

**COMPLEXES OF GERMYLENES AND
GERMACARBOXYLIC ACID DERIVATIVES**

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COMPLEXES OF GERMYLENES AND GERMACARBOXYLIC ACID DERIVATIVES

by

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Submitted

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Dedicated to My Family

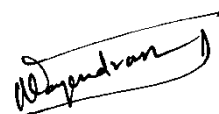
Certificate

This is to certify that the thesis entitled “**Complexes of Germylenes and Germacarboxylic Acid Derivatives**” being submitted by **Mr. Mahendra Kumar Sharma** (Entry no. 2012CYZ8156) to Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of research work carried out by him. Mr. Mahendra Kumar Sharma has worked under my supervision and has fulfilled all the requirements for the submission of his PhD thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of PhD degree.

The work exemplified in this thesis has not been submitted, in part or full, to other University or Institute for the award of any degree or diploma.

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A handwritten signature in blue ink that reads "Mahendra". The name is written in a cursive style, with the first letter 'M' being large and circular, and the rest of the name following in a fluid, connected script.

Mahendra

Abstract

The thesis entitled “*Complexes of Germylenes and Germacarboxylic Acid Derivatives*” presents the details about the coordination chemistry of *N*-heterocyclic germylenes (NHGes) and their oxidation products (i.e; germaacid chlorides, germaesters and so forth). The thesis is divided into the six chapters. A brief description about each chapter is given below:

Chapter 1: This chapter will briefly introduce *N*-heterocyclic germylenes (NHGes) and stannylenes (NHSns). Subsequently, the use of these compounds (as well their oxidation products) as ligands for the formation of (a) transition metal complexes and (b) complexes with main group elements. On the basis of these discussions, the objectives of this thesis are mentioned at the end of this Chapter.

Chapter 2: This chapter will provide information about the methods/techniques used for the (a) drying of solvents (used in synthesis and NMR spectroscopic studies), (b) drying of gases, (c) preparation and purification of starting materials, and (d) handling of air and moisture sensitive compounds. The sources for various commercially available chemicals are provided. Details regarding the instruments used for the characterization of compounds are mentioned. The information regarding software used for theoretical studies is also given.

Chapter 3: Examples of germaacid chloride, germaester, *N*-germaacyl pyrrole, and germacarboxylic acid are not known till now. Here, germaacid chloride ($(i\text{-Bu})_2\text{ATiGe}(\text{O})(\text{Cl})\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ (**308**), germaester ($(i\text{-Bu})_2\text{ATiGe}(\text{O})(\text{OSiPh}_3)\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ (**309**), and *N*-germaacyl pyrrole ($(i\text{-Bu})_2\text{ATiGe}(\text{O})(\text{NC}_4\text{H}_4)\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$ (**312**), with Cl-Ge=O, Ph₃SiO-Ge=O, and C₄H₄N-Ge=O moieties are stabilized as their B(C₆F₅)₃

complexes, respectively. Reaction of compound **312** with thiophenol produced $B(C_6F_5)_3$ complex of germaacyl thioester $(i-Bu)_2ATI\text{Ge}(O)(SPh)\rightarrow B(C_6F_5)_3$ (**314**) with a PhS-Ge=O moiety. Further, an attempted synthesis of complex of germacarboxylic acid leading to a germylene with a weakly coordinating hydroxide $(i-Bu)_2ATI\text{Ge}\cdots(OH)\rightarrow B(C_6F_5)_3$ (**315**) is also reported.

Chapter 4: *N*-heterocyclic germanium(II) isocyanate $[(i-Bu)_2ATI]\text{GeNCO}$ (**401**) and isothiocyanate $[(i-Bu)_2ATI]\text{GeNCS}$ (**402**) (ATI = aminotroponimate) complexes are synthesized through reactions of (chloro)germylene $[(i-Bu)_2ATI]\text{GeCl}$ (**204**) with NaOCN and KSCN, respectively. Interestingly, these germanium(II) pseudohalides react differently in comparison to the corresponding germanium(II) halides $[(i-Bu)_2ATI]\text{GeX}$ (X = Cl **204**, F **208**, Br **209**). Thus, reactions of compounds **401-402** with *cis*- $[M'(CO)_4(COD)]$ (M' = Mo, W) gave metallogermynes *trans*- $\{[(i-Bu)_2ATI]\text{GeNCO}\}_2\text{Mo}(CO)_4$ (**404**), *trans*- $\{[(i-Bu)_2ATI]\text{GeNCS}\}_2\text{Mo}(CO)_4$ (**405**), and *trans*- $\{[(i-Bu)_2ATI]\text{GeNCO}\}_2\text{W}(CO)_4$ (**411**), in which, germanium atoms coordinated to molybdenum are in *trans* orientation with respect to each other. Whereas, reactions of (fluoro)germylene $[(i-Bu)_2ATI]\text{GeF}$ (**208**), (chloro)germylene $[(i-Bu)_2ATI]\text{GeCl}$ (**204**), and (bromo)germylene (**209**) with *cis*- $[M'(CO)_4(COD)]$ (M' = Mo, W) afforded *cis*- $\{[(i-Bu)_2ATI]\text{GeF}\}_2\text{Mo}(CO)_4$ (**407**), *cis*- $\{[(i-Bu)_2ATI]\text{GeCl}\}_2\text{Mo}(CO)_4$ (**408**), *cis*- $\{[(i-Bu)_2ATI]\text{GeBr}\}_2\text{Mo}(CO)_4$ (**409**), and *cis*- $\{[(i-Bu)_2ATI]\text{GeCl}\}_2\text{W}(CO)_4$ (**410**) containing coordinated germanium atoms in *cis* orientation.

