)), 0.82 (t, 3H, B-CH(CH$_2$-C*H*$_3$)(CH$_3$)), 0.68 (d, 3H, B-CH(CH$_2$-CH$_3$)(C*H*$_3$)), 0.62 (d, 3H, B-CH(CH$_2$-CH$_3$)(C*H*$_3$)), 0.58 (m, 1H, B-CH(C*H*$_2$-CH$_3$)(CH$_3$), 0.24-0.16, 0.09– -0.08 (m, 3H, B-C*H*(CH$_2$-CH$_3$)(CH$_3$)) ppm. ^{13}C{^{1}H} NMR(125.77 MHz, C_7D_8): δ 165.4, 145.9, 141.5, 125.0, 124.4, 94.2, 69.8, 31.0, 30.8, 30.4, 28.5, 25.2, 25.0, 24.8, 24.7, 20.5, 20.3, 19.9, 15.41, 15.22, 15.11 ppm. ^{11}B NMR (128.38 MHz, C_7D_8) : δ –4.7 ppm (d, $^1J_{BH}$ = 55 Hz, B, BR). IR (Nujol, cm^{-1}) : $\tilde{\nu}$ 2377.21, 2346.89, 1932.06, 1624.06, 1551.52, 1511.58, 1404.65, 1311.02, 1261.36, 1222.12, 1164.31, 1097.60, 1054.10, 1020.09, 925.73, 868.55, 785.96, 757.73, 741.99, 722.78, 664.57, 619.22. MS (70 eV): *m/z* (%): 403.3 (100) [L^+-Me]. Anal. Calcd for $C_{45}H_{77}BN_2OSr$ (760.54): C 71.07, H 10.20, N 3.68. Found: C 70.42, H 9.90, N 3.70.

10.4.14. Synthesis of [LCa(thf)(μ-C≡CPh)$_2$CaL] (**14**)

A solution of PhC≡CH (0.296 g, 2.897 mmol) in THF (10 mL) was added to a solution of LCaN(SiMe$_3$)$_2$(thf) (2.00 g, 2.897 mmol) in THF (30 mL) at –5 °C. The solution was allowed to warm to room temperature and stirred for 30 minutes. All volatiles were removed in vacuum. The residue was dissolved in a 1:1 mixture of toluene-THF mixture, and keeping a concentrated solution for 4 h at room temperature resulted in colorless crystals of compound **14**. Yield: (0.796 g, 0.669 mmol, 46.18%); Mp: 378–380 °C (decomp). ^{1}H NMR (500 MHz, THF-d_8): δ 7.12–6.98 (m, 22 H, Ar-*H*), 4.74 (s, 2H, γ-C*H*), 3.34 (sept, 8H, C*H*(CH_3)$_2$), 1.65 (s, 12H, C*H*$_3$), 1.33–1.31 (d, 24H, CH(C*H*$_3$)$_2$, 1.19–1.18 (d, 24H, CH(C*H*$_3$)$_2$) ppm. ^{13}C {^{1}H} NMR(125.77 MHz, THF-d_8): δ 165.60, 148.93, 143.95, 142.76, 131.67, 130.84, 127.97, 124.33, 124.18, 124.11, 107.71, 94.46, 28.73, 25.79, 25.02, 24.96 ppm. MS (EI, 70 eV): *m/z* (%): 1116.6 (100) [M$^+$-thf]. Anal. Calcd for $C_{78}H_{100}Ca_2N_4O$ (1189.81): C 78.74, H 8.47, N 4.71. Found: C 77.78, H 9.39, N 4.71.

11.4.15. Synthesis of [LSr(thf)(μ-C≡CPh)]$_2$ (**15**)

Compound **15** was prepared by the same method as for compound **14** with **1** (2.00 g, 2.711 mmol) and phenyl acetylene (0.277 g, 2.711mmol). Single crystals of **15** were obtained from a solution of 1:1 mixture of *n*-hexane and THF at room temperature. Yield: (1.001 g, 0.738 mmol, 54.42%); Mp: 179–181°C (decomp); ^{1}H NMR (500 MHz, C_6D_6): δ 7.18–7.03 (m, 22 H, Ar-*H*), 4.60 (s, 2H, γ-C*H*), 3.45 (m, 8H, O-C*H*$_2$-CH$_2$), 3.33 (sept, 8H, C*H*(CH_3)$_2$), 1.64 (s, 12H, C*H*$_3$), 1.28 (m, 8H, O-CH$_2$-C*H*$_2$), 1.22–1.21 (d, 24H, CH(C*H*$_3$)$_2$), 1.19–1.17 (d, 24H, CH(C*H*$_3$)$_2$) ppm. ^{13}C {^{1}H} NMR(125.77 MHz, C_6D_6): δ 164.33, 147.05, 146.14, 142.03, 131.78, 127.98, 126.61, 126.55, 124.17, 123.99, 120.76, 94.08, 68.31, 28.25, 25.48, 25.39, 24.55, 24.43 ppm; IR (nujol): $\tilde{\nu}$ 3379, 2959, 2925, 2854, 2586, 2161, 1758, 1661, 1625, 1553, 1463, 1380, 1322, 1258, 1170, 1102, 1038, 928, 894, 787, 758, 695, 626, 486 cm^{-1}. MS (EI, 70 eV): *m/z* (%): 403.3 (100) [L$^+$-Me]. Anal. Calcd for $C_{82}H_{108}N_4O_2Sr_2$ (1357.00): C 72.58, H 8.02, N 4.13. Found: C 71.11, H 8.70, N 4.07.

