BIS(GERMYLENES) AND a-DPM STABILIZED GERMYLENES: SYNTHESES, REACTIVITIES, AND PHOTOPHYSICAL PROPERTIES

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

December 2024

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by

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Submitted

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

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

December 2024

Dedicated to My Father

Certificate

This is to certify that the thesis entitled **"Bis(germylenes) and a-DPM Stabilized Germylenes: Syntheses, Reactivities, and Photophysical Properties"** being submitted by **Mr. Prakash Chandra Joshi (Entry Number: 2018CYZ8478)** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of original research work carried out by him under my supervision and guidance. The thesis has met the required standards for the degree.

The results presented in this thesis have not been submitted in part or in whole to any other university or institute to obtain any degree or diploma.

Prof. S. Nagendran

Thesis Supervisor

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Acknowledgments

I still remember that crisp morning in early December 2018 when my heart pounded with excitement and nervousness. I had just been selected for a Ph.D. program at IIT Delhi, a dream I had nurtured for years. Stepping into Prof. S. Nagendran's office, I felt a surge of anticipation. His words resonated with a depth of wisdom and kindness that immediately put me at ease as we spoke. At that moment, amidst our conversation about my future and aspirations, I felt an undeniable connection and a sense of purpose. It was clear that under his guidance, I could explore the realms of my research with confidence and clarity.

Deciding to pursue my Ph.D. under Prof. Nagendran wasn't just a choice; it was the beginning of a journey filled with hope, determination, and the unwavering support of a mentor who believed in my potential. That day began a transformative chapter in my life that I would cherish forever. As I near the completion of my thesis, having spent almost five years under his guidance and mentorship, I am filled with a profound debt of gratitude to my academic advisor, Prof. S. Nagendran, for his unparalleled guidance and support throughout both my academic endeavors and personal growth.

His mentorship has offered me the opportunity to master a variety of new synthetic methods and to glean novel research perspectives from his extensive expertise and experience. Despite encountering numerous obstacles during my Ph.D. studies, the constant encouragement and unwavering support from my supervisor fortified my resolve, enabling me to navigate through those challenges. I am deeply appreciative of the autonomy he allowed me in the laboratory and his confidence in my capabilities. Serving under his guidance has been an extraordinary experience, significantly broadening my understanding of group 14 and organometallic chemistry. I remain forever grateful for his significant role in my academic and professional development. I would like to express my

sincere gratitude to Prof. Moumita Majumdar (IISER Pune) for reviewing my thesis and providing invaluable suggestions.

I am deeply grateful to Prof. Anil J Elias, Prof. Nidhi Jain, Prof. J. D. Singh, and Prof. C K. Hazra for their invaluable guidance throughout my coursework at IIT Delhi. My heartfelt thanks to my SRC committee members, Prof. A. J. Elias, Prof. Sayantan Paria, and Prof. Bhabani K. Satapathy for their critical insights and support during my comprehensive exam, SRC presentation and Ph.D. synopsis activities. I want to express my gratitude to the current and former department heads for their support in providing the necessary research facilities during my tenure.

I would like to express my gratitude to Prof. Subrata Kundu, Prof. Biswarup Chakraborty, and Prof. Sandeep Gupta for always giving me big brother vibes and helping me with my research needs.

I thank Mr. V. K. Sharma and Mr. Kanon in the glass-blowing facility for fabricating glassware for me. I thank Mr. Keshav, Mr. Alok, Mr. Manoj, and Miss Poornima for their help in recording NMR spectra. I want to give a vote of thanks to the chemistry department office staff and instrumentation lab staff for helping me in all my official and instrumental lab activities. I am thankful to Mr. Narinder Nath and Mr. Ghanshyam Sharma for their timely help in providing liquid nitrogen.

It is with immense gratitude that I extend my heartfelt thanks to my senior lab colleagues, Dr. Dharmendra Singh, Dr. Pritam Mahawar, Dr. Jyoti Shukla, Dr. Priyanka Kundu, Dr. Pinky Yadav, Dr. Vivek Kumar Singh, and Dr. Pratima Shukla. Their support and inspiration have been pivotal throughout my thesis journey. I also want to express my profound appreciation to my current lab mates, Dr. Hemant Kumar, Mr. Vishal Singh, Mr. Upendra Yadav, Miss Tanya Batra, Miss Ameesha Bansal, Miss Priti Yadav, Miss Namrita, Miss Vishakha, Miss Mehak, Mr. Anmol Mishra, Shivam Panwar, and Salar Ahmed as well as my former lab mates, Dr. Arvind Kumar Jaiswal, Mr. Akhil Paliwal, Miss Rashmi Jena, Mr. Shubham, Miss Komal, Miss Meenu Sharma, and Miss Shipra

