

**SYNTHESES, REACTIVITIES, AND APPLICATIONS OF Ge(II)
COMPOUNDS AND CATALYTIC APPLICATIONS OF Sn(II)
HALIDES**

PRATIMA SHUKLA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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COMPOUNDS AND CATALYTIC APPLICATIONS OF Sn(II)
HALIDES**

by

PRATIMA SHUKLA

DEPARTMENT OF CHEMISTRY

Submitted

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



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APRIL 2024

Dedicated to My Family

Certificate

This is to certify that the thesis entitled “**Syntheses, Reactivities, and Applications of Ge(II) Compounds and Catalytic Applications of Sn(II) Halides**” being submitted by **Miss. Pratima Shukla** 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 her under my supervision and guidance. The thesis has reached the standards fulfilling for 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.

Prof. S. Nagendran

Thesis Supervisor

Department of Chemistry

Indian Institute of Technology Delhi

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Abstract

The thesis entitled “*Syntheses, Reactivities, and Applications of Ge(II) Compounds and Catalytic Applications of Sn(II) Halides*” present the detail about the synthesis and reactivity of air and water stable dipyrinate germylenes and germacarbonyl compounds, along with its metal complexation and catalysis using commercially available tin(II) halides. This thesis is divided into six chapters. A brief description about each chapter is given below:

Chapter 1: This chapter briefly discusses various *N*-heterocyclic germylenes, which include the reactivity of germylenes, such as substitution, oxidative addition, and metal complexation. Based on these aspects, the scope and objectives of the thesis are mentioned.

Chapter 2: In this chapter, techniques commonly employed for cleaning and drying glassware, purifying and drying solvents utilized in synthesis and NMR spectroscopic studies, and drying gases are discussed. The preparation and purification of starting materials and ways of handling air and moisture-sensitive compounds are presented. Also, the sources of various commercially available chemicals, details of the instruments used to characterize synthesized compounds, and software utilized for theoretical studies and solving crystal structures are given.

Chapter 3: Low-valent main group compounds that fluoresce in the solid state were previously unknown. To address this, we investigated room-temperature photoluminescence from a series of crystals of germylenes **302-307** in this chapter; they exhibited emissions nearly reaching the NIR. Germylene carboxylates **302-307** were synthesized by reacting dipyrinatogermylene pyrrolide **301** with carboxylic acids such as acetic acid, trifluoroacetic acid, benzoic acid, *p*-cyanobenzoic acid, *p*-nitrobenzoic acid, and acetylsalicylic acid.

Chapter 4: Metallylenes and metallacarbonyl compounds are the heavier analogous of carbenes and carbonyl compounds. The use of these compounds to stabilize mercury complexes was not known until now, and this issue is addressed in this chapter by forming the mercury complexes of germylene pyrrolide **301** and germacarbonyl compounds **404-405** with Ge=E bonds (E = S **404**, Se **405**). Compounds **301** and **404-405** gave mercury halide complexes **401-403** and **406-411** upon reactions with mercury(II) halides. As compounds **301**, **404**, and **405** formed complexes with mercury halides (HgCl₂ and HgBr₂) even at a significantly low concentration (75 μM), and the resultant mercury complexes (**401**, **402**, **406**, **407**, **409**, and **410**) were reasonably water stable, the possible utility of compounds **301**, **404**, and **405** for mercury remediation was studied. It was found that they could remove mercury with an efficiency >99% in 10 min from a contaminated water sample having 20 mg/L of mercury halide.

Chapter 5: Though a few examples of germylene carboxylates are reported, their reactivity is hardly explored; this chapter is devoted to exploring their reactivity. The reaction of dipyrinatogermylene acetate **302** with trimethylsilyl cyanide, trimethylsilyl azide, and trimethylsilyl iodide afforded air and water stable germylene cyanide **501**, germylene azide **502**, and germylene iodide **503**, respectively. However, compound **302** didn't undergo an oxidative addition reaction with elemental chalcogens. Considering this, the reactivity of aminotroponiminatogermylene acetate **504** with elemental chalcogens was checked. Compound **504** reacted with elemental sulfur and selenium to afford germathioacid anhydride **505** and germaselenoacid anhydride **506**, respectively, with a heterogenous (E)Ge-O-C(O) moiety. The reaction of compound **504** carried out with tris(pentafluorophenyl)borane to isolate the corresponding adduct as a precursor for synthesizing the germanium analog of acid anhydride through the acceptor-first approach gave an unexpected adduct

507 with O→B bond instead of the expected one with a Ge→B bond. All the newly synthesized compounds were characterized by multinuclear NMR spectroscopy and SCXRD techniques.

Chapter 6: A variety of carbodiimides are dihydroborylated by pinacolborane (HBpin) using commercially available tin(II) halides [SnBr_2 (**601**) and SnCl_2 (**602**)] as catalysts at room temperature (21 °C) in short reaction times (0.13 to 6 h). The reaction mechanism for the dihydroboration of carbodiimides has been illustrated through DFT calculations; the rate-determining step is the transfer of the first hydrogen atom from a pinacolborane molecule to carbodiimide.

