

**DIPYRRINATE AND AMINOTROPONIMINATE LIGAND
STABILIZED Ge(II) AND Ge(IV) COMPOUNDS: SYNTHESIS,
REACTIVITY, AND BIOLOGICAL APPLICATIONS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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REACTIVITY, AND BIOLOGICAL APPLICATIONS**

By

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Submitted

*In fulfilment of the requirements of the degree of Doctor of Philosophy
to the*



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DECEMBER 2021

Dedicated to My Parents

Certificate

This is to certify that the thesis entitled “**Dipyrrinate and Aminotroponimate Ligand Stabilized Ge(II) and Ge(IV) Compounds: Synthesis, Reactivity, and Biological Applications**” being submitted by **Mr. Pritam Mahawar** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of the original, bonafide research work carried out by him under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results exemplified in this thesis have not been submitted in part or full to any other University or institute to award any degree or diploma.

Dr. S. Nagendran

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Abstract

The thesis entitled “*Dipyrinate and Aminotroponimate Ligand Stabilized Ge(II) and Ge(IV) Compounds: Synthesis, Reactivity, and Biological Applications*” presents the details about the synthesis, and reactivity of water stable dipyrinate germylenes and germacarbonyl compounds, along with the oxidation products of aminotroponimate germylene metal complexes. This thesis is divided into the six chapters. A brief description about each chapter is given below:

Chapter 1: This chapter describes *N*-heterocyclic germylenes by talking about their synthesis and reactivity (nucleophilic substitution and oxidation). The applications of germylenes and germacarbonyl compounds as ligands for the isolation of transition metal complexes are also briefed. Based on these discussions, the scope and objectives of the thesis are mentioned.

Chapter 2: This chapter presents the methods employed for cleaning and drying of glassware, purification and drying of solvents (used in synthesis and NMR spectroscopy), and drying of gases. Additionally, preparation and purification of starting materials and handling of air and moisture-sensitive compounds are discussed. The source of various commercially available chemicals is provided. Details regarding instruments used to characterize the synthesized compounds and software used for theoretical studies are also presented.

Chapter 3: The germylenes require an inert atmosphere for their stability. If they are made stable under ambient conditions, their applications in various fields can be explored. Accordingly, this chapter will describe the synthesis of air, water, and culture-medium stable germylene hydroxide DPMGeOH (**303**) and its biological applications. Compound **303** was synthesized under ambient conditions from germylene monochloride DPMGeCl (**302**) using an excess of cesium carbonate. The reactions of air and water stable germylene monochloride DPMGeCl (**302**) with alcohols,

methylating agent (MeOTf), and fluorinating agent (CsF) offered germylene alkoxides DPMGeOR (R = Me (**304**), Et (**305**), ⁱPr (**306**)), cationic germanium(IV) compound DPMGeCl(Me)(OTf) (**307**), and germylene monofluoride DPMGeF (**308**), respectively. Interesting conversion of germylene alkoxides **304-306** to germylene hydroxide **303** is also discussed. The air stabilities of compounds **302-304** were monitored for up to 10 days and were stable. The compounds **302**, **303**, and **304** were stable in water for 36 h, 5 d, and 6 h, respectively. The antiproliferative effects of germylene **303** on human cancer lines (HeLa, MCF7, and Huh7) and normal epithelial cells (Vero) were studied using MTT, Trypan blue, and colony formation assays. Compound **303** exhibits comparable/better antiproliferative effects than that of cisplatin, depending on the cell studied. The cytotoxicity of compound **303** on normal epithelial cells is minimal, and this aspect is similar/marginally better to that of the currently used anticancer drugs.

Chapter 4: As the isolation of air and water stable germylenes and the demonstration of their biology applications were possible, the synthesis of hitherto unknown air and water stable germacarbonyl compounds with Ge=E bonds (E = S/Se) are attempted in this chapter. The starting materials used to synthesize these germacarbonyl compounds are dipyrromethene ligand stabilized hydroxygermylene **303**, ethoxygermylene **305**, phenylgermylene **401**, thienylgermylene **404**, and aminogermylene **411**. Germylenes **401**, **404**, and **411** were isolated using monochlorogermylene **302**. The reactions of germylenes **401**, **404**, **303**, **305**, and **411** with elemental sulfur and selenium powder in toluene at ambient conditions afforded the corresponding germacarbonyl compounds, i.e., germanones **402-403**, **405-406**, germacarboxylic acids **407-408**, germaesters **409-410**, and germaamides **412-413** with Ge=E bonds (E = S/Se), respectively. Interestingly, all these compounds are air and water stable. The attempted synthesis of germaaldehyde **A** through the reaction of germylene hydroxide **303** and alkoxides **304-305** independently with water borane

adduct ($\text{H}_2\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3$) afforded a germylene cation **414** with a weakly coordinating $[(\text{OH})\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion. Preliminary reactivity studies of the first air and water stable germacarbonyl compounds **412-413** with copper(I) halides resulted in the first air and water stable germaamides stabilized monomeric (**415, 416**) and dimeric copper(I) halides complexes (**417-420**).

