

Abstract

The thesis entitled “**Ligand Stabilized Monochloro Metallylenes: Synthesis and Reactivities**” presents the details about the synthesis and reactivity (substitution and adduct formation reactions) of various germynes and stannynes. The thesis is divided into seven chapters. A brief description of each chapter is given below:

Chapter 1: This chapter provides a brief overview of germynes and stannynes; their synthesis and reactivity (such as nucleophilic substitution and adduct formation reactions) are discussed. Based on these discussions, the scope and objectives of the thesis are also mentioned.

Chapter 2: This chapter describes various basic aspects, such as cleaning and drying of glass apparatus, drying of solvents used in synthesis and NMR spectroscopic studies, drying of gases, handling of air and moisture sensitive compounds, synthesis of reported compounds, and commercial sources of chemicals. Further, details regarding instruments used during/for synthesis and characterization, and software used are also discussed.

Chapter 3: *N*-heterocyclic germylene acetate [(*i*-Bu)₂ATIGe(OAc)] (**301**) has been isolated through the reaction of aminotroponimino germylene monochloride [(*i*-Bu)₂ATIGeCl] (**102**) with sodium acetate (ATI = aminotroponimino) (OAc = OCOCH₃). However, an alternate to compound **301** did not work; the reaction of compound **102** with silver acetate (AgOAc) for 12 h produced digermylene oxide stabilized AgCl complex [({(*i*-Bu)₂ATIGe}₂O)₂(Ag₄Cl₄)] (**302**) with an Ag₄Cl₄ core. The reaction of compound **102** with AgOAc when carried out only for 30 min, afforded germylene acetate stabilized AgCl complex [({(*i*-Bu)₂ATIGe(OAc)}₂(AgCl)] (**303**) with a monomeric AgCl core. Interestingly, stirring a THF solution of compound **303** overnight gave compound **302**. The reactions of germylene acetate **301** with TMSCN, TMSCl, and TMSI afforded germylene cyanide [(*i*-Bu)₂ATIGeCN] (**304**),

germylene monochloride **102** and germylene iodide [(*i*-Bu)₂ATIGeI] (**305**), respectively, via the elimination of TMSOAc. Further, the germylene acetate stabilized platinum(II) complex *cis*-[{{(*i*-Bu)₂ATIGe(OAc)}₂(PtCl₂)] (**306**) is obtained through the reaction of compound **301** with PtCl₂(COD) (COD = 1,5-cyclooctadiene). In contrast, the treatment of compound **301** with 1.5 equiv of ZnI₂ resulted in dianion separated bis(germylene cation) [{{(*i*-Bu)₂ATIGe}₂(Zn₂I₆)] (**307**). Compounds **301-307** have been characterized by NMR spectroscopy and the solid-state structures of compounds **301-303** and **306-307** were confirmed through single-crystal X-ray diffraction studies.

Chapter 4: The isolation of the first air-stable *N*-heterocyclic germylene stabilized palladium(II) complexes is achieved by reacting aminotroponiminatogermylene monochloride [{{(*i*-Bu)₂ATIGeCl}] (**102**) with various palladium(II) precursors (ATI = aminotroponimate). Accordingly, the synthesis and characterization of germylene palladium(II) complexes [{{(*i*-Bu)₂ATIGeCl}₂PdCl₂] (**401**), [{{(*i*-Bu)₂ATIGe(Cl)PdCl₂}₂] (**402**) and [{{(*i*-Bu)₂ATIGe(Cl)Pd(allyl)Cl}] (**403**) are described in this chapter. Complexes **401** and **403** are stable in air for 10 d, while the dimeric complex **402** is stable for 5 h only. A preliminary study shows that complexes **401-403** are active as catalysts for Suzuki-Miyaura coupling reactions in aqueous medium. The solid-state structures of complexes **401-403** have been confirmed by single-crystal X-ray diffraction studies, and details are furnished.

