Bulky Guanidinate Ligand Stabilized Main Group Metal Complexes: Synthesis, Characterization and Reactivity Studies

By

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STATEMENT BY AUTHOR

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Milan Kr. Barman

DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

Milan Kr Barman

List of Publications

1. Baishya, A.; **Barman, M. K**.; Peddarao, T.; Nembenna, S, Catalytic C-N bond formation in guanylation reaction by N-heterocyclic carbene supported magnesium(II) and Zn(II) amide complexes. ***J. Organomet. Chem***. **2014,** *769*, 112-118.

2. **Barman, M. K**.; Baishya, A.; Peddarao, T.; Nembenna, S., Guanidinate stabilized germanium(II) and tin(II) amide complexes and their catalytic activity for aryl isocyanate cyclization. ***J. Organomet. Chem.*** **2014,** *772–773*, 265-270.

3. **Barman, M. K.**; Baishya, A.; Nembenna, S., Bulky guanidinate stabilized homoleptic magnesium, calcium and zinc complexes and their catalytic activity in the Tishchenko reaction. ***J. Organomet. Chem.*** **2015,** *785*, 52-60.

4. Baishya, A.; Peddarao, T.; **Barman, M. K.**; Nembenna, S., Catalyst free C–N bond formation by the reaction of amines with diimides: Bulky guanidines. ***New J. Chem.*** **2015,** *39*, 7503-7510.

5. **Barman, M. K.**; Nembenna, S., Mixed guanidinato-amido Ge(IV) and Sn(IV) complexes with Ge=E (E = S, Se) double bond and SnS_4, Sn_2Se_2 rings. ***RSC Adv.***, **2016,** *6*, 338-345.

6. **Barman M. K**.; Sinha, A. K; Nembenna, S., An efficient and recyclable thiourea supported copper(I) chloride catalyst for azide-alkyne cycloaddition reactions. ***Green Chem.*** **2016,** *18*, 2534-2541.

7. Baishya, A.; Kumar. L.; **Barman, M. K.**; Peddarao, T.; Nembenna, S., Air stable N-heterocyclic carbene-carbodiimide (NHC-CDI) adducts: Bulky amidinates. ***Chemistry Select,*** **2016,** *3*, 498-503.

8. Peddarao, T.; Baishya, A.; **Barman, M. K.**; Kumar, A.; Nembenna, S., Metal-free access of bulky N, N'-diarylcarbodiimides and their reduction: Bulky N, N'-diarylformamidines, ***New. J. Chem.***, **2016**, *40*, 7627-7636.

9. Jakhar, V. K.‡, **Barman, M. K.**‡, Nembenna, S. "Alminium mono hydride catalysed selective Hydroboration of carbonyl compounds" ***Org. lett.*** **2016**, *18*, 4710−4713. (‡ equal contribution)

Manuscripts submitted or in preparation

10. **Barman, M. K.**, A. Baishya; Nembenna, S., 'Guanidinato calcium and zinc amide complexes as catalysts for the intramolecular hydroamination reactions' *Manuscript submitted.*

11. **Barman, M. K.**, Nembenna, S. 'Magnesium amides as pre-catalysts for the chemoselective hydroboration of ester' *Manuscript submitted.*

12. **Barman, M. K.**, Peddarao, T., Nembenna, S. 'Guanidinato stabilized aluminum amides as efficient homogeneous catalysts for Tishchenko reaction' *Manuscript in preparation.*

13. **Barman, M. K.**, Baishya, A., Nembenna, S. 'Bis(guanidinate) supported Group 14 metallynes (LML) and their oxidative additions with chalcogens' *Manuscript in preparation.*

14. **Barman, M. K.**, S. Nembenna, "Heterobimetallic (Group1/2) mixed metal amides bearing bridging amido and *N,N'*-chelated guanidinate ligand" *Manuscript under preparation.*

Conferences

1. 'Symposium in Chemistry', **Chemical Research Society of India (CRSI-2011**), Attended in **NISER,** Bhubaneswar (02-06 February, 2011).
2. Attended the '**Indo-Europian Symposium** on ***Inorganic and catalysis'*** in **NISER** Bhubaneswar (12-16 February, 2012).
3. Presented poster in **Indo-French Symposium** on '***Functional Metal-Organics: Applications in Materials and Catalysis'*** in **NISER** Bhubaneswar (24-26 February, 2014).
4. Attended the Symposium on '***Supramolecular chemistry'*** in **KIIT** Bhubaneswar (12-16 February, 2014).

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Dedicated to my eldest brother

Late Sri Tapan Seth……

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Synopsis

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1. Name of the Student: **Milan Kr. Barman**

2. Name of the Constituent Institution: **National Institute of Science Education and Research (NISER)**
   1. Enrolment No. : **CHEM07201004014**

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The general formula of guanidines is $R_1–N=C(NR_2R_3)NR_4R_5$, in which the carbon atom of the N_3C functional Group is connected to one imino and two amino nitrogen atoms. In 1970, Lappert and co-workers reported the first transition metal guanidinate complex. Since then, a large number of guanidinate supported coordination complexes involving metals from across the periodic table have been described. In recent years, the chemistry of guanidinate stabilized low valent and/or low oxidation state metal complexes with metal-metal (single or multiple bonded) or metal with non-bonded electrons or both is the emerging area. To isolate such unusual molecules the utilization of bulky guanidine ligand systems are very important, because these can provide steric and/or electronic protection from processes such as disproportionation,

oligomerization etc.

Main Group metal complexes bearing guanidinate ligands is less developed in comparison to transition metal chemistry. Although, there have been some bench mark inventions, most importantly, bulky guanidinate supported low oxidation state magnesium(I) complex with Mg-Mg bond and Ga(I) heterocycle bearing bulky guanidine ligand.

In this regard, various main Group metal complexes have been synthesized bearing bulky guanidinate ligands. Accordingly, this thesis describes synthesis, structural and spectroscopic characterization of main Group metal complexes and their reactivity studies towards catalytic transformations such as Tishchenko reaction, hydroamination reaction, and hydroboration of ester, cyclotrimerization reaction and oxidative additions with chalcogens.

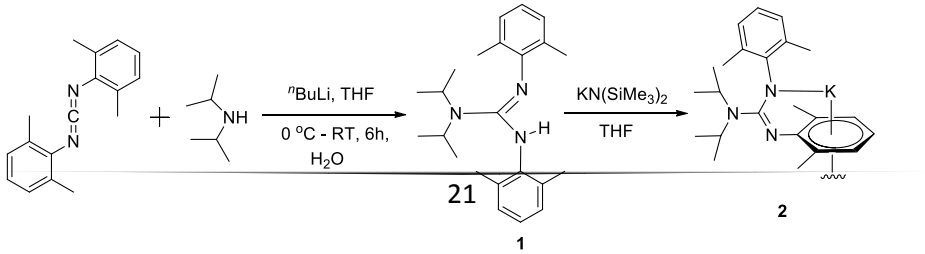
Chapter 1 General Introduction

Chapter 1 describes a brief introduction to the chemistry that is related to the work carried out throughout the thesis. This chapter comprises a concise description about the synthesis of different bulky guanidine ligand and bonding modes etc. Next, a summary of literature review of low oxidation state complexes containing main Group metal ions. Finally, the scope and objective of the work carried out in this thesis are presented.

Chapter 2: This chapter has been divided into two parts.

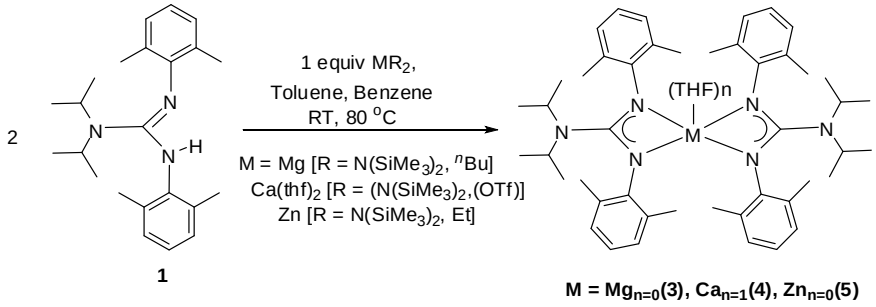
<u>Part A:</u> Bulky guanidinate stabilized homoleptic magnesium, calcium and zinc complexes and their catalytic activity in the Tishchenko reaction

This part describes synthesis of guanidinate ligand L^1H (**1**) [L = {ArNC (N^iPr_2)NAr} (Ar = 2,6-Me_2-C_6H_3)}] which reacts with potassium bis(trimethylsilyl)amide forms potassium salt of the ligand$(LK)_n$(**2**) (Scheme 1).

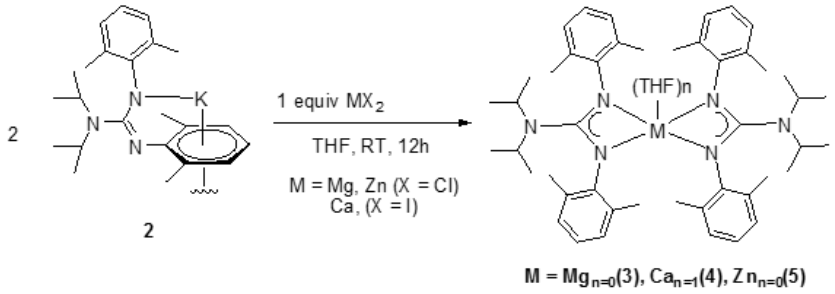


Scheme 1: Synthesis of bulky guanidine LH and its potassium salt LK

Next, i) a) Direct addition of one equivalent of metal amide [M{N(SiMe$_3$)$_2$}$_2$] (M = Mg, Ca(thf)$_2$ and Zn) to LH (two equiv), subsequent release of two equivalents NH(SiMe$_3$)$_2$ and afforded homoleptic complexes b) Deprotonation of LH (two equiv) upon treatment with magnesium/zinc dialkyls(one equiv) *viz.* ^{n}Bu$_2$Mg/Et$_2$Zn, evolution of butane/ethane gas and formation homoleptic magnesium and zinc complexes (Scheme 2). And also, LCaL(**4a**) was obtained by the deprotonation of LH (two equiv) upon treatment with Ca(OTf)$_2$ at 100 ^{o}C for 2 d in C$_6$D$_6$ in J Young valve NMR tube. ii) Easy deprotonation of LH by treating with metal amide *i.e.* KN(SiMe$_3$)$_2$ led to the formation of LK, *in situ* generated two equivalents of LK and subsequent treatment with one equivalent of metal dihalide MX$_2$ (M = Mg, Ca, Zn; X = Cl or I) led to the formation of LM(thf)L complexes (Scheme 2 & 3).

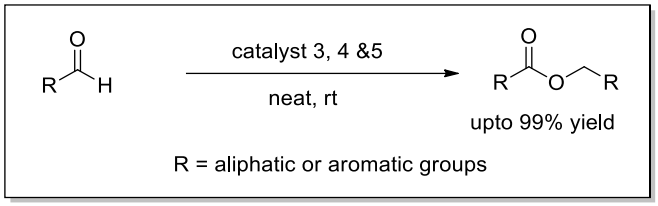


Scheme 2. Syntheses of **3-5**; by metalation of neutral guanidine (LH) with MR$_2$



Scheme 3. Syntheses of **3-5**; by salt metathesis reaction between LK and MX_2

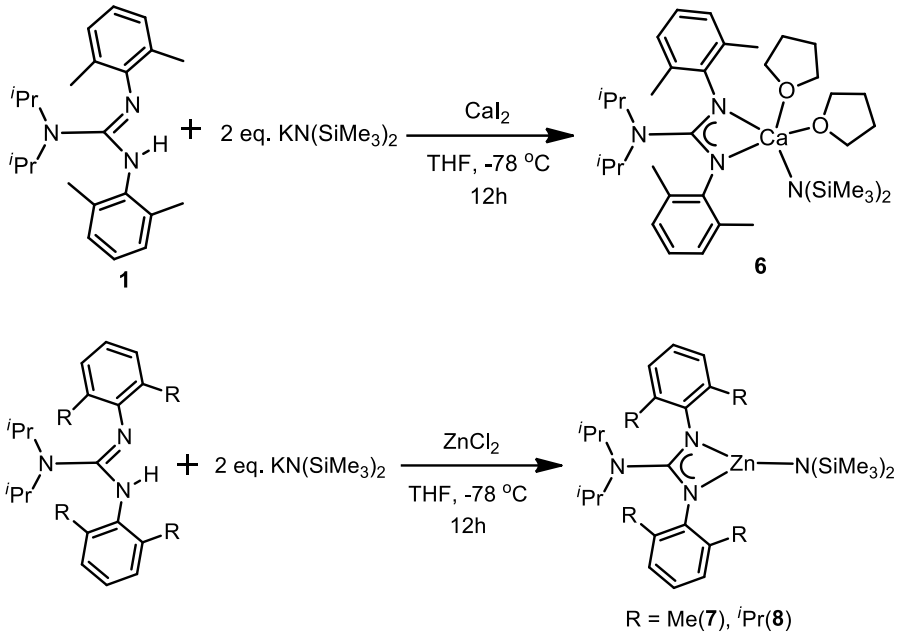
Finally, three homoleptic complexes $Mg[^{i}Pr_2NC\{N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]_2$, $Ca[^{i}Pr_2NC\{N\text{-}2,6\text{-}Me_2C_6H_3\}_2]_2(THF)$, $Zn[^{i}Pr_2NC\{N\text{-}2,6\text{-}Me_2C_6H_3\}_2]_2$ were used as catalysts for dimerization of aldehydes to form the corresponding symmetric esters, or Tishchenko reaction (or Claisen-Tishchenko reaction) (Scheme 4).



Scheme 4: Dimerization of various aldehyde to corresponding ester.

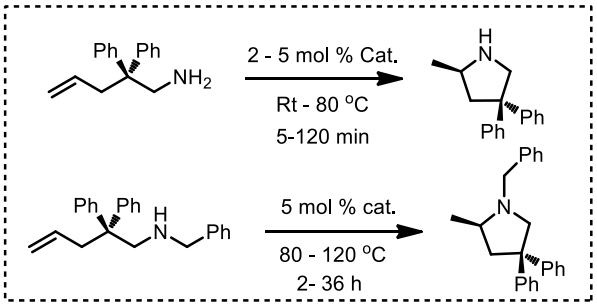
<u>Part B:</u> Guanidinato calcium and zinc amide complexes as catalysts for the intramolecular Hydroamination

This part presents synthesis of guanidinate ligand stabilized heteroleptic calcium and zinc amide complexes $\{[ArNC(N^{i}Pr_2)NAr]CaN(SiMe_3)_2(THF)_2\}$ [Ar=2,6- Me_2-C_6H_3(**6**)], $\{[ArNC(N^{i}Pr_2)NAr]ZnN(SiMe_3)_2\}$ [Ar=2,6- Me_2-C_6H_3(**7**) and Ar = 2,6- $^{i}Pr_2$-C_6H_3(**8**)]. LH was treated with 2 equiv. of $KN(SiMe_3)_2$ and formation of LK, *in situ* generated LK and subsequent treatment with one equivalent of metal dihalide MX_2 (M=Ca, X= I_2; M= Zn, X =Cl) at -78 ^{o}C led to the formation of $LMN(SiMe_3)_2(thf)_n$ (M = Ca(**6**), n=2; Zn(**7** & **8**), n=0) complexes (Scheme 5).



Scheme 5: Synthesis of guanidinato calcium(top) and zinc(bottom) amide complexes

These heteroleptic calcium and zinc amide complexes have shown excellent catalytic activity towards intramolecular hydroamination reaction for both primary and secondary amines (Scheme 6).



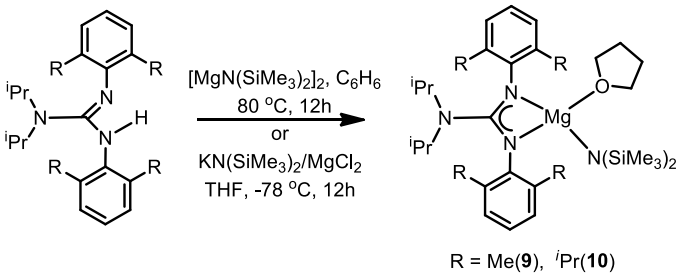
Scheme 6: Hydroamination reactions for primary and secondary amines utilising calcium and zinc amide catalysts

Chapter 3 has been divided into two parts

<u>Part A:</u> Guanidinato magnesium amide complexes as catalyst for hydroboration of Ester

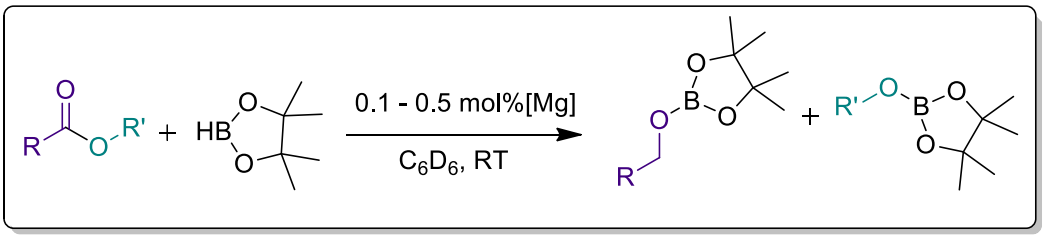
This part reveals heteroleptic magnesium amide complexes supported by guanidinate ligand

{[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)$_2$}[Ar=2,6- Me$_2$-C$_6$H$_3$(**9**) and Ar = 2,6- iPr$_2$-C$_6$H$_3$(**10**)] synthesized by direct addition of one equivalent of metal bis(amide) [Mg{N(SiMe$_3$)$_2$}$_2$] to L^{1}H (one equiv), subsequent release of one equivalent of NH(SiMe$_3$)$_2$ and afforded heteroleptic complexes **9** & **10** or deprotonation of LH by treating with metal amide *i.e.* KN(SiMe$_3$)$_2$ led to the formation of LK, *in situ* generated LK and subsequent treatment with one equivalent of metal dihalide MgCl$_2$ led to the formation of LMgN(SiMe$_3$)$_2$ (thf) complexes (Scheme 7).



Scheme 7: Synthesis of {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)}[Ar=2,6- Me$_2$-C$_6$H$_3$(**9**) and Ar = 2,6- ^{i}Pr$_2$-C$_6$H$_3$(**10**)]

Guanidinate ligand stabilized magnesium amide complexes used as pre-catalyst (0.1 – 0.5 mol %) with excellent catalytic activity under solvent free conditions (Scheme 8).

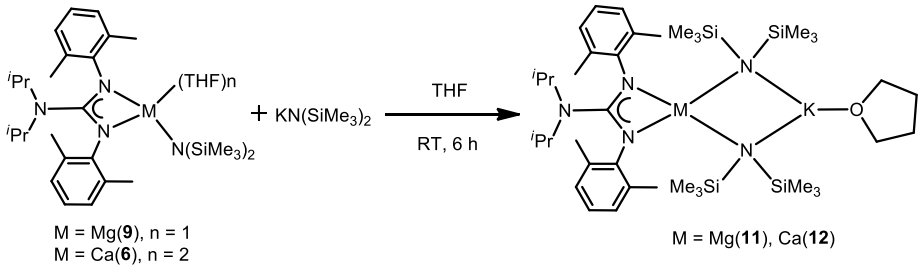


Scheme 8: Magnesium amide catalysed hydroboration of ester

<u>Part B:</u> Heterobimetallic (Group1/2) systems bearing bridging amido and *N,N'*-chelated guanidinate ligand

In this section guanidinate stabilized Group1/2 mixed dimetal amides have been discussed. The metals are magnesium, potassium {[ArNC(N^{i}Pr$_2$)NAr]Mg{N(SiMe$_3$)$_2$}$_2$K(THF)}(**11**) and calcium, potassium {[ArNC(N^{i}Pr$_2$)NAr]Ca{N(SiMe$_3$)$_2$}$_2$K(THF)}(**12**). Mixed metal amides are

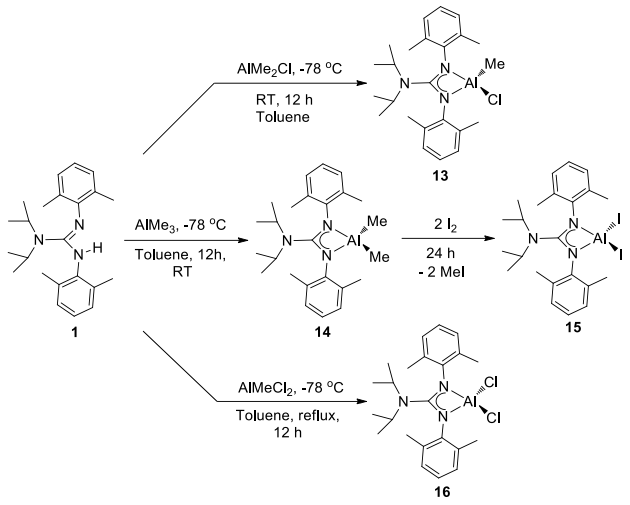
synthesized by guanidinato magnesium and calcium amides {[ArNC(N^iPr_2)NAr]MN($SiMe_3$)$_2$($THF)_n$} [Ar=2,6- Me_2-C_6H_3] (M = Mg(**9**), n = 1, M = Ca (**6**), n = 2) with one equivalent of potassium bisamide *i.e.* KN($SiMe_3$)$_2$ in THF at room temperature (Scheme 9). All the compounds were characterized by multi nuclear NMR and X-ray studies.



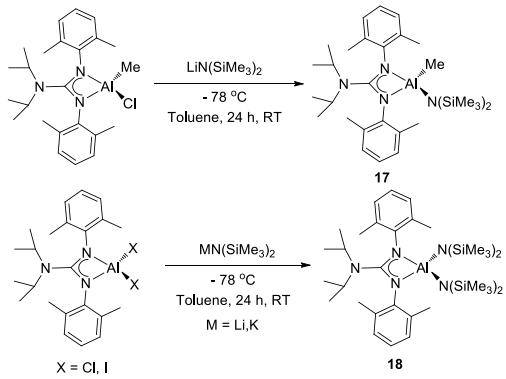
Scheme 9: Synthesis mixed metal complexes

<u>Chapter 4:</u> Guanidinato stabilized aluminum amides as efficient homogeneous catalysts for Tishchenko reaction

Chapter 4 Reaction of neutral guanidinate ligand with $AlMe_3$, $AlMeCl_2$ and $AlMe_2Cl$ evolution of methane gas and formation of L^1AlMe_2, $L^1AlMeCl$ and L^1AlCl_2 [L^1 = {ArNC (N^iPr_2) NAr}(Ar = 2,6- $^iPr_2$-C_6H_3)}]. Further, treatment of L^1AlMe_2 with molecular iodine (I_2) led to the formation of L^1AlI_2 (See Scheme 10). Again reaction with one equivalent of $L^1AlMeCl$ with one equivalent of lithium amide *i.e.* LiN($SiMe_3$)$_2$ led to the formation of $L^1AlN(SiMe_3)_2$ and reaction with L^1AlI_2 with two equivalent of potassium amide *i.e.* KN($SiMe_3$)$_2$ formation of $L^1Al\{N(SiMe_3)_2\}_2$(Scheme 11). Both compounds $L^1AlN(SiMe_3)_2$ and $L^1Al\{N(SiMe_3)_2\}_2$ show good to excellent catalytic activity for dimerization of aldehyde i.e. Tishchenko reaction in neat condition at 80 ^oC with 2 mol% catalyst.



Scheme 10: Synthesis of Guanidinate stabilized Aluminium halide complexes



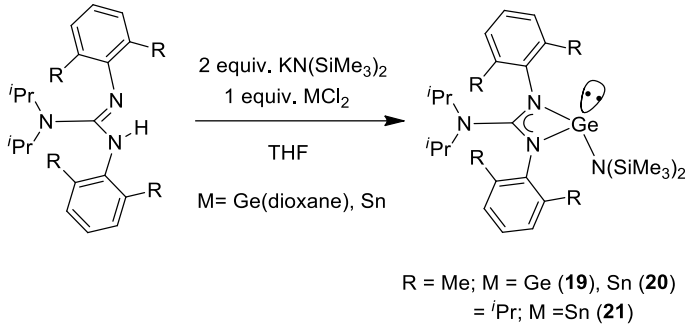
Scheme 11: Synthesis of guanidinate aluminium amide complexes.

Chapter 5 has been divided into two parts

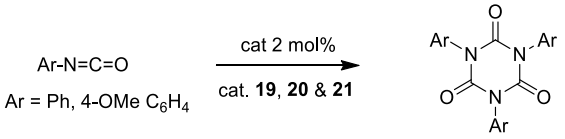
<u>Part A:</u> Guanidinate stabilized germanium(II) and tin(II) amide complexes and their catalytic activity for aryl isocyanate cyclization

This part presents bulky guanidinate supported low valent germanium (II) and tin (II) amide complexes. Reaction of one equivalent of free bulky guanidine either L^1H or L^2H with two equivalents of potassium hexamethyldisilazide *i.e.,* $KN(SiMe_3)_2$ in tetrahydrofuran at 0 ^oC and followed by metathesis reaction with one equivalent of metal dihalide of germanium(dioxane) or tin in THF at 0 ^oC led to the formation of corresponding guanidinate supported metal amides

(Scheme 12). Furthermore, we have shown these are effective catalysts for the cyclotrimerization of arylisocyanates.



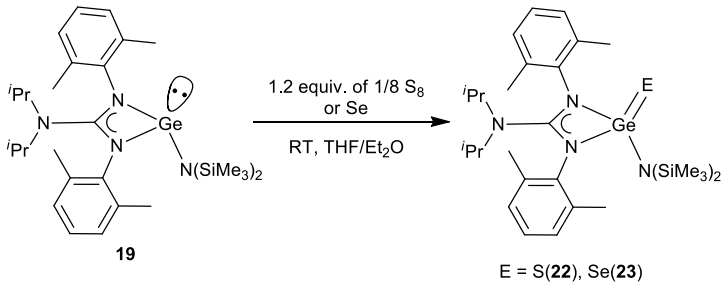
Scheme 12: Synthesis of guanidinate supported germanium and tin amides



Scheme 13: Compounds **19-21** catalyzed cyclotrimerization of arylisocyanates

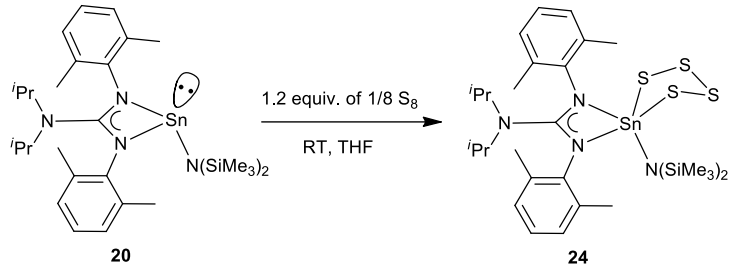
<u>Part B:</u> Mixed guanidinato-amido Ge(IV) and Sn(IV) complexes with Ge=E (E = S, Se) double bond and SnS_4, Sn_2Se_2 rings

Part B deals with the reactivity studies of guanidinate supported germanium and tin amides with chalcogens. Reaction with elemental sulphur and selenium with germanium amide formation of guanidinate supported germathioamide [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)]; (Ar = 2,6– Me$_2$–C$_6$H$_3$) (**22**) and germaselanoamide [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(Se)](**23**) (Scheme 14)



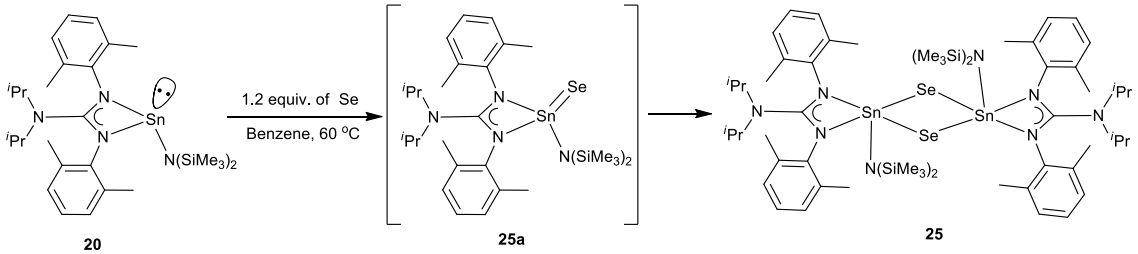
Scheme 14: Synthesis of germathioamide and germaselanoamide

Reaction of guanidinate tin amide with elemental sulphur led to the formation of guanidinato cyclic tetrasulfido tin [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S$_4$)](**24**) complex (Scheme 15).



Scheme 15: Synthesis of guanidinato tetrasulfido complex.

Furthermore, dimeric bridged seleno tin [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–Se)}$_2$](**25**) was synthesized from guanidinato tin amide and selenium powder at 60 ^{o}C in benzene (Scheme 16).

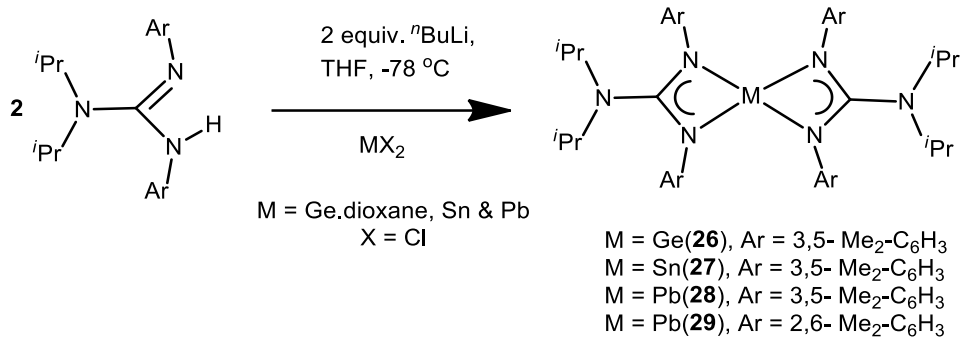


Scheme 16: Synthesis of dimeric bridged seleno complex

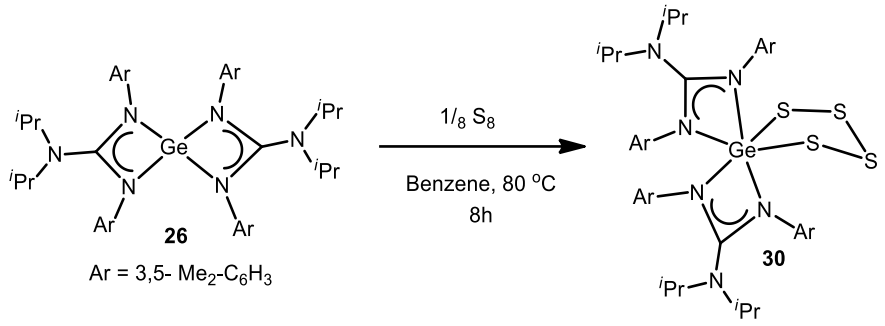
<u>Chapter 6:</u> Bis(guanidinate) supported Group 14 metallynes (LML) and their oxidative additions with chalcogens

Chapter 6 contains guanidinato homoleptic Group 14 complexes and their reactivity towards chalcogens. Homoleptic Ge(II), Sn(II) and Pb(II) complexes are prepared by employing salt elimination reactions from two equivalent of guanidinate lithium salt and one equivalent of Gecl$_2$.dioxane, SnCl$_2$ and PbCl$_2$, respectively in THF at room temperature (Scheme 17). Guanidinato Germenium (IV) and Tin (IV) complexes were synthesized; the reactions were performed in benzene solvent at 80 ^{o}C through an oxidative addition (Scheme 18, 19 & 20). Driving force of the reaction is oxidation state changes from M(II) to stable oxidation state

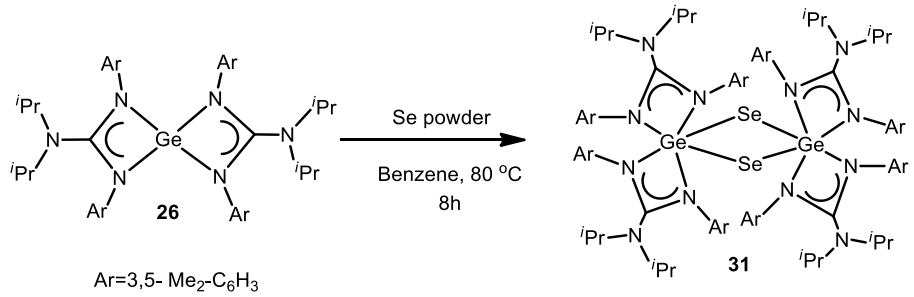
M(IV)(M = Ge and Sn).



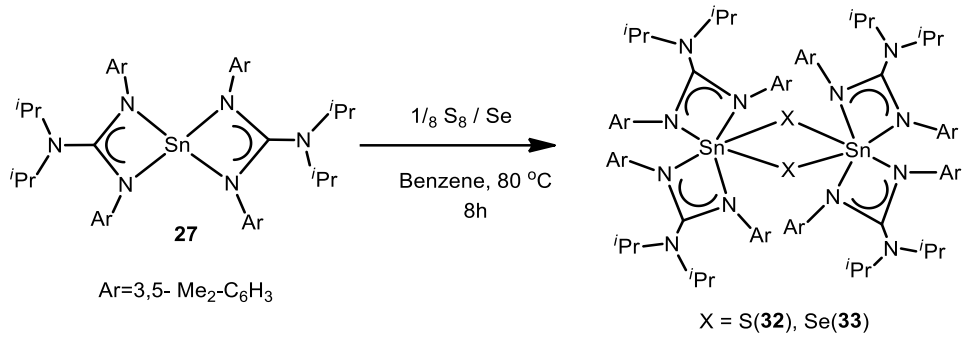
Scheme 17: Synthesis of LML[M= Ge(II), Sn(II) & Pb(II)]



Scheme 18: Synthesis of homoleptic germanium tetrasulfido complex



Scheme 19: Synthesis of $(\mu\text{–Se})_2[L^1GeL^1]_2$



Scheme 20: Synthesis of $(\mu\text{–E})_2[L^1SnL^1]_2$(E = S/Se)

Summary: A wide range of s – and p- block and zinc complexes bearing bulky guanidinate ligands have been synthesised and structurally characterized. Further, reactivity studies of these complexes with chalcogens or applications as catalysts in organic transformations have been elucidated.

List of Abbreviations

δ	chemical shift
λ	wavelength
μ	bridging
av.	average
C	Celsius
calcd.	Calculated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopetadienyl
EI	electron impact ionization
equiv.	Equivalents
TON	Turn over number
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
XRD	X-ray diffraction
$CDCl_3$	Chloroform-d
C_6D_6	Benzene-d_6
ppm	parts per million
q	quartet
R	organic substituents
s	singlet
d	doublet
dd	doublet of doublet
t	triplet
sept	septet
m	multiplet
br	broad
THF	tetrahydrofuran
L^1	{ArNC (N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3)
L^2	{ArNC (N^iPr_2)NAr} (Ar = 2,6- $^iPr_2$-C_6H_3)
L^3	{ArNC (N^iPr_2)NAr} (Ar = 3,5- Me_2-C_6H_3)

Introduction

This unit of the thesis gives the background and a brief overview of the area in a different sections of the present work.

1.1. Guanidinate ligands

After one hundred and fifty-three years the synthesis of the first guanine[1], guanidine are still considered to be amongst the most attractive structure for organic and inorganic chemists. The general formula of guanidines is R_1–N=C(NR_2R_3)NR_4R_5

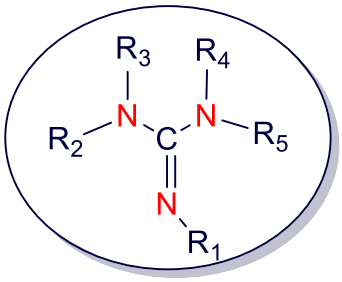


Figure 1.1. General formula for substituted guanidine.

Guanidines are compounds containing N_3C core, in which central sp^2 hybridized carbon atom is connected to one imino Group and two amino Groups. The Y-shaped CN3 functional Group i.e. demanded to be responsible for the stability of its cationic (guanidinium) and anionic (guanidinate) derivatives[2]. The main advantage of the guanidinate ligand is that they can allow almost countless variation in the substitution pattern. This made guanidinate ligand rival or even better in their versatility than the cyclopentadienyls. This, combined with the easy accessibility of this ligand surely made tremendous popularity in recent years. The design of new guanidinate ligands follows different paths depending on the envisaged purpose (new structures, catalytic activity, and volatility).

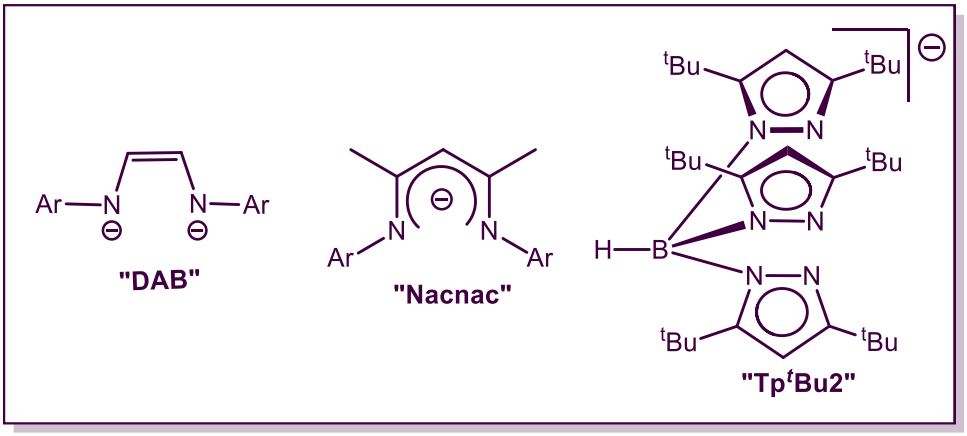


Figure 1.2. Some commonly used bulky ligands.

A wide variety of bulky monodentate, bidentate and higher denticity ligands have been developed. These can provide steric, electronic protection from oxidation, disproportionation, hydrolysis and oligomerization. In Figure 1.2 presents some of the most common ligands that have been successfully employed. These are the dianionic diazabutadiene (DAB), diketaminate(Nacnac) in which N-centers are substituted with 2, 6-diisopropylphenyl substituent. To prepare stable five and six membered heterocycles these ligands have been used by many research groups. The most important heterocycles are Group 13 elements in the +1 oxidation state, viz. [:M(DAB)])]− (M=B[3] or Ga[4]) and [:M(Nacnac)] (M=Al[5], Ga[6], In[7] or Tl[8]). These low oxidation state Groups 13 metal complexes metal center possess a singlet lone pair of electron which are the analogues of the immensely important N-heterocyclic carbene(NHC) class of ligand. Therefore, the coordination chemistry and reactivity of the metallacycles have been widely explored.[9]

Among the bidentate anionic ligand systems are listed in Figure 1.3 Amidinates and guanidinates are the most easily accessible ligand systems in the series.

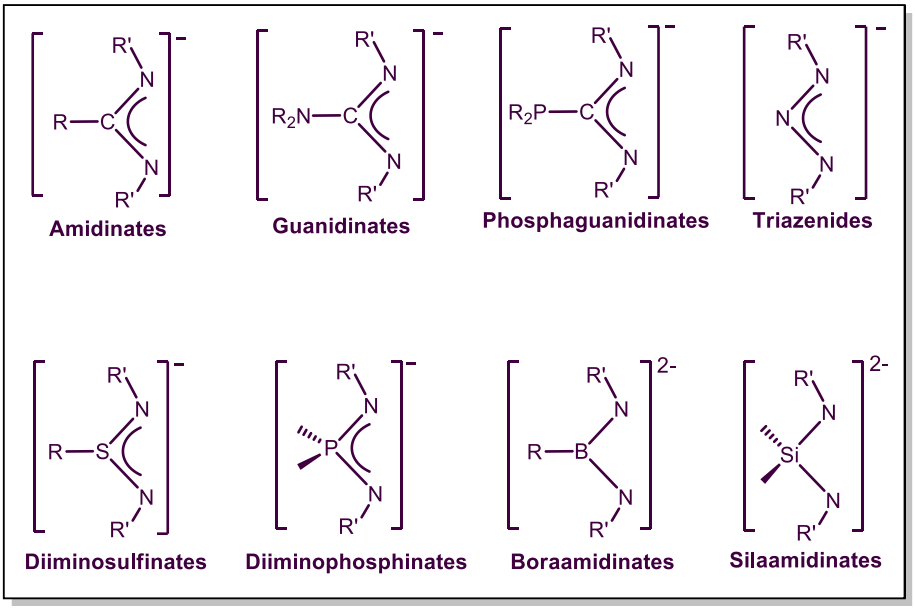


Figure 1.3. Different bidentate ligand systems[27b]

The general formula of guanidinate anion is $[(RN)_2CNR'_2]^-$ (R, R' = alkyl, aryl, silyl etc.) which is closely related to the amidinates $[(RN)_2CR']^-$. In 1970, Lappert and co-workers reported the first transition metal guanidinate complex.[10] Since then, a large number of guanidinate supported coordination complexes involving metals from across the periodic table have been described. Where the guanidinate have displayed various coordination modes, but two most common modes are *N*,*N'*-chelating and bridging mode. The bite angles of N–M–N of chelating guanidinate ligands are generally acute *ca*. 65°[11]. The bridging coordination mode is generally happen for transition metal complexes, e.g. the metal metal bonded paddlewheel or lantern compounds established by the Cotton Group[12]. Bridging mode coordination also can occur for p- block elements[11]. The reason behind this is the close to parallel alignment of the N-lone pairs in guanidinate ligands. In contrast, the use of bulky substituent's at N-centers can cause the ligand N-lone pairs to converge, thereby enforcing *N*,*N'*-chelation of metal centers.

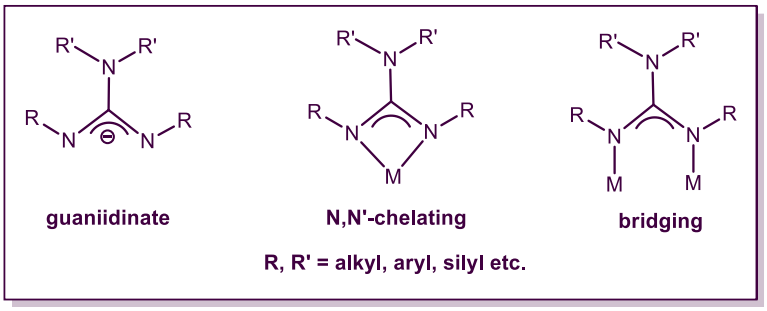


Figure1.4. Common bridging mode anionic guanidinates

Accordingly, in the literature several research Group utilized amidinate ligand to access low oxidation state metallacycles, but related guanidinate appear to be more stabilizing compared with amidininate ligand. The reasons are bulky amino substituents of the backbone C-centers of guanidinates can be more easily incorporated than the alkyl or aryl C-substituents of amidinates. This enriches the ability to chelate metal centers of guanidinate relative to amidinates. And also guanidinates have three possible resonance forms (Figure 1.5) one of which does not occur for amidinates. The resonance structure of two coordinating N-centers have formal negative charges, which makes guanidinates more electron rich compare to amidinates.

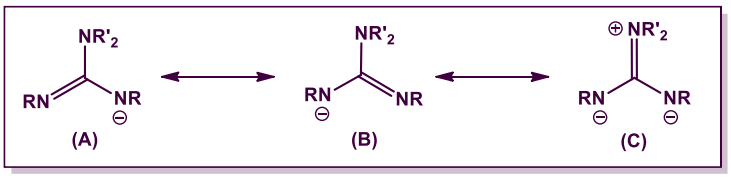


Figure 1.5. Different resonance forms of guanidinate anions

Guanidine contains strong basic properties and it is considered as an organic super base with amine basicity due to resonance stabilization of its conjugated acids.[2, 13] In fact, guanidines are stronger base compare to the other nitrogen based compounds such as amines, diamines, pyridines, pyrroles and amidines. Moreover, some biguanidine derivatives are more basic than the classical 'Proton Sponge'[14].

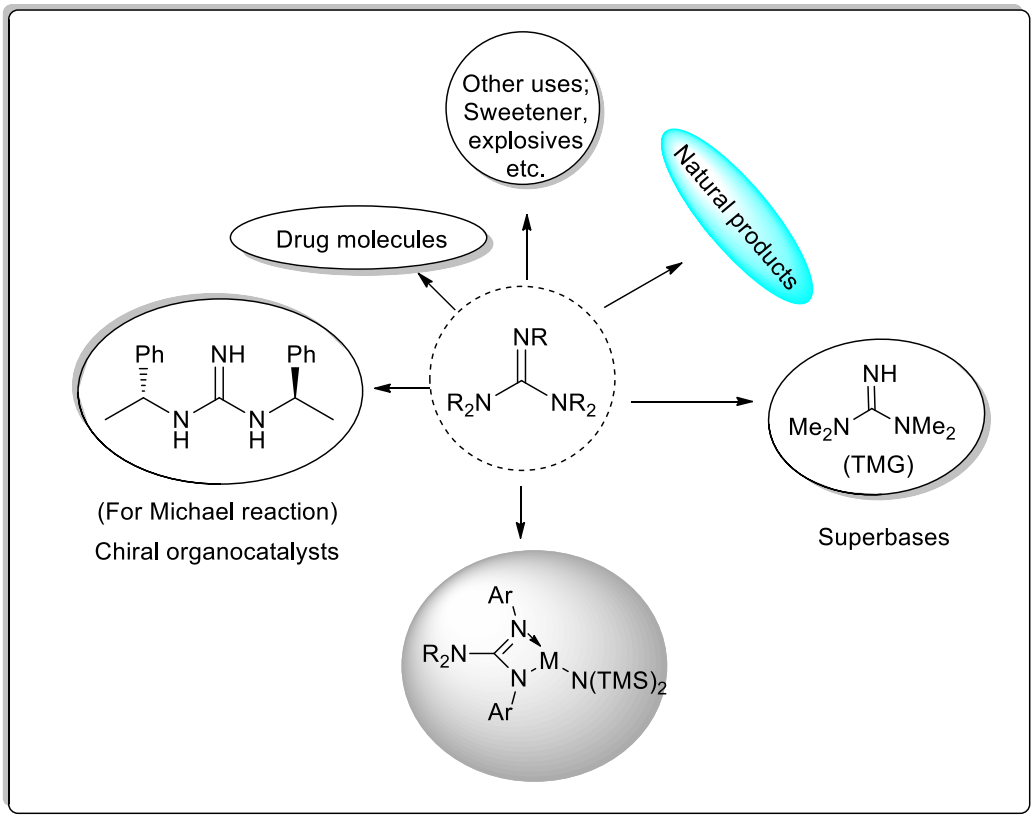


Figure 1.6. Examples of guanidines as fragments.[1b]

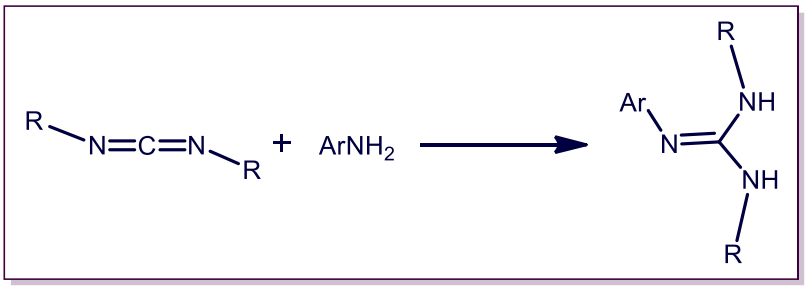
A wide variety of chiral guanidine compounds has been used as asymmetric catalyst for various reactions.[15] The guanidine moiety is an important substructure in many molecules with biological importance such as arginine, creatine phosphates, and purines.[16] Furthermore many natural products directly isolated from terrestrial, marine and freshwater microorganisms, marine and terrestrial invertebrates, marine sponges, and higher plants with prominent pharmacological and biological activities are also based on these entities.[17] Long years ago guanidine containing drugs were shown to have pharmaceutical properties.[18] In fact some of the guanidine containing drugs is top selling pharmaceuticals.

In 2006 Coles specified to summarize the role of guanidine ligand in coordination chemistry *i.e.* 'Guanidine framework constitutes a versatile ligand-set for use in coordination chemistry.'[19] The physical and chemical properties of this ligand make them very useful anionic N-donor ligand in coordination chemistry.[11,20] Bearing this mono anionic and

bidentate guanidine ligand various metal complexes have been synthesized throughout the periodic table.

1.2. Guanidine Synthesis

Several synthetic methods have been reported for the preparation of guanidines[9e]. Guanidines are generally synthesized via the reaction of an amine compound with a suitable electrophilic guanylating reagent. Various guanylating reagents, including thioureas, isothiourea, amidine sulfonic acids, cyanamides, carbodiimides, trifyl guanidines and carboximidamide are developed in order to obtain guanidine efficiently (Figure 1.7)[21]. Out of these procedures mentioned above the most efficient and atom economical way to synthesize guanidine is from carbodiimides i.e. Direct guanylation of amine with symmetrical and unsymmetrical carbodiimides (Scheme 1.1).



Scheme 1.1. Addition of amine to carbodiimides

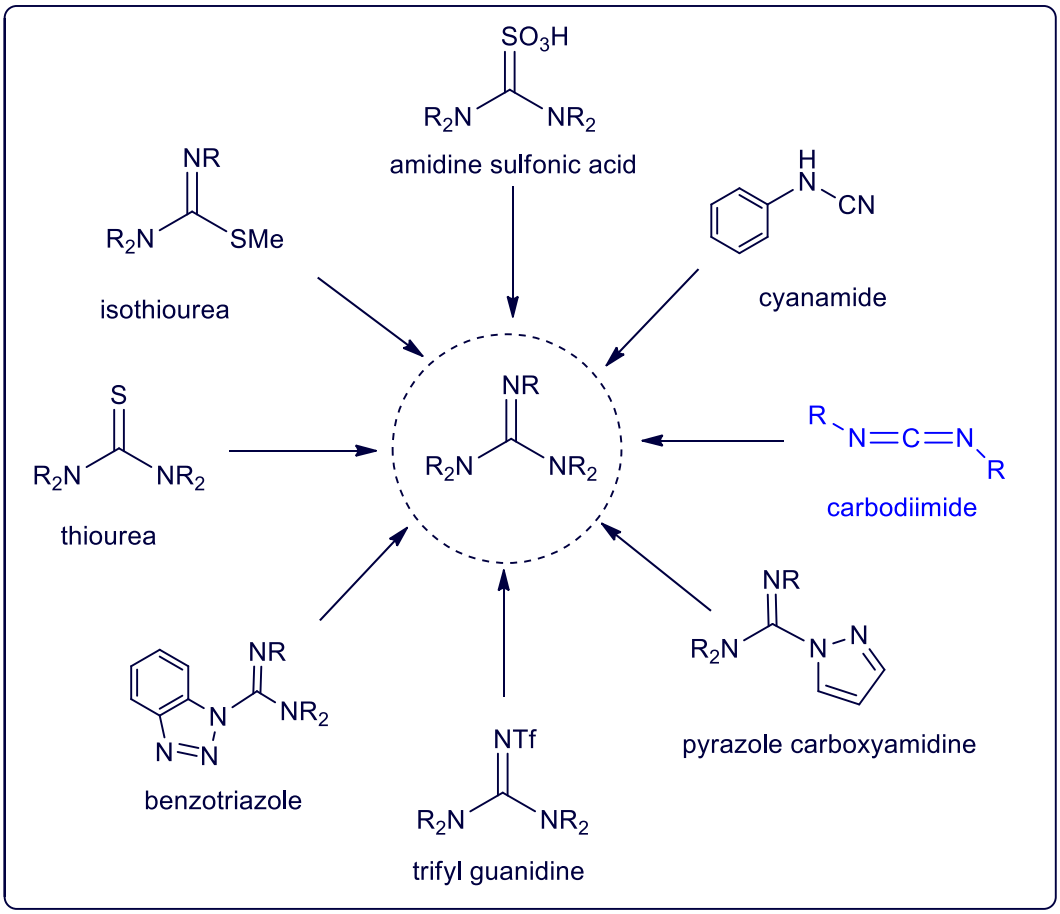


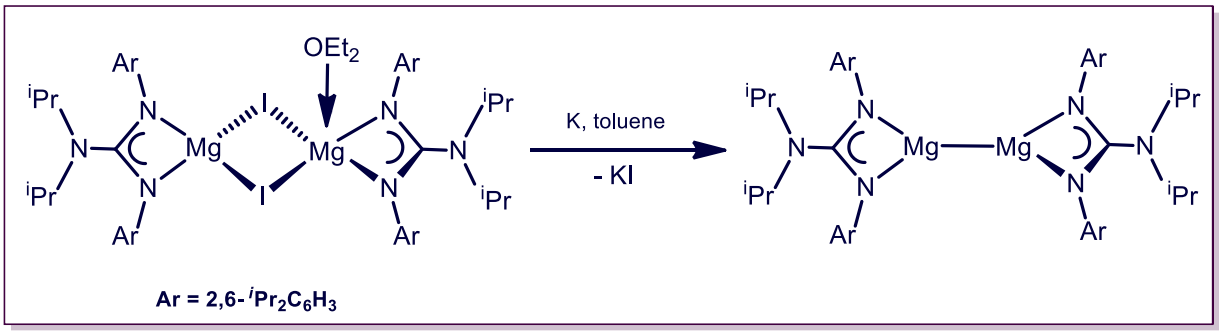
Figure 1.7. Classical guanidine synthesis

Under harsh reaction condition aliphatic amines undergo this reaction gives moderate yield[22]. But less nucleophilic aromatic amines do not react even after heating also. Thus, catalytic procedure for the synthesis of guanidines from the diverse library of amines and carbodiimides appeared in the literature. The first catalytically synthesis of guanidines with good yield from aromatic amines was reported by Richeson et al. in 2003[23]. Many metal (Transition, Lanthanide, actinide and main group) catalysed gunylation reactions were reported in literature[24]. In this regard in our lab we have developed NHC stabilized Mg and Zn complexes and used as excellent catalyst for C-N bond formation reaction[25]. But surprisingly there was no report on catalyst free C-N bond formation reaction. By taking advantage of bulky aromatic carbodiimide i.e. electrophilic C- center compare to aliphatic carbodiimide reacts with amine and formation of guanidine with good to excellent yield[26].

1.3. Coordination chemistry with guanidine ligand

1.3.1 Group 2

In 1970 Lappert and co-workers reported the first guanidinate stabilized transition metal complex.[10] Since then, various guanidinate stabilized coordination complexes involving metals from across the periodic table have been documented.[11, 19, 27] Despite the major research interest in main group and transition metal guanidinates, only a handful of guanidinate supported homoleptic magnesium, calcium and zinc complexes have been reported, which are stabilized by less bulky guanidinate ligand.[28] Few examples of sterically encumbered (bulky) guanidinate[29] supported alkaline earth metal complexes have been reported in the literature; most importantly low oxidation state magnesium(I) complex with Mg–Mg bond.[30]



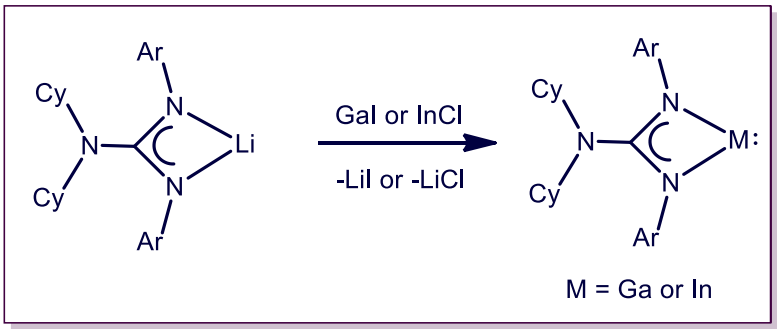
Scheme 1.2. Synthesis of magnesium (I) compounds with Mg-Mg bond

Recently, Westerhausen and co-workers reported the structurally characterized bulky guanidinate supported homoleptic and heteroleptic heavier alkaline earth metal complexes.[31] Very recently, Fortier and co-workers reported the "super bulky" guanidinates of alkali metals,[32] however, no reports on alkaline earth metal guanidinates.

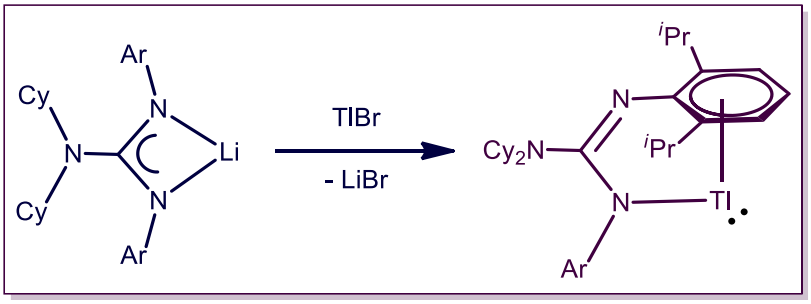
1.3.2. Group 13

The coordination chemistry of Group 13 element complexes are widely established. The most studied compounds are the diyls :MR (M= Group 13 element, R = bulky alkyl, aryl, C_5Me_5 –

etc. Currently the chemistry related with Group 13 metal(I) heterocycles is rapidly emerging. *β*-Diketaminate ligand stabilized six membered neutral heterocycles [:M(Nacnac)] (M=Al[5], Ga[6], In[7] or Tl[8]) and DAB stabilized five membered anionic heterocycles which are valence isoelectronic analouges of the typical N-heterocyclic carbene (NHC) class of ligand.