10.4.16. Synthesis of [L^{1}Al(Me)(μ-OSr·thf)]$_2$ (**16**)

To a solution of LAl(OH)Me (0.953 g, 2 mmol) in THF (20 mL) was added a solution of Sr[N(SiMe$_3$)$_2$]$_2$·2thf (1.105g, 2 mmol) in THF (20 mL) at room temperature and stirred for 1.5 days. Removal of all the volatiles *in vacuo* gave **16** as a pale greenish yellow solid. Analytically pure **16** was obtained by crystallizing the sample from a 1:1 mixture of *n*-hexane-THF at –5 °C. Yield: (1.03 g, 0.811 mmol, 81.23%); Mp: 252–254 °C. ^{1}H NMR (500 MHz, C_7D_8, –50 °C): δ 7.33–7.31, 7.25–7.17, 7.12–7.10 (m, 12 H, *m-, p*-Ar-*H*), 4.83 (sept, 2H, C*H*(CH_3)$_2$), 4.67 (s, 2H, γ-C*H*), 3.94 (sept, 2H, C*H*(CH_3)$_2$, 3.86 (2 sept merged together, 4H, C*H*(CH_3)$_2$), 3.36 (s, 2H, NCC*H*$_2$), 3.33 (m, 8H, O-C*H*$_2$-CH$_2$), 2.79 (s, 2H, NCC*H*$_2$), 1.81–1.80 (d, 6H, CH(C*H*$_3$)$_2$), 1.73 (s, 6H, CH_3), 1.53–1.52 (d, 6H, CH(CH_3)$_2$), 1.50–1.49 (d, 6H, CH(CH_3)$_2$), 1.44 (2d merged together, 12H, CH(CH_3)$_2$), 1.39–1.37 (d, 6H, CH(CH_3)$_2$), 1.32–1.31 (d, 6H, CH(CH_3)$_2$), 1.17–1.16 (d (broad), 6H, CH(CH_3)$_2$), 1.13 (m, 4H, O-CH$_2$-CH_2), –1.06 (s, 6H, Al*Me*) ppm. ^{13}C {^{1}H} NMR(125.77 MHz, C_7D_8): δ 163.94, 158.96, 146.76, 146.46, 146.03, 144.21, 144.00, 142.47, 125.80, 125.60, 124.28, 123.67, 123.10, 122.47, 88.87, 73.00, 68.19, 28.44, 28.17, 27.92, 27.40, 26.98, 26.90, 26.49, 25.27, 25.06, 24.77, 24.41, 23.81, 23.44, 22.98, –11.86 ppm. IR (Nujol, cm^{-1}) : $\tilde{\nu}$ 3451, 3057, 1624, 1556, 1514, 1407, 1323, 1302, 1253, 1178, 1102, 1035, 934, 799, 775, 759, 721, 692, 650. MS (70 eV): *m*/*z* (%): 403 (100) [L$^+$-Me]. Anal. Calcd for $C_{68}H_{102}Al_2N_4O_4Sr_2$ (1268.76): C 64.37, H 8.10, N 4.42; Found: C 62.10, H 8.32, N 4.14.

10.4.17. Synthesis of Cp*$_2$Zr(Me)-O-SrN(SiMe$_3$)$_2$(thf)$_3$ (**17**)

A solution of Cp*$_2$Zr(Me)OH (0.394 g, 1 mmol) in *n*-hexane–THF was slowly added drop by drop to a stirred solution of Sr[N(SiMe$_3$)$_2$]$_2$·2thf (0.552g, 1 mmol) in *n*-hexane–THF (30 mL) at 0 °C. The reaction mixture was warmed to room temperature and was stirred for additional 2 days. After removal of all the volatiles, the residue was extracted with *n*-hexane-THF mixture (30 mL) and was concentrated. The solution was stored at –32 °C in a freezer for one day to obtain colorless crystals of **17**. Yield: (0.553 g, 0.645 mmol, 64.48 %). Mp: 283–285 °C. ^{1}H NMR (500 MHz, THF-d$_8$): δ 1.81 (s, 30H, Cp**Me*), -0.05 (s, 18H, (Si*Me$_3$*)$_2$), –0.89 (s, 3H, Zr-C*H$_3$*). ^{13}C NMR (125.77 MHz, THF-d$_8$): δ 113.08 (Cp*), 17.16 (Zr-*C*H$_3$), 11.39 (Cp*-*Me*), 5.36 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{39}H_{75}NO_4Si_2SrZr$, (M = 857.03): C 54.66, H 8.82, N 1.63. Found: C 50.83, H 8.29, N 1.60. The low value for carbon probably due to the high air-sensitivity of the compound and/or partial loss of coordinate thf molecule.