Chapter 5: The catalytic utility of germylene stabilized zinc complexes is rare, and there is no report on their use as hydroboration catalysts. This chapter addresses this issue by studying the aminotroponimate germylenes stabilized zinc complexes. The reactions of monochlorogermylene $[(^i\text{Bu})_2\text{ATiGeCl}]$ (**101q**), germylene pyrrole $[(^i\text{Bu})_2\text{ATiGeNC}_4\text{H}_4]$ (**101r**), and aminogermylene $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2]$ (**101v**) with ZnI_2 in tetrahydrofuran resulted in the germylene stabilized zinc iodide complexes $[(^i\text{Bu})_2\text{ATiGeCl}\rightarrow\text{ZnI}_2(\text{THF})]$ (**501**), $[(^i\text{Bu})_2\text{ATiGeNC}_4\text{H}_4\rightarrow\text{ZnI}_2(\text{THF})]$ (**502**), and $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2\rightarrow\text{ZnI}_2(\text{THF})]$ (**503**), respectively. The synthesis of germylene stabilized dimeric zinc complexes with Zn_2I_4 core $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2\rightarrow(\text{ZnI}_2)]_2$ (**504**) and $[(^i\text{Bu})_2\text{ATiGe}^i\text{Pr}\rightarrow(\text{ZnI}_2)]_2$ (**505**) are also reported. Further, the catalytic application of germylene stabilized zinc complex $[(^i\text{Bu})_2\text{ATiGe}^i\text{Pr}\rightarrow(\text{ZnI}_2)]_2$ (**505**) for the hydroboration of aldehydes and ketones is shown. Compounds **501-505** were characterized through multinuclear NMR spectroscopy, and single-crystal X-ray diffraction studies were performed on compounds **502-505**.

Chapter 6: As the reactivity of germylene stabilized zinc complexes are hardly known, this chapter is devoted to the study of their reaction with chalcogens with an objective to isolate Lewis acid (ZnI_2) stabilized germacarbonyl compounds. Here, the synthesis of germaacid chloride $[(^i\text{Bu})_2\text{ATiGe}(\text{E})\text{Cl}\rightarrow\text{ZnI}_2(\text{THF})]$ ($\text{E} = \text{S}$ (**601**), Se (**602**)) and the germaamides $[(^i\text{Bu})_2\text{ATiGe}(\text{E})\text{N}(\text{TMS})_2\rightarrow\text{ZnI}_2(\text{THF})]$ ($\text{E} = \text{O}$ (**604**), S (**607**), Se (**608**)) are reported as their zinc

iodide complexes. The synthesis of bisgermacarbonyl compounds, i.e., bisgermaamide $[(^i\text{Bu})_2\text{ATiGe}(\text{O})\text{N}(\text{TMS})_2 \rightarrow (\text{ZnI}_2)]_2$ (**605**) and bisgermanones $[(^i\text{Bu})_2\text{ATiGe}(\text{E})^i\text{Pr} \rightarrow (\text{ZnI}_2)]_2$ (E = O (**609**), S (**610**), Se (**611**)) as their dimeric zinc iodide complexes are also discussed. Further, attempted reactions of germylene pyrrole stabilized zinc complex **502** with N_2O and S/Se leading to the formation of a cationic cyclotrigermoxane **603** with capping μ_3 -oxo ligand and an unidentified mixture of products are discussed, respectively.

सार

थीसिस शीर्षक " डाइपाइरिनेट और एमिनोट्रोपोनिमिनेट लिगेंड स्टेबिलाइज्ड Ge(II) और Ge(IV) कंपाउंड्स: सिंथेसिस, रिएक्टिविटी, और बायोलॉजिकल एप्लीकेशन" पानी के स्थिर डिपाइरिनेट जर्माइलीन और जर्माकार्बोनील यौगिकों के संश्लेषण, और प्रतिक्रियाशीलता के साथ एमिनोट्रोपोनिमिनाटो जर्माइलीन धातु परिसरों के ऑक्सीकरण उत्पाद के बारे में विवरण प्रस्तुत करता है। यह थीसिस छह अध्यायों में विभाजित है। प्रत्येक अध्याय के बारे में संक्षिप्त विवरण नीचे दिया गया है:

