

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

RAHUL KUMAR



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2015**

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

by

RAHUL KUMAR

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi

September, 2015

Dedicated to My Parents

Certificate

This is to certify that the thesis entitled “**Low-valent Chemistry of Group 14 Elements Studied using Bulky Aminotroponimate 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

Prof. S. Nagendran

Thesis Supervisor

Department of Chemistry

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110 016, India

Acknowledgements

This journey started in July 2008 when I got a great opportunity to join in Prof. Selvarajan Nagendran's research group as his first PhD student. I was in front of several challenging tasks such as setting up a laboratory that can manipulate air and moisture sensitive compounds, establishing a new chemistry, and so forth. However, with the help of my supervisor, I was able to accomplish all these tasks and for which I am grateful to him.

Further, I feel privileged to convey my deep and wholehearted gratitude to my thesis supervisor for his prolific supervision, extreme support, motivation, and care. From his vast knowledge and experience, I could learn several new synthetic tricks and gained a lot of new research ideas. The freedom that he gave helped a lot to develop my confidence and independency.

I wish to convey my sincere thanks to Prof. A. Ramanan, Prof. J. D. Singh, Prof. N. G. Ramesh, and Prof. Sameer Sapra for teaching me material characterization, inorganic and organic synthesis, and supramolecular chemistry during my course work at IIT Delhi. I am very much thankful to Prof. A. J. Elias, Prof. Ravi Shankar, Prof. Josemon Jacob (CPSC), and Prof. S. Malaichamy (DU) for giving me their valuable suggestions during my comprehensive examination, fellowships extension, and PhD synopsis.

In would like to thank Prof. G. Rajaraman (IIT Mumbai), Prof. B. Jayaram, and Dr. G. Mukherjee for their support during theoretical studies. I also thank Prof. Pramit K. Chowdhury and Prof. J. Jacob for allowing me to use their lab facilities whenever I need.

I thank the present and past heads of the chemistry department for providing all the facilities to conduct my research.

I thank Mr. V. K. Sharma for fabricating several glassware for me. Further, I thank Mr. Keshav, Mr. Munalal, and Mr. Alok for their help in recoding the NMR spectra. I am grateful to the chemistry department office staffs and instrumentation lab staffs for helping me in all my official and instrumental lab activities, respectively. I am thankful to all the staff members in the liquid nitrogen plant. Further, I am thankful to all the staff members at Kumaon hostel for their care during my stay at IIT Delhi.

Words are not enough to express my heartfelt appreciation and affection towards my lab mates Mr. Dhirendra Yadav, Mr. Chandan Jha, Mr. Surendar Karwasara, Mr. Soumen Sinhababu, and Mr. Mahendra Kumar Sharma who have helped me a lot during my work for this thesis. They gave me brotherly support during tough times, bond of friendship, fruitful scientific interactions, and wonderful research environment in the lab. I sincerely thank all the following past and present MSc, MTech, and summer research students for their support: Mr. Somnath, Umesh, Pankaj, Subrata, Vikas, Seshagiri, Manoj, Sameer, Nikhil, Sunil, Ravi, Saddam, Santigopal, Nimai, Anup, Samir, Deborta, Dharmendra, Raghav, and Ms Rupali and Amanpreet.

I acknowledge the following colleagues from other research groups at IIT Delhi for their constant motivation: Dr. Udit, Vinod, Dinesh, Nem, Monika, Dharmendra, Piyush, Senthil, Dheeraj, Usha, Richa, Prabhu, Kamalakanta, Neeru, Praduman, Gyan, Om, Kamal, Amit, Shrinivas; Mr. Vineet Latayan, Pramod, Balender, Manoj, Hemant, Alpesh, Jatinder, Vikas Dahiya, Bijesh, Vineet Soni, Sandeep Dhaka, Manu, Rishi, Sandeep Tripathi, Rajendra, Jogendra, Vikas Arora, Sanjeeb, Saurabh; Ms. Preeti, Nisha, Ashima, Sakshi, and Sushma.

For unconditional help and continuous motivation, I acknowledge my friends Mr. Vipin Dhankad and Mrs. Balee Dhankad, Dr. Rahul Dhaka and Smt. Dr. Sarita Dhaka, Dr.