Scheme 1.3. Synthesis of Ga(I) and In(I) heterocycles



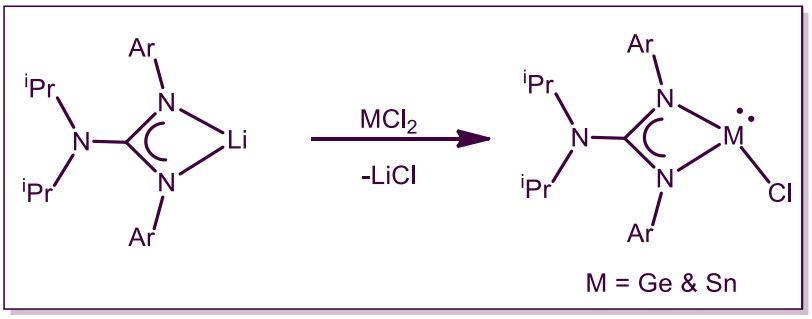
Scheme 1.4. Synthesis of Tl(I) heterocycles

Same research group have been isolated low valent four membered Ga(I) heterocycle using same bulky guanidinate ligand.[33] Which are also the typical N- heterocyclic carbene (NHC) class of ligand. The gallium heterocycle has considered as an anionic gallium and its nucleophilicity is revealed that it has formed complexes with more than 40 s-, p-, d-, and f-block elements.[9f, 34]

1.3.3. Group 14

The chemistry of amidinato Group 14 complexes in both the +2 and +4 oxidation states is well established and has been reviewed.[11] Surprisingly, only a handful examples of Group 14 complexes incorporating guanidinate ligands have been reported.[35] The earlier demonstrated that the properties of bulky Ar-substituted guanidinates suggested that Group 14 metal(I) complexes might be accessible *via* the reduction of compounds of the type, [(guanidinate)$M^{II}X$] (M= Group 14 element; X= halide). Very recently, Tracke and co-workers succeeded to synthesize the first donor-stabilized silylenes that contain guanidinato ligand.[36] Germylenes, stannylenes, and plumbylenes with guanidinato ligands have already been synthesized, starting from suitable germanium(II), tin(II), or lead(II) precursors.[29, 37]

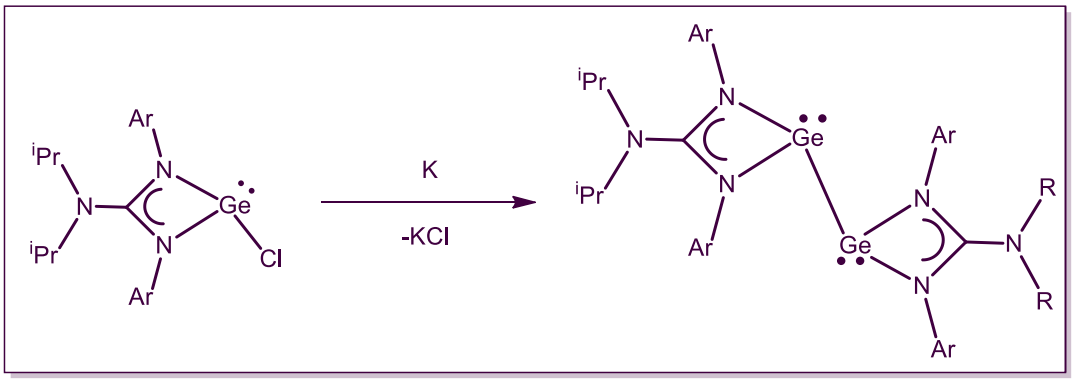
A series of guanidinato Group 14 halides have been synthesized by salt elimination reactions (Scheme 1.5).[37c-f] In the solid state structure all the Ge(II) and Sn(II) complexes are monomeric in nature, whereas the lead(II) species are dimeric through weak chloride bridges.[37e] In contrast, the more sterically hindered lead *β*-diketiminatecomplexes, [(Nacnac)$Pb^{II}X$], are monomeric.[38]



Scheme 1.5. guanidinato Group 14 halides

Very recently, Jones and co-workers have been reported guanidinate stabilized Ge(I) complex containing Ge-Ge bond[39] with non-bonded electrons at each metal center. Reductions of

LGeCl with potassium mirror in toluene at room temperature over 3–4 hours afforded deeply coloured solutions of the germanium(I)dimers (Scheme 1.6)[29].

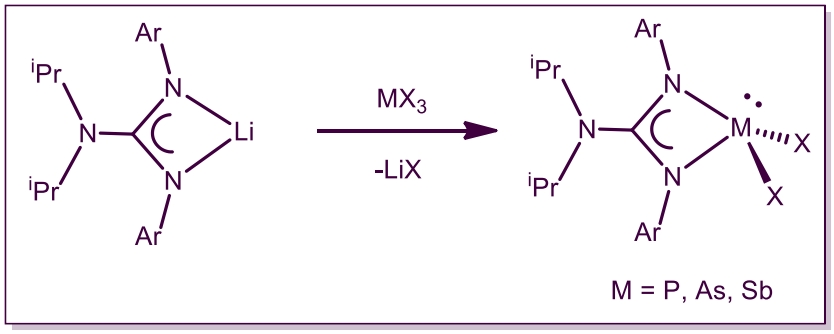


Scheme 1.6. Guanidinate stabilized Ge(I) complex containing Ge-Ge bond

On the other hand, the chemistry of the related amidinate and *β*-diketiminate supported low valent and/or low oxidation of main Group metal complexes is well documented.[40]

1.3.4. Group 15

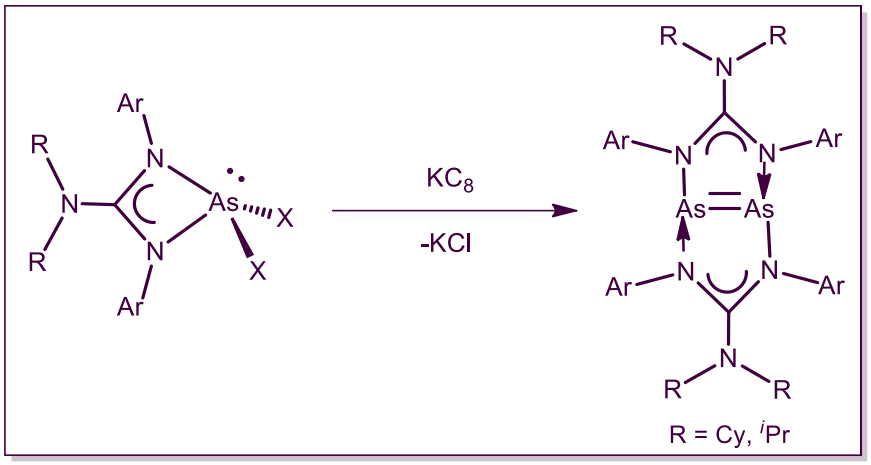
The coordination chemistry of Group 15 metals with guanidinato and amidinato ligand is not well developed as those of Groups 13 and 14.[11, 27a] Additionally, prior to the development of bulky Aryl substituted guanidinate ligands, there were no reports of such complexes with the Group 15 element in the +1 oxidation state. Different +3 oxidation state precursors to guanidinate dipnictenes have been synthesized (Scheme1.7).[41]



Scheme 1.7. Synthesis of Group 15 metal (III) precursors

Using the P, As and Sb complexes have been treated with KC_8. For the phosphorus complexes, mixtures of many P-containing products were obtained. Deposition of antimony

metal for the reduction of the Sb complexes, while reduction of the As-complexes formation of the first examples of base stabilized amidodiarsenes.[42] Only *β*−diketiminato complex to contain a Group 15 element center in the +1 oxidation state, *viz.* $[(\eta^1\text{-N-L})_2As–As=As(\eta^2\text{-N,N'-L})]$ (L = $[(ArNCH)_2CPh]-$), was successively prepared by the reduction of $[LAsI_2]$ with KC_8 **(**Scheme 1.8). [43]



Scheme 1.8. Synthesis of As(I) complex

1. 4. Reactivity Studies

1.4.1 Catalysis

Generally organometallic chemistry is considered the important for homogeneous catalysis, Although it is century old, but still today a very dynamic discipline.[44] We have seen two Nobel prizes related to organometallics and its application in catalysis (2001: Knowles, Noyori, and Sharpless; 2005: Chauvin, Grubbs, and Schrock).

Importantly, transition metal chemistry forms the heart of catalysis. Due to the availability of d-orbitals, this allows for the changes in the metal's oxidation states, helps in many catalytic cycles. The transition metal chemistry are also responsible for activation of a large variety of bonds, containing H-H, C=O, C=C, and C≡C. Transition metals having partially filled d-orbitals, is not a requirement for catalytic transformations. Transition metal with d^0 – orbital are among the most active transition metal catalysts,[45] and also lanthanide metal chemistry

has made an significant contribution to the catalysis field.[46] Later, procedures are controlled by metal Lewis-acidity, ligand-basicity, steric and electronic factors, rather than by redox processes and/or orbital overlap.

For its catalytic potential main group organometallic chemistry has never been recognised. The limited examples are mainly Lewis-acidic catalysis with late main group elements such as Al, B, or Sn.[46d] The basic features of the early main group metal complexes (Group 1 and 2), however, are not much utilised and are only opening to gain momentum. Early main group metal complexes behave like typical organolanthanide-like. For example, σ-bond metathesis reaction and addition to saturated bonds. As these reactions are also the basis for lanthanide catalysis, so, it is not surprising that this class of compounds can also be used in catalytic transformations.

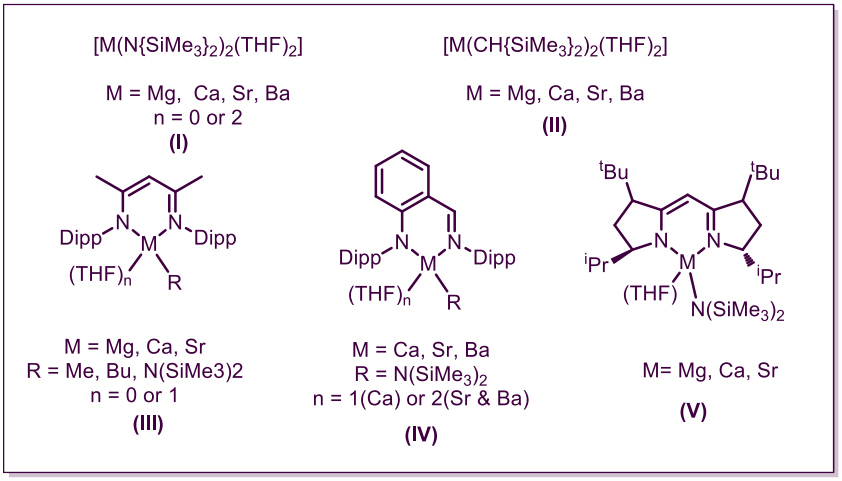
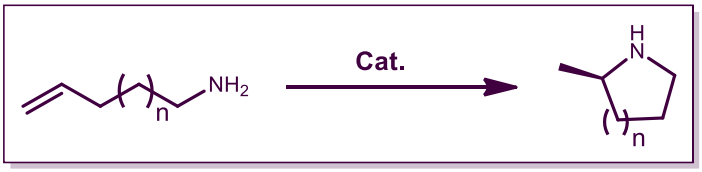


Figure 1.8. Different pre-catalyst exploited in Group 2 mediated catalysis.

Well-known ligands and their Group 2 complex related to this work are summarized in figure 1.8. Different ligand stabilized homoleptic Group 2 pre-catalysts including those bulky amides [47, 48] and alkyls.[49]

Hill and co-workers reported alkaline earth amides as catalyst for Tishchenko reaction[50]. Related Coles and their group demonstrated bicyclic guanidine stabilized magnesium amide complexes and used as a precatalyst for Tishchenko reaction[51].

Group 2 mediated Lewis acid catalysis undergone a significant interest in the different organic transformation such as ring opening polymerization of cyclic esters such as γ-caprolactone and rac-lactide.[52] In most of the recent advances the use of alkaline earth compounds in molecular catalysis have been derived from the perspective that the d^0 valence electronic configuration of a M^{2+} centre will render it some level of 'lanthanide mimetic' character. The reactivity of alkaline earth metal amides and alkyls with alcohols, pyrroles, alkynes, phosphines and C–H acidic heterocycles has been revealed to formation of alkoxide,[53] pyrrolide,[54] acetylide,[55] phosphide[56] and carbanion[57] fragments. First example of Group 2 mediated molecular catalysis for intramolecular hydroamination of aminoalkenes and -alkynes (Scheme 1.9).[58]



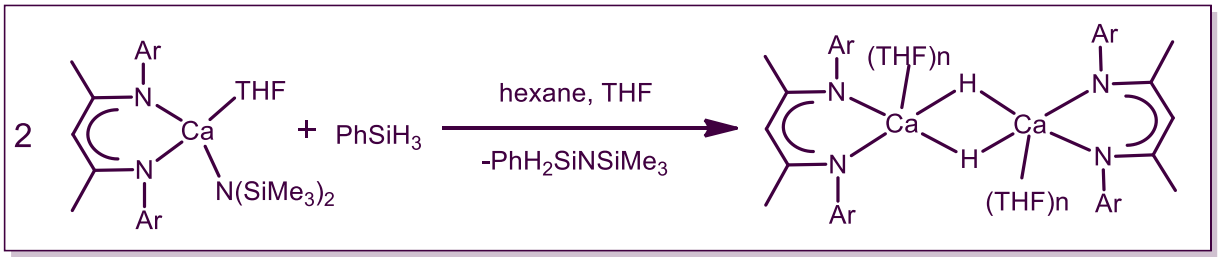
Scheme 1.9. Group 2 catalysed hydroamination of aminoalkenes[47]

Although initial reports are *β*-diketaminate ligand stabilized calcium amide complex(1f), this reactivity was found in different Group 2 metal complexes in wider range including III,[59] I, and II.[59d,60] Mechanistic investigation has been employed by Hill and co-workers for both homoleptic Group 2 bis(amides) I, II along with the *β* -diketiminato ligated magnesium, calcium and strontium pre-catalysts III (See figure 1.8).

Wide range of nitrogen containing five membered or six membered heterocycles was obtained from the reaction with quantitative yield under mild reaction condition. Seven membered rings also isolated but only with specific catalyst and moderate yield.

Kinetic analysis between diketaminate Mg and Ca amide complexes (see figure 1.8), indicated a difference of the rate of reaction of the Group 2 metal centre. Calcium-catalysed intramolecular hydroamination was comparatively faster than magnesium.

Initial rate of the reactions done with the Group 2 bis(amides), and di-*n*-butylmagnesium appealed a rate dependence was in the order Sr > Ca >> Ba > Mg. So the extremely slow rate of conversion by both barium and magnesium pre-catalysts, due to the inability of the diffuse barium centre to sufficiently polarise the C=C bond and due to the reduced polarising ability of the far less polar Mg–N bond respectively.



Scheme 1.10. Synthesis of *β*-diketiminato calcium hydride.

For the Extension of this Group 2 catalysed heterofunctionalisation chemistry for the hydrogenation, hydrosilylation and hydroboration reaction people have focused on the isolation of metal hydrides. In recently there has been significant progress on the isolation of magnesium and calcium hydride species. These studies were started by Harder's group and they report of a *β*-diketiminate-supported calcium hydride complex (Scheme 1.10**)**.[61] Subsequently Jones and co-workers reported a variety of similar *β*-diketiminate-supported magnesium hydrides,[62] Using phenylsilane, bond metathesis route produce a variety of higher hydrides reported by the groups of Hill,[63] Harder[64] and Okuda.[65] Okuda and co-workers

shows using homoleptic calcium silyl, $[Ca(SiPh_3)_2(THF)_4]$, hydrosilylation of α-phenyl- and α-methylstyrene with triphenylsilane.[66]

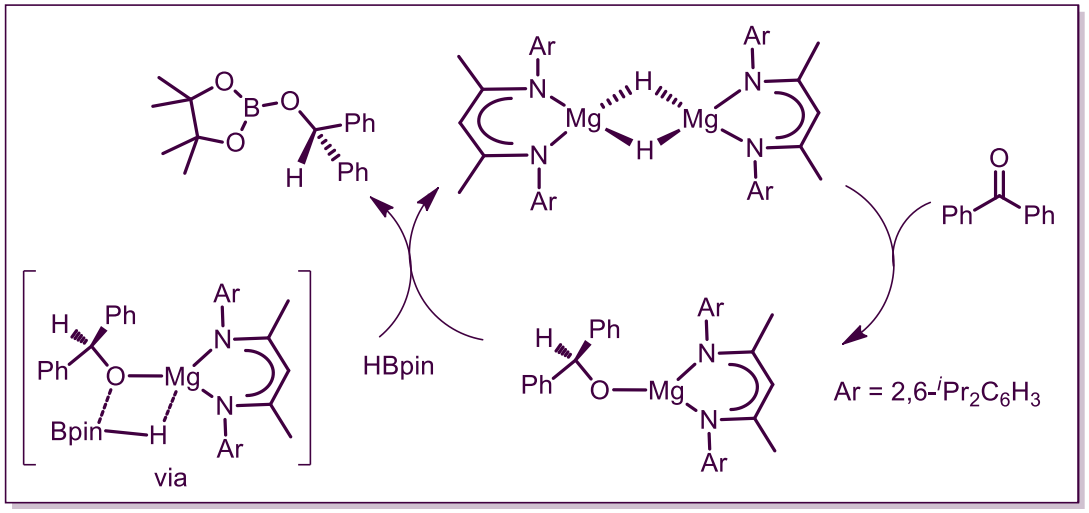


Figure 1.9. Hydroboration of aldehyde and ketone[67]

Harder was then able to demonstrate hydrogenation of diphenylethylene and styrene derivatives using metal hydride.[61] Hill and co-workers reported magnesium hydride catalysed hydroboration of aldehyde and ketone (Figure 1.9)[67]. Similarly, β-diketiminato stabilized magnesium n-butyl complex was used as an efficient pre-catalyst for the hydroboration of pyridines (Scheme 1.10), [68]

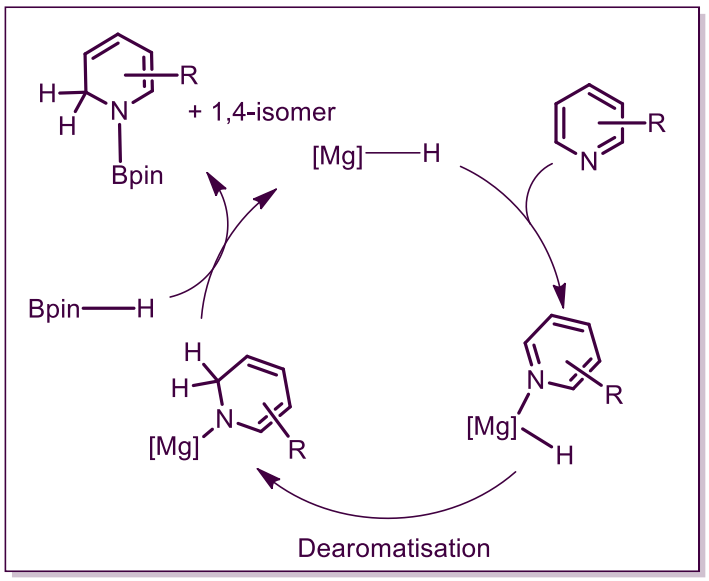
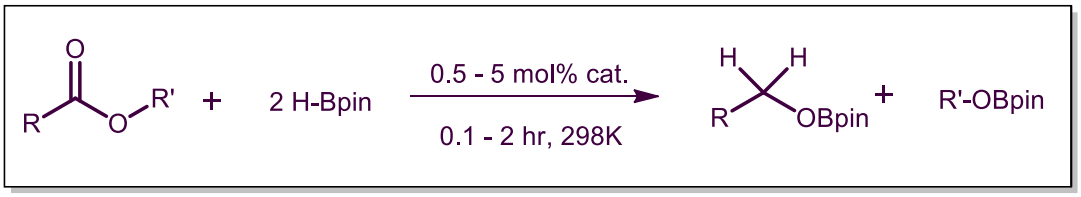


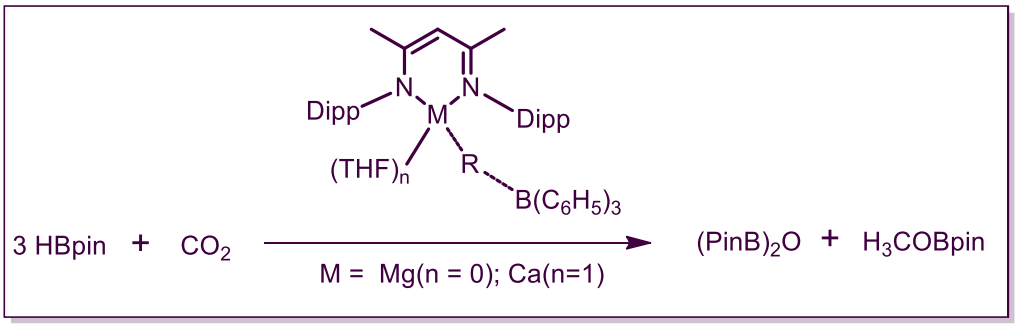
Figure 1.10. Hydroboration of pyridine. [47]

Harder has also demonstrated that a bis(*β*-diketiminate) ligand stabilized bis(magnesium) hydride used for the stoichiometric dearomatisation of pyridines with a preference for 1,2-addition.[69] In related work Sadow and co-workers have been reported catalytic hydroboration of esters using magnesium pre-catalyst (Scheme 1.11)[70]



Scheme 1.11. Hydroboration of ester[47]

Using similar catalyst system Sadow and co-workers employed hydroboration of amides which occurred with their deoxygenation to amines[71]. *β* -diketiminate supported magnesium and calcium borohydrides, which were used as a catalyst for the highly selective reduction of CO_2 to the methanol in the presence of HBpin (Scheme 1.12).[72]



Scheme 1.12. Hydroboration of CO_2

1.5. Summary

It is apparent that Group 2 metal catalysts are potentially sustainable reagent in homogenous catalysis has developed tremendously in past decade. Despite the many described main group metal catalyst above, however the scope and absolute activity of bond activation processes are relatively less when compared to the transition metal catalysts. Furthermore many mechanistic deduction, clear conceptual framework to facilitated the development of s- and p- block catalysts are somewhat lacking.

1.6. References

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Bulky guanidinate stabilized homoleptic magnesium, calcium and zinc complexes and their catalytic activity in the Tishchenko reaction

Bulky guanidinate stabilized homoleptic complexes of $[L^1M(thf)_nL^1]$ [L = {ArNC(N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3)]; M = Mg, Ca, and Zn; n = 0-1) have been synthesized with three different synthetic routes. First, treatment of bis{bis(trimethylsilyl)amide}s of Mg, Ca, and Zn *i.e.* $[M\{(N(SiMe_3)_2\}_2]$ (M = Mg, $Ca(thf)_2$, and Zn) with free guanidine ligand (L^1H) at 80 °C, elimination of $NH(SiMe_3)_2$ and formation of $[L^1M(thf)_nL^1]$ (M = Mg, Ca and Zn; n = 0-1) (**3-5**) complexes occurred. Second, the reaction of two equivalents of potassium salt of L^1H with metal dihalides *via* salt metathesis led to the formation of homoleptic complexes. Third, the reaction between MR_2 (M = Mg, Ca, Zn; R = alkyl or OTf) and L^1H at reflux temperature, formation of bis(guanidinate) magnesium, calcium, and zinc complexes have been observed. The solid state structures of L^1H(**1**), L^1K(**2**) and all three bis(guanidinate) magnesium, calcium and zinc complexes (**3-5**) were confirmed by X-ray structural analysis. Furthermore, dimerization of a range of aromatic, heteroaromatic and aliphatic aldehydes (Tishchenko reaction) has been demonstrated by using catalysts **3-5**.

2.A.1. Introduction

In recent years, the utilization of main group compounds as catalysts[1] is an attractive area of research; especially compounds containing Mg, Ca and Zn elements, due to their low toxicity, large abundance and inexpensive. Accordingly, magnesium, calcium and zinc metal complexes have been reported for their activity as catalysts in a wide range of chemical transformations including, dimerization of aldehydes[2] (the Tishchenko reaction), ring

opening polymerization,[3] hydroboration,[4] hydroamination,[5] guanylation,[6] coupling of alkynes with carbodiimides[7] and cross dehydrocoupling.[8] Various homoleptic and heteroleptic magnesium, calcium and zinc complexes have been reported, which are stabilized by a wide variety of nitrogen based ancillary ligands, such as *β*-diketiminates,[9] formamidinate,[10] amidinates,[11] iminopyrroles,[12] dipyrromethenes,[13] aminotropniminates,[5b, 5c], 1,4-diaza-1,3 butadiene,[14] aminopyridinates[15] tris(pyrozolyl)borate)[16] etc. Furthermore, by using another type of anicillary ligand *i.e.* guanidinate, Lappert and co-workers reported the first guanidinate transition metal complex in 1970.[17] Since then, many guanidinate stabilized coordination complexes involving metals from across the periodic table have been documented.[18] Despite the significant research interest in main group and transition metal guanidinates, only a handful of guanidinate supported homoleptic complexes of magnesium, calcium and zinc have been reported, which are stabilized by less bulky guanidinate ligand. [5a, 7, 11c,19] Very few examples of sterically encumbered (bulky) guanidinate[20] supported alkaline earth metal complexes have been reported in the literature; most importantly low oxidation state magnesium(I) complex with Mg–Mg bond.[21] Recently, Westerhausen and co-workers reported the structurally characterized bulky guanidinate supported homoleptic and heteroleptic heavier alkaline earth metal complexes.[22] Very recently, Fortier and co-workers reported the "super bulky" guanidinates of alkali metals,[23] however, no reports on alkaline earth metal guanidinates.

Herein, we report the structurally characterized new bulky guanidine ligand L^1H **(1)** and its potassium salt *i.e.,* L^1K (**2**) and three bulky guanidinate supported homoleptic complexes of magnesium, calcium and zinc (**3-5**), respectively. In addition, a range of aromatic, heteroaromatic and aliphatic aldehydes was converted into corresponding esters *i.e.* Tishchenko reaction by using precatalysts **3-5.**

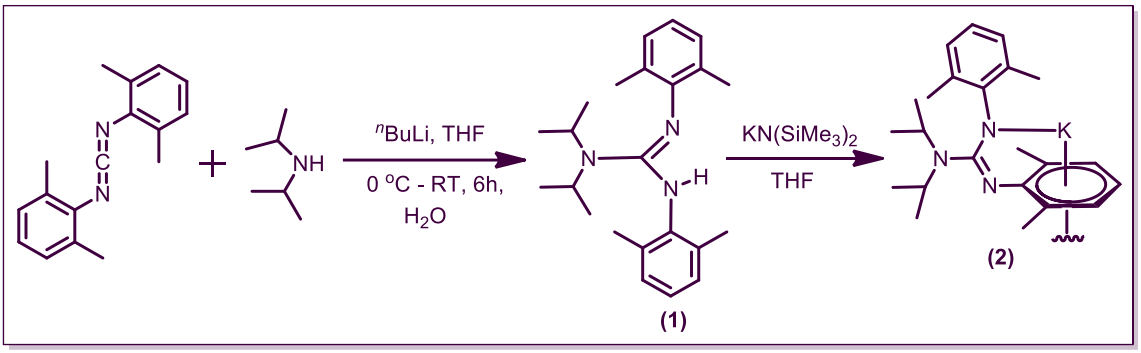
2.A.2. Results and discussion

2.A.2.1. *Synthesis of L^1H(**1**), L^1K(**2**) and $L^1M(thf)_nL^1$ (M = Mg, Ca and Zn) (**3-5**) complexes.*

Guanidinate ($[RNC(NR_2)NR]^-$) ligands are highly versatile and readily available systems play an important role in stabilizing complexes of main group, transition and lanthanide elements. The steric and electronic properties of guanidines can be readily tuned by changing the substituents at the nitrogen atoms of the ligand core. These ligands have displayed various coordination modes; more dominantly are bridging and chelating modes, which depend upon the nature and steric bulk of the substituent (R), and the metal involved.

In 2009 Jones and co-workers reported the bulky guanidine L^2H or (PrisoH) [L^2 = Priso$^-$ = {ArNC (N^iPr_2)NAr} (Ar = 2,6- $^iPr_2$-C_6H_3)}] by treating metallated amide with ^{dipp}carbodiimide *i.e.* ArN=C=NAr (Ar = 2,6- $^iPr_2$-C_6H_3) and followed by aqueous work up.[24] In our hands, deprotanation of L^2H upon treatment with MR_2 (M = Mg, Ca; R = $N(SiMe_3)_2$ or salt metathesis reaction between potassium salt of L^2H *i.e.*, L^2K with MX_2 (M = Mg, Ca; X= halide) led to the formation of mixture of products; major product free ligand (L^2H) was noticed by NMR analysis of reaction mixture. Moreover, during the course of this study, Westerhausen and co-workers have reported[22] the homoleptic strontium complex L^2SrL^2 and unsuccessful to produce, L^2CaL^2. Although, a saturated hexane solution of heteroleptic complex, $L^2Ca(N(SiMe_3)_2(THF)$, was kept at room temperature for several months led to the formation of homoleptic L^2CaL^2. This is presumably due to the steric nature of the ligand, 2,6- $^iPr_2$-C_6H_3 or dipp substituent present on the nitrogen atoms. We presumed less bulky group *i.e.* xyl or 2,6- Me_2-C_6H_3 instead of dipp (2,6- $^iPr_2$-C_6H_3) substituent, which is attached to the chelating nitrogen atoms of the guanidine core, might be suitable in isolation of homoleptic alkaline earth metal complexes. Thus, we targeted to prepare a new bulky guanidine ligand *i.e.* L^1H (**1**) [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3)], which is less

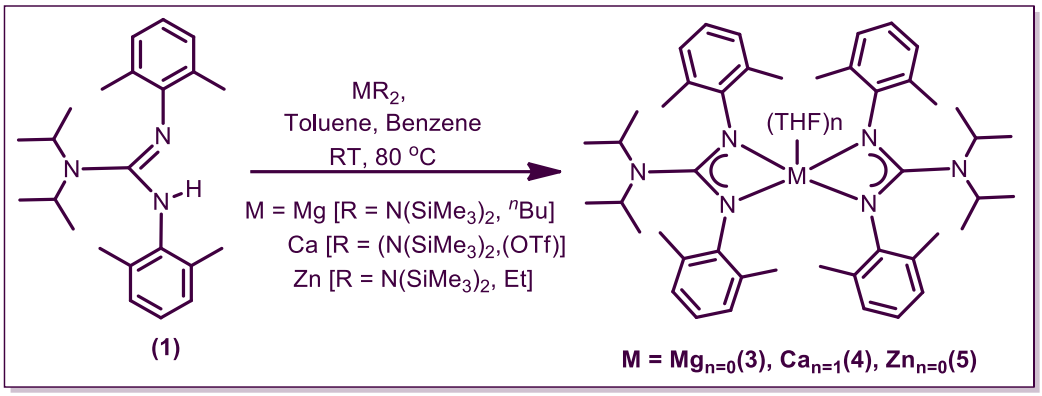
bulky in comparison to L^2H. New bulky guanidine ligand *i.e.*, L^1H (**1**) can be prepared by using ^{xyl}carbodiimide *i.e.* ArN=C=NAr (Ar = 2,6- Me_2-C_6H_3) and following the same method reported by Jones and co-workers (Scheme 2.A.1). Very recently, our group reported the structurally characterized low valent germanium and tin amide complexes by utilizing bulky guanidine L^1H.[25]



Scheme 2.A.1. Syntheses of bulky guanidine L^1H (**1**) and its potassium salt L^1K (**2**)

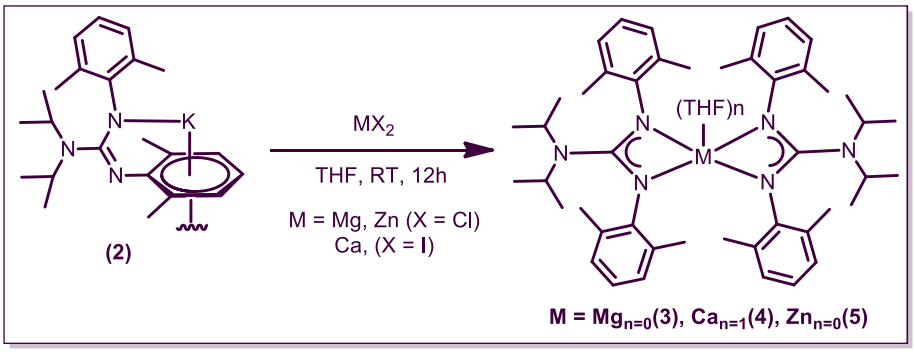
Deprotanation of L^1H (**1**) ligand upon treatment with one equivalent of potassium bis(trimethylsilyl)amide in tetrahydrofuran at ambient temperature led to the formation L^1K(**2**) (Scheme 2.A.1).

Generally, three procedures allow the synthesis of guanidinates of alkaline earth metals. i) Metallation of neutral guanidines with MR_2 (R = amide, alkyl etc.) ii) Salt metathesis reaction of alkali metal guanidinates with MX_2 (X = halide) iii) Addition of MR_2 to carbodiimide allows the synthesis of guanidinates. Furthermore, Cheng et al. reported[26] the ligand exchange reaction between guanidinate supported yttrium dihalide with allyl magnesium halide (in ethereal solvent) allows the formation of heteroleptic guanidinate magnesium halide. By employing above two methods, homoleptic complexes of magnesium, calcium and zinc *i.e.*, $L^1M(thf)_nL^1$ (M = Mg, Ca and Zn; n = 0-1) (**3**-**5**), respectively, were prepared (Scheme 2.A.2).



Scheme 2.A.2 Syntheses of **3-5**; by metalation of neutral guanidine (L^1H) with MR_2

i) a) Direct addition of one equivalent of metal amide $[M\{N(SiMe_3)_2\}_2]$ (M = Mg, $Ca(thf)_2$ and Zn) to L^1H (two equiv), subsequent release of two equivalents $NH(SiMe_3)_2$ and afforded homoleptic complexes b) Deprotanation of L^1H (two equiv) upon treatment with magnesium/zinc dialkyls(one equiv) *viz.* $^nBu_2Mg/Et_2Zn$, evolution of butane/ethane gas and formation homoleptic magnesium and zinc complexes (Scheme 2.A.2). And also, L^1CaL^1 (**4a**) was obtained by the deprotanation of L^1H (two equiv) upon treatment with $Ca(OTf)_2$ at 100 °C for 2 d in C_6D_6 in J Young valve NMR tube. ii) Easy deprotonation of L^1H by treating with metal amide *i.e.* $KN(SiMe_3)_2$ led to the formation of L^1K, *in situ* generated two equivalents of L^1K and subsequent treatment with one equivalent of metal dihalide MX_2 (M = Mg, Ca, Zn; X = Cl or I) led to the formation of $L^1M(thf)L^1$ complexes (Scheme 2.A.3).



Scheme 2.A.3. Syntheses of **3-5**; by salt metathesis reaction between L^1K and MX_2

Furthermore, efforts were made to prepare homoleptic guanidinate complexes of magnesium, calcium and zinc, by insertion of MR_2 *i.e.* $[M\{N(SiMe_3)_2\}_2]$ (M = Mg, $Ca(thf)_2$, Zn) into ^{xyl}carbodiimide and turned to be unsuccessful. And also the reaction of $^{i}Pr_2NH$ (two equiv), $[Mg\{N(SiMe_3)_2\}_2]$ (one equiv) and ^{xyl}carbodiimide either in tetrahydrofuran or hexane at room temperature or elevated temperature was failed to produce homoleptic magnesium complex.

2.A.2.2. Spectroscopic characterization

Both compounds L^1H (**1)** and L^1K (**2)** were characterized by ^1H, $^{13}C\{^1H\}$ NMR, IR and mass spectrometry analyses. The ^1H NMR spectrum exhibits a singlet at 4.79 ppm for the N–H resonance. The $^{13}C\{^1H\}$ NMR spectrum, the carbon atom of the guanidine core *i.e.*, N3*C* resonates at 148.7 ppm, that is well in agreement with other reported bulky guanidines (N3*C* 140-159 ppm).[24]

Guanidines often display several isomeric and tautomeric forms, due to C–N bond rotation and C=N bond isomerization (E_{anti}, E_{syn}, Z_{anti}, Z_{syn}), [27] this can lead to complicated NMR spectra for such compounds. However, ^1H and $^{13}C\{^1H\}$ NMR spectra for L^1H clearly indicate the existence of one isomer in solution. The infrared spectrum of the guanidine L^1H displays an N–H stretching frequency at 3366 cm^{-1} and C=N stretching frequency at 1623 cm^{-1}. A complete disappearance of N–H resonance was observed in the ^1H NMR spectrum for compound L^1K (**2**). In the $^{13}C\{^1H\}$ NMR, N3*C* peak resonates at 157 ppm which is shifted downfield in comparison to L^1H (N3*C* 148.7 ppm).

Bis(guanidinate) metal complexes (**3-5**) are freely soluble in organic solvents and that are moderately air and moisture sensitive. All these compounds are characterized by ^1H, $^{13}C\{^1H\}$ NMR, IR and mass spectrometry analyses. Reproducible microanalyses on compounds **2-5** could not obtained after several attempts. The lack of ν(N–H) absorption in the infrared and

the absence of a N–H resonance in the ^{1}H NMR spectra indicate complete deprotanation of the guanidine in isolated homoleptic magnesium, calcium and zinc complexes (**3-5)**. The ^{1}H NMR spectra of **3**, **4** and **5** display one chemically equivalent set of isopropyl methyl groups, one isopropyl methine resonance and one aryl methane resonance, which can be attributed to the symmetrical coordination of two ligand systems to the metal site (C_2 symmetrical). There is a downfield shift of the guanidine backbone N*C*N resonance to 170-171 ppm in the ^{13}C{^{1}H} NMR spectra of these complexes compared to the free guanidine and its potassium salt values. This suggests that the metal atom is coordinated by the two N-donor guanidinate ligands. ESI mass spectra for compounds **2-5** show peak at *m/z* 352 corresponds to molecular ion peak for free guanidine ligand, this suggests that the decomposition of these air and moisture sensitive compounds. Therefore, no molecular ion peaks for compounds **2-5** were detected in the ESI mass spectra.

2.A.2.3 Crystallographic characterization

Molecular structures for compounds **1-2** are depicted in Figure **2.A.1** and Figure **2.A.2**, respectively.

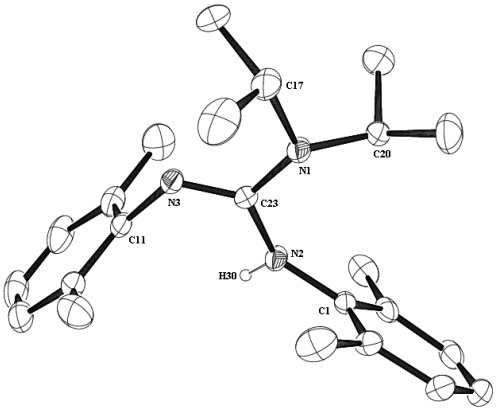


Figure 2.A.1. Molecular structure of **1.** Hydrogen atoms, except H30 are omitted for clarity. Selected bond lengths[Å] and bond angles[deg] for **1**: C1–N2 1.4260(15), C11–N3 1.4071(16), C23–N1 1.3789(15), C23–N2 1.3912(15), C23–N3 1.2815(15), N2–H30 0.842(14); N3–C23–N2 121.94(11), N3–C23–N1 120.1510, N1–C23–N2 117.90(10), C23–N3–C11 121.98(10), C23–N2–C1 130.69(10).

The compounds **1** and **2** display solid state structures comparable to those of previously characterized bulky guanidine (L^1H) and its alkali salt $(L^1K)_n$ compounds.[24] Four different isomeric forms exist for guanidine and related amidines, due to C–N bond rotation and C=N bond isomerization (E_{anti}, E_{syn}, Z_{anti}, Z_{syn}). The guanidine ligand **1** exists in the *Z- anti* form which is most common for (bulky)guanidines.[24] The carbon atom of the guanidine core N3*C*, is connected to one imino and two amino nitrogen atoms, which are confirmed by the C–N bond distances (C23– N3 1.2815(15), C23–N2 (1.3912(15) and C23–N1 1.3789(15) Å). Solid state structure of L^1K reveals that it is in polymeric in form and adopts *Z-anti* configuration, but with more localized coordinated NCN fragment (C39–N1 1.342(4) C39–N3 1.321(4) Å). Furthermore, the arene-K interaction in the compound $(L^1K)_n$ close to η^6, this leads to a one dimensional polymeric structure. The bond length of N(3)–K(1) = 2.749(2) Å is well in agreement with that of (L^2K) ((K(1) –N(1) 2.755(3) Å).

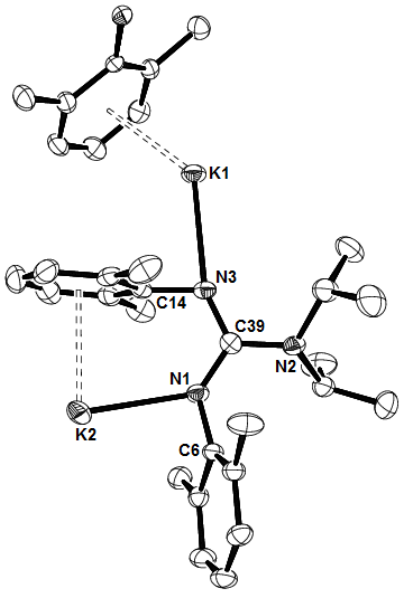


Figure 2.A.2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles[deg] for **2**: K1–N3 2.749(2), K1–Ar centroid 2.9565(12), K2–N1 2.694(3), K2–Ar centroid 2.8867(13), C39–N1 1.342(4), C39–N3 1.321(4), C39–N2 1.402(4), C6–N1 1.389(4), C14–N3 1.406(4); C39–N1–K2 129.9(2), C39–N3–K1 157.0(2), N1–C39–N3 120.2(3), N1–C39 –N2 121.4(3), N2–N3–C39 118.4(3), C39–N2–C33 115.4(3), C39–N2–C36 116.9(3), C33–N2–C36 121.4(3).

The molecular structure for compounds **3, 4** and **5** are represented in Figure **2.A.3**, Figure **2.A.4** and Figure **2.A.5**, respectively. The asymmetric unit of compound **3** contains two crystallographically independent and almost identical molecules. Sterically encumberd bis(guanidinate) magnesium complex **3** crystallizes as unsolvated, in contrast to less bulky bis(guanidinate) magnesium complexes, in those one thf molecule is coordinated to magnesium atom [Mg{(^{i}PrN)$_2$CN^{i}Pr$_2$}(THF)] and [Mg{(Me$_3$Si)$_2$NC(N^{i}Pr$_2$)}$_2$(THF)].[7]

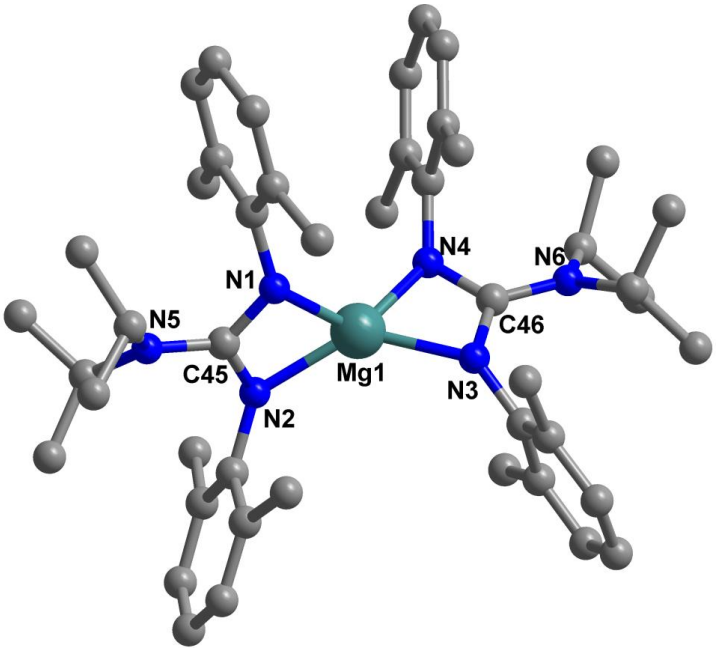


Figure 2.A.3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles[deg] for **3** : Mg1–N1 2.040(3), Mg1–N2 2.051(2), Mg1–N3 2.042(2), Mg1–N4 2.047(2), C45–N1 1.346(3), C45–N2, C45–N5 1.390(4), C46–N4 1.349(3), C46–N3 1.353(3), C46–N6 1.383(3); N1–Mg1–N2 66.67(10), N3–Mg1–N4 66.51(9), N1–C45–N2 113.1(2), N4–C46–N3 112.2(2), C45–N1–Mg1 90.38(17), C45–N2–Mg1 89.82(17), C46–N4–Mg1 90.60(16), C46–N3–Mg1 90.68(16).

Like the magnesium complex **3**, the zinc atom is in a distorted tetrahedral environment. In both compounds **3** and **5,** MgNCN and ZnNCN four membered heterocycles are planar and twisted with respect to each other. The average Mg–N and Zn–N bond distances in compounds (**3** and **5)** 2.045 Å and 2.0097 Å. are similar. The NC(backbone)N bond angles in compounds **3** and **5** 112.2(2)^{o} and 110.67(14)^{o}, respectively are well in agreement with bis(guanidinate) magnesium and zinc complexes in [Mg{(^{i}PrN)$_2$CN^{i}Pr$_2$}(THF)],[19d][Mg{(Me$_3$Si)$_2$NC(N^{i}Pr$_2$)}$_2$(THF)], [7][Zn{(Me$_3$Si)$_2$NC(NCy$_2$)}$_2$],[19e] [Zn{(Me$_3$Si)$_2$NC(N^{i}Pr$_2$)}$_2$] and [Zn{Et$_2$NC(NCy$_2$)}$_2$][19a]

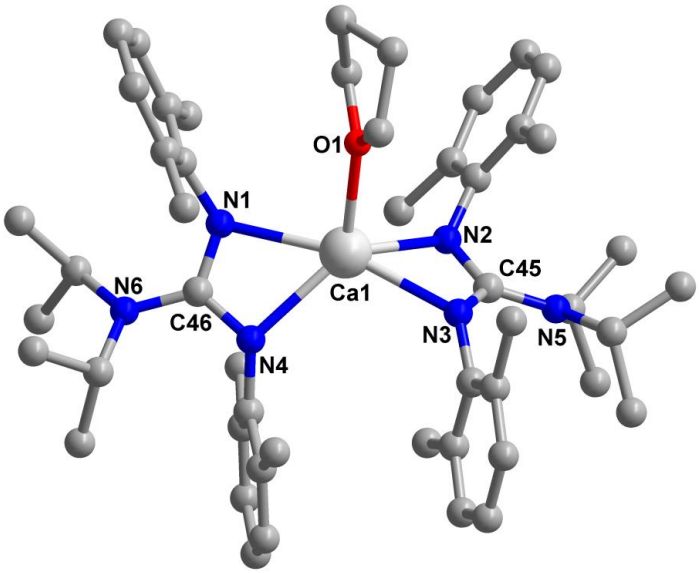


Figure 2.A.4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles[deg] for **4**: Ca1–N1 2.412(2), Ca1–N4 2.380(2), Ca1–N2 2.349(2), Ca1–N3 2.3976(19), Ca1–O1 2.3646(17) , C45–N3 1.339(3), C45–N2 1.348(3), C45–N5 1.394(3), C46–N1 1.337(3), C46–N4 1.345(3), C46–N6 1.399(3); N1–Ca1–N4 56.239(66), N2–Ca1–N3 56.72(7), N1–C46–N4 114.7(2), C45–N3–Ca1 93.43(13), C45–N2–Ca1 95.33(14), C46–N4–Ca1 95.09(14), C46–N1–Ca1 123.8(2), N(1) –C(46) –N(4) 114.7(2), N(2) –C(45) – N(3) 114.12(19), N(1) –Ca(1) –O(1) 89.53(6), N2–Ca1–O1 98.08(6).

In contrast to molecular structure of L^2SrL^2, the L^1CaL^1 (**4**) is solvated by one molecule of tetrahydrfuran and it is pentacoordinated and distorted square pyramidal geometry (Figure 2.A.4). The Ca–N bond lengths are in average 2.40 Å and Ca–O bond length is 2.3646(17) Å. The Ca–N bond distance *av.* 2.384, which is 0.339 Å longer than that of Mg–N and Zn–N bond distances (av. 2.027), this is expected due to the large ionic radii of Ca(II) ion in comparison to Mg(II) and Zn(II) ions

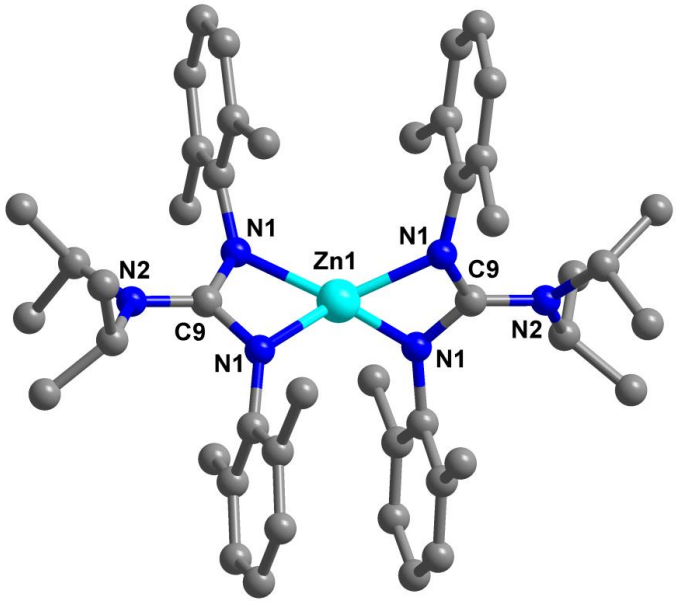


Figure 2.A.5. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles[deg] for **5**: Zn1–N1 2.0097(10), Zn1–N1^{i} 2.0097(10), Zn1-N1^{ii} 2.0097(10), Zn1-N1^{iii} 2.0097(10), N1–C9 1.3521(13), N1^{i}–C9 1.3521(13), N2–C9 1.377(2); N1^{i} –Zn1–N1 67.20(6), N1^{ii}–Zn1–N1^{iii} 67.20(6), N1^{i}–C9–N1 110.67(14), N1^{ii}–C9^{ii}–N1^{iii} 110.67(14), C9– N1– Zn1 91.06(8), N1^{i}–C9–N2 124.66(7).

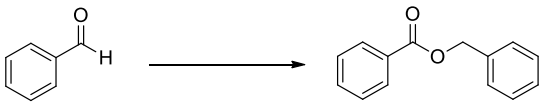
2.A.3. Catalytic activity

Catalytic studies: Bis(guanidinate) supported Mg(II), Ca(II) and Zn(II) complexes as catalysts for Tishchenko reaction

The dimerization of aldehydes to form the corresponding symmetric esters, or Tishchenko reaction (or Claisen-Tishchenko reaction), has been known for more than a century. This reaction exemplifies an atom-efficient synthesis of esters and it is industrially viable. A large number of compounds containing main group,[28] transition[29] and lanthanide[30] elements have been used as catalysts for this reaction. Hill et al., have shown [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] acts as precatalyst for the intramolecular and intermolecular dimerization of aldehydes.[2a] Coles and co-workers have reported cyclic guanidinate metal complexes as active precatalysts for the

Tishchenko reaction. [2b, 2c] Very recently, Lappert and co-workers reported the dimerization of aldehydes by using various zinc complexes, including bis(guanidinate) zinc complexes.[19a] To the best of our knowledge, there have been no reports on bis(guanidinate) magnesium and calcium compounds use as catalysts for the Tishchenko reaction.

Table 2.A.1. Homoleptic Mg(II), Ca(II) and Zn(II) catalyzed dimerization of benzylbenzoate



Catalyst	Temp. (^oC)	Mol % of cat.	Time (h)	Yield[a] (%)	Ref.
3	25	2	21	95	b
3	25	5	18	98	b
4	25	2	23	90	b
4	25	5	20	93	b
5	80	2	36	85	b
5	80	5	24	85	b
$[Mg\{N(SiMe_3)_2\}_2]$(**2.a.6**)	25	1	6	98	b
$[Mg\{N(SiMe_3)_2\}_2]$(**2.a.6**)	25	2	4	98	b
$[Zn\{N(SiMe_3)_2\}_2]$	80	2	12	<10	b
$[Ca\{N(SiMe_3)_2\}_2(THF)_2]$	25	1	24	97	2a
$[Zn\{Et_2NC(NCy)_2\}_2]$	80	5	12	96	19a

` [a] NMR yield. [b] This work, solvent free.

Our initial trial reaction was done by choosing benzaldehyde as a substrate, and bis(guanidinate) magnesium, calcium and zinc complexes were screened as catalysts for the Tishchenko reaction (Table 2.A.1). From the Table 2.A.1, it is very clear that good to excellent yields (85-98%) were obtained when each **3-5** was used as catalyst for the dimerization of benzaldehyde. The catalytic activity of bis(guanidinate) magnesium, calcium

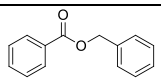
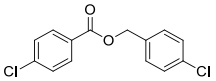
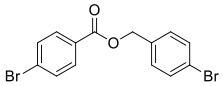
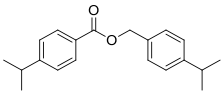
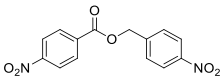
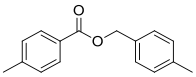
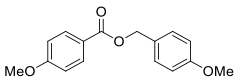
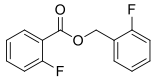
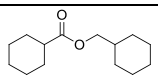
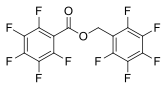
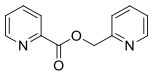
and zinc complexes for this reaction is in the order of Mg≈Ca>Zn. These compounds **3-5** show catalytic activity in line with the $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ and better than Lappert's homoleptic zinc guanidine complex. Then, our attention turned to compare the catalytic activities of these compounds with $[Mg\{N(SiMe_3)_2\}_2]$(**2.a.6**) and $[Zn\{N(SiMe_3)_2\}_2]$ for the dimerization of benzaldehyde at same reaction conditions. Surprisingly, we noticed very poor catalytic activity from $[Zn\{N(SiMe_3)_2\}_2]$, however $Mg\{N(SiMe_3)_2\}_2$(**2.a.6**) shows excellent catalytic activity. Furthermore, the esterification of benzaldehyde was examined on a time scale vs. yield using 5 mol% **3**, **4** and **5** (Figure 2.A.6) at room temperature conditions, however, for **5** catalyzed reaction at 80 ^{o}C.

During the initial 4 h, in contrast to compound **5**, which is showing less than 50% yield of benzylbenzoate, compounds **3** and **4** produce more than 70%. After 18 h, compounds **3** and **4** exhibit catalytic activities for the formation of ester is more than 90% when compared with **5** (75%). This represents a marked increase in the catalytic activity of compounds **3** and **4** over the time period when compared with **5**. Thus, both compound **3** and **4** are exhibiting almost same catalytic activity.

In view of the above results, a variety of aromatic, heteroaromatic and aliphatic aldehydes, were examined, using **3** and **2.a.6** as catalysts at 2 mol% loading under solvent free conditions (Table 2.A.2, entries 1-24). Complexes **3** and **2.a.6** show good to excellent catalytic activity for the dimerization of various aldehydes (Table 2.A.2, entries 1-24, except entries 13-14 and 23-24). In all cases, the preparative scale yields paralleled those observed by NMR (aliquot of reaction mixture) and products were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy methods. This study showed that **3** was an effective catalyst for both inter and intramolecular Tishchenko reaction. Various electron donating and electron withdrawing aromatic, heteroaromatic and aliphatic aldehydes have been used for the

intermolecular dimerization. However, only one example has been shown for the intra molecular Tishchenko reaction.

Table 2.A.2 Compounds **3** and **2.a.6** catalyzed dimerization of various aldehydes[a]

Entry	Cat.	Product	Temp. (°C)	Time (h)	Yield (%)[d]
1	**3**		25	21	95(92)
2	**2.a.6**		25	4	98
3	**3**		80	8	95(90)
4	**2.a.6**		80	4	96
5	**3**		80	8	96(92)
6	**2.a.6**		80	4	97
7	**3**		25	18	90(84)
8	**2.a.6**		25	4	93
9[b]	**3**		25	12	98(91)
10[c]	**2.a.6**		25	2	99
11	**3**		80	24	88(82)
12	**2.a.6**		25	4	90
13	**3**		80	24	15
14	**2.a.6**		25	6	70
15	**3**		80	24	94(89)
16	**2.a.6**		25	6	90
17	**3**		25	12	92(90)
18	**2.a.6**		25	4	93
19	**3**		80	20	90(83)
20	**2.a.6**		25	6	96
21	**3**		80	1	99(95)
22	**2.a.6**		80	2	99
23	**3**		80	24	20
24	**2.a.6**		80	12	20

[a] 2 mol% catalyst, Solvent free; [b] Solvent, toluene; [c] C_6D_6; [d] NMR yield(Isolated Yield)

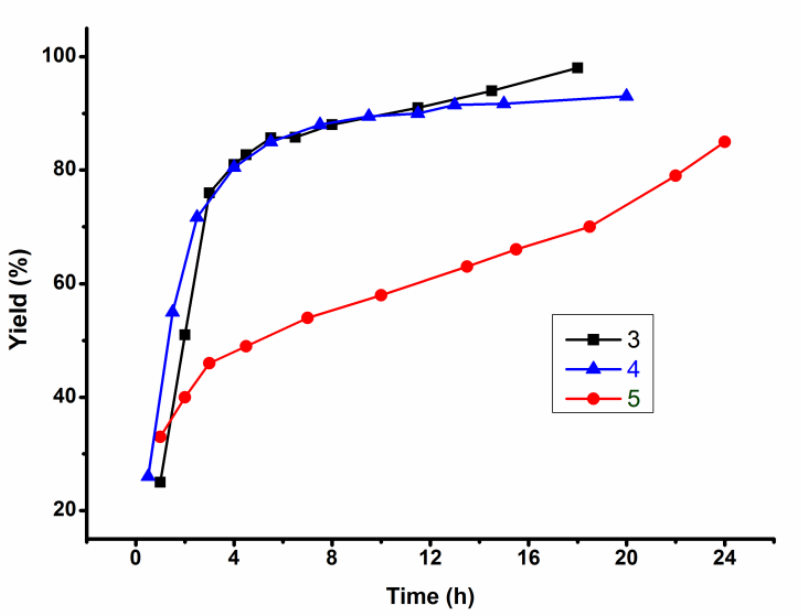


Figure 2.A.6. NMR monitoring of the reaction progress: benzyl benzoate formation vs. time; catalyst **3**, **4** and **5** (5 mol %) and benzaldehyde was stirred at room temperature and 80 ^{o}C for **5**.