10.4.18. Synthesis of [LMg(μH)$_2$AlH(Me)]·thf (**18**)

A 1 M solution of AlH$_3$·NMe$_3$ in toluene (2 mL, 2.00 mmol) was added to a THF (40 mL) solution of LMgMe·thf (1.06 g, 2.00 mmol) at –40 °C. The solution was allowed to warm to room temperature and was stirred for 12 h. All volatiles were removed and the residue was dissolved in toluene. The solution was concentrated and stored at –5 °C in a freezer to obtain colorless crystals of compound **18**. Yield: (0.975 g, 1.74 mmol, 87.05%); Mp: 177-179 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.16–7.15 (m, 6 H, *m*-, *p*-Ar-*H*), 4.80 (s, 1H, γ-C*H*), 3.74 (m, 4H, O-C*H$_2$*-CH$_2$), 3.35 (br, 2H, Mg(μH)$_2$Al), 3.17 (sept, 4H, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, C*H$_3$*), 1.30–1.29

(d, 12H, CH(C*H*$_3$)$_2$), 1.26 (m, 4H, O-CH$_2$-C*H*$_2$), 1.22–1.20 (d, 12H, CH(C*H*$_3$)$_2$), –0.68, –0.69 (s, 3H, Al*Me*) ppm. ^{13}C {^{1}H} NMR(125.77 MHz, C$_6$D$_6$): δ 169.18, 145.70, 142.42, 125.53, 123.85, 95.05, 70.57, 28.40, 25.32, 25.09, 24.66, 24.44, –16.2 ppm. MS (70 eV): *m/z* (%): 202.1 (100) [DippNCCH$_3$]$^+$. Anal. Calcd for $C_{34}H_{55}AlMgN_2O$ (559.1): C 73.04, H 9.92, N 5.01. Found: C 72.40, H 9.95, N 5.07.

10.4.19. Synthesis of [LMg(μ-S$_2$)MgL]·2thf (**19**)

A toluene solution of [LMg(μH)$_2$AlH(Me)]·thf (**18**) (1.12 g, 2.00 mmol) was added to a suspension of sulfur (0.06 g, 2.00 mmol) in toluene at –40 °C. Then the solution was taken to room temperature and stirred for 1 day. Insoluble part was filtered off and the solution was concentrated. Yellow crystals of **19** were obtained by storing the solution at –32 °C in a freezer for 2 days. Yield: (0.11 g, 0.10 mmol, 10.1%); Mp: 239–241 °C (decomp). ^{1}H NMR (500.132 MHz, C$_6$D$_6$): δ 7.12–7.05 (m, 12H, *m*-, *p*-Ar-H), 4.79 (s, 2H, γ-C*H*), 3.66 (m, 8H, O-C*H*$_2$-CH$_2$), 3.14 (sept, 8H, C*H*(CH$_3$)$_2$), 1.66 (s, 12H, C*H*$_3$), 1.40 (m, 8H, O-CH$_2$-C*H*$_2$), 1.21–1.20 (d, 24H, CH(C*H*$_3$)$_2$), 1.11–1.10 (d, 24H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H}NMR (125.77 MHz, C$_6$D$_6$): δ 168.56, 146.01, 142.40, 129.28, 125.64, 124.69, 123.34, 94.29, 69. 35, 28.30, 25.48, 25.20, 24.64, 24.49 ppm. MS (70 eV): *m/z* (%): 946.6 (100) [M$^+$-2thf].

10.4.20. Synthesis of LAl(NH$_2$)Me (**20**)

Dry ammonia gas was passed through a solution of **8** (0.531g, 1 mmol) in toluene (20 mL) at room temperature under stirring and the gas stream of ammonia was disconnected after 15 min. The stirring again continued for half an hour and the excess ammonia was released through a mineral oil bubbler attached to the flask. All volatiles were removed in vacuum and the residue was extracted with *n*-pentane (20 mL) containing a little toluene. The solution was concentrated and kept at –32 °C for two day to get pale yellow crystals suitable for single crystal X-ray diffraction. Yield: (0.398 g, 0.837 mmol, 83.61%); Mp: 138–140 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 7.16–7.10 (m, 6H, Ar-*H*), 4.89 (s, 1H, γ-C*H*), 3.63 (sept, 2H, C*H*(CH$_3$)$_2$), 3.32 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.35–1.34 (2d, 12H, CH(C*H*$_3$)$_2$), 1.24–1.23 (d, 6H, CH(C*H*$_3$)$_2$), 1.10–1.08 (d, 6H, CH(C*H*$_3$)$_2$), –0.20 (brs, 2H, AlN*H*$_2$), –0.91 (s, 3H, Al-*Me*) ppm. ^{13}C{^{1}H}NMR (125.77 MHz, C$_6$D$_6$): δ 168.79, 145.30, 143.61, 141.16, 127.08, 124.81, 123.94, 96.82, 28.91, 28.10, 26.58, 24.95, 24.50, 24.17, 23.36, -13.33 ppm. EI-MS (70 eV): *m*/*z* (%):

461.3 (100) [M^+-CH_3+H], 475.3(5) [M^+]. Anal. Calcd for $C_{30}H_{46}AlN_3$ (475.69): C 75.75, H 9.75, N 8.83. Found: C 72.30, H, 9.56, N 6.05. Satisfactory elemental analysis data for the compound was not obtained due to its extreme air and moisture sensitivity.

