# LOW-VALENT CHEMISTRY OF GROUP 14 ELEMENTS STUDIED USING BULKY AMINOTROPONIMINATE LIGANDS

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*by*

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*Submitted*

*in fulfillment of the requirements of the degree of*

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*to the*


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*Dedicated to My Parents*

# Certificate

This is to certify that the thesis entitled "**Low-valent Chemistry of Group 14 Elements Studied using Bulky Aminotroponiminate Ligands**" being submitted by **Mr. Rahul Kumar** (Entry No.: 2008CYZ8012) to **Indian Institute of Technology Delhi**, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. **Mr. Rahul Kumar** 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.

Date: 03-09-2015
Place: New Delhi

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# Abstract

The thesis entitled *"Low-valent Chemistry of Group 14 Elements Studied using Bulky Aminotroponiminate Ligands"* presents the details about the synthesis, characterization, reactivity, theoretical study, and utility of various aminotroponiminate (ATI) ligand stabilized compounds with heavier group 14 elements in their formal oxidation state of +2. The thesis is divided into the six chapters. A brief description about each chapter is given below:

***Chapter 1:*** In this chapter, a brief overview on the heavier analogues of carbenes is discussed. Several recent developments in the low-valent chemistry of heavier group 14 elements studied through the monoanionic bidentate ligands are discussed. Consequently, the objectives of this thesis are mentioned.

***Chapter 2:*** This chapter first describes the source of various chemicals used for this thesis. The experimental procedures for the following routine activities in an organometallic lab are mentioned: cleaning and drying of glassware; drying of solvents and gases; purification of reagents and products; handling of air, moisture, and thermally sensitive compounds; preparation of known compounds. The details regarding the instruments used for the characterization of novel compounds are furnished. Further, the details about the software used for theoretical studies are mentioned.

***Chapter 3:*** This chapter contains the details regarding the multi-step synthesis of bulky aminotroponiminate ligand stabilized germylene monochlorides [LGeCl] (L = (*t*-Bu)$_2$ATI and (*i*-Bu)$_2$ATI). The suitability of these new germylene monochlorides to react further is

demonstrated through their reactions with $Fe_2(CO)_9$. The reactions of [(*t*-Bu)$_2$ATIGeCl] with lithium derivatives of alkynes and sodium azide are also given.

***Chapter 4:*** The use of germylene monochloride complexes [LGeCl] in the synthesis of germanium analogues of carbonyl compounds such as esters [LGe(E)O*t*-Bu] (E = S, Se, Te), amides [LGe(E)N(SiMe$_3$)$_2$] (E = S, Se, Te), ynones [(*t*-Bu)$_2$ATIGe(E)C≡CPh] (E = S, Se), and acid bromides [(*i*-Bu)$_2$Ge(E)Br] is shown. The reaction of germylene alkoxide complexes [LGeO*t*-Bu] with elemental chalcogens (S, Se, Te) afforded the first examples of germathioester [LGe(S)O*t*-Bu], germaselenoester [LGe(Se)O*t*-Bu], and germatelluroester [(*i*-Bu)$_2$ATIGe(Te)O*t*-Bu] complexes. Similarly, the synthesis of germathioamide [LGe(S)N(SiMe$_3$)$_2$], germaselenoamide [LGe(Se)N(SiMe$_3$)$_2$], germatelluroamide [(*i*-Bu)$_2$ATIGe(Te)N(SiMe$_3$)$_2$], germathioynone [(*t*-Bu)$_2$ATIGe(S)C$_2$Ph], and germaselenoynone [(*t*-Bu)$_2$ATIGe(Se)C$_2$Ph] complexes is shown through the oxidative addition of elemental chalcogens to the corresponding germylene precursors [LGeN(SiMe$_3$)$_2$] and [(*t*-Bu)$_2$ATIGeC≡CPh]. The reaction of germylene amides [LGeN(SiMe$_3$)$_2$] with Me$_3$SiBr (TMSBr) has resulted in the corresponding germylene monobromide complexes [LGeBr]. Likewise, germachalcogenoamide complexes [(*i*-Bu)$_2$ATIGe(E)N(SiMe$_3$)$_2$] (E = S, Se) also reacted with TMSBr at elevated temperatures to afford the germachalcogenoacid bromide [(*i*-Bu)$_2$ATIGe(E)Br] complexes as the first examples.