Chapter 5: Though, cyanogermylene $[L(CN)\text{Ge}]$ is known, isocyanogermylene $[L(\text{NC})\text{Ge}]$ is not known till now. Similar is the situation with tin, where, and isocyanostannylyene $[L(\text{NC})\text{Sn}]$ is not yet isolated. These issues are addressed in this work through the successful isolation of germylene isocyanides

$[\text{ATI}(\text{NC})\text{Ge}:\rightarrow\text{M}'(\text{CO})_4]_2$ ($\text{M}' = \text{Mo}$ **501** and W **502**) and stannylene isocyanides $[\text{ATI}(\text{NC})\text{Sn}:\rightarrow\text{M}'(\text{CO})_4]_2$ ($\text{M}' = \text{Mo}$ **503** and W **504**) as their metal carbonyl complexes using a simple route.

Chapter 6: Though, germylene stabilized platinum(0) complexes are known, platinum(II) complexes stabilized through germylenes are not known till now, and this issue is addressed in this work. Reactions of chlorogermylene **204** and alkylgermylene **207** with $\text{Pt}(\text{cod})\text{Cl}_2$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) in a 2:1 ratio resulted in germylene stabilized platinum(II) chloride complexes $\text{cis-}\{(\text{iBu})_2\text{ATIGeCl}\}_2\text{PtCl}_2$ (**601**) and $\text{cis-}\{(\text{iBu})_2\text{ATIGe}(\text{iPr})\}_2\text{PtCl}_2$ (**602**), respectively. Reactions of compound **602** with trimethylsilylcyanide (TMSCN) and trimethylsilylazide (TMSN_3) produced platinum(II) cyanide $\text{trans-}\{(\text{iBu})_2\text{ATIGe}(\text{iPr})\}_2\text{Pt}(\text{CN})_2$ (**603**) and platinum(II) azide $\text{cis-}\{(\text{iBu})_2\text{ATIGe}(\text{iPr})\}_2\text{Pt}(\text{N}_3)_2$ (**604**) in almost quantitative yields, respectively. Interestingly, the chlorine analogue $\text{trans-}\{(\text{iBu})_2\text{ATIGe}(\text{Cl})\}_2\text{Pt}(\text{CN})_2$ (**605**) of compound **603** is obtained through a reaction of cyanogermylene $(\text{iBu})_2\text{ATIGe}(\text{CN})$ with $\text{Pt}(\text{cod})\text{Cl}_2$. In contrast to these reactions, reaction of compound **602** with silver triflate (AgOTf) gave a dimeric platinum(II) ionic complex $[\{(\text{iBu})_2\text{ATIGe}(\text{iPr})\}_2\text{PtCl}]_2[\text{OTf}]_2$ (**606**). Compound **606** can be converted to a monomeric platinum(II) ionic complex $[\{(\text{iBu})_2\text{ATIGe}(\text{iPr})\}_2\text{PtCl}(\text{DMAP})][\text{OTf}]$ (**607**) up on its treatment with two equiv of DMAP (DMAP = N,N -dimethylamino)pyridine). The ability of platinum(II) cyanide **603** to act as a catalyst for the cyanosilylation of aldehydes is also shown.