2.A.4. Conclusions

Synthesis and crystal structures of bulky guanidine ligand (L^1H) and its potassium salt (L^1K) have been described. Utilizing these precursors three homoleptic complexes of magnesium, calcium and zinc *i.e.,* $L^1M(thf)L^1$ (**3-5**) have been synthesized with two standard synthetic procedures *i.e.,* i) deprotanation of L^1H with MR_2 and ii) metathesis reaction between L^1K and MX_2. However, insertion MR_2 into bulky aryl carbodiimide reaction was unsuccessful. X-ray crystal structural analysis revealed that both complexes of Mg and Zn, crystallize as C_2 symmetric with coordination number four, but the complex of Ca crystallizes as C_2 symmetric with mono etherate with coordination number five. Furthermore, we have shown the efficacy of these compounds in organic transformation reaction *i.e.* Tishchenko reaction. All these compounds **3-5** exhibit as good to excellent catalysts for the conversion of aldehydes into esters.

Table 2.A.3. Crystal data for compounds **1-5**

Compounds	**1**	**2**	**3**	**4**	**5**
CCDC	984875	984876	984877	984878	984879
Formula	C_{23} H_{33} N_3	C_{46} H_{64} K_2 N_6	$C_{92}H_{128}Mg_2N_{12}$	$C_{50}H_{72}CaN_6O$	$C_{46}H_{64}N_6Zn$
Mol.mass	351.52	779.23	1450.68	813.22	766.42
Size (mm)	0.09 x 0.06 x 0.034	0.04 x 0.028 x 0.018	0.093 x 0.075 x 0.053	0.12 x 0.08 x 0.052	0.22 x 0.15 x 0.1
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space Group	$P\bar{1}$	*P*2(1)/c	$P\bar{1}$	*P*2(1)/n	*Fddd*
a (Å)	8.7245(2)	11.070(6)	13.394(7)	11.497(8)	8.577(2)
b (Å)	10.7448(2)	18.648(9)	16.798(8)	29.855(2)	28.275(8)
c (Å)	12.4415(3)	22.237(13)	21.985(11)	14.776(9)	34.657(10)
α (°)	110.4650(10)	90	111.455(3)	90.000	90.000
β (°)	91.8350(10)	103.351(4)	93.475(3)	111.477(4)	90.000
γ (°)	97.2020(10)	90	105.182(3)	90.000	90.000
*V (*Å3)	1080.46(4)	4466(3)	4375(2)	4720(3)	8405(5)
Z	2	4	2	4	8
ρ (gcm^{-3})	1.081	1.159	1.101	1.144	1.211
μ (Mo-*Kα*) (mm^{-1})	0.064	0.250	0.078	0.175	0.623
T (K)	296	100	100	100	100
θ (max.)	27.88	25.74	26.05	27.55	25.5
Unique reflections	5141	8530	17171	10829	1959
F(000)	384	1680	1576	1768	3296
R(int)	0.0256	0.1248	0.0744	0.1420	0.0403
Parameters	247	550	987	539	126
*R*1	0.0518	0.0566	0.0605	0.0508	0.0263
w*R*2	0.1433	0.1104	0.1444	0.1082	0.0810
GOF	1.064	1.006	1.000	1.014	1.047

2.A.5. References

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Guanidinato calcium and zinc amide complexes as catalysts for the intramolecular hydroamination

Abstract

Mixed guanidianto-amido supported complexes of calcium, $L^1CaN(SiMe_3)_2{\cdot}2THF$ (**6**) [L^1 = {$ArNC(N^iPr_2)NAr$} (Ar = 2,6-Me_2-C_6H_3)] and zinc, $L^1ZnN(SiMe_3)_2$ (**7**) & $L^2ZnN(SiMe_3)_2$ (**8**) [L^2 = {$ArNC(N^iPr_2)NAr$} (Ar = 2,6- $^iPr_2$–C_6H_3)] were synthesized by salt metathesis method and characterized by multinuclear (^1H, ^{13}C, ^{29}Si) NMR, elemental analysis, spectrometry and single crystal X-ray diffraction methods. Interestingly, complex **6** exhibits as an excellent precatalyst for intramolecular hydroamination of various primary aminoalkenes in the absence of any additional activator (co-catalyst). However, both **6** and **7** show excellent catalytic activity of hydroamination of various secondary amines in the presence of co catalyst.

2.B.1. Introduction

Synthesis of nitrogen containing compounds like enamine and imines by the catalytic addition of amine containing N–H bonds to multiple C–C bonds is most atom efficient method. Consequently, this method has received[1] much attention and various metals, metal amides[2] were used in the hydroamination of alkenes[3] and alkynes.[4] The homogeneous catalyst has shown the capability to catalyze this process that spans the periodic tables from Group 1 to 12.[3f,4b,4c,5,6] In recent year's heavier Group 2 homogeneous catalysts have witnessed considerable development in this field. Various organometallic compounds of heavier alkaline earth metal have been used as suitable initiator for catalytic heterofunctionalization of unsaturated substrate[2g,7], polymerization of lactides and lactones[8], polymerization of styrene[9], cyclotrimerization of isocyanate[10], dimerization of aldehyde to corresponding ester *i.e.* Tishchenko reaction[11]. Recently, Hill et al., reported heteroleptic

precatalyst of Group 2(Ca, Sr and Ba) in the form LMX where X is reactive substituent. In this studied they have shown Group 2 LMX compounds will undergo Schlenk equilibration in solution to L_2M and MX_2, a catalyst damage and/or loss of ligand control over reactivity may effect of this redistribution in solution. On the series of the heteroleptic compounds (LMX, M= Ca, Sr and Ba) LCaX is the stable with respect to Schlenk–like redistribution in solution[12]. Later this complex has become a model complex and a useful precatalyst for hydroamination reaction.

Zinc complexes have been used broadly in organic synthesis[13]. Roesky et al reported aminotroponimate methyl zinc complex[14a,7c,7d,] and diketaminate stabilized zinc complex as a catalyst for intramoleular hydroamination reaction[15]. The resultant zinc complex shows additional advantage comparative to the other metal catalyst i) high tolerance towards polar functional group and ii) comparative stable towards air and moisture to the other metal catalyst.

In recent year's guanidinate ligand in coordination chemistry have emerged improved attention[16]. Because of the monoanionic, variation of substituents at N center, tunable the steric and electronic factor in the N center it plays a significant role on metal center. Using this guanidinate ligand in 2007 Jones et al. reported Mg(I)[17] complex containing Mg–Mg bond. Same group have been reported Ga(I)[18] complex, Ge(I) complex with Ge–Ge bond along with non–bonded electrons at each metal centre[19]. Very recently we have developed guanidinate stabilized homoleptic Mg(II), Ca(II) and zinc complexes and have effectively used as a catalyst in Tishchenko reaction[11b] and low valent Ge(II) and Sn(II) amides and their catalytic use in cyclotrimerization of aryl isocyanate. [10b]

Herein, we report the synthesis of guanidinate stabilized heteroleptic calcium [{ArNC(N^{i}Pr$_2$)NAr]CaN(SiMe$_3$)$_2$(THF)$_2$}(Ar=2,6-Me$_2$–C$_6$H$_3$)(**6**) and zinc [{ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$)$_2$}(Ar = 2,6- Me$_2$–C$_6$H$_3$(**7**) & 2,6- ^{i}Pr$_2$–C$_6$H$_3$(**8**)); complexes where Ar is the sterically demanding 2,6–di–isopropylphenyl group and 2,6–di–methyl phenyl group. These complexes are stable in solution and competence as active precatalyst for hydroamination reaction.

2.B.2. Result and Discussion

2.B.2.1. Synthetic aspects

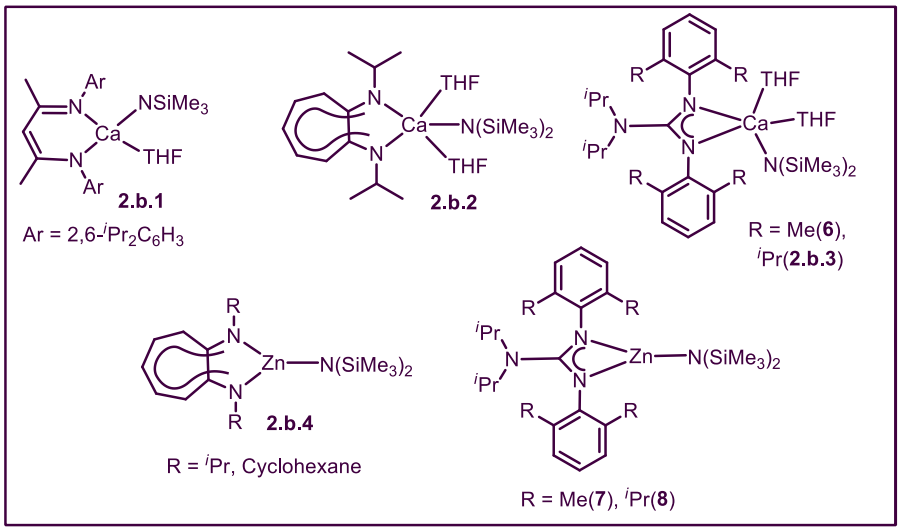
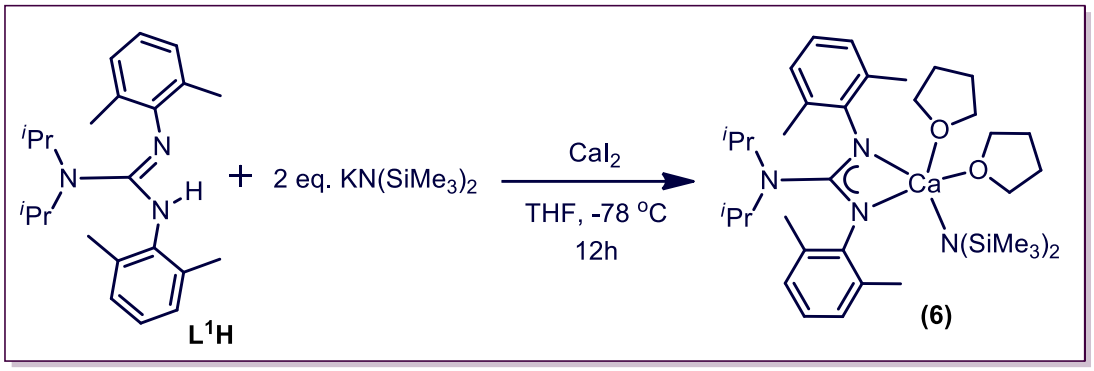


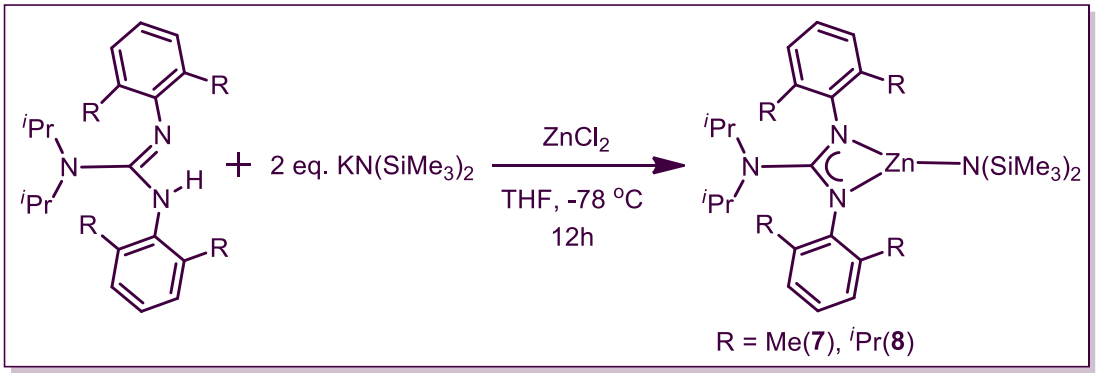
Figure 2.B.1. Bidentate calcium and zinc amide complexes

Previous studies by our group, we have demonstrated that guanidinate ligand {ArNC(N^{i}Pr$_2$)NAr} (Ar = 2,6– Me$_2$–C$_6$H$_3$))(L^{1}H) reacts with ^{n}BuLi or KN(SiMe$_3$)$_2$ formed their corresponding lithium or potassium salt of the ligand[11b].



Scheme 2.B.1. Synthesis of Guanidinate-stabilized calcium amide complex (**6**).

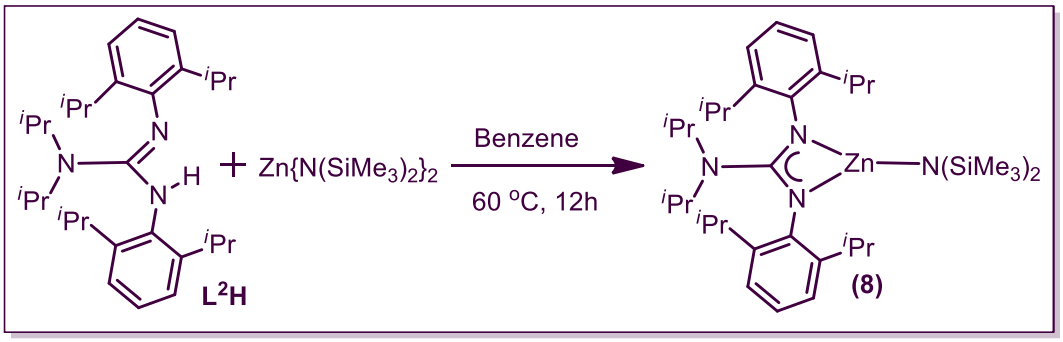
Very Recently Westerhausen and their group attempted to synthesize homoleptic calcium (L^2CaL^2) complex using guanidine ligand {ArNC (N^iPr_2)NAr} (Ar = 2,6– $^iPr_2$–C_6H_3))(L^2H) but they came up with different product i.e. heteroleptic [{$(Me_3Si)_2N$}(thf)–Ca(Priso)] and [(thf)Ca(Priso)(μ–I)]$_2$ instead of [Ca(Priso)$_2$] due to steric factor of bulky aryl–isopropyl Group. After reducing the steric strain by introducing phenyl Group at backbone instead of diisopropyl amino they were able to make desire homoleptic calcium compound[20].



Scheme 2.B.2. Synthesis of Guanidinate-stabilized zinc amide complexes by salt metathesis reaction (**7 & 8**).

Using our ligand ^{Xyl}Priso{ArNC(N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3)(L^1H) to make heteroleptic calcium amide complex {[ArNC(N^iPr_2)NAr]CaN$(SiMe_3)_2(THF)_2$} two synthetic procedures were applied, in the first case one equivalent of neutral guanidine L^1H and one equivalent of metal amides, [Ca{$N(SiMe_3)_2$}$_2$$(THF)_2$] was mixed in THF and stirred for 12 h

at room temperature but finally homoleptic L^1CaL^1 was came out with a THF unit. But in salt metathesis case controlling the reaction temperature and stoichiometry attempts were made to synthesize heteroleptic calcium complex with our ligand ^{Xyl}Priso{ArNC (N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3). Reaction of one equivalent of free guanidine either L^1H with two equivalents of potassium hexamethyldisilazide *i.e.*, $KN(SiMe_3)_2$ in tetrahydrofuran at 0 °C and followed by metathesis reaction with one equivalent of calcium diiodide in THF at –78 °C led to the formation of corresponding guanidinate supported calcium amide complex (Scheme 2.B.1). Suspended type solution solvent was removed and extracted with n-hexane, solution volume reduced and kept at 0 °C. X–Ray quality crystal was obtained after one day from the hexane solution. The resulted structure of single crystal x–ray shown in figure 2.B.2.



Scheme 2.B.3. Synthesis of guanidinate-Stabilized Zinc amide complexes (**8**).

Similarly, compound **7** and **8** were made, treating the neutral guanidine ligand L^1H or L^2H (1 eq) with zinc trimethylsilylamide(1 equiv.) or salt metathesis reaction i.e. one equivalent of ligand L^1H or L^2H, two equivalent of $KN(SiMe_3)_2$ mixed in tetrahydrofuran at 0 °C, stirred at room temperature for four hours and then it was added slowly to the one equivalent of zinc chloride in THF at –78 °C. Slowly came to room temperature and stirred at this temperature for 24 h (Scheme 2.B.2). Brownish color solution solvent was removed in vacuum, extracted with hexane (40 mL), filtered through celite and clear solution volume was reduced and kept for crystallization at –30 °C. Products were obtained as a colorless crystals.

Suitable for X–ray quality crystals came after 2–3 days. Crystalline compounds of **7** & **8** were isolated in yield of 85% and 88% respectively.

All the compounds were characterised by standard analytical/spectroscopic method *i.e.* C, H, N analysis/^{1}H and ^{13}C and ^{29}Si NMR and the molecular structures were confirmed by single crystal X–ray crystallography.

The ^{1}H and ^{13}C and ^{29}Si NMR spectra showed the expected set of signals for both the compounds. Absences of free ligand NH proton at 4.79 and 5.15 ppm revealed that the formation of new product. Characteristic sharp singlet for $N(SiMe_3)_2$ which shows at δ = 0.1 to 0.15 ppm in ^{1}H NMR spectra. Whereas in ^{13}C NMR spectra for $N(SiMe_3)_2$ peak shows in the range from δ = 2–5 ppm and for guanidine ligand backbone N*C*N it came around 160–170 ppm.[20-21, 10b, 11b] In ^{29}Si NMR spectra $N(SiMe_3)_2$ peak shows at 0 to –5 ppm.

2.B.3.2. X–ray Crystal Structures of 6, 7 and 8

Suitable crystals of **6** were obtained after one day from saturated hexane solution at 0 ^{o}C. Compounds **7** & **8** were crystalized in saturated hexane solution with few drops of THF at –30 ^{o}C. Colorless block type crystals came after 2–3 days for compound **7** and one week for compound **8**. Complex **6** was crystalized in orthorhombic space group *Pca*2(1) respectively, with one molecule in asymmetric unit. The X–Ray structure of **6** the metal centre is in distorted trigonal bipyramidal in geometry. In the solid state structure the central metal coordination no is five. The central atom is provided with σ–bonded hexamethydisilazide residue, one nitrogen atom and also by two THF molecules. Another two nitrogen atom from the backbone of the ligand.

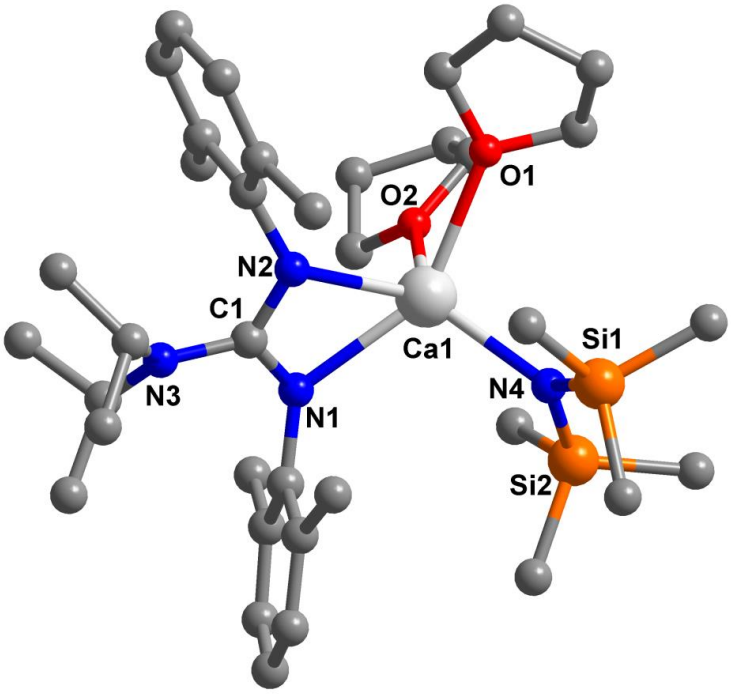


Figure 2.B.2: Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] for **6**: Ca1–N1 2.411(3), Ca1–N2 2.403(3), Ca1–N4 2.322(3), C1–N3 1.411(4), Ca1–O1 2.427(2), Ca1–O(2) 2.421(2), Si1–N4 1.690(3), Si2–N4 1.682(3); N2–C1–N1 115.22(3), N4–Ca1–N1 108.40(9), N4–Ca1–N2 131.82(10), N1–Ca1–O1 146.67(9), N1–Ca1–O2 99.52(8), N2–Ca1–O1 92.35(9), N2–Ca1–O2 108.80(10), O2–Ca1–O1 79.43(8), Si2–N4–Si1 123.30(15), N1–C1–N3 122.36(3), C1–N1–C2 121.35(3).

The Ca–N bonding distances of the guanidinato ligand are in a similar range [Ca–N1 2.411(3) Å and Ca–N2 2.403(3) Å]. In contrast, the Ca–N bond of the bis(trimethylsilylamido) group is considerably shorter [Ca–N4 2.322(3) Å], which is an effect of the stronger electrostatic interaction. The Ca1–O1 and Ca1–O2 bond distances are in comparable range 2.427(2) & 2.421(2). The bis (trimethylsilyl)amido ion is having short Si–N bond length 1.686 Å, that impose a large Si2–N4–Si1 bond angle of 123.31(15)^{o} due to the bulkiness of two $SiMe_3$ group[22].

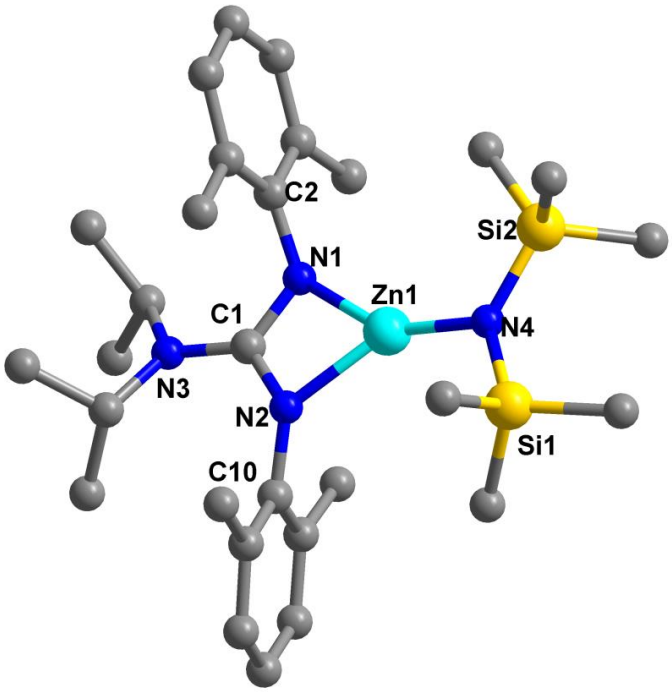


Figure 2.B.3: Molecular structure of **7.** Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] **7**: Zn1–N1 1.993(2), Zn1–N2 2.023(3), Zn1–N4 1.858(2), Si2–N4 1.714(3), Si1–N4 1.709(3), N3–C1 1.376(4), C1–N2 1.354(4), C1–N1 1.356(4), N1–C2 1.424(4), N2–C(10) 1.428(4); N4–Zn1–N1 149.26(12), N4–Zn1–N2 142.73(12), N1–Zn1–N2 67.48(11), N2–C1–N1 110.8(3), N2–C1–N3 124.5(3), N1–C1–N3 124.67(3), C1–N2–Zn1 90.2(2), C1–N1–C2 124.68(3), C1–N1–Zn1 91.41(18), C2–N1–Zn1 129.07(19), Si1–N4–Si2 126.01(15), Si1–N4–Zn1 114.12(16), Si2–N4–Zn1 119.19(14).

Compound **7** and **8** crystallize in monoclinic and triclinic space group *P*2(1)/*c* and $P\bar{1}$ respectively having each one molecule to their corresponding metal complex in the one unit cell. In both the compounds the central Zn atom is in trigonal planar geometry which coordinates with two guanidinate nitrogen atom (N1 and N2) and another nitrogen atom attached with bis (trimethylsilyl)amido group (i.e. N4). The bulky bis(trimethylsilyl)amido group is almost in same plane with the guanidinate ligand. Therefore, bis(trimethylsilyl)amido group does not have any important effect on the structural parameters. The Zn–N bond distances of backbone guanidinate ligand for both the

compounds [Zn1–N1 1.993(2) Å and Zn1–N2 2.023(3) Å (**7**), Zn1–N1 2.0044(14) Å and Zn1–N2 2.0023(15) Å (**8**)] are similar in range as we have shown in earlier for compound **7**. But the Zn–N bond of the bis(trimethylsilyl)amido group is considerably shorter [Zn–N4 1.858(2) Å(**7**) and Zn–N4 1.8689(15) Å (**8**)], which is also the effect of stronger electrostatic interaction[14e].

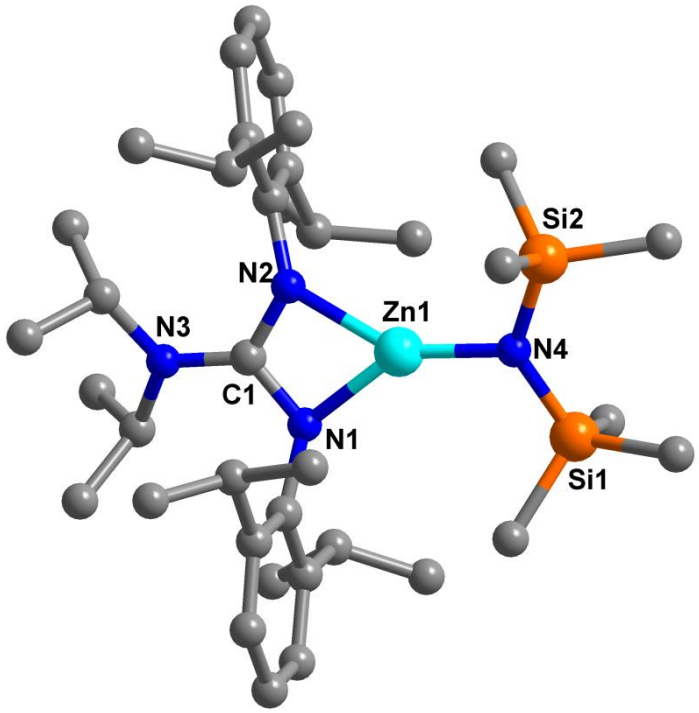
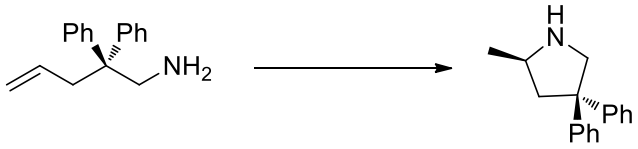


Figure 2.B.4: Molecular structure of **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] for **8**: Zn1–N1 2.0044(14), Zn1–N2 2.0023(15), Zn1–N4 1.8689(15), Si1–N4 1.7166(15), Si2–N4 1.7151(15), N3–C1 1.366(2), C1–N2 1.356(2), C1–N1 1.356(2), C2–N1 1.427(2), N2–C14 1.427(2); N2–Zn1–N1 67.29(6), N4–Zn1–N2 147.31(6), N4–Zn1–N1 145.39(6), N2–C1–N1109.92(14), N2–C1–N3125.20(15), N1–C1–N3124.88(15), Si2–N4–Zn1115.11(8), Si1–N4–Zn1114.05(8), Si2–N4–Si1130.64(9).

2.B.4. Catalytic intramolecular hydroamination reaction

Compounds **6**, **7** and **8** were tested for intramolecular hydroamination/cyclization reaction of primary and secondary aminoalkenes (Table 2.B.1 & 2.B.3).

Table 2.B.1. Cyclization of 2,2-diphenylpent-4-en-1-amine[a]



Entry	Precatalyst	Cat. mol%	Time (min)	Temp (°C)	Conv. (%)[b,c]
1	**2.b.1**	10	15	25	>99[2g]
2	**2.b.2**	10	15	25	99 [7c]
3	**2.b.2**	2	60	25	99 [7c]
4	[{ArNC(N^{i}Pr$_2$)NAr]CaN(SiMe$_3$)$_2$}(**6**)[e]	2	30	25	>99
5	**6**	5	15	25	>99
6	**6**	10	5	25	>99
7	{ArNC(N^{i}Pr$_2$)NAr}CaN(SiMe$_3$)$_2$] (**2.b.3**)[f]	2	30	25	>99
8	**2.b.3**	5	15	25	>99
9	[{ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$)$_2$}(**7**)[e]	2.5	480	80	>99[g]
10	[{ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$)$_2$}(**7**)[e]	5	120	80	>99[h]
11	[{ArNC(N^{i}Pr$_2$)NAr}ZnN(SiMe$_3$)$_2$](**8**)[f]	2.5	480	80	>99[g]

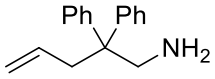
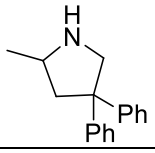
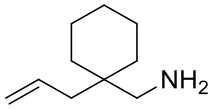
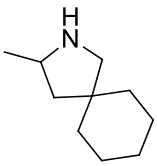
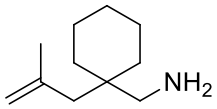
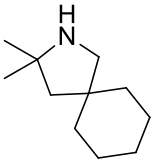
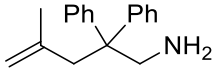
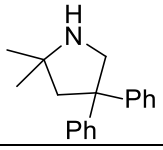
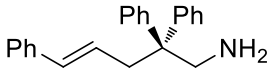
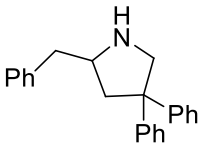
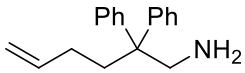
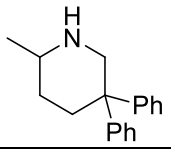
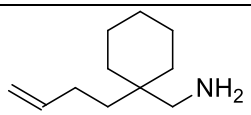
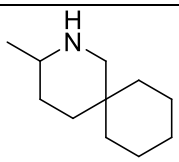
[a]Reactions are in NMR scale, catalyst in 0.5 mL of C_6D_6. [b]Calculated by ^{1}H NMR spectroscopy. [c]Hexamethylbenzene added as internal standard. [d]See reference no. [e](Ar = 2,6– Me_2–C_6H_3), [f](Ar = 2,6– ^{i}Pr$_2$–C_6H_3). [g]Co–Catalyst [PhNMe$_2$H] [B(C_6F_5)$_4$] 2.5 mol% was used. [h]Co–Catalyst [PhNMe$_2$H] [B(C_6F_5)$_4$] 5 mol% was used.

2.B.5. Intramolecular hydroamiation of primary aminoalkenes

Recent literature have revealed that organo calcium and zinc base complexes can catalyse for the activation of primary and secondary aminoalkenes. Our objective was to assess the catalytic activity of compounds **6**, **7** and **8** compared to the reported *β*–diketiminato stabilized calcium amide complex(**2.b.1**)[2g], Aminotroponiminate Calcium Amide complex(**2.b.2**)[7c] and

Aminotroponiminate Zinc Amide complexes(**2.b.4**)[14e] towards intramolecular hydroamination of aminoalkenes.

Table 2.B.2. Intramolecular hydroamination reaction of terminal aminoalkenes catalysed by 6 & 7[a]

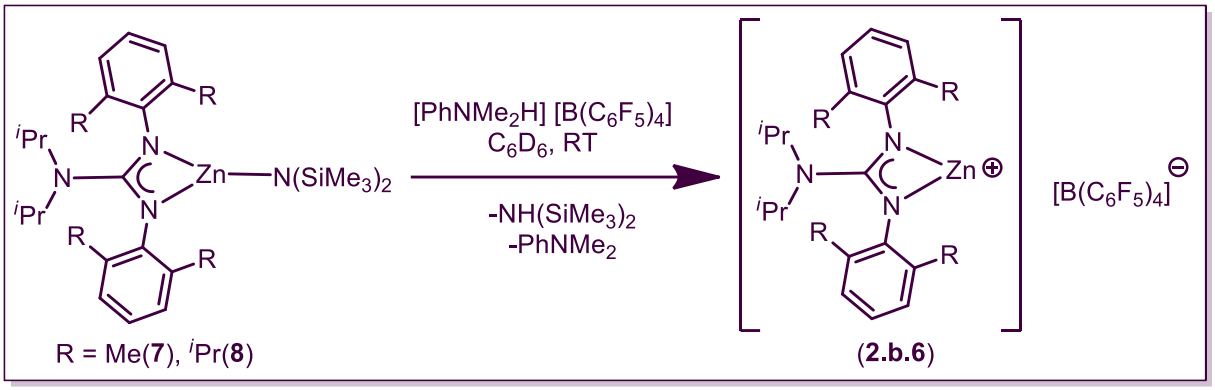
Entry	Substrate	Product	Catalyst (mol%)	Time (min)	Temp (^oC)	Conv. (%)[b]
1			6(2)	20	25	>99
2			7(5)	120	80	>99
3			6(2)	20	25	99
4			7(5)	120	80	99
5			6(2)	25	25	99
6			7(5)	120	80	98
7			6(2)	25	25	98
8			7(5)	120	80	97
9			6(2)	20	25	99
10			7(5)	120	80	98
11			6(10)	120	60	97[c]
12			7(5)	180	80	95
13			6(10)	150	60	99[c]
14			7(5)	180	80	96

[a]*Reaction conditions:* For catalyst **6** amine (20µl) and catalyst (2 mol%); for catalyst **7** amine (20 µl) catalyst (5 mol%) and activator (5 mol%) in C_6D_6(0.5 mL), NMR scale . [b]Determined by ^{1}H-NMR spectroscopy using internal standard. [c]catalyst **6** (10 mol%) was used.

After synthesis and purified of the above compounds (**6**, **7** & **8**) we started our study with unactivated primary amino alkenes. Initially, the reaction of catalyst **6** with dry, degassed aminoalkenes proceeds regiospecifically. And it results primary aminoalkenes are immediately converted to their corresponding cyclic product within very less time in very high yields under very mild condition (25–60 ^{o}C) with low catalyst loading(2 mol %). In Table 2.B.1 result of the various primary aminoalkenes are summarized.

Initially, intramolecular hydroamination reaction was done using compounds **7** & **8** without adding any activator at room temperature. After 24h with heating at 80 ^{o}C there was no detectable resonance of hydroamination product in ^{1}H NMR spectrum. Now to improve the catalytic activity of compound **7** & **8** an equimolar quantity of activator [$PhNMe_2H$] [$B(C_6F_5)_4$] (with respect to the catalyst) was added as a co catalyst and after 2 – 3 h at 80 ^{o}C the expected cyclic amine was formed with quantitative yield. The screening results of the reaction time and yields are shown in table 2.B.1. This improve in catalytic activity may be attributed to the in situ generation of the coordinatively unsaturated cationic zinc species[23], in which the activator acts as amide($–NHSiMe_3)_2$ –abstracting agent. In case of 2,2–diphenylhex–5–en–1–amine(entry11) and (1–(but–3–en–1–yl)cyclohexyl)methanamine(entry 13) using catalyst **6** (2 mol%) at room temperature there was <10% conversion after 24h then for improve the yield of the reaction catalyst mol% was increased from 2 to 10 mol% and heated at 60 ^{o}C and the reaction was completed with quantitative conversion after 2 – 2.5 hours. But in case of catalyst **7** same as like other primary amine reactions.

The reaction of catalyst **7** & **8** and co catalyst with equimolar mixture in ^{1}H NMR spectrum of the reaction mixture shows peak at δ = 0.1 i.e. free $NH(SiMe_3)_2$. Indicating the activation of primary aminoalkenes happens through amine activation pathway.

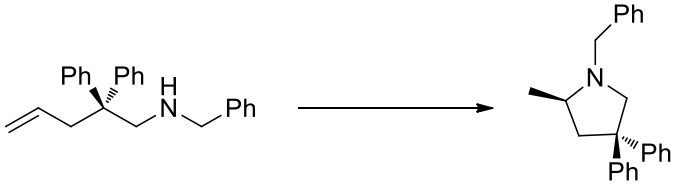


Scheme 2.B.4. Synthesis of Zinc-centered cation of compounds **7** & **8**

2.B.6. Intramolecular Hydroamiation of secondary aminoalkenes

Promising catalytic reactivity showed by complex **6**, **7** & **8** for unactivated primary aminoalkenes to cyclic amine, we presume that these catalysts will also be proficient for intramolecular hydroamination of secondary aminoalkenes.

Table 2.B.3. Cyclization of N-benzyl-2,2-diphenylpent-4-en-1-amine



Entry	Catalyst	Cat. mol%	Time (h)	Temp (°C)	Conv. (%)[b, c]
1	[{ArNC(N^{i}Pr$_2$)NAr]CaN(SiMe$_3$)$_2$} (**6**)	5	24	120	95
2	[{ArNC(N^{i}Pr$_2$)NAr}CaN(SiMe$_3$)$_2$] (**2.b.3**)	5	23	120	93
3	[{ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$)$_2$} (**7**)	2.5	12	80	94
4	[{ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$)$_2$} (**7**)	5	2	80	99
5	[{ArNC(N^{i}Pr$_2$)NAr}ZnN(SiMe$_3$)$_2$] (**8**)	2.5	12	80	94
6	[{ArNC(N^{i}Pr$_2$)NAr}ZnN(SiMe$_3$)$_2$] (**8**)	5	2	80	98
7	[{ATI(^{i}Pr)$_2$}Zn{N(SiMe$_3$)$_2$}]	2.5	1.5	80	29[14e]
8	[{ATI(Cy)$_2$}Zn{N(SiMe$_3$)$_2$}]	2.5	12	80	64[14e]
9	[{PhS–ATI(^{i}Pr)$_2$}Zn{N(SiMe$_3$)$_2$}]	2.5	12	80	87[14e]

[a]Reactions are in NMR scale, catalyst and co–catalyst [PhNMe$_2$H] [B(C$_6$F$_5$)$_4$](with respect to catalyst) in 0.5 mL of C$_6$D$_6$. [b]Calculated by ^{1}H NMR spectroscopy. [c]Hexamethylbenzene was added as internal standard. [d]See reference no.

For secondary aminoalkenes intramolecular hydroamination reaction was carried out in NMR scale in C_6D_6 using compounds **6** (10 mol%) without addition of any activator at room temperature to 120 ^oC. After 48h there was no noticeable change in ^1H NMR spectrum of secondary aminoalkene. Now to improve the catalytic activity of compound **6** (5 mol %) for secondary aminoalkene (2–methyl–4,4–diphenylpyrrolidine)[23] an equimolar quantity of activator $[PhNMe_2H]$ $[B(C_6F_5)_4]$ (5 mol% with respect to the catalyst) was added as a co catalyst and heated in a preheated oil bath at 120 ^oC. After 24 h the expected product cyclic amine was formed with quantitative yield. Reaction progress was monitered by different time interval and it has presented as stack plot in Fig. 2.B.6. From the figure we can clearly see the cyclic product formation. The screening results are shown in table 2 for the reaction time and yields.

Catalyst **7** & **8** displayed similar catalytic activity for secondary aminoalkenes to that of previously explained primary aminoalkenes in the presences externally added activator. Finaly, we have demonstrated intramolecular hydroamination of wide range of secondary aminoalkenes. All the cases it shows very excellent yield. Furthermore, catalyst **7** have been reused upto five consecutive cycle and we got upto 70 % conversion at the last cycle (see Fig. 2.B.5).

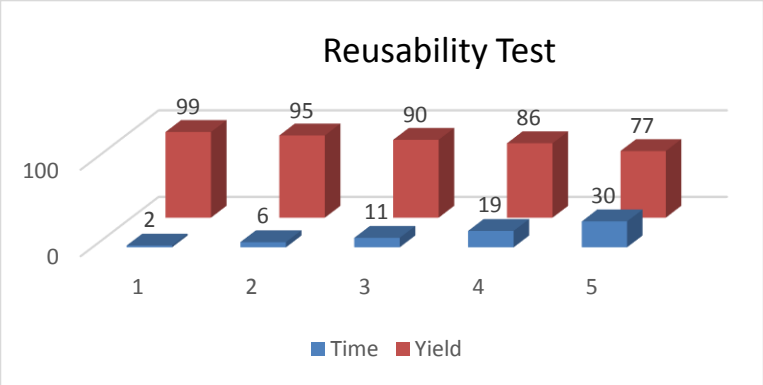
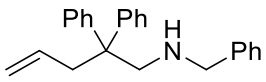
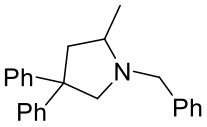
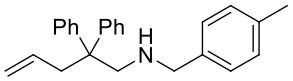
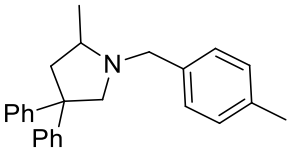
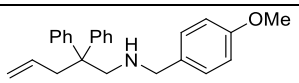
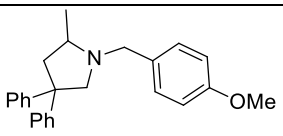
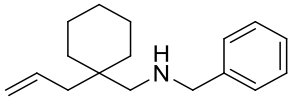
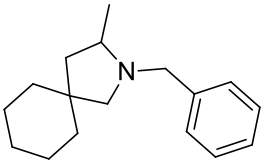
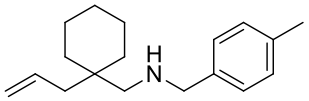
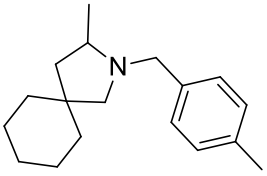
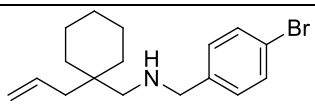
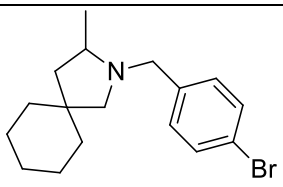
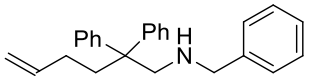
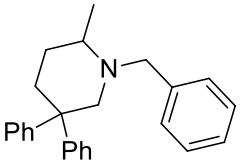
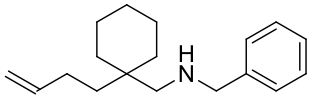
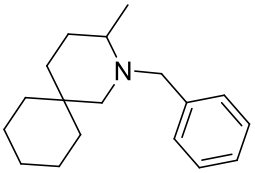


Figure 2.B.5. Catalyst longevity test for the hydroamination product of N-benzyl-2,2-diphenylpent- 4-en-1-amine with catalyst **7** in C_6D_6(NMR scale) at 80 ^oC.

Table 2.B.4. Intramolecular Hydroamination Reaction of secondary Aminoalkenes Catalysed by 6 & 7[a]

Entry	Substrate	Product	Catalyst	Time (h)	Temp (°C)	Conv. (%)[b]
1			6	24	120	>95
2			7	2	80	99
3			6	34	120	95
4			7	4	80	96
5			6	36	120	94
6			7	4	80	97
7			6	24	120	98
8			7	2	80	99
9			6	30	120	95
10			7	4	80	95
11			6	26	120	96
12			7	3	80	98
13			6	34	120	93
14			7	4	80	94
15			6	36	120	94
16			7	4	80	95

[a]*Reaction conditions:* For catalyst **6** & **7** amine (20µl), catalyst (5 mol%) and activator (5 mol%) in C_6D_6(0.5 mL), NMR scale . [b]Determined by ^{1}H-NMR spectroscopy using internal standard.

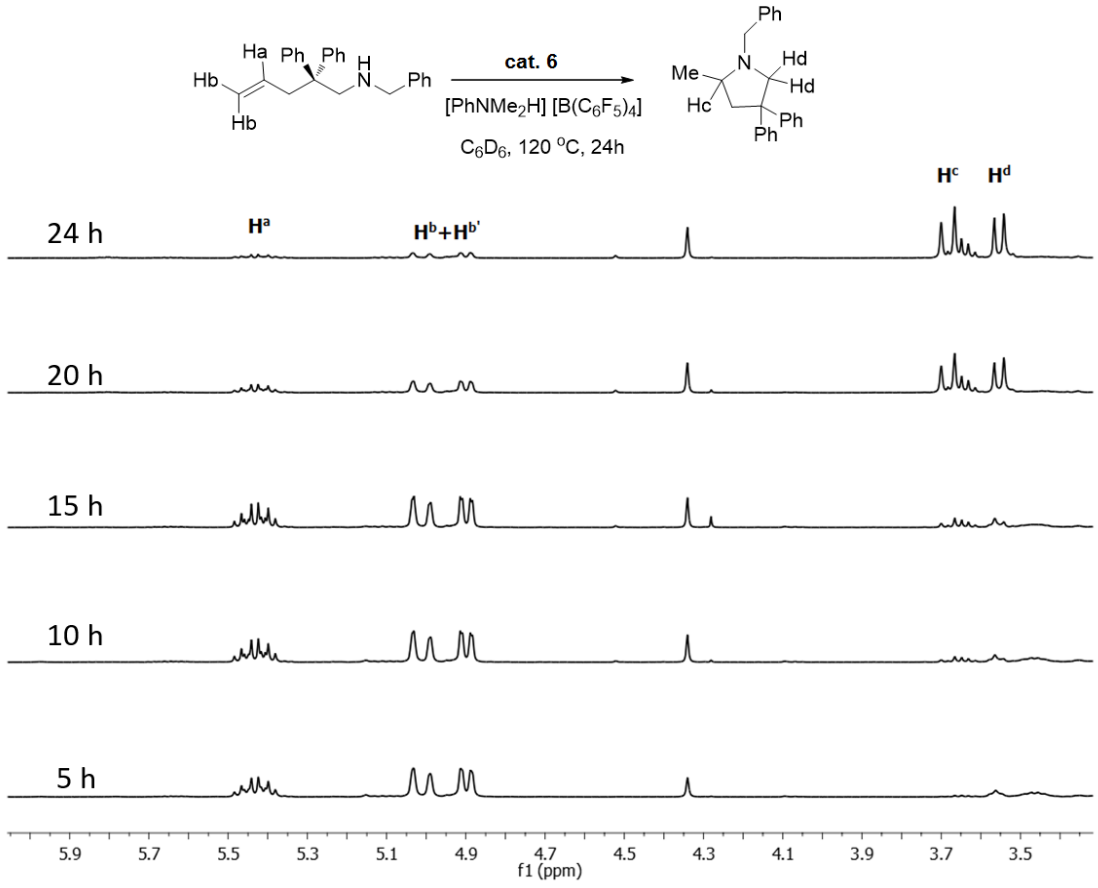


Figure 2.B.6. Stack plots of ^{1}H NMR spectrum for the reaction of N–(2,2–diphenylpent–4–en–1–yl)–4–methylaniline with **6** as catalyst at different time intervals.

2.B.7. Conclusion

Three heteroleptic calcium and zinc complexes bearing bulky guanidinato and amido ligands have been synthesized and structurally characterized. Considering the fact that metal complexes bearing amido ligand group have wide applications in homogeneous catalysis, we tested these metal complexes for hydroamination reactions. All these three metal complexes exhibit as excellent precatalysts for intramolecular hydroamination of both alkenes bearing primary amine and secondary amino group. These are important precursors for isolation of guanidianto supported hydride and hydroxides, alkoxides etc. Such studies are in progress in our laboratory and we publish in due course.

Table 2.B.5. Crystal data for compounds **6**, **7** and **8**

Formula	$C_{37}H_{66}CaN_4O_2Si_2$(**6**)	$C_{37}H_{66}N_4Si_2Zn$(**7**)	$C_{29}H_{50}N_4Si_2Zn$(**8**)
Mol.mass	695.20	688.49	576.28
Temperature	100 K	100 K	100 K
Size (mm)	0.2 x 0.16 x 0.14	0.28 x 0.26 x 0.23	0.1 x 0.087 x 0.065
Crystal system, space Group	Orthorhombic, *Pca*2(1)	Monoclinic, *P*2(1)/*c*	Triclinic, $P\bar{1}$
a (Å)	18.302(18)	17.428(7)	a = 9.710(4) Å
b (Å)	12.818(12)	12.746(5)	b = 11.479(4) Å
c (Å)	17.682(15)	18.721(7)	c = 16.187(7) Å
α (°)	90	90	70.395(2)
β (°)	90	101.187(2)	84.806(2)°
γ (°)	90	90	77.247(2)°
*V (*Å3)	4148(2)	3288(2)	1657.4(12)Å^3
Z, Calculated density	4, 1.113 Mg/m^3	4, 1.121 Mg/m^3	2, 1.155 Mg/m^3
Absorption coefficient	0.243 mm^{-1}	0.689 mm^{-1}	0.835 mm^{-1}
F(000)	1520	1496	620
Theta range for data collection	2.23 to 25.30 deg.	1.19 to 25.50 deg	1.34 to 25.75°.
Limiting indices	–22<=h<=14, –10<=k<=15, –21<=l<=20	–21<=h<=21, –15<=k<=15, –22<=l<=22	–11<=h<=11, –13<=k<=14, –19<=l<=19
Reflections collected / unique	21514 / 6619 [R(int) = 0.0599]	48524 / 7598 [R(int) = 0.0434]	17884/6231 [R(int) = 0.1456]
Completeness to theta	99.1 %	99.9 %	98.6 %
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.7452 and 0.6422	0.7461 and 0.6652	0.7453 and 0.5967
Data / restraints / parameters	6619 / 1 / 429	7598 / 0 / 415	6231 / 0 / 339
Goodness–of–fit on F^2	1.019	1.040	0.923
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.1014	R1 = 0.0307, wR2 = 0.0745	R1 = 0.0471, wR2 = 0.1059

2.B.8. References

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Magnesium amides as catalysts for the hydroboration of ester under solvent free condition

Abstract

Two examples of structurally characterized bulky guanidinate supported heteroleptic magnesium(II) amide complexes {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)}[Ar=2,6– Me$_2$–C$_6$H$_3$(**9**) and 2,6– ^{i}Pr$_2$–C$_6$H$_3$(**10**)] are synthesized by two synthetic routes; i) salt metathesis method ii) deprotonation of free ligand with metal bis(amide). Further, magnesium bis{bis(trimethylsilyl)amide} i.e. Mg{N(SiMe$_3$)$_2$}$_2$(**2.a.6**) and bulky guanidinate stabilized magnesium amide complexes (**9**) and (**10**)] are reported as highly proficient catalysts for the hydroboration of ester with pinacolborane under neat and very mild reaction conditions.

3.A.1. Introduction

In organic synthesis reduction of ester to alcohol is a very important transformation[1]. Alcohols are very significant starting material for manufacturing bioactive compounds, pharmaceuticals and agrochemicals. For the synthesis of alcohol from their corresponding ester is a very straightforward process[2]. Using the hydride sources like $LiAlH_4$, $LiBH_4$, DIBAL–H are still difficult to do the reduction of ester to their corresponding alcohol[3]. Metal catalysed hydrosilylation and hydroboration recations are useful method for the reduction of ester. Although there are some drawbacks like very high temperature, high pressure, and low selectivity nevertheless, metal catalysed hydrogenation is an important methodology for the reduction of ester[4].

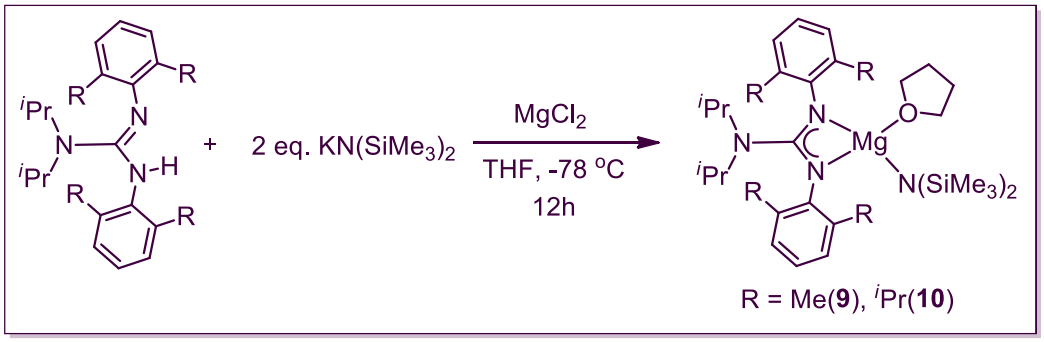
Compared to ester hydrogenation of ketone has focused in more/catalytic hydrogenation of ester is much less in literature compared to ketone[5]. Various catalysts (from transition metal to main group metal) were used for reduction of ester or amides. First transition metal was

used for reduction of ester in 1973 by Tsurugi[6] and using titanium alkoxides or titanocene with triethoxysilane or PMHS for reduction of ester by Bucwald in early 1990s[7]. Transition metal catalysts like titanium[7], vanadium[8], zinc derivatives[9], molybdenum[10], ruthenium[11], rhodium[12], iron[13], manganese[14] and palladium[15] were also used for such reaction. Recently Nolan and their group reported KOH catalysed hydrosilylation of esters and amides[16]. Lewis acids also exhibited good catalytic activity towards the reduction of ester[17].

Group 2 metal catalysed hydrosilylation, hydroboration of aldehyde, ketone, pyridine, imine and isonitriles are also reported very recently[18]. However hydrosilylation of ester reports[9a, 11b, 13a,16] are there but hydroboration of ester examples are few in literature[19]. Ester hydroboration is thermodynamically more challenging than aldehyde.

Very recently Sadow and their group has reported magnesium catalysed hydroboration of ester through zwitterionic mechanism[19] keeping in mind we tried this reaction with free magnesium bis(amide) i.e. $Mg\{N(SiMe_3)_2\}_2$ in different reaction conditions(see Table 3.A.1) and it shows very good catalytic activity. During this studies, we developed two complexes (**9** & **10**) of magnesium amide stabilized by guanidinate ligand for the comparison of catalytic activity with the magnesium bis(amide) (see Table 3.A.1). Herein, we report guanidinate supported heteroleptic Mg(II) amide and $Mg\{N(SiMe_3)_2\}_2$ compounds utilized as precatalysts for the hydroboration of ester under solvent free conditions. To the best of our knowledge there have been no reports on the heteroleptic guanidinate supported Mg(II) amide complexes and which are employed for hydroboration of ester reaction.

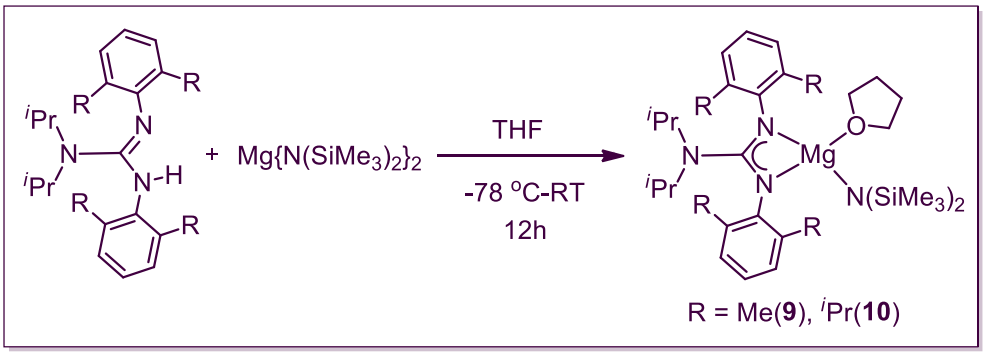
3.A.2. Results and discussion:



Scheme 3.A.1. Synthesis of {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)})}[Ar=2,6– Me$_2$–C$_6$H$_3$ (**9**), Ar=2,6– ^{i}Pr$_2$–C$_6$H$_3$(**10**)]

Bulky guanidinato magnesium amide complexes have been synthesized by two different syntetic methods; i) salt metatheis method and ii) deprotnation of free ligand with metal bis(amide).

The reaction with neutral guanidines L^{1}H [L = {ArNC (N^{i}Pr$_2$)NAr} (Ar = 2,6- Me$_2$-C$_6$H$_3$ & 2,6- ^{i}Pr$_2$-C$_6$H$_3$)] with Mg{N(SiMe$_3$)$_2$}$_2$ in THF at -78 ^{o}C and Salt metathesis reaction of alkali metal guanidinates(L^{1}K) with MgCl$_2$ (X = halide) led to the formation of desired compound (Scheme 3.A.1 & 3.A.2).



Scheme 3.A.2. Synthesis of {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)}[Ar=2,6– Me$_2$–C$_6$H$_3$ (**9**), Ar=2,6– ^{i}Pr$_2$–C$_6$H$_3$(**10**)]

X-ray quality crystals were obtained from saturated hexane solution with few drops of THF at -30 ^{o}C. Both compounds **9** and **10** were characterized by multi nuclear NMR (^{1}H, ^{13}C, ^{29}Si), X-ray crystallographic studies and elemental analysis. In ^{1}H NMR spectra characteristic N(SiMe$_3$)$_2$ peak appears at 0.11 to 0.33 ppm which is similar with reported LMgN(SiMe$_3$)$_2$ compounds[20]. In ^{13}C{^{1}H} NMR spectrum, the carbon atom of the guanidine core *i.e.*, N3*C* resonates at 148.7 ppm, that is well in agreement with other reported bulky guanidines (N3*C* 140-159 ppm)[21]. In ^{29}Si NMR, N(*Si*Me$_3$)$_2$ peak shows at -8 ppm which is the range for four coordinated amido compound reports in literature.

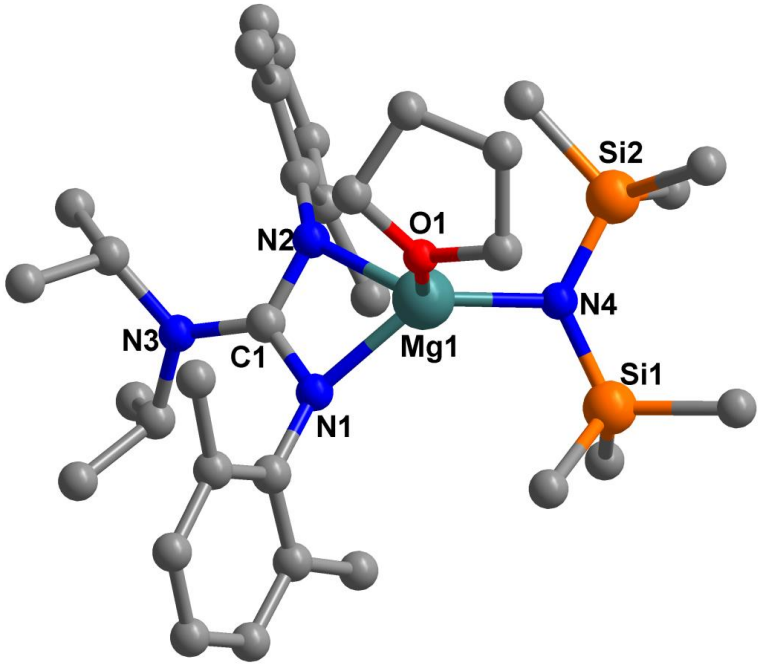


Figure 3.A.1. Molecular structure of **9.** Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] for **9.** Mg1–N1 2.0987(18), Mg1–N2 2.0747(18), Mg1–O1 2.0359(17), Mg1–N4 1.9904(18), N1–C1 1.347(3), N2–C1 1.355(3), N3–C1 1.392(2), Si1–N4 1.6907(18), Si2–N4 1.7008(18); N2–Mg1–N1 65.37(7), N4–Mg1–N1 131.29(8), O1–Mg1–N1 112.12(7), O1–Mg1–N2 109.27(7), N4–Mg1–O1 104.02(7), N1–C1–N2 113.03(17), N1–C1–N3 124.57(18), Si1–N4–Si2 125.87(10), Si1–N4–Mg1 116.48(9), Si2–N4–Mg1 117.64(9), C1–N2–Mg1 91.21(12), C1–N1–Mg1 90.39(12).

