Precursors for N-Heterocyclic Carbenes (NHC) for NHC-Stabilized Germylenes

M.Sc. Thesis

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Department of Chemistry Indian Institute of Technology Indore June 2021

Precursors for N- Heterocyclic Carbenes (NHC) for NHC-Stabilized Germylenes

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Submitted in partial Fulfilment of the requirements for the award of the degree

Of

Master of Science by ADITYA RAJ (1903131010)



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Precursors** for N- Heterocyclic Carbenes (NHC) for NHC-Stabilized Germylenes" is the partial fulfilment of the requirements for the award of the degree of MASTER of SCIENCE and submitted in the **Department of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from March 2021 to June 2021 under the supervision of Dr. Dipak Kumar Roy.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.



(Aditya Raj)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Classically the catalytic activities for small molecule activation are widely represented by the use of transition metals and their compounds, but due to toxicity, low abundance, and high cost, the steps are moving towards main group elements and their compounds. Germylenes has greater potential to take charge.

In this report we have reported, the synthesis of different DAD i.e., DIPP DAD, MES DAD from glyoxal and butan-2,3-dione and further their imidazolium salt, for the purpose of synthesis of their respective carbene that can be used for complexation with $GeCl_2$ to obtain stable germylenes and study their catalytic ability in small molecules activation like CO_2 and H_2 .

In addition, with an aid of ¹H, ¹³C NMR spectroscopy, and Mass spectrometry techniques these molecules were characterized.

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ABBREVIATIONS

mL	Millilitre
g	Gram
hr	Hour
K	Kelvin
%	Percentage
Mol	Mole
°C	Degree Celsius
0	Degree
min	Minute

ACRONYMS

DMF	Dimethylformamide
NHC	N- heterocyclic carbene
cAAC	Cyclic Alkyl Amino Carbene
NHGe	N- heterocyclic germylene
Dipp	Di isopropyl phenyl
DAD	Di aza diene
EA	Ethyl acetate
TMSCI	Trimethyl silyl chloride
THF	Tetrahydrofuran
TMEDA	Tetra methyl ethylene diamine
MES	Mesitylene
PXRD	Powder X-ray Diffraction
NMR	Nuclear magnetic resonance
XRD	X-ray Diffraction

CHAPTER 1

1.1 Introduction

Activation of small molecules and catalysis of different types of reaction is a need and requirement of easy and less time-consuming completion of many reactions. Last several years witnessed the typical way of doing this is by activation via transition-metal complexes and transition metal organometallic compounds [1,2]. But due to toxicity and low metal abundance and higher economic factors, the use of transition metal complexes for this purpose has been shifting towards main group compounds due to its low toxic effect on environment and eco system and better economic point of view [3].

One of the astounding main-group molecules which have activating tendency of small molecule are N-heterocyclic carbene (NHC) and heavier tetrylenes of group 14 elements which are heavier analogues of carbene. NHC proved to be an effective ligand for stabilising low coordinate elements in various oxidation states that are difficult to get using other methods [4]. This opens up a lot of possibilities for characterising and learning about the bonding in these reactive species, as well as exploring their distinct reactivities and catalytic potential.

Mostly the stable N-Heterocyclic carbenes (NHCs) are singlet carbenes with a divalent carbenic core that is directly bound to at least one nitrogen atom inside the heterocycle. Carbenes have traditionally been thought to be so reactive that they have only been studied indirectly, such as by trapping reactions [5]. Many of them can be isolated as pure substances, despite the fact that they are fairly reactive (i.e., they dimerize). In the singlet form, persistent carbenes are found. Steric hindrance by bulky groups allow to stabilize the carbene in free state. Thermodynamically stable singlet carbenes can be isolated and stored for an indefinite period. Others gradually dimerise with time. Since carbenes in the triplet state have short half-lives, they can be detected but not processed. The divalent carbon species became common and available class of compound with the discovery of first stable NHC in the beginning of 90s by Arduengo [6]. N-heterocyclic carbenes, in contrast to other carbenes, are nucleophilic and having electro rich carbenic core which