सारांश

Ge(II) यौगिकों के संश्लेषण, प्रतिक्रियाशीलता, और अनुप्रयोग और Sn(II) हैलाइड्स के उत्प्रेरक अनुप्रयोग" शीर्षक वाली थीसिस हवा और पानी के स्थिर डिपिरिनेट जर्मलीन और जर्मेकार्बोनील यौगिकों के संश्लेषण और प्रतिक्रियाशीलता के साथ-साथ इसकी धातु संरचना के बारे में विवरण प्रस्तुत करती है और व्यावसायिक रूप से उपलब्ध Sn(II) हैलाइडों का उपयोग करके उत्प्रेरण। यह थीसिस छह अध्यायों में विभाजित है। प्रत्येक अध्याय का संक्षिप्त विवरण नीचे दिया गया है:

अध्याय 1: यह अध्याय संक्षेप में विभिन्न एन-हेटरोसायक्लिक जर्माइलीन पर चर्चा करता है, जिसमें जर्मलीन की प्रतिक्रियाशीलता, जैसे प्रतिस्थापन, ऑक्सीडेटिव जोड़ और धातु जटिलता शामिल है। इन पहलुओं के आधार पर, थीसिस के दायरे और उद्देश्यों का उल्लेख किया गया है।

अध्याय 2: इस अध्याय में, विभिन्न प्रकार की तकनीकों का पता लगाया गया है जो आमतौर पर कांच के बर्तनों की सफाई और सुखाने, संश्लेषण और एनएमआर स्पेक्ट्रोस्कोपिक अध्ययन में उपयोग किए जाने वाले सॉल्वेंट्स को शुद्ध करने और सुखाने और गैसों को सुखाने के लिए उपयोग की जाती हैं। इसके अतिरिक्त, शुरुआती सामग्रियों की तैयारी और शुद्धिकरण, साथ ही हवा और नमी-संवेदनशील यौगिकों की हैंडलिंग पर भी चर्चा की जाती है। इसके अलावा, विभिन्न व्यावसायिक रूप से उपलब्ध रसायनों के स्रोतों के बारे में जानकारी, साथ ही संश्लेषित यौगिकों को चिह्नित करने के लिए उपयोग किए जाने वाले उपकरणों और सैद्धांतिक अध्ययन और क्रिस्टल संरचना को हल करने के लिए उपयोग किए जाने वाले सॉफ्टवेयर का विवरण।

अध्याय 3: निम्न-वैलेंट मुख्य समूह यौगिक जो ठोस अवस्था में प्रतिदीप्त होते हैं, पहले अज्ञात थे। इसे संबोधित करने के लिए, हमने इस अध्याय में जर्मलीन **302-307** के क्रिस्टल की एक श्रृंखला से कमरे के तापमान फोटोल्यूमिनेशन की जांच की; उन्होंने उत्सर्जन को लगभग एनआईआर तक पहुँचने का प्रदर्शन किया। जर्माइलीन कार्बोक्सिलेट्स **302-307** को एसिटिक एसिड, ट्राइफ्लूरोएसिटिक एसिड, बेंजोइक एसिड, *p*-सायनोबेंजोइक एसिड, *p*-नाइट्रोबेंजोइक एसिड और एसिटाइलसैलिसिलिक एसिड जैसे कार्बोक्जिलिक एसिड के साथ डिपाइरिनेटोजर्माइलीन पाइरोलाइड **301** पर प्रतिक्रिया करके संश्लेषित किया गया।

अध्याय 4: मेटालिलीन और मेटालैकार्बोनील यौगिक कार्बन और कार्बोनील यौगिकों के भारी समकक्ष हैं। पारा परिसरों को स्थिर करने के लिए इन यौगिकों का उपयोग अब तक ज्ञात नहीं था, और इस मुद्दे को इस अध्याय में Ge=E बांड (E = S **404**, Se **405**) के साथ जर्माइलीन पाइरोलाइड **301** और जर्मेकार्बोनील यौगिक **404-405** के पारा परिसरों का निर्माण करके संबोधित किया

गया है। यौगिक **301** और **404-405** ने पारा (II) हैलाइड के साथ प्रतिक्रिया करने पर पारा हैलाइड कॉम्प्लेक्स **401-403** और **406-411** दिए। चूंकि यौगिक **301**, **404**, और **405** ने काफी कम सांद्रता ($75 \mu\text{M}$) पर भी पारा हैलाइड्स (HgCl_2 और HgBr_2) के साथ कॉम्प्लेक्स का गठन किया, और परिणामी पारा कॉम्प्लेक्स (**401**, **402**, **406**, **407**, **409**, और **410**) थे यथोचित जल स्थिर, पारा उपचार के लिए यौगिक **301**, **404**, और **405** की संभावित उपयोगिता का अध्ययन किया गया। यह पाया गया कि वे 20 मिलीग्राम/लीटर मरकरी हैलाइड वाले दूषित पानी के नमूने से 10 मिनट में 99% से अधिक दक्षता के साथ पारा हटा सकते हैं।