10.4.21. Synthesis of LAl(OPh)Me (**21**)

A solution of phenol (0.094 g, 1 mmol) in toluene (10 mL) was added to a solution of **8** (0.531 g, 1 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 1 h and all volatiles were removed *in vacuo*. The remaining residue was extracted with *n*-hexane (25 mL). The solution was concentrated and stored at -32 °C in a freezer. Pale yellow crystals of **21** were formed after one day. Yield: (0.507 g, 0.917 mmol, 91.68 %); Mp: 128–130 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.25–7.21, 7.14–7.06, 6.88–6.82 (m, 6H, Ar-*H*), 5.14 (s, 1H, γ-C*H*), 3.32 (sept, 2H, C*H*(CH_3)$_2$), 3.21 (sept, 2H, C*H*(CH_3)$_2$), 1.55 (s, 6H, C*H*$_3$), 1.31–1.30 (d, 6H, CH(C*H*$_3$)$_2$), 1.11–1.10 (d, 6H, CH(C*H*$_3$)$_2$), 1.08–1.07 (d, 6H, CH(C*H*$_3$)$_2$), 1.02–1.01(d, 6H, CH(C*H*$_3$)$_2$), –0.69 (s, 3H, Al-*Me*) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 170.29, 159.25, 145.63, 143.30, 140.36, 129.18, 128.30, 127.52, 124.96, 124.07, 120.83, 118.00, 98.39, 28.90, 27.82, 25.43, 24.75, 24.38, 24.14, 23.35, –14.0 ppm. ^{27}Al{^{1}H} NMR (186.46 MHz): No resonances were observed. EI-MS (70 eV): *m*/*z* (%): 537.5 (100) [M^+-Me], 552.5 (3) [M]$^+$. Anal. Calcd for $C_{36}H_{49}AlN_2O$ (552.77): C 78.22, H 8.93, N 5.07. Found: C 77.29, H, 8.58, N 4.96.

10.4.22. Synthesis of L^{2}AlCl(Me) (**22**)

A toluene solution (20 mL) of Ph_2PCl (0.221 g, 1 mmol) was added to a cooled toluene (30 mL) solution (–60 °C) of L^{1}AlMe·thf (0.531, 1 mmol). After the addition was complete, the solution was raised to room temperature and stirred for 10 h. All volatiles were removed in vacuum and the residue was dissolved in *n*-hexane (20 mL). Concentration followed by keeping the solution at –5 °C for one day afforded pale yellow crystals of **22**. Yield: (0.634 g ,0.933 mmol, 93.3%); Mp: 169–170 °C. ^{1}H NMR (500.13 MHz, C_6D_6) δ 7.38–6.93 (several multiplets, 16H, Ar-*H*), 5.18–5.17 (d, 1H, γ-C*H*), 4.09 (sept, 1H, C*H*(CH_3)$_2$), 3.70 (sept, 1H, C*H*(CH_3)$_2$), 3.33 (sept, 1H, C*H*(CH_3)$_2$), 3.26 (sept, 1H, C*H*(CH_3)$_2$), 3.20–3.17 (d, 1H, NCC*H*$_2$), 3.01–2.98 (d, 1H, NCC*H*$_2$), 1.50–1.48 (d, 3H, CH(C*H*$_3$)$_2$), 1.46–1.45 (d, 3H, CH(C*H*$_3$)$_2$), 1.43 (s, 3H, C*H*$_3$), 1.30–1.26 (four doublets, 12H, CH(C*H*$_3$)$_2$), 1.12–1.10 (d, 3H, CH(C*H*$_3$)$_2$), 1.03–1.02 (d, 3H, CH(C*H*$_3$)$_2$), –0.59 (s, 3H, Al-*Me*) ppm; ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6) δ 171.19, 170.40, 170.30, 146.72, 145.92, 144.34, 143.01, 139.63, 139.26, 138.84, 138.82, 138.71, 133.48, 133.32, 133.02, 132.87, 129.12, 129.02, 128.95, 128.90, 128.79, 128.73, 125.44, 125.38, 124.53, 123.98, 100.09, 99.98, 36.63, 36.45, 29.22, 28.92, 28.47, 28.08, 27.59, 27.15, 25.36, 25.31, 25.16, 24.80, 24.66, 24.63, 24.23, 23.76, 23.36, –11.6 ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6) δ –15.18 ppm. EI-MS (70 eV): *m*/*z* (%): 663.3 (100) [M^+-Me], 678.4 (22) $[M]^+$. Anal. Calcd for $C_{42}H_{53}AlClN_2P$ (679.29): C 74.26, H 7.86, N 4.12. Found: C 74.04, H 8.34, N 4.18.