सारांश

"कॉम्प्लेक्स ऑफ जर्मिलीस एंड जर्माकार्बोक्विरजलिक एसिड डेरिवेटिव्स", एन-हेटरोसाइकलिक जर्मिलीस (एनएचजीएस) और उनके ऑक्सीकरण उत्पादों (यानी, जर्माएसिड क्लोराइड, जर्माएस्टर और अन्य) के समन्वयन रसायन के बारे में विवरण प्रस्तुत किया गया है। यह थीसिस छह अध्यायों में विभाजित है प्रत्येक अध्याय के बारे में एक संक्षिप्त विवरण नीचे दिया गया है:

अध्याय 1: यह अध्याय संक्षेप में एन-हेटरोसाइकलिक जर्मिलीस (एनएचजीएस) और स्टैनीलीस (एनएचएसएन) का परिचय देगा। इसके बाद, इन यौगिकों (साथ ही उनके ऑक्सीकरण उत्पादों) का प्रयोग (ए) संक्रमण धातु कॉम्प्लेक्स और (बी) मुख्य समूह तत्वों के साथ कॉम्प्लेक्स के गठन के लिए लिगंड के रूप में प्रयोग का विवरण देगा। इन चर्चाओं के आधार पर, इस अध्याय के अंत में इस शोध के उद्देश्यों का उल्लेख किया गया है।

अध्याय 2: इस अध्याय में (ए) विलायक द्रवों को सुखाने (संश्लेषण और एनएमआर स्पेक्ट्रोस्कोपिक अध्ययन में प्रयुक्त), (बी) गैसों को सुखाने, (सी) प्रारंभिक सामग्रियों की तैयारी और शुद्धि, और (डी) हवा और नमी संवेदनशील यौगिकों के संचालन के लिए इस्तेमाल किए जाने वाले तरीकों / तकनीकों के बारे में जानकारी प्रदान की जाएगी। विभिन्न व्यावसायिक रूप से उपलब्ध रसायनों के स्रोत प्रदान किए जाते हैं। यौगिकों के लक्षण वर्णन के लिए इस्तेमाल किए गए उपकरणों के बारे में विवरण का उल्लेख किया गया है। सैद्धांतिक अध्ययन के लिए प्रयुक्त सॉफ्टवेयर के बारे में जानकारी भी दी गई है।

अध्याय 3: जर्माएसिड क्लोराइड, जर्माएस्टर, एन-जर्माएसिल पायरॉल और जर्माकार्बोकिर्जलिक एसिड के उदाहरण अब तक ज्ञात नहीं हैं। यहां, जर्माएसिड क्लोराइड $(i\text{-Bu})_2\text{ATiGe(O)(Cl)} \rightarrow \text{B(C}_6\text{F}_5)_3$ (308), जर्माएस्टर $(i\text{-Bu})_2\text{ATiGe(O)(OSiPh}_3) \rightarrow \text{B(C}_6\text{F}_5)_3$ (309), और एन-जर्माएसिल पायरॉल $(i\text{-Bu})_2\text{ATiGe(O)(NC}_4\text{H}_4) \rightarrow \text{B(C}_6\text{F}_5)_3$ (312), क्रमशः Cl-Ge=O , $\text{Ph}_3\text{SiO-Ge=O}$, and $\text{C}_4\text{H}_4\text{N-Ge=O}$ मोईटीज के साथ उनके $\text{B(C}_6\text{F}_5)_3$ कॉम्प्लेक्स के रूप में स्टेबिलाइज़्ड किए गये हैं। यौगिक 312 की क्रिया थिओफेनॉल (PhSH) के साथ करवाने पर जर्मासायल थियोस्टर $(i\text{-Bu})_2\text{ATiGe(O)(SPh)} \rightarrow \text{B(C}_6\text{F}_5)_3$ (314) उत्पाद के रूप में PhS-Ge=O मोईटीज के साथ इसके $\text{B(C}_6\text{F}_5)_3$ कॉम्प्लेक्स के रूप में प्राप्त हुआ। इसके अलावा, जर्माकार्बोकिर्जलिक एसिड कॉम्प्लेक्स के संश्लेषण के दौरान प्राप्त एक कमजोर समन्वयशील हाइड्रॉक्साइड $(i\text{-Bu})_2\text{ATiGe}\cdots(\text{OH}) \rightarrow \text{B(C}_6\text{F}_5)_3$ (315) रिपोर्ट किया गया है।