also got stability with both electron donating and electron withdrawing nature of N-centres. NHCs form stronger bonds with metal centres in comparison to most of classical ligands, such as phosphines, because of their strong sigma electron-donating properties [7]. In organometallic chemistry NHCs were first recognised as ubiquitous ligand because of these beneficial properties. Because of their distinctive features, such as strong -donor abilities well as easy structural and electronic tinkering, N-heterocyclic carbenes (NHCs) have been studied intensively in many domains for the past two decades. The NHCs capacity to behave like transition metal in small molecule activation has recently been discovered, which supports efforts to use NHCs to activate small molecules in a similar way to transition metal centres [8]. The frustrated Lewis Pairs which is metal free have been shown to H₂ activation [9], and these species have been used to catalytically hydrogenate reactive unsaturated compounds [10]. N- heterocyclic carbenes have also been used as Lewis bases for frustrated lewis pairs (FLPs) [11]. The activation barrier of H₂ addition to cAAC (cyclic Alkyl amino Carbene) (Scheme-1) was found to be more thermodynamically and kinetically favourable than the activation barrier of bis(amino)carbenes. Initial attempts were unsuccessful for activation of CO with various persistent carbene. The first CO fixation to a stable singlet carbene was reported by Bertrand et al.(reference) At normal temperature, the electrophilic cAAC interacts with CO to form the aminoketene. Since cAAC was developed to decrease singlet to triplet energy gap by lowering the energy gap of LUMO, so that the effective activation of CO is conceivable. Nucleophilic NHCs also activates CO₂ a weak electrophile. The direct fixation of CO₂ to NHCs and NHC salts generating imidazolium carboxylates was reported by Louie et al. in 2004 [12]. The Bertrand group has recently reported direct CO₂ fixation to cAAC and anti-Bredt NHC [13].



Scheme 1. Activation of H₂ by cAAC.

Germylene is a germanium analogue of carbene. The ground state of germylene is mostly in singlet due to larger HOMO-LUMO gap than that of carbene. So lone pair of electrons in germylene present in sp^2 orbital which has much greater s-character and a vacant p-orbital. Germylenes are stabilized either by adding bulky substituent of GeR₂ or an electronegative element directly attached to Ge, which determent it's HOMO and also prevents from oligomerisation [14]. Well known stable germylenes are: Meller germylenes (fig-2), six membered N-heterocyclic germylenes (fig-3) [15], boryls substituted pendent N-heterocyclic germylene (fig-4) [16], During activation of small molecules and catalysis Ge goes from Ge(+2) oxidation state to Ge(+4) oxidation state which is generally square planar or tetrahedral by oxidising itself by undergoing oxidative addition.



Fig. 1. General representation of germylene





Fig.3. Miller germylene



Fig.4. N- borylated NHGe





Scheme 3. Synthesis of germylene by GeCl₂.dioxane

Our aim is to synthesize NHC stabilized germylenes. In this connection we started to synthesize NHC.

Several ways of synthesis of substituted diamines based on the required properties of NHC precursor, which can be categorised into three major strategies: [17,18,19] (a) formation of a bis imine and reduction; (b) bis acylation of two amines and reduction;(c) mono alkylation and monoacylation of two amines followed by reduction.

In a typical synthetic procedure in condensation and reduction method (a), an aryl or alkylamine is first condensed with glyoxal, then reduced to the corresponding diamine, which is then extracted as the dihydrochloride salt. The product formed as imidazolium salt is cyclized by triethyl formate as precarbenic unit (and if starting from the free diamine, one equivalent of acid). This route of synthesis is the most popular and standard protocol for obtaining common imidazolium salts, since this applies to wide variety of amines. Mol and colleagues first announced the synthesis of the mixed adamantyl/mesityl N-heterocyclic precursor 1-(1-adamantyl)-3mesityl-imidazoliniumchloride by reacting an amine with oxalyl chloride, then reacting a another amine with the intermediate acyl chloride under biacylation reduction method. The resulting oxalamide was then reduced and cyclized with triethyl orthoformate. The modular synthesis of N-heterocyclic carbene precursors starting from

chloroacetylchloride was stated by Kotschy and colleagues as acylation/ alkylation reduction route.