Bajpai, Hemaang Bhartiya for their invaluable suggestions, enriching scientific discussions, and for cultivating a warm and friendly lab environment. I want to express my profound gratitude to my master's students: Manoj Kumar, Abhishek Kushwaha, Satyam Dubey, Vikash Giri, and Miss Aditi Garg. Your remarkable dedication and enthusiasm have significantly enriched our intellectual journey, creating an exceptional atmosphere of trust and collaboration. I deeply appreciate your unwavering belief in my efforts and your relentless hard work, often extending into the late-night hours, driven purely by our shared goals. Your contributions have been pivotal and invaluable to our collective success. I'd also like to express my sincere appreciation to our summer interns B Mugesh, P Rahul, Prachi Singh, Himani Bisht, Vishal Singh, and Prachi Dilwalia, who made the summer work period an exciting experience despite the typically sluggish feel of the hot weather.

I wanted to express my deepest gratitude to my friends from my graduation time: Himanshu Pandey, Rakesh Joshi, Saurabh Joshi, Deepak Suyal, Neeraj Pandey, Mahipal Darmal, Jitendra Goswami, Gaurav Tatrari, Dashrath Singh Bisht, Shyam Dutt Sanwal, Rajesh Mathpal, Awantika Joshi, Manisha Kabdwal, Nitika Bisht, Shikha Joshi, Bhawna Joshi, Diksha Sanwal, Anisha Mishra, Mehak, Priyanka Sahjlan and some from the Ph.D tenure Naved Akhtar, Neha Antil, Parul Saini, Abhishek Nair, Sanjay Singh, Vikash Dikshit, Rajat Joshi. A special thanks to my friend Shailendra Singh Surya. Your unwavering support and encouragement during my Ph.D. journey meant the world to me. Whether it was through late-night research sessions, words of encouragement, or simply being there to listen, you all played an integral role in helping me achieve this milestone. Thank you for believing in me, even when I doubted myself. Your friendship has been a beacon of light in times of stress and uncertainty. I couldn't have done this without you, and I am forever grateful for your presence in my life.

I express my deepest gratitude to the seniors of IIT Delhi, Upanshu Gangwar, Manjeet, Sanjay Singh, Moumita Bera, Bharti Singh, and Shailabh Tiwari for their unwavering support throughout my Ph.D. journey. Your guidance, encouragement, and wisdom have been invaluable to me.

Similarly thanks to my juniors Naveen Sihag, Ruchi Sharma, Swati Jain, Saleem Hafeez, Bindusagar Das, Ritu, Chinmoy Majumder, Himanshu Nath, Pabitra Kumar Nayak, Raju Sen, Chhaya Thadhani, Haribrahma Singh, Prabuddhakant Mishra and Navdeep Singh Thayat for your admiration and support throughout my Ph.D. journey. Knowing that I have inspired and motivated you is one of the greatest rewards of my academic career. Your encouragement and positive energy have been a tremendous source of strength for me. I am deeply grateful for your kind words and for the respect you have shown me. I *would like to express my heartfelt gratitude to Manish Tripathi's family. The support I received from your family has been invaluable to me. Your encouragement and unwavering support have played a crucial role in my journey, helping me to become an example for society. I am deeply grateful for everything you have done.*

I would like to express my heartfelt gratitude to my brother-in-law, Mohan Pant, and elder sister, Prema Pant, for their support of my parents and home. Achieving this milestone was possible because of their efforts, which allowed me to focus entirely on my research without worrying about home. I want to thank my younger sister, Hema Bhatt, and my brother-in-law, Tanuj Bhatt, who have been faithful companions throughout my entire Ph.D. journey. Their unwavering faith and constant support have meant the world to me. I am also deeply grateful to my elder sister, Kamla Pandey, for her continuous motivation.

Finally, I would like to express my profound affection and respect for all my family members for their unwavering support and encouragement. I extend my warmest appreciation to my parents, Mr.

Shyam Datt Joshi and Mrs. Janki Joshi, for their sacrifices, love, and blessings. It was their belief in me that kept me moving forward.

I acknowledge the Council of Scientific and Industrial Research (CSIR) in New Delhi, India, for the senior research fellowships.