10.4.23. Synthesis of Eight-membered Aluminum Complex (**23**)

A toluene solution (15 mL) of **8** (0.531g, 1.0 mmol) was added to a solution of benzophenone (0.364 g, 2.0 mmol) in toluene (15 mL) at –60 °C. The solution was raised to room temperature and stirred for 12 h. The solvent from the flask was removed and the residue was dissolved in a mixture of toluene/*n*-hexane. On concentration and subsequently storing the solution at –32 °C in a freezer for one week gave colorless crystals of compound **23**. Yield: (0.706 g, 0.858 mmol, 85.74%); Mp: 244–246 °C. ^1H NMR (500 MHz, C_6D_6): δ 8.09–8.08, 7.54–7.52, 7.19–6.81 (m, 26H, Ar-*H*), 5.87 (s, 1H, γ-C*H*), 4.06–4.03 (d, 1H, NCCH_2), 3.96–3.94 (d, 1H, NCCH_2), 3.89 (sept, 1H, C*H*$(CH_3)_2$), 2.23 (2 sept, 2H, C*H*$(CH_3)_2$), 2.09 (s, 3H, CH(C$H_3)_2$), 1.57–1.56 (d, 3H, CH(C$H_3)_2$), 1.43 (sept, 1H, C*H*$(CH_3)_2$), 1.18–1.17 (d, 3H, CH(C$H_3)_2$), 1.16–1.15 (d , 3H, CH(C$H_3)_2$), 1.09–1.08 (d, 3H, CH(C$H_3)_2$), 1.01–1.00 (d, 3H, CH(C$H_3)_2$), 0.78–0.77 (d, 3H, CH(C$H_3)_2$), 0.76–0.75 (d, 3H, CH(C$H_3)_2$), 0.44–0.42 (d, 3H, CH(C$H_3)_2$), –0.31 (Al-*Me*) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ 190.96, 169.94, 155.34, 152.10, 150.08, 145.50, 142.08, 141.71, 138.84, 137.84, 137.48, 134.21, 130.24, 129.28, 128.51, 128.41, 127.53, 126.55, 126.28, 126.05, 125.64, 125.39, 125.27, 125.22, 124.61, 124.33, 123.83, 123.04, 122.52, 78.89, 78.45, 67.28, 45.05, 28.93, 27.91, 27.28, 26.05, 25.47, 25.36, 24.74, 23.84, 21.71, 21.37, 20.70, –13.62 ppm. ^{27}Al NMR (75 MHz, C_6D_6) : No resonance was observed. EI-MS (70 eV): *m*/*z* (%):822.5 (100) [M^+]. Anal. Calcd for $C_{56}H_{63}AlN_2O_2$ (823.09): C 81.72, H 7.71, N 3.40. Found: C 79.95, H 7.84, N 3.33.

10.4.24. Synthesis of Heterobimetallic Complex **24** Containing Aluminum and Germanium

A toluene solution (15 mL) of LGeCl (0.525 g, 1.0 mmol) was added to a solution of **8** (0.531g, 1.0 mmol) in toluene (15 mL) at –20 °C. The solution was raised to room temperature and stirred for 2 h. The solvent was removed and the residue was dissolved in a mixture of toluene/*n*-hexane

(0.25:1). On concentration and subsequently storing the solution at –32 °C gave red crystals of compound **24**. Yield: (0.856 g, 0.870 mmol, 86.9%); Mp: 206–209 °C.^{1}H NMR (500 MHz, C_6D_6, 323 K): δ 7.17–6.90 (m, 12H, Ar-*H*), 4.65 (s, 1H, γ-C*H*), 4.17 (s, 1H, γ-C*H*), 3.87 (sept, 1H, C*H*(CH_3)$_2$), 3.77 (sept, 1H, C*H*(CH_3)$_2$), 3.40 (2sept, 1H, C*H*(CH_3)$_2$), 3.30 (sept, 1H, C*H*(CH_3)$_2$), 3.18 (sept, 1H, C*H*(CH_3)$_2$), 3.06 (sept, 1H, C*H*(CH_3)$_2$), 2.39–2.37 (d, 1H, NCC*H$_2$*), 2.20–2.19 (d, 1H, NCC*H$_2$*), 1.48–1.47 (d, 3H, CH(C*H*$_3$)$_2$), 1.43–1.04 (48H, CH(C*H*$_3$)$_2$ and C*H*$_3$), 0.98–0.96 (d, 3H, CH(C*H*$_3$)$_2$), 0.62–0.61 (d, 3H, CH(C*H*$_3$)$_2$), –0.81 (s, 3H, Al-*Me*) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ 176.24, 167.36, 167.07, 166.62, 146.61, 145.90, 145.18, 145.00, 144.15, 143.88, 140.91, 140.79, 140.64, 139.90, 129.47, 129.28, 127.53, 127.42, 127.05, 127.01, 125.90, 125.55, 125.18, 125.00, 124.84, 123.91, 123.79, 123.56, 100.71, 96.49, 40.76, 29.42, 29.09, 28.74, 28.57, 28.19, 28.06, 27.97, 27.43, 27.10, 26.50, 26.26, 25.46, 25.37, 25.24, 25.06, 24.92, 24.87, 24.69, 24.50, 24.45, 24.24, 24.14, 23.77, 23.62, 23.54, 23.41, –11.02 ppm. ^{27}Al NMR (75 MHz, C_6D_6) : No resonance was observed. MS (70 eV): *m*/*z* (%):479.2 (100) [LAlCl]$^{+}$. Anal. Calcd for $C_{59}H_{84}AlClGeN_4$ (984.40): C 71.99, H 8.60, N 5.69. Found: C 71.26, H 8.91, N 5.55.