Compounds **9** & **10** crystallize in the monoclinic system with *P* 21/*n* and *C*2/*c* space group respectively. The molecular structure, selected bond distances and bond angles have depicted in the figure 3.A.1 and 3.A.2. In solid state structure both the compound bonded to the guanidinate ligand in [*N,N'*] chelate fashion and the other sites are occupied by N atom of the amido ligand and coordinated with oxygen atom(from THF solvent), resulting in distorted tetrahedral geometry. Mg–N(amido) bond distances Mg1–N4 1.9904(18) Å in (**9**) and Mg1–N4 1.9995(16) Å in (**10**), are comparable with Mg–N(amido) bond distance in compound Mg(hpp)(N{SiMe$_3$}$_2$) Mg–N4 1.9798(14) Å[20a].

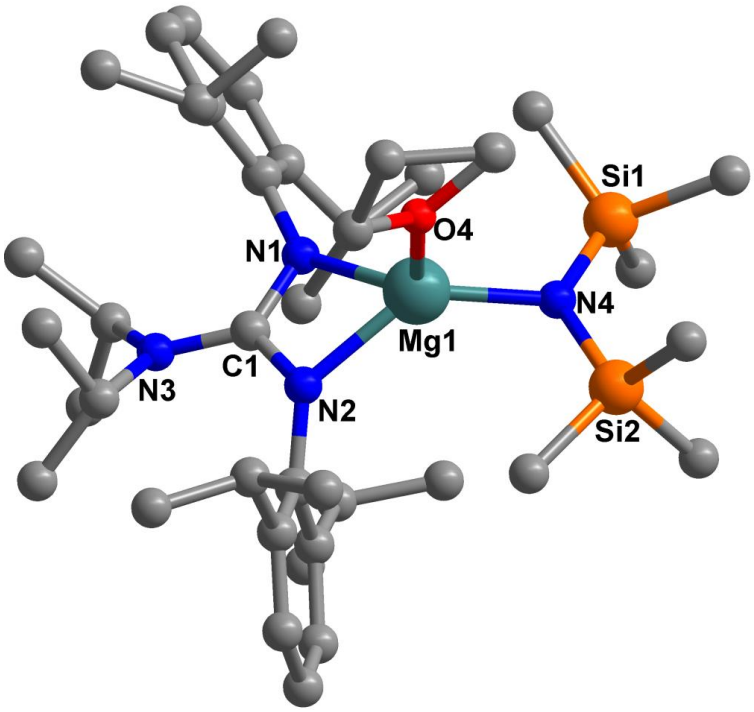


Figure 3.A.2. Molecular structure of **10.** Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] for **10.** Mg1–N1 2.0996(16), Mg1–N2 2.0724(15), Mg1–N4 1.9995(16), Mg1–O4 2.0649(14), Si1–N4 1.7015(17), Si2–N4 1.7036(17), N1–C1 1.350(2), N2–C1 1.365(2), N3–C1 1.386(2); N2–Mg1–N1 65.11(6), N4–Mg1–O4 99.67(7), N1–C1–N2 111.59(15), O4–Mg1–N1 113.60(6), O4–Mg1–N2 107.57(6), N1–C1–N3 126.73(15), C1–N1–Mg1 91.14(10), Si1–N4–Si2 124.06(9), Si1–N4–Mg1 119.83(9), Si2–

N4–Mg1 116.08(8).

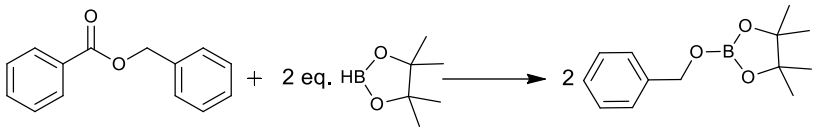
For comparison of catalytic reactivity of free magnesium bis(amide)[22], we developed two guanidinate stabilized magnesium amide complexes {[ArNC(N^iPr_2)NAr]MgN($SiMe_3$)$_2$(THF)$_2$}[Ar=2,6– Me_2–C_6H_3 (**9**) and Ar = 2,6– iPr_2–C_6H_3 (**10**)].

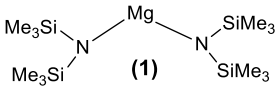
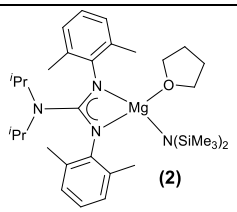
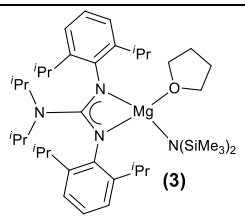
3.A.3. Catalytic studies

We started our investigation with the reduction of ester (benzyl benzoate) as a model substrate with 2.1 equiv. of pinacolborane(HBpin) under various condition and with different magnesium amide catalysts (**2.a.6**, **9** & **10**) (Scheme 3.A.1 and Table 3.A.1) are readily transformed to alkoxyboronic acid pinacol esters (ROBpin). Initially with free magnesium bis{bis(trimethylsilylamide)} (0.1 to 2 mol%) as catalyst with benzyl benzoate (0.25 mmol) and of pinacolborane(HBpin)(0.525 mmol) in C_6D_6 and solvent free condition at room temperature in NMR scale and neat in large scale hydroboration occurs rapidly to form $PhCH_2OBpin$. Reaction was monitored by ^1H NMR spectroscopy and after certain time (10 to 45min) reaction completed with quantitative conversion with high TON.

Catalyst **9** and **10** were used from 0.1 to 0.5 mol% for benzylbenzoate(1equiv.), pinacolborane(2.1eq) (See Table 3.A.1) and all the different concentration of catalyst loading hydroboration occurs very fast with quantitative conversion (TON>900). Reaction was monitor in time interval by ^1H NMR spectroscopy and conversion of product was calculated by corresponding peak intensity of ester and PhCH_2OBpin. In Product $PhCH_2OBpin$ the B–O bond was confirmed by ^{11}B NMR spectrum disappearance of HBpin starting material peaks and appearances of new peak at 22 –23 ppm matching with compound in literature[19]. In ^1H NMR spectrum complete consumption of pinacolborane peak at 0.99ppm (singlet) and appearance of new peak at 1.07ppm.

Table 3.A.1: Variation of catalysts and optimization of reaction condition[a]



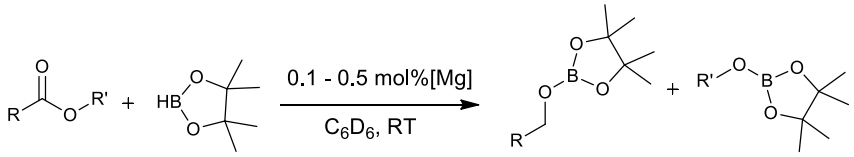
Catalyst(1-3)	Cat. mol%	Time (min)	Solvent	Yield (%)[b]
	1	10	neat	>99
	1	30	C_6D_6	>99
	0.5	15	neat	>99
	0.5	45	C_6D_6	>98
	0.2	20	neat	>99
	0.1	30	neat	>99
	0.5	15	neat	>99
	0.5	45	C_6D_6	>99
	0.2	20	neat	>99
	0.1	25	neat	99
	0.5	15	neat	>99
	0.5	50	C_6D_6	>99
	0.2	15	neat	>98
	0.1	20	neat	98

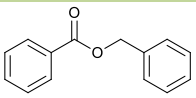
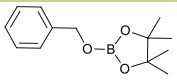
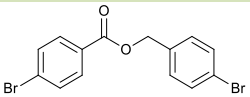
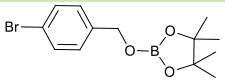
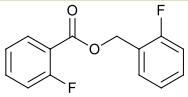
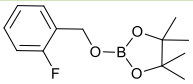
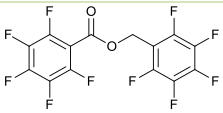
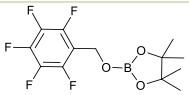
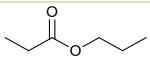
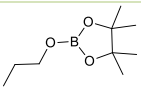
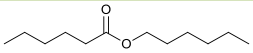
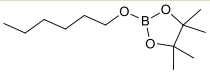
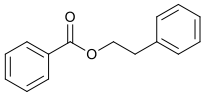
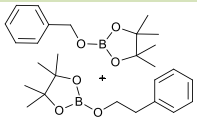
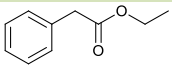
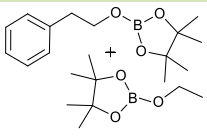
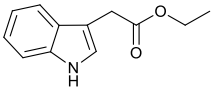
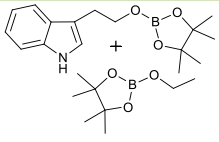
[a]Conditions: Benzyl benzoate (0.25 mmol), Pinacolborane(0.55 mmol), 25 ^oC, C_6D_6 in NMR scale. [b]NMR yields.

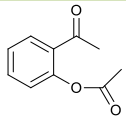
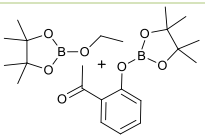
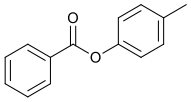
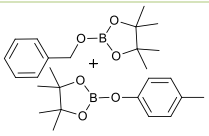
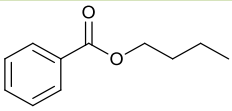
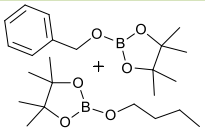
For catalyst **10** also in different concentration reaction was performed with benzyl benzoate, more than 90% product formation was there for all the different concentration, which is comparable with catalyst **9** (See Table 3.A.1). For all three (**2.a.6**, **9** & **10**) catalyst comparison one kinetic studies was done with 0.5 mol% catalyst. In the figure yield vs. time plot have shown and it was noticed that for catalyst **2.a.6** reaction proceeds gradually but in case of catalyst **9** within 15 min >85% conversion was completed and for complete

conversion it was taking rest of the time. Similar observation of catalyst **2.a.6** was noticed for catalyst **10**.

Table 3.A.2. Scope of hydroboration of ester substrate[a]



Entry	Substrate	Cat	Product	T (min)	Yield[b] (isolated)
1		2.a.6		30	>99 (97[c])
2		9		25	>99
3		2.a.6		35	>99 (91[c])
4		9		30	>99
5		2.a.6		20	>99 (92[c])
6		9		20	>99
7		2.a.6		30	>99 (90[c])
8		9		30	>99
9		2.a.6		15	>99
10		9		10	>99
11		2.a.6		15	>99
12		9		10	>99
13		2.a.6		20	>99
14		9		20	>99
15		2.a.6		20	>99
16		9		15	>99
17		2.a.6		30	>99
18		9		25	>99

19		2.a.6		30	>99
20		9		30	>99
21		2.a.6		25	>99
22		9		25	>99
23		2.a.6		25	>99
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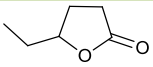
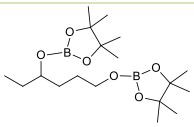
25		2.a.6		15	>99
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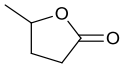
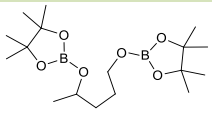
27		2.a.6		15	>99
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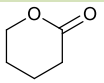
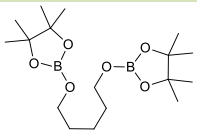
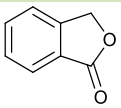
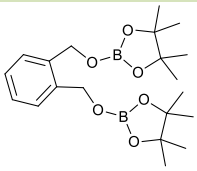
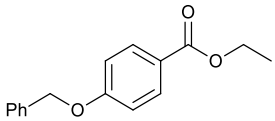
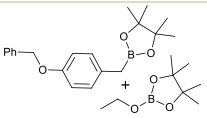
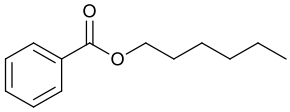
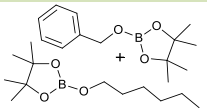
29		2.a.6		15	>99
30		9		15	>99
31		2.a.6		20	>99
32		9		15	>99
33		2.a.6		30	>99
34		9		20	>99
35		2.a.6		20	>99
36		9		15	>99

[a]Conditions: Benzyl benzoate (1 equiv.), Pinacolborane(2.1 equiv), 25 °C, C_6D_6 in NMR scale. [b]NMR yields. [c]Ester (1 mmol), pinacolborane (2.1 mmol), neat, room temparature.(Isolated yield by column chromatography).

The success of this reaction promote us explore the substrate scope to other commercially available esters. Result of these catalytic ester hydroboration using 0.1 mol% catalyst of **2.a.6** and **9** in neat at room temperature summarized in Table 3.A.2. A variety of esters were reduced proficiently, including aromatic, aliphatic, heteroaromatic and

heterocyclic symmetric and unsymmetrical esters to their corresponding alkoxyboronic acid pinacol esters (ROBpin). In aromatic symmetric ester substituent in different position has not effect on product yield (Table 3.A.2 entry 3–6). Substituent in all five position of aromatic ring did not take more time compare to less substituents aromatic ring and not decreased the yield also (Table 3.A.2 entry 7–8) (TON>900). In addition for aliphatic esters reaction time was reduced compare to the aromatic esters. In fact other esters like heteroarenes, heterocyclic and cyclic esters are forming their corresponding product with excellent yield (Table 3.A.2 entries 17–36) (TON>990).

3.A.4. Kinetic studies

Furthermore, kinetic studies were done for the hyroboration of ester using benzyl benzoate as substrate catalysed by **2.a.6** and **9** in C_6D_6. Kinetic experiment was monitored by ^{1}H NMR spectroscopy. To check the order of the ester hydroboration reaction for benzyl benzoate, the reaction was carried out with 0.1 mol % of **9** and 0.25 mmol of benzyl benzoate. A straight line with a negative slope was noticed from the plot of $\ln(C/C_0)$ vs time (see figure 3.A.3). This reveals that it is a pseudo first order rate of reaction. Moreover, to determine the order of the reaction with respect to the catalyst concentration, the hydroboration of benzyl benzoate was done by keeping same concentration of substrate (0.25mmol) with varied concentration of catalyst **2.a.6** (from 0.1 mol % to 1 mol %). From the plot of k_{obs} vs catalyst concentration exposes a linear increase of the reaction rate with respect to the catalyst concentration. That confirms a first order dependency with respect to the catalyst concentration. This was again confirmed by Vant hoff plot i.e. $\ln k_{obs}$ vs ln[cat] showing a linear graph and the slope value was determined to be 1.0 (slope = order of the reaction).

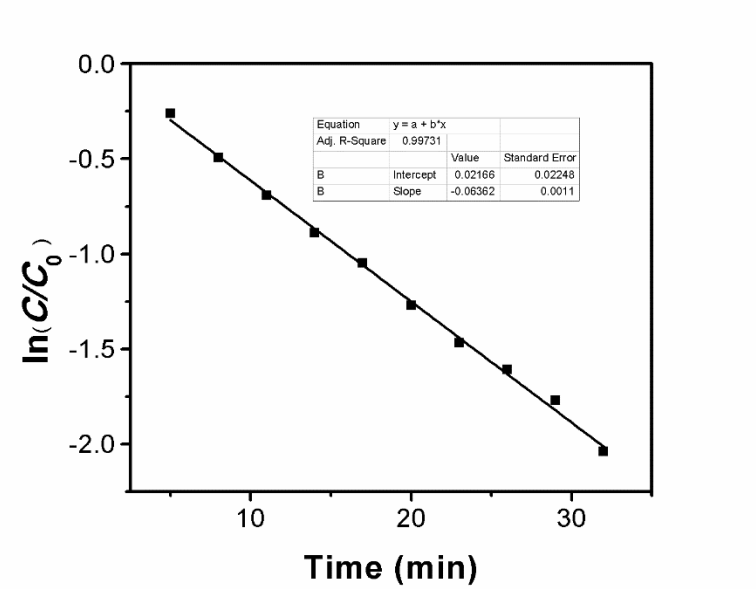


Figure 3.A.3. Kinetic studies of hydroboration of ester.

3.A.5. Conclusion

In summary, we have demonstrated a very straightforward and efficient catalysts $Mg\{N(SiMe_3)_2\}_2$ (**2.a.6)** , $L^1Mg\{N(SiMe_3)_2\}_2$ (**9)** [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3)] and $L^2Mg\{N(SiMe_3)_2\}_2$ (**10**) [L^2 = {ArNC (N^iPr_2)NAr} (Ar = 2,6– $^iPr_2$–C_6H_3)], further we have demonstrated their excellent catalytic activity for hydroboration of ester under very mild reaction condition. Further investigations into the reactivity of such complexes and directed towards the mechanism of this reaction, especially the nature of the active catalytic species, are underway in our laboratory.

Table 3.A.3. Details of the crystal structure determination of **9** & **10**

Empirical formula	$C_{33}H_{58}MgN_4OSi_2$ **(9)**	$C_{41}H_{74}MgN_4OSi_2$ **(10)**
Formula weight	607.32	719.53
Temperature	100(2) K	100(2) K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic
Space Group	*C* 2/*c*	*P* 21/*n*
Unit cell dimensions	a = 30.059(5)Å α= 90 b = 19.808(5)Å β=107.486(5)° c = 15.024(5)Å γ = 90	a=10.752(5)Å α = 90° b =6.875(5)Å β=117.992(5)° c=11.551(5)Å γ = 90°
Volume	7899(4) $Å^3$	4368(3) $Å^3$
Z	8	4
Density (calculated)	1.021 Mg/m^3	1.094 Mg/m^3
Absorption coefficient	0.133 mm^{-1}	0.129 mm^{-1}
F(000)	2656	1584
Crystal size	0.2 x 0.23 x 0.26 mm^3	0.18 x 0.21 x 0.25 mm^3
Theta range for data collection	1.283 to 30.585°.	2.061 to 29.626°
Index ranges	–42<=h<=42, –28<=k<=28, –21<=l<=21	–14<=h<=14, –51<=k<=51, –15<=l<=15
Reflections collected	77623	64589
Independent reflections	12074 [R(int) = 0.0573]	11918 [R(int) = 0.0593]
Completeness to theta = 25.240°	99.9 %	99.5 %
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	12074 / 0 / 384	11918 / 0 / 460
Goodness–of–fit on F^2	1.063	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.2126	R1 = 0.0602, wR2 = 0.1286
R indices (all data)	R1 = 0.0877, wR2 = 0.2249	R1 = 0.0773, wR2 = 0.1355
Largest diff. peak and hole	2.400 and –0.369 e.$Å^{-3}$	0.445 and –0.277 e.$Å^{-3}$

3.A.6. References

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Heterobimetallic (Group1/2) systems bearing bridging amido and *N,N'*-chelated guanidinate ligand

Abstract

Heterobimetalic systems of K/Mg and K/Ca bearing bridged two amido ligands and *N,N'* chelated guanidinate ligand {(ArNC(N^iPr_2)NAr)Mg{μ-$N(SiMe_3)_2$}$_2$K (THF)}[Ar=2,6– Me_2–C_6H_3](**11**) and {(ArNC(N^iPr_2)NAr)Ca{μ-$N(SiMe_3)_2$}$_2$K (THF)}[Ar=2,6– Me_2–C_6H_3](**12**) have been synthesized by the treatment of $L^1MgN(SiMe_3)_2$(THF) (**9**) or $L^1CaN(SiMe_3)_2(THF)_2$ (**6**) [L^1= {ArNC(N^iPr_2)NAr}] with $KN(SiMe_3)_2$ in THF at room temperature. Both compounds **11** & **12** were characterized by mutinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis. In solid state structures we have noticed that heterobimetallic Mg(μ_2-N)$_2$K four membered ring structure in compound **11** and Ca(μ_2-N)$_2$K ring in compound **12**.

3.B.1. Introduction

In recent years alkali and alkaline earth metal amides are the most widely used class of organometallic reagents.[1,2]. Their application as a reagent in different organic synthesis[3], salt metathesis[4,5] reagent for the synthesis of inorganic compounds[6] also as catalysis in polymerization reaction[7], Tishchenko reaction[8], hydroamination reaction[9]. Hexamethyldisilazane (HMDS) is one of the utmost studied amide ligands for different synthetic applications as well as for structural investigations.[10] Commercially available amide like LiHMDS, NaHMDS and KHMDS those approaching one hundred crystal structures containing these bases have appeared.[10] Similarly alkaline metal bis(trimethylsilylamide) plays an important role to developing organometallic chemistry.[11] Various ligand stabilized metal amide complexes have been synthesized directly using neutral ligand and alkali or alkaline earth metal (bisamide).[12] Additionally numerous examples of heterobimetallic

HMDS complexes with two different alkali metals (Li-Na, Li-K, and Na-K)[13] are known in literature and several examples of heterodimetallics HMDS compounds with alkali metal with alkaline earth metals (Li-Mg,[14] Li-Ca,[15] K-Mg,[16] Rb-Mg,[16] and K-Ca[17]) also known in literature. Heterobimetallic compound with only alkaline earth metal amides also known in literature.[18]

But surprisingly, N -donar bidentate monoanionic ligand stabilized Heterobimetallic complex containing a pair of alkaline earth metal and alkali metal are not known in literature. Earlier in our work we have demonstrated guanidinate ligand stabilized heteroleptic magnesium [{L^1MgN$(SiMe_3)_2$}(THF)] (**9**) and calcium amide [{L^1CaN$(SiMe_3)_2$}$(THF)_2$] (**6**) complexes. Starting with these heteroleptic Mg and Ca metal amide complexes, herein we reports first guanidinate ligand stabilized Heterobimetallic mixed alkali and alkaline earth metal amide complexes.

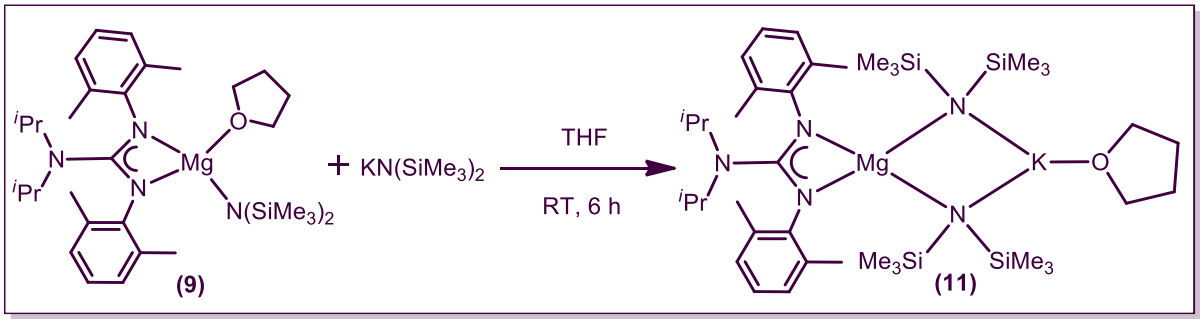
3.B.2. Results and Discussion

3.B.2.1. Synthesis and NMR spectroscopic data

Earlier from our group we have synthesized mixed guanidinato–amido Mg(II) and Ca(II) complexes by treating with one equivalent of free guanidine ligand L^1H [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3)] and one equivalent of magnesium bis{bis(trimethylsilyl)amide} i.e. [Mg{$N(SiMe_3)_2$}$_2$] in THF or reaction of one equivalent of free guanidine either L^1H [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3) with two equivalents of potassium hexamethyldisilazide *i.e.*, $KN(SiMe_3)_2$ in THF at 0 ^oC and followed by metathesis reaction with one equivalent of magnesium chloride/calcium iodide in THF at –78 ^oC led to the formation of corresponding guanidinate supported magnesium/calcium amides. Further, these guanidinato magnesium and calcium amides were reacted with potassium hexamethyldisilazide *i.e.*, $KN(SiMe_3)_2$ in THF at room temperature and stirring for another 4–6 h and formation of mixed metal amides. Crystalline compounds were isolated

from saturated hexane solution at 0 ^{o}C after one day. Compound **12** also have been prepared by treating with one equivalent of L^1H and excess of potassium hexamethyldisilazide *i.e.*, $KN(SiMe_3)_2$ in THF at 0 ^{o}C and followed by metathesis reaction with 1.2 equivalent of calcium iodide at –78 ^{o}C. After coming room temperature stirred for another 24h. Formation of compound **12** suggest that, initial formation of $[\{L^1CaN(SiMe_3)_2\}(THF)_2]$ (**6**) and further reaction with excess $KN(SiMe_3)_2$ and formation of desired compound.

Both the compounds were characterized by spectroscopic method i.e. multinuclear NMR(^{1}H, ^{13}C, ^{29}Si), analytical method i.e. C, H, N analysis and the molecular structures were confirmed by single crystal X–ray crystallographic studies.



Scheme 3.B.1. Synthesis of compound **11**

In ^{1}H NMR compound **11** and **12** display two singlet at 0.13 and 0.19 ppm and 0.09 and 0.1 ppm for the $N(Si\mathit{Me}_3)_2$ moiety, where the compound **9**, $L^1MgN(SiMe_3)_2(THF)$ and **6**, $L^1CaN(SiMe_3)_2(THF)_2$ the $N(Si\mathit{Me}_3)_2$ moiety resonate at 0.33 and 0.1 ppm. In ^{1}H NMR spectrum of **11** displayed that the aryl methyl protons *i.e.*, Ar–CH_3 of as one singlet at 2.46 ppm, in contrast to the corresponding precursor complex (**9**) in which it is showing two resonances at 2.21 and 2.46 ppm. However, compound **12**, the aryl methyl protons *i.e.*, Ar–CH_3 of resonate at two different peak at 2.33 and 2.59 ppm. Rest other peaks are matching with backbone guanidine ligand. Coordinated THF molecule with potassium metal showed two different peak at 1.35 and 3.63 ppm for compound **11** and 1.41 and 3.51 ppm for compound **12**.

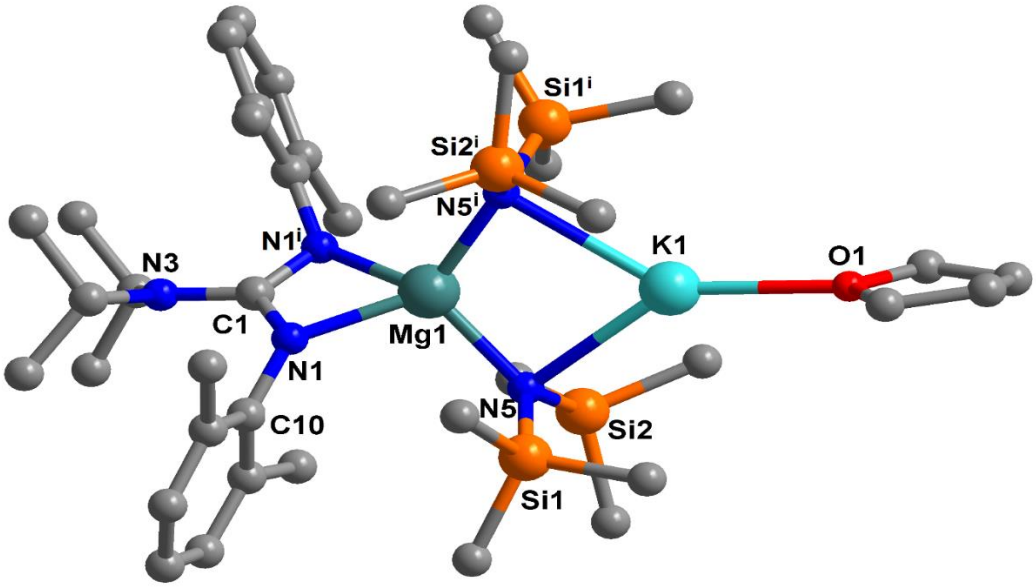
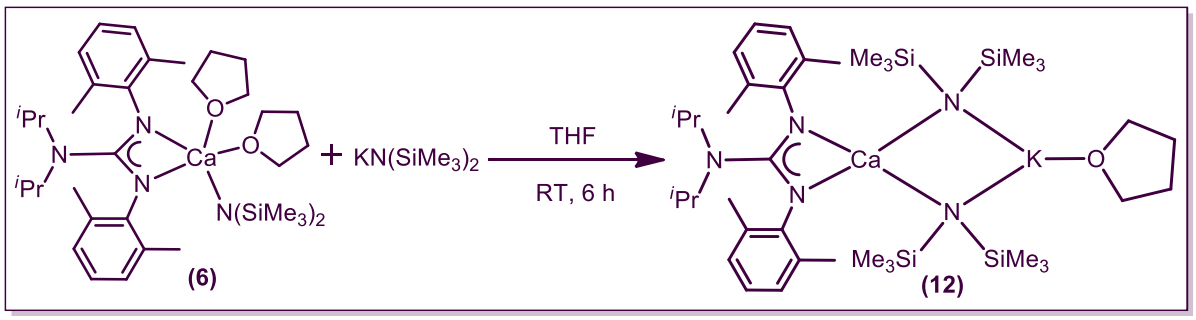
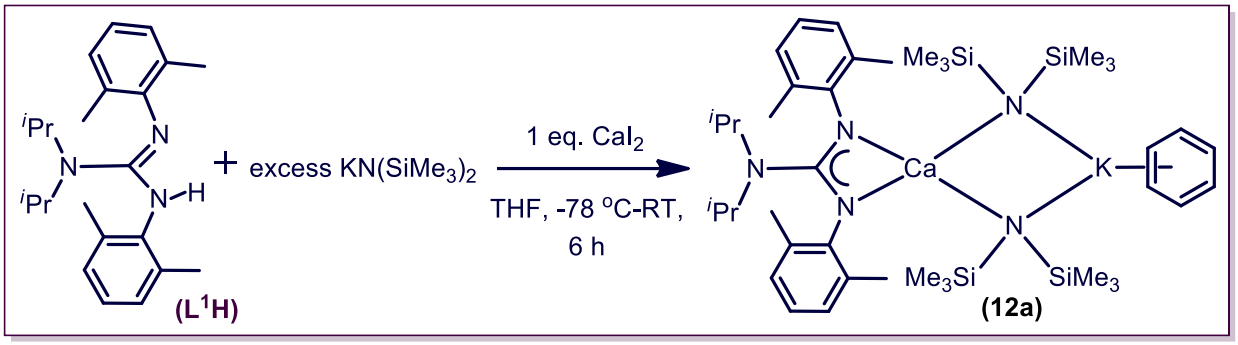


Figure 3.B.1: Molecular structure of **11**. Selected bond lengths (Å) and bond angles (deg) for **11**: Mg1–N1 2.1510(19), Mg1–N5 2.1162(18), K1–N5 2.872(2), K1–O1 2.646(3), Si2–N5 1.7139(19), Si1–N5 1.7201(19); $N1^{i}$–Mg1–N1 63.17(9), N1–C1–$N1^{i}$ 113.6(2), $N5^{i}$–Mg1–N5 107.64(11), $N5^{i}$–K1–N5 72.98(7), Si2–N5–Si1 119.53(10), Mg1–N5–K1 89.69(7).

to the corresponding ligand[19] of these metal complexes and other reported free tetra substituted guanidines (148–160 ppm).[20, 8b] The Si(CH_3)$_3$ peak of compound **11** resonate at 5.2 & 6.8 ppm and for compound **12,** 2.27 & 6.04 ppm respectively. ^{29}Si NMR showed signals at –21.5 ppm which is up field as compare to $L^1MgN(SiMe_3)_2(THF)$(**9**) (–8.11 ppm) and –15.6 ppm in **12** i.e. also up field as compare to $L^1CaN(SiMe_3)_2(THF)_2$ (**6**) (1.89 ppm).



Scheme 3.B.2. Synthesis of compound **12**



Scheme 3.B.3. Synthesis of compound **12a**

3.B.2.2. Single crystal X–ray structural characterization of compound 11 and 12

Crystals of the complexes {(ArNC(N^{i}Pr$_2$)NAr)MgK{N(SiMe$_3$)$_2$}$_2$(THF)}[Ar=2,6– Me$_2$–C$_6$H$_3$] (**11**) and {(ArNC(N^{i}Pr$_2$)NAr)MgK{N(SiMe$_3$)$_2$}$_2$(THF)}[Ar=2,6– Me$_2$–C$_6$H$_3$] (**12**) suitable for X-ray crystallographic analysis were grown from saturated hexane solution at 0 ^{o}C. Both the compounds were crystallise in monoclinic system with space group *C*2/*c*. Molecular structure, selected bond length and bond angles of compound **11** and **12** have represented in figure 3.B.1 and 3.B.2. X-ray crystallographic studies revealed that four membered MgKN$_2$ ring in compound **11**, where Mg centre is bonded to the guanidinate ligand in [*N*,*N'*] chelated fashion and the other sites are occupied by two bridged bis(trimethylsilyl)amido ligand, ensuing in distorted tetrahedral geometry. And another metal center i.e. K which is connected with two nitrogen atom of two bridged bis(trimethylsilyl)amido ligand and one oxygen atom of coordinated THF molecule and the metal center is distorted trigonal planar in geometry.

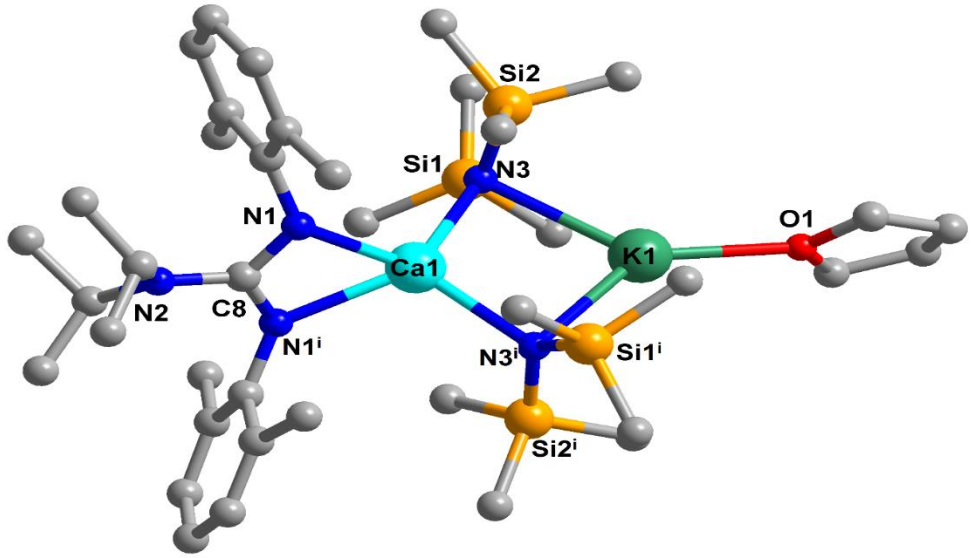


Figure 3.B.2: Molecular structure of **12**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **12**: Ca1–N1 2.3919(16), Ca1–N3 2.3890(17), Si1–N3 1.6976(18), Si2–N3 1.6994(18), N1–C(8) 1.348(2), K1–O1 2.635(3), K1–N3 2.8588(19); N1–Ca1–$N1^{i}$ 56.79(7), N3–Ca1–$N3^{i}$ 101.97(9), Ca1–N3–K1 88.53(5), $N3^{i}$–K1–N3 80.98(7), Si1–N3–Si2 125.19(10).

The Mg1–N5(bridged) bond distance 2.1162(18) in compound **11** is well agreement with Mg-N(bridged) bond distance 2.125(4) reported mixed Mg and Li amide complex $[\{(Me_3Si)_2N\}_3LiMg]$[14a] and mixed Mg-Ca metal amides $[CaMg\{N(SiMe_3)_2\}_4]$(2.145(5))[18b]. The Mg1–N5 bond distance is slightly longer than the guanidinate ligand stabilized magnesium amide {[ArNC($N^{i}Pr_2$)NAr]MgN($SiMe_3$)$_2$(THF)}[Ar=2,6– Me_2–C_6H_3(2)] Mg-N(terminal) bond distance 1.9904(18)Å, $[CaMg\{N(SiMe_3)_2\}_4]$ 1.975(7)[18b] and $[\{(Me_3Si)_2N\}_3LiMg]$ 1.998(4) Å.[14a]

Similarly, in compound **12,** Ca centre is bonded to the guanidinate ligand in [*N*,*N'*] chelate fashion and the other sites are occupied by two N atom of the two amido ligand, and K metal center is connected with two nitrogen atom of two amido ligand and one oxygen atom of coordinated THF molecule. The geometry of both the Ca & K metal centers are similar with

compound **11,** distorted teterahedral and trigonal planar in geometry. The key bond length and bond angles of compound **12** are listed in figure 3.B.2.

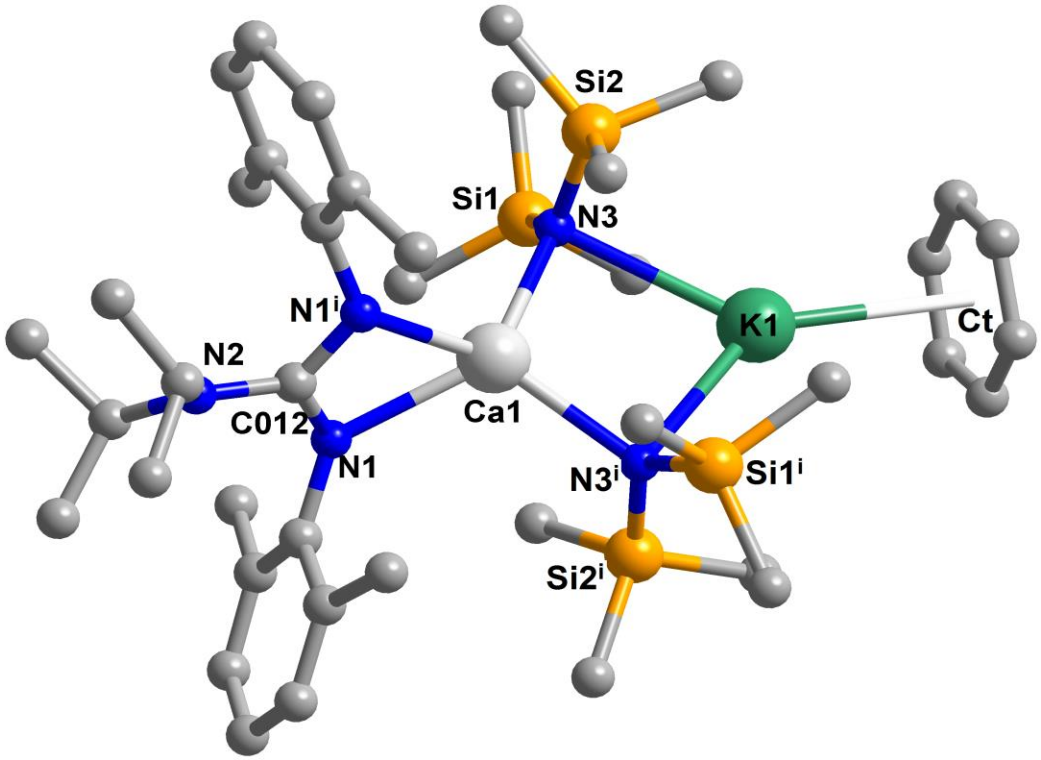


Figure 3.B.3: Molecular structure of **12a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **12a:** Ca1–N1 2.388(3), Ca1–N3 2.390(3), K1–N3 2.935(3), Si1–N3 1.698(3), Si2–N3 1.701(3), K1–Ct1 3.357(4), N1–C(012) 1.349(3); $N1^{i}$–Ca1–N1 56.99(13), N3–Ca1–$N3^{i}$ 103.81(13), Ca1–N3–K1 88.25(9), Si1–N3–Si2 123.74(17), N1–C(012)–$N1^{i}$ 115.2(4), N3–K1–$N3^{i}$ 79.70(11).

Ca1–N3 bond distance(bridging amide) in compound **12** of 2.3890(17) Å is very similar to those of 2.430(6) Å in $[Ca_2\{N(SiMe_3)_2\}_4]$ and 2.467(3) in compound $[CaMg\{N(SiMe_3)_2\}_4]$[18b]. The terminal Ca1–N^{t} bond lengthens by 0.24 Å on moving from compound **9,** 2.3919(16) to **11** Mg–N^{t} 2.1510(19) Å. Also in compound **12,** the Ca1–N^{b} bond 2.3919(16) Å lengthens by 0.273 Å compare with the compound Mg1–N^{b} bond distance in **11,** 2.1162(18) Å. The K1–N5 distance 2.872(2) Å in compound **11** is very similar with

compound **12**, K1–N3 2.8588(19) Å. But the K1–N5 distance 2.872(2) Å is comparatively longer than the mixed-alkali-metal HMDS, K-N 2.832 (3)[13]. The $N5^{i}$–K1–N5 72.98(7)^{o} bond angle of compound **11** is smaller than the compound **12**, $N3^{i}$–K1–N3 80.98(7)^{o}.

The most notable difference in bond angles of compound **11** and **12** i.e. N3–Ca1–$N3^{i}$ 101.97(9) with compared to the reported mixed metal amides. Specially the $N5^{i}$–Mg1–N5 107.64(11) angle widens by 6.4^{o} compare with [CaMg{$N(SiMe_3)_2$}$_4$] compound $N(1)^{b}$-Mg(1)-$N(2)^{b}$ 101.24(10). And N3–Ca1–$N3^{i}$ 101.97(9) angle widens by 19.64^{o} than compound [CaMg{$N(SiMe_3)_2$}$_4$] [$N(1)^{b}$-Ca(1)-$N(2)^{b}$ 82.33(8)][18b]. The Mg1–N1 2.1510(19) Å bond lengths of compound **11** are shorter by 0.24 Å than compound **12** Ca1–N1 2.3919(16) Å. The variation of bond length and angles between compound **11** and **12** can be justified by the relative Lewis acidities of the metals. Magnesium metal ionic radii 0.86 Å is considerably smaller than calcium ionic radii 1.26 Å.[21] Furthermore, when the compound **12** is crystallize in benzene the potassium metal centre environment changes which was coordinated with two bridging nitrogen and one thf molecule now instead of THF it has been coordinated with benzene(See figure 3.B.3). The compound **12a** was crystallize in monoclinic system with space group *C*2/*c*. Selected bond length and bond angles of compound **12a** depicted in figure 3.B.3. Both the metal centres one is four coordinate and one is three coordinated, similar with compound **12.**

Table 3.B.1. X-ray crystallographic data for compounds **11, 12 & 12a**

Compounds	**11**	**12**	**12a**
Formula	$C_{39}H_{74}KMgN_5OSi_4$	$C_{39}H_{76}CaKN_5OSi_4$	$C_{41}H_{74}CaKN_5Si_4$
Mol.mass	804.80	822.58	828.59
Size (mm)	0.25 x 0.2 x 0.17	0.28 x 0.22 x 0.18	0.16 x 0.13 x 0.1
Crystal system	monoclinic	monoclinic	monoclinic
Space Group	*C* 2/*c*	*C* 2/*c*	*C* 2/*c*
a (Å)	15.909(6)	15.9663(4)	17.572(3)
b (Å)	19.750(6)	20.2476(5)	18.310(2)
c (Å)	15.052(4)	15.0315(3)	16.325(2)
α (°)	90	90	90
β (°)	97.703(3)	97.6990(10)	111.985(7)
γ (°)	90	90	90
*V (*Å3)	4687(2)	4815.6(2)	4870.7(11)
Z	4	4	4
ρ (gcm^{-3})	1.141	1.135	1.130
μ (Mo-*K*α) (mm^{-1})	0.263	0.349	0.345
T (K)	100	100	100
θ (max.)	28.760	33.391	26.02
Unique reflections	6088	7231	4752
F(000)	1752	1792	1800
R(int)	0.0915	0.0600	0.1013
Parameters	243	274	247
*R*1	0.0484	0.0488	0.0550
w*R*2	0.1069	0.1258	0.0933
GOF	1.010	1.033	0.965

3.B.3. Conclusion

In conclusion, we have demonstrated that heterobimetallic (Group 1/2) systems containing Mg-K and Ca-K metal atoms, bearing bridged amido groups and *N,N'* -chelated guanidinate ligand which is connected to Group 2 metal atoms. These compounds can be synthesized by the reaction of $L^1MgN(SiMe_3)_2(THF)$(**9**) and $L^1CaN(SiMe_3)_2(THF)_2$ (**6**) with $KN(SiMe_3)_2$ in THF at room temperature. All the compounds were well characterized by multinuclear NMR, X-ray crystallographic studies and elemental analysis. To the best of our knowledge these are first examples of guanidinate ligand stabilized heterobimetallic mixed metal amide complexes. These heterobimetallic compounds are important precursor for the synthesis of soluble mixed metal hydride. Such investigations are underway in our laboratory.

3.B.4. References

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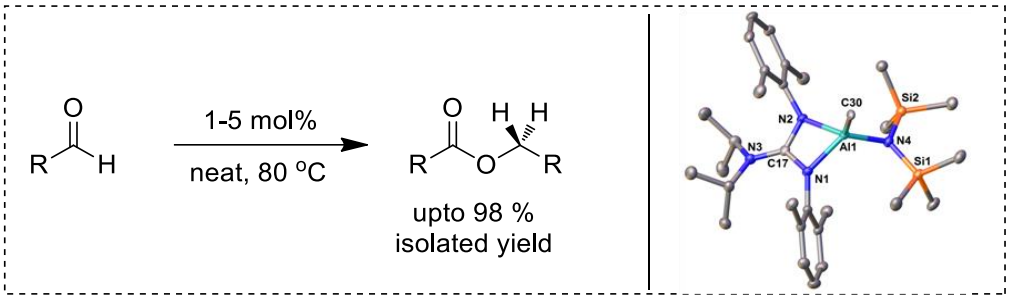
Guanidinato stabilized aluminum amides as efficient homogeneous catalysts for Tishchenko reaction

Abstract

Guanidinate supported mixed alkyl/amide aluminum(III) $L^1Al(Me)N(SiMe_3)_2$ **(17)** and aluminum(III) bis(amide) $L^1Al\{N(SiMe_3)_2\}_2$ **(18)** [L^1 = {ArNC(N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3)] complexes were synthesized by treatment of $L^1AlMeCl$, L^1AlCl_2/L^1AlI_2 with $LiN(SiMe_3)_2$ or $KN(SiMe_3)_2$ in toluene at –78 °C. Further, the aluminum mono and bis(amide) complexes **17** and **18** were shown to be highly efficient homogenous precatalysts for the dimerization of aldehyde to ester *i.e.* Tishchenko reaction in solvent free condition.



4.1. Introduction

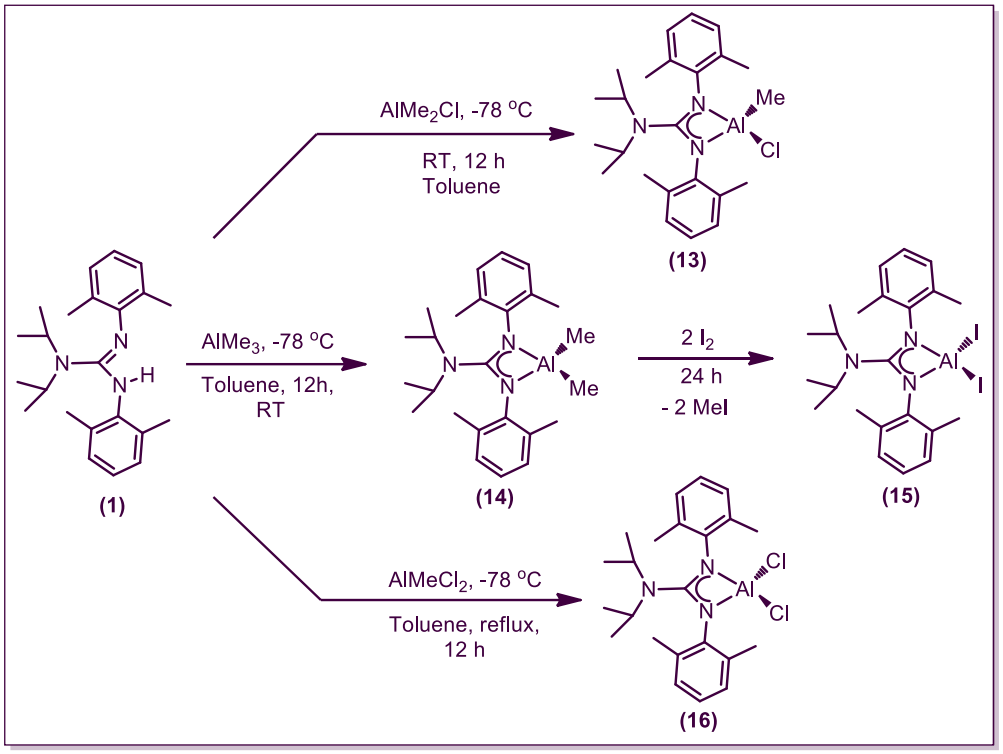
Dimerization of aldehyede to the corresponding carboxylic ester or Tishchenko reaction (or Claisen–Tishchenko reaction)[1] is known for about a century. The development of compounds and their capability to synthesis of ester from aldehydes (Tishchenko– reaction) leftovers and attractive aspiration for organic and inorganic chemists[2]. The reaction shows it is an industrially important procedure to synthesis of ester by dimerization of aldehydes which has found many applications in industries like foodstuff and fragrance. To catalyze the

reaction various transition metal and main group metal catalysts are reported in the literature. The originally studied catalyst for Tishchenko reactions were aluminium alkoxides[3]. Recently lanthanides[4] and actinides[5], particularly lanthanide formamidinates[6] showed active catalysts for the Tishchenko reaction. Furthermore, Hill and co–workers reported alkaline earth metal (Ca, Sr, Ba) amides[7] as precatalysts for making ester. Very recently Coles *et al.*, reported magnesium compounds supported bicyclic guanidinate[8] and amidinate ligands[9] as an active catalysts for the Tishchenko reaction. In this regard, we also reported that guanidinate stabilized homoleptic Mg(II), Ca(II) and Zn(II) complexes are active catalysts for Tishchenko reaction[10].

Aluminum amides have found ubiquitous application as precursors for AlN materials[11] and are of interest in catalysis and organic synthesis[12]. A range of applications of these complexes in organic transformation similar to hydroamination catalysis[13] have made metal imides as attractive target. The alkyl/amide functionalities have an important role on the reactivity of the metal complex[14]. The amido group which plays the role as a good leaving group. The supporting ligand *i.e.* guanidinate ligand also play significant role on metal center by providing steric and electronic support. As a result guanidinate ligand has received improved attention to coordination with Group 13 metals[15]. Although a handful example of aluminum based catalysts have been employed in literature for dimerization of aldehyde i.e. Tishchenko reaction however those catalyst produce less in yield for aromatic aldehydes. Therefore design a aluminum based catalyst still an attractive goal for Tishchenko reaction.

Herein, we report guanidinate ligand stabilized aluminium mono $L^1Al(Me)N(SiMe_3)_2$ (**17)** and bis(amide) $L^1Al\{N(SiMe_3)_2\}_2$ **(18)** complexes are the efficient precatalysts for the Tishchenko reaction.

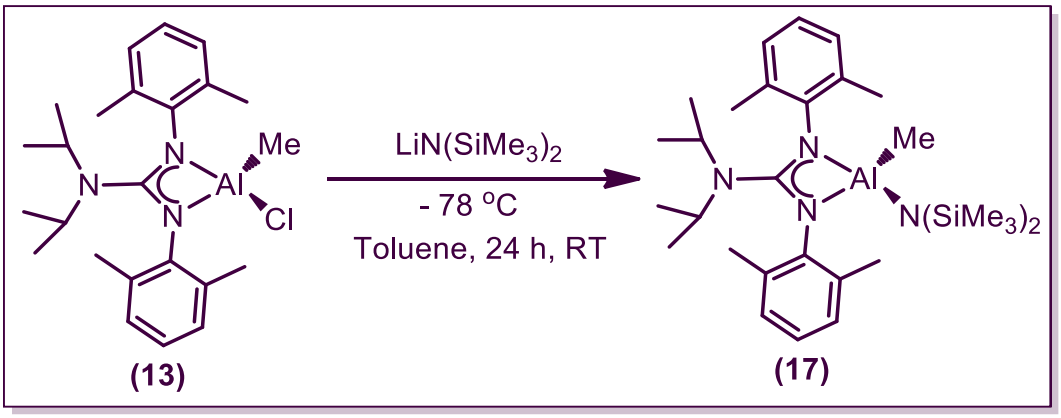
4.2. Results and discussion



Scheme 4.1. Synthesis of guanidinate supported aluminum halides

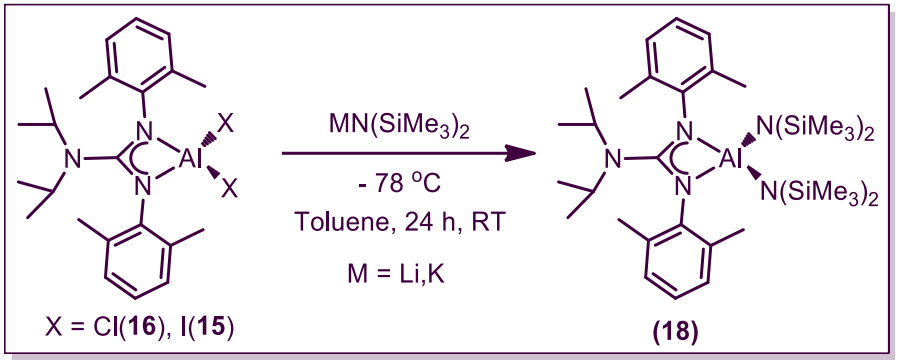
Bulky guanidine ligand (L^1H) [L = {ArNC (N^iPr_2)NAr} (Ar = 2,6– Me_2–C_6H_3)] is prepared according to the literature procedure[16]. Free ligand (L^1H) upon treatment with $AlMe_3$ in toluene at room temperature, evolution of methane gas formation of L^1AlMe_2 (**14**). $L^1AlMeCl$ **(13)** and L^1AlX_2{X=Cl **(16)**, I **(15)**} were prepared by reaction L^1H with $AlMe_2Cl$ in toluene at room temperature and $AlMeCl_2$ in toluene at reflux condition. L^1AlI_2 was prepared by previously reported procedure by Roesky and co–workers *i.e.* diaklyl complex undergo substitution with I_2 in toluene solution at r.t to form corresponding dihalide species[17]. $L^1AlMeCl$ **(13)** and L^1AlI_2 **(15)** both the compounds were isolated as colorless crystalline compound in toluene at –20 °C. Compound $L^1Al(Me)N(SiMe_3)_2$ (**17**) was prepared in a very good yield by the reaction of $L^1AlMeCl$ **(13)** with one equivalent of $LiN(SiMe_3)_2$ in toluene

(Scheme 4.2) at –70 °C and after coming to r.t stirred for another 12 hours. Crystals were obtained in toluene solution at –30 °C as colorless block.



Scheme 4.2. Synthesis of compound $L^1Al(Me)N(SiMe_3)_2$(17)

In ^{1}H NMR spectrum **17** display one singlet at δ = –0.13 ppm for the resonance of methyl proton Al(*Me*) at δ = 0.19 ppm corresponding to the methyl proton resonance of the N(Si*Me*$_3$)$_2$ group. In ^{29}Si NMR spectrum displays one singlet at δ = –5 ppm for N(*Si*Me$_3$)$_2$ group. The remaining resonances are attributed to the guanidinate ligand. Aluminium bis(amide), $L^1Al\{N(SiMe_3)_2\}_2$ **(18)** was obtained by treating L^1AlCl_2 **(16)** or L^1AlI_2 **(15)** with lithium bis(trimethylsilylamide) or potassium bis(trimethylsilylamide) at –70 °C and at r.t and it was stirred for another 12 hours. The ^{1}H NMR spectrum of **18** shows two singlets (δ = 0.13 and 0.23 ppm) with equally intense for the N(SiMe$_3$)$_2$ group and corresponding resonance in the ^{29}Si NMR spectrum (δ = –20.44 and –20.52 ppm).



Scheme 4.3. Synthesis of compound $L^1Al\{N(SiMe_3)_2\}_2$ (18)

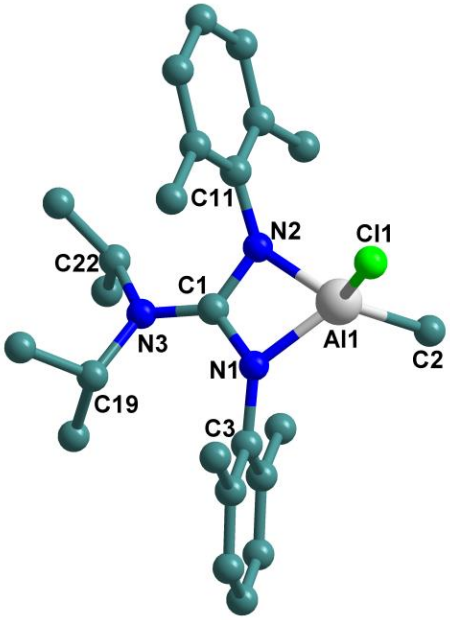


Figure 4.1. Molecular structure of **L^1AlMeCl**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **13**. Al1–N1 1.895(3), Al1–N2 1.885(3), Al1–C2 1.966(4), Al1–Cl1 1.966(4), N1–C1 1.367(4), N2–C1 1.355(5), N1–C3 1.437(5), N3–C1 1.355(5), N3–C22 1.492(5); N2–Al1–N1 70.87(14), N1–Al1–C2 117.28(15), N2–Al1–C2 124.37(16), N1–Al1–Cl1 118.22(12), N2–Al1–Cl1 112.66(11), C2–Al1–Cl1 109.33(13), N2–C1–N1 107.2(3), N3–C1–N1 126.2(3).