Pramod Baliyan, Dr. Sushil Vashistha, Dr. Rajesh Chhatra and Smt. Dr. Usha Chhatra, Dr. Rajan Rathi, Dr. Deepak Tyagi, Dr. Anuj Panwar, Dr. Satendra Dahima, Dr. Surbhi Arya, Dr. Amit Rawat, Mr. Arun Baliyan, Mr. Vikas Latiyan, Mr. Ashok Hinwar; Mr. Rajkumar Rawat, Mr. Bobby, Mr. Sohan Pal, Mr. Vikes, Mr. Bijesh Deol, Mr. Ankur Chauhan, Mr. Rajeev Tomar, Mr. Kuldeep Singh; and Ms. Nivedita Choudhary.

I acknowledge CSIR, New Delhi, for the financial assistance.

I express my intense affection and respect to my family members, who sacrificed their needs and worked very hard for years to support my education. My parents Shri Virendar Pal and Smt. Bharat Wati have always been blessing me with their love and care. They taught me high moral values which helped me in shaping up my educational, social, and spiritual growth. I am extremely lucky to have the blessings of my in-laws Shri Naresh Pal and Smt. Usha Devi. For their extreme care and love, I thank my sisters Anju and Manju, my sister in-law Chhaya my brothers in-law Pankaj, Bhuvnesh and Ashish, and my nephew Rajan and my niece Shagun and Palak. I sincerely appreciate to my loving wife Bhavna and my cute son Aaryansh for their extream supports, love, care, and having a huge belief in me. Finally, I thank God for offering me good health and wisdom to carry out the piece of work discussed in this thesis.

Rahul Kumar

Abstract

The thesis entitled “*Low-valent Chemistry of Group 14 Elements Studied using Bulky Aminotroponimate Ligands*” presents the details about the synthesis, characterization, reactivity, theoretical study, and utility of various aminotroponimate (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 aminotroponimate ligand stabilized germylene monochlorides [LGeCl] (L = (*t*-Bu)₂ATI and (*i*-Bu)₂ATI). The suitability of these new germylene monochlorides to react further is

demonstrated through their reactions with $\text{Fe}_2(\text{CO})_9$. The reactions of $[(t\text{-Bu})_2\text{ATiGeCl}]$ with lithium derivatives of alkynes and sodium azide are also given.