10.4.25. Synthesis of Heterobimetallic Complex **25** Containing Aluminum and Tin

Compound **25** was prepared by the same method as compound **24** with **8** (0.531 g, 1.00 mmol) and LSnCl (0.573 g, 1.00 mmol). Single crystals of **25** were obtained from a saturated solution of *n*-hexane at room temperature. Yield: (0.887 g, 0.861 mmol, 86.03%); Mp: 189–194 °C. ^{1}H NMR (500 MHz, C_6D_6, 323 K): δ 7.17–6.96 (m, 12H, Ar-*H*), 4.65 (s, 1H, γ-C*H*), 4.01 (s, 1H, γ-C*H*), 3.87 (sept, 1H, C*H*(CH_3)$_2$), 3.79 (sept, 1H, C*H*(CH_3)$_2$), 3.41 (sept, 1H, C*H*(CH_3)$_2$), 3.35 (4 sept, 4H, C*H*(CH_3)$_2$), 3.22 (sept, 1H, C*H*(CH_3)$_2$), 2.36–2.35 (d, 1H, NCC*H$_2$*), 1.87–1.85 (d, 1H, NCC*H$_2$*), 1.47 (s, 3H, C*H*$_3$), 1.46 (s, 3H, C*H*$_3$), 1.42–1.41 (d, 3H, CH(C*H*$_3$)$_2$), 1.39–1.38 (d, 3H, CH(C*H*$_3$)$_2$), 1.37–1.36 (d, 3H, CH(C*H*$_3$)$_2$), 1.27–1.23 (4d and s, 15H, CH(C*H*$_3$)$_2$ and C*H*$_3$), 1.15–1.13 (d, 3H, CH(C*H*$_3$)$_2$), 1.11–1.10 (d, 3H, CH(C*H*$_3$)$_2$), 1.07 (3d, 9H, CH(C*H*$_3$)$_2$), 1.013–1.006 (d, 3H, CH(C*H*$_3$)$_2$), 0.99–0.97 (d, 3H, CH(C*H*$_3$)$_2$), 0.86–0.85 (d, 3H, CH(C*H*$_3$)$_2$), –0.74 (s, 3H, Al-*Me*) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 298 K): δ 177.21, 167.23, 167.11, 166.61, 146.68, 146.29, 144.30, 144.24, 144.04, 143.64, 143.57, 142.40, 141.84, 140.71, 140.54, 127.53, 127.32, 127.09, 126.75, 125.72, 125.48, 125.08, 125.04, 124.84, 124.77, 124.03, 123.96, 123.77, 98.81, 96.82, 46.88, 29.24, 28.82, 28.74, 28.60, 28.53, 28.44, 28.01, 27.97, 27.23, 27.03, 26.53, 26.05, 25.34, 25.28, 25.25, 25.23, 25.01, 24.80, 24.72, 24.67, 24.60, 24.46, 24.35, 24.02, 23.94, 23.82, 23.72, 23.41, –11.1 ppm. ^{119}Sn NMR (75 MHz, C_6D_6, 298K) : δ 71.54 (s, Sn, L*Sn*). ^{27}Al NMR (75 MHz, C_6D_6, 298 K) : No resonance was observed. MS (70 eV): *m*/*z* (%): 479.2 (100) $[LAlCl]^+$. Anal. Calcd for $C_{59}H_{84}AlClN_4Sn$ (1030.47): C 68.77, H 8.22, N 5.44. Found: C 69.22, H 8.62, N 4.95.