Finally, I express my deepest gratitude to Almighty God for blessing me with the health, wisdom, and courage to undertake and complete the work presented in this thesis. Your divine guidance and support have been my constant source of strength throughout this journey.

Prakash Chandra Joshi

Abstract

The thesis titled "**Bis(germylenes) and a-DPM Stabilized Germylenes: Syntheses, Reactivities, and Photophysical Properties**" provides detailed information about the isolation, characterization, reactivity, and optical properties of various bis(germylenes) and aza-dipyrrinatogermylenes. The thesis is divided into six chapters, each of which is briefly described below:

Chapter 1: This section highlights *N*-heterocyclic metallylenes and mainly focuses on *N*-heterocyclic bis(metallylenes). The synthesis and reactivity of these compounds, including nucleophilic substitution, reduction, oxidation, and metal complexation, are discussed. Additionally, the objectives and scope of the thesis are outlined based on these discussions.

Chapter 2: This chapter describes the methods used for (a) cleaning and drying glassware and (b) purifying and drying solvents that are commonly used in synthesis and NMR spectroscopy. It details the preparation and purification of starting materials and handling air and moisture-sensitive compounds. The sources of commercially available chemicals, information about instruments used to characterize the synthesized compounds, and the software used for theoretical studies are also presented.

Chapter 3*:* The activation of chemical bonds by germylenes is well-known; however, the same by bis(germylenes) is hardly known. Therefore, this chapter presents the synthesis of a non-functionalized bis(germylene) **300** that was obtained by reducing germylene monochloride [(*i*-Bu)$_2$ATIGeCl] (**105f**). The activation of the C-X and M-Cl bonds of haloalkanes and halides of metal/metalloids through this newly formed bis(germylene) **300** is demonstrated.

Chapter 4: Anticipating the potential of pyrrole-imine dimeric ligands (like **401**) to stabilize bis(metallylenes), this chapter reports the isolation of such derivatives **402**-**407** along with

bis(aluminum(III)) derivatives **408**-**409**. Compound **401** has been designed with bulky substituents to stabilize low-valent main-group compounds. It was synthesized by formylating mesityl pyrrole and reacting the resultant formylated derivative with hydrazine hydrate using acetic acid as a catalyst. The bis(tetrylenes) **402**-**404** were synthesized by reacting ligand **401** with Lappert's metallylenes, $E[N(TMS)_2]_2$ (E = Ge, Sn, Pb). Representative reactivity studies of these compounds were performed using compound **402,** and germylene derivatives **405**-**407** were isolated. The bis(dimethylaluminum) complex **408** was isolated by treating compound **401** with trimethylaluminium. Compound **408** was converted to bis(diiodoaluminum(III)) derivative **409** with the anticipation that it would be a suitable precursor to isolate the bis(aluminum(I)) compound. All the novel compounds are thoroughly characterized through various state-of-the-art techniques.

Chapter 5: The first examples of bis(germylenes) **503**-**507** and bis(germacarbonyl compounds) **508**-**510**, stable in air and water, are reported. The bis(dipyrrinate) stabilized bis(germylene monochloride) **503** is isolated starting from a bis(dipyrromethene) **502**. It reacts with alcohols, phenol, and sodium pyrrolide to afford bis(germylene alkoxides) **504**-**505**, bis(germylene phenoxide) **506**, and bis(germylene pyrrolide) **507**. Compounds **505** and **507** react with elemental sulfur and selenium, resulting in bis(germacarbonyl) compounds **508**-**510**. The optical properties of compounds **502**-**510** are also studied experimentally and computationally.

Chapter 6: The possibility of using aza-dipyrromethene (a-DPM) ligands to stabilize compounds containing low-valent main group elements is demonstrated through the isolation of germylenes, a-DPM(*p*-tol)GeCl (**602**), a-DPM(Naph)GeCl (**605**), and a-DPM(Naph)GeN(TMS)$_2$ (**606**) (*tol* = tolyl, Naph = naphthyl). Because of the presence of the aza-DPM ligand, these germylenes exhibit an absorption maximum at around 640 nm, a highly redshifted value previously unknown for germylenes.