Molecular structure for compounds **13** and **15** are depicted in figure **4.1** and **4.2**. Both the compound crystallizes in the monoclinic space group *P*2(1)/*c and P*2(1)/*n*. In compound **15** the Al center is coordinated to two nitrogen atom of guanidinate ligand and two iodine atoms. The Al center is distorted tetrahedral in geometry. The Al–I1 and Al1–I2 bond length is

2.5080(10), 2.5055(12) which is well agreement with reported guanidinate Al–I bond length. The C-N bond distances linked with the sp^2 carbon (C17) of the ligand are almost equal (see figure 4.1) and are significantly shorter than a usual C–N single bond, suggesting that the three C-N bond hold a partial double-bond character with typical C17–N1, C17–N2 and C17–N3 distance of N1 C17 1.372(3), N2 C17 1.356(3), and 1.343(3) Å respectively. The Al1–C2 1.966(4) and Al1–Cl1 1.966(4) bond distances are closely related with compounds reported by Bergman and co-workers.

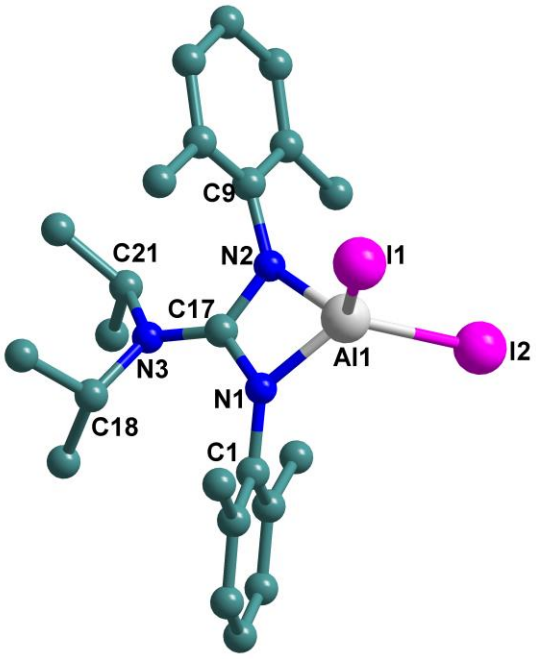


Figure 4.2. Molecular structure of **L^1AlI_2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **15**: Al1–I1 2.5080(10), Al1–I2 2.5055(12), Al1–N1 1.871(2), Al1–N2 1.875(2), N1–C17 1.372(3), N2–C17 1.356(3), N1–C1 1.437(3), N3–C17 1.344(3), N3–C21 1.493(3); N1–Al1–N2 71.72(10), N1–Al1–I2 119.49(8), N1–Al1–I1 117.11(7), N2–Al1–I1 114.33(7), N2–Al1–I2 118.95(7), I2–Al1–I1 110.60(3), N2–C17–N1 107.1(2), N3–C17–N2 127.0(2), C1–N1–Al1 135.76(17), C17–N3–C21 119.2(2).

Single crystal X–ray confirmed compound **17** crystallize in the monoclinic space group *P*2(1)/*n*. The amido group and the CH_3 groups are positioned opposite sides of the four

membered CN_2Al ring. The Al–C30 bond length 1.976(2) of the Al–methyl moiety is within the expected range for Al alkyl complexes[18]. The Al–N4 bond length 1.844(2) is close to the predicted range of 1.79–1.85 Å[19].

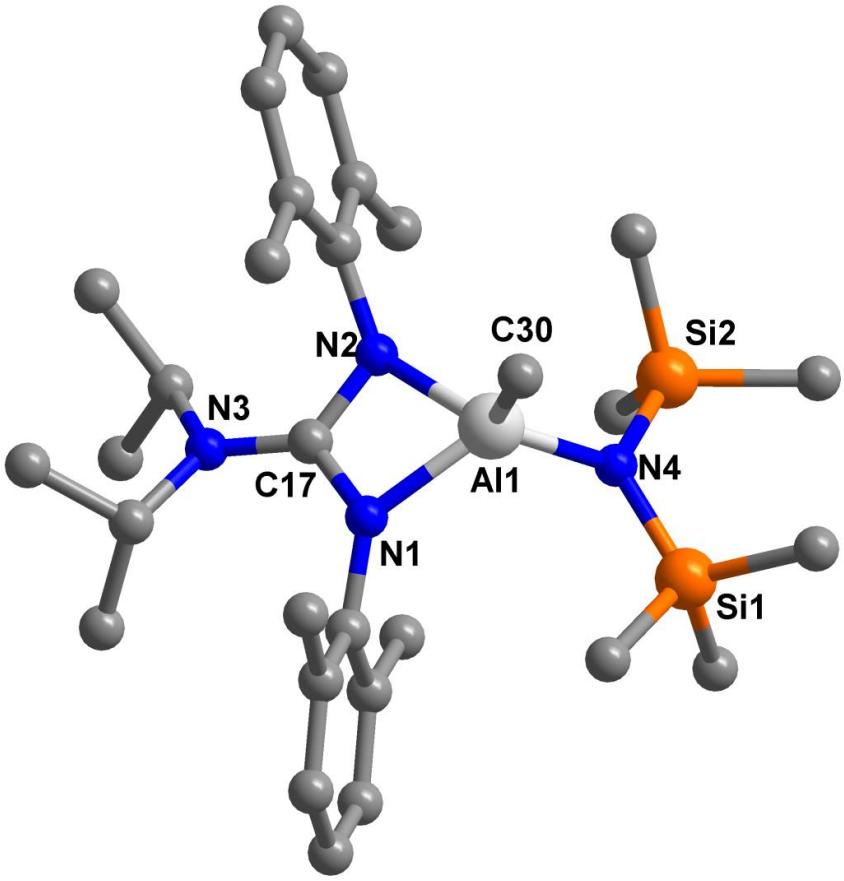
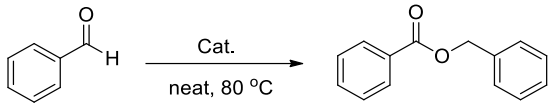


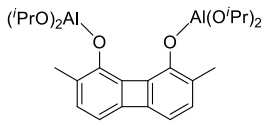
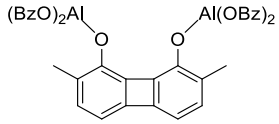
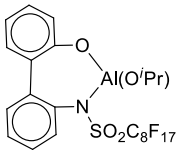
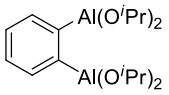
Figure 4.3. Molecular structure of $L^1Al(Me)N(SiMe_3)_2$ (**17**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **17**. Al1–N1 1.921(2), Al1–N2 1.962(2), Al1–N4 1.844(2), Al1– C30 1.976(2), Si1–N4 1.730(2), Si2–N4 1.725(2), N1–C17 1.353(3), N3–C17 1.355(3), C1–N2 1.444(3); N1–Al1–N2 68.83(9), N4–Al1–N1 118.69(10), N(4)–Al1–N2 118.58(10), N2–Al1–C30 118.50(10), N4–Al1–C30 111.90(10), N1–Al1–C30 114.15(10), Si2–N4–Si1 121.69(12), Si2–N4–Al1 117.99(12), Si1–N4–Al1 119.88(12), N1–C17–N2 107.5(2), C9–N1–Al1 135.20(17), N1–C17–N2 107.5(2).

4.3. Catalytic Studies

By employing both the compounds $L^1Al(Me)N(SiMe_3)_2$ (**17)** and $L^1Al\{N(SiMe_3)_2\}_2$ **(18)** we have demonstrated the catalytic activity towards Tishchenko reaction i.e. dimerization of aldehydes to ester. The standard reaction of benzaldehyde to form benzyl benzoate was chosen with 1–5 mol% catalyst at 80 ^oC (Table 4.1). Reactions were carried out in solvent free (neat) condition as well as in solvent C_6D_6 in NMR scale. In neat condition reaction is faster compare to in solvent, but both the cases yields are comparable. Using same catalyst loading reaction was performed in both neat and solvent (benzene) condition in different time interval. From the progress of the reaction it was noticed that in solvent condition reaction is going slowly compared to neat condition. The reactions were monitored and yield was calculated by ^1H NMR spectroscopy from the reaction mixture. The increase in the intensity of proton signal of benzyl group, simultaneous with a decrease in the proton signal of aldehyde in the ^1H NMR spectrum provided evidence for the formation of benzyl benzoate.

Table 4.1. Tishchenko reaction of benzaldehyde giving benzyl benzoate.



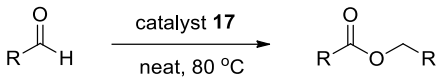
Entry	Catalyst	Cat. load. (mol%)	Conditions[a] Time(h)	Yield[b]	Ref.
1	$Al(OiPr)_3$	1	r.t.,-	51	4b
2		1	r.t., 5	67	3d
3		1	r.t., 5	76	3e
4		2	r.t., 5	68	3e
5		1	r.t., 23	58	3g
6	**17**	1	80, 14	92	
7	**17**	2	80, 10	94	
8	**17**	5	80, 8	95	
9	**18**	2	80, 24	85	
10	**18**	5	80, 18	87	

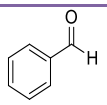
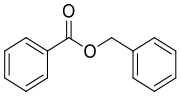
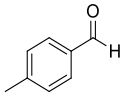
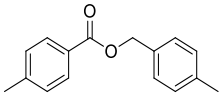
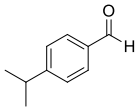
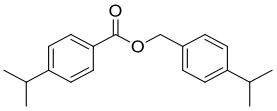
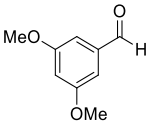
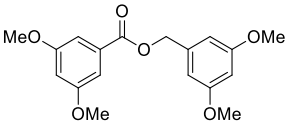
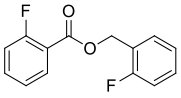
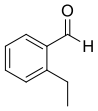
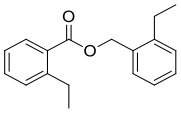
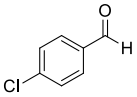
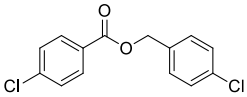
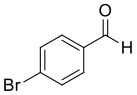
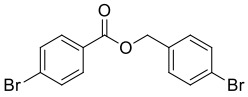
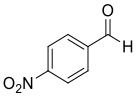
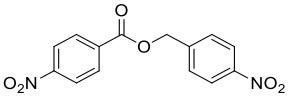
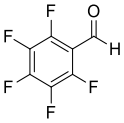
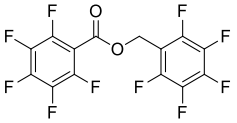
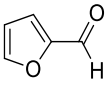
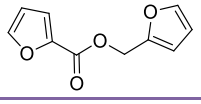
[a] Temparature in °C and Time in hour. [b] Isolated yield after purification by column chromatography.

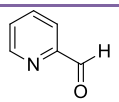
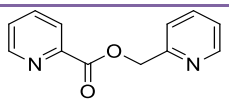
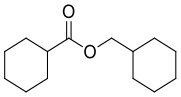
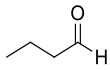
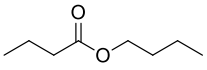
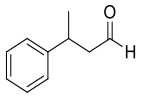
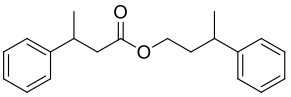
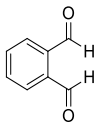
There was no side product in the reaction mixture without corresponding ester product. The reactions were done in preparative scale in solvent free condition to determine the isolated yield and full characterization of the product. A comparison between compound **17** and **18** with reported aluminum catalyst (Table 4.1, entries 1–10), In table 1 using standard aluminium catalyst $Al(OiPr)_3$ led to a low yield of product (Table 4.1, entry 10)[4b]. Other aluminium based catalysts (Table 4.1, entries 2–5)[3d,3e,3g] also did not reach the level of

activity of compound **17**. This because of ligand effect. Basicity of the ligand bound to the metal and the Lewis acidity of the metal center play vital role in the catalytic activity. Between compound **17** and **18**, **17** shows slightly better catalyst than **18**.

Table 4.2. Esterification of aldehydes.



entry	Substrate(R)	cat. load [mol %]	Time [h]	product	Yield [%][a]
1		2	10		93
2		2	10		85
3		2	10		84
4		2	24		-
5		2	10		84
6		5	24		-
7		2	10		90
8		2	10		91
9		2	10		90[b]
10		2	15		83
11		5	24		10[c]

12		5	24		20[c]
13		1	5		98
14		1	4		97
15		1	6		95
16		1	1		94

[a] Isolated yields. [b] solvent, toluene, 80 ^{o}C. [c] NMR yield.

After completion of the reaction GC–MS was taken from the reaction mixture there with product mass another one mass peak is showing at 265 which is one product $PhCON(SiMe_3)_2$ of the catalytic cycle.

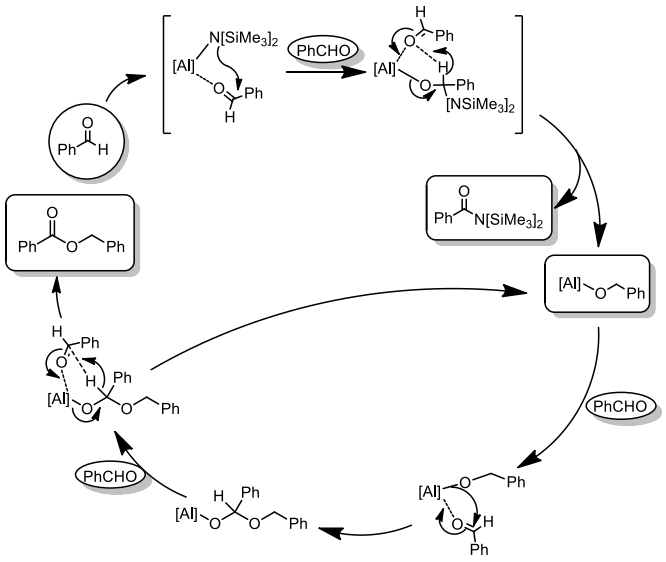


Fig. 4.4. Proposed mechanism for Tishchenko reaction using catalyst **17** and **18**

The success of this reaction of benzaldehyde promotes us to explore the substrate scope to other commercially available aldehydes. Result of this catalytic dimerization of aldehydes using 2 mol% catalyst of **17** in neat at 80 ^{o}C summarized in Table 4.2. A variety of aldehydes were used effectively, including aromatic, aliphatic and heterocyclic aldehydes to their

corresponding esters. For aromatic aldehydes substituent in different position of the ring has not effect on product yield (Table 4.2, entry 1–9) except entry no 4 and 6. Substituent in all five position of aromatic ring yield also good (Table 4.2, entry 10). In addition for aliphatic aldehydes catalyst loading was 1 mol% and time (4–6h) also less compare to aromatic aldehydes. The dimerization of pivaldehyde was faster than any other aldehyde with quantitative yield within an hour (Table 4.2, entry 16). Other aldehydes like heterocyclic are forming their corresponding product with less yield *i.e.* up to 20% (Table 4.2 entries 11 & 12).

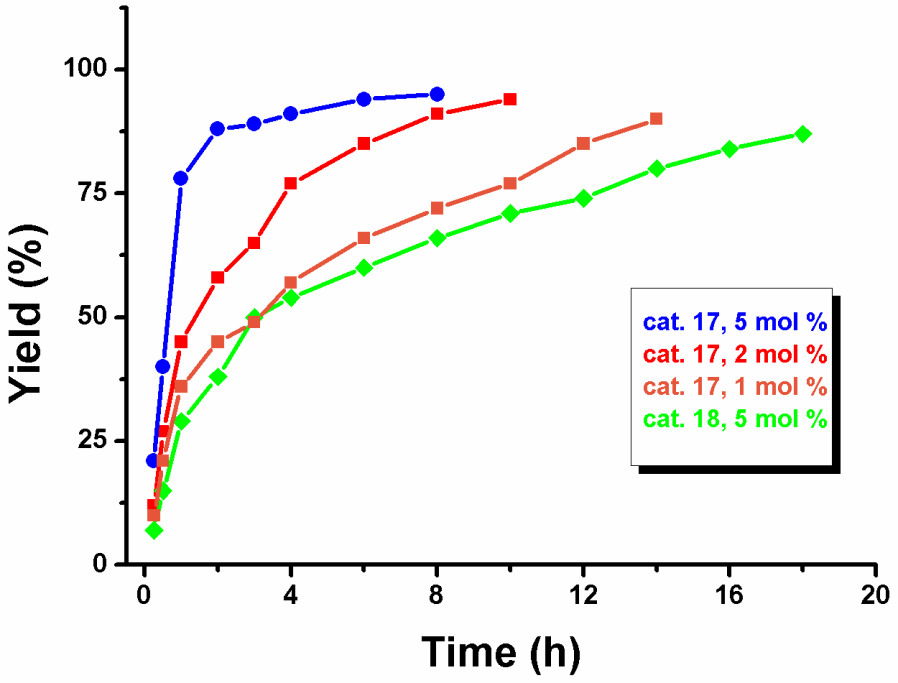


Fig. 4.5. Yield vs time plot at different catalyst loading.

From the plot of yield vs time it was noticed that using catalyst **17,** 80% of product was forming within one hour later the reaction becoming slow and it taking another 7 hours to complete the reaction.

Table 4.3. Crystallographic data of compounds **13, 15** & **17**

Formula	$C_{24}H_{35}N_3AlClN_3$**(13)**	$C_{23}H_{32}AlI_2N_3$**(15)**	$C_{30}H_{53}AlN_4Si_2$**(17)**
Mol.mass	427.98	631.30	552.92
Temperature	100 K	100 K	100 K
Size (mm)	0.1 x 0.087 x 0.065	0.15 x 0.11 x 0.09	0.21 x 0.17 x 0.11
Crystal system, space Group	Triclinic, $P\bar{1}$	Monoclinic, *P*2(1)/*c*	Monoclinic, *P*2(1)/*n*
a (Å)	9.341(19) Å	15.134(5)	9.396(3)
b (Å)	9.379(17) Å	9.710(3)	11.854(4)
c (Å)	15.764(3) Å	18.027(6)	29.828(9)
α (°)	101.106(13)	90.000	90.000
β (°)	95.420(13)	107.081(2)	98.264(2)
γ (°)	112.417(12)	90.000	90.000
V (Å3)	1231.1(10)	2532.2(17)	3288(2)
Z, Calculated density	2, 1.154 Mg/m^3	4, 1.656 Mg/m^3	4, 1.117 Mg/m^3
Absorption coefficient	0.205 mm^{-1}	2.533 mm^{-1}	0.159 mm^{-1}
F(000)	460	1240	1208
Theta range for data collection	2.68 to 25.50°.	2.36 to 25.49 deg.	1.38 to 25.50 deg
Reflections collected / unique	16837/4579 [R(int) = 0.0580]	31222 / 4709 [R(int) = 0.0350]	39417 / 6118 [R(int) = 0.1040]
Completeness to theta	99.7 %	100.0 %	100.0 %
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.7458 and 0.6622	0.7461 and 0.4742	0.7457 and 0.6333
Data / restraints / parameters	4579 / 6 / 259	4709 / 0 / 270	6118 / 0 / 349
Goodness–of–fit on F^2	1.050	1.037	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0772, wR2 = 0.2002	R1 = 0.0216, wR2 = 0.0489	R1 = 0.0503, wR2 = 0.1223

4.4. Conclusion

In summary, we have synthesized bulky guanidinate ligand supported Al(III), mixed alkyl/halide(**13**), dialkyl(**14**) and dihalide(**15** & **16**) complexes. Furthermore, guanidinato mixed alkyl/amide complex(**17**) has been prepared by reaction with alkyl/halide(**13**) and lithium bis(trimethylsilylamide) in toluene. Similarly, aluminium bis(amide) (**18**) complex has been synthesized by reaction with dihalide (**15** & **16**) complexes with either lithium or potassium bis(trimethylsilylamide) in toluene. Both the compounds **17** and **18** display excellent catalytic activity for Tishchenko reaction *i.e.* aldehydes to give their corresponding carboxylic ester.

4.5. References

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Guanidinate stabilized germanium(II) and tin(II) amide complexes and their catalytic activity for aryl isocyanate cyclization

Two different synthetic routes for the preparation of guanidinate stabilized germanium(II) and tin(II) amide complexes have been established. First, the reaction of one equiv of bulky guanidine ligand either L^1H or L^2H [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3) and L^2 = {Ar'NC (N^iPr_2) NAr'}(Ar' = 2,6- $^iPr_2$-C_6H_3)] with two equiv. of $KN(SiMe_3)_2$ and one equiv of metal dihalide *i.e.*, MCl_2{M = Ge(dioxane) and Sn} led to the formation of guanidinate supported germanium(II) amide, *i.e.*, $L^1GeN(SiMe_3)_2$ (**19)** and tin amide, *i.e.*, $L^1SnN(SiMe_3)_2$ (**20**) and $L^2SnN(SiMe_3)_2$ (**21**) complexes, respectively. Second, deprotanation of L^1H upon treatment with $M[N(SiMe_3)_2]_2$ (M = Ge and Sn) in C_6D_6 at 80 ^oC for 12 h, afforded the compounds $L^1MN(SiMe_3)_2$ M = Ge(**19**) and Sn(**20**), respectively. X-ray crystal structures of **19** and **20** revealed that both are in monomeric and metal centers in distorted tetrahedral environments with one vertex occupied by a stereo chemically active lone pair of electrons.

5.A.1. Introduction

In 1970, Lappert and co-workers reported the first transition metal guanidinate complex.[1] Since then, a large number of guanidinate supported coordination complexes involving metals from across the periodic table have been described.[2] In recent years, the chemistry of guanidinate stabilized low oxidation state metal complexes with metal-metal (single or multiple bonded) or metal with non bonded electrons or both is the emerging area.[3] To isolate such unusual molecules the utilization of bulky guanidine ligand systems are very important, because these can provide steric and/or electronic protection from processes such

as disproportionation, oligomerization etc. In this context, some benchmark inventions in the main group chemistry, notably, in 2007, Jones et al. reported bulky guanidinate stabilized magnesium complex with Mg–Mg bond, where the magnesium oxidation state is +1.[4] Same research group has also been isolated guanidinate stabilized low valent Ga(I)[5] complex and Ge(I) complex containing Ge–Ge bond[6] with non bonded electrons at each metal centre. On the other hand, the chemistry of the related amidinate and *β*-diketiminate supported low valent and/or low oxidation of main group metal complexes is well documented.[7] In Group 14 low valent heteroleptic complexes, particularly, low valent amides, Richeson and co-workers reported amidinate germanium(II) and tin(II) amides.[8] Roesky et al., demonstrated the amidinate and *β*-diketiminate stabilized tin amides.[9] In 2004, Lappert et al. reported structurally characterized *β*-diketiminate stabilized low valent tin compounds including tin amide compound.[10] In contrast, guanidinate supported low valent Group 14 complexes are poorly developed. Although, there are some reports on guanidinate supported germylenes, stannylenes and plumbylenes.[11] Very recently, Tacke et al. reported the structurally characterized guanidinate supported silicon amide complex.[12] Recently, Růžička and his co-workers described guanidinate stabilized tin amide complexes, but those are not structurally characterized.[13] However, in 2009, Chen, Rheingold and co-workers reported the structurally characterized germanium(II) amido complex, which is prepared by the insertion of carbodiimide into the Ge–N bond in diaminogermylene.[14] Apart from this, to the best of our knowledge no other structurally characterized guanidinate supported germanium(II) and tin(II) amide complexes are reported in the literature.

5.A.2. Synthesis of Guanidinato Germanium(II) and Tin(II) amides

Guanidines are compounds containing N_3C core, in which central sp^2 hybridized carbon atom is connected to one imino group and two amino groups. Various synthetic routes have been reported for the preparation of guanidines.[15] Among all, the important and widely used method of preparation, is the addition of metallated amides to bulky aryl carbodiimides (RN=C=NR), and followed by aqueous work up led to the formation of bulky aryl guanidines.

For this work we chose two bulky guanidine L^1H and L^2H [L^1 = {$ArNC(N^iPr_2)NAr$} (Ar = 2,6- Me_2-C_6H_3) and [L^2 = {$Ar'NC(N^iPr_2)NAr'$}(Ar' = 2,6- $^iPr_2$-C_6H_3)] ligand systems (Figure 5.A.1).

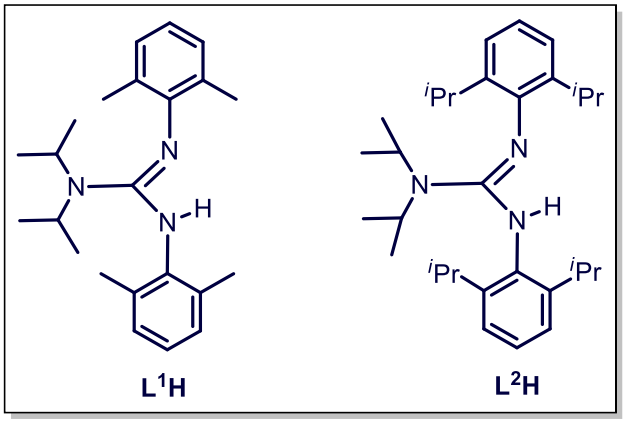
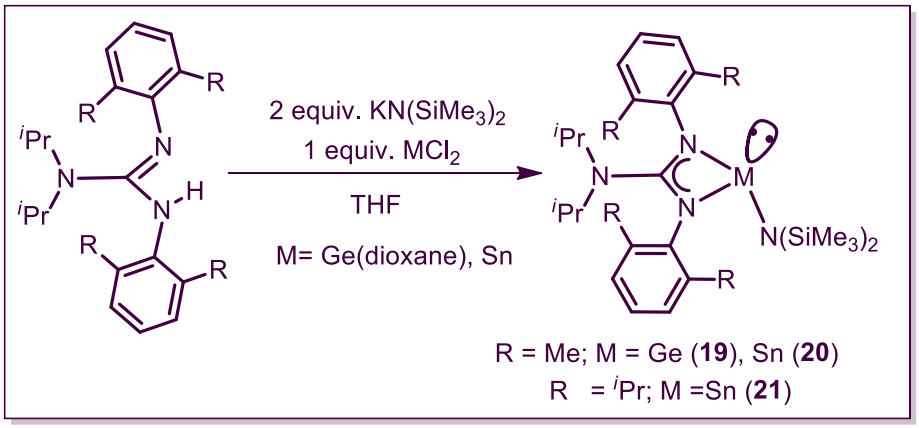


Figure 5.A.1. bulky guanidine ligands, L^1H and L^2H

L^2H reported by Jones and co-workers by treating metallated amide (LiN^iPr_2) with ^{dipp}carbodiimide *i.e.*, (ArN=C=NAr); (Ar = 2, 6- $^iPr_2$-C_6H_3) and followed by aqueous work up.[16] Thus, bulky aryl carbodiimides are important precursors for the preparation guanidines and related amidines. Classical method of preparation of bulky aryl carbodiimides is the desulphurization of thiourea in the presence of HgO and magnesium sulphate in toluene at reflux temperature.[17] Recently, our group has been investigated the new synthetic route for an

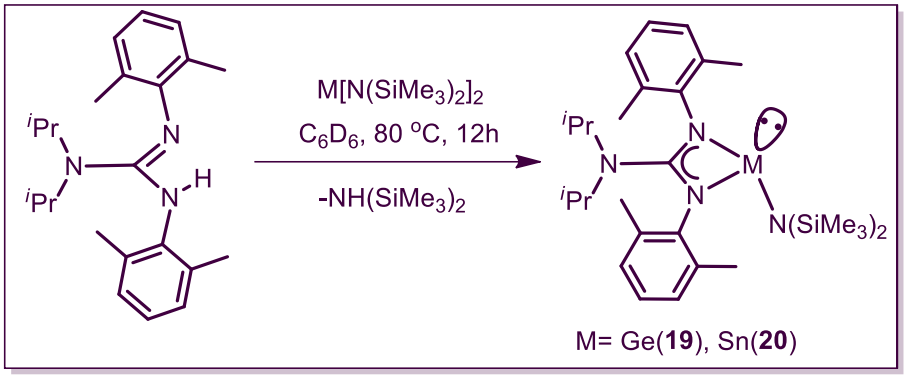
easy access of various bulky aryl symmetrical and unsymmetrical carbodiimides by the desulphurization of the corresponding thioureas. L^1H has been prepared by using ^{xyl}carbodiimide *i.e.* (ArN=C=NAr); (Ar = 2,6- Me_2-C_6H_3) and following the same method reported by Jones and co-workers.

Reaction of one equivalent of free bulky guanidine either L^1H or L^2H with two equivalents of potassium hexamethyldisilazide *i.e.*, $KN(SiMe_3)_2$ in tetrahydrofuran at 0 ^oC and followed by metathesis reaction with one equivalent of metal dihalide of germanium(dioxane) or tin in THF at 0 ^oC led to the formation of corresponding guanidinate supported metal amides (Scheme 5.A.1).



Scheme 5.A.1. Syntheses of compounds **19**-**21**.

Alternatively, we have investigated another synthetic route for the preparation of guanidinate supported germanium(II) and tin(II) amide complexes. For this synthetic route, NMR scale reactions were conducted by using Young valve NMR tube. Treatment of L^1H with $M[N(SiMe_3)_2]_2$ (M = Ge or Sn) in C_6D_6 at 80 ^oC for 12 h, afforded the guanidinate germanium(II) and tin(II) amide complexes, **19** and **20**, respectively. Deprotonation of N–H moiety of L^1H upon treatment with metal bis(amide) through an elimination of $NH(SiMe_3)_2$ which resonates at 0.9 ppm was observed in ^1H NMR spectroscopy (Scheme 5.A.2).



Scheme 5.A.2. Synthesis of compounds **19** and **20**

All these compounds (**19 - 21**) are readily soluble in organic solvents such as tetrahydrofuran, diethyl ether, toluene, benzene and hexane. Compounds **19, 20,** and **21** were isolated as colorless, crystalline solids in 88%, 86% and 75% yields, respectively.

5.A.3 Spectroscopic Characterization

Moreover, compounds **19-21** were characterized by multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR and IR spectroscopy methods. Furthermore, compounds **19** and **20** were confirmed by single crystal X-ray structural analysis.

^{1}H and ^{13}C NMR spectra display the expected set of ligands proton and carbon signals. In the ^{1}H NMR, the complete disappearance of N–H proton of L^{1}H and L^{2}H ligand systems gives a clue for the formation of new products. And also appearance of amido resonance *i.e.*, MN(SiMe$_3$)$_2$, in compounds **19-21** (0.13 - 0.26 ppm) indicates the formation of guanidinate stabilized metal amido substituent. In the ^{13}C NMR, N3*C* resonance exhibit for compounds **19, 20** and **21** at 165, 168.6 and 163.6 ppm, respectively. This is typical N3*C* resonance range (163 – 168.5 ppm) in ^{13}C NMR spectra, which is well in agreement with other related guanidinate metal complexes. The chemical shifts of all the ^{13}C and ^{1}H NMR signals observed for **19-21** appears slightly downfield from the corresponding signals in the free L^{1}H an L^{2}H. ^{29}Si NMR spectra for **19-21** exhibit in the range of – 3.68 to – 4.10 ppm. This is the

expected ^{29}Si NMR range for the four coordinated silicon atom.[18] Efforts were made to get high resolution mass spectra for compounds **19-21** and turned to be unsuccessful.

5.A.4. Crystallographic Characterization

Maintaining a *n*-hexane solution of **19** at –30 ºC overnight resulted in colorless single crystals suitable for X-ray structure analysis. Compound **19** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 5.A.1).

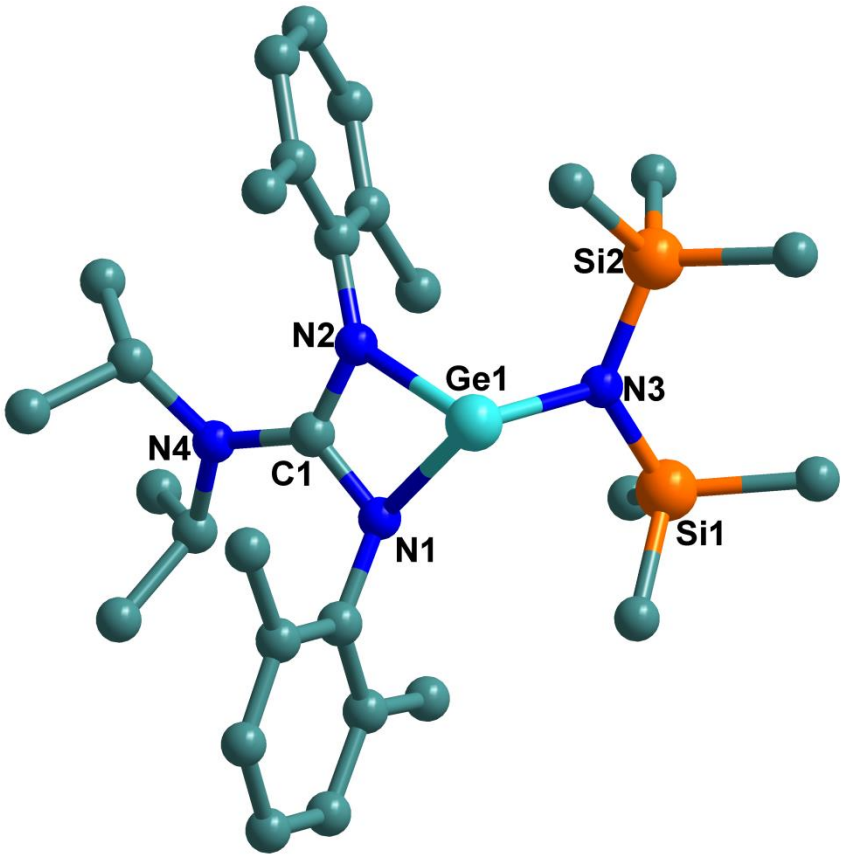


Figure 5.A.1. Molecular Structure of **19.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge1–N3 1.9395(12), Ge1–N1 2.0994(12), Ge1 –N2 2.0424(11), Si1–N3 1.7292(13), Si2 –N3 1.7352(13), N1–C1 1.3614(18), N2–C1 1.3407(18), N4–C1 1.3716(17), N1–C8 1.4411(18); N2–Ge1–N1 64.12(5), N3–Ge1–N1 105.80(5), N3–Ge1–N2 102.15(5), Si1–N3–Si2 125.34(7), Si1–N3–Ge1 117.18(7), N1–C1–N2 108.95(13), C1–N1–Ge1 91.22(8).

The metal center of compound **19** resides in distorted tetrahedral environment with one vertex occupied by a stereo chemically active lone pair of electrons. The sum of angles around the germanium atom is 271.92°. An overall pyramidal ligand array around the germanium center which consist with one bidentate guanidinate and the bis(trimethylsilyl) amido nitrogen center. The Ge–N_{amido} bond distance in **19** 1.9395(12) Å is slightly longer than those of Chen, Rheingold and coworker's guanidinate Ge amide complex[14] *i.e.*, [Ge^{II}(N($SiMe_2CH_2CH_2Me_2Si$))(^{i}PrNCN($SiMe_2CH_2CH_2Me_2Si$)N^{i}Pr] (1.880(2) Å) and Richeson's amidinato germanium amide complex $Ge^{II}[N(SiMe_3)_2][Me_3SiNC(^{t}Bu)NSiMe_3]$ (Ge–N_{amido} (1.9101 (19) Å).[8b]

The bond distances between germanium atom and two nitrogen atoms of the guanidinate ligand, *i.e.* Ge1 –N1 2.0994(12) Å and Ge1–N2 2.0424(11) Å are well in agreement with bond distances observed in [Ge^{II}(N($SiMe_2CH_2CH_2Me_2Si$))(^{i}PrNCN($SiMe_2CH_2CH_2Me_2Si$)N^{i}Pr] (Ge1–N1 2.0133(17), Ge-N2 2.0328(17) Å) and $Ge^{II}[N(SiMe_3)_2][Me_3SiNC(^{t}Bu)NSiMe_3]$ (Ge1–N1 2.037(2), Ge–N2 2.042(2) Å). However, these bond lengths are slightly longer in comparison to the other reported values [1.993(3) and 2.003(3) Å in [Ge^{II}(Giso)Cl] [Giso = {(2,6-$C_6H_3{}^{i}Pr_2N)_2CNCy_2$}][6]

The molecular structure of **20** has been determined by single crystal X-ray diffraction analysis (Figure 5.A.2). Colorless crystals of **20** suitable for single crystal X-ray analysis were obtained from a *n*-hexane solution at –30 °C after 1 day. Compound **20** crystallizes in the monoclinic space Group *P*2(1)/*n*. Selected bond lengths and bond angles are given in the caption of Figure 5.A.2. The geometry and the coordination number of the tin atom in compound **20** are same as those observed in compound **19**. However, N3–Sn1–N4 bond angle 59.13(17)° in **20** which is acute than that of compound **19 (**N2–Ge1–N1 64.12(5) °). The Sn–N_{amido} bond distance in compound **20** is 2.149(5) Å is longer than that of Ge–N_{amido}

bond distance of **19 (**1.9395(12) Å), this is expected due to the large covalent radii of tin element (1.39 Å) in comparison to that of germanium atom (1.20 Å).[19] However, $Sn–N_{amido}$ bond length is well in agreement with related amidinate stabilized tin(II) amide complexes such as $Sn^{II}[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ (2.121 (5) Å) and $Sn^{II}[N(SiMe_3)_2][^tBu NC(Ph)N^tBu]$ (2.116 (6) Å).

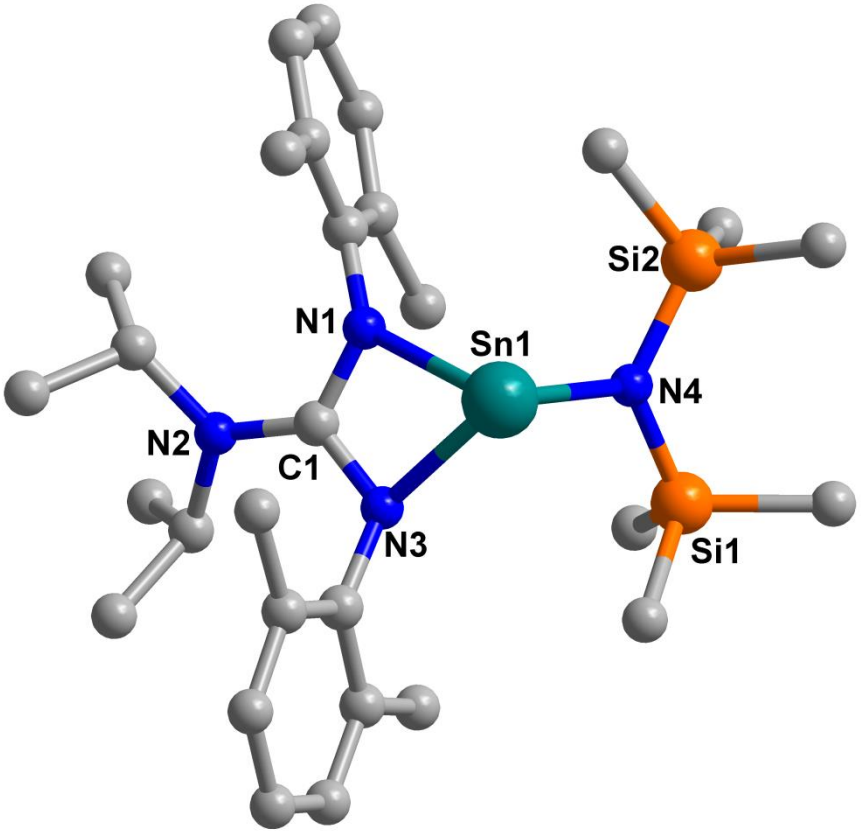


Figure 5.A.2. Molecular Structure of **20.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) of **20**: Sn1–N1 2.149(5), Sn1–N3 2.275(5), Sn1–N4 2.234(4), Si1 –N1 1.716(5), Si2– N1 1.723(6), C17 –N4 1.334(8), C17 –N3 1.364(7), C17–N2 1.380(7), N4–C1 1.414(7); N3–Sn1–N4 59.13(17), N1–Sn1–N3 102.4(18), N1–Sn1–N4 101.19(18), N4–C17–N3 111.1(5), Si1–N1 –Si2 124.2(3), Si1–N1 –Sn1 116.9(3), C17–N4–Sn1 95.6(3).

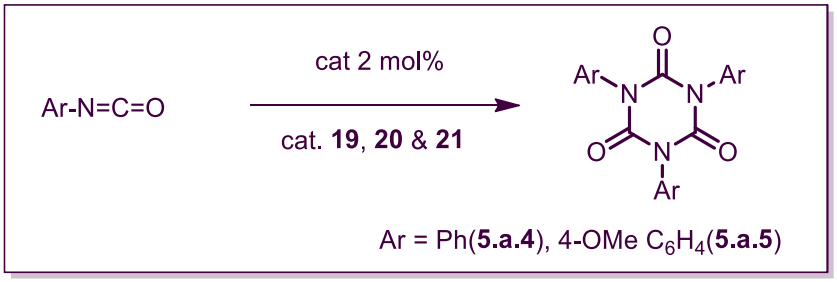
The bond lengths between tin and two nitrogen atoms of the guanidinate ligand *i.e.* Sn1 **–**N3 2.275(5) Å and Sn1**–**N4 2.234(4) Å are longer than those observed in compound **19** (Ge1 **–**N1

2.0994(12) Å and Ge1–N2 2.0424(11) Å). The C–N bond distances in both compound **19** (C1–N1 (1.3614(18) Å) and C1–N2 (1.3407(18) Å)) and **20** (C17–N3 (1.364(7) Å) and C17–N4 (1.334(8) Å)) are consistent with delocalization of the π bond in the N–C–N core of the ligand.

5.A.5. Reactivity Studies

5.A.5.1. Catalytic cyclotrimerization of arylisocyanates with complexes 19-21

In recent years, the main group organometallic chemistry has been accepted for its catalytic potential, and promising alternative to expensive transition and lanthanide based catalysis.[20] We were inspired by the work done by two research groups, Richeson and Harder for the catalytic cyclotrimerization of arylisocyanates by using amidinate supported Group 14 metal complexes and iminophosphorane chelated calcium carbene, respectively.[8b, 21] We presumed such catalytic studies might be attractive targets by employing the bulky guanidinate supported low valent germanium(II) and tin(II) amide complexes. In this connection, we have observed that guanidinate supported germanium(II) and tin(II) amides are very good catalysts for the cyclotrimerization of aryl isocyanates to produce triaryl isocyanurates (Scheme 5.A.3).



Scheme 5.A.3. Compounds **19-21** catalyzed cyclotrimerization of arylisocyanates

Triarylisocyanurates, the aromatic compounds obtaining from cyclotrimerization of arylisocyanates, are used to upgrade the physical properties of a wide range of polyurethanes and coating materials.[22] And also, these are very effective activators for anionic polymerization of caprolactams to nylon-6.[23]

Various isocyanate trimerization catalysts have been described, with a majority of the conventional catalysts being anions or neutral Lewis bases.[24] Recently, Louie et al., has shown *N*-heterocyclic carbenes as efficient catalysts for the cyclotrimerization of isocyanates.[25] And also, organometallic compounds which include both transition[26] and lanthanide[27] based catalysts for trimerization of isocyanates is well documented. On the other hand main group organometallic compounds based catalysis of cyclotrimerization of aryl isocyanate is poorly documented, though there are some reports.[28]

Table 5.A.1. Data for the catalytic cyclotrimerization of aryl isocyanates[a]

Entry	Substrate	Catalyst	Time (min)	Isolated Yield (%)
1	C_6H_5NCO	**19**	60	93
2	*P*-$MeOC_6H_4NCO$	**19**	60	94
3	C_6H_5NCO	**20**	30	95
4	*P*-$MeOC_6H_4NCO$	**20**	30	96
5	C_6H_5NCO	**21**	20	97
6	*P*-$MeOC_6H_4NCO$	**21**	20	96
7	*P*-$MeOC_6H_4NCO$	$Ge[N(SiMe_3)_2]_2$[b]	1440	83
8	*P*-$MeOC_6H_4NCO$	$Sn[N(SiMe_3)_2]_2$	480	91
9	C_6H_5NCO	$[Me_3SiNC(^tBu)NSiMe_3]Sn[N(SiMe_3)_2]$[c]	210	94
10	C_6H_5NCO	$[Me_3SiNC(^tBu)NSiMe_3]Ge[N(SiMe_3)_2]$[c]	16	98
11	C_6H_5NCO	$Sn[Me_3SiNC(Me)NSiMe_3]_2$ [c]	10	35(52% dimer)
12	C_6H_5NCO	$[CyNC(Me)NCy]Sn[N(SiMe_3)_2]S_4$ [c]	12	95
13	C_6H_5NCO	$[CyNC(^tBu)NCy]Sn[N(SiMe_3)_2]S_4$ [c]	60	68

[a]all reactions were carried out in neat aryl isocyanate (substrates) at room temperature and catalysts **19-21** in 2 mol%.[b]5 mol % catalyst was used. [c] data from ref.[8]

The addition of complexes **19-21** (2 mol %) to neat aryl isocyanates and followed by stirring at room temperature for 1 h led to the formation of cyclotrimerized products, *i.e*., triarylisocyanurates in quantitative yields. Our catalysts show a high degree of selectivity of

only triaryl isocyanurate formation (93–96% yield). No other isomeric products were observed. Moreover, catalysts **19-21** can be recovered and confirmed by the ^{1}H NMR without any decomposition products. The catalytic activity of guanidinate stabilized germanium(II) and tin(II) amide complexes **19-21** along with data for some related catalysts is summarized in Table 5.A.1.

From Table 5.A.1 (Entries 1-6), it is very clear that more bulky guanidinate stabilized tin(II) amide catalyst **21** is showing slightly better catalytic activity compare to **19** and **20.** Further**,** we extended these studies to test the catalytic activity of germanium bis(amide) and tin bis(amide) compounds (Entry 7 & 8). These compounds show less activity compare to catalysts **19-21** (Entries 1-6). This suggests that basicity of the proligand attached to metal site and Lewis acidity of the metal center play a role in the activity of these complexes. And also, it might be a solubility effect. Homoleptic metal catalysts may form polymeric insoluble structures in solution. However, the bulky guanidine ligand which is attached to metal atom keeps the catalyst active in solution. Furthermore, it is very important to note that bulky guanidinato stabilized tin(II) amide complex which is better catalyst than other related amidinato tin(II) amide complexes (Entries 9-13).

5.A.6 Conclusion

In conclusion, we have presented the synthesis and characterization of three new metal complexes of bulky guanidinate stabilized germanium(II) and tin(II) amides, which can be readily prepared by two synthetic routes; i) deprotonation of free bulky guanidine ligand with two equiv of $KN(SiMe_3)_2$ and followed by metathesis reaction with one equiv of metal dihalide of germanium or tin ii) deprotonation of ligand with metal bis(amide) of germanium or tin. Furthermore, compounds **19** and **20** were confirmed by single crystal X-ray structural

analysis, and revealed that both are monomeric in nature. Moreover, compounds **19-21** display excellent catalytic activity for the cyclotrimerization of aryl isocyanurates.

Table 5.A.2. Crystallographic details for **19** and **20.**

Compound	**19**	**20**
Formula	C_{29} H_{50} Ge N_4 Si_2	C_{29} H_{50} Sn N_4 Si_2
CCDC	984884	984883
Mol.mass	583.50	629.60
Temperature	100 K	100 K
Size (mm)	0.065 x 0.051 x 0.038	0.051 x 0.038 x 0.024
Crystal system, space Group	Triclinic, $P\bar{1}$	Monoclinic, $P2(1)/n$
a (Å)	8.9831(2)	8.983(12)
b (Å)	12.2308(2)	12.081(17)
c (Å)	16.3278(3)	29.469(4)
α (°)	70.6050(10)	90.000
β (°)	86.1720(10)	96.122
γ (°)	69.0760(10)	90.000
*V (*Å3)	1577.81(5)	3180(2)
Z, Calculated density	2, 1.228 Mg/m^3	4, 1.315
Absorption coefficient	1.070 mm^-1	0.902 mm^-1
F(000)	624	1320
Theta range for data collection	3.57 to 30.53 deg.	2.84 to 28.36 deg
Limiting indices	-12<=h<=10, -17<=k<=17, -22<=l<=23	-6<=h<=11, -16<=k<=16, -39<=l<=33
Reflections collected / unique	28696 / 9470 [R(int) = 0.0372]	28298 / 7794 [R(int) = 0.1355]
Completeness to theta	98.1 %	98.2 %
Absorption correction	SPHERE	SPHERE
Max. and min. transmission	0.7461 and 0.6296	0.7457 and 0.4420
Data / restraints / parameters	9470 / 0 / 339	7794 / 0 / 339
Goodness-of-fit on F^2	1.040	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0772	R1 = 0.0726, wR2 = 0.1806

5.A.7 References

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Mixed guanidinato-amido Ge(IV) and Sn(IV) complexes with Ge=E (E = S, Se) double bond and SnS_4, Sn_2Se_2 rings

The first bulky guanidinate supported germathioamide [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$(S)]; (Ar = 2,6– Me_2–C_6H_3) (**22**) and germaselanoamide [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$(Se)] **(23)** complexes with Ge=S (**22**) and Ge=Se (**23**) moieties, have been synthesized and structurally characterized. Both compounds **22** and **23** were prepared by the oxidative addition of elemental sulfur and selenium, respectively, to the heteroleptic germylene complex [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$](**19**) in THF/ether at room temperature. Similarly, reaction of compound [{ArNC(N^iPr_2)NAr}SnN($SiMe_3$)$_2$] (**20**) with equimolar amount of elemental chalcogens (S and Se) led to the formation of cyclic tetrasulfido tin [{ArNC(N^iPr_2)NAr}SnN($SiMe_3$)$_2$(S_4)] (**24**) with SnS_4 ring and dimeric bridged seleno tin [{ArNC(N^iPr_2)NArN($SiMe_3$)$_2$Sn(μ–Se)}$_2$] (**25**) with Sn_2Se_2 ring, respectively. All compounds **22-25** were confirmed by multinuclear NMR spectroscopy, elemental analysis and single crystal X-ray structural analysis.

5.B.1 Introduction

In recent years there has been rapid progress in the synthesis of molecular compounds with formal double bonds between the heavier Group 14 and 16 elements M=E (M = Si, Ge, Sn; E = S, Se, Te).[1] The synthesis of such species is quite challenging due to the high polarity and/or weak π-orbital overlap in the M=E bonds.[1,2] Therefore, to isolate such highly reactive molecules, synthetic chemists have been utilized a wide variety of bulky ligand systems such as diketiminate,[3] amidinate,[4] aminotroponiminate (ATI),[5] diamido,[6] iminophosphonamide,[7] N-heterocyclic carbene(NHC)[8] and related ligands.[9] The oxidative addition reaction of

chalcogens to either homoleptic or heteroleptic tetrelenes (MR_2) is the general synthetic approach for the multiple bonded (M=E) compounds. The reactivity studies of heteroleptic six or five membered Ge(II) and Sn(II) heterocycles is well documented.[1] In contrast, there have been limited reports of the reactivity of heteroleptic four membered Ge(II) and Sn(II) heterocycles.[10] Although, since the first guanidinate metal complex by Lappert in 1970,[11] various guanidinate supported Ge(II) and Sn(II) complexes with their reactivity studies have been reported.[12] Surprisingly, there have been no reports on oxidative addition of chalcogens to guanidinate supported Ge(II) and Sn(II) amide complexes. However, Richeson and co-workers reported oxidative addition of chalcogens to the mixed (amidinato) (amido) germanium(II) and tin(II) complexes.[13] (see Figure 5.B.1). Especially of great interest are compounds with amido substituent, where the amido - $\{N(SiMe_3)_2\}$ can easily be replaced to synthesize a variety of new compounds. More importantly, Hill and co-workers have shown that the catalytic activity of main group complexes bearing M-$\{N(SiMe_3)_2\}$ group, in which M-amide acts as a precatalyst.[14] Very recently, Coles[15] thoroughly reviewed on main group metal complexes of which bearing a bis-trimethylsilylamido ligand, $[N\{SiMe_3\}_2]^-$. This ligand was widely utilized due to its bulkiness, lipophilicity, the simplicity of its ^1H NMR spectra and lack of β-hydrogen atoms. Moreover, the anion $[N\{SiMe_3\}_2]^-$ is readily formed upon deprotonation of the commercially available hexamethyldisilazane (HMDS), facilitating its use in coordination chemistry. In this regard, we have previously reported that NHC supported magnesium and zinc bis(amide) complexes as precatalysts for guanylation reactions.[16] And also, we have reported that structurally characterized heteroleptic bulky guanidinate ligand[17] $[\{ArNC(N^iPr_2)NAr\}^-$; (Ar = 2,6– Me_2–C_6H_3)] stabilized germanium(II) and tin(II) amide complexes *i.e.*, $[\{ArNC(N^iPr_2)NAr\}GeN(SiMe_3)_2]$(**19**), $[\{ArNC(N^iPr_2)NAr\}SnN(SiMe_3)_2]$(**20**).[17a] Herein, we report the oxidative addition of

chalcogens (S and Se) to the guanidinate supported Ge(II) (**19**) and Sn(II) (**20**) amide complexes.

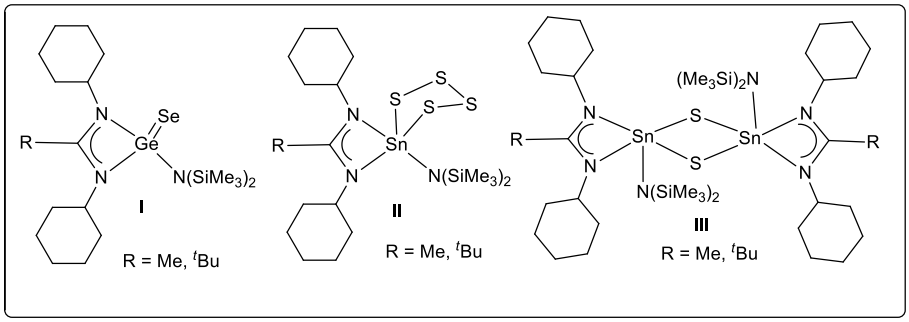
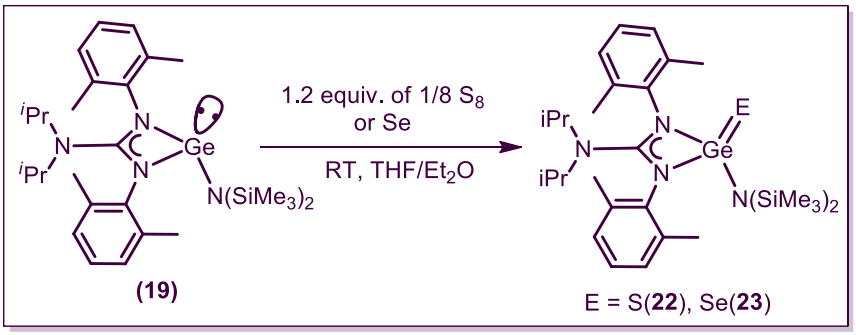


Figure 5.B.1. Four membered germanium and tin chalcogenido heterocycles bearing amido group

5.B.2. Results and discussion

5.B.2.1 Synthesis and spectroscopic characterization of complexes 22-25

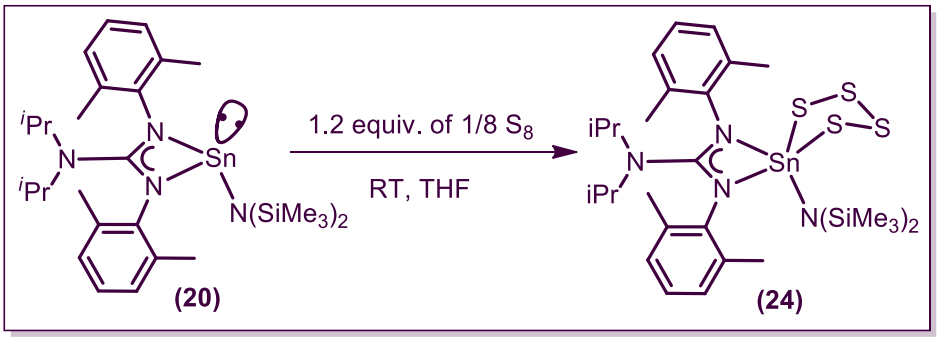
The reaction of compound [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$] (**19**) with equimolar amount of elemental sulfur powder in THF at room temperature led to the formation of thermally stable mixed guanidinato/amido supported germanium(IV) complex with Ge=S moiety (*vide supra*) [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)] (**22**) (Scheme 5.B.1).



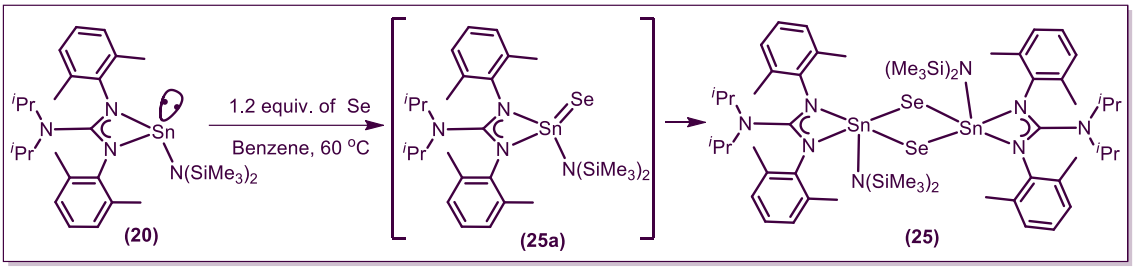
Scheme 5.B.1. Synthesis of (guanidinato) (amido) germanium sulphide (**22**) and selenide (**23**) complexes.

Similarly, the reaction of compound **19** with one equivalent of selenium powder in diethyl ether afforded the germanium complex with Ge=Se moiety [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(Se)] **(23).** Both compounds **22** and **23** are colourless crystalline, thermally stable, air and moisture sensitive solids. These are well soluble in organic solvents such as diethyl ether, THF, toluene, benzene and sparingly soluble in *n*-hexane.

In a manner similar to the syntheses of complexes **22** and **23,** the reaction of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**20**) with an excess or exact amount of elemental sulfur in THF at room temperature, gave the exclusively tetrasulphido tin(IV) complex [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S$_4$)] (**24**) as a stable light orange crystal in good yield (Scheme 5.B.2). Further, we treated one equivalent of elemental selenium with compound **20** at room temperature in THF. The ^{1}H NMR and ^{29}Si NMR spectra of aliquot indicate the presence of mixture of compounds, exhibiting two peaks at 0.41 and 0.49 ppm for N(Si*Me*$_3$)$_2$ moiety in ^{1}H NMR spectrum and showing two peaks at 5.22 and 5.32 ppm, for N(*Si*Me$_3$)$_2$ in ^{29}Si NMR spectrum. From these spectroscopic observations, we presume that mixture of products are [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–Se)}$_2$] (**25**) (*vide supra*) and [{ArNC(N^{i}Pr$_2$)NAr}N(SiMe$_3$)$_2$Sn=Se] (**25a**) (Scheme 5.B.3).