With the purpose of synthesising germylenes with good sigma donating Nheterocyclic carbenes as ligand, we synthesized first MES DAD, DIPP DAD [20,21], precursor for synthesis of corresponding NHC by paraformaldehyde as precarbenic unit which was first synthesized by Bildstein and co-workers in 1999. Our purpose was for complexation of these carbene with Ge to germylenes and studying their properties, reactivities and activation capability for small molecules like H_2 , CO_2 etc.

1.2 Objective

Objective of my research work is to synthesizing stable Germylenes of different imidazolium carbene ligands and different substituents on it, which helps to make them stable and isolable. Studying the characteristics of substituents, and how much it helps in stabilizing germylenes, also to get its thermal stability. Further focus is to finding the reactivities and activation capability of small molecules like H₂, CO, etc. of synthesized germylenes. It will be also exciting to observe to how much extent this carbene analogue germylene is capable to replace transition metal complex and transition metal organometallic compounds in catalysing activity and activation of small molecules and in different reactions.



Scheme 4 Activation of small molecules by germylene.

CHAPTER 2

2. Experimental Section

All the chemicals used were bought from Alfa Aesar, Merck, and Sigma-Aldrich, and used without further purification. Solvents used were purified by distillation. 500 MHz (¹H NMR) and 126 MHz (¹³C NMR) were recorded in CDCl₃ on a Bruker 500 spectrometer at 298 K using TMS (tetramethyl silane) as external standard. In ¹H NMR Chemical shifts were reported in ppm relative to the centre of singlet at 7.26 ppm for CDCl₃ and in ¹³C NMR it is relative to the centre of triplet at 77.0 ppm for CDCl₃.

2.1 Synthesis of Dipp DAD

A solution of glyoxal (1 eq.) in MeOH was added to a warmed solution (50 °C) solution of DAD (2 eq.) and acetic acid (1.5 mL) solution in MeOH. After 30 minutes, the product began to crystallise. The mixture was stirred at room temperature for 10 hours. The resulting yellow suspension was filtered and washed with MeOH, yielding a yellow crystal. The product yield was 25 %.



Scheme –5 Synthesis of Dipp DAD

2.2 Synthesis of Dipp imidazolium salt

A solution of Dipp DAD (1 eq.) and paraformaldehyde (1.03 eq.) in ethyl acetate was heated to 70 $^{\circ}$ C and stirred till most of the paraformaldehyde was dissolved and temperature reduced to 50 $^{\circ}$ C. A solution of TMSCl (1.03 eq.) in ethyl acetate (8mL) was added dropwise with vigorous stirring. Then the mixture was stirred for another two hours at 70 $^{\circ}$ C with

reflux before being cooled in an ice bath. Filtered reaction mixture was washed with ethyl acetate and ether. The pinkish-red precipitate was then dried and suctioned. The yield of our product was 77.09%.



Scheme -6 Synthesis of Dipp imidazolium salt

2.3 Synthesis of MES DAD

A solution of glyoxal (1 eq.) in MeOH was added to a warmed solution (50 °C) solution of MES (2 eq.) and acetic acid (1.5 mL) solution in MeOH. The product started to crystalize after15 minutes. The mixture was stirred at room temperature for 10 hours. Then the resulting yellow suspension was filtered and washed with MeOH before being dried in a vacuum to obtain yellow crystal with good yield.



Scheme- 7 Synthesis of MES DAD.

2.4 Synthesis of MES imidazolium salt

A solution of MES DAD (1 eq.) and paraformaldehyde (1.03 eq.) in ethyl acetate was heated to 70 °C and stirred till most of the paraformaldehyde was dissolved. A solution of TMSCl (1.03 eq.) in ethyl acetate was (8 mL) was added dropwise with vigorous stirring. Then for another two hours the mixture was stirred at 70 °C with reflux before being cooled in an ice bath. Filtered reaction mixture was washed with ethyl acetate and ether. The pinkish-red

precipitate was then dried and suctioned. The yield of our product was 36.22%.



Scheme –8 Synthesis of MES imidazolium salt.

CHAPTER 3

3. Result and discussion

3.1 Dipp DAD

After synthesis the product was characterized by ¹H NMR and ¹³C NMR.