Chapter 5: Aminotroponiminatogermylene stabilized Ru(II) complexes and reactivity studies on *N*-heterocyclic germylene stabilized ruthenium(II) complexes were not known. Therefore, this work reports the synthesis of aminotroponiminatogermylene stabilized ruthenium(II) complexes [L₁Ge(X){RuCl₂(Y)}] (L₁ = (*i*-Bu)₂ATI; (ATI = aminotroponimate), X = Cl **501**, NC₄H₄ **502**, Y = η⁶-*p*-cymene), and the reactivity studies on complex **502**. *N*-pyrrolylgermylene stabilized Ru(II) complex **502** reacts with H₂O and SnCl₂ to afford hydroxygermylene

stabilized ruthenium(II) complex $[L_1Ge(OH)\{RuCl_2(Y)\}]$ (**503**) and a bimetallic complex $[L_1Ge(NC_4H_4)\{Ru(SnCl_3)Cl(Y)\}]$ (**504**), respectively. The chlorogermylene analogue $[L_1GeCl\{Ru(SnCl_3)Cl(Y)\}]$ (**505**) of complex **504** is also isolated by reacting complex **504** with chlorotrimethylsilane.

Chapter 6: The reaction of aminotroponiminatogermylene pyrrole $[(i-Bu)_2ATIGe(NC_4H_4)]$ (**102a**) with dimesitylboronic acid afforded germylene dimesitylboroxide $[(i-Bu)_2ATIGe(OB(Mes)_2)]$ (**601**) (ATI = aminotroponimate; mes = mesityl). The reaction of compound **601** with $GeCl_2 \cdot (1,4-dioxane)$ and $SnCl_2$ produced dimesitylboroxide stabilized germylene monochloride $[\{(Mes)_2BOGe(Cl)\}_2]$ (**602**) and stannylene monochloride $[\{(Mes)_2BOSn(Cl)\}_2]$ (**603**), respectively. Compound **102** was formed as a side product in these reactions, which was not separable until now. However, the reactions of the *in-situ* generated lithium salt of dimesitylboronic acid with $GeCl_2 \cdot (1,4-dioxane)$ and $SnCl_2$ in a 1:1 molar ratio offered exclusively compounds **602** and **603**, respectively. Compounds **601-603** were characterized through multinuclear NMR spectroscopy, and single-crystal X-ray diffraction studies were performed on compounds **602** and **603**.

Chapter 7: Novel chiral *N*-heterocyclic germylene $[(L)GeCl]$ (**701**) containing chiral amidooxazolate is isolated as a stable species (L = (4*S*)-4,5-dihydro-2-[2'-(2,6-diisopropylanilino)phenyl]-4-*iso*-propyloxazole). The first examples of chiral germylene acetate $[(L)GeOAc]$ (**702**), triflatogermylene $[(L)GeOTf]$ (**704**), isocyanatogermylene $[(L)GeNCO]$ (**705**), and siloxygermylene $[(L)GeOSiPh_3]$ (**706**) are obtained through the nucleophilic substitution reactions of chiral germylene **701** with suitable reagents (OAc = $OCOCH_3$; OTf = OSO_2CF_3). Chiral cyanogermylene $[(L)GeCN]$ (**703**) is synthesized through the reaction of compound **702** with $TMSCN$. The coordinating ability of chiral germylene **701** towards ruthenium(II) and palladium(II) precursors were examined and chiral germylene-

ruthenium(II) ($[(L)Ge(Cl) RuCl_2(p\text{-cymene})]$ (**707**)) and -palladium(II) ($[(L)Ge(Cl)PdCl_2]_2$ (**708**) and $[(L)Ge(Cl)PdCl_2(t\text{-BuNC})]$ (**709**)) complexes are isolated. Compounds **701-709** were characterized through multinuclear NMR spectroscopy, and single-crystal X-ray diffraction studies were performed on compounds **701-702**, and **705-707**.