10.4.26. Synthesis of Heterobimetallic Complex **26** Containing Aluminum and Bismuth

To a clear solution of **8** (0.531 g, 1.0 mmol) in toluene (15 mL) a toluene solution of $[1,8\text{-}C_{10}H_6(NSiMe_3)_2BiNMe_2]$ (0.553 g, 1.0 mmol) was added at –20 °C (15 mL) and solution was raised to room temperature and stirred for 1 h. The solution was removed under vacuum to get a reddish solid. The solid was washed with a minimum amount of *n*-pentane to obtain analytically pure compound **26**. Yield: (0.847 g, 0.837 mmol, 83.61%); Mp: 79–82 °C.^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.32-6.86 (m, 11H, Ar-*H*), 4.91 (s, 1H, γ-C*H*), 3.47 (sept, 1H, C*H*$(CH_3)_2$), 3.38 (sept, 1H, C*H*$(CH_3)_2$), 3.16 (sept, 1H, C*H*$(CH_3)_2$), 2.95 (sept, 1H, C*H*$(CH_3)_2$), 2.70 (s, 6H, AlN*Me*$_2$), 2.38-2.36 (d, 1H, NCC*H*$_2$), 1.83-1.82 (d, 1H, NCC*H*$_2$), 1.74 (s, 3H, C*H*$_3$), 1.38-1.37 (d, 3H, CH(C*H*$_3$)$_2$), 1.34 (2d, 6H, CH(C*H*$_3$)$_2$), 1.31-1.29 (d, 3H, CH(C*H*$_3$)$_2$), 1.22-1.21 (d, 3H, CH(C*H*$_3$)$_2$), 1.10-1.09 (d, 3H, CH(C*H*$_3$)$_2$), 0.92-0.91 (2d, 3H, CH(C*H*$_3$)$_2$), 0.64-0.63 (d, 3H, CH(C*H*$_3$)$_2$), 0.37 (s, 9H, NSi(C*H*$_3$)$_3$), 0.2 (s, 9H, NSi(C*H*$_3$)$_3$), -0.97 (s, 3H, Al-*Me*) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6, 298K): δ 169.82, 168.32, 148.41, 148.12, 145.67, 145.08, 144.98, 143.56, 141.22, 140.97, 138.24, 130.92,127.24, 127.14, 126.67, 126.57, 124.84, 124.72, 124.08, 123.95, 121.15, 120.85, 118.14, 116.08, 96.60, 63.35, 43.4, 28.81, 28.60, 28.14, 28.01, 26.56, 26.13, 26.01, 25.42, 24.86, 24.67, 24.63, 23.64, 23.60, 3.32, 3.07,-14.9 ppm. ^{29}Si NMR (75 MHz, C_6D_6, 298K) : δ 5.01 and 4.99 (s, 2Si, *Si*Me$_3$) ppm. ^{27}Al NMR (75 MHz, C_6D_6, 298K) : No resonance was observed. MS (70 eV): *m*/*z* (%): 996.5 (100) $[M^+\text{-}Me]$, 1011.5 (5) $[M]^+$. Anal. Calcd for $C_{48}H_{73}AlBiN_5Si_2$ (1012.26): C 56.95, H 7.27, N 6.92. Found: C 55.48, H 7.32, N 6.04.

10.4.27. Synthesis of Trimetallic Complex **27** Containing Aluminum and Zinc

A toluene solution of **8** (1.062 g, 2.0 mmol) was cooled to –40 °C and to this solution was added 0.5 equiv of $ZnMe_2$ (2 M solution in toluene) under stirring. The solution was warmed to room temperature and stirred for 12 h. The solvent was removed in vacuum and washed with a little amount of *n*-hexane. X-ray quality crystals were obtained when a concentrated solution of **27** in *n*-hexane-THF mixture was stored at -5 °C in a freezer. Yield: (0.834 g, 0.823 mmol, 82.33%); Mp: 162 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.15-7.07 (m, 12H, Ar-*H*), 5.09 (s, 2H, γ-C*H*), 3.48, 3.47 (2sept, 8H, C*H*(CH_3)$_2$), 1.68 (s, 6H, C*H*$_3$), 1.44 (s, 4H, NCC*H*$_2$), 1.35-1.34 (d, 12H, CH(C*H*$_3$)$_2$), 1.31-1.29 (d, 12H, CH(C*H*$_3$)$_2$), 1.19-1.18 (d, 24H, CH(C*H*$_3$)$_2$), -0.52 (s, 12H, Al-*Me*) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6, 298K): δ 177.17, 167.62, 144.76, 144.71, 142.48, 141.47, 126.92, 124.95, 124.43, 96.69, 28.77, 28.51, 28.28, 25.46, 25.44, 24.77, 23.59, -10.26 ppm. ^{27}Al NMR (75 MHz, C_6D_6, 298K) : Resonance was silent. MS (70 eV): *m*/*z* (%): 403 (100) [L$^+$-Me]. Anal. Calcd for $C_{62}H_{92}Al_2N_4Zn$ (1012.79): C 73.53; H 9.16, N 5.53; found: C 71.46, H 9.17, N 5.11. An attempt to acquire satisfactory elemental analysis data for the compound was not successful because of its air and moisture sensitivity.

Handling and Disposal of Solvents and Residual Wastes

1. The recovered solvents were condensed into a liquid nitrogen cold-trap under *vacuo* and collected in halogen-free or halogen-containing solvent containers, and stored for disposal.
2. Used NMR solvents were classified into halogen-free or halogen-containing solvents and disposed accordingly.
3. The acid-bath used for cleaning glassware collected in containers and stored for disposal.
4. The residue of the base-bath used for cleaning glassware was poured into a container for waste disposal.
5. Sodium metal used for drying solvents was collected and reacted carefully with *iso*-propanol and poured into the base-bath for cleaning glassware.
6. Ethanol and acetone used for low temperature reactions for cold-baths (with solid CO_2 or liquid N_2) were subsequently used for cleaning glassware.