अध्याय 4: एन-हेटरोसायक्लिक जर्मिलीन(II) आइसोसाइनेट $[(i\text{-Bu})_2\text{ATI}]\text{GeNCO}$ (401) और आइसोथियोसाइनेट $[(i\text{-Bu})_2\text{ATI}]\text{GeNCS}$ (402) (एटीआई = एमिनोट्रोपोनिमेट) कॉम्प्लेक्स को (क्लोरो)जर्मिलीन $[(i\text{-Bu})_2\text{ATI}]\text{GeCl}$ (204) की प्रतिक्रियाओं क्रमशः NaOCN और KSCN के जरिये संश्लेषित किया जाता है। दिलचस्प है कि ये जर्मिलीन(II) सुडोहेलाइड्स, इनके अनुरूपी जर्मिलीन(II) हेलाइड्स $[(i\text{-Bu})_2\text{ATI}]\text{GeX}$ ($\text{X} = \text{Cl}$ 204, F 208, Br 209) की तुलना में अलग तरह से प्रतिक्रिया करते हैं। इस प्रकार, यौगिकों 401-402 की प्रतिक्रियाएं सीस- $[\text{M}'(\text{CO})_4(\text{COD})]$ ($\text{M}' = \text{Mo}, \text{W}$) के साथ मेटलोजर्मिलींस ट्रांस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeNCO}\}_2\text{Mo}(\text{CO})_4$ (404), ट्रांस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeNCS}\}_2\text{Mo}(\text{CO})_4$ (405), और ट्रांस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeNCO}\}_2\text{W}(\text{CO})_4$ (411), देता हैं, जिनमें क्रमशः मोलिब्डेनम और टंगस्टेन के समन्वित जर्मिनियम परमाणु एक दूसरे के संबंध में ट्रांस ओरिएंटेशन में हैं। जबकि, (फ्लूरो)जर्मिलीन $[(i\text{-Bu})_2\text{ATI}]\text{GeF}$

$\text{Bu}_2\text{ATI}]\text{GeF}$ (208), (क्लोरो)जर्मिलीन $[(i\text{-Bu})_2\text{ATI}]\text{GeCl}$ (208) और (ब्रोमो)जर्मिलीन $[(i\text{-Bu})_2\text{ATI}]\text{GeBr}$ (208) की प्रतिक्रियाएँ सीस- $[\text{M}'(\text{CO})_4(\text{COD})]$ ($\text{M}' = \text{Mo}, \text{W}$) के साथ मेटलोजर्मिलींस सीस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeF}\}_2\text{Mo}(\text{CO})_4$ (407), सीस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeCl}\}_2\text{Mo}(\text{CO})_4$ (408), सीस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeBr}\}_2\text{Mo}(\text{CO})_4$ (409), और सीस- $\{[(i\text{-Bu})_2\text{ATI}]\text{GeCl}\}_2\text{W}(\text{CO})_4$ (410) देता हैं, जिसमें समन्वित जर्मिनियम परमाणु सीस ओरिएंटेशन में होते हैं।

अध्याय 5: हालांकि, साइनोजर्मिलींस $[\text{L}(\text{CN})\text{Ge}:]$ ज्ञात है, लेकिन आइसोसाइनोजर्मिलींस $[\text{L}(\text{NC})\text{Ge}:]$ अब तक ज्ञात नहीं है। इसी तरह टिन के साथ स्थिति है, जहां, आइसोसाइनोस्टेनीलींस $[\text{L}(\text{NC})\text{Sn}:]$ अब तक ज्ञात नहीं है। इन मुद्दों को सफलतापूर्वक जर्मिलींस आइसोसाइनाइड $[\text{ATI}(\text{NC})\text{Ge}:\rightarrow\text{M}'(\text{CO})_4]_2$ ($\text{M}' = \text{Mo}$ 501 and W 502) और स्टेनीलींस आइसोसाइनाइड $[\text{ATI}(\text{NC})\text{Sn}:\rightarrow\text{M}'(\text{CO})_4]_2$ ($\text{M}' = \text{Mo}$ 503 and W 504) के धातु कार्बोनिल कॉम्प्लेक्स के रूप में एक सरल मार्ग का उपयोग करते हुए बनाया गया है।