सारांश

"बिस(जर्माइलीनस्) और ए-डीपीएम स्थिर जर्माइलीनस्: संश्लेषण, प्रतिक्रियाएँ, और प्रकाश-भौतिक गुण" शीर्षक वाली थीसिस विभिन्न बिस(जर्माइलीनस्) और एजा-डिपिरिनाटोजर्माइलीनस् के संश्लेषण, लक्षण वर्णन, प्रतिक्रियाशीलता और प्रकाश-भौतिक गुणों के बारे में विस्तृत जानकारी प्रदान करती है। थीसिस को छह अध्यायों में विभाजित किया गया है, जिनमें से प्रत्येक को संक्षेप में नीचे वर्णित किया गया है:

अध्याय 1: यह खंड एन-हेट्रोसायक्लिक मेटलाइलीन पर प्रकाश डालता है और मुख्य रूप से एन-हेटरोक्साइक्लिक बीएस (मेटलाइलीन) पर केंद्रित है। इन यौगिकों का संश्लेषण और प्रतिक्रियाशीलता जैसे न्यूक्लियोफिलिक प्रतिस्थापन, अपचयन अभिक्रिया, ऑक्सीकरण और धातु जटिलता पर चर्चा की जाती है। इसके अतिरिक्त, इन चर्चाओं के आधार पर थीसिस के उद्देश्यों और दायरे को रेखांकित किया गया है।

अध्याय 2: यह अध्याय (a) कांच के बने पदार्थ की सफाई और सुखाने और (b) विलायक को शुद्ध करने और सुखाने के लिए उपयोग की जाने वाली विधियों का वर्णन करता है जो आमतौर पर संश्लेषण और एनएमआर स्पेक्ट्रोस्कोपी में उपयोग किए जाते हैं। यह प्रारंभिक सामग्री की तैयारी और शुद्धिकरण और हवा और नमी-संवेदनशील यौगिकों को संभालने का विवरण देता है। व्यावसायिक रूप से उपलब्ध रसायनों के स्रोत, संश्लेषित यौगिकों को चिह्नित करने के लिए उपयोग किए जाने वाले उपकरणों के बारे में जानकारी, और सैद्धांतिक अध्ययन के लिए उपयोग किए जाने वाले सॉफ़्टवेयर भी प्रस्तुत किए जाते हैं।

अध्याय 3: जर्माइलीन के माध्यम से रासायनिक बंधन और छोटे अणु सक्रियण लोकप्रिय शोध विषय हैं। जर्माइलीनस् द्वारा रासायनिक बंधों की सक्रियता सर्वविदित है; हालांकि, बिस(जर्माइलीनस्) द्वारा शायद ही जाना जाता है। इसलिए, यह अध्याय एक गैर-कार्यात्मक बिस(जर्माइलीन) **300** के संश्लेषण को प्रस्तुत करता है जो जर्माइलीन मोनोक्लोराइड [(i-Bu)$_2$ATIGeCl] (**105f**) को अपचयन करके प्राप्त किया गया था। इस नवगठित बिस(जर्माइलीन) **300** के माध्यम से हैलोऐल्केन और धातु/उपधातु के हलाइड्स के सी-एक्स और एम-सीएल बॉन्ड की सक्रियता का प्रदर्शन किया गया है।

अध्याय 4: बिस(मेटलाइलीन) को स्थिर करने के लिए पायरोल-इमाइन डिमेरिक लिगैंड (जैसे **401**) की क्षमता का अनुमान लगाते हुए, यह अध्याय ऐसे डेरिवेटिव **402**-**407** के साथ बिस(एल्यूमीनियम (III)) डेरिवेटिव **408**-**409** के संश्लेषण की रिपोर्ट करता है। यौगिक **401** को लो-वैलेंट मुख्य-समूह यौगिकों को स्थिर करने के लिए भारी प्रतिस्थापन के साथ डिजाइन किया गया है। इसे

मेसिटिल पायरोल को फॉर्माइल करके और उत्प्रेरक के रूप में एसिटिक एसिड का उपयोग करके हाइड्राज़ीन हाइड्रेट के साथ परिणामी फॉर्माइलेटेड व्युत्पन्न पर प्रतिक्रिया करके संश्लेषित किया गया है। बिस(टेट्राइलीन) **402-404** को लैपर्ट के मेटलाइलीन के साथ लिगैंड **401** की प्रतिक्रिया करके संश्लेषित किया गया है। इन यौगिकों के प्रतिनिधि प्रतिक्रियाशीलता अध्ययन यौगिक **402** का उपयोग करके किए गए है, और जर्माइलीन डेरिवेटिव **405-407** को अलग किया गया है। बिस (डाइमिथाइलएलुमिनम) यौगिक **408** को ट्राइमिथाइल्युलुमिनियम के साथ यौगिक **401** का प्रतिक्रिया करके अलग किया गया है। यौगिक **408** को बिस में परिवर्तित किया गया था(डायोडोएल्यूमिनियम(III)) व्युत्पन्न **409** इस प्रत्याशा के साथ कि यह बिस को अलग करने के लिए एक उपयुक्त यौगिक (एल्यूमीनियम (I)) अग्रदूत होगा। यह उपन्यास यौगिकों को विभिन्न अत्याधुनिक तकनीकों के माध्यम से अच्छी तरह से चित्रित किया गया है।