अध्याय 1: इस अध्याय में एन-हेटरोसायक्लिक जर्माइलीन के संश्लेषण और प्रतिक्रियाशीलता (न्यूक्लियोफिलिक प्रतिस्थापन और ऑक्सीकरण) के बारे में वर्णन किया गया है। संक्रमण धातु परिसरों के अलगाव के लिए लिगेंड के रूप में जर्माइलीन और जर्माकार्बोनील यौगिकों के अनुप्रयोगों के बारे में भी जानकारी दी गई है। इन चर्चाओं के आधार पर थीसिस के दायरे और उद्देश्यों का उल्लेख किया गया है।

अध्याय 2: यह अध्याय कांच के बर्तनों की सफाई और सुखाने, सॉल्वेंट्स की शुद्धि और सुखाने (संश्लेषण और एनएमआर स्पेक्ट्रोस्कोपी में प्रयुक्त), और गैसों के सुखाने के लिए नियोजित विधियों को प्रस्तुत करता है। इसके अतिरिक्त, प्रारंभिक सामग्री की तैयारी और शुद्धिकरण और हवा और नमी-संवेदनशील यौगिकों की हैंडलिंग पर चर्चा की गई है। विभिन्न व्यावसायिक रूप से उपलब्ध रसायनों के स्रोत प्रदान किए गए हैं। सैद्धांतिक अध्ययन के लिए इस्तेमाल किए गए संश्लेषित यौगिकों और सॉफ्टवेयर को चिह्नित करने के लिए उपयोग किए जाने वाले उपकरणों के बारे में विवरण भी प्रस्तुत किया गया है।

अध्याय 3: जर्माइलीन को अपनी स्थिरता के लिए एक निष्क्रिय वातावरण की आवश्यकता होती है। यदि उन्हें परिवेशी परिस्थितियों में स्थिर बनाया जाता है, तो विभिन्न क्षेत्रों में उनके अनुप्रयोगों का पता लगाया जा सकता है। तदनुसार, यह अध्याय हवा, पानी और culture-माध्यम स्थिर जर्माइलीन हाइड्रॉक्साइड DPMGeOH

(303) और इसके जैविक अनुप्रयोगों के संश्लेषण का वर्णन करेगा। यौगिक 303 को सीज़ियम कार्बोनेट की अधिकता का उपयोग करके जर्माइलीन मोनोक्लोराइड DPMGeCl (302) से परिवेशी परिस्थितियों में संश्लेषित किया गया था। एल्कोहल, मिथाइलेटिंग एजेंट (MeOTf), और फ्लोरिनेटिंग एजेंट (CsF) के साथ हवा और पानी स्थिर जर्माइलीन मोनोक्लोराइड DPMGeCl (302) की प्रतिक्रियाओं ने जर्माइलीन एल्कोक्साइड DPMGeOR ($\text{R} = \text{Me}$ (304), Et (305), $i\text{Pr}$ (306)) की पेशकश की। , धनायनित Ge(IV) यौगिक DPMGeCl(Me)(OTf) (307), और जर्माइलीन मोनोफ्लोराइड DPMGeF (308), क्रमशः। जर्माइलीन एल्कोक्साइड 304-306 का जर्माइलीन हाइड्रॉक्साइड 303 में दिलचस्प रूपांतरण पर भी चर्चा की गई है। यौगिकों 302-304 की वायु स्थिरता की निगरानी 10 दिनों तक की गई और वे स्थिर थे। यौगिक 302, 303, और 304 पानी में क्रमशः 36 h, 5 d, और 6 h के लिए स्थिर थे। मानव कैंसर लाइनों (HeLa , MCF7 , and Huh7) और सामान्य उपकला कोशिकाओं (Vero) पर जर्माइलीन 303 के एंटीप्रोलिफेरेटिव प्रभावों का अध्ययन एमटीटी, ट्रिपैन ब्लू और कॉलोनी गठन परख का उपयोग करके किया गया था। कंपाउंड 303 अध्ययन किए गए सेल के आधार पर सिस्प्लैटिन की तुलना में तुलनीय/बेहतर एंटीप्रोलिफेरेटिव प्रभाव प्रदर्शित करता है। सामान्य उपकला कोशिकाओं पर यौगिक 303 की साइटोटोक्सिसिटी न्यूनतम है, और यह पहलू वर्तमान में उपयोग की जाने वाली एंटीकैंसर दवाओं के समान/मामूली रूप से बेहतर है।