अध्याय 6: यद्यपि, जर्मिलीन स्टेबिलाइज़्ड प्लैटिनम(0) कॉम्प्लेक्सस बनाये गये हैं, लेकिन जर्मिलीन के माध्यम से स्टेबिलाइज़्ड प्लैटिनम(II) कॉम्प्लेक्सस अब तक ज्ञात नहीं हैं, और इस मुद्दे को इस काम में संबोधित किया है। 2:1 अनुपात में (क्लोरो)जर्मिलीन 204 और (एल्किल)जर्मिलीन 207 की प्रतिक्रियाएं $\text{Pt}(\text{cod})\text{Cl}_2$ (सीआडि = 1,5-साइक्लोआक्टैडिन) के साथ क्रमशः जर्मिलीन स्टेबिलाइज़्ड प्लैटिनम(II) क्लोराइड कॉम्प्लेक्सस सीस- $\{(i\text{-Bu})_2\text{ATI}]\text{GeCl}\}_2\text{PtCl}_2$ (601) और सीस- $\{(i\text{-Bu})_2\text{ATI}]\text{Ge}(\text{Pr})\}_2\text{PtCl}_2$ (602) देती है। यौगिक 602 की प्रतिक्रियाएं ट्राइमिथिलसिलीसाइनाइड (TMSCN) और ट्राइमिथिलसिलीएजाइड (TMSN₃) के साथ क्रमशः प्लैटिनम(II) साइनाइड ट्रान्स- $\{(i\text{-Bu})_2\text{ATI}]\text{Ge}(\text{Pr})\}_2\text{Pt}(\text{CN})_2$ (603) और प्लैटिनम(II) एजाइड सीस- $\{(i\text{-Bu})_2\text{ATI}]\text{Ge}(\text{Pr})\}_2\text{Pt}(\text{N}_3)_2$ (604) लगभग मात्रात्मक देती है। दिलचस्प बात यह है कि, क्लोरीन एनालॉग ट्रान्स- $\{(i\text{-Bu})_2\text{ATI}]\text{Ge}(\text{Cl})\}_2\text{Pt}(\text{CN})_2$ (605) यौगिक 603 का $\text{Pt}(\text{cod})\text{Cl}_2$ की प्रतिक्रिया साइनोजर्मिलीन से प्राप्त होता है। इन प्रतिक्रियाओं के विपरीत,

सिल्वर ट्राइफ्लेट (AgOTf) की प्रतिक्रिया यौगिक **602** के साथ, ने एक डाईमरिक प्लैटिनम(II) आयनिक कॉम्प्लेक्स $[\{(\text{tBu})_2\text{ATiGe}^i\text{Pr}\}_2\text{PtCl}]_2[\text{OTf}]_2$ (**606**) दिया। यौगिक **606**, डीएमएपी (डीएमएपी = (एन, एन-डायमिथाइलमिनोपिरिडीन) के दो समकक्षों के साथ एक मोनोमेरिक प्लैटिनम(II) आयनिक कॉम्प्लेक्स $[\{(\text{tBu})_2\text{ATiGe}^i\text{Pr}\}_2\text{PtCl}(\text{DMAP})][\text{OTf}]$ (**607**) में परिवर्तित किया गया है। यौगिक प्लैटिनम(II) साइनाइड **603** की क्षमता साइनोसिलाइलेशन अभिक्रिया के लिए उत्प्रेरक के रूप में कार्य करने के लिए दिखाई गई है।

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List of Symbols and Abbreviations

ATI	aminotroponimate	K	kelvin
%	percentage	Kcal	kilocalorie
°	degree	LA	Lewis acid
°C	degree centigrade	Me	methyl
Å	angstrom	Mes	mesityl
Anal	analysis	mg	milligram
bs	broad singlet	MHz	megahertz
Calcd	calculated	min.	minute
cm	centimeter	mL	milliliter
cod/COD	cyclooctadiene	mmol	mill mole
Cp	cyclopentadienyl	Mp	melting point
coe	cyclooctene	NBO	natural bond orbital
CO	carbon monoxide	<i>n</i> -Bu	<i>normal</i> -butyl
Cy	cyclohexyl	NHC	<i>N</i> -heterocyclic carbene
cym	cyamene	NHSi	<i>N</i> -heterocyclic silylene
DCM	dichloromethane	NHGe	<i>N</i> -heterocyclic germylene
dd	double doublet	NHSn	<i>N</i> -heterocyclic stannylene
dec	decomposition	nm	nanometer
deg	degree	NMR	nuclear magnetic resonance
DFT	density functional theory	<i>n</i> -Pr	<i>normal</i> -propyl
Dip	2,6-diisopropylphenyl	OTf	triflate
DMAP	<i>N,N</i> - dimethylaminopyridine	Ph	phenyl
dme	dimethoxyethane	ppm	parts per million

Et	ethyl	Py	pyridyl
ex.	excess	Pz	pyrazolyl
g	gram	rt	room temperature
h	hour	<i>t</i> -Bu	<i>tert</i> -butyl
Hz	Hertz	thf/THF	tetrahydrofuran
<i>i</i> -Bu/ ^{<i>i</i>} Bu	<i>iso</i> -butyl	TMS	trimethylsilyl
<i>i</i> -Pr	<i>iso</i> -propyl	WBI	Wiberg bond index
<i>J</i>	coupling constant	δ	(delta) chemical shift