Chapter 4: The use of germylene monochloride complexes $[\text{LGeCl}]$ in the synthesis of germanium analogues of carbonyl compounds such as esters $[\text{LGe(E)Ot-Bu}]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$), amides $[\text{LGe(E)N}(\text{SiMe}_3)_2]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$), ynones $[(t\text{-Bu})_2\text{ATiGe(E)C}\equiv\text{CPh}]$ ($\text{E} = \text{S}, \text{Se}$), and acid bromides $[(i\text{-Bu})_2\text{Ge(E)Br}]$ is shown. The reaction of germylene alkoxide complexes $[\text{LGeOt-Bu}]$ with elemental chalcogens ($\text{S}, \text{Se}, \text{Te}$) afforded the first examples of germathioester $[\text{LGe(S)Ot-Bu}]$, germaselenoester $[\text{LGe(Se)Ot-Bu}]$, and germatelluroester $[(i\text{-Bu})_2\text{ATiGe(Te)Ot-Bu}]$ complexes. Similarly, the synthesis of germathioamide $[\text{LGe(S)N}(\text{SiMe}_3)_2]$, germaselenoamide $[\text{LGe(Se)N}(\text{SiMe}_3)_2]$, germatelluroamide $[(i\text{-Bu})_2\text{ATiGe(Te)N}(\text{SiMe}_3)_2]$, germathioynone $[(t\text{-Bu})_2\text{ATiGe(S)C}_2\text{Ph}]$, and germaselenoynone $[(t\text{-Bu})_2\text{ATiGe(Se)C}_2\text{Ph}]$ complexes is shown through the oxidative addition of elemental chalcogens to the corresponding germylene precursors $[\text{LGeN}(\text{SiMe}_3)_2]$ and $[(t\text{-Bu})_2\text{ATiGeC}\equiv\text{CPh}]$. The reaction of germylene amides $[\text{LGeN}(\text{SiMe}_3)_2]$ with Me_3SiBr (TMSBr) has resulted in the corresponding germylene monobromide complexes $[\text{LGeBr}]$. Likewise, germachalcogenoamide complexes $[(i\text{-Bu})_2\text{ATiGe(E)N}(\text{SiMe}_3)_2]$ ($\text{E} = \text{S}, \text{Se}$) also reacted with TMSBr at elevated temperatures to afford the germachalcogenoacid bromide $[(i\text{-Bu})_2\text{ATiGe(E)Br}]$ 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 $[\text{LGe-O-GeL}]$. 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 $[{(i-Bu)_2ATIGe(Te)}_2O]$ complexes with $(E)Ge-O-Ge(E)$ moieties. Reaction of compound $[{(t-Bu)_2ATIGe}_2O]$ with trimethylsilyl cyanide (TMSCN) gave the first example of a germylene monocyanide complex $[(t-Bu)_2ATIGeCN]$. 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 $[(t-Bu)_2ATIGeOC(H)(CN)R]$ ($R = H, i-Pr, t-Bu, CH(Ph)CH_3, C_6F_5$). 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 $[(t-Bu)_2ATISnCl]$ and $[(i-Bu)_2ATISnCl]$ with $LiN(SiMe_3)_2$ and sodium pyrrolide have afforded the stannylene amide $[(t-Bu)_2ATISnN(SiMe_3)_2]$ and stannylene pyrrolide $[(i-Bu)_2ATISnpy]$ ($py = \text{pyrrolide}$) complexes, respectively. Further, the reactions of compound $[(t-Bu)_2ATISnN(SiMe_3)_2]$ with $TMSBr$ and $TMSCN$ gave stannylene monobromide $[(t-Bu)_2ATISnBr]$ and stannylene monocyanide $[(t-Bu)_2ATISnCN]$ complexes, respectively. The utility of stannylene monocyanide complex in the activation of aldehydes is shown through the formation of cyanostannylated product $[(t-Bu)_2ATISnOC(H)(CN)C(CH_3)_3]$. Also, the attempted synthesis of aminotroponiminatosilylene monochlorides $[LSiCl]$ is discussed.

Table of Contents

Certificate.....	i
Acknowledgements.....	iii
Abstract.....	vii
List of Figures.....	xv
List of Tables.....	xix
List of Symbols and Abbreviations.....	xxi
Chapter 1: Introduction	
1.1 Metallylenes.....	1
1.2 Recent Developments in Functionalized Metallylene Chemistry.....	4
1.2.1 Substitution Reactions of Metallylenes.....	4
1.2.2 Metallylenes as Neutral Donors: Adduct Forming Reactions.....	10
1.2.3 Oxidative Addition/Insertion Reactions of Metallylenes.....	16
1.2.4 Reduction Reactions of Metallylenes.....	21
1.2.5 Miscellaneous Reactions of Metallylenes.....	24
1.3 ATI Ligand in Germylene Chemistry.....	29
1.4 Objectives.....	31
References.....	32
Chapter 2: General Experimental Techniques	
2.1. Reagents, Solvents, and Starting Materials.....	39
2.2. Cleaning and Drying of Glassware.....	42
2.3. Drying of Solvents and Gases.....	43
2.3.1. Purification and drying of solvents.....	43
2.3.2. Drying of gases.....	44
2.4. Purification of Reagents.....	44

2.5. Handling and Sampling of Compounds	45
2.6. Details of Instruments Used.....	45
2.7. Details of Software Used	46
References.....	47

Chapter 3: Aminotroponiminatogermylene Monochlorides: Synthesis and Reactivity Studies

3.1 Introduction.....	49
3.2 Results and Discussion	54
3.2.1. Synthesis and Spectra	54
3.2.2. X-ray Crystal Structures of Compounds 101 , 103-104 , 106-108 , and 110-116	61
3.3 Conclusions.....	75
3.4 Experimental Section.....	75
3.4.1 Synthetic Details	75
3.4.2 X-ray Structure Determination of Compounds 101 , 103-104 , 106-108 , and 110-116	86
References.....	93

Chapter 4: Germachalcogenoester, -amide, -acid halide, and -ynone Complexes with Ge=E Bonds (E = S, Se, Te)