Figure- 6 depicts the ¹H NMR of the DIPP DAD salt with the chemical shift value as,

¹H NMR (500 MHz, CDCl₃) δ = 8.10 (s, 1H), 7.23 – 7.11 (m, 3H), 2.94 (sept, J = 6.9 Hz, 2H), 1.21 (d, J = 6.9 Hz, 12H).

Figure- 7 shows ¹³C NMR characterization with chemical shift as, ¹³C NMR (126 MHz, CDCl₃) δ 163.25, 148.16, 136.87, 125.27, 123.33, 28.35, 23.53.



Fig. –5 Dipp DAD



Fig. -6¹H NMR of Dipp DAD.



Fig. –7¹³C NMR of Dipp DAD

3.2 Dipp Imidazolium salt

In this method we used activator TMSCl instead of HCl. When we used HCl as activator, the characterization data does not match with required product. We successfully synthesized the product DIPP Imidazolium salt of off-white colour in 77.09% yield.



Fig. – 8 Dipp Imidazolium salt

Figure- 9 depicts the ¹H NMR of the DIPP Imidazolium salt with the chemical shift value as, ¹H NMR 500 MHz (CDCl₃): $\delta = 8.15(d, 2H), 7.57(t, 2H), 7.35(d, 4H), 2.45(sept., 4H), 1.29(d, 6H), 1.25(d, 6H).$ Figure- 10 shows ¹³C NMR characterization with chemical shift as, ¹³C NMR 126 MHz (CDCl₃): $\delta = 171.27, 145.14, 138.70, 132.29, 130.01, 126.95, 124.85, 29.26, 24.89, 23.86.$ Which are matching well with reported data [11].



Fig.-9 ¹H NMR of Dipp Imidazole salt



Fig. –10¹³C NMR of Dipp Imidazole salt

3.3 MES DAD

After synthesis of the product, it was characterized by ¹H NMR and ¹³C NMR. Figure- 12 depicts the ¹H NMR of the DIPP DAD salt with the chemical shift value as,

¹H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.23 – 7.11 (m, 3H), 2.94 (sept, *J* = 6.9 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 12H).

Figure- 13 shows ¹³C NMR characterization with chemical shift as, ¹³C NMR (126 MHz, CDCl₃) δ 163.25, 148.16, 136.87, 125.27, 123.33, 28.35, 23.53 Which are matching well with reported data. So, we successfully synthesized MES DAD of yellow coloured crystal.



Fig.- 11 MES DAD



Fig.-12¹H NMR of MES DAD



3.4 MES imidazolium salt

After synthesis of the product, it was characterized by ¹H NMR.

Figure- 15 depicts the ¹H NMR of the DIPP Imidazolium salt with the chemical shift value as, ¹H NMR 500 MHz (CDCl₃): δ =11.10 (s, 1H), 7.55 (d, J = 1.5 Hz, 7H), 7.05 (s, 14H), 2.35 (s, 21H), 2.21 (s, 44H).

Which are matching well with reported data. So, we successfully synthesized MES Imidazolium salt.



Fig.- 14 MES Imidazolium salt



Fig.- 15¹H NMR of MES Imidazolium salt.

CHAPTER 4

4. Conclusion future outlook

From here we conclude that, for the purpose of synthesizing NHC stabilized germylenes and studying its ability to activate small molecules, we have synthesized DIPP DAD, MES DAD, and their respective imidazolium salt and characterized them with ¹H NMR, ¹³C NMR.

In this context we targeted to synthesize NHC (for stabilizing germylene as a ligand), because of strong sigma donating ability and easy electron tinkering. NHC are singlet carbene with divalent carbenic core. NHC are electron rich and nucleophilic species unlikely to other carbenes which are electron deficient and very reactive. In comparison to most of classical ligands e.g. phosphine, NHC form stronger bonds with metal centre. There are several classic paths to synthesize substituted diamines based on the characteristics of the target NHC precursors.

Our target was for synthesis of these NHC stabilized germylene and studying their properties, reactivity and activation capability for small molecule like H₂, CO₂.

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