Scheme 5.B.2 Synthesis of tetrasulphido tin(IV) complex (**24**).



Scheme 5.B.3 Synthesis of dimeric bridged μ-selenotin(IV) complex (**25**).

Further, the same reaction was performed in benzene solvent at 60 °C, instead of THF, which undergo rapid reaction to yield exclusively the tin complex [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–Se)}$_2$] (**25**) as a light yellow crystalline solid with high yield. Like complexes **22** and **23**, both compounds **24** and **25** are soluble in organic solvents, thermally stable, air and moisture sensitive. All compounds **22-25** were characterized by multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR spectroscopy, elemental analysis and single crystal X-ray spectroscopy methods.

^{1}H NMR spectra of **22** and **23** showed that the aryl methyl protons *i.e.*, Ar-C*H*$_3$ of guanidinate ligand are magnetically non-equivalent and resonating as two singlets at 2.45 and 2.97 ppm (**22**) and 2.46 and 2.99 ppm (**23**)**.** In contrast, only one signal observed in corresponding precursor complex in **19** at 2.58 ppm. Interestingly, the ^{1}H NMR spectrum of **24** exhibited that the aryl methyl protons *i.e.*, Ar-C*H*$_3$ of guanidinate ligand as one singlet at 2.45 ppm, in contrast to the corresponding precursor complex (**20**) in which it is showing two resonances at 2.50 and 2.60 ppm. However, ^{1}H NMR spectrum of complex **25** shows two singlets at 2.47 and 3.00 ppm. And also, ^{1}H NMR spectra exhibit singlet at 0.32 (**22**), 0.34(**23**), 0.3(**24**) and 0.48(**25**), respectively for the N(Si*Me*$_3$)$_2$ moiety, these resonances are shifted downfield as compared to the compounds **19** (0.26 ppm) and **20** (0.2 ppm)[17a] and other signals such as Ar-*H*, C*H*(CH$_3$)$_2$ and CH(C*H*$_3$)$_2$ for all compounds (**22-25**) were as expected for the guanidinate ligand.

^{13}C NMR spectra of compounds **22, 23, 24** and **25** show a characteristic peak for the N_3C carbon atom of the guanidinate ligand 167.7, 167.9, 168.0 and 169.9 ppm respectively, these values are significantly shifted downfield as compared to the corresponding ligand[17b] of these metal complexes and other reported free tetra substituted guanidines (148-160 ppm).[18]

^{29}Si{^{1}H} spectra of compounds **22** and **23** showed signals at 3.31(**22**) and 3.02 (**23**) ppm respectively, and these values are shifted downfield as compared to the compound **19** (–3.68 ppm). Similarly, ^{29}Si{^{1}H} spectrum of compounds **24** and **25** exhibited signals at 5.52(**24**) and 5.25(**25**) ppm respectively, these values are also shifted downfield as compared to the compound **20** (–3.69 ppm).[17b]

Further efforts were made to isolate tin complexes such as [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S)] with Sn=S and [{ArNC(N^{i}Pr$_2$)NArN(SiMe$_3$)$_2$Sn(μ–S)}$_2$] with Sn_2S_2 ring. Accordingly, sulfur was added to a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**20**) in C_6D_6 and followed by heating at 60 ºC for 12, in which ^{1}H NMR spectrum reveals mixture of products. And also, we investigated the reaction of compound **24** with three equivalents of triphenylphosphine to possibly afford the monomer [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$(S)] with a formal Sn=S bond, instead a mixture of products, including compound **19** was observed in the ^{1}H NMR spectrum.

5.B.2.2. Single crystal X-ray structural characterization of complexes 22-25

Crystals of the complex [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$(S)] (**22**) suitable for X-ray diffraction were grown from its diethyl ether with few drops of toluene solution at –30 ºC. Compound **22** crystallizes in the monoclinic system with *C*2/*c* space group. The molecular structure, selected bond distances and bond angles have depicted in the figure 5.B.1.

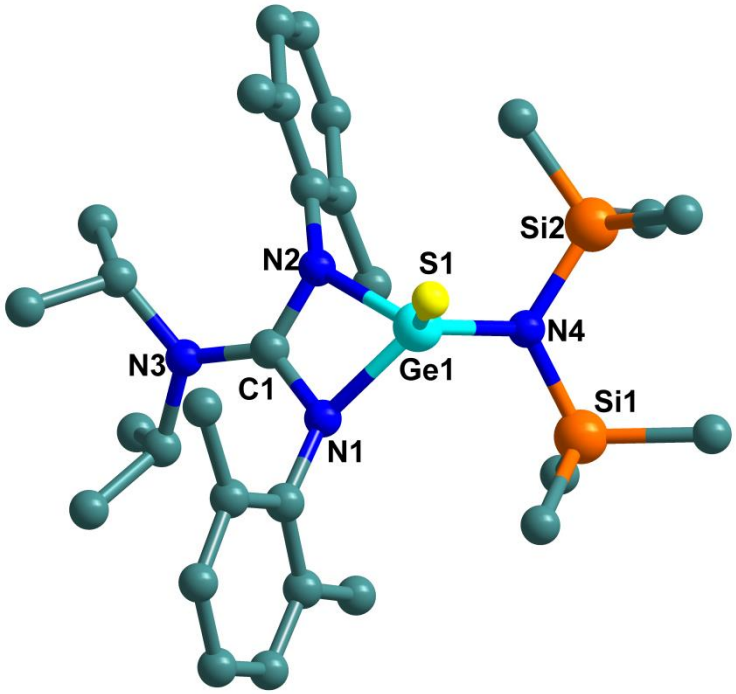


Figure 5.B.1. Molecular structure of **22**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **22**: Ge1–S1 2.0735(15), Ge1–N1 1.984(4), Ge1–N2 1.949(4), Ge1–N4 1.843(4), C1–N1 1.359(6), C1–N2 1.351(6), N3–C1 1.355(6), N1–C2 1.443(6), Si1–N4 1.753(5), Si2–N4 1.759(4); N2–Ge1–N1 67.56(17), N4–Ge1–N1 113.06(17), N4–Ge1–N2 110.24(18), N1–Ge1–S1 119.36(12), N4–Ge1–S1 117.44(14), N2–C1–N1 107.6(4), N3–C1–N1 126.9(5), Si1–N4–Si2 119.8(2), Si1–N4–Ge1 118.9(2), Si2–N4–Ge1 117.6(2).

The solid state structure of **22** reveals that the Ge centre is bonded to the guanidinate ligand in [*N,N'*] chelate fashion and the other sites are occupied by N atom of the amido ligand and sulfur atom, resulting in a distorted tetrahedral geometry. The most characteristic feature of the complex **22** is the presence of Ge=S bond and it is the first example of a monomeric germathioamide with germanium in a four membered heterocycle ring. The Ge1–S1 bond distance 2.0735(15) Å in compound **22** is well in agreement with other reported germanium complexes bearing Ge=S moiety; [PhNC(Me)CHC(Me)NPh](Cl)Ge=S] (2.074(1) Å)[19] [2,6-^{i}Pr$_2$(C$_6$H$_3$N)P(Ph$_2$)(N^{t}Bu)]GeS(Cl)] (2.048(2) Å,[7] [CH{MeCN(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$]Ge(S)Cl

2.053(6) Å,[20] [CH{MeCN(2,6- $^{i}Pr_2$ C_6H_3)}$_2$]Ge(S)SH 2.064(4) Å.[21] The Ge1–S1 bond distance 2.0735(15) Å for compound **22** is more consistent with a double bond than a single bond. Because, theoretical calculations for $H_2Ge=S$ molecule predicted that the 2.04 Å[19, 22] for Ge=S bond. However, Ge–S single covalent bond distance is 2.26 Å. The Ge=S bond length is slightly longer than the other kinetically stabilized germanechalcogenones.[23] And also, the Ge1–S1 bond distance 2.0735(15) Å in compound **22** is well in agreement with Okazaki and coworker's heavy ketone Tb(Tip)Ge=S (2.049(3) Å.[1k]

Due to the change of germanium centre environment from tricoordinate to tetra coordinate the Ge–N(amido) bond distance in **22** Ge1–N4 1.843(4) Å, is shorter by 0.0965 Å than that of the corresponding distance in **19** (Ge1–N3 1.9395(4) Å). For the same reason the Ge1–N1 bond distance also shorter by 0.114 Å than corresponding bond length of Ge1–N1 in compound **19**. The N2–Ge1–N1 bond angle 67.56(17)^{o} is slightly wider than the corresponding bond angle observed in **19** (N2–Ge1–N1 (64.12(4)^{o}).

The compound **23** crystallizes in the monoclinic system with $P2_1/c$ space group. Both compounds **22** and **23** are isostructural. Compound **23** is the first example of bulky guanidinate supported germanium selenoamide. However, closely related amidinate supported germanium selenoamide complexes are reported by Richeson and co-workers.[13a] The molecular structure, selected bond distances and bond angles have shown in figure 5.B.2.

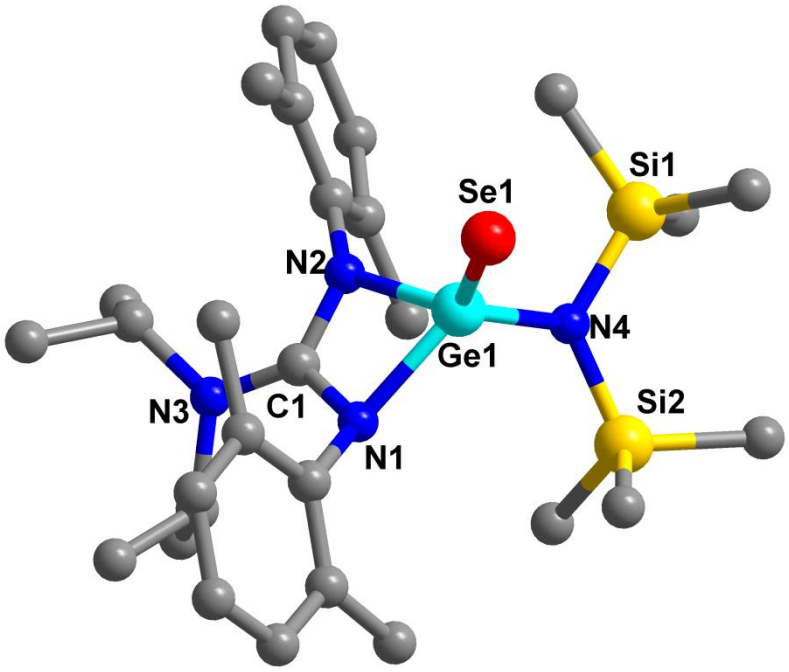


Figure 5.B.2. Molecular structure of **23**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **23**: Ge1–Se1 2.2061(4), Ge1–N1 1.973(2), Ge1–N2 1.959(2), Ge1–N4 1.850(2), Si1–N4 1.760(3), Si2–N4 1.735(3), N2–C1 1.342(3), N1–C1 1.342(3), N3–C1 1.345(3); N2–C1–N1 107.5(2), N2–Ge1–N1 67.87(9), N4–Ge1–N1 113.12(12), N4–Ge1–N2 104.26(10), N4–Ge1–Se1 116.96(8), N2–Ge1–Se1 124.73(6), N1–Ge1–Se1 120.22(7), Si1–N4–Ge1 116.55(15), Si2–N4–Ge1 117.32(17), Si2–N4–Si1 122.72(15), N3–C1–N1 124.5(2).

The Ge1–Se1 bond length 2.2061(4) Å in **23** was found to be identical with other germanium complexes containing Ge=Se moiety; [{2,6-^{i}Pr$_2$(C$_6$H$_3$N)P(Ph$_2$)(N^{t}Bu)}GeSe(O^{t}Bu)] (2.2003(2) Å),[7] [{C$_6$H$_{11}$NC(Me)NC$_6$H$_{11}$}Ge{N(SiMe$_3$)$_2$}Se] (2.2113(3) Å),[13a] [PhNC(Me)CHC(Me)NPh](Cl)Ge=Se (2.210(1) Å),[19] germaselenoesters [(*t*-Bu)$_2$ATI]Ge(Se)O^{t}-Bu (2.2193(7) Å),[5e] (η^4-Me$_8$taa)GeSe (2.247(1) Å).[24] However, Ge1–Se1 bond length 2.2061(4) Å in **23** is slightly longer than that of Okazaki and coworker's heavy ketone, *i.e.,* Tbt(Tip) Ge=Se (Ge=Se 2.180(2) Å).[1k] The short Ge–Se bond length is revealing of a double bond or a Ge–Se bond with an added percentage of ionic character. The

Ge–N(amido) bond distance in **23** Ge1–N4 1.850(2) Å, is shorter by 0.0895 Å than that of the corresponding distance in **19** (Ge1–N3 1.9395(4)). The N2–Ge1–N1 bond angle 67.87(9)^{o} is slightly wider than the corresponding bond angle observed in **19** (N2–Ge1–N1 (64.12(4)^{o}).

Further, we have performed theoretical calculations to confirm the presence of double bond between germanium and sulphur or selenium atoms (see Figure 5.B.5 and 5.B.6). The Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory. The atomic coordinates were taken from the .cif files of compounds **22** & **23** and no further geometry optimization was carried out. The Wiberg Bond Index (WBI) of Ge–S in compound **22** and Ge–Se in compound **23** are 1.49 and 1.52, respectively, indicating the existence of double bond between germanium and sulfur or selenium atoms.

Single crystals of **24** were obtained from diethyl ether and few drops of toluene solution at –30 ^{o}C. Compound **24** crystallizes in the triclinic space group $P\bar{1}$ (see Figure 5.B.3).

This complex shows the Sn centre in a distorted five co–ordinated geometry consisting of (*N,N'*) chelate guanidinate, amido and (S1 and S4) chelate tetrasulphido ligands. The noteworthy feature of this molecule is five membered SnS_4 ring. In this structure, five membered SnS_4 is in distorted half chair conformation. The bond angle S1–Sn1–S4 of compound **24** is 95.43(5)^{o} is comparable to the structurally characterized SnS_4 rings.[13b, 25] The average S–S bond distance (2.045 Å) in SnS_4 (S1–S2 2.043(2), S2–S3 2.036(2), S(3)–S(4) 2.057(2) Å) is good in agreement with the average S–S bond distance (2.050 Å) for orthorhombic sulfur.

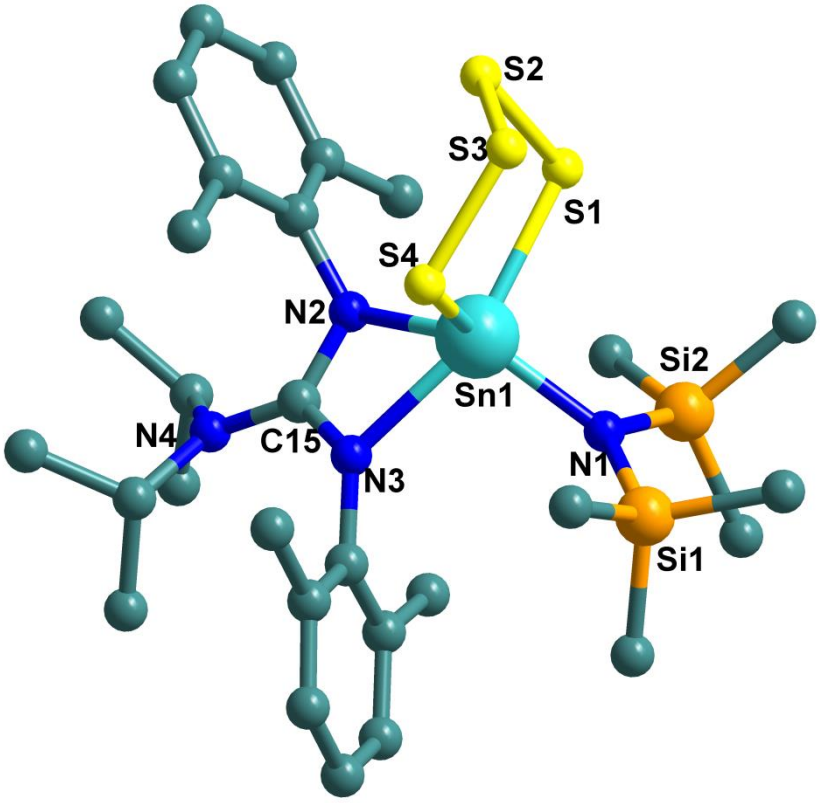


Figure 5.B.3. Molecular structure of **24**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **24**: Sn1–S1 2.4997(16), Sn1–S4 2.456 (15), Sn1–N1 2.062(4), Sn1–N2 2.167(4), Sn1–N3 2.240(4), Si1–N1 1.745(4), Si2–N1 1.748(5), N2–C(15) 1.354(6), N3–C(16) 1.421(6), N4–C(15) 1.358(6), S1–S2 2.043(2), S2–S3 2.036(2); N1–Sn1–N2 128.31(16), N1–Sn1–N3 99.28(16), N2–Sn1–N3 60.5(16), N1–Sn1–S1 97.95(12), N1–Sn1–S4 119.18(12), N3–C(15)–N2 110.2(4), N3–C(15)–N4 125.8(5), Si1–N1–Si2 119.0(2), Si1–N1–Sn1 121.9(2), Si2–N1–Sn1 118.4(2), S3–S4–Sn1 101.10(7), S2–S1–Sn1 97.82(7), S3–S2–S1 101.28(9), S(4)–Sn(1)–S(1) 95.43(5).

Sn–N(amido) bond distance in **24** Sn1–N1 2.062(4) Å, is shorter by 0.087 Å than that of the corresponding distance in **20** (Sn1–N1 2.149(5)). Sn–N(amido) bond distance in **24** Sn1–N1 2.062(4) Å is comparable with related amidinate stabilized tetrasulfido tin(IV) complexes [{$C_6H_{11}NC(^tBu)NC_6H_{11}$}Sn(N($SiMe_3$)$_2$)($S_4$)] (2.065(2) Å). The Sn1–N3 2.275(5) bond

distance in compound **24** slightly longer by 0.0054 Å than corresponding bond length of Sn1–N4 2.234(4) in compound **20** and Sn1–N2 2.167(4) bond distance is shorter by 0.108 Å compare to the Sn1–N3 2.275(5) in compound **20**.

Compound **25** (see Figure 5.B.4) also crystallizes in the triclinic space group $P\bar{1}$ which is dimeric species with bridging seleno ligand. The alternative tin and selenium atom in four membered [Sn(μ–Se)]$_2$ ring core is planar. The central Sn atom coordination is covered by amido and bidentate guanidinate ligand and two bridged seleno [Sn(μ–Se)]$_2$ unit.

Sn–N(amido) bond distance in **25** Sn1–N7 2.062(10) and Sn2–N8 2.083(10)Å, is shorter by 0.087 and 0.066 Å than that of the corresponding distance in starting material **20** (Sn1–N1 2.149(5)). The bridged Sn1–Se1 2.5676(17), Sn1–Se2 2.5658(18) bond distance in compound **25** is slightly longer than bridged seleno amide compound [{Sn(N(SiMe$_3$)$_2$)$_2$(μ-Se)}$_2$] Sn–Se 2.538(1) and 2.544(1) Å[26] and Sn–Se 2.528 Å in [{Sn(L$_1$)(μ -Se)}$_2$].[6] These Bond lengths of N1–Sn1 and N2–Sn1 in compound **25** are comparatively shorter than the compound **20.** The bond angle of N1–Sn1–N2 59.7(4)^o is very similar with the free guanidinate tin amide (**20**) N3–Sn1–N4 59.13(17) ^{o}. Bond angles of Sn1–Se1–Sn2 89.51^o and Sn1–Se2–Sn2 89.37^o are wider than compound [{Sn[N(SiMe$_3$)$_2$]$_2$(μ-Se)}$_2$] Sn–Se–Sn' (85.09^o). Se2–Sn2–Se1 90.62(6)^o bond angle is shorter than [{Sn(N(SiMe$_3$)$_2$)$_2$(μ-Se)}$_2$] Se–Sn–Se' (94.91^o) and compound [{Sn(L$_1$)(μ -Se)}$_2$] 97.5^o. These difference of bond length and bond angles of compound **25** with [{Sn(N(SiMe$_3$)$_2$)$_2$(μ-Se)}$_2$] and [{Sn(L$_1$)(μ -Se)}$_2$] due to environment change of metal center from tetra coordinate to pentacoordinate.

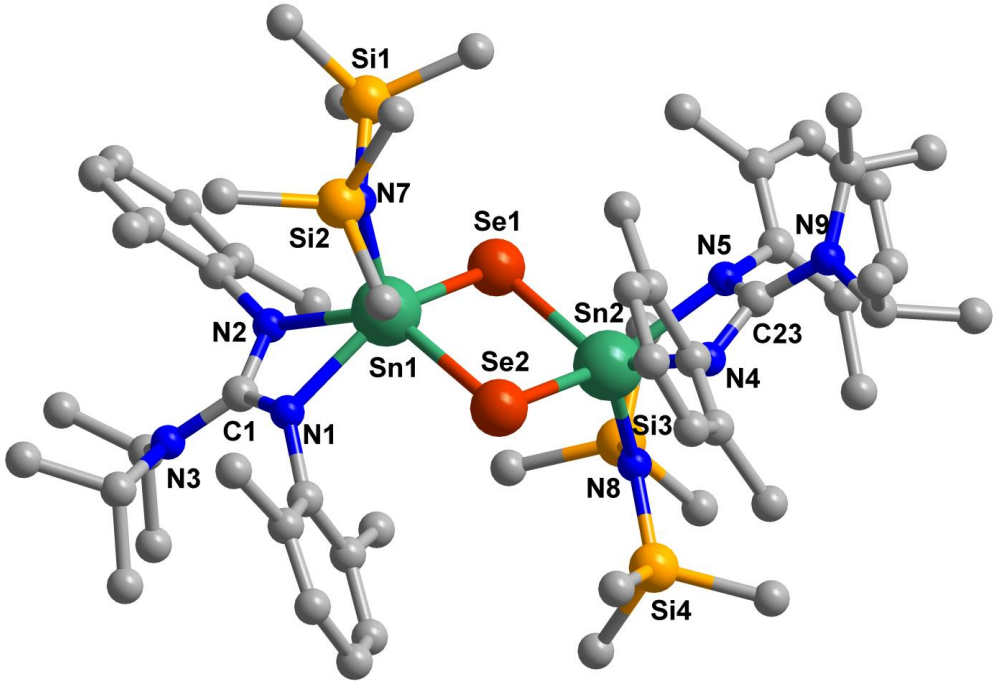
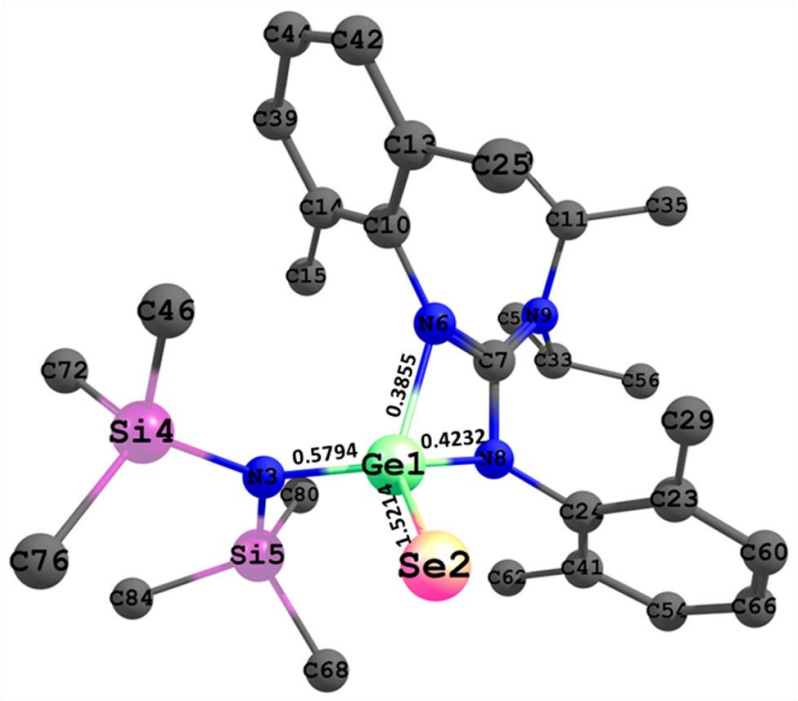


Figure 5.B.4. Molecular structure of **25**. Selected bond lengths (Å) and bond angles (deg) for **25**: Sn1–Se1 2.5676(17), Sn1–Se2 2.5658(18), Sn2–Se1 2.5662(18), Sn2–Se2 2.5616(17), Sn1–N1 2.231(10), Sn1–N2 2.270(11), Sn1–N7 2.062(10), Sn2–N4 2.222(10), Sn2–N5 2.268(10), Sn2–N8 2.083(10), N1–C1 1.332(16), N3–C1 1.411(14), N4–C23 1.338(16), N9–C23 1.403(15), Si1–N7 1.764(12), Si2–N7 1.733(11), Si3–N8 1.761(11), Si4–N8 1.719(11); N1–Sn1–N2 59.7(4), N7–Sn1–N1 110.6(4), N7–Sn1–N2 103.2(4), C1–N1–Sn1 94.3(8), N1–Sn1–Se2 88.7(3), N2–Sn1–Se2 138.5(3), N1–Sn1–Se1 140.5(3), N8–Sn2–N4 110.9(4), N8–Sn2–N5 102.0(4), N4–Sn2–N5 59.7(4), N8–Sn2–Se2 113.3(3), N4–Sn2–Se2 88.5(3), Se2–Sn2–Se1 90.62(6), Sn2–Se1–Sn1 89.37(6), Si4–N8–Si3 120.7(6), Si4–N8–Sn2 121.1(6).

5.B.3. Computational studies

The Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory.

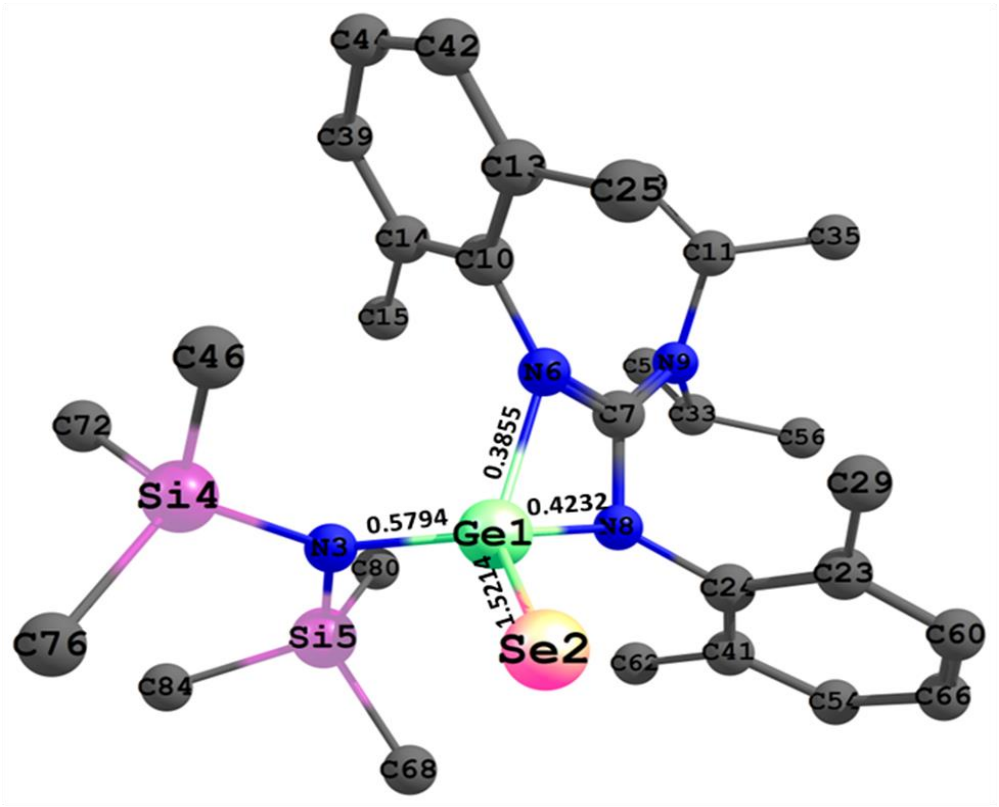
The Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory. The atomic coordinates were taken from the .cif files of compounds **22** & **23** and no further geometry optimization was carried out. The Wiberg Bond Index (WBI) of Ge–S in compound **22** and Ge–Se in compound **23** are 1.49 and 1.52, respectively, indicating the the existence of double bond between germanium and sulfur or selenium atoms.



(40.48%) 0.6362*Ge 1 s(54.66%)p 0.82(45.01%)d 0.01(0.33%)

(59.52%) 0.7715* S 2 s(16.57%)p 5.02(83.16%)d 0.02(0.27%)

Figure 5.B.5 Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory for compound **22**



(44.79%) 0.6693*Ge 1 s(55.41%)p 0.80(44.22%)d 0.01(0.37%)

(55.21%) 0.7430*Se 2 s(13.36%)p 6.47(86.53%)d 0.01(0.11%)

Figure 5.B.6. Wiberg Bond Index (WBI) was computed at B3LYP/6-31+G(d) level of theory for compound **23**

Table 5.B.1. Crystal data for compounds **22-25**

Compounds	**22**	**23**	**24**	**25**
CCDC	1436337	1436338	1436339	1436340
Formula	$C_{71}H_{104}Ge_2N_8S_2Si_4$	$C_{29}H_{50}GeN_4SeSi_2$	$C_{58}H_{100}N_8S_8Si_4Sn_2.C_4H_{10}O$	$C_{58}H_{100}N_8Se_2Si_4Sn_2$
Mol.mass	1391.32	662.46	1589.79	1417.12
Size (mm)	0.28 × 0.16 × 0.11	0.2 × 0.15 × 0.12	0.22 × 0.17 × 0.15	0.13x 0.087 x 0.058
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space Group	*C* 2/*c*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	37.184(6)	18.6303(10)	12.328(3)	13.142(13)
b (Å)	10.4649(15)	10.2343(5)	18.377(4)	14.843(17)
c (Å)	26.604(8)	18.6276(9)	18.647(4)	18.533(2)
α (°)	90	90	106.217(5)	96.409(7)
β (°)	131.927(3)	90.622(3)	107.376(4)	91.916(6)
γ (°)	90	90	94.718(4)	110.364(6)
V (Å3)	7702(4)	3551.5(3)	3807.8(15)	3357.9(19)
Z	4	4	2	2
ρ (gcm^{-3})	1.200	1.239	1.387	1.402
μ (Mo-$K\alpha$) (mm^{-1})	0.940	1.977	0.982	1.940
T (K)	100	100	100	100
θ (max.)	25.329	26	25.552	25.80
Unique reflections	7025	6983	41667	12769
F(000)	2952.0	1384.0	1660.0	1456
R(int)	0.0637	0.0430	0.0724	0.1469
Parameters	411	348	796	696
*R*1	0.0622	0.0377	0.0466	0.0908
w*R*2	0.1663	0.0859	0.1032	0.2035
GOF	1.075	1.050	1.013	0.973

5.B.4. Conclusion

In summary, we have synthesized and structurally characterized first mixed guanidinato/amido ligands supported germanium complexes with Ge=E (E= S or Se) double bond by oxidative addition of elemental sulfur or selenium to the [{ArNC(N^iPr_2)NAr}GeN($SiMe_3$)$_2$](**19**). Further, [{ArNC(N^iPr_2)NAr}SnN($SiMe_3$)$_2$] (**20**) upon treatment with sulfur and selenium led to the formation of cyclic tetrasulphido and μ–seleno tin complexes bearing five membered SnS_4 and four membered Sn_2Se_2 rings, respectively.

5.B.5. References

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Bis(guanidinate) supported Group 14 metallynes (LML) and their oxidative additions with chalcogens

Abstract

A series of structurally characterized bis(guanidinate) supported heavier Group 14 metallynes such as germylene (L^3GeL^3), stannylene (L^3SnL^3) and plumbylene (L^1PbL^1) & (L^3PbL^3) have been synthesized by salt metathesis reaction, i.e. the treatment of corresponding lithium salt of guanidinate ligand(L^1 or L^3) with metal dihalides (M= Ge·dioxane, Sn and Pb) [L^1 = {ArNC (N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3) and L^3 = {Ar'NC (N^iPr_2) NAr'}(Ar' = 3,5- Me_2-C_6H_3)]. The reactivity of homoleptic germylene and stannylene towards chalcogens (S and Se) have been explored, in which oxidative addition occurred and led to the formation of bis(guanidinate) supported germanium tetrasulfido, dimeric bridged seleno complex and dimeric bridged sulfido and seleno tin complexes. All bis(guanidinate) supported Group 14 metallynes and oxidative addition products of germylene and stannylne complexes were characterized by multi nuclear NMR, elemental analysis and X-ray crystal structural analysis. Attempts to synthesis oxidative addition products of homoleptic plumbylne complexes with chalcogens were unsuccessful.

6.1. Introduction

Group 14 low valent carbene analogues germylenes, stannylenes, and plumbylenes have attracted much attention in fundamental chemistry because of their particular structures and high reactivities[1]. Among the stabilization strategies of germylenes, stannylenes and plumbylenes the intermolecular coordination have produced a great interest in the last decades mainly with the use of N- donor ligands. Using bidentate and monoanionic ligand backbone metal guanidinates[2] and amidinates[3] show cyclic structures with electron pair

conjugation. Due to the potential stabilization of low valent metal center and reactive intermediates[4] these compound attracted much attention.

In the Group 14 divalent derivatives one of the utmost characteristic features is their high potential as building blocks in organometallic chemistry; e.g., their oxidation by elemental chalcogens produces a usual and clean route to double bonded species M=E (M = Si, Ge, Sn; E = S, Se, Te).[5] Even though several germanium and tin compounds with double bond to chalcogens have been isolated using kinetic or thermodynamic stabilization.[6]

Germylene and stannylene plays an important role in the activation of small molecules and other functional groups. Recently, two research groups Power[7] and Jones[8] independently reported Ge-Ge bonded complex [R_1GeGeR_1] [R_1 = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2$)$_2$] which is kinetically stabilized by bulky aryl group, [R_2GeGeR_2] [R_2 = $N(SiMe_3)(Ar^*)$; Ar^* = $C_6H_2Me\{C\text{-}(H)Ph_2\}_2$-2,4,6], [Ar'GeGeAr'] [Ar' = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2$)$_2$],[9] and [Ar'SnSnAr'] activated H_2 and P_4. Roesky and co-workers demonstrated activation of small molecule using low valent Group 14 complex stabilized by diketaminate ligand[10]. Moreover, germanium(II) hydride used catalytically to promote hydroboration reaction *via* the activation of ketone[11]. Very recently, Nagendran and co-workers reported germanium(II) cyanides[12] [(L2)GeCN] (L2 = aminotroponiminate) and Fulton et al., germanium(II) alkoxide[13] [L1GeOi Pr] which they used for activation of aldehydes and alkoxides, which showed that low valent Group 14 germylenes are potential catalyst for organic reactions. Driess and co-workers first reported a N-heterocyclic ylide-like germylene that was capable of activating halohydrocarbon,[14] ammonia,[15] water, phenol, and carboxylic acid.[16]

From our group we have reported guanidinate stabilized heteroleptic low valent Group 14 Ge(II) and Sn(II) amide complexes and that demonstrated good catalytic behaviour in cyclotrimerization reaction[17]. Furthermore, we showed those germylene and stannylene

reactivity studies towards chalcogens to form germethioamide, germeselenoamide, tetrasulfido tin and dimeric bridged seleno complexes[18]. Although several amidinate stabilized homoleptic Group 14 complexes are known in literature but guanidinate stabilized homoleptic germylenes, stannylenes, and plumbylenes are very limited in the literature[19].

Very recently Růžička and co-workers reported $(L)_2Sn$[19b] and they showed reactivity of $(L)_2Sn$ with a series of diones and describe the structure and properties of the products of such an oxidation[19h]. There are several reports on oxidation of tin(II) compounds by halides[20], alkyl- or arylhalides[21], organometallic halides[22] and oxygen-containing compounds[23]. But there were no reports on oxidative addition of homoleptic Group 14 germylene and stannylene with chalcogens(S and Se).

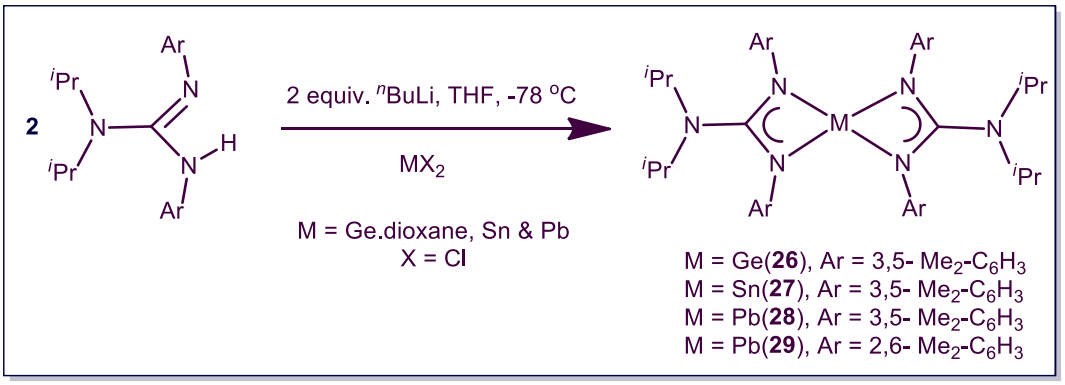
Herein, we report a series of structurally characterized bis(guanidinate) supported Group 14 metallynes by the salt metathesis method. Further, we have demonstrated the oxidative addition reactions between bis(guanidinate) stabilized both germylene and stannylene with chalcogens.

6.2. Results and Discussion

6.2.1. Synthesis

Preparation of homoleptic Ge(II), Sn(II) & Pb(II) guanidinates are presented in Scheme **6.1**. The homoleptic guanidinate compounds using ligand 2,3–bis(2,6–dimethylphenyl)–1,1–diisopropylguanidine(**L^3**) were prepared with quantitative yield at room temperature by reacting with MCl_2 in a 1:1 stoichiometry. Recently Gibson and co–workers have reported that equimolar reaction with $SnCl_2$ with Li(Priso) formation of a mixture of compounds *i.e.* [{ArNC(Me)NAr}SnCl] and [Sn{ArNC(Me)NAr}$_2$] respectively. Using guanidinate ligands(same aromatic substituents) 2,3–bis(2,6–dimethylphenyl)–1,1–diisopropylguanidine(^{xyl}Priso) and 2,3–bis(2,6–diisopropylphenyl)–1,1–diisopropylguanidine(^{Dipp}Priso) fails to make homoleptic guanidinate complexes as a single

product instead of mixture of products (free ligand with desired product) even at higher temperature also. Due to bulkiness of the ligand ^{Dipp}Priso it is difficult to make homoleptic Mg(II), Ca(II) and Zn(II) complexes have shown in earlier in our work[23]. For Group 14 metal Ge(II), Sn(II) it was noticed similar observation for ^{xyl}Priso except Pb(II). So we used less bulky substituent instead of sterically more hindered ligand. By employing salt elimination reactions from guanidinate lithium or potassium salt and $GeCl_2$.dioxane, $SnCl_2$ and $PbCl_2$, respectively in THF at room temperature. ^{n}BuLi was added to the THF solution of ^{Xyl}Priso at 0 ^{o}C to make the lithium salt. Then these LLi was added drop by drop to their corresponding metal salt.

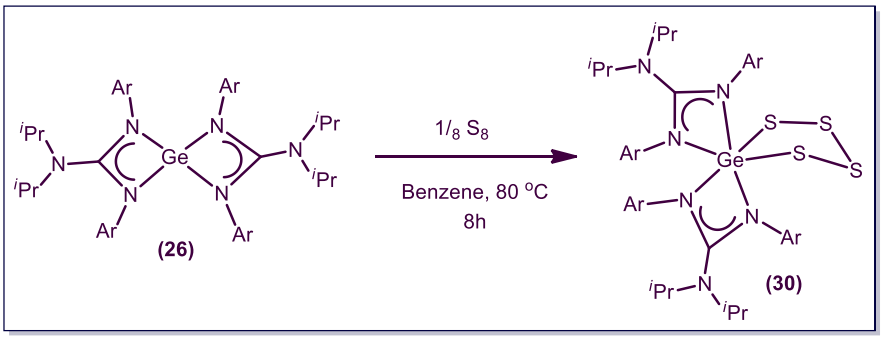


Scheme 6.1. Synthesis of homoleptic Ge(II), Sn(II) and Pb(II) complexes.

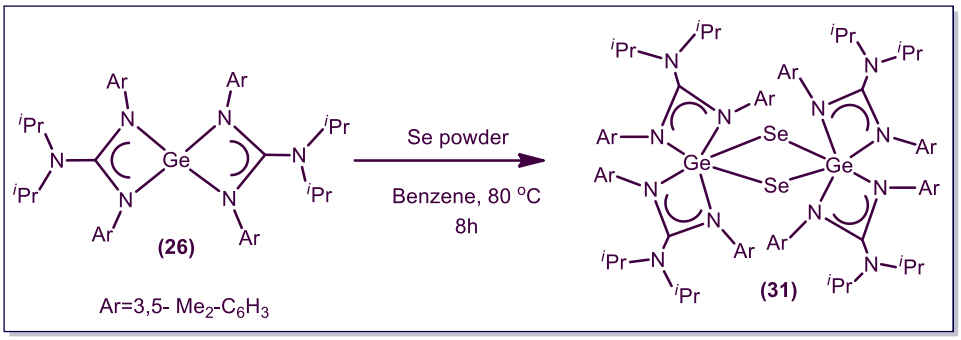
Various oxidative addition with compound Ge[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$(**26)** and Sn[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$(**27)** with chalcogens have demonstrated in scheme **6.2, 6.3** and **6.4**. Guanidinato Germenium(IV) and Tin(IV) complexes **30**–**33**, the reactions were performed in benzene solvent at 60 – 80 ^{0}C through an oxidative addition. Driving force of the reaction is oxidation state changes from M(II) to stable oxidation state M(IV)(M = Ge and Sn). Very recently Aleš Růžička and their group reported tin(II) guanidinate with oxidative cycloaddition[19h] and oxidative addition of tin(II) amidinate[25]. According to their report homoleptic amidinate tin(II) did not react with elemental sulfur due to their insufficient

oxidizing strength. Keeping on mind, It was our interest to know that guanidinate stabilized homoleptic gr 14 complexes Ge, Sn and Pd will react with chalcogens or not?

First we started homoleptic germanium complex (**26**) with chalcogens i.e. sulfur, selenium and Tellurium. After mixing both the compound **26** and elemental sulfur in benzene solvent at 60 ^{0}C tetrasulfido Ge(IV) has formed instead of bridged (μ–S)$_2$L$_2$Ge complex i.e. confirmed by X–ray crystallographic analysis. Similar reaction with elemental selenium, formation of bridged (μ–Se)$_2$L$_2$Ge complex was confirmed by NMR spectroscopy. The reactivity of compound **26** with sulfur and selenium because of the allotropes of sulfur refers to the many allotropes of the element sulfur. Tetrasulfur is one of them. So in case reaction of sulfur with **26** there is a chance to form L$_2$GeS$_4$ (tetrasulfur) but for Se allotropes there is polymeric form and temperature dependent. Several attempts were made to get X–ray quality crystal of compound **31** but unsuccessful. Similarly with elemental Tellurium there was no reaction up to 80 ^{o}C and above this temperature but there was decomposition of the homoleptic Ge(II) compound to free ligand monitored by ^{1}H NMR spectroscopic studies.



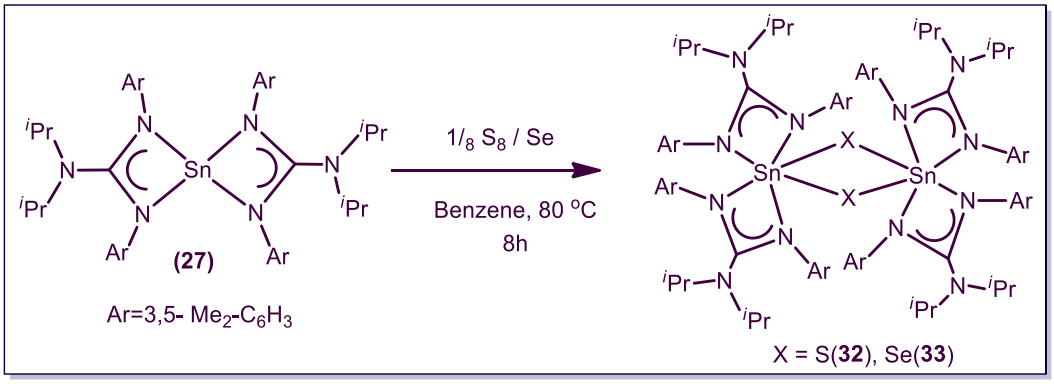
Scheme 6.2. Synthesis of germanium tetrasulfido complex.



Scheme 6.3. Synthesis of dimeric bridged seleno Ge(IV) complex.

Similar reaction was performed homoleptic tin(II) complex and chalcogens(i.e. S, Se and Te) at 80 °C in benzene as solvent. For sulfur and selenium, both the cases bridged (μ–S)$_2$L$_2$Sn(**32**) and (μ–Se)$_2$L$_2$Sn(**33**) complexes were formed as orange color crystalline solid with very good yield. But there was no reaction with elemental tellurium powder and similar observation like earlier with homoleptic germanium complexes (**26**). Due to large size of Te compared to Se, formation of bridged tellurium compound is sterically hindered. But smaller size Se it is easily forming bridged seleno complex with Ge as wel as Sn metal.

Surprisingly, homoleptic plumbylene did not react with elemental chalcogens even at higher temperature also.



Scheme 6.4. Synthesis of dimeric bridged sulfur and seleno Sn(IV) complexes.

6.2.2 NMR Spectroscopic studies in solution

Compounds (**26–29**) are free soluble in organic solvents like hexane, toluene, tetrahydrofuran etc. and compounds **30–33** are hexane insoluble but soluble in toluene, tetrahydrofuran and partially soluble in benzene. All the compounds are thermally stable but sensitive towards air and moisture. Purity of the compounds (**26**–**33**) and the structural behaviour of homoleptic metal complexes as well as their oxidative products were examined by multinuclear NMR (^{1}H, ^{13}C) spectroscopic studies in C_6D_6, $CDCl_3$ and Tol–d_8, THF–d_8 solvents. The ^{1}H NMR spectra of homoleptic Ge, Sn and Pb complexes shows similar kind of NMR resonance. Due to symmetry independent group in each homoleptic M(II) complexes ^{1}H NMR spectra expose one set of signals. In aliphatic region ^{1}H NMR resonance singlet at δ = 2.3 ppm for aryl methane protons which can be attributed to the symmetrical coordination of two ligand systems to the metal site (C_2 symmetrical) and one doublet at δ = 0.82– 0.92 ppm due to one chemically equivalent set of iso–propyl methyl groups for compounds **26**, **27**, **28** & **29**.

In ^{13}C NMR spectra of homoleptic compounds (**26–29**) signals for the N*C*N carbon atom are found around 164–168 ppm i.e. comparable with the reported amidinate and guanidinate homoleptic Ge, Sn and Pb complexes[R].

As the oxidative addition products are easily soluble in toluene, but partially soluble in benzene. So ^{1}H NMR spectra were recorded in C_6D_6, toluene–d_8, THF–d_8 and compounds **30**–**33** also shows symmetric behaviour in both C_6D_6 and toluene– d_8 solvents. In ^{13}C NMR spectra the ipso carbon resonance is showing same region like homoleptic complexes.

6.2.3. X–ray crystallographic studies

Molecular structure of compounds **26, 27, 28** & **29** are represented in figure **6.1, 6.2, 6.3 & 6.4** respectively. Single crystal suitable for X–ray diffraction were grown from saturated hexane solution at 0 ^{o}C. Colorless crystals were isolated in quantitative yield.

Compounds **26**–**29** are monomeric and four coordinate with a distorted sawhorse coordination geometry. Metal center surrounded by four nitrogen atom of two guanidinate ligand and one position is occupied by stereochemically active lone pair of electron. The geometry of the metal center is distorted trigonal bipyramidal.

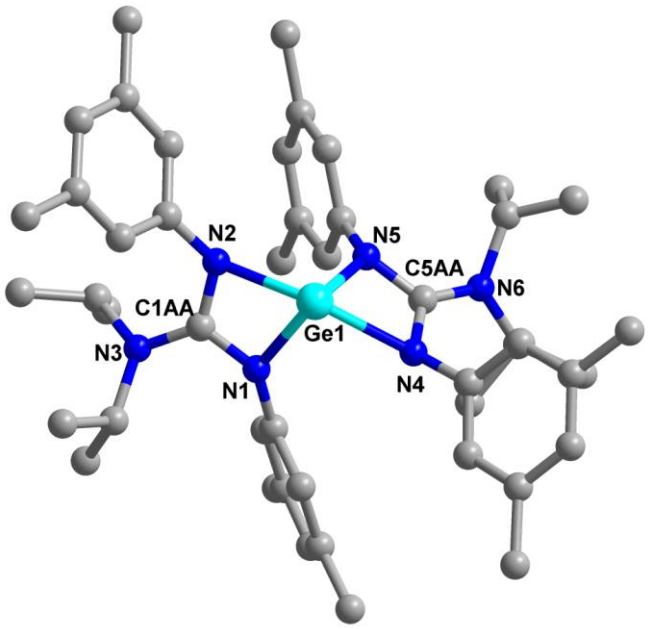


Figure 6.1. Molecular structure of L^3GeL^3. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **26**: Ge1– N1 2.012(2), Ge1–N2 2.206(2), Ge1–N4 2.232(2), Ge1–N5 1.994(3), N1–C1aa 1.353(3), N2–C1aa 1.331(3), N3–C1AA 1.376(3), C5AA–N6 1.369(4); N5–Ge1–N1 98.79(10), N1–Ge1–N2 62.62(8), N5–Ge1–N4 62.53(9), N2–C1AA–N1 109.9(2), N4–C5AA–N5 110.0(3).

Compound **26** crystallises in triclinic system with space group $P\bar{1}$. In compound **26** the axial distance of Ge1–N2 2.206(2) Å and Ge1–N4 2.232(2) Å are considerably longer than the equatorial bond distance of Ge1–N1 2.012(2) Å and Ge1–N5 1.994(3) Å. Elongation of bond length (Ge1–N2 and Ge1–N4) compare to heteroleptic guanidinate stannylene due to the high steric demands of the ligand[26]. The bond angle of axial N2–Ge1–N4 138.94^o is very small compared to the standard tbp geometry bond angle i.e. 180 ^{o}C and that is because of ring

strain of compound **26**. The equatorial bond angle N1–Ge1–N5 98.80° is also less. One crystallographic C_2 axis have made two ligands equivalent.

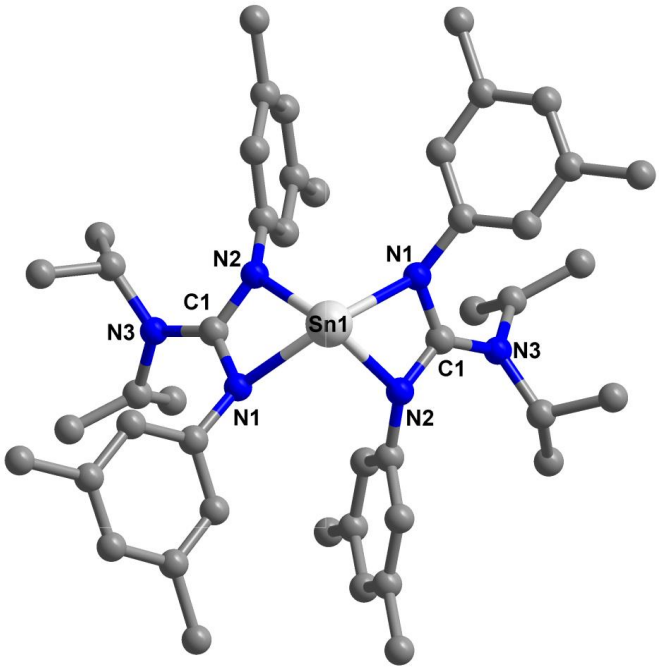


Figure 6.2. Molecular structure of L^3SnL^3. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **27**: Sn1–N1 2.3160(19), Sn1–N2 2.2242(19), N2–C1 1.345(3), N1–C1 1.343(3), N3–C1 1.373(3), N1–C2 1.415(3), N2–C10 1.417(3); N2–Sn1–N1 58.45(6), C1–N1–Sn1 93.06(13), C1–N2–Sn1 97.14(13), N1–C1–N2 111.25(19), C1–N1–C2 122.71(19), C1–N2–C10 124.28(19), C10–N2–Sn1 131.85(14), C2–N1–Sn1 131.74(15), N1–C1–N3 124.70(19), N2–C1–N3 124.04(19).

Compound **27** crystallizes in the monoclinic system with *C*2/c space group. Colorless crystal of **27** revels that one half of the molecule present in the asymmetric unit. By symmetric transformation the whole molecule can be generated. Axial bond distance Sn1–N1 2.3160(19) Å is slightly longer than the Sn1–N2 2.2242(19) Å bond distance that features is related to the earlier reported homoleptic amidinated or guanidinated tin(II) complexes. For

compound **27** the pseudoaxial vector is well–defined by N1–Sn1–N1' with an angle of 120.55°. This largest bond angle value N1–Sn1–N1' 120.55° in compound **27** represents the configuration of the metal center is distorted square pyramidal in comparison with the homoleptic bis(guanidinato)tin(II) complex reported by Richeson[19f] as distorted pseudo trigonal bipyramidal with a pseudoaxial vector with an angle of 140.4(3)°. This large distortion from the linearity is due to the restricted bite angle(°) of the ligand. Sum of the angle around N2 is 353.26° but sum of the angle in N1 center is 347.53°. The backbone of the ligand three nitrogen atoms are in same plane. N1–C1 1.343(3) and N2–C1 1.345(3) bond distances are almost same, signifying the π bond delocalization is not fixed between N1–C1 and N2–C1.

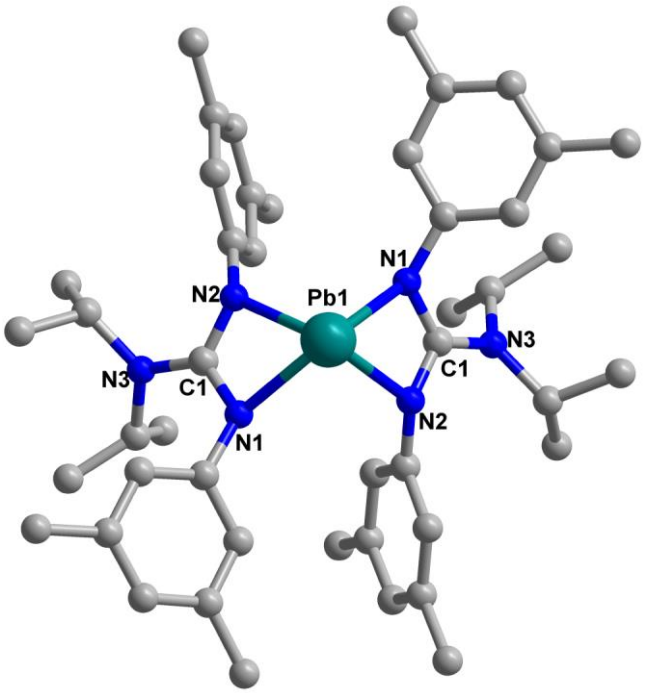


Figure 6.3. Molecular structure of L^3PbL^3. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **28**: Pb1–N1 2.385(3), Pb1–N2 2.363(4), Pb1–$N1^i$ 2.385(3), N1–C1 1.343(5), N2–C1 1.344(5), N3–C1 1.382(5), N2–C2 1.402(5); N2–Pb1–N1 56.39(11), N1–C1–N2 113.2(4), N2–C1–N3 123.0(4), C1–N2–C2 124.0(3).

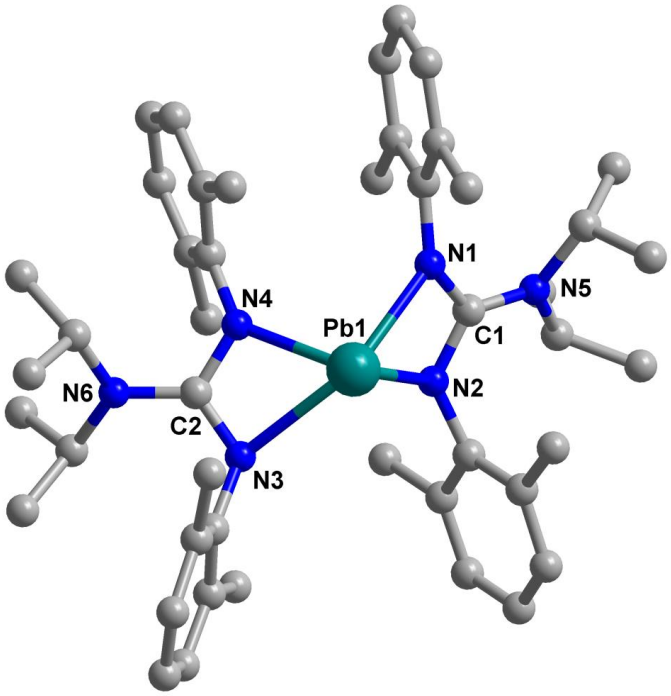


Figure 6.4. Molecular structure of L^1PbL^1. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **29**: Pb1–N1 2.399(4), Pb1–N2 2.318(4), Pb1–N3 2.594(4), Pb1–N(4) 2.277(4), N1–C1 1.350(6), N5–C1 1.366(6); N2–Pb1–N1 56.03(14), N4–Pb1–N3 54.65(13), N1–C1–N2 109.9(4), N3–C2–N4 113.8(4), N1–C1–N5 125.3(4).