4.1 Introduction.....	100
4.2 Results and Discussion	108
4.2.1. Synthesis and Spectra	108
4.2.2. Crystal Structures of Compounds 201 , 203-207 , and 210-220	124
4.2.3 Theoretical Studies on Compounds 207 , 214 , and 219-220	142
4.3 Conclusions.....	150
4.4 Experimental Section.....	151
4.4.1 Synthetic Details	151

4.4.2 X-ray Structure Determination for Compounds 201 , 203-207 , and 210-220	163
4.4.3 Computational Details	171
References	174

Chapter 5: Digermylene Oxide and Germylene Monocyanide Complexes: Synthesis and Reactivity Studies

5.1 Introduction	180
5.2(a) Results and Discussion: Digermylene Oxide and Germaacid Anhydride Complexes	184
5.2(a).1 Synthesis and Spectra	184
5.2(a).2 Crystal Structures of Compounds 301-307	193
5.2(a).3 Theoretical Studies on Compounds 301-307	201
5.2(b) Results and Discussion: Germylene Monocyanide and Its Catalytic Activities	215
5.2(b).1 Synthesis and Spectra	215
5.2(b).2 Crystal Structures of Compounds 308-312	221
5.3 Conclusions	226
5.4 Experimental Section	228
5.4.1 Synthetic Details	228
5.4.2 X-ray Structure Determination for Compounds 301-312	238
5.4.3 Computational Details	242
References	254

Chapter 6: Synthesis and Reactivity Studies on Aminotroponiminatostannylene Monochlorides and the Attempted Synthesis of Aminotroponiminatosilylene Monochlorides

6.1 Introduction	260
6.2 Results and Discussion	262
6.2.1 Synthesis and Spectra	262
6.2.2 X-ray Crystal Structures of Compounds 401-403 , 405 , 406 , and 408	269

6.3 Conclusions.....	275
6.4 Experimental Section.....	276
6.4.1 Synthetic details.....	276
6.4.2 X-ray Data Collection for Compounds 401-403, 405, 406 and 408	281
References.....	285
Author's Profile	287
Research Publications	288

List of Figures

Figure No.	Figure Caption	Page No.
3.1	Molecular structure of 2-(<i>t</i> -butylamino)tropone 101	62
3.2	Molecular structure of 2-(1-adamantylamino)tropone 103	63
3.3	Molecular structure of aminotroponimine 104	64
3.4	Molecular structure of aminotroponimine 106	65
3.5	Molecular structure of lithium salt 107	66
3.6	Molecular structure of lithium salt 108	67
3.7	Molecular structure of aminotroponiminatogermylene monochloride 110	68
3.8	Molecular structure of aminotroponiminatogermylene monochloride 111	69
3.9	Molecular structure of aminotroponiminatogermylene monochloride stabilized iron(0) tetracarbonyl complex 112	70
3.10	Molecular structure of aminotroponiminatogermylene monochloride stabilized iron(0) tetracarbonyl complex 113	71
3.11	Molecular structure of alkynyl germylene derivative 114	72
3.12	Molecular structure of alkynyl germylene derivative 115	73
3.13	Molecular structure of aminotroponiminatogermylene azide 116	74
4.1a	UV-vis spectra of compounds 204, 211, 215, and 219	121
4.1b	UV-vis spectra of compounds 206, 213, 216, and 220	122
4.1c	UV-vis spectra of compounds 207 and 214	122
4.2	Molecular structure of germylene alkoxide complex 201	125
4.3	Molecular structure of germathioester complex 203	127
4.4	Molecular structure of germathioester complex 204	128
4.5	Molecular structure of germaselenoester complex 205	129
4.6	Molecular structure of germaselenoester complex 206	129
4.7	Molecular structure of germatelluroester complex 207	131
4.8	Molecular structure of germathioamide complex 210	132
4.9	Molecular structure of germathioamide complex 211	133
4.10	Molecular structure of germaselenoamide complex 212	134