अध्याय 5: हालाँकि जर्मलीन कार्बोक्सिलेट्स के कुछ उदाहरण बताए गए हैं, लेकिन उनकी प्रतिक्रियाशीलता का शायद ही पता लगाया गया है; यह अध्याय उनकी प्रतिक्रियाशीलता की खोज के लिए समर्पित है। ट्राइमिथाइलसिलिल साइनाइड, ट्राइमिथाइलसिलिल एज़ाइड और ट्राइमिथाइलसिलिल आयोडाइड के साथ डिपाइरिनैटोगर्मिलीन एसीटेट **302** की प्रतिक्रिया से क्रमशः हवा और पानी में जर्मलीन साइनाइड **501**, जर्मलीन एज़ाइड **502** और जर्मलीन आयोडाइड **503** स्थिर हो गए। हालाँकि, यौगिक **302** में मौलिक चालकोजेन के साथ ऑक्सीडेटिव जोड़ प्रतिक्रिया नहीं हुई। इसे ध्यान में रखते हुए, मौलिक चाकोजेन के साथ एमिनोट्रोपोनिमिनोटोजर्मिलीन एसीटेट **504** की प्रतिक्रियाशीलता की जाँच की गई। यौगिक **504** ने मौलिक सल्फर और सेलेनियम के साथ प्रतिक्रिया करके क्रमशः जर्मेथियोएसिड एनहाइड्राइड **505** और जर्मेसेलेनोएसिड एनहाइड्राइड **506** को विषम जीई-ओ-सी (ओ) अंश के साथ प्रदान किया। स्वीकर्ता-प्रथम दृष्टिकोण के माध्यम से एसिड एनहाइड्राइड के जर्मेनियम एनालॉग को संश्लेषित करने के लिए अग्रदूत के रूप में संबंधित जोड़ को अलग करने के लिए ट्राइस (पेंटाफ्लोरोफेनिल) बोरेन के साथ किए गए यौगिक **504** की प्रतिक्रिया ने अपेक्षित के बजाय $\text{O} \rightarrow \text{B}$ बांड के साथ एक अप्रत्याशित जोड़ **507** दिया, $\text{Ge} \rightarrow \text{B}$ बांड के साथ। सभी नए संश्लेषित यौगिकों को बहु-परमाणु एनएमआर स्पेक्ट्रोस्कोपी और एससीएक्सआरडी तकनीकों द्वारा चित्रित किया गया था।

अध्याय 6: पिनाकोलबोरेन (एचबीपिन) का उपयोग करके विभिन्न प्रकार के कार्बोडायमाइड्स डाइहाइड्रोबोरेशन को कम प्रतिक्रिया समय (0.13 से 6 h) में कमरे के तापमान (21°C) पर उत्प्रेरक के रूप में व्यावसायिक रूप से उपलब्ध टिन (II) हैलाइड्स [SnBr_2 (**601**) और SnCl_2 (**602**)] के माध्यम से किया जाता है। कार्बोडायमाइड्स के डाइहाइड्रोबोरेशन की प्रतिक्रिया तंत्र को डीएफटी गणना के माध्यम से चित्रित किया गया है। उत्प्रेरण का दर-निर्धारण चरण पिनाकोलबोरेन अणु से कार्बोडायमाइड भाग की ओर पहले हाइड्रोजन परमाणु का स्थानांतरण 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	Kg	Kilogram
bs	broad singlet	LUMO	lowest unoccupied molecular orbital
Calcd	calculated	L	Litre
CDI	carbodiimide	m/z	mass-to-charge ratio
cm	centimeter	Me	methyl
cp	cyclopentadienyl	M	Molar
COD	cyclooctadiene	Mes	mesityl
DCM	dichloromethane	mg	milligram
Dipp	2,6-diisopropylphenyl	MHz	megahertz
d	doublet	min	minute
dd	double doublet	mL	milliliter
DFT	density functional theory	MO	molecular orbital
deg	degree	Mp	melting point
DME	dimethoxyethane	MS	mass spectrometry
EI	electron ionization	mmol	millimole
ESI	electrospray ionization	NHC	<i>N</i> -heterocyclic carbene
Et	ethyl	NHGe	<i>N</i> -heterocyclic germylene
g	gram		

ⁱ Bu	iso-butyl	nm	nanometer
ppm	parts per million	ⁿ Pr	<i>normal</i> -propyl
ppb	parts per billion	S	Solvent
Ph	phenyl	t(pseudo)	pseudo triplet
rt	room temperature	T	temperature
^s Bu	sec-butyl	t	triplet
s	singlet	^t Bu	tert-butyl
NMMO	<i>N</i> -methyl morpholine <i>N</i> -oxide	THF	tetrahydrofuran
NMR	nuclear magnetic resonance	UV	ultra violet