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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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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Surendar Karwasara

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 aminotroponiminate (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*-aminotroponiminatogermylenepyrrole [$(Bu^{i}_2ATI)GeNC_4H_4$] and its terminal chalcogenides [$(Bu^{i}_2ATI)Ge(E)NC_4H_4$] (E = S, Se). Compound $(Bu^{i}_2ATI)GeNC_4H_4$ was synthesized from $(Bu^{i}_2ATI)GeCl$ through its reaction with sodium pyrrolide. The terminal chalcogenides [$(Bu^{i}_2ATI)Ge(E)NC_4H_4$] were synthesized from the reaction of $(Bu^{i}_2ATI)GeNC_4H_4$ with S and Se. The reactions of $(Bu^{i}_2ATI)GeNC_4H_4$ and $(Bu^{i}_2ATI)Ge(E)NC_4H_4$ (E = S/Se) with thio

and selenophenol resulted in novel germylene derivatives [$(Bu^{i}_{2}ATI)GeSPh$ and $(Bu^{i}_{2}ATI)$-$GeSePh$] and germaesters [$(Bu^{i}_{2}ATI)Ge(E)SPh$ and $(Bu^{i}_{2}ATI)Ge(E)SePh$], respectively.

Chapter 4: Isolation of the first silathiogermylene [$(Bu^{i}_{2}ATI)GeSSiMe_3$] and its utility in the single-step synthesis of trichalcogenodigermaacid anhydrides [$\{(Bu^{i}_{2}ATI)Ge(E)\}_2E$] (E = S, Se, Te) is described in this chapter. The synthesis of $(Bu^{i}_{2}ATI)GeSSiMe_3$ was achieved through the reaction of $(Bu^{i}_{2}ATI)GeCl$ with lithiated trimethylsilathiol. The reaction of $(Bu^{i}_{2}ATI)GeSSiMe_3$ with elemental chalcogens (S, Se, Te) occured in an unprecedented manner resulting in the trichalcogenodigermaacid anhydrides [$\{(Bu^{i}_{2}ATI)Ge(E)\}_2E$].

Chapter 5: This chapter presents a comparative reactivity study on the silathiogermylene [$(Bu^{i}_{2}ATI)GeSSiMe_3$] and siloxygermylenes [$(Bu^{i}_{2}ATI)GeOSiR_3$] (R = Me, Ph) with reagents such as elemental chalcogens (S, Se), diironnonacarbonyl ($Fe_2(CO)_9$) and *N*-methylmorpholine-*N*-oxide (nmmo). Further, the reactivity studies on *O*-silylgermaesters [$(Bu^{i}_{2}ATI)Ge(E)OSiR_3$] (E = S, Se; R = Me, Ph) are also discussed.

Chapter 6: Synthesis and reactivity of the first *O*,*S*-heterocyclic stannylenes [$(C_5H_4NOS)_2Sn$ and $(C_5H_4NOS)SnCl$] containing a novel Sn(II)-O(0) bond are discussed in this chapter. Stannylenes [$(C_5H_4NOS)_2Sn$] and [$(C_5H_4NOS)SnCl$] were synthesized through the reaction of sodium 2-mpno [$(C_5H_4NOS)Na$] with $SnCl_2$ in 2:1 and 1:1 molar ratios, respectively. The reaction of $(C_5H_4NOS)_2Sn$ with $SbCl_3$ and $GeCl_2{\cdot}dioxane$ resulted in a diantimony oxide [$\{(C_5H_4NOS)SbCl\}_2O$] and the first *O*,*S*-heterocyclic germylene [$(C_5H_4NOS)GeCl$], respectively. $(C_5H_4NOS)SnCl$ reacted with indium(I) chloride (InCl) to give indium(III) complex [$(C_5H_4NOS)InCl_2{\cdot}(thf)_2$]. The computational studies performed on $(C_5H_4NOS)_2Sn$, $(C_5H_4NOS)SnCl$, and [$(C_5H_4NOS)GeCl$ to analyze their FMOs (frontier molecular orbitals).

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List of Symbols and Abbreviations

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

rt	room temperature	ΔH	change in enthalpy
Bu^t	*tertiary*-butyl		
thf	tetrahydrofuran		