4.11	Molecular structure of germaselenoamide complex 213	135
4.12	Molecular structure of germatelluroamide complex 214	135
4.13	Molecular structure of germathioynone complex 215	137
4.14	Molecular structure of germaselenoynone complex 216	137
4.15	Molecular structure of aminotroponiminatogermylene monobromide 217	139
4.16	Molecular structure of aminotroponiminatogermylene monobromide 218	139
4.17	Molecular structure of germathioacid bromide complex 219	141
4.18	Molecular structure of germaselenoacid bromide complex 220	142
4.19	The NBO computed orbital interactions (from the second order perturbation theory analysis) in the Ge=Te bonds in compounds 207 and 214	144
4.20	Interaction of the lone pairs on oxygen (of -Ot-Bu) and nitrogen (of -N(SiMe ₃) ₂) atoms with the antibonding orbitals of Ge-Te bonds in compounds 207 and 214	145
4.21	MOs of compounds 207 and 214 that show the σ -bonds between the tellurium and germanium atoms	146
4.22	FMOs of compounds 207 and 214	147
4.23	NBO interactions between the filled <i>p</i> -orbitals of bromine atoms and the vacant <i>sp</i> ^x hybrid orbitals of germanium atoms in compounds 219 and 220	148
4.24	NBO interactions between the lone pairs of bromine atoms and the σ^* -orbitals of the Ge-E bonds in compounds 219 and 220	150
4.25	NBO interactions between the filled orbitals of halogen atoms (X) and the vacant orbitals of germanium atoms in compounds 219a-220a (X = Cl) and 219b-220b (X = F)	173
5.1	UV-vis spectra of compounds 302 , 304 , 306 , and 307	191
5.2	Molecular structure of digermylene oxide complex 301	194
5.3	Molecular structure of digermylene oxide complex 302	195
5.4	Molecular structure of dithiogermaacid anhydride complex 303	197
5.5	Molecular structure of dithiogermaacid anhydride complex 304	197
5.6	Molecular structure of diselenogermaacid anhydride complex 305	199
5.7	Molecular structure of diselenogermaacid anhydride complex 306	199
5.8	Molecular structure of ditellurogermaacid anhydride complex 307	200

5.9	NBO orbitals of compounds 301 , 303 , and 305 showing the significant oxygen to germanium donor interactions along with their stabilization energies in kcal/mol	204
5.10	Molecular orbitals showing the overlap between oxygen and germanium atoms in compounds 301 , 303 , and 305	205
5.11	AIM calculations showing critical points for compound 301	206
5.12	AIM calculations showing critical points for compound 303	206
5.13	AIM calculations showing critical points for compound 305	207
5.14	π -antibonding interaction between oxygen and germanium atoms in compounds 301 , 303 , and 305	208
5.15	MOs of compounds 303 and 305 that show the mixing of Ge–O and Ge=E antibonding orbitals	209
5.16	MO of compound 307 that shows the σ -bond between the tellurium and germanium atoms along the Ge–Te bond axes	210
5.17	π -bonding interaction between germanium and E atoms in compound 303 and 305 , π -antibonding interaction between germanium and E atoms in compound 303 and 305 , interaction of the lone pair of electrons of nitrogen with Ge–E antibonding orbital in compound 303 and 305 , interaction of the lone pair of electrons of oxygen with Ge–E antibonding orbital in compound 303 and 305 (E = S 303 , Se 305)	211
5.18	π -antibonding and σ -bonding interactions between germanium and tellurium atoms in compound 307 , interaction of the lone pair of electrons of oxygen with Ge–Te antibonding orbital in compound 307	212
5.19	FMOs of compounds 301 , 303 , 305 , and 307	214
5.20	Molecular structure of germylene monocyanide complex 308	223
5.21	Molecular structure of germylene alkoxide complexe 309	224
5.22	Molecular structure of germylene alkoxide complexe 310	225
5.23	Molecular structure of germylene alkoxide complexe 311	225
5.24	Molecular structure of germylene alkoxide complexe 312	226
5.25	MOs of compound 302 that involve in the electronic transitions shown in	250

	Table 5.1	
5.26	MOs of compound 304 that involve in the electronic transitions shown in Table 5.1	251
5.27	MOs of compound 306 that involve in the electronic transitions shown in Table 5.1	252
5.28	MOs of compound 307 that involve in the electronic transitions shown in Table 5.1	253
6.1	Molecular structure of aminotroponiminatostannylene monochloride 401	270
6.2	Molecular structure of aminotroponiminatostannylene monochloride 402	271
6.3	Molecular structure of stannylene amide complex 403	272
6.4	Molecular structure of aminotroponiminatostannylene monobromide 405	273
6.5	Molecular structure of stannylene monocyanide complex 406	274
6.6	Molecular structure of aminotroponiminatodichlorosilane 408	275

