

SYNTHESIS AND REACTIVITY OF BASE-STABILIZED Ge(II) COMPOUNDS, THEIR TERMINAL CHALCOGENIDES, AND BASE-STABILIZED Sn(II) COMPOUNDS

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by

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Submitted

in fulfillment of the requirements of the degree of

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Dedicated to My Family

Certificate

This is to certify that the thesis entitled “**Synthesis and reactivity of base-stabilized Ge(II) compounds, their terminal chalcogenides, and base-stabilized Sn(II) compounds**” being submitted by **Mr. Surendar Karwasara** to **Indian Institute of Technology Delhi**, for the award of the degree of **Doctor of Philosophy**, is a record of bona-fide research work carried out by him. **Mr. Surendar Karwasara** 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 embodied 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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Abstract

As evident from the title “*Synthesis and reactivity of base-stabilized Ge(II) compounds, their terminal chalcogenides, and base-stabilized Sn(II) compounds*” the thesis deals with the synthesis, reactivity, and theoretical studies on the aminotroponimate (ATI) ligand stabilized Ge(II) compounds (germylenes), their terminal chalcogenide derivatives, and 2-mercaptopyridine-*N*-oxide (2-mpno) ligand stabilized Sn(II) compounds (stannylenes). The thesis comprises six chapters and a brief description of each chapter is given below:

Chapter 1: Here, an overview of germylene and stannylene chemistry is provided. The synthesis and interesting reactivity of selected germylenes and stannylenes are discussed with an emphasis on germylenes. Finally, the objectives of the thesis are mentioned.

Chapter 2: In this chapter, the information about the chemicals used in this thesis is given. Apart from that, the general experimental techniques and procedures such as: cleaning and drying glassware; drying solvents and gases; purification of reagents; handling air-, moisture- and thermally-sensitive compounds; synthesis of reagents and starting materials; and instrumental details are provided. The details of software used for theoretical studies are also mentioned in this chapter.

Chapter 3: This chapter includes the details of synthesis and reactivity of *N*-aminotroponimatogermylenepyrrole [(Bu^{*i*}₂ATI)GeNC₄H₄] and its terminal chalcogenides [(Bu^{*i*}₂ATI)Ge(E)NC₄H₄] (E = S, Se). Compound (Bu^{*i*}₂ATI)GeNC₄H₄ was synthesized from (Bu^{*i*}₂ATI)GeCl through its reaction with sodium pyrrolide. The terminal chalcogenides [(Bu^{*i*}₂ATI)Ge(E)NC₄H₄] were synthesized from the reaction of (Bu^{*i*}₂ATI)GeNC₄H₄ with S and Se. The reactions of (Bu^{*i*}₂ATI)GeNC₄H₄ and (Bu^{*i*}₂ATI)Ge(E)NC₄H₄ (E = S/Se) with thio

and selenophenol resulted in novel germylene derivatives $[(\text{Bu}^i_2\text{ATI})\text{GeSPh}]$ and $(\text{Bu}^i_2\text{ATI})\text{-GeSePh}$ and germaesters $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\text{SPh}]$ and $(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\text{SePh}$, respectively.

Chapter 4: Isolation of the first silathiogermylene $[(\text{Bu}^i_2\text{ATI})\text{GeSSiMe}_3]$ and its utility in the single-step synthesis of trichalcogenodigermaacid anhydrides $[\{(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\}_2\text{E}]$ (E = S, Se, Te) is described in this chapter. The synthesis of $(\text{Bu}^i_2\text{ATI})\text{GeSSiMe}_3$ was achieved through the reaction of $(\text{Bu}^i_2\text{ATI})\text{GeCl}$ with lithiated trimethylsilathiol. The reaction of $(\text{Bu}^i_2\text{ATI})\text{GeSSiMe}_3$ with elemental chalcogens (S, Se, Te) occurred in an unprecedented manner resulting in the trichalcogenodigermaacid anhydrides $[\{(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\}_2\text{E}]$.