***Chapter 5:*** Digermylene oxides contain a Ge(II)-O-Ge(II) moiety and only a very few of them are known. Also, the synthetic routes for their preparations are not simple and straightforward. This chapter addresses this issue by devising a simple and high yielding route for the preparation of digermylene oxides [LGe-O-GeL]. Reactions of these compounds

with elemental chalcogens afforded the first example of dithiogermaacid anhydride [L(S)Ge-O-Ge(S)L], diselenogermaacid anhydride [L(Se)Ge-O-Ge(Se)L], and ditellurogermaacid anhydride [{(*i*-Bu)$_2$ATIGe(Te)}$_2$O] complexes with (E)Ge-O-Ge(E) moieties. Reaction of compound [{(*t*-Bu)$_2$ATIGe}$_2$O] with trimethylsilyl cyanide (TMSCN) gave the first example of a germylene monocyanide complex [(*t*-Bu)$_2$ATIGeCN]. Due to the high reactivity of the Ge(II)-CN bond, this compound activates several aldehydes (RCHO) at room temperature to result in the corresponding cyanogermylated products [(*t*-Bu)$_2$ATIGeOC(H)(CN)R] (R = H, *i*-Pr, *t*-Bu, CH(Ph)CH$_3$, C$_6$F$_5$). Germylene monocyanide complex also works as a useful catalyst for the cyanosilylation reaction of aldehydes using TMSCN and is the first isolable and structurally characterized germylene to act as a catalyst.

***Chapter 6:*** In this chapter, the facile synthesis of stannylene monochloride complexes [LSnCl] is described. Reactivity studies on them and some of their derivatives are also reported. The reactions of compounds [(*t*-Bu)$_2$ATISnCl] and [(*i*-Bu)$_2$ATISnCl] with LiN(SiMe$_3$)$_2$ and sodium pyrrolide have afforded the stannylene amide [(*t*-Bu)$_2$ATISnN(SiMe$_3$)$_2$] and stannylene pyrrolide [(*i*-Bu)$_2$ATISnpy] (py = pyrrolide) complexes, respectively. Further, the reactions of compound [(*t*-Bu)$_2$ATISnN(SiMe$_3$)$_2$] with TMSBr and TMSCN gave stannylene monobromide [(*t*-Bu)$_2$ATISnBr] and stannylene monocyanide [(*t*-Bu)$_2$ATISnCN] complexes, respectively. The utility of stannylene monocyanide complex in the activation of aldehydes is shown through the formation of cyanostannylated product [(*t*-Bu)$_2$ATISnOC(H)(CN)C(CH$_3$)$_3$]. Also, the attempted synthesis of aminotroponiminatosilylene monochlorides [LSiCl] is discussed.

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# List of Symbols and Abbreviations

| | |
|---|---|
| ATI | aminotroponiminate |
| % | percentage |
| ° | degree |
| °C | degree centigrade |
| $\mu$M | micro molar |
| Å | angstrom |
| Ad | adamantyl |
| AIM | atoms in molecules |
| Anal | analysis |
| au | atomic unit |
| bcp | bond critical point |
| 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 |
| ESI | Electrospray ionization |
| h | hour |
| HOMO | highest occupied molecular orbital |
| HRMS | high-resolution mass spectrometry |
| Hz | Hertz |
| *i*-Bu | *iso*-butyl |
| *i*-Pr | *iso*-propyl |
| IR | infra red |
| *J* | coupling constant |
| K | Kelvin |
| Kcal | kilocalorie |
| LUMO | lowest unoccupied molecular orbital |
| m/z | mass-to-charge ratio |
| Me | methyl |
| Mes | mesityl |
| mg | milligram |
| MHz | megahertz |
| min. | minute |
| mL | milliliter |
| mmol | mill mole |
| MO | molecular orbital |
| Mp | melting point |
| MS | Mass spectrometry |
| NBO | natural bond orbital |
| NHC | *N*-heterocyclic carbene |
| nm | nanometer |
| NMR | nuclear magnetic resonance |

| | |
|---|---|
| Et | ethyl |
| ex. | excess |
| FMO | frontier molecular orbitals |
| g | gram |
| Ph | phenyl |
| ppm | parts per million |
| Py | pyridyl |
| Pz | pyrazolyl |
| rcp | ring critical point |
| rt | room temperature |
| *t*-Bu | *tert*-butyl |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| NPA | natural population analysis |
| *n*-Pr | *normal*-propyl |
| NRT | natural resonance theory |
| OTf | triflate |
| tmeda | tetramethylethylenediamine |
| TMS | trimethylsilyl |
| UV | ultra violet |
| Vis | visible |
| WBI | Wiberg bond index |
| $\delta$ | (delta) chemical shift |
| $\Delta G$ | change in free energy |
| $\Delta H$ | change in enthalpy |
| $\lambda$ | (lambda) wave length |