अध्याय 4: चूंकि हवा और पानी के स्थिर जर्माइलीन का अलगाव और उनके जीव विज्ञान अनुप्रयोगों का प्रदर्शन संभव था, इस अध्याय में अब तक अज्ञात हवा और पानी के स्थिर जर्माकार्बोनील यौगिकों के Ge=E बांड ($\text{E} = \text{S/Se}$) के संश्लेषण का प्रयास किया गया है। इन जर्माकार्बोनील यौगिकों को संश्लेषित करने के लिए उपयोग की जाने वाली प्रारंभिक सामग्री हैं डाइपाइरोमेथीन लिगैंड स्टेबलाइज्ड हाइड्रॉक्सीजर्माइलीन 303, एथोक्सीजर्माइलीन 305, फेनिलजर्माइलीन 401, थिएनिलजर्माइलीन 404 और एमिनोजर्माइलीन 411। जर्माइलीन 401, 404, और 411 को मोनोक्लोरोजर्माइलीन 302, का उपयोग करके संश्लेषित किया गया था।

जर्माइलीन्स 401, 404, 303, 305, और 411 परिवेशी परिस्थितियों में टोल्यूनि में मौलिक सल्फर और सेलेनियम पाउडर के साथ संबंधित जर्मेकार्बोनिल यौगिकों को वहन करता है, अर्थात्, जर्मेनोन 402-403, 405-406, जर्माकारबोक्सिलिक एसिड 407-408, जर्मेस्टर 409-410, और जर्माइड्स 412-413 $\text{Ge}=\text{E}$ बांड ($\text{E} = \text{S/Se}$) के साथ, क्रमशः। दिलचस्प बात यह है कि ये सभी यौगिक हवा और पानी स्थिर हैं। जर्माइलीन हाइड्रॉक्साइड 303 और एल्कोक्साइड 304-305 की स्वतंत्र रूप से पानी के बोरेन एडक्ट ($\text{H}_2\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$) की प्रतिक्रिया के माध्यम से जर्माइलीन धनायनित 414 एक कमजोर समन्वय $[(\text{OH})\text{B}(\text{C}_6\text{F}_5)_3]^-$ आयन के साथ वहन किया। कॉपर(I) हलाइड्स के साथ जर्माकार्बोनिल यौगिकों 412-413 के प्रारंभिक प्रतिक्रियाशीलता अध्ययन के परिणामस्वरूप पहली हवा और पानी स्थिर जर्माइड्स स्थिर मोनोमेरिक (415, 416) और डिडाइमेरिक कॉपर(I) हलाइड्स कॉम्प्लेक्स (417-420) भी प्रस्तुत किया गया है।

अध्याय 5: जर्माइलीन स्थिर जिंक कॉम्प्लेक्स की उत्प्रेरक उपयोगिता दुर्लभ है, और हाइड्रोबोरेशन उत्प्रेरक के रूप में उनके उपयोग पर कोई रिपोर्ट नहीं है। यह अध्याय इस मुद्दे को अमीनोट्रोपोनिमिनेट जर्माइलीन स्थिर जिंक कॉम्प्लेक्स का अध्ययन करके संबोधित करता है। मोनोक्लोरोजर्माइलीन $[(^i\text{Bu})_2\text{ATiGeCl}]$ (101q), जर्माइलीन पाइरोल $[(^i\text{Bu})_2\text{ATiGeNC}_4\text{H}_4]$ (101r), और एमिनोजर्माइलीन $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2]$ (101v) की टेट्राहाइड्रोफुरन में ZnI_2 के साथ प्रतिक्रिया के परिणामस्वरूप जर्माइलीन स्थिर जिंक आयोडाइड कॉम्प्लेक्स $[(^i\text{Bu})_2\text{ATiGeCl} \rightarrow \text{ZnI}_2(\text{THF})]$ (501), $[(^i\text{Bu})_2\text{ATiGeNC}_4\text{H}_4 \rightarrow \text{ZnI}_2(\text{THF})]$ (502), और $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2 \rightarrow \text{ZnI}_2(\text{THF})]$ (503), क्रमशः। Zn_2I_4 कोर के साथ $[(^i\text{Bu})_2\text{ATiGeN}(\text{TMS})_2 \rightarrow (\text{ZnI}_2)]_2$ (504) और $[(^i\text{Bu})_2\text{ATiGe}^i\text{Pr} \rightarrow (\text{ZnI}_2)]_2$ (505) जर्माइलीन स्थिर डिमेरिक जिंक कॉम्प्लेक्स के संश्लेषण की भी रिपोर्ट की गई है। इसके अलावा, एल्डिहाइड और कीटोन के हाइड्रोबोरेशन के लिए जर्माइलीन स्थिर जिंक कॉम्प्लेक्स $[(^i\text{Bu})_2\text{ATiGe}^i\text{Pr} \rightarrow (\text{ZnI}_2)]_2$ (505) के उत्प्रेरक अनुप्रयोग को दिखाया गया है। यौगिकों 501-505 को बहु-