Chapter 5: This chapter presents a comparative reactivity study on the silathiogermylene $[(\text{Bu}^i_2\text{ATI})\text{GeSSiMe}_3]$ and siloxygermylenes $[(\text{Bu}^i_2\text{ATI})\text{GeOSiR}_3]$ (R = Me, Ph) with reagents such as elemental chalcogens (S, Se), diironnonacarbonyl ($\text{Fe}_2(\text{CO})_9$) and *N*-methylmorpholine-*N*-oxide (nmmo). Further, the reactivity studies on *O*-silylgermaesters $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\text{OSiR}_3]$ (E = S, Se; R = Me, Ph) are also discussed.

Chapter 6: Synthesis and reactivity of the first *O,S*-heterocyclic stannylenes $[(\text{C}_5\text{H}_4\text{NOS})_2\text{Sn}]$ and $(\text{C}_5\text{H}_4\text{NOS})\text{SnCl}$ containing a novel Sn(II)-O(0) bond are discussed in this chapter. Stannylenes $[(\text{C}_5\text{H}_4\text{NOS})_2\text{Sn}]$ and $[(\text{C}_5\text{H}_4\text{NOS})\text{SnCl}]$ were synthesized through the reaction of sodium 2-mpno $[(\text{C}_5\text{H}_4\text{NOS})\text{Na}]$ with SnCl_2 in 2:1 and 1:1 molar ratios, respectively. The reaction of $(\text{C}_5\text{H}_4\text{NOS})_2\text{Sn}$ with SbCl_3 and $\text{GeCl}_2\cdot\text{dioxane}$ resulted in a diantimony oxide $[\{(\text{C}_5\text{H}_4\text{NOS})\text{SbCl}\}_2\text{O}]$ and the first *O,S*-heterocyclic germylene $[(\text{C}_5\text{H}_4\text{NOS})\text{GeCl}]$, respectively. $(\text{C}_5\text{H}_4\text{NOS})\text{SnCl}$ reacted with indium(I) chloride (InCl) to give indium(III) complex $[(\text{C}_5\text{H}_4\text{NOS})\text{InCl}_2\cdot(\text{thf})_2]$. The computational studies performed on $(\text{C}_5\text{H}_4\text{NOS})_2\text{Sn}$, $(\text{C}_5\text{H}_4\text{NOS})\text{SnCl}$, and $[(\text{C}_5\text{H}_4\text{NOS})\text{GeCl}]$ to analyze their FMOs (frontier molecular orbitals).

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List of Symbols and Abbreviations

ATI	aminotroponimate	h	hour
%	percentage	HOMO	highest occupied molecular orbital
°	degree	Hz	Hertz
°C	degree centigrade	Bu ⁱ	<i>iso</i> -butyl
Å	angstrom	Pr ⁱ	<i>iso</i> -propyl
Anal	analysis	<i>J</i>	coupling constant
bs	broad singlet	K	kelvin
Calcd	calculated	Kcal	kilocalorie
cm	centimeter	LUMO	lowest unoccupied molecular orbital
COD	cyclooctadiene	Me	methyl
Cp	cyclopentadienyl	Mes	mesityl
Cy	cyclohexyl	mg	milligram
dcm	dichloromethane	MHz	megahertz
dd	double doublet	min.	minute
dec	decomposition	mL	milliliter
deg	degree	mmol	mill mole
DFT	density functional theory	MO	molecular orbital
DME	dimethoxyethane	Mp	melting point
dmpe	bis(dimethylphosphino)ethane	NHC	<i>N</i> -heterocyclic carbene
EI	electron ionization	nm	nanometer
Et	ethyl	NMR	nuclear magnetic resonance
ex.	excess	Pr ⁿ	<i>normal</i> -propyl
FMO	frontier molecular orbitals	OTf	triflate
g	gram	tmeda	tetramethylethylenediamine
Ph	phenyl	TMS	trimethylsilyl
ppm	parts per million	δ	(delta) chemical shift
Py	pyridyl	ΔG	change in free energy

rt	room temperature	ΔH	change in enthalpy
Bu ^t	<i>tertiary</i> -butyl		
thf	tetrahydrofuran		