अध्याय 5: हवा और पानी में स्थिर बिस(जर्माइलीन) **503-507** और बिस(जर्माकार्बोनिल यौगिक) **508-510** के पहले उदाहरण बताए गए हैं। बिस(डिपाइरिनेट) स्थिर बिस(जर्माइलीन मोनोक्लोराइड) **503** को बिस(डिपिरोमेथीन) **502** से शुरू करके संश्लेषण किया जाता है। यह अल्कोहल, फिनोल और सोडियम पाइरोलाइड के साथ प्रतिक्रिया करता है ताकि बिस(जर्माइलीन एल्कॉक्साइड) **504-505**, बिस(जर्माइलीन फेनोक्साइड) **506**, और बिस(जर्माइलीन पाइरोलाइड) **507** को वहन किया जा सके। यौगिक **505** और **507** मौलिक सल्फर और सेलेनियम के साथ प्रतिक्रिया करते हैं, जिसके परिणामस्वरूप बिस(जर्माकार्बोनिल) यौगिक **508-510** होते हैं। यौगिकों **502-510** के ऑप्टिकल गुणों का भी प्रयोगात्मक और कम्प्यूटेशनल रूप से अध्ययन किया जाता है।

अध्याय 6: लो-वैलेंट मुख्य समूह तत्वों वाले यौगिकों को स्थिर करने के लिए एज़ा-डिपिरोमेथीन (a-DPM) लिगैंड का उपयोग करने की संभावना जर्माइलीनस्, a-DPM(*p*-tol)GeCl (**602**), a-DPM(Naph)GeCl (**605**), और a-DPM (Naph)GeN(TMS)$_2$ (**606**) (*tol* = tolyl, Naph = naphthyl) के संश्लेषण को प्रदर्शित करती है। एज़ा-डीपीएम लिगैंड की उपस्थिति के कारण, ये जर्माइलीनस् लगभग **640** nm पर अधिकतम अवशोषण प्रदर्शित करते हैं, जो जर्माइलीनस् के लिए पहले से अज्ञात एक अत्यधिक रेडशिफ्ट मूल्य है।

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ATI	aminotroponiminate	h	hour
%	percentage	HOMO	highest occupied molecular orbital
°	degree	HRMS	high-resolution mass spectrometry
°C	degree centigrade	Hz	*Hertz*
μM	micro molar	*i*-Bu	*iso*-butyl
Å	angstrom	*i*-Pr	*iso*-propyl
ε	extinction coefficient	IR	infra-red
δ	(delta) chemical shift	*J*	coupling constant
λ	(lambda) wavelength	K	Kelvin
Dipp	diisopropylphenyl	Kcal	kilocalorie
au	atomic unit	Kg	kilogram
bs	broad singlet	LUMO	lowest unoccupied molecular orbital
Calcd	calculated	L	Litre
COE	cyclooctaene	m/z	mass-to-charge ratio
cm	centimeter	Me	methyl
cp	cyclopentadienyl	M	Molar
COD	cyclooctadiene	Mes	mesityl
DCM	dichloromethane	mg	milligram
d	doublet	MHz	megahertz
dd	double doublet	min	minute
DFT	density functional theory	mL	milliliter
deg	degree	MO	molecular orbital
nbd	norboranadiene	Mp	melting point
EI	electron ionization	MS	mass spectrometry
ESI	electrospray ionization	mmol	millimole
Et	ethyl	NHC	*N*-heterocyclic carbene
g	gram	NHGe	*N*-heterocyclic germylene
i-Bu	iso-butyl	nm	nanometer

ppm	parts per million	*n*-Pr	normal propyl
ppb	parts per billion	S	Solvent
Ph	phenyl	t(pseudo)	pseudo triplet
rt	room temperature	T	temperature
n-Bu	normal butyl	t	triplet
TMS	Trimethyl silyl	ad	adamantyl
s	singlet	*t*-Bu	tert-butyl
TMEDA	tetramethyl ethylenediamine	THF	tetrahydrofuran
NMR	nuclear magnetic resonance	UV	ultraviolet
DPM	dipyrromethene	a-DPM	aza-dipyrromethene