Amounts of various types of disposable wastes generated during the work:

Halogen-containing solvent waste	5 L
Halogen-free solvent waste	16 L
Acid waste	12 L
Basic waste	20 L

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List of Scientific Contributions

Publications

1 "*A Reactivity Change of a Strontium Monohydroxide by Umpolung to an Acid*"; **Sankaranarayanapillai Sarish**, Sharanappa Nembenna, Selvarajan Nagendran, Herbert W. Roesky, Aritra Pal, Regine Herbst-Irmer, Arne Ringe, and Jörg Magull *Inorg. Chem.* **2008**, *47*, 5971–5977.

2 "*Well-Defined Hydrocarbon Soluble Strontium Fluoride and Chloride Complexes of Composition* $[LSr(thf)(\mu\text{-}F)_2Sr(thf)_2L]$ *and* $[LSr(thf)(\mu\text{-}Cl)_2Sr(thf)_2L]$"; **Sankaranarayana Pillai Sarish**, Herbert W. Roesky, Michael John, Arne Ringe and Jörg Magull *Chem. Commun.* **2009**, 2390–2392.

3 "*Addition of Dimethylaminobismuth to Aldehydes, Ketones, Alkenes, and Alkynes*"; Bijan Nekoueishahraki, **Sankaranarayana Pillai Sarish**, Herbert W. Roesky, Daniel Stern, Carola Schulzke, and Dietmar Stalke *Angew. Chem.* **2009**, *121*, 4587–4590; *Angew. Chem., Int. Ed.* **2009**, *48,* 4517–4520.

4 "*Facile Access of Well-Defined Stable Divalent Lead Compounds with Small Organic Substituents*"; Anukul Jana, **Sankaranarayana Pillai Sarish**, Herbert W. Roesky, Carola Schulzke, Alexander Döring and Michael John *Organometallics* **2009**, *28*, 2563–2567.

5 "*Synthesis and Characterization of Alkynyl Complexes of Groups 1 and 2*"; Andreas Stasch, **Sankaranarayana Pillai Sarish**, Herbert W. Roesky, Kathrin Meindl, Fabio Dall´Antonia, Thomas Schulz, and Dietmar Stalke *Chem. Asian J.* **2009**, *4*, 1451–1457.

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7 "*A Rational Design for an Efficient Synthesis of a Monomeric Tin(II) Hydroxide*"; Anukul Jana, **Sankaranarayana Pillai Sarish**, Herbert W. Roesky, Carola Schulzke and Prinson P. Samuel *Chem. Commun.*, **2010**, *46*, 707–709.

8 "*Heavier Alkaline Earth Metal Borohydride Complexes Stabilized by β-diketiminate Ligand";* **Sankaranarayana Pillai Sarish,** Anukul Jana, Herbert W. Roesky, Thomas Schulz, Michael John, and Dietmar Stalke *Inorg. Chem.* **2010**, *49*, 3816–3820.

9 "*A [I-Ca-I-Ca-I-Ca-I]*$^{2+}$ *Chain Stabilized by Two Chelating β-Diketiminate Ligands*"; **Sankaranarayana Pillai Sarish**, Anukul Jana, Herbert W. Roesky, Thomas Schulz, and Dietmar Stalke *Organometallics* ***2010**, 29,* 2901–2903.

10 "*A New Entry into Aluminum Chemistry:* L^1*AlMe·thf, a Versatile Building Block for Bimetallic and Polymetallic Complexes*" **Sankaranarayana Pillai Sarish,** Bijan Nekoueishahraki, Anukul Jana, Herbert W. Roesky, Thomas Schulz, and Dietmar Stalke *Chem. Eur. J.* **2010**, Manuscript submitted.

Lebenslauf

Name	Sarish Sankaranarayana Pillai
Geboren	4th May 1980 in Cheppad
Staatsangehörigkeit	indisch

Schulbesuch

1985 – 1994	Primary School (Class I-IX)
1994 – 1995	Secondary School Examinations (Class X)

Studium

1995 – 1997	Pre-Degree, University of Kerala, Kerala, Indien
1997 – 2000	B. Sc. in Chemie, University of Kerala, Kerala, Indien
2000 – 2002	M. Sc. in Chemie, University of Kerala, Kerala, Indien
2003 – 2005	M. Tech. in Industrial Catalysis, Cochin University of Science and Technology, Kochi, Indien

Promotion

2006 April – present Experimentelle Promotionsarbeit im Institut für

Anorganische Chemie Göttingen unter der Leitung

von Prof. Dr. Dr. h.c. mult. H. W. Roesky

Ph.D. Thesis "*β*−Diketiminate Ligands as Supports for Alkaline Earth and Aluminum Complexes: Synthesis, Characterization, and Reactivity Studies"