

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

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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 germynes **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 analogues 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 (HgCl<sub>2</sub> and HgBr<sub>2</sub>) 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 dihydroborated by pinacolborane (HBpin) using commercially available tin(II) halides [SnBr<sub>2</sub> (**601**) and SnCl<sub>2</sub> (**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.