The structure of homoleptic guanidinate lead(II) complexes (**28** & **29**) using guanidinate ligand [^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$] and [^{i}Pr$_2$NC{N–2,6–Me$_2$–C$_6$H$_3$}$_2$] were determined by X–ray diffaraction (Figure **6.3** & **6.4**). Both the compounds crystallises in monoclinic system with *C*2/*c* space group. Bond lengths and bond angles are shown in figure **6.3** & **6.4**. In compound **28** & **29** molecular geometry is similar like compound **26** & **27**, distorted trigonal bypyramid and one pseudo equitorial position is occupied by one lone pair of electron. The lone pair lies on molecular C_2 axis. Compound **28** Axial bond length Pb1–N1 2.399(4), Pb1–N3 2.594(4) Å is longer than the equatorial bond length Pb1–N2 2.318(4), Pb1–N(4) 2.277(4) Å which is similar to the reported homoleptic amidinate lead(II) complexes. This Pb–N bond distances are comparable with the homoleptic amidinate lead(II) complexes described by Junk and co–workers[27].

For compound **29** observation is same like compound **28** and geometry of the metal center also distorted trigonal bypyramidal and one pseudoequitorial position is occupied by one lone pair of electron. Compound **29** shows that one half of the molecule present in the asymmetric unit. The distortion between both the compounds **28** & **29** from their ideal geometry is maybe the reason by aromatic π–π stacking interaction in compound **28** but not in compound **29**.

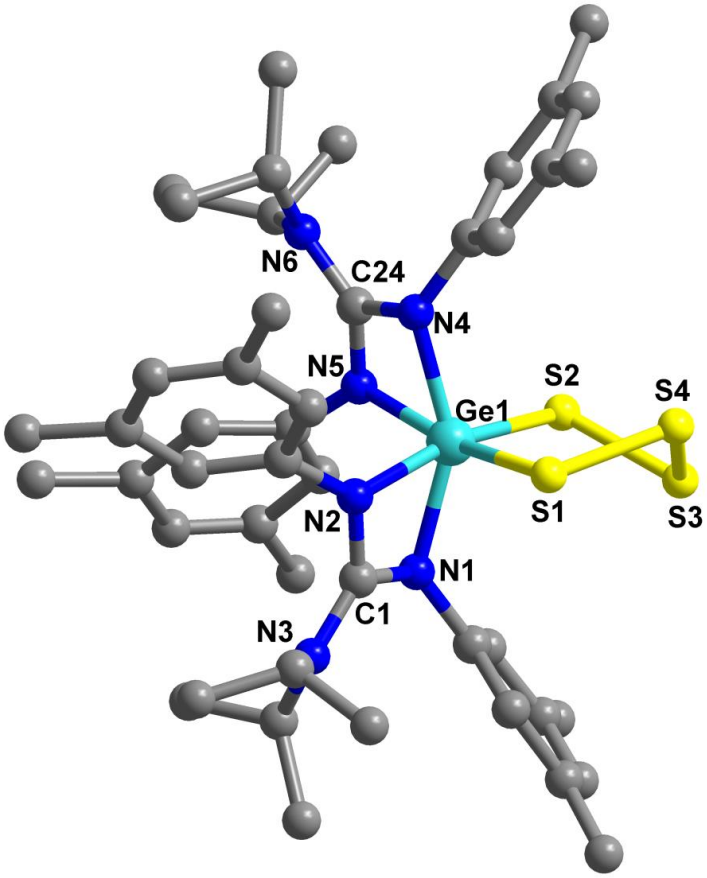


Figure 6.5. Molecular structure of $L^3{}_2GeS_4$. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **30**: Ge1–S1 2.3331(19), Ge1–S2 2.331(2), Ge1–N1 2.005(5), Ge1–N2 2.012(5), Ge1–N4 1.992(4), Ge1–N5 2.016(5), C1–N1 1.338(8), C1–N2 1.343(7), C1–N3 1.367(8), N6–C24 1.361(7), C24–N4 1.358(7), C24–N5 1.340(7), S2–S3 2.190(4), S4–S3 2.060(5); S2–Ge1–S1 98.14(9), N1–Ge1–N2 65.07(19), N4–Ge1–N5 65.54(19), N1–C1–N2 107.4(5), N5–C24–N4 107.0(5), N1–Ge1–N5 94.6(2), N4–Ge1–N1 150.9(2), N4–Ge1–N2 94.27(19), N2–Ge1–N5 94.8(2), S4–S1–Ge1 105.50(12), S3–S2–Ge1 99.93(13), S4–S3–S2 101.16(15).

Crystal for compound **30** suitable for X-ray diffraction grown from ether solution at -20 ^{o}C. It crystallises in triclinic system with $P\bar{1}$ space group. Selected bond length and bond angle have shown with molecular structure in figure 5. This is first example of homoleptic guanidinato germanium tetrasulfido complex. Metal center chelating with two N-C-N ligand and two sulfur from tetrasulfido group. The chelating Ge1–N1, Ge1–N2, Ge1–N(4) and Ge1–N(5) bond distances are 2.005(5), 2.012(5), 1.992(4) and 2.016(5) which are slightly shorter than the homoleptic guanidinate germylene complex described earlier. Hexacoordinate germanium metal center is distorted pseudooctahedral geometry. MS_4 ring is in distorted half chair conformation where the two central sulfur atoms in the S_4 unit lie opposite side of the two plane of M–N–C–N. In compound **30** metal atom is symmetrically bound with the two equal metal sulfur bond lengths [Ge1–S1 2.3331(19) and Ge1–S2 2.331(2) Å]. The average S-S bond length (2.087 Å) in sulfur chain are slightly longer than the average S–S bond distance (2.050 Å) for orthorhombic sulfur. S2–Ge1–S1 98.14(9)^{o} bond angle is comparable with the L_2GeS4 compound reported by Renji Okazak i.e 98.4(1)^{o} [6].

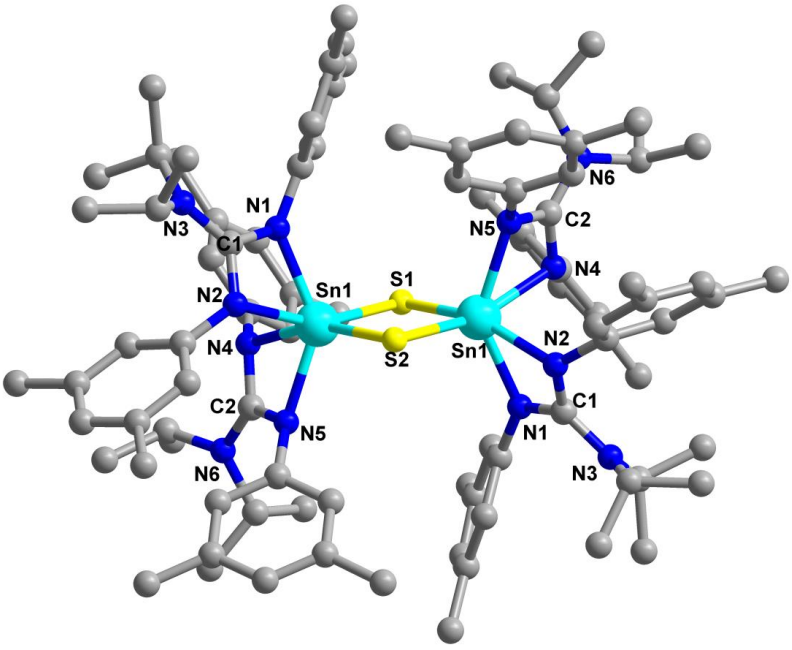


Figure 6.6. Molecular structure of **{L^{3}Sn(μ–S)}$_2$**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **32**: Sn1–N1 2.1871(18), Sn1–N2 2.2337(18), Sn1–N4 2.2262(17), Sn1–N5 2.1941(17), Sn1–S1 2.4321(7), Sn1–S2 2.4508(7), N1–C1 1.346(3), N(3)–C1 1.374(3); N1–Sn1–N2 60.05(6), N5–Sn1–N4 60.21(6), S1–Sn1–S2 91.72(3), N1–Sn1–N4 87.38(6), N4–Sn1–N2 88.49(7), N1–Sn1–N5 139.32(7), N1–Sn1–S1 97.965, N1–Sn1–S2 109.90(5), N2–C1–N1 110.56(18), N1–C1–N(3) 124.46(19).

Structural analysis of compound **32** reveals that it is a dimeric complex with bridging sulfur ligand. It crystallised in monoclinic space group *C*2/*c*. The central tin atom coordination geometry is distorted pseudooctahedral. One C_2 axis lies on perpendicular to nearly square (Sn-μ-S)$_2$ ring. From the figure **6.6** it is clear that the structural feature in this molecule is bridged S bond. The bond length of Sn1–S1 2.4321(7), Sn1–S2 2.4508(7) Å are comparable reported in the literature Sn-S bond distance (2.434(2) Å, 2.476(2) Å) of structurally reported [(CyNC(Me)NCy)$_2$Sn(μ-S)]$_2$ compound[19f]. Sn-N bond distances Sn1–N1 2.1871(18), Sn1–N2 2.2337(18) Å are slightly shorter than [(CyNC(Me)NCy)$_2$Sn(μ-S)]$_2$ i.e. Sn1-N1, 2.226(5) and Sn1-N2, 2.264(4) Å. N1–Sn1–N2 60.05(6) bond angle is slightly longer than N1-Sn1-N2

57.1(2) in amidinate $[(CyNC(Me)NCy)_2Sn(\mu\text{-}S)]_2$. Another bond angle S1–Sn1–S2 91.72(3)^o is wider than S1-Sn1-S1a, 88.95(5)^o in $[(CyNC(Me)NCy)_2Sn(\mu\text{-}S)]_2$[19f].

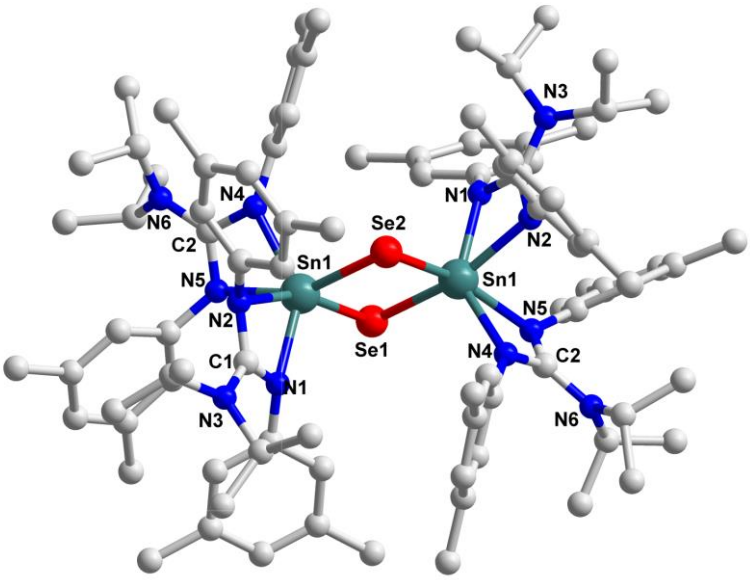


Figure 6.7. Molecular structure of **{L^{3}Sn(μ–Se)}$_2$**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **33**: Sn1–N1 2.200(4), Sn1–N2 2.236(4), Sn1–N4 2.192(4), Sn1–N5 2.244(4), Sn1–Se1 2.5759(6), Sn1–Se2 2.5621(6), N4–C2, N(6)–C2 1.375(6); N1–Sn1–N2 60.06(13), N4–Sn1–N5 59.59(14), Se2–Sn1–Se1 92.996(17), N4–Sn1–N1 139.14(14), N4–Sn1–N2 87.29(14), N2–Sn1–N5 88.21(14), N1–Sn1–N5 93.14(14), N5–C2–N4 110.4(4), N4–C2–N(6) 124.4(4)

For compound **33** (figure 6.**7**) similar kind of structural behaviour shows like compound **32** dimeric species with bridging seleno ligand. In this also central metal coordination geometry is distorted psudooctahedral with C_2 axis perpendicular through square $(Sn\text{-}\mu\text{-}Se)_2$ ring. The four membered ring core of $[Sn(\mu–Se)]_2$ is co planar. The bridged Sn1–Se1 2.5759(6), Sn1–Se2 2.5621(6) bond lengths are comparable with $\{[ArNC(N^iPr_2)NAr]\ N(SiMe_3)_2Sn(\mu–Se)\}_2$ Sn1–Se1 2.5676(17), Sn1–Se2 2.5658(18) reported by our group[18].

Table 6.1. Crystal data for compounds **26-30, 32 and 33**

Compounds	**26**	**27**	**28**	**29**	**30**	**32**	**33**
Formula	$C_{46}H_{64}GeN_6$	$C_{46}H_{64}N_6Sn$	$C_{46}H_{64}N_6Pb$	$C_{49}H_{71}N_6Pb$	$C_{50}H_{64}GeN_6S_4$	$C_{116}H_{152}N_{12}S_2Sn_2$	$C_{116}H_{152}N_{12}Se_2Sn_2$
Mol.mass	773.62	819.72	908.22	951.30	949.90	2015.99	2109.79
Size (mm)	0.22 X 0.17 X 0.1	0.25 x 0.24 x 0.23	0.25 × 0.22 × 0.19	0.13 × 0.098 × 0.059	0.22x0.16x 0.13	0.24 × 0.2 × 0.17	0.26 × 0.21 × 0.15
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	*C* 2/c	C 2/c	*P*2(1)/c	$P\bar{1}$	*C* 2/c	*C* 2/c
a (Å)	10.5001(5)	22.256(11)	22.573(2)	19.451(8)	11.680(5)	28.408(3)	28.6724(11)
b (Å)	14.4044(7)	7.966(4)	7.804(7)	15.043(6)	11.748(5)	15.812(13)	15.8581(5)
c (Å)	14.7225(8)	24.991(10)	24.986(2)	15.887(6)	19.257(8)	26.594(3)	26.6415(9)
α (°)	97.446(3)	90	90	90.000	82.965(2)	90.000	90.000
β (°)	90.402(4)	98.471(4)	97.758(4)	100.156(2)	82.365(3)	113.947(8)	114.049(3)
γ (°)	96.346(3)	90	90	90.000	70.554(2)	90.000	90.000
V (Å3)	2193.92(19)	4382(3)	4361(3)	4576(2)	2460.9(16)	10917(4)	11062.1(7)
Z	2	4	4	4	2	4	4
ρ (gcm^{-3})	1.171	1.242	1.383	1.381	1.282	1.227	1.267
μ (Mo–$K\alpha$) (mm^{-1})	0.735	0.620	3.906	3.726	0.832	0.623	1.161
T (K)	100	100	100	100	100	100	100
θ (max.)	27.377	25.50	29.99	27.56	25.439	30.60	25.027
Unique reflections	9723	4080	6147	10544	8997	16721	9725
F(000)	828	1728	1856	1956	1004	4256	4400
R(int)	0.0481	0.0424	0.1086	0.0875	0.0627	0.0646	0.0600
Parameters	494	248	248	539	566	612	612
*R*1	0.0575	0.0290	0.0447	0.0412	0.0798,	0.0395	0.0429
w*R*2	0.1546	0.0691	0.1108	0.0891	0.2063	0.0980	0.1003
GOF	1.024	1.034	1.050	1.018	1.051	1.073	1.028

6.3. Conclusion

In conclusion, we have demonstrated bis(guanidinate) ligand stabilized homoleptic germylene, stannylene and plumbylene complexes and their oxidative additions with chalcogens. Germylene reacts with elemental sulfur led to the formation of tetrasulfido bis(guanidinato) Ge(IV), $L^3{}_2GeS_4$ (**30**) complex and reaction with selenium powder formed dimeric bridged seleno complex $\{L^3Ge(\mu–Se)\}_2$(**31**). Furthermore, stannylene reacts with elemental sulfur and selenium forms dimeric bridged sulfur/seleno $\{L^3Sn(\mu–S)\}_2$(**32**) and $\{L^3Sn(\mu–Se)\}_2$(**33**) complexes. These are the first examples of guanidinate supported homoleptic germanium tetrasulfido and germanium and tin dimeric bridged complexes.

6.4. References

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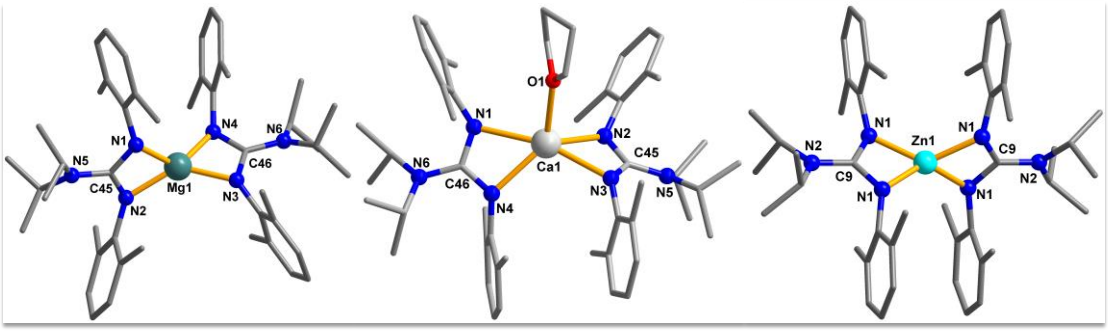
Summary

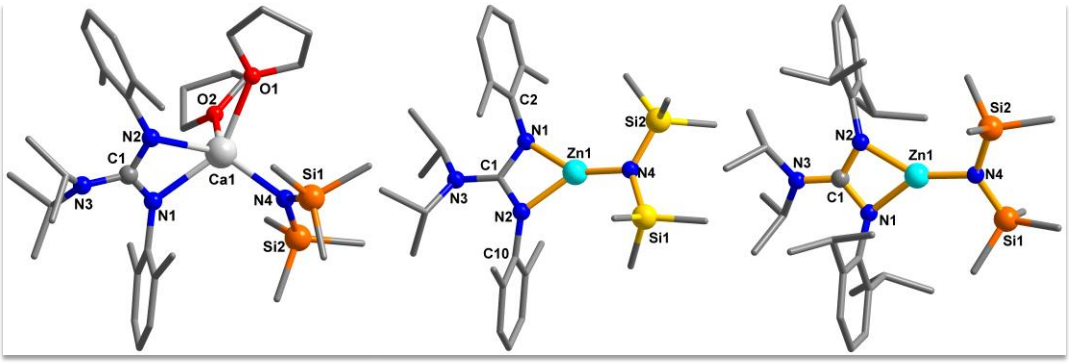
In this thesis synthesis and reactivity studies of bulky guanidinate supported main group complexes that include Group 2, 13 and Group 14 elements are reported.

- Initially, we have demonstrated the synthesis of new bulky guanidine ligand (L^1H) and its potassium salt, which are confirmed by X-ray crystallography. By using these precursors, bulky guanidinate homoleptic Mg(II), Ca(II) and Zn(II) complexes have been synthesized by two synthetic routes i) deprotonation of the free ligand with MR_2 (R= amide, alkyl, etc.) ii) Salt metathesis reaction of alkali metal guanidinates with metal diahalide. Further, we have shown that these three homoleptic complexes are effiecient catalysts for Tishchenko reaction *i.e.* dimerization of aldehyde to ester at very mild reaction conditions.

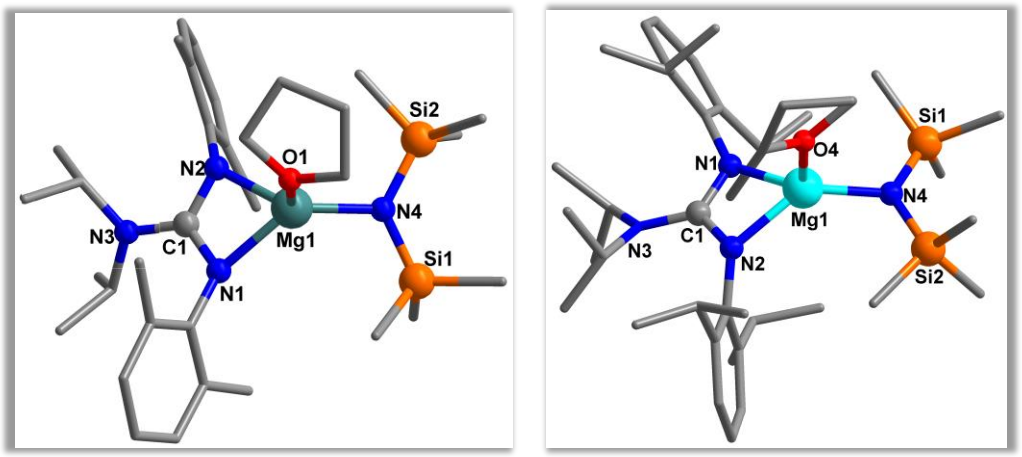


- It is always quite challenging to synthesize heteroleptic alkaline earth metal complexes, because such complexes are more prone to undergo Schlenck equilibrium $2LMX \leftrightarrow LML + MX_2$. In recent years, mainly Hill and Harder and few other research groups have independently utilized heteroleptic alkaline earth metal complexes as catalysts for various organic transformations such as hydroamination, hydrosilyation, guanylation etc., in which L acts as a spectatator ligand and X ligand participate in the reaction. In view of this, we have synthesized and structurally characterized heteroleptic bulky guanidinate stabilized Ca(II) and Zn(II) metal amide

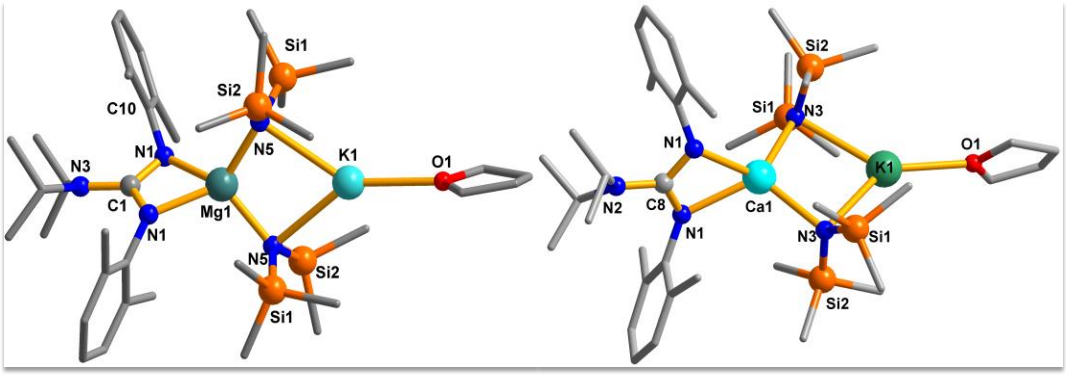
complexes. These heteroleptic calcium and zinc amide complexes have shown excellent catalytic activity towards intramolecular hydroamination reaction for both primary and secondary amines.



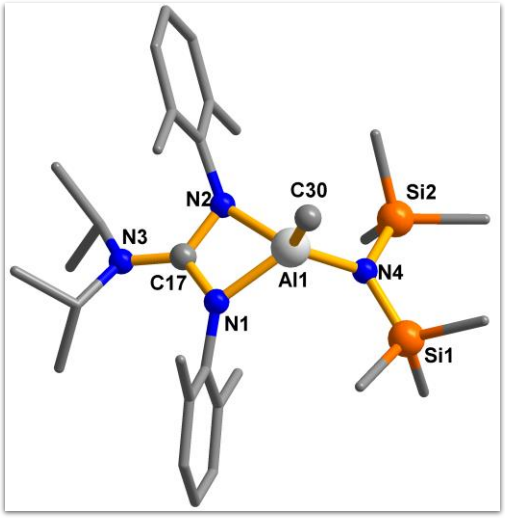
- We also synthesized and structurally characterized of two examples of hetroleptic guanidinate supported Mg(II) amide complexes. Both the compounds were synthesized by salt metathesis reaction as well as deprotonation of neutral ligands with metal bis(amides) in THF solvent. In the literature there are many reports on hydroboration of carbonyls, pyridine, imine and isonitriles but hydroboration of ester examples are few in literature. Ester hydroboration is thermodynamically more challenging than aldehyde. So here these magnesium amide complexes have been shown as active precatalysts for hyboration of ester with excellent catalytic activity (0.1 to 0.5 mol%) under solvent free conditions.



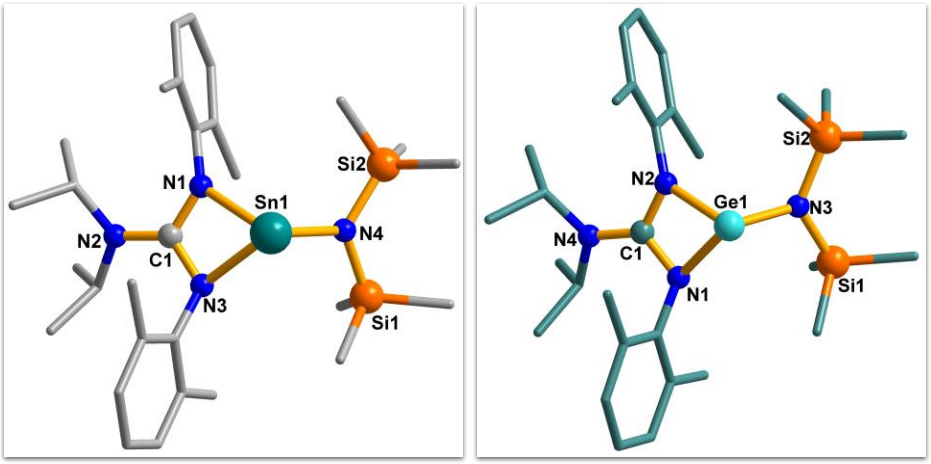
- In the literature few examples of heterobimetallics HMDS compounds with alkali metal with alkaline earth metals (Li-Mg, Li-Ca, K-Mg, Rb-Mg, and K-Ca) are known. Heterobimetallic compounds with only alkaline earth metal amides are also known in the literature. Herein, we have demonstrated the first examples of guandinate ligand stabilized Heterobimetallic mixed alkali and alkaline earth metal amide (Mg-K and Ca-K) complexes. All the compounds were well characterized by multinuclear NMR, X-ray crystallographic studies and elemental analysis.



- Bulky guanidinate supported aluminum (III) mixed alkyl/amide and bis (amide) complexes have been synthesized. The amido group which plays the role as a good leaving group. The supporting ligand *i.e.* guanidinate ligand also play significant role on metal center by providing steric and electronic support. Both the mono and bis (amide) aluminum complexess show good to excellent catalytic activity for dimerization of aldehyde *i.e.* Tishchenko reaction in neat condition at 80 ^{o}C with 2 mol% catalyst.

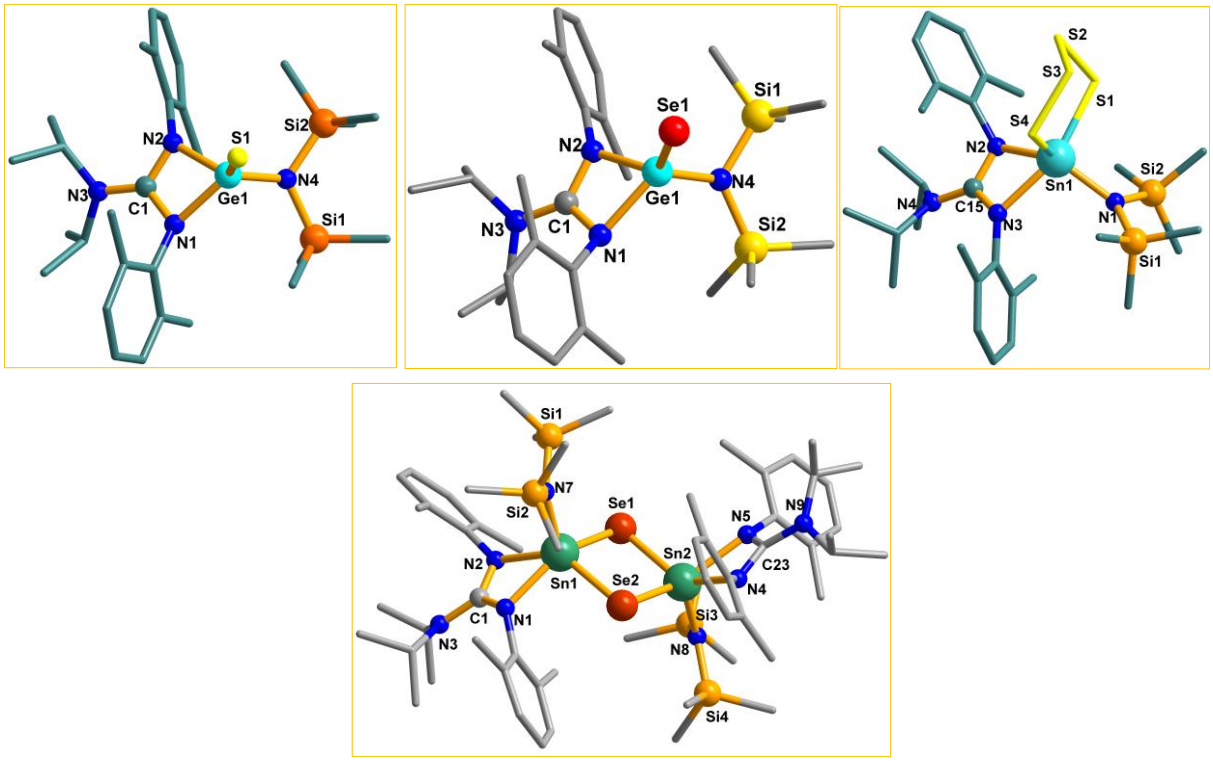


- We reported synthesis of guanidinate ligand stabilized three coordinated low valent Ge(II) and Sn(II) metal amide complexes and demonstrated the reactivity of Ge(II) and Sn(II) complexes as catalyst for cyclotrimerization reaction.

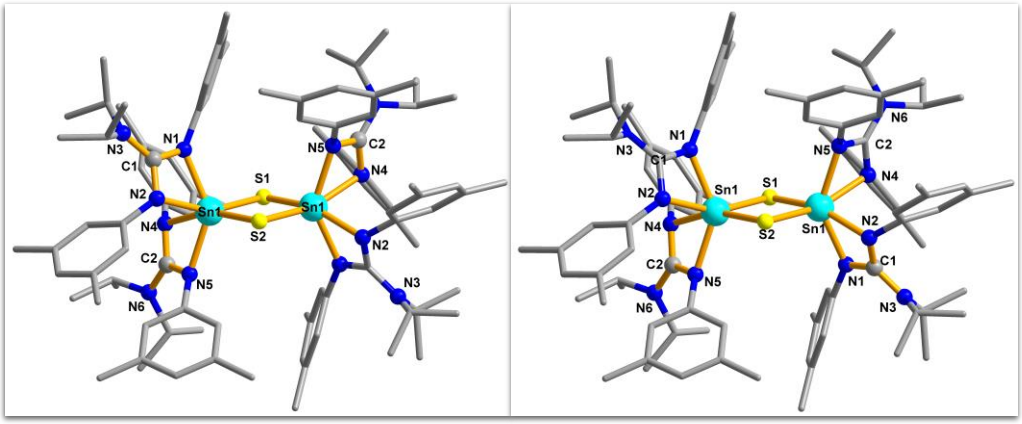


- The synthesis of molecular compounds with formal double bonds between the heavier Group 14 and 16 elements M=E (M = Si, Ge, Sn; E = S, Se, Te) is quite challenging due to the high polarity and/or weak π-orbital overlap in the M=E bonds. Surprisingly, there have been no reports on oxidative addition of chalcogens to guanidinate supported Ge(II) and Sn(II) amide complexes. Herein, we have demonstrated the reactivity of first isolable guanidinato Ge(II) and Sn(II) towards chalcogens (S and Se). Reaction with elemental sulphur and selenium with germanium amide formation

of guanidinate supported germathioamide and germaselanoamide. Reaction of guanidinate tin amide with elemental sulphur led to the formation of guanidinato cyclic tetrasulfido tin complex and dimeric bridged seleno tin was synthesized from guanidinato tin amide and selenium powder.



- Guanidinate ligand supported low valent homoleptic germylene, stannylene and plumbylene complexes are reported and the reactivity of homoleptic germylene and stannylene towards chalcogens (S and Se) have been explored, in which oxidative addition occurred and led to the formation of bis(guanidinate) supported germanium tetrasulfido, dimeric bridged seleno complex and dimeric bridged sulfido and seleno tin complexes. These are the first examples of guanidinato Ge(IV) and Sn(IV) complexes with chalcogens. Attempts to synthesis oxidative addition products of homoleptic plumbylne complexes with chalcogens were unsuccessful.


N1
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N5
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S1
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Sn1
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N3
N6
N1
N3
C1
N2
N4
C2
N5
N6
Sn1
S1
S2
Sn1
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C1
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N3

CHAPTER 8

Experimental Section

8.1. General procedure

All stoichiometric reaction and catalytic reactions were carried out under atmosphere of high purity nitrogen gas using standard Schlenk–line and cannula techniques or nitrogen filled MBraun glove box. Solvents *n*-hexane, benzene, toluene, pentane, tetrahydrofuran and diethyl ether were dried with appropriate drying agents and degassed prior to use. All glassware was oven-dried at 120 ^{o}C for at least 24h, assembled hot and cooled under high vacuum prior to use.

8.2 Physical measurement

Melting Point Melting points were measured on an electro thermal apparatus and are uncorrected.

NMR Spectra NMR spectra were recorded on Bruker AV 400 MHz spectrometer for ^{1}H NMR (^{13}C{^{1}H} NMR 100 MHz and ^{29}Si{^{1}H} NMR 80 MHz). Deuterated NMR solvents C_6D_6, C_7H_8, $CDCl_3$ and THF-d_8 were dried over sodium before distillation under nitrogen and storage over molecular sieves. Heteroatom NMR spectra were recorded 1H decoupled with the exception of ^{19}F. Chemicals shifts are reported in ppm with reference to residual deutorited solvent peak foe ^{1}H nucleai, external standard was used $SiMe_4$ for ^{29}Si nuclei, $BF_3{\cdot}OEt_2$ for ^{11}B nuclei and $CFCl_3$ for ^{19}F.

IR Spectra were recorded in Perkin-Elmer FT–IR Spectrometer.

Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer.

Elemental Analysis Elemental analyses were performed in a Vario Micro Cube Elementar CHNS /O analyzer.

8.3 Starting Materials

$^{i}Pr_2NH$, $^{n}BuLi$ (1.6 M in hexane, Aldrich), $LiN(SiMe_3)_2$ (Aldrich), $KN(SiMe_3)_2$ (Aldrich), $Zn\{N(SiMe_3)_2\}_2$ (Aldrich), $ZnCl_2$ (Aldrich), $ZnEt_2$ (1.0 M solution in hexane, (Aldrich)), $Mg^{n}Bu_2$ (1 M solution in heptane, (Aldrich)), $MgCl_2$(Aldrich), CaI_2 (Aldrich), $Ca(OTf)_2$ (Aldrich), $Sn[N(SiMe_3)_2]_2$ (Aldrich), $Ge[N(SiMe_3)_2]_2$[1], $AlMe_3$(2.0 M in hexane, Across), $AlMe_2Cl$(0.9 M in hexane, Aldrich), $AlMeCl_2$(1.0 M in hexane, Across), Sulfur and selenium powders(Aldrich), L^2H,[2] $[Mg\{N(SiMe_3)_2\}_2]$[3] and $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$[4], $[PhNMe_2H][B(C_6F_5)_4]$ (Stream chemicals). Amonoalkenes substrate both primary and secondary 2,2-diphenylpent-4-en-1-amine,[5] (1-allylcyclohexyl)methanamine, (1-(2-methylallyl)cyclohexyl) methanamine,[6] 4-methyl-2,2-diphenylpent-4-en-1-amine, (E)-2,2,5-triphenylpent-4-en-1-amine,[7] 2,2-diphenylhex-5-en-1-amine,[8] (1-(but-3-en-1-yl)cyclohexyl)methanamine,[7] N-benzyl-2,2-diphenylpent-4-en-1-amine,[9] N-(4-methylbenzyl)-2,2-diphenylpent-4-en-1-amine, N-(4-methoxybenzyl)-2,2-diphenylpent-4-en-1-amine, 1-(1-allylcyclohexyl)-N-benzylmethanamine[10], 1-(1-allylcyclohexyl)-N-(4-methylbenzyl)methanamine, 1-(1-allylcyclohexyl)-N-(4-bromobenzyl)methanamine,[10] N-benzyl-2,2-diphenylhex-5-en-1-amine,[11] N-benzyl-1-(1-(but-3-en-1-yl)cyclohexyl)methanamine[5] were prepared according to the literature procedure. All the aldehyde and esters substrate were purchased from Sigma-Aldrich, Alfa aesar chemicals and used as received without any further purification.

8.4. Crystallographic data

X-ray crystal structure determination

After removing the crystal from Schlenk flask immediately coated with silicon oil on a glass slide. On a glass fiber suitable crystals were mounted at temperature 100K and it was controlled using an Oxford Cryostream 700 instrument. Crystal data were collected with a

Bruker AXS SMART Apex CCD detector and with an INCOATEC micro source (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). The software SADABS was used for absorption correction SHELXTL[12] and OLEX2[13] for space group, structure determination and refinements. The least-squares refinement techniques on F^2 were done until the model converged. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model.

8.5. Synthesis of Compounds

8.5.1. Synthesis of L^1H **(1)**

^{n}BuLi (1.6 M solution in hexane, 11.29 mL, 18.07 mmol, 1.04 equiv) was added to a solution of ^{i}Pr$_2$NH (1.82 g, 18.07 mmol, 1.04 equiv) in THF (30 mL) at 0 ^{o}C and the resultant solution stirred for 1 h. ArN=C=NAr (Ar = 2,6-Me$_2$-C$_6$H$_3$) in THF (30 mL) (4.303 g, 17.21 mmol, 1.0 equiv) was then added, the resultant solution was stirred for overnight. All volatiles were removed under reduced pressure and diethyl ether and water added to the residue. The mixture was stirred for 30 minutes to give two clear phases. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles evaporated under vacuum to get yellow solid. The solid residue was recrystallized as colorless crystals from hexane. Yield: (4.80 g, 79.4 %). Mp = 128-130 ^{o}C. ESI-HRMS: calcd for $C_{23}H_{34}N_3$ [M+H]+: 352.2753; found: 352.2747. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.14 - 6.93 (t, 2H, ArH), 6.82 (d, 2H, *J* = 8 Hz, ArH), 6.76 (t, 2H, ArH), 4.79 (s, 1H, NH), 3.44 (sept, *J* = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 2.42 (s, 6H, CH(CH$_3$)$_2$), 2.06 (s, 6H, CH(CH$_3$)$_2$), 1.21 (d, *J* = 8 Hz, 12H, CH$_3$) ppm. ^{13}C{^{1}H}NMR (100 MHz, C_6D_6, 25 °C): δ = 148.7 (NCN), 148.5 (Ar-C), 139.3 (Ar-C), 134.9 (Ar-C), 130.3 (Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 125.8 (Ar-C), 122.2 (Ar-C), 48.2 (N-^{i}Pr-

CH), 22.4 (Ar-CH_3), 19.6 (^{i}Pr-CH_3), 19.4 (^{i}Pr-CH_3) ppm ; IR (KBr) ν (cm-1): 3366 (m, N-H), 2966 (m), 1623 (s, C=N), 1587 (s), 1341 (s), 1188 (m), 1135 (m), 1090 (m), 777 (m), 758 (m).

8.5.2. Synthesis of $(LK)_n$ **(2)**

Tetrahydrofuran (30 mL) was added to a mixture of $KN(SiMe_3)_2$ (0.090 g, 0.439 mmol, 1.03 equiv) L^{1}H (0.150 g, 0.426 mmol, 1.0 equiv) and the resulting solution stirred vigorously for 12 h at room temperature. All volatiles were removed under reduced pressure and residue washed with *n*-hexane (10 mL). Solid extracted from toluene (40 mL). The solution was concentrated from reduced pressure ca. 15 mL and cooled 0 ^{o}C to obtain colorless crystals suitable for X-ray diffraction analysis. Yield: (0.160 g, 96%). Mp >300 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 6.89 (d, *J* = 8Hz, 4H, Ar-*H*), 6.57 (s, 2H, Ar-H), 3.70 (sept, *J* = 6.66 Hz, 2H, C*H*$(CH_3)_2$), 2.24 (s, 12H, C*H*$_3$), 1.235 (d, *J* = 4Hz, 12H, CH(C*H*$_3)_2$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 157.0 (N*C*N), 155.5 (Ar-*C*), 130.9 (Ar-*C*), 128.9 (Ar-*C*), 117.6 (Ar-*C*), 47.7 (N-^{i}Pr-*C*H), 23.5 (Ar-*C*H_3), 20.3

(^{i}Pr-CH_3) ppm. ^{1}H NMR (400 MHz, THF-d_8, 25 °C,): δ = 6.78 (d, *J* = 4 Hz, 4H, Ar-H), 6.32 (t, *J* = 8 Hz, 2H, Ar-H), 3.62 (sept, *J* = 6.6 Hz, 2H, $CH(CH_3)_2$), 2.23 (s, 12H, CH_3), 1.20 (d, *J* = 8 Hz, 12H, $CH(CH_3)_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ = 156.4(NCN), 143.5(Ar-C), 130.3(Ar-C), 127.9(Ar-C), 115.5(Ar-C), 47.4(N-^{i}Pr-CH), 23.1(^{i}Pr-CH3), 20.1 (Ar-CH3) ppm. IR (KBr) ν (cm^{-1}): 2924(w), 2725(s), 1616(s), 1587(s), 1457(w), 1376(m), 1305(m), 722(s).

8.5.3. Synthesis of $Mg[^{i}Pr_2NC\{N\text{-}2,6\text{-}Me_2\text{-}C_6H_3\}_2]_2$ **(3)**

Method A: A Schlenk tube charged with L^1H (0.200 g, 0.568 mmol, 2.0 equiv) and $[Mg\{N(SiMe_3)_2\}_2]$ (0.098 g, 0.284 mmol, 1.0 equiv). To the above mixture benzene (15 mL) was added and heated at 80 °C for 24 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL) and concentrated to about 5 mL and finally stored in –30 °C. Colorless crystals of compound **3** suitable for X-ray diffraction analysis are formed after one day. Yield: (0.165 g, 80%).

Method B: L^1H (0.500 g, 1.42 mmol, 1.0 equiv) and $KN(SiMe_3)_2$ (0.297 g, 1.49 mmol, 1.05 equiv) were placed in a Schlenk tube and THF (10 mL) was added at room temperature and stirring was continued overnight. The resulting solution was added drop by drop to a stirred suspension of $MgCl_2$ (0.035 g, 0.355 mmol, 0.5 equiv) in THF (5 mL) at room temperature under stirring for another 24 h. Removal of all volatiles and recrystallized from *n*-hexane (20 mL) gave **3** Yield: (0.417 g, 81%).

Method C: To a solution of L^1H (0.200 g, 0.568 mmol, 2 equiv) in toluene (20 mL) was slowly added drop by drop a solution of $^{n}Bu_2Mg$ (1M solution in heptane) (0.35 mL, 1.25 equiv) at room temperature. The stirring was continued for 12 h. The solvent was removed and solid compound **3** obtained. Yield: (0.173 g, 84 %)**:** Mp = 90-95 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 6.99 (d, *J* = 8Hz, 8H, Ar-H), 6.91-6.87 (m, 4H, Ar-H), 3.86 (sept, *J* = 6.66 Hz, 4H, $CH(CH_3)_2$), 2.23 (s, 24H, CH_3), 0.68 (d, *J* = 8 Hz, 24H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 171.3 (N*C*N), 148.0 (Ar-C), 133.1 (Ar-C), 128.8 (Ar-C), 122.9 (Ar-C), 51.0 (N-iPr-CH), 24.5 (Ar-CH_3), 19.3 (^{i}Pr-CH_3) ppm. IR (KBr) ν (cm^{-1}): 2927(w), 2726(s), 1456(m), 1376(s), 1303(m), 722(s).

8.5.4. Synthesis of Ca[^{i}Pr$_2$NC{N-2,6-Me$_2$C$_6$H$_3$}$_2$]$_2$(THF) **(4)**

The compound **4** was synthesized by following similar procedures to that employed for the preparation of **3** and using appropriate precursors

Method A: L^{1}H (0.250 g, 0.711 mmol, 2.0 equiv) and [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (0.178 g, 0.355 mmol, 1.0 equiv); Yield: (0.239 g, 83%).

Method B: L^{1}H (0.500 g, 1.42 mmol, 1.0 equiv), K{N(SiMe$_3$)$_2$} (0.297 g, 1.49 mmol, 1.05 equiv), CaI$_2$ (0.211 g, 0.711 mmol, 0.5 equiv) in THF (10 mL). Yield: (0.482 g, 83.5 %): M. p. = 145-148 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.01 (d, *J* = 8 Hz, 8H, Ar-H) , 6.87 (t, *J* = 8 Hz, 4H, Ar-H), 3.83 (sept, 4H, *J* = 6.66 Hz, CH(CH$_3$)$_2$), 3.25(m, 4H, OCH$_2$CH$_2$(THF)), 2.25 (s, 24 H, CH$_3$), 1.13 (m, 4H, OCH$_2$CH$_2$, (THF)), 0.79 (d, *J* = 8 Hz, 24H, CH(CH$_3$)$_2$), ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 170.0 (NCN), 150.8 (Ar-C), 131.8 (Ar-C), 128.8 (Ar-C), 121.0 (Ar-C), 68.8 (THF), 50.5 (N-^{i}Pr-CH), 25.6 (THF), 25.0 (Ar-CH$_3$),19.8 (^{i}Pr-CH$_3$). IR (KBr) ν (cm^{-1}): 2925(w), 2726(s), 1459(m), 1377(s), 1304(m), 722(s).

8.5.4a. Synthesis of Ca[^{i}Pr$_2$NC{N-2,6-Me$_2$C$_6$H$_3$}$_2$]$_2$ **(4a)**

To a mixture of L^{1}H and Ca(OTf)$_2$ in a J Young valve NMR tube was added 0.6 mL C$_6$D$_6$ and further heated to 100 ^{o}C for 48 h and led to the formation of LCaL (**4a**); LH (0.020 g, 0.0568 mmol, 2.0 equiv) and Ca(OTf)$_2$ (0.011 g, 0.0284 mmol, 1.02 equiv) ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C,): δ = 6.86-6.84 (m, 12H, Ar-*H*), 2.78 (sept, 4H, *J* = 6.66 Hz, C*H*(CH$_3$)$_2$), 2.28 (s, 24 H, C*H*$_3$), 0.955 (d, *J* = 4 Hz, 24H, CH(C*H*$_3$)$_2$) ppm

8.5.5. Synthesis of $Zn[^{i}Pr_2NC\{N\text{-}2,6\text{-}Me_2C_6H_3\}_2]_2$ **(5)**

The compound **5** was synthesized by following similar procedures to that employed for the preparation of **3** and using appropriate precursors

Method A: L^1H (0.2 g, 0.568 mmol, 2.0 equiv) and $[Zn\{N(SiMe_3)_2\}_2]$ (0.114 mL, 0.284 mmol, 1.0 equiv). Yield: (0.176 g, 81%).

Method B: L^1H (0.250 g, 0.711 mmol, 1.0 equiv) and $K\{N(SiMe_3)_2\}$ (0.149 g, 0.746 mmol, 1.05 equiv) in THF (10 mL) at room temperature and stirring was continued overnight. The resulting solution was added drop by drop to a stirred suspension of $ZnCl_2$ (0.048 g, 0.355 mmol, 0.5 equiv) in THF (5 mL); Yield: (0.204 g, 75%).

Method C: L^1H (0.5 g, 1.42 mmol, 2 equiv) and Et_2Zn(1M solution in hexane) (0.86 mL, 1.2 equiv); Yield: (0.452 g, 83%). Mp = 155-159 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C,): δ = 6.98 (d, *J* = 8Hz, 8H, Ar-*H*), 6.91-6.88 (m, 4H, Ar-*H*), 3.88(sept, *J* = 7.33 Hz, 4H, C*H*$(CH_3)_2$), 2.28 (s, 24H, C*H*$_3$), 0.68 (d, *J* = 4Hz, 24H, CH(C*H*$_3)_2$) ppm. ^{13}C {^1H} NMR (100 MHz, C_6D_6): *δ* = 170.2 (N*C*N), 147.3 (Ar-*C*), 133.9 (Ar-*C*), 128.7 (Ar-*C*), 123.3 (Ar-*C*), 51.3 (N-*i*Pr-*C*H), 24.4 (Ar-*C*H_3), 19.2 (*i*Pr-*C*H_3) ppm. IR (KBr) ν (cm^{-1}): 2925(w), 2726(s), 1457(m), 1376(s), 1305(m), 1154(m), 722(s).

8.5.6. General procedure for the Tishchenko reaction

The required amount of catalyst and aldehyde both were placed in a dry sample vial with a stirring bar inside the glove box. Subsequently, sealed vial brought outside the glove box and stirred at room temperature or heated to 80 ^{o}C till completion of the reaction. The reaction was monitored by thin layer chromatography (TLC) and aliquot of reaction mixture by NMR spectroscopy. Final product was purified by column chromatography (Hexane/diethyl ether (98:2))

8.5.6.1. Benzyl benzoate **(2.a.7a)**[14]

0.184 g of light yellowish oil were obtained from the benzaldehyde (0.943 mmol, 0.1 g).

^{1}H NMR ($CDCl_3$, 400MHz): 5.38 (s, 2H,CH_2O),7.357.47(m,7H,aromatic), 7.54-7.59 (m, 1H, aromatic), 8.08-8.1 47 (m, 2H, aromatic), ^{13}C NMR: δ 66.8, 128.3, 128.3, 128.5, 128.7, 129.8, 130.2, 133.1, 136.2, 166.5 ppm.

8.5.6.2. 4-Chlorobenzyl 4-chlorobenzoate **(2.a.7b)**[14]

0.180 g of light yellow oil were obtained from 4-chlorobenzaldehyde (0.711 mmol, 0.1 g)

^{1}H NMR ($CDCl_3$, 400MHz): 5.31 (s, 2H, CH_2O), 7.36-7.42 (m, 6H, aromatic), 7.98-8.0 (m, 2H, aromatic). ^{13}C NMR: δ 66.1, 128.3, 128.8, 128.8, 129.6, 131.0, 134.2, 134.3, 139.6, 165.4 ppm

8.5.6.3. 4-Bromobenzyl 4-bromobenzoate **(2.a.7c)**[14]

0.290 g of light yellow oil were obtained from 4-bromobenzaldehyde (0.85 mmol, 0.158 g)

^{1}H NMR ($CDCl_3$, 400MHz): 5.29 (s, 2H, CH_2O), 7.33-7.47 (m, 7H, aromatic), 7.54-7.59 (m, 1H, aromatic), 8.08-8.10 (m, 2H, aromatic). ^{13}C NMR: δ 66.8, 128.3, 128.3, 128.5, 128.7, 129.8, 130.2, 133.1, 136.2, 166.5 ppm

8.5.6.4. 4-isopropylbenzyl 4-isopropylbenzoate **(2.a.7d)**[15]

0.168 g yellowish color oil were obtained from the reaction of 4-isopropylbenzaldehyde (0.1 g, 0.674 mmol). (84% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 1.24-1.25 (d, J(H,H), 4 Hz, 6H; (CH_3)$_2$CH, 1.266-1.268 (d, J(H,H). 0.8 Hz, 6H); (CH_3)$_2$C*H*, 2.88-2.99 (sept, J(H,H), 6.28 Hz, 2H; 5.32 (s, 2H, CH_2O), 7.23-7.29 (m, 4H, aromatic), 7.36-7.38 (d, J(H,H), 8 Hz, 2H, aromatic); 7.98-8.01 (d, J(H,H), 12Hz, 2H, aromatic). ^{13}C NMR: 166.7, 154.5, 149.1, 133.7, 130.0, 128.4, 126.7, 126.6, 66.5, 34.4, 34.0, 24.1, 23.8 ppm.

8.5.6.5. 4-nitrobenzyl 4-nitrobenzoate **(2.a.7e)**[14]

0.182 g pale yellow color oil were obtained from 4-nitrobenzaldehyde (0.1 g, 0.661 mmol). (91% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 5.50 (s, 2H, C*H*$_2$O), 7.61-7.63 (d, J(H,H), 8 Hz, 2H, aromatic); 8.24-8.32 (m, 6H, aromatic). ^{13}C NMR: δ 66.2, 123.8, 124.1, 128.8, 131.0, 134.9, 142.4, 148.1, 150.9, 164.4 ppm.

8.5.6.6. 4-methylbenzyl 4-bromobenzoate **(2.a.7f)**[14]

0.164 g of light yellow color oil were obtained from 4-methylbenzaldehyde (0.1 g, 0.832 mmol). (82% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 2.37 (s, 3H, C*H*$_3$), 2.41(s, 3H, C*H*$_3$), 5.32 (s, 2H, C*H*$_2$O), 7.19-7.24 (m, 4H, aromatic), 7.34-7.36 (d, J(H,H), 8 Hz, 2H, aromatic), 7.96-7.98 (d, J(H,H), 8 Hz, 2H, aromatic). ^{13}C NMR: 21.3, 21.7, 66.6, 127.6, 128.4, 129.1, 129.3, 129.8, 133.3, 138.1, 143.7, 166.6.

8.5.6.7. 2-fluorobenzyl 2-fluorobenzoate **(2.a.7g)**

0.178 g, of yellow color oily compound were obtained from the reaction of 2-fluorobenzaldehyde (0.1 g, 0.805 mmol). (89% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 5.45 (s, 2H, C*H*$_2$O), 7.07-7 (m, 4H, aromatic), 7.30-7.36 (m, 1H, aromatic), 7.49-7.55 (m, 2H, aromatic), 7.94- 7.98 (m, 1H, aromatic), ^{13}C NMR: δ 61.0, 61.0, 115.5, 115.7, 117.0, 117.2, 118.5, 118.6, 123.0, 123.2, 124.1, 124.1, 124.3, 124.3, 130.3, 130.3, 130.6, 130.6, 132.3, 134.7, 134.8, 159.8, 160.9, 162.3, 163.5, 164.1, 164.2

8.5.6.8. Cyclohexylmethyl cyclohexanecarboxylate **(2.a.7h)**[16]

0.180 g pale yellow color compounds were obtained from cyclohexanecarboxaldehyde (0.1 g, 0.891 mmol).(90% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 0.92-1.01 (2H, m), 1.17-1.30 (6H, m), 1.39-1.48 (2H, m), 1.57-1.74 (9H, m), 1.89-1.92 (2H, m), 2.28 (tt, J(H,H), 4 Hz, 1H), 3.865 (d, J(H,H), 4 Hz, 2H, C*H*$_2$O), 5.49 (s, 2H, C*H*$_2$O). ^{13}C NMR: δ 25.64, 25.86, 25.94, 26.54, 29.24, 29.83, 37.34, 43.50, 69.42, 176.40 ppm.

8.5.6.9. Pentafluorobenzyl pentafluorobenzoate **(2.a.7i)**[17]

0.166 g of pale yellow color oily compound was obtained from the (0.1 g, 0.510 mmol). (83%)

^{1}H NMR ($CDCl_3$, 400MHz): 5.49 (s, 2H, C*H*$_2$O). ^{13}C NMR: δ 55.2, 107.27 (td, J(C,F), 16 Hz), 108.44 (td, J(C,F), 16 Hz), 136.39-147.35 (m), 158.56 ppm.

8.5.6.10. Phtalide **(2.a.7j)**[14]

0.095 g of pale yellow color oil were obtained from *ortho*-phthaldialdehyde (0.1 g, 0.745 mmol). (95% yield).

^{1}H NMR ($CDCl_3$, 400MHz): 5.33 (s, 2H, C*H*$_2$O), 7.49-7.56 (m, 2H, aromatic); 7.69 (td, J(H,H), 5.33 Hz, 1H, aromatic), 7.94(d, J(H,H), 8 Hz, 1H, aromatic). ^{13}C NMR: δ 69.76, 122.22, 125.79, 125.82, 129.13, 134.12, 146.63, 171.23 ppm.

8.5.7. Synthesis of compound [ArNC(N^iPr_2)NAr]CaN($SiMe_3$)$(THF)_2$ (Ar = $C_6H_3Me_2$–2,6) **(6)**

A Solution of ligand precursor [^{i}Pr$_2$NC{N–2,6–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (L^1H) (0.5 g, 1.42 mmol) and KN($SiMe_3$)$_2$ (0.574 g, 2.87 mmol) in THF(15 mL) was stirred for four hours. The mixture was added drop by drop to the stirred suspension of CaI_2 (0.417 g, 1.42 mmol) solution in THF (5 mL) at –78 ^{o}C. The reaction mixture slowly came to room temperature and it was stirred for an additional 24h. Suspended type solution solvent was removed in vacuo and the

residue was extracted with hexane 40 mL. The mixture was left to settle down and white color precipitate(KI) was filtered through celite and the yellow colour clear solution concentrated in vacuo about to 10 mL and kept for crystallization in 0 °C. Colourless crystals came after one day of compound **6** which is suitable for X–ray diffraction analysis.

Yield: (0.173 g, 84 %) mp 140–145 °C, ^{1}H NMR (400 MHz, C_6D_6) δ = 7.11 (d, *J* = 7.4 Hz, 4H, Ar–H), 6.93 (t, *J* = 7.4 Hz, 2H, Ar–H), 3.87 (sept, *J* = 8Hz, 2H, C*H*$(CH_3)_2$), 3.52 (br, 8H, THF), 2.59 (s, 12H, CH_3), 1.39 (br, 8H, THF), 0.75 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 0.10 (s, 18H, Si(C*H*$_3)_3$); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 172.5 (N*C*N), 151.1 (Ar–*C*), 132.6 (Ar–*C*), 130.1 (Ar–*C*), 121.4 (Ar–*C*), 67.9 (THF), 50.2 (N–iPr–*C*H), 25.7 (THF), 24.7 (Ar–*C*H$_3$), 23.0 (Ar–*C*H$_3$), 20.5 (^{i}Pr–*C*H$_3$), 20.2 (^{i}Pr–*C*H$_3$), 6.4 (Si–*C*); ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C): 1.89 N*Si*$(CH_3)_3$).