नाभिकीय NMR स्पेक्ट्रोस्कोपी के माध्यम से चित्रित किया गया था, और एकल-क्रिस्टल एक्स-रे विवर्तन अध्ययन 502-505 यौगिकों पर किए गए थे।

अध्याय 6: जैसा कि जर्माइलीन स्थिर जिंक कॉम्प्लेक्स की प्रतिक्रियाशीलता शायद ही ज्ञात हो, यह अध्याय काल्कोजन के साथ उनकी प्रतिक्रिया के अध्ययन के लिए समर्पित है जिसका उद्देश्य लुईस एसिड (ZnI_2) स्थिर जर्माकार्बोनिल यौगिकों को अलग करना है। यहाँ, जर्माएसिड क्लोराइड $[(^iBu)_2ATiGe(E)Cl \rightarrow ZnI_2(THF)]$ ($E = S$ (601), Se (602)) और जर्माइड्स $[(^iBu)_2ATiGe(E)N(TMS)_2 \rightarrow ZnI_2(THF)]$ ($E = O$ (604), S (607), Se (608)) को उनके जिंक आयोडाइड परिसरों के रूप में सूचित किया जाता है। बिस्जर्माकार्बोनिल यौगिकों का संश्लेषण, अर्थात्, बिस्जर्माइड $[(^iBu)_2ATiGe(O)N(TMS)_2 \rightarrow (ZnI_2)]_2$ (605) और बिस्गर्मनोन्स $[(^iBu)_2ATiGe(E)^iPr \rightarrow (ZnI_2)]_2$ ($E = O$ (609), S (610), Se (611)) के रूप में उनके डिमरिक जिंक आयोडाइड परिसरों की भी चर्चा की गई है। इसके अलावा, N_2O और S/Se के साथ जर्माइलीन पाइरोल स्थिर जिंक कॉम्प्लेक्स 502 की कोशिश की गई प्रतिक्रियाओं से क्रमशः μ_3 -ऑक्सो लिगेंड कैपिंग के साथ एक धनायनित साइक्लोट्रिगर्मोक्सेन 603 का निर्माण होता है और उत्पादों के एक अज्ञात मिश्रण पर चर्चा की जाती है।

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List of Symbols and Abbreviations

ATI	aminotroponimate	h	hour
%	percentage	HOMO	highest occupied molecular orbital
°	degree	HRMS	high-resolution mass spectrometry
°C	degree centigrade	Hz	<i>Hertz</i>
μ M	micro molar	ⁱ Bu	<i>iso</i> -butyl
Å	angstrom	ⁱ Pr	<i>iso</i> -propyl
ϵ	extinction coefficient	IR	infra-red
δ	(delta) chemical shift	<i>J</i>	coupling constant
λ	(lambda) wave length	K	Kelvin
Anal	analysis	Kcal	kilocalorie
au	atomic unit	LUMO	lowest unoccupied molecular orbital
bs	broad singlet	m/z	mass-to-charge ratio
Calcd	calculated	Me	methyl
cm	centimeter	Mes	mesityl
COD	cyclooctadiene	mg	milligram
Cp	cyclopentadienyl	MHz	megahertz
coe	cyclooctene	min	minute
DCM	dichloromethane	mL	milliliter
d	doublet	MO	molecular orbital
dd	double doublet	Mp	melting point
DFT	density functional theory	MS	mass spectrometry
deg	degree	mmol	milli mole
DME	dimethoxyethane	NHC	<i>N</i> -heterocyclic carbene
EI	electron ionization	NHGe	<i>N</i> -heterocyclic germylene
ESI	electrospray ionization	nm	nanometer
Et	ethyl	NMR	nuclear magnetic resonance
g	gram	ⁿ Pr	<i>normal</i> -propyl

OTf	triflate	S	Solvent
ppm	parts per million	t _(pseudo)	pseudo triplet
Py	pyrrole	T	temperature
Ph	phenyl	t	triplet
rt	room temperature	^t Bu	<i>tert</i> -butyl
^s Bu	<i>sec</i> -butyl	THF	tetrahydrofuran
s	singlet	UV	ultra violet