List of Tables

Table No.	Table Caption	Page No.
3.1	Crystal data and structure refinement parameters for compounds 101 , 103-104 , 106-108 , and 110-116	86
4.1	⁷⁷ Se NMR spectroscopic data for compounds containing Ge=Se bonds	118
4.2	Observed and calculated UV-vis absorption maxima of compounds 219 , 220 , 207 , and 214	123
4.3	Wiberg bond indices and NPA charges of the atoms connected to the germanium atoms in compounds 207 and 214	145
4.4	Ionicities and WBI of Ge–X bonds and hybridizations and NPA charges of the atoms in the Ge–X bonds in compounds 219(a-b) , 220(a-b) and 219-220 . The WBI of Ge=E bonds in these compounds are also tabulated (X = a halogen atom; E = a chalcogen atom)	147
4.5	Crystal data and structure refinement parameters for compounds 201 , 203-207 , and 210-220	163
4.6	Selected bond lengths of compounds 207 and 214 obtained from calculations. The values in the parentheses are the corresponding values obtained from experimental studies	172
4.7	Selected bond angles of compounds 207 and 214 obtained from calculations. The values in the parentheses are the corresponding values obtained from experimental studies	172
5.1	Observed and calculated UV-vis absorption maxima of digermylene oxide complex 302 and its chalcogen derivatives 304 , 306 , and 307	191
5.2	B3LYP computed total energies along with the reaction enthalpies and free energies for the steps 1 and 2 in Scheme 5.2	202
5.3	NPA charges on the germanium atoms and other atoms connected to them in compounds 301 , 303 , 305 , and 307	204
5.4	The electron charge density, electronic energy density for Ge–O (in compounds 301 , 303 , and 305) and Ge=E (in compounds 303 and 305) bonds at the bond	207

	critical points (bcps)	
5.5	Crystal data and structure refinement parameters for compounds 301-312	238
5.6	Variation of the Ge–O–Ge angles in compounds 301 , 303 , and 305 based on the basis set used with respect to the experimental values	244
5.7	Comparison of the important bond angles and lengths in compounds 301 , 303 , and 305 obtained from experimental studies with the corresponding values calculated using DFT calculations	245
5.8	Comparison of the important bond angles and lengths in compound 307 obtained from experimental studies with the corresponding values calculated using DFT calculations	248
6.1	Crystal data and structure refinement parameters for compounds 401-403 , 405 and 406	281

List of Symbols and Abbreviations

ATI	aminotroponimate	h	hour
%	percentage	HOMO	highest occupied molecular orbital
°	degree	HRMS	high-resolution mass spectrometry
°C	degree centigrade	Hz	Hertz
μ M	micro molar	<i>i</i> -Bu	<i>iso</i> -butyl
Å	angstrom	<i>i</i> -Pr	<i>iso</i> -propyl
Ad	adamantyl	IR	infra red
AIM	atoms in molecules	<i>J</i>	coupling constant
Anal	analysis	K	Kelvin
au	atomic unit	Kcal	kilocalorie
bcp	bond critical point	LUMO	lowest unoccupied molecular orbital
bs	broad singlet	<i>m/z</i>	mass-to-charge ratio
Calcd	calculated	Me	methyl
cm	centimeter	Mes	mesityl
COD	cyclooctadiene	mg	milligram
Cp	cyclopentadienyl	MHz	megahertz
Cy	cyclohexyl	min.	minute
DCM	dichloromethane	mL	milliliter
dd	double doublet	mmol	mill mole
dec	decomposition	MO	molecular orbital
deg	degree	Mp	melting point
DFT	density functional theory	MS	Mass spectrometry
DME	dimethoxyethane	NBO	natural bond orbital
dmpe	bis(dimethylphosphino)ethane	NHC	<i>N</i> -heterocyclic carbene
EI	electron ionization	nm	nanometer
ESI	Electrospray ionization	NMR	nuclear magnetic resonance

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