8.5.8. Synthesis of compound [ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$) (Ar = $C_6H_3Me_2$–2,6) **(7)**

Inside the glovebox L^{1}H (0.5 g, 1.422 mmol, 1.0 equiv) and KN(SiMe3)$_2$ (0.57 g, 2.85 mmol, 2.01 equiv) were mixed into a dry Schlenk flask and dry THF (10 ml) was added at room temperature and the mixture was stirring for 3 hours. The resulting solution was added drop by drop to a stirred suspension of $ZnCl_2$ (0.269 g, 1.422 mmol, 1.0 equiv) in THF (5 ml) at –78 °C and after coming room temperature stirring for additional 24 h. The suspended solution was removed *in* vacuo and hexane (30 mL) was added. The resultant solution was stirred for 30 minutes and then allowed to settle down and filter through to celite and clear solution volume was reduced and few drops of THF was added and kept at –30 °C. Colorless crystal came after 4 days. Yield: (0.71 g, 85 %). Mp 120 – 125 °C, ^{1}H NMR (400 MHz, C_6D_6) δ = 6.97 (d, *J* = 7.4 Hz, 4H, Ar–H), 6.91–6.87 (m, 2H, Ar–H), 3.87 (sept, *J* = 6.6 Hz 2H, C*H*$(CH_3)_2$), 2.40 (s, 3H, Ar–C*H*$_3$), 2.27 (s, 9H, Ar–C*H*$_3$), 0.68 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3)_2$), 0.20 (s, 18H, Si(C*H*$_3)_3$); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 169.9

(N*C*N), 147.0 (Ar–*C*), 133.5 (Ar–*C*), 128.4 (Ar–*C*), 123.0 (Ar–*C*), 51.00 (N–iPr–*C*H), 24.1 (Ar–CH_3), 18.9 (^{i}Pr–*C*H_3), 5.1 (Si–*C*); ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C): 0.51 (N*Si*$(CH_3)_3$). Anal Calcd for $C_{29}H_{50}N_4Si_2Zn$; C, 60.44; H, 8.75; N, 9.72. found C, 60.92; H, 8.31; N, 10.09.

8.5.9. Synthesis of compound [ArNC(N^{i}Pr$_2$)NAr]ZnN(SiMe$_3$) (Ar = $C_6H_3{}^i$Pr$_2$–2,6) **(8)**

Same as described for compound **7**. Suitable for x–ray crystal came after 4 days at –30 °C in hexane solution with few drops of THF. Yield: (0.70 g, 88 %). Mp <40 °C(low melting solid).

^{1}H NMR (400 MHz, C_6D_6) δ = 7.10 (d, *J* = 1.8 Hz, 2H, Ar–*H*), 7.05 (t, *J* = 4 Hz, 4H, Ar–*H*), 3.65 (sept, 6H, C*H*$(CH_3)_2$), 1.40 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.29 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3)_2$), 1.24 (d, *J* = 6.9 Hz, 24H, CH(C*H*$_3)_2$), 0.75 (d, *J* = 7.1 Hz, 3H, CH(C*H*$_3)_2$), 0.20 (s, 18H, Si(C*H*$_3)_3$); ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 170.4 (N*C*N), 143.4(Ar–*C*), 143.0 (Ar–*C*), 133.7 (Ar–*C*), 125.5 (Ar–*C*), 124.0(Ar–*C*), 123.7 (Ar–*C*), 51.0 (N–iPr–*C*H), 29.5 (^{i}Pr–*C*H_3), 28.2 (^{i}Pr–*C*H_3), 25.4 (^{i}Pr–*C*H_3), 23.9 (^{i}Pr–*C*H_3), 23.4 (^{i}Pr–*C*H_3), 22.9 (^{i}Pr–*C*H_3), 5.6 (Si–*C*); ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C): 0.80 (N*Si*$(CH_3)_3$). Anal Calcd for $C_{37}H_{66}N_4Si_2Zn$: C, 64.55; H, 9.66; N, 8.14. Found C, 64.93; H, 9.82; N, 7.75.

8.5.10. General procedure for the intramolecular hydroamination of primary aminoalkenes.

For catalyst 6

Inside the glovebox an oven dried NMR tube was charged with aminoalkene (20µL) and a solution of catalyst (2-10 mol%) in C_6D_6 with hexamethylbenzene (known amount) was added to the NMR tube containing aminoalkene. NMR tube was closed and immediately NMR was taken. Reaction progress was monitored by ^{1}H NMR spectroscopy and NMR

yields were calculated by comparing the integration of well resolved ^{1}H NMR signal of cyclic amine with that of internal standard (Hexamethyl benzene).

For catalyst 7 & 8

Inside the glovebox an oven dried NMR tube was charged with aminoalkene (20μL) and a solution of catalyst (2.5–5 mol%), equimolar amount of co-catalyst $[PhNMe_2H][B(C_6F_5)_4]$ (2.5–5 mol%) in C_6D_6 with hexamethylbenzene (known amount) was added to the NMR tube containing aminoalkene. Sealed NMR tube was taken out from the glovebox and heated at 80 ^oC on a preheated oil bath until to finish the reaction.

8.5.11. General procedure for the intramolecular hydroamination of secondary aminoalkenes.

For catalyst 6

Young valve NMR tube was charged with secondary aminoalkene (20 μL). A solution of catalyst (5 mol%), co-catalyst $[PhNMe_2H][B(C_6F_5)_4]$ (5 mol%) and internal standard hexamethyl benzene(known amount) in 0.5 mL of C_6D_6 was added to the NMR tube. NMR tube was sealed inside the box and started to heat at 120 ^oC in a preheated oil bath. Reaction progress was examined by ^{1}H NMR spectroscopy. NMR yield was determined by same like earlier.

For catalyst **7** & **8** procedure is same but temperature was 80 ^oC instead of 120 ^oC.

8.5.12. Reaction monitor of hydroamination product for secondary aminoalkene catalysed by **6**

Reaction progress of secondary amine i.e. N-benzyl-2,2-diphenylpent-4-en-1-amine using catalyst 3 was monitor by ^{1}H NMR spectroscopic studies. Figure contains NMR stack plot which clearly shows that the clean conversion of substrate to their cyclic product where the

olefinic proton (H_a, $H_{b+b'}$) resonance of starting material decreases and the product peak (H_c and H_d) resonances are increases.

8.5.13. Synthesis of {[ArNC(N^iPr_2)NAr]MgN($SiMe_3$)$_2$(THF)}[Ar=2,6– Me_2–C_6H_3] **(9)**

Method A In a Schlenk tube L^1H (1.00 g, 2.84 mmol, 1.0 equiv) was dissolved in THF(15 mL) and the solution was added drop by drop at -78 ^oC to an another Schlenk tube charged with [Mg{N($SiMe_3$)$_2$}$_2$] (0.979 g, 2.84 mmol, 1.0 equiv) in THF(5 mL). After completion of addition reaction mixture slowly came to room temperature and at this temperature it was stirred for another 12 h. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL) filtered through celite and concentrated to about 5 mL and finally stored at –30 ^oC. Colorless crystals of compound **9** suitable for X–ray diffraction analysis are formed after one day. Yield: (1.38 g, 80%).

Method B.

L^1H (0.500 g, 1.42 mmol, 1.0 equiv) and KN($SiMe_3$)$_2$ (0.582 g, 2.91 mmol, 2.05 equiv) were placed in a Schlenk tube and THF (10 mL) was added at room temperature and stirring was continued up to four hours. The resulting solution was added drop by drop to a stirred suspension of $MgCl_2$ (0.135 g, 1.42 mmol, 1.0 equiv) in THF (5 mL) at -78 ^0C. After coming to room temperature stirring was continued for another 24 h. Removal of all volatiles and recrystallized from *n*–hexane (20 mL) gave **9** Yield: (0.675 g, 78%).

Mp = 150 – 155 ^oC; ^1H NMR (400 MHz, C_6D_6) δ 7.08–6.99 (m, 4H, Ar–*H*), 6.95 – 6.86 (m, 2H, Ar–*H*), 3.86 (sept, *J* = 6 Hz, 2H, C*H*(CH_3)$_2$), 3.59 (t, 4H, THF), 2.46 (s, 3H, Ar–C*H*$_3$), 2.21 (s, 9H, Ar–C*H*$_3$), 1.25 (m, 4H, THF), 0.73 (d, *J* = 7.0 Hz, 5H, CH(C*H*$_3$)$_2$), 0.33 (s, 18H, NSi(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 170.6(N*C*N), 148.4(Ar–*C*), 132.9(Ar–*C*), 128.47(Ar–*C*), 122.2(Ar–*C*), 69.1(THF), 50.7(N–*i*Pr–*C*H), 25.1(THF), 24.5 (*i*Pr–*C*H$_3$),

19.3(Ar–*C*H_3), 6.1(Si–*C*) ppm. ^{29}Si NMR (80 MHz, C_6D_6) δ –8.11 ppm. Anal. Calcd. $C_{33}H_{58}MgN_4OSi_2$: C, 65.26; H, 9.63; N, 9.23. Found: C, 65.06; H, 10.03; N, 8.93.

8.5.14. Synthesis of {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$}[Ar=2,6– ^{i}Pr$_2$–C$_6$H$_3$] **(10a)**

In a Schlenk tube L^{2}H (1.00 g, 2.15 mmol, 1.0 equiv) and [Mg{N(SiMe$_3$)$_2$}$_2$] (0.74 g, 2.15 mmol, 1.0 equiv) were mixed inside the glovebox. To the above mixture benzene (15 mL) was added and heated at 80 ^{o}C for 12 h. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL) and concentrated to about 5 mL, few drops of thf was added and finally stored in –30 ^{o}C. Crystal did not come after 2 days. Solvent was removed dried in vacuum off-white solid compound came. Yield: (1.09 g, 78 %).

^{1}H NMR (400 MHz, C_6D_6) δ 7.10 – 7.08 (m, 6H, Ar–*H*), 4.01(sept, 2H, C*H*(CH$_3$)$_2$), 3.61 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.29 (dd, *J* = 11.1, 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 0.69 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.22 (s, 18H, NSi(C*H*$_3$)$_3$) ppm.

8.5.15. Synthesis of {[ArNC(N^{i}Pr$_2$)NAr]MgN(SiMe$_3$)$_2$(THF)}[Ar=2,6– ^{i}Pr$_2$–C$_6$H$_3$] **(10)**

L^{2}H (0.50 g, 1.07 mmol, 1.0 equiv) and [Mg{N(SiMe$_3$)$_2$}$_2$] (0.371 g, 1.07 mmol, 1.0 equiv). Yield: (0.61 g, 76%).

Mp = 162 – 165 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.18 (d, *J* = 2.4 Hz, 4H, Ar–*H*), 7.14–7.10 (m, 2H, Ar–*H*), 4.08 (sept, 2H, C*H*(CH$_3$)$_2$), 3.93 (s, 4H, THF), 3.60 (sept, 4H, C*H*(CH$_3$)$_2$), 1.36 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.25 (t, 4H, THF), 0.80 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.11 (s, 18H, NSi(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 170.7(N*C*N), 145.3(Ar–*C*), 143.2(Ar–*C*), 124.0(Ar–*C*), 123.9(Ar–*C*), 70.0(THF), 50.3(N–*i*Pr–*C*H), 28.0(*i*Pr–*C*H$_3$), 26.6(*i*Pr–*C*H$_3$), 25.0(THF), 24.2(*i*Pr–*C*H$_3$), 23.9(*i*Pr–*C*H$_3$), 5.9(Si–*C*). ^{29}Si NMR (80 MHz, C_6D_6) δ – 8.36 ppm. Anal. Calcd. $C_{41}H_{74}MgN_4OSi_2$: C, 68.44; H, 10.37; N, 7.79; Found: C, 68.16; H, 10.13; N, 7.56.

8.5.16. Synthesis of boronic esters

8.5.16.1. 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4a)**[18]

^{1}H NMR (400 MHz, C_6D_6) δ 7.30 (d, J = 7.4 Hz, 2H), 7.16 – 7.10 (m, 2H), 7.09 – 7.02 (m, 1H), 4.94 (s, 2H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.69 (s).

8.5.16.2. 2-((4-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4b)**[19]

^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 4.73 (s, 2H), 1.03 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.62 (s).

8.5.16.3. 2-((2-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4c)** [20]

^{1}H NMR (400 MHz, C_6D_6) δ 7.45 – 7.41 (m, 1H), 6.85 – 6.80 (m, 2H), 6.77 – 6.72 (m, 1H), 5.10 (s, 1H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.69 (s).

8.5.16.4. 4,4,5,5-tetramethyl-2-((perfluorophenyl)methoxy)-1,3,2-dioxaborolane **(3.a.4d)**

^{1}H NMR (400 MHz, C_6D_6) δ 4.77 (s, 2H), 1.05 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.52.

8.5.16.5. 4,4,5,5-tetramethyl-2-propoxy-1,3,2-dioxaborolane **(3.a.4e)**[21]

^{1}H NMR (400 MHz, C_6D_6) δ 3.83 (t, J = 6.6 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.06 (s, 12H), 0.81 (t, J = 7.4 Hz, 3H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.54.

8.5.16.6. 2-(hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4f)**[20]

^{1}H NMR (400 MHz, C_6D_6) δ 3.87 (t, J = 6.5 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.29 – 1.21 (m, 2H), 1.20 – 1.13 (m, 4H), 1.07 (s, 12H), 0.81 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) 82.35, 65.05, 32.0, 31.9, 25.7, 24.7, 23.0, 14.2.

8.5.16.7. 4,4,5,5-tetramethyl-2-phenethoxy-1,3,2-dioxaborolane **(3.a.4g)**

^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, J = 7.5 Hz, 2H), 7.15 – 7.09 (m, 3H), 7.08 – 7.06 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 4.92 (s, 2H), 4.06 (t, J = 6.9 Hz, 2H), 2.74 (t, J = 6.9 Hz, 2H), 1.04 (s, 12H), 1.00 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.38.

8.5.16.8. 3-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)-1H-indole **(3.a.4h)**

^{1}H NMR (400 MHz, C_6D_6) δ 7.67 (d, J = 7.7 Hz, 1H), 7.22 – 7.03 (m, 2H), 7.09 (d, J = 7.8 Hz, 1H), 7.03 (s, 1H), 6.60 (d, J = 2.1 Hz, 1H), 4.25 (t, J = 6.9 Hz, 2H), 3.91 (q, J = 7.0 Hz, 2H), 3.06 (t, J = 6.9 Hz, 2H), 1.11 (d, J = 7.0 Hz, 3H), 1.05 (s, 12H), 0.99 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 136.7, 122.5, 122.0, 119.5, 119.4, 112.5, 111.2, 82.4, 82.3, 65.5, 60.7, 28.3, 24.7, 24.6, 17.5. ^{11}B NMR (128 MHz, C_6D_6) δ 22.47.

8.5.16.9. 1-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)phenyl)ethanone **(3.a.4i)**

^{1}H NMR (400 MHz, C_6D_6) δ 7.64 – 7.60 (m, 1H), 6.99 – 6.96 (m, 3H), 5.66 (q, J = 6.4 Hz, 1H), 1.81 (s, 3H), 1.51 (d, J = 6.5 Hz, 3H), 1.01 (s, 12H), 1.00 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) 168.0, 147.4, 136.6, 127.7, 126.7, 125.8, 122.6, 82.7, 82.2, 67.7, 24.2, 24.1, 20.0; ^{11}B NMR (128 MHz, C_6D_6) δ 22.33.

8.5.16.10. 4,4,5,5-tetramethyl-2-(p-tolyloxy)-1,3,2-dioxaborolane **(3.a.4j)**[22]

^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, J = 7.4 Hz, 2H), 7.15 – 7.13 (m, 4H), 7.04 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 4.93 (s, 2H), 2.02 (s, 3H), 1.02 (s, 12H), 1.01 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.42.

8.5.16.11. 2-butoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4k)**[22]

^{1}H NMR (400 MHz, C_6D_6) δ 7.31 (d, J = 7.2 Hz, 2H), 7.13 (t, J = 7.4 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 4.95 (s, 2H), 3.93 (t, J = 6.5 Hz, 2H), 1.54 – 1.47 (m, 2H), 1.36 – 1.26 (m, 2H), 1.07 (s, 12H), 1.04 (s, 12H), 0.80 (t, J = 7.4 Hz, 3H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.54.

8.5.16.12. 4,4,5,5-tetramethyl-2-((4-((3,3,4,4-tetramethylborolan-1-yl)oxy)hexyl)oxy)-1,3,2-dioxaborolane **(3.a.4l)**

^{1}H NMR (400 MHz, C_6D_6) δ 4.11 – 4.05 (m, 1H), 3.97 – 3.87 (m, 2H), 1.80 – 1.61 (m, 2H), 1.54 – 1.49 (m, 2H), 1.47 – 1.33 (m, 2H), 1.06 (s, 24H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR

(101 MHz, C_6D_6) δ 82.3, 82.2, 75.6, 64.9, 32.5, 29.8, 28.1, 24.6, 24.6, 10.0; ^{11}B NMR (128 MHz, C_6D_6) δ 22.68.

8.5.16.13. 4,4,5,5-tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)oxy)pentyl)oxy)-1,3,2-dioxaborolane **(3.a.4m)**[18]

^{1}H NMR (400 MHz, C_6D_6) δ 4.32 – 4.24 (m, 1H), 3.94 – 3.84 (m, 2H), 1.75 – 1.58 (m, 2H), 1.57 – 1.44 (m, 2H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.06 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 82.3, 82.2, 70.6, 64.9, 34.7, 28.1, 24.6, 24.7, 22.8; ^{11}B NMR (128 MHz, C_6D_6) δ 22.15.

8.5.16.14. 1,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane **(3.a.4n)**

^{1}H NMR (400 MHz, C_6D_6) δ 3.83 (t, *J* = 6.5 Hz, 4H), 1.47 (dt, *J* = 14.3, 6.9 Hz, 4H), 1.36 – 1.28 (m, 2H), 1.06 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 82.3, 64.9, 31.6, 24.7, 22.1; ^{11}B NMR (128 MHz, C_6D_6) δ 22.38.

8.5.16.15. 1,2-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene **(3.a.4o)**

^{1}H NMR (400 MHz, C_6D_6) δ 7.50 (dd, *J* = 5.5, 3.4 Hz, 2H), 7.09 (dd, *J* = 5.7, 3.4 Hz, 2H), 5.06 (s, 4H), 1.03 (s, 24H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.8.

8.5.16.16. 2-(4-(benzyloxy)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3.a.4p)**

^{1}H NMR (400 MHz, C_6D_6) δ 7.28 (t, *J* = 8.9 Hz, 4H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.13 – 7.10 (m, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.97 (s, 2H), 4.71 (s, 2H), 3.94 (q, *J* = 7.0 Hz, 2H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.09 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 158.8, 137.7, 132.5, 128.8, 128.6, 127.9, 127.6, 115.0, 82.6, 82.3, 69.9, 66.7, 60.6, 24.9, 24.7, 17.5; ^{11}B NMR (128 MHz, C_6D_6) δ 22.44.

8.5.17. Synthesis of {(ArNC(N^iPr_2)NAr)MgK{$N(SiMe_3)_2$}$_2$(THF)}[Ar=2,6– Me_2–C_6H_3] **(11)**

In a dry glovebox 0.25 g of solid [L^1Mg$N(SiMe_3)_2$(THF)][L^1= {ArNC (N^iPr_2)NAr} (Ar = 2,6- Me_2-C_6H_3)] (**9**) (0.493 mmol, 1 equiv.) and 0.109 g of $KN(SiMe_3)_2$ (0.542 mmol, 1.1 equiv.) were added to a Schlenk tube. The Schlenk tube was taken out from the glovebox and

charged with 10 ml of THF. The clear solution was stirred at room temperature for 6h. Solvent was removed and extracted with hexane(20 mL) and the solution was concentrated in vacuo to 5 mL and kept for crystallization at 0 ^{o}C. Clear, colorless crystals were obtained on standing overnight.

Yield (0.29 g, 73 %); Mp = 140 – 145 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.07 (d, J = 8Hz, 4H, Ar–*H*), 6.87 – 6.95 (m, 2H, Ar–*H*), 3.87 (sept, J = 6 Hz, 2H, C*H*$(CH_3)_2$), 3.63 (br, 4H, THF), 2.46 (s, 12H, Ar–C*H*$_3$), 1.23 (m, 4H, THF), 0.74 (d, J = 8 Hz, 12H, CH(C*H*$_3)_2$), 0.19 (s, 18H, NSi(C*H*$_3)_3$), 0.13 (s, 18H, NSi(C*H*$_3)_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 172.5(N*C*N), 148.4(Ar–*C*), 133.3(Ar–*C*), 128.8(Ar–*C*), 122.8(Ar–*C*), 56.4 (THF), 50.8 (N–*i*Pr–*C*H), 25.2 (THF), 24.6 (*i*Pr–*C*H$_3$), 19.9 (Ar–*C*H$_3$), 7.1(Si–*C*), 5.5 (Si–*C*) ppm. ^{29}Si NMR (80 MHz, C_6D_6) δ = 21.5 ppm. Anal. Calcd. for $C_{39}H_{77}MgKN_5OSi_4$: C, 57.99; H, 9.61; N, 8.67. Found: C, 57.46; H, 9.23; N, 8.93.

8.5.18. Synthesis of {(ArNC(N^{i}Pr$_2$)NAr)CaK{N(SiMe$_3)_2$}$_2$(THF)}[Ar=2,6– Me$_2$–C$_6$H$_3$] **(12)** [L^{1}CaN(SiMe$_3)_2$(THF)$_2$][L^{1}= {ArNC (N^{i}Pr$_2$)NAr} (Ar = 2,6- Me$_2$-C$_6$H$_3$)] (**6**) (0.2 g, 0.287 mmol, 1 equiv.) and 0.082 g of KN(SiMe$_3)_2$ (0.063 g, 0.316 mmol, 1.1 equiv.).

Yield: (0.185 g, 85 %); Mp = 150 – 155 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.11 (d, J = 8Hz, 3H, Ar–*H*), 6.93 (t, J = 8Hz, 1H, Ar–*H*), 6.87 (d, J = 8Hz, 2H, Ar–*H*), 3.87 (sept, J = 6 Hz, 2H, C*H*$(CH_3)_2$), 3.51 (br, 4H, THF), 2.59 (s, 9H, Ar–C*H*$_3$), 2.33 (s, 3H, Ar–C*H*$_3$), 1.44–1.40 (m, 4H, THF), 0.75 (d, J = 8 Hz, 12H, CH(C*H*$_3)_2$), 0.1 (s, 18H, NSi(C*H*$_3)_3$), 0.09 (s, 18H, NSi(C*H*$_3)_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 172.3(N*C*N), 150.7(Ar–*C*), 132.3(Ar–*C*), 128.5(Ar–*C*), 121.1(Ar–*C*), 67.5(THF), 48.8(N–*i*Pr–*C*H), 46.9(N–*i*Pr–*C*H), 25.3 (THF), 24.3 (*i*Pr–*C*H$_3$), 22.7 (Ar–*C*H$_3$), 20.1(Ar–*C*H$_3$), 19.7(Ar–*C*H$_3$), 6.0 (Si–*C*), 2.2 (Si–*C*) ppm. ^{29}Si NMR (80 MHz, C_6D_6) δ = –15.6 ppm. Anal. Calcd. for $C_{39}H_{77}MgKN_5OSi_4$: C, 56.88; H, 9.42; N, 8.5. Found: C, 56.43; H, 9.23; N, 8.83.

8.5.18. Synthesis of {(ArNC(N^iPr_2)NAr)CaK{$N(SiMe_3)_2$}$_2$(Benzene)}[Ar=2,6– Me_2–C_6H_3] **(12a)**

Same with compound **12**

8.5.20. Synthesis of [L^1AlMeCl] (**13)**

To a solution of L^1H (0.5 g, 1.422 mmol, 1.0 equiv) in toluene Diimethyl aluminum Chloride (1.63 ml, 0.9 M in hexane, 1.03 equiv) was added drop by drop at 0 ^oC and stirred at room temperature for another 12 h. Solvent volume was reduced and stored in –20 ^oC freezer. Colorless crystals suitable for X–ray diffraction analysis came after one day. Yield: (0.45 g, 74%). Mp 188 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): δ 6.87– 6.92 (m, 6H, Ar–*H*), 3.78(sept, 2H, C*H*(CH_3)$_2$), 2.58 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), , 0.66 (d, *J*= 8Hz, 12H, CH(CH_3)$_2$), –0.18(s, 3H, Al(CH_3)Cl) ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 166.7, 141.7, 134.0, 129.1, 125.2, 50.8, 23.4, 19.6, 19.1, –8.9 ppm.

8.5.21. Synthesis of [L^1AlMe$_2$] (**14)**

To a solution of L^1H (0.50 g, 1.422 mmol, 1.0 equiv) in toluene(15 mL) trimethyl aluminium (0.74 ml, 2.0 M in hexane, 1.03 equiv) was added drop by drop at 0 ^oC and at room temperature under stirring for another 12 h. Solvent volume was concentrated to about 5 ml and finally stored in a -20 ^oC freezer. Colorless crystalline compound isolated for chacterization after one day. Yield: (0.502 g, 86 %). Mp 135 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): ^{1}H NMR (400 MHz, C_6D_6) δ 6.96 (d, *J* = 8 Hz, 4H), 6.90 (dd, *J* = 8 Hz, 2H), 3.80 (sept, *J* = 6.6 Hz, 2H), 2.41 (s, 12H), 0.71 (d, *J* = 8 Hz, 12H); ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 165.7, 143.5, 134.4, 129.2, 124.8, 50.7, 24.0, 19.6, -8.2 ppm.

8.5.22. Synthesis of [L^1AlI$_2$] (**15)**

Solid Iodine (0.717 g, 2.84 mmol, 2.0 equiv) was added to a solution of L^1AlMe$_2$ (0.579 g, 1.422 mmol, 1.0 equiv) in toluene at room temperature and stirring for another 24 h. After removal of all the volatiles, the residue was extracted with excess toluene (20 ml) filtered and

concentrated to about 5 ml and finally stored in a –20 ^{o}C freezer. Upon storing overnight colorless crystalline material was formed for X–ray diffraction analysis. Yield: (0.715 g, 79 %). Mp 182 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): δ 6.88 (s, 6H, Ar–*H*), 3.79 (sept, 2H, C*H*$(CH_3)_2$), 2.53 (s, 12H, C*H*$_3$), 0.62 (d, *J* = 4Hz, 12H, CH(C*H*$_3)_2$), ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 166.9, 140.0, 134.6, 129.3, 126.0, 51.2, 23.5, 20.6 ppm. IR (KBr) ν (cm^{-1}): 2921, 2825, 2637, 1425, 1367, 1035, 877, 852, 762.

8.5.23. Synthesis of [L^{1}AlCl$_2$] (**16)**

To a solution of L^{1}H (0.5 g, 1.422 mmol, 1.0 equiv) in toluene(20 mL) Methyl aluminum dichloride (1.46 ml, 1.0 M in hexane, 1.03 equiv) was added drop by drop at 0 ^{o}C and reflux for another 12 h. Solution was filtered through filter cannula and concentrated to about 5 ml and finally stored in a –30 ^{o}C freezer. Crystalline compound isolated after one day. Yield: (0.530 g, 83%). Mp 178 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): δ 6.89–6.93 (m, 5H, Ar–*H*), 6.69(s, 1H, Ar–*H*), 3.74(sept, 2H, C*H*$(CH_3)_2$), 2.44(s, 12H, C*H*$_3$), 0.56 (d, *J* = 8Hz, 12H, CH(C*H*$_3)_2$), ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 162.6, 138.8, 136.6, 129.1, 126.9, 51.2, 22.9, 19.4 ppm.

8.5.24. Synthesis of [L^{1}Al(Me)N(SiMe$_3)_2$] (**17)**

To a solution of **13** (1 gm, 2.34 mmol, 1.0 equiv) in toluene(20 ml) Lithium bis trimethylsilylamide (0.431 g, 2.57 mmol, 1.1 equiv) was added drop by drop at –78 ^{o}C, after coming at room temperature it was stirring for another 24 h. After removal of all the volatiles, dried for 2h in high vacuum and the residue was extracted with toluene (30 ml) and filter through celite and solution was concentrated to about 5 ml and finally stored in a –30 ^{o}C freezer. Colorless crystals of compound suitable for X–ray diffraction analysis are obtained after one day. Yield: (1.2 gm, 76%). Mp = 115 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): δ 6.95– 6.98 (m, 2H, Ar–*H*), 6.91– 6.94 (m, 4H, Ar–*H*), 3.84 (sept, 2H, C*H*$(CH_3)_2$), 2.52 (s,

6H, CH_3), 2.39 (s, 6H, CH_3), 0.63 (d, J = 8Hz, 12H, CH(CH_3)$_2$), 0.19 (s, 18H, Si(CH_3)$_3$), –0.13(s, 3H, Al(CH_3) ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 170.1, 143.4, 135.3, 135.3, 129.1, 129.0, 125.2, 51.1, 24.1, 20.3, 19.6, 5.0, –4.7 ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = – 3.5 (NSi(CH$_3$)$_3$) ppm. IR (KBr) ν (cm^{-1}): 2925, 2852, 2727, 2672, 1457, 1376, 1306, 1246, 950, 890, 834, 767, 722.

8.5.25. Synthesis of [L^{1}Al{N(SiMe$_3$)$_2$}$_2$] **(18)**

To a solution of **16** (0.5 g, 2.34 mmol, 1.0 equiv) in toluene(20 ml) Lithium bis trimethylsilylamide (0.431 g, 2.57 mmol, 2.05 equiv) was added drop by drop at –78 °C and after coming at room temperature it was stirring for another 24 h. After removal of all the volatiles, the residue was extracted with toluene (30 ml) and filter through celite and solution was removed and dried to isolate the compound. Yield: (0.45 g, 81%). Mp = 121 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C,): δ 6.89–93 (m, 6H, Ar–H), 3.83(sept, 2H, CH(CH$_3$)$_2$), 2.68 (s, 6H, CH_3), 2.45 (s, 6H, CH_3), 0.59 (d, J = 4Hz, 12H, CH(CH$_3$)$_2$), 0.23 (s, 18H,Si(CH_3)$_3$), 0.13(s, 18H,Si(CH_3)$_3$) ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6): δ 170.6, 141.8, 136.2, 135.1, 129.6, 128.8, 126.0, 51.6, 23.9, 21.6, 20.2, 7. 2, 5.0 ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C): δ = – 20.44, –2.52 (NSi(CH$_3$)$_3$) ppm. IR (KBr) ν (cm^{-1}): 2923, 2854, 2720, 2668, 1458, 1376, 1300, 1254, 930, 722.

8.5.26. General procedure for the Tishchenko reaction

The required amount of catalyst and aldehyde both were placed in a dry sample vial with a stirring bar inside the glove box. Subsequently, sealed vial brought outside the glove box and heated to 60–80 °C till completion of the reaction. The reaction was monitored by thin layer chromatography (TLC) and aliquot of reaction mixture by NMR spectroscopy. Final product was purified by column chromatography (Hexane/diethyl ether (98:2)).

8.5.26.1. Synthesis of Butylbutyrate (4.7a)[23]

0.140 g pale yellow color compounds were obtained from butyraldehyde (0.72 g, 1 mmol). (Yield 97%). ^{1}H NMR ($CDCl_3$, 400MHz, 298K): δ = 0.93 (t, J = 4 Hz, 3H), 0.95 (t, J = 4 Hz, 3H), 1.33–1.41 (m, 2H), 1.59–1.68(m, 4H), 2.28 (t, J = 8 Hz, 2H), 4.07 (t, J = 6 Hz, 2H) ppm.

8.5.26.2. Synthesis of 3–phenylbutyl 3–phenylbutanoate (4.7b)

0.190 g pale yellow color compounds were obtained from 3–phenylbutanal (0.1 g, 0.675 mmol). (Yield 95%). ^{1}H NMR ($CDCl_3$, 400MHz, 298K): δ = 1.21–1.25 (m, 3H), 1.28–1.30 (m, 3H, CH_3), 1.79–1. 85 (m, 2H, CH_3), 2.48–2.63(m, 2H, CH_3CH_2), 2.71 (sept, J = 6.6 Hz, 1H, CH(CH_3)Ph), 3.22–3.29 (m, 1H, CH(CH_3)Ph), 3.84–3.91 (m, 1H, CH_2O), 3.93–3.4(m, 1H, CH_2O), 7.11–7.14 (m, 2H, aromatic), 7.16–7.23(m, 5H, aromatic), 7.28–7.32 (m, 3H, aromatic) ppm. ^{13}C {^{1}H}NMR: δ =22.1, 22.3, 36.6, 36.9, 43.0, 43.0, 62.9, 126.3, 126.5, 126.9, 127.0, 128.6, 128.6, 145.8 146.4, 172.5 ppm.

8.5.27 Synthesis of [L^{1}GeN($SiMe_3$)$_2$] **(19)**

A solution of L^{1}H (0.25 g, 0.711 mmol, 1.0 equiv) in THF (10 mL) was added drop by drop to a stirred suspension of KN($SiMe_3$)$_2$ (0.29 g, 1.43 mmol, 2.01 equiv) in THF (5 mL) at 0 °C and stirring was continued for 12 h at room temperature. The resulting solution was added drop by drop to a stirred suspension of $GeCl_2$ (dioxane) (0.165 g, 0.711 mmol, 1.0 equiv) in THF (5 mL) at 0 °C under stirring for another 24 h at room temperature. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL) and concentrated to about 5 mL and finally stored in a –30 ^{o}C freezer. Colorless crystals of compound suitable for X–ray diffraction analysis are obtained after one day. Yield: 0.73 g (88%). Mp = 120 – 122 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.26 (s, 18H, NSi(CH_3)$_3$), 0.67 (d, J = 8Hz, 12H, CH(CH_3)$_2$), 2.58 (s, 12H, CH_3), 3.90 (sept, J = 8Hz, 2H, CH(CH_3)$_2$), 6.87–6.93 (m, 4H, Ar–

H), 7.00 (d, *J* = 8Hz, 2H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 5.6 (Si–*C*), 20.7 (Ar–*C*H_3), 21.0(Ar–*C*H_3), 24.6 (*i*Pr–*C*H_3), 50.7 (N–*i*Pr–*C*H), 125.6 (Ar–*C*), 129.6 (Ar–*C*), 129.6 (Ar–*C*), 136.0 (Ar–*C*), 136.3 (Ar–*C*), 144.3 (Ar–*C*), 165.0 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 °C,): δ = – 3.68 (N*Si*$(CH_3)_3$) ppm. IR (KBr) ν (cm^{-1}): 2924(s), 2854(s), 1459(m), 1377(s), 932(w), 721(m).

8.5.28 Synthesis of [L^1SnN$(SiMe_3)_2$] **(20)**

A solution of L^1H (0.5 g, 1.422 mmol, 1.0 equiv.) in THF (10 mL) was added drop by drop to a stirred suspension of $KN(SiMe_3)_2$ (0.57 g, 2.85 mmol, 2.01 equiv) in THF (5 mL) at 0 °C and stirring was continued overnight at room temperature. The resulting solution was added drop by drop to a stirred suspension of $SnCl_2$ (0.269 g, 1.422 mmol, 1.0 equiv) in THF (5 mL) at 0 °C and continued the stirring for another 24 h at room temperature. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL) and concentrated to about 5 mL and finally stored in a –30 °C freezer. Colorless crystals of compound suitable for X–ray diffraction analysis are formed after one day. Yield: 0.71 g (86 %). Mp = 125 –127 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.20 (s, 18H, NSi(C*H*$_3$)$_3$), 0.66 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$), 2.50 (s, 6H, C*H*$_3$), 2.60 (s, 6H, C*H*$_3$), 3.84 (sept, *J* = 8Hz, 2H, C*H*$(CH_3)_2$), 6.85–6.88 (t, 2H, Ar–*H*), 6.93 (d, *J* = 8 Hz, 2H, Ar–*H*), 7.01 (d, *J* = 8 Hz, 2H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 5.4 (Si–*C*), 20.6 (Ar–*C*H_3), 20.7 (Ar–*C*H_3), 24.8 (N–^{i}Pr–*C*H_3), 51.0 (*iP*r–*C*H), 125.1 (Ar–*C*), 129.4 (Ar–*C*), 129.6 (Ar–*C*), 134.9 (Ar–*C*), 135.8 (Ar–*C*), 145.2 (Ar–*C*), 168.5 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (100 Hz, C_6D_6, 25 °C): –3.69 N*Si*$(CH_3)_3$) ppm. IR (KBr) ν (cm^{-1}): 2923(s), 2853(s), 1462(m), 1377(m), 721(m).

8.5.29 Synthesis of [$L^2SnN(SiMe_3)_2$] **(21)**

The compound was synthesized by using a similar procedure to that employed for the preparation of **20,** but by using L^2H (0.25 g, 0.539 mmol), $KN(SiMe_3)_2$ (0.217 g, 1.08 mmol) and $SnCl_2$ (0.103 g, 0.539 mmol).Yield: 0.3 g (75%). M. p. = 141 – 142 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.13 (s, 18H, Si(CH_3)$_3$), 0.76 (d, J = 8Hz, 12H, CH(CH_3)$_2$), 1.28 (d, J = 8Hz, 6H, CH(CH_3)$_2$), 1.345 (d, J= 4Hz, 12H, CH(CH_3)$_2$), 1.50 (d, J = 8Hz, 6H, CH(CH_3)$_2$), 3.62 (sept, J = 7Hz, 2H, CH(CH$_3$)$_2$), 3.76 (sept, J = 6Hz, 2H, CH(CH$_3$)$_2$), 4.03 (sept, J = 6.6Hz, 2H, CH(CH$_3$)$_2$), 7.04–7.10 (m, 6H, Ar–H) ppm. ^{13}C {1H} NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 5.8 (Si–C), 23.9 (iPr–CH$_3$), 24.4 (iPr–CH$_3$), 24.6 (iPr–CH$_3$), 27.3 (iPr–CH$_3$), 28.5 (N–iPr–CH$_3$), 28.7 (iPr–CH), 28.8 (iPr–CH), 50.5 (N–iPr–CH), 124.7 (Ar–C), 125.8 (Ar–C), 142.5 (Ar–C), 144.0 (Ar–C), 145.6 (Ar–C), 163.5 (NCN) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 ^{o}C,): – 4.10 (NSi(CH$_3$)$_3$) ppm. IR (KBr) ν (cm^{-1}): 2921(w), 2726(m), 1456(m), 1377(m), 1306(m), 936(w), 722(s).

8.5.30 General procedure for the synthesis of triarylisocyanurate

8.4.30.1 Synthesis of $(PhNCO)_3$ **(5.a.4)**[24]

To a complex **19** (0.029 g, 0.0462 mmol) neat phenyl isocyanate (0.275 g, 2.31 mmol) was added. After 60 minutes the reaction mixture became solidified. The resulting white solid was crushed into powder and washed with benzene 5 times (5 mL x 5) repeatedly, filtered off and dried in vacuum and yielded of $(PhNCO)_3$. The product was confirmed by ^{1}H NMR and melting point with the reported samples.

Yield: 0.256 g (93%). M. p. = 280 °C (lit. M. p. 280– 281 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.39 –7.42 (m, 6H, C_6H_5), 7.44 –7.52 (m, 9H, C_6H_5) ppm.

8.5.30.2 Synthesis of (*p*– OMePhNCO)$_3$ **(5.a.5)**[25]

To a complex **19** (0.020 g, 0.0308 mmol) neat *p*–methoxyphenyl isocyanate (0.23 g, 1.54 mmol) was added. After 60 minutes a white color solid was formed. The crude solid was washed with benzene 5 times (5 mL x 5) and dried in vacuum. The desired product (*p*–OMePhNCO)$_3$ collected in 94% yield.

Yield: 0.216 g (94%). Mp = 257 °C (lit. M. p. 261 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.72 (s, 9H, OCH_3), 6.875 (d, 12H, *J* = 12Hz, C_6H_4), 7.16–7.19 (t, 6H, C_6H_4) ppm.

8.5.31 Synthesis of [L^{1}GeN(SiMe$_3$)$_2$(S)] **(22)**

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$] (**19**) (0.150 g, 0.257 mmol, 1.0 equiv) in THF (10 mL) was added 1.2 equiv of sulfur (0.010 g, 0.312 mmol, 1.2 equiv) at room temperature and stirred for another 12 h and noticed the formation of a clear yellow solution. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (10 mL) and few drops of toluene was added and stored at –30 ^{o}C. Colourless crystals of compound suitable for X–ray diffraction analysis are obtained after one day. Yield 0.14 g (88%); Mp 182 – 187 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 0.32 (s, 18H, NSi(C*H*$_3$)$_3$), 0.57 (d, *J* = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.45 (s, 6H, C*H*$_3$), 2.97 (s, 6H, C*H*$_3$), 3.85 (sept, *J* = 8.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.89–6.91 (m, 6H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 5.2 (Si–*C*), 20.3 (Ar–*C*H$_3$), 21.5(Ar–*C*H$_3$), 23.7 (*i*Pr–*C*H$_3$), 52.3 (N–*i*Pr–*C*H), 127.2 (Ar–*C*), 128.9 (Ar–*C*), 130.0 (Ar–*C*), 135.9 (Ar–*C*), 139.1 (Ar–*C*), 140.1 (Ar–*C*), 167.7 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 ^{o}C,): δ = 3.31 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}GeN_4SSi_2$ (615.61): C, 56.58; H, 8.19; N, 9.10. Found C, 56.28; H, 8.02; N, 8.91.

8.5.32 Synthesis of [L^1GeN(SiMe$_3$)$_2$(Se)] **(23)**

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}GeN(SiMe$_3$)$_2$](**19**) (0.250 g, 0.428 mmol, 1.0 equiv) in diethyl ether (15 mL) was added one equiv of selenium powder (0.04 g, 0.507 mmol, 1.2 equiv) at room temperature and stirring was continued for another 12 h. The reaction mixture was filtered through Celite and a clear yellow solution was reduced (7 mL) and kept it for crystallization at –30 ^{o}C. Colourless crystals for X–ray diffraction analysis were obtained after one day.

Yield 0.245 g (86%); Mp 190 – 195 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 0.34 (s, 18H, NSi(C*H*$_3$)$_3$), 0.57 (d, *J* = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 2.46 (s, 6H, C*H*$_3$), 2.99 (s, 6H, C*H*$_3$), 3.84 (sept, *J* = 8.0 Hz, 2H, C*H*(CH$_3$)$_2$), 6.88–6.91 (m, 6H, Ar–*H*) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 5.3 (Si–*C*), 20.4 (Ar–*C*H$_3$), 22.1(Ar–*C*H$_3$), 23.7 (*i*Pr–*C*H$_3$), 52.2 (N–*i*Pr–*C*H), 127.2 (Ar–*C*), 128.3 (Ar–*C*), 130.1 (Ar–*C*), 135.9 (Ar–*C*), 139.0 (Ar–*C*), 140.1 (Ar–*C*), 167.9 (N*C*N) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 ^{o}C,): δ = 3.02 (N*Si*(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}GeN_4SeSi_2$ (662.51): C, 52.57; H, 7.61; N, 8.46. Found C, 52.07; H, 7.21; N, 8.36

8.5.33 Synthesis of [L^1SnN(SiMe$_3$)$_2$(S$_4$)] **(24)**

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**20**) (0.270 g, 0.428 mmol, 1.0 equiv) in THF (10 mL) was added 1.2 equiv of sulfur (0.017 g, 0.531 mmol, 1.2 equiv) in THF (2 mL) at room temperature and stirred for another 12 h and noticed the formation of a clear yellow solution. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (8 mL) and few drops of toluene was added and stored at –30 ^{o}C. Colourless crystals of compound suitable for X–ray diffraction analysis are obtained after one day.

Yield 0.29 g (89%); Mp 195 – 200 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 0.30 (s, 18H, NSi(CH_3)$_3$), 0.55 (d, J = 8.0 Hz, 12H, CH(CH_3)$_2$), 2.54 (s, 12H, CH_3), 3.78 (sept, J = 8.0 Hz, 2H, CH(CH$_3$)$_2$), 6.87 (m, 6H, Ar–H) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 6.4 (Si–C), 20.7 (Ar–CH$_3$), 24.0 (Ar–CH$_3$), 52.9 (N–iPr–CH), 126.4 (Ar–C), 129.2 (Ar–C), 136.4 (Ar–C), 141.9 (Ar–C), 167.9 (NCN) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 ^{o}C,): δ = 5.54 (NSi(CH$_3$)$_3$) ppm. Anal Calcd for $C_{29}H_{50}N_4S_4Si_2Sn$ (757.88): C, 45.96; H, 6.65; N, 7.39. Found C, 45.43; H, 6.39; N, 6.82.

8.5.34 Synthesis of [{L^{1}SnN(SiMe$_3$)$_2$(μ–Se)}$_2$] **(25)**

To a solution of [{ArNC(N^{i}Pr$_2$)NAr}SnN(SiMe$_3$)$_2$] (**20**) (0.2 g, 0.317 mmol, 1.0 equiv) in benzene (20 mL) was added one equiv. of selenium powder (0.03 g, 0.38 mmol, 1.2 equiv) at room temperature and the reaction mixture was heated to 60 ^{o}C and continued the stirring for 12 h and a yellowish solution with some black colour precipitate was observed. All the volatiles were removed and extracted with diethyl ether (20 mL). Filtered through Celite using frit, solvent volume was reduced (8 mL) and few drops of toluene was added and stored at –30 ^{o}C. The reaction mixture was filtered through Celite and a clear yellow solution was reduced (8 mL) and kept it for crystallization at –20 ^{o}C. Colourless crystals for X–ray diffraction analysis were obtained after one day. Yield 0.19 g (85%); Mp 215 – 220 ^{o}C; ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ = 0.49 (s, 18H, NSi(CH_3)$_3$), 0.58 (d, J = 4.0 Hz, 12H, CH(CH_3)$_2$), 2.47 (s, 6H, CH_3), 3.03 (s, 6H, CH_3), 3.87 (sept, J = 7.3 Hz, 2H, CH(CH$_3$)$_2$), 6.84–6.91 (m, 4H, Ar–H), 7.05 (d, J = 8.0 Hz, 2H, Ar–H) ppm. ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ^{o}C): δ = 7.1 (Si–C), 20.6 (Ar–CH$_3$), 22.7(Ar–CH$_3$), 24.4 (iPr–CH$_3$), 52.6 (N–iPr–CH), 125.8 (Ar–C), 129.1 (Ar–C), 129.4 (Ar–C), 136.1 (Ar–C), 138.0 (Ar–C), 143.1 (Ar–C), 169.9 (NCN) ppm. ^{29}Si {^{1}H} NMR (80 MHz, C_6D_6, 25 ^{o}C,): δ = 5.24 (NSi(CH$_3$)$_3$) ppm. Anal

Calcd for $C_{58}H_{100}N_8Se_2Si_4Sn_2$ (1417.15): C, 49.16; H, 7.11; N, 7.91. Found C, 48.63; H, 7.01; N, 7.54.

General procedure for preparation of LML (L = L^1 & L^3, M = Ge, Sn, Pb)

^{n}BuLi was added to a solution of L^3H [^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$] in THF (20 mL) at 0 ^{o}C the solution became yellowish in colour and stirred for 4 h. The resultant solution was added drop by drop to a stirred solution of MX_2 (M = Ge, Sn, Pb; X = Cl) in THF (5 mL) at 0 ^{o}C and continued the stirring for another 24 h. Removal of all volatiles, extracted with *n*- hexane (40 mL) and filter through Celite, from the yellow colour solution solvent volume was reduced and kept for crystallization at 0 ^{o}C. Colourless crystals came after one day.

8.5.35. Synthesis of L^3GeL^3 **(26)**

[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (L^3H) (1 g, 2.84 mmol), ^{n}BuLi (1.6 M solution in hexane, 1.86 mL, 2.98 mmol), $GeCl_2$. dioxane (0.335 g, 1.42 mmol), 20 mL of THF. Yield: 0.97 g (88%) off–white solid. Mp = 135 – 140 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6) δ 6.87 (s, 8H, Ar*H*), 6.690 (s, 4H, Ar*H*), 3.71 (sept, *J* = 6.6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.30 (s, 24H, C*H*$_3$), 0.71 (d, *J* = 8 Hz, 24H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H}NMR (100 MHz, C_6D_6, 25 °C): δ 161.9 (N*C*N), 147.8 (Ar–*C*), 137.5 (Ar–*C*), 124.6 (Ar–*C*), 124.2 (Ar–*C*), 49.7 (N–^{i}Pr–*C*H), 22.0 (Ar–*C*H$_3$), 21.5 (^{i}Pr–*C*H$_3$). Anal Calcd for $C_{46}H_{64}GeN_6$ (773.68): C, 71.41; H, 8.34; N, 10.86. Found C, 71.11; H, 8.12; N, 10.38.

8.5.36 Synthesis of L^3SnL^3 **(27)**

[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (L^3H) (1 g, 2.84 mmol), ^{n}BuLi (1.6 M solution in hexane, 1.86 mL, 2.98 mmol), $SnCl_2$ (0.267 g, 1.42 mmol), 20 mL of THF. Yield: 0.98 g (84%) off–white solid. Mp 170 – 175 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6) δ 6.80 (s, 8H, Ar*H*), 6.68 (s, 4H, Ar*H*), 3.76 (sept, *J* = 6.6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.31 (s, 24H, C*H*$_3$), 0.82 (d, *J* = 8 Hz, 24H,

$CH(CH_3)_2$); $^{13}C\{^1H\}$NMR (100 MHz, C_6D_6, 25 °C): δ 164.4 (N*C*N), 148.6 (Ar–*C*), 137.7 (Ar–*C*), 124.3 (Ar–*C*), 123.9 (Ar–*C*), 50.0 (N–^{i}Pr–*C*H), 22.1 (Ar–*C*H_3), 21.6 (^{i}Pr–*C*H_3); Anal Calcd for $C_{46}H_{64}SnN_6$ (819.75): C, 67.40; H, 7.87; N, 10.25; Found C, 67.12; H, 7.39; N, 10.52.

8.5.37 Synthesis of L^3PbL^3 **(28)**

[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (L^3H) (1 g, 2.84 mmol), ^{n}BuLi (1.6 M solution in *n*-hexane, 1.86 mL, 2.98 mmol), $PbCl_2$ (0.396 g, 1.42 mmol), 20 mL of THF. Yield: 1.15 g (89%) off–white solid. Mp = 172 – 176 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.66 (s, 8H, Ar*H*), 6.61 (s, 4H, Ar*H*), 3.81 (sept, *J* = 6.6 Hz, 4H, C*H*$(CH_3)_2$), 2.30 (s, 24H, C*H*$_3$), 0.91 (d, *J* = 8 Hz, 24H, $CH(CH_3)_2$); $^{13}C\{^1H\}$NMR (100 MHz, C_6D_6, 25 °C): δ 165.1 (N*C*N), 149.1 (Ar–*C*), 137.4 (Ar–*C*), 123.8 (Ar–*C*), 123.6 (Ar–*C*), 49.7 (N–^{i}Pr–*C*H), 22.1 (Ar–*C*H_3), 21.6 (^{i}Pr–*C*H_3); Anal Calcd for $C_{46}H_{64}PbN_6$ (908.24): C, 60.83; H, 7.10; N, 9.25; Found C, 60.45; H, 7.33; N, 8.89.

8.5.38 Synthesis of L^1PbL^1 **(29)**

[^{i}Pr$_2$NC{N–2,6–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (L^1H) (1 g, 2.84 mmol), ^{n}BuLi (1.6 M solution in *n*-hexane, 1.86 mL, 2.98 mmol), $PbCl_2$ (0.396 g, 1.42 mmol), 20 mL of THF. Yield: 1.05 g (81%) off–white solid. Mp = 165 – 170 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.89 (d, *J* = 8Hz, 8H, Ar*H*), 6.58 (t, *J* = 6Hz, 4H, Ar*H*), 3.69 (sept, *J* = 6.6 Hz, 4H, C*H*$(CH_3)_2$), 2.24 (s, 24H, C*H*$_3$), 1.2 (d, *J* = 4 Hz, 24H, $CH(CH_3)_2$); $^{13}C\{^1H\}$NMR (100 MHz, C_6D_6, 25 °C): δ 157.4 (N*C*N), 155.9 (Ar–*C*), 130.8 (Ar–*C*), 128.4 (Ar–*C*),117.0 (Ar–*C*), 47.7 (N–^{i}Pr–*C*H), 23.4 (Ar–*C*H_3), 20.3 (^{i}Pr–*C*H_3); Anal Calcd for $C_{46}H_{64}PbN_6$ (908.24): C, 60.83; H, 7.10; N, 9.25; Found C, 60.51; H, 6.83; N, 8.81.

8.5.39 Synthesis of $L^3{}_2GeS_4$ **(30)**

In a Schlenk tube both the compounds L^3GeL^3 (0.3 g, 0.388 mmol) and elemental sulfur (0.014 g, 0.426) were mixed inside glove box and benzene (10 mL) was added as a solvent.

The reaction mixture was heated at 80 ºC for 8h with a color change to light yellowish. After evaporation of benzene in *vacuo* the crude product was washed with cold *n*- hexane to get light yellowish pure crystalline compound **30** (0.31 g, 89%). Single crystals suitable for XRD analyses were obtained in a saturated solution of 5 mL of ether and few drops of toluene cooled to –30 ºC. Mp = 225–230 ºC. ^{1}H NMR (400 MHz, THF) δ 7.02 (s, 4H, Ar*H*), 6.93 – 6.64 (m, 8H, Ar*H*), 3.63 (sept, J = 6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.35 (s, 12H, C*H*$_3$), 2.18 (s, 12H, C*H*$_3$), 0.88 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$), 0.82 (d, *J* = 8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, THF) δ 164.0 (N*C*N), 138.5 (Ar–*C*), 137.6 (Ar–*C*), 126.6 (Ar–*C*), 125.1 (Ar–*C*), 52.0 (N–^{i}Pr–*C*H), 23.3 (^{i}Pr–*C*H$_3$), 21.7 (Ar–*C*H$_3$), 21.5 (Ar–*C*H$_3$). Anal Calcd for $C_{46}H_{66}GeN_6S_4$ (904.34): C, 61.12; H, 7.36; N, 9.30. Found C, 61.50; H, 7.01; N, 9.82.

8.5.40 Synthesis of {L^{3}Ge(μ–Se)}$_2$ **(31)**

Same procedure as compound **30**

L^{3}GeL^3 (0.2 g, 0.258 mmol, 1 equiv.) and selenium powder (0.021 g, 0.258 mmol, 1equiv.), 10 mL of benzene. Yield: 0.178 g (81%). Mp = 235–240 ºC. ^{1}H NMR (400 MHz, C_6D_6): δ 6.97 (s, 8H, Ar*H*), 6.87 (s, 8H, Ar*H*), 6.71 (d, *J* = 8Hz, 8H, Ar*H*), 3.69 (sept, *J* = 6.6 Hz, 8H, C*H*(CH$_3$)$_2$), 2.30 (s, 24H, C*H*$_3$), 2.22 (s, 24H, C*H*$_3$), 0.79 (d, *J* = 4 Hz, 24H, CH(C*H*$_3$)$_2$), 0.68 (d, *J* = 8 Hz, 24H, CH(C*H*$_3$)$_2$). Anal Calcd. for $C_{92}H_{132}Ge_2N_{12}Se_2$ (1709.31): C, 64.64; H, 7.78; N, 9.83; Found C, 64.25; H, 7.41; N, 10.22.

8.5.41 Synthesis of {L^{3}Sn(μ–S)}$_2$ **(32)**

A Schlenk tube charged with L^{3}SnL^3 (0.230 g, 0.281 mmol) and elemental sulfur (0.01 g, 0.309 mmol). To the above mixture benzene (10 mL) was added and the reaction mixture was heated at 70 ºC for 8 h with a color change to light yellowish colour solution. The resultant yellowish colour solution filtered through Celite and reduced (4 mL) and kept it for crystallization at room temperature. Colourless crystals of compound **32** suitable for X–ray

diffraction analysis are formed after one day. Yield: 0.19 g (79 %). Mp = 240–245 ^{o}C. ^{1}H NMR (400 MHz, Tol) δ 6.97 (s, 16H, Ar*H*), 6.63 (s, 8H, Ar*H*), 3.72 (sept, *J* = 6.6 Hz, 8H, C*H*(CH$_3$)$_2$), 2.22 (s, 24H, C*H*$_3$), 2.22 (s, 24H, C*H*$_3$), 0.79 (d, *J* = 8 Hz, 48H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, Tol) δ 164.5(N*C*N), 163.4 (N*C*N), 145.0 (Ar–*C*), 138.1(Ar–*C*), 138.1(Ar–*C*), 137.5 (Ar–*C*), 126.3 (Ar–*C*), 125.9(Ar–*C*), 124.9 (Ar–*C*), 124.6 (Ar–*C*), 51.8 (N–^{i}Pr–*C*H), 51.7 (N–^{i}Pr–*C*H), 32.4 (Ar–*C*H$_3$), 22.3 (^{i}Pr–*C*H$_3$), 21.7 (Ar–*C*H$_3$), 21.3 (^{i}Pr–*C*H$_3$), 14.7(^{i}Pr–*C*H$_3$). Anal Calcd for $C_{92}H_{132}Sn_2N_{12}S_2$ (1707.66): C, 64.71; H, 7.79; N, 9.84; Found C, 64.35; H, 7.91; N, 10.22.

8.5.42 Synthesis of {L^{3}Sn(μ–Se)}$_2$ **(33)**

Same procedure as earlier compound **32**

Sn[^{i}Pr$_2$NC{N–3,5–Me$_2$–C$_6$H$_3$}$_2$]$_2$ (0.250 g, 0.305 mmol) and selenium powder (0.024 g, 0.305 mmol), 10 ml of benzene. Yield: 0.21 g (76 %). Single crystals suitable for X-ray diffraction analyses were obtained saturated solution of **33** in benzene at room temperature. Mp = 250–255 ^{o}C. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.86 (s, 12H, Ar*H*), 6.64 (s, 12H, Ar*H*), 3.87 (br, 8H, C*H*(CH$_3$)$_2$), 2.27 (s, 48H, C*H*$_3$), 1.02 (d, *J* = 4 Hz, 48H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 163.0 (N*C*N), 150.9 (Ar–*C*), 148.6(Ar–*C*), 138.4 (Ar–*C*), 138.4 (Ar–*C*), 136.5(Ar–*C*), 128.5 (Ar–*C*), 125.0 (Ar–*C*), 123.6 (Ar–*C*), 120.5 (Ar–*C*), 116.6 (Ar–*C*), 50.9 (N–^{i}Pr–*C*H), 47.6 (N–^{i}Pr–*C*H), 22.8 (Ar–*C*H$_3$), 21.5 (^{i}Pr–*C*H$_3$), 21.4 (Ar–*C*H$_3$), 21.3 (^{i}Pr–*C*H$_3$). Anal Calcd for $C_{92}H_{132}Sn_2N_{12}Se_2$ (1801.45): C, 61.34; H, 7.39; N, 9.33; Found C, 61.05; H, 7.78